Development and Exploration of Schiff base Ruthenium Carbene Catalysts for Olefin Metathesis

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‘Facts per se can neither prove nor refute anything. Everything is decided by the interpretation and explanation of the facts, by the ideas and the theories.’

Ludwig von Mises
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The undertaking of a research project is not a one-man job but is only possible by the help of financers, colleagues, friends and family.

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The formation of a chemical bond is the fountainhead of chemical science and since most chemistry concerns organic molecules, the formation of carbon-carbon bonds is of primordial importance in chemistry. Catalysts on the other hand, are substances which increase the rate of a chemical reaction. This is accomplished by lowering the activation energy in the transition state by an association of the starting product to the catalyst. After dissociation, the original catalyst is regenerated and a new product is formed. The use of a catalyst can provide fast reaction to the required products which are otherwise not obtained due to excessive activation energies. Moreover, higher productivity for a reaction can be obtained since only the productive, aimed reaction is accelerated and unwanted side reactions remain slow. This is the reason why most industrial reactions are performed in the presence of a catalyst and not by textbook chemistry.

Olefin metathesis is a reaction which inter-switches the double bonds of two molecules: $C_A=C_B + C_C=C_D \rightarrow C_A=C_C + C_B=C_D$. This is a fundamental carbon-carbon coupling reaction. Due to the high activation energy for this reaction it only proceeds in the presence of a catalyst. Only half a century ago the first catalysts which catalyze this reaction were found. These were valuable in polymerizations and later in the SHOP (Shell Higher Olefin Process). However, little was known about the catalyst mechanism and inner workings so the development of superior catalysts remained difficult. This spurred great interest in the scientific community to unravel these ‘black-box’ catalysts. In 2005 R. Y. Chauvin, R.R. Schrock and H. Grubbs were awarded the Nobel prize for their contributions to these understandings. Y. Chauvin had proposed the metallacyclobutane mechanism for the reaction and R.R. Schrock had developed a series of ‘Schrock-carbenes’ based on W and Mo which are stable and active for the olefin metathesis reaction. R.H. Grubbs had also been working long in this area when he developed in the early nineties the first stable Ru-carbene active for olefin metathesis. The Ru-catalysts have proven to be very active for olefin metathesis and extremely tolerant – compared to Schrock catalysts – towards functional groups. This has led an always increasing number of researchers to synthesize a vast number of ‘Grubbs catalysts’ which even further improved the activity and tolerance. These combined efforts have led olefin metathesis from the industrial applications back into the organic chemist lab. Due to the high number of catalysts which are already commercially available the metathesis reaction has become a tool to the organic chemist and pharmacist which eventually influences faster and less costly synthesis procedures for medicines and related products.

Previously, our research group had synthesized several Grubbs type catalysts substituted with bidentate O,N Schiff base ligands. These catalysts proved efficient for several types of olefin metathesis reactions. Moreover, these species proved efficient for atom transfer radical reactions.
current research project consisted of the optimization of these catalysts and the exploration of new catalytic applications for them.
Outline

This work consists of two parts. The first part contains an extensive overview on Ru metathesis catalysts made up to date, an overview of contemporary thinking in organometallic chemistry and the description on the inner workings of the catalyst. A second part describes the practical investigations which were performed. Schiff base substituted catalysts are central in this section. First several Schiff base complexes were synthesized, the complexes were optimized and suitable applications were investigated. During this research, also secondary metathesis turned out to be important in the description of the catalysts. Further optimization of the catalyst was attempted in the adaptation of the NHC ligand using guidelines which were established in the theoretical part.

Chapter 1 is an introductory chapter describing metathesis as a reaction, the early catalyst developments and a detailed overview of most of the catalyst developments in the field of Ru-based catalysts.

Chapter 2 contains a lengthy exposition on contemporary organometallic thinking but textbook organometallic chemistry falls out of this context. Most of the chapter deals with carbene ligands and phosphines are also elaborately discussed. Moreover, the olefin ligands and description of total metal-ligand complexes are discussed. Most of the material handled stems from computational investigations. Furthermore, emphasis is directed on the separation of σ-bonding and π-backbonding effects of the ligands and more specific on the effects of the π-backbonding to the metal ligand complex.

Chapter 3 deals with the computational investigations performed on the Grubbs catalyst. A detailed overview and discussion is presented together with guidelines to obtain active catalysts. This is performed in accordance to the contemporary organometallic thinking proposed in Chapter 2.

Chapter 4 contains most of the experimental results obtained with Schiff base catalysts and contains 3 topics: Monometallic catalysts, a bimetallic catalyst and secondary metathesis. The monometallic Schiff base catalyst synthesis and a detailed structural analysis are described. Moreover, this type of Schiff base catalyst was tuned to obtain different characteristics. These catalysts were also intensively investigated for several applications in order to find segments of the metathesis-realm in which these catalysts outperform all others. Secondly, many attempts were made to synthesize a Schiff base substituted catalyst. Thirdly, the investigation of the 1,5-cyclooctadiene polymerization has created an opportunity to study the secondary metathesis events. Due to the interesting results, this investigation was performed very elaborately.
Chapter 5 is the practical application of the knowledge gathered in Chapters 2 and 3. In these chapters, the requisites for an active catalysts were investigated. In chapter 4 the Schiff base catalysts were synthesized, and the variation of the Schiff base was investigated, however, the opportunity to change the rest of the catalyst still remained. To investigate these variations, the substitutions were performed on the classic Grubbs catalyst, since this catalyst still holds as the standard for comparison and that a Schiff base substitution can always be added afterwards.

In this investigation we have prepared an (amino)(amido)NHC ligand and substituted it on the Grubbs catalyst. This first synthesis of an (amino)(amido)NHC ligand represent the exploration of a new class of the NHCs. In this context it is interesting to note that NHC ligands have dominated organometallic chemistry over the last 10 years.

Also some interesting features of organometallics in general were explored using $\nu$(CO) frequencies.

Chapter 6 contains a detailed description of all the experimental procedures which were applied in chapters 4 and 5.

Chapter 7 summarizes the conclusions which have been taken from this work.

Chapter 8 shows a small summary of this work in Dutch.
List of abbreviations

[M] Metal complex
acac Acetyl acetonate
ADMET Acyclic Diene METathesis Polymerization
Ar Aromatic group
ATRP Atom Transfer Radical Polymerization
Ax Axial
b Backdonation
BDE Bond Disruption Enthalpies
BDE Bond Dissociation Enthalpy
BE Binding Energy
BINAP 2,2’-bis(diphenylphosphino)-1,1’-binaphtyl
BMI-PF$_6$ 1-butyl-3-methyl-imidazolium hexafluorophosphate
CAAC Cyclic Alkyl Amino Carbene
CDA Charge Decomposition Analysis
CM Cross Metathesis
CO $Cis$-Cyclocotene
COD $Cis,cis$-1,5-cyclooctadiene
Cp Cyclopentadienyl
Cp* Pentamethylcyclopentadienyl
CSOV Constrained Space Orbital Variation
Cy Cyclohexyl
D Donation
$D_0$ M-L bond energy
$D_0'$ M-CO bond energy
DCD (Dewar-Chatt-Duncanson) model
DCPD Dicyclopentadiene
Decypb 1,4-bis(dicyclohexylphosphino)butane
DEDAM DiEthylDiAllylMalonate
DEDAM-1 4,4-dicarboxyloxy-2-methyl-1,6-heptadiene
DEDAM-2 4,4-dicarboxyloxy-1,2-dimethyl-1,6-heptadiene
DFT Density Functional Theory
Dme Dimethoxyethane
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<tr>
<td>Dppb</td>
<td>1,4-Bis(diphenylphosphino)butane</td>
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<tr>
<td>Dtbp</td>
<td>Bis(di-tert-butylphosphino)methane</td>
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<tr>
<td>E_{ar}</td>
<td>Aromatic effect in QALE (not restricted to aromatic groups)</td>
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<td>EDA</td>
<td>Energy Decomposition Analysis</td>
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<tr>
<td>EN</td>
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<td>ETS</td>
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<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>NAO$_{x}$</td>
<td>NAO with the metal valence scale extended with the p-orbitals</td>
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<tr>
<td>NTDAA</td>
<td>N-tosyl-diallylamine</td>
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ORSAM  Orbitally Ranked Symmetry Analysis Method
ORTEP  Oak Ridge Thermal Ellipsoid Plot
OS     Oxidation State
PA     Proton Affinity
PDI    Polydispersity Index
PEG    PolyEthylene Glycol
PHC    P-heterocyclic carbene
Phoban  Phosphabicyclononanes
QALE   Quantitative Analysis of Ligand Effects
QM     Quantum Mechanical
QSAR   Quantitative structure-activity relationship
RCM    Ring Closing Metathesis
RIM    Reaction Injection Molding
RLS    Rate Limiting Step
ROM    Ring Opening Metathesis
ROMP   Ring Opening Metathesis polymerization
RRM    Ring-Rearrangement Metathesis
SEP    Semi-empirical quantum mechanics
SIMES  1,3-dimesityl-4,5-dihydroimidazol-2-ylidene
SM     Self Metathesis
S-T    Singlet-Triplet
t,t,t-CDT Trans,trans,trans-cyclododecatriene
T_g    Glass transition temperature
THF    Tetrahydrofuran
TM     Transition Metal
TMSD   Trimethyl Silyl Diazo Methane
TOF    Turn Over Frequency
TON    Turn Over Number
TS     Transition State
VB     Valence Bond
VSEPR  Valence Scale Electron Pair Repulsion
\Delta E(\pi_L) Out of plane \pi orbital interaction energy term in EDA
\Delta E^{\text{elstat}} Electrostatic energy term in EDA
\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}
\Delta E^{\text{orb}} Orbital interaction energy term in EDA
\Delta E^{\text{Pauli}} Pauli repulsion energy term in EDA
\Delta E^{\text{prep}} Energy term in EDA necessary to excite the parts from their separate optimal geometries into their bonded geometries.
\Delta E_{\pi} \pi orbital interaction energy term in EDA
\Delta E_{\pi||} In plane \pi orbital interaction energy term in EDA
\Delta E_{\sigma} \sigma orbital interaction energy term in EDA
\Delta G_s Solution free energies
\theta  Steric parameter in QALE
\theta_{st} Steric threshold in QALE
\pi_p \pi-acidity in QALE
\nu_{CO} CO stretching frequency in IR
$\chi_d$  σ-donor capacity in QALE
# List of most used molecules

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Chapter 1

Olefin Metathesis

The goal of this first chapter is to present a short résumé of the early developments in metathesis and an extensive overview of the well defined ruthenium based homogeneous catalysts for this reaction. For the interested reader ‘Handbook of Metathesis’\(^1\) is recommended which was here used as a guideline for the introductory part on the early developments.

1.1 Introduction

‘Metathesis’ is a word derived from the two Greek words *meta* (change) and *thesis* (position).\(^2\) Olefin metathesis is the exchange of double bonds between olefins. A model reaction of the interchanged double bonds between the carbon atoms is depicted below.

\[
\begin{align*}
\text{A} & \quad \text{C} \\
\text{B} & \quad \text{D}
\end{align*}
\quad \leftrightarrow \quad
\begin{align*}
\text{A} & \quad \text{C} \\
\text{B} & \quad \text{D}
\end{align*}
\]

*Figure 1.1: Olefin metathesis.*

No classical orbital attack is possible to obtain these products because the energies of the potential TS’s (Transition State) are too high. This problem is circumvented through the introduction of a catalyst which is a chemical compound that remains unchanged in the overall reaction scheme but assists the reagents and products in the reaction mechanism, causing a drop in the activation barriers and consequently a faster reaction. It is important to note that a catalyst can only speed up the reaction to thermodynamic equilibrium but can never change that particular equilibrium. In 2005 the Nobel Prize for chemistry was awarded to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock for the development of catalysts and the elucidation of the mechanism for olefin metathesis. Yves Chauvin
was awarded for unravelling the mechanism\(^3\). His team proposed a reaction with a metal carbene complex as initiator going through a cycle of reversible steps. Firstly, the metal carbene reacts with an olefin in a concerted mechanism and forms a cyclobutane ring. The cyclobutane ring subsequently flips open either into the initiating species or productively into a new metal carbene fragment. A new substrate olefin can now again react with the carbene centre to ultimately get the metathized product and the carbene initiator. The cycle can reinitiate now. The reaction is characterised by a series of reversible steps, which lead to a thermodynamic equilibrium of reaction products.

![Metalloyclobutane mechanism of metathesis.](image)

Richard Schrock was awarded the Nobel Prize for being the first to have discovered an alkylidene complex and for having developed a whole family of tungsten and more important molybdenum alkylidene complexes (vide infra)\(^4\). Robert Grubbs was honoured for his development of ruthenium catalysts, which up till now are by far the most tolerant to functional groups and simultaneously compete with the most active Schrock catalysts in catalytic activity (vide infra). The metathesis reaction is a versatile tool with a large variety of applications both in polymer chemistry and organic synthesis. The basic transformation reactions include Ring Opening Metathesis polymerization (ROMP), Ring Closing Metathesis (RCM), Acyclic Diene METathesis Polymerization (ADMET), Ring Opening Metathesis (ROM) and Cross Metathesis (CM).

In RCM, CM and ADMET the formation of a volatile compound and an internal olefine is the driving force for the reaction. To favour RCM, low concentrations of substrate can be used to prevent oligomerization obtained by the competitive ADMET reaction. Furthermore the stability of the ring is of paramount importance in this competition as RCM is favoured with the formation of stable rings. On the other hand, in ROMP and ROM high ring strain is necessary to overcome the loss in entropy during the reaction. Cross metathesis deals with linear transformations and the substitution pattern determines the equilibrium of homodimerization vs. heterodimerization.
Evolution of high oxidation state Schrock carbenes

The first catalyzed metathesis reactions were reported by the industry after the polymerization of ethylene was discovered by Ziegler. Thereupon, a series of black box catalysts were developed without any mechanistical understanding.

Calderon suggested that the polymerization of cyclic alkenes to polyalkenemers and the disproportionation of acyclic alkenes are the same type of reaction and baptized it olefin metathesis. At DuPont Tebbe reported the fully characterized Tebbe complex. It was demonstrated to be a catalyst for the degenerate metathesis of terminal olefins and the propagating species was characterized. Subsequently his group and others reported on the formation of several Titanium-cyclobutane species from the reaction with Tebbe complex.

Furthermore, the intermediate methylene species was trapped by a variety of reagents. This methylene species and the existence of metallocyclobutane rings delivered strong evidence for the Chauvin mechanism. Though the titanium catalysts showed very low activity for metathesis, they provided an excellent model for the reaction. This was a big step forward since the industrial applied metathesis catalysts up to that point were ill defined tungsten and molybdenum species and none of the known carbene complexes at that time showed any metathesis activity. However, the \( \text{Cp}_2\text{Ti(CH}_2\text{)} \) complex is fundamentally different from all other carbene complexes discovered since Fischer’s first reports in 1964. The Fischer carbenes are polarized with a \( \delta^+ \) on the carbene and a \( \delta^- \) on the metal. In contrast
this new carbene, later named as alkylidene or Schrock-carbene, is polarized $\delta^+$ on the metal and $\delta^-$ on the carbon.\(^1\)

Tebbe who carried out this research in the mid 70’s did not publish the results until 1978.\(^1\) A concurrent development of tantalum carbene complexes was originally reported by Richard R. Schrock. In 1974 Schrock et al. described the serendipitous discovery of a carbene formation.\(^4\) In an attempt to synthesize a penta alkyl tantalum complex Ta(CH\(_2\)CMe\(_3\))\(_5\), a (Me\(_3\)CCH\(_2\))\(_3\)Ta=CHCMe\(_3\) tantalum ylide was obtained that bears similarity to a phosphorous ylide (hence alkylidene).\(^1\)

\[
\begin{align*}
\text{Ta(CH}_2\text{t-Bu)}_3\text{Cl}_2 & \xrightarrow{2 \text{ LiCH}_2\text{CMe}_3} \text{t-BuCH}_2\text{Ta}=\text{H} \equiv \text{CMe}_3 \\
& \xrightarrow{-2 \text{ LiCl} - \text{CMe}_4} \text{t-BuCH}_2\text{Ta} = \text{H} \equiv \text{CMe}_3
\end{align*}
\]

**Figure 1.5:** Ta olefin metathesis catalyst.

The carbene was believed to result from an $\alpha$-hydrogen abstraction which is accelerated with increasing bulk, leading to the first example of a M=CHR complex. The complex is sensitive to oxygen, water and a variety of functional groups and reacts with carbonyls in a Wittig-like manner.\(^1\) These phosphorous ylide characteristics suggest that the metal is in a V+ oxidation state.\(^1\) Later Schrock et al. synthesized a tantalum methylene complex Cp\(_2\)Ta(CH\(_2\)Me) using more sterically demanding ligands with the anti-Fischer (Schrock) polarisation of $\delta^+$ on the metal and $\delta^-$ on the carbon.\(^1\) The observation of tantalum cyclobutane and cyclopentane complexes\(^11\) and the first productive metathesis of a simple olefin obtained with a well characterized catalyst\(^12,13\), led to better insights in the metathesis reaction. A high oxidation state is required for the formation of alkylidene complexes and the presence of alkoxides is preferential to chlorines to promote metathesis.\(^1\)

At that time the synthesis of a new metathesis active complex W(O)(CH-t-Bu)(PMe\(_3\))\(_2\)Cl\(_2\), which formed in an attempt to create an alkoxide carbene [(t'-Bu-O)_\(_2\)W=CH-t-Bu], was reported.\(^14,15\)

\[
\begin{align*}
\text{t-Bu-O} & \xrightarrow{+ \text{Ta(CH}_2\text{t-Bu)(PMe}_3\text{)}_2\text{Cl}_3} \text{W(O)} \equiv \text{C} \equiv \text{O} \\
& \xrightarrow{\text{-Ta(O-t-Bu)}_4\text{Cl}} \text{W(O)} \equiv \text{C} \equiv \text{O}
\end{align*}
\]

**Figure 1.6:** W-based olefin metathesis catalysts.

The complex is active only in the presence of a trace of AlCl\(_3\). Concurrently the Osborn group had developed a cationic complex [W(CH-t-Bu)(OCH-t-Bu)_2X]^+AlX\(_4^-\), which was the first well defined catalyst that engaged in metathesis with analogous activity to the earlier black box systems.\(^16-20\)

Furthermore, analogous systems were synthesized with tungsten alkylidyne moieties and the alkoxide catalysts of the type (OR)\(_3\)W=C-t-Bu proved to be highly active for alkyne metathesis.\(^1,21-25\) The expected intermediate alkylidyne and tungsten cyclobutadiene species can be observed in alkyne

\(^1\)For a detailed analysis see chapter 2
It became clear that complexes with chlorines like (dimethoxyethane)Cl₃W≡C₅Bu are prone to side reactions that destroy the alkylidyne and alkylidene and that bulky electron withdrawing alkoxides could solve this issue.²⁶

This led to the introduction of sterically demanding imido ligands as alkoxide-mimics. Upon treatment of W≡C₅Bu(NHar)Cl₂(dme) with a catalytic amount of Et₃N, a quantitative conversion to W=CH₅Bu(NHar)(OR)₂(dme) is obtained.²¹,²⁷ Upon substitution of the chlorines with bulky alkoxide-ligands, the complex W=CH₅Bu(NHar)(OR)₂ is formed. Catalysts of this type show good activity for the metathesis of internal olefins.

In the search for catalysts being more tolerant to functional groups this methodology was applied to synthesize analogue molybdenum species. The first synthesis dates from 1987²⁸, while three years later a more practical synthesis was developed²⁹.

![Figure 1.7: Preparation of Mo-based olefin metathesis catalyst.](image)

Although Mo=CHR(NAr)(OTf)₂(dme) is relatively stable towards triflic acid, it reacts even with alkoxides that are poor nucleophiles.¹ These molybdenum catalysts are stable as long as the alkoxide ligands hinder the metal centre with sufficient steric bulk.²¹ One advantage of Mo versus W is that molybdenum intermediates generally lose olefin more readily than the tungsten intermediates and consequently show better activity at lower temperatures.¹ This technology led to one of the fastest initiating species known up to this date.

![Figure 1.8: Efficient Mo-based olefin metathesis catalyst.](image)

Recent developments in the area of Mo-catalysts deal with the incorporation of enantiomere pure bidentate alkoxide ligands and a series of different imido ligands. These species have proved to be excellent catalysts for the enantioselective Ring-Closing, Ring-Opening and Cross Metathesis reactions.¹,³⁰-⁴⁶

Rhenium complexes were also explored but they did not prove to be as active as tungsten and molybdenum complexes.¹
1.3 Development of ruthenium catalysts into well defined carbenes

The first metathesis catalysts involved molybdenum oxide on alumina with alkyl aluminiums or aluminium hydrides and hydrogen and thereafter they consisted of ill-defined mixtures of WCl₆ and MoCl₅. RuCl₃ in ethanol was found to be an initiator for metathesis in 1965. However the importance of the discovery was not appreciated until Grubbs and co-workers worked it out 3 decades later.¹

In 1988 Novak, associated with Grubbs, investigated the polymerization of 7-oxonorbornene. Ruthenium trichloride was found to polymerize olefins and could even generate high molecular weight polymers in water.¹⁴⁷,⁴⁸ It was assumed that these polymers were obtained through a metal carbene species which appeared to be tolerant to water and oxygen.¹ Furthermore it was demonstrated that a strained olefin and a ruthenium(II) metal centre are the keys to an active catalyst.¹⁴⁷,⁴⁹ At that time Johnson, also associated with Grubbs, developed a series of vinylalkylidene W(VI) species through the addition of 3,3 disubstituted cyclopropenes to reduced W(IV) precursors.¹

In this context that Nguyen, also associated with Grubbs, has developed the first well defined ruthenium species that is active for metathesis and which would later be called the first member of the Grubbs catalysts.¹⁵⁰

![Figure 1.9: First stable carbene formation on Ru.](image)

1.1 is active for the living ROMP, it is stable for days in the presence of water, alcohol or an ether solution of HCl and does not react in a Wittig-type reaction with either ketones or aldehydes.⁵⁰ This high functional group tolerance combined with a well defined organometallic species would herald a new dawn in the metathesis technology.¹

One year later, Grubbs et al. reported that substitutions of the chlorine ligands with a variety of electron withdrawing anionic ligands, copying the early transition metal metathesis chemistry, does not increase the propagation rate of the ruthenium.⁵¹ However, the substitution of the triphenylphosphine ligands with better σ-donating alkyl ligands like PCy₃ or P(°Pr)₃ led to such an increase of the propagation rate for norbornene that little of the catalyst had initiated when the polymerization was finished.⁵¹ In contrast to 1.1, complex 1.2 catalyzes the ROMP of less strained olefins like cis-cyclooctene (CO), cyclooctadiene (COD), 7-oxonorborne derivatives and cyclopentene (CP).⁵¹ 1.2 remains tolerant to functional groups and CH₂Cl₂ was found to be the optimal solvent.⁵¹
Olefin metathesis

Very soon a variety of applications such as RCM, ADMET and the RIM of DCPD were investigated in the Grubbs group\textsuperscript{52-56} as well in other groups\textsuperscript{57-59}. The initial synthetic pathway of 1.2 is not suitable for large scale production and therefore efforts were concentrated on developing a new large scale synthesis. Herein the reaction of RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3} with diazocompounds\textsuperscript{60,61}, especially phenyldiazomethane that can be handled relatively safely on a large scale, proved to be an excellent strategy for the large scale synthesis of the commercially available 1.3, better known as the 1\textsuperscript{st} generation Grubbs catalyst.\textsuperscript{1}

The $k_i$ (initiating constant)/$k_p$ (propagating constant) ratio of the benzylidene 1.3 compared to 1.2 is 1000 times higher which should allow full initiation leading to living polymers, since chain transfer and termination reactions are formally not present\textsuperscript{60}. In Chapter 4, we will comment elaborately on the transfer reactions caused by secondary metathesis. This affords polymers with narrow molecular weight distributions (PDI < 1.1).

Some other synthetic methods for the synthesis of ruthenium carbenes are listed below.\textsuperscript{1,62-70} The carbene transformation is accomplished through reaction with dichloromethane\textsuperscript{62}, alkynes\textsuperscript{63,65}, propargyl chlorines\textsuperscript{63,64}, vinyl chlorines\textsuperscript{64}, sulphur ylides\textsuperscript{67}, cyclopropenes\textsuperscript{50}, dichloromethylbenzene\textsuperscript{68}, propargyl alcohol\textsuperscript{69-71} or dichloromethyl chalcogenides.\textsuperscript{72,73}
Figure 1.12: Different types of carbene formation for Ru catalysts.
1.4 Development of 2\textsuperscript{nd} generation Grubbs catalysts

The biggest improvement since the development of 1.3 was the substitution of a phosphine with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (SIMES or H\textsubscript{2}IMES) in 1999 which leads to 1.4. This complex is known as the commercially available 2\textsuperscript{nd} Grubbs generation catalyst.\textsuperscript{74}

![Figure 1.13: Standard second generation Grubbs catalyst.](image)

Encouraged by the landmark breakthrough of Arduengo et al. who synthesized the first stable N-heterocyclic carbene (NHC) in 1991,\textsuperscript{75} these new type of ligands were explored rapidly (see chapter 2). The NHC’s are bulky molecules and act as strong \(\sigma\)-donors and weak \(\pi\)-acceptors in organometallic compounds which make them excellent \textit{phosphine-mimics}. Herrmann et al. initiated the race in 1998 by introducing a series of 2-imidazolin-2-ylidenes on the Grubbs 1\textsuperscript{st} generation catalyst. Complex 1.5 was found to be more active for the polymerization of COD than 1.3. Furthermore, it showed excellent activity for RCM.\textsuperscript{76}

![Figure 1.14: Double NHC substitution on the Grubbs catalyst.](image)

One year later both Herrmann et al.\textsuperscript{77,78} and Nolan et al.\textsuperscript{71,79,80} almost concurrently reported on the incorporation of one unsaturated NHC ligand on a ruthenium biphosphine benzylidene. Herrmann et al. concluded that the mono-substituted Grubbs catalyst 1.6 shows superior activity over 1.3 and 1.5.\textsuperscript{77} The better activity of 1.6 over 1.5 can be attributed to the high strength of the Ru-NHC bond which makes it more difficult to initiate an active species. That same year Grubbs et al. reported on the introduction of dihydroimidazol-2-ylidenes on 1.3\textsuperscript{74} leading to the 2\textsuperscript{nd} generation Grubbs catalyst 1.4 (vide supra).
Grubbs et al. showed that substitution with H$_2$IMES improved the activity of the catalyst compared to the introduction of the analogue unsaturated carbene IMES. Furthermore, the introduction of a NHC enhanced the thermal stability and inertness to moisture and oxygen. The carbene substituted catalysts also perform well in the RCM for tri- and even tetra-substituted cycloalkene products, in contrast to their parent catalyst $\mathbf{1.3}$. H$_2$IMES together with H$_2$IPr (1,3-Bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene, remain of the best carbene ligands for metathesis systems up to the present.

It was proposed that the NHC ligands improve metathesis activity due to an increased NHC-metal bond strength. The NHC–metal bond is characterized by a strong σ-donation and a weak π-back donation from the metal (Chapter 2). It has been generally accepted that the higher σ-donation of the saturated carbenes leads to an increase in activity but these arguments have been strongly under attack by observations that the IMES and H$_2$IMES ligands show similar bond strengths for several complexes (Chapter 2).

As a consequence of the Grubbs influence, H$_2$IMES is accepted to be a significant better ligand in promoting metathesis in the classical Grubbs systems and $\mathbf{1.4}$ is now the most widely used catalyst. However Nolan et al. observed through ν$_{CO}$ stretching frequencies that the saturated NHC ligands are slightly less electron-donating than their unsaturated analogues in Ni(CO)$_3$L complexes. Furthermore examination of the BDEs (Bond Disruption Enthalpies) for the reaction of [Cp*RuCl]$_4$ with 4 equivalents of carbene can not explain the high activity of H$_2$IMES compared to the other carbenes in catalysts for metathesis. Nolan et al. suggested that mainly steric factors are responsible for the observed differences in the BDEs between the carbenes. These observations are however contradictory to all the recent attempts to increase activity in catalysts by trying to incorporate more electron-donating carbenes. All this can only suggest that the carbene-metathesis puzzle is not yet finished and that breakthroughs in this area are still possible. (Chapters 3 and 5)

Nolan et al. observed that the initiation is slower for catalysts bearing IMES compared to PCy$_3$. However when RuCHPh(Cl)$_2$(PCy)$_3$IMES is initiated, it exhibits superior properties upon $\mathbf{1.3}$.

Grubbs et al. reported on a mechanistic study focussing on the coordination properties of $\mathbf{1.3}$ and $\mathbf{1.4}$.

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$\mathbf{1.3}$: First mono-NHC substituted Grubbs catalyst.

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$\text{Figure 1.15:}$ First mono-NHC substituted Grubbs catalyst.
Olefin metathesis

The exchange rate constant for coordinated phosphines of \( \textbf{1.3} \) was found to be 100 times higher compared to \( \textbf{1.4} \). The initiation constant is independent of the olefin concentration over a wide range which supports the dissociative mechanism. Furthermore, it was observed that the \( k_1/k_2 \) ratio for \( \textbf{1.3} \) is 4 orders of magnitude higher than that of \( \textbf{1.4} \). Grubbs et al. concluded that the high activity of the N-heterocyclic carbene-coordinated catalyst \( \textbf{1.4} \), which previously had been attributed to its increased ability to promote phosphine dissociation (increasing \( k_1 \)), instead appears to be caused by the improved selectivity for binding \( \pi \)-acidic olefin substrates on the 14 electron species in the presence of \( \sigma \)-donating free phosphines.\(^{94}\)

Figure 1.16: Dissociative mechanism.

\[
\begin{align*}
\text{Cl} & \quad \text{R} \quad \text{Cl} & \quad \text{L} \quad \text{PCy}_3 \\
\text{Cl} & \quad \text{R} \quad \text{Cl} & \quad \text{L} \quad \text{PCy}_3 \\
\end{align*}
\]

\[
\begin{align*}
k_1 & \quad \text{R} \quad \text{PCy}_3 \\
+ \text{PCy}_3 & \quad \text{k}_1 \\
\text{R} \quad \text{PCy}_3 \\
\end{align*}
\]

\[
\begin{align*}
k_2 & \quad \text{R} \quad \text{PCy}_3 \\
\text{Cl} & \quad \text{k}_2 \\
\text{Cl} \quad \text{R} \quad \text{PCy}_3 \\
\end{align*}
\]

\[
\begin{align*}
k_3 & \quad \text{R} \quad \text{PCy}_3 \\
\text{Cl} & \quad \text{k}_3 \\
\text{Cl} \quad \text{R} \quad \text{PCy}_3 \\
\end{align*}
\]

\[
\begin{align*}
k_4 & \quad \text{R} \quad \text{PCy}_3 \\
\text{Cl} & \quad \text{k}_4 \\
\text{Cl} \quad \text{R} \quad \text{PCy}_3 \\
\end{align*}
\]

Mol et al. revealed the activity of the previously published complex of \( \textbf{1.7} \) substituted on \( \textbf{1.3} \){\(^{95}\)} for a series of reactions.\(^{95}\) The \( \textbf{1.7} \) substituted catalyst shows highly increased activity for the SM (Self Metathesis) of 1-octene (TON= 630 000) compared to \( \textbf{1.4} \) and a slightly higher TON for the RCM of DEDAM.\(^{95, \text{VI}}\)

Verpoort and Ledoux made a quest to incorporate an alkyl substituted NHC onto the Grubbs complex since the alkyl ligands and hence the NHC lone pair should be more electron donating. First, they attempted to incorporate a series of alkylated NHC ligands on \( \textbf{1.3} \) but no complexes could be isolated due to the low stability.\(^{96}\) However, substitution of \( \textbf{1.8} \)-\( \textbf{1.9} \) in a subsequent publication on \( \textbf{1.35} \) (vide infra) led to Grubbs-Hoveyda N-alkyl NHC complexes as the first alkyl-NHC Grubbs complexes synthesized.\(^{97}\) Unfortunately, the activity for metathesis could not match that of \( \textbf{1.4} \).\(^{97}\)

In the quest for an improved better carbene ligand to promote metathesis, Herrmann et al. explored the possibility to coordinate the acyclic \( \textbf{1.10} \), a much more donating ligand than H\(_2\)IMES, on \( \textbf{1.3} \).\(^{98}\) However, in the reaction mixture no alkylidene could be detected and an attack of the free carbene on the alkylidene was postulated.\(^{99}\) Buchmeiser et al. prepared the six ring analogue of H\(_2\)IMES and observed that its donor capacity is nearly as high as the acyclic \( \textbf{1.10} \).\(^{100}\) The 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene was substituted on the Grubbs catalyst \( \textbf{1.3} \), however no comparative results were presented with the H\(_2\)IMES ligand.\(^{101}\) Grubbs et al. synthesized a similar six-membered carbene \( \textbf{1.11} \) and observed that the corresponding catalyst was slower than \( \textbf{1.4} \) for the polymerization of COD.\(^{102}\) The drop in activity was assigned to the steric bulk which would disfavour olefin bonding, which is highly in contrast to contemporary reasoning on metathesis activity (Chapter 3).\(^{103}\)

\(^{\text{VI}}\) However the activity is substrate dependant and the activity of \( \textbf{1.7} \) for the SM of trans-4-decene and methyl oleate remains well beyond that of \( \textbf{1.4} \).
Grubbs et al. prepared a four-membered NHC 1.12 that shows a $^{13}$C NMR signal for the free carbene at $\delta = 285$ ppm, significantly downfield of the classical NHCs. However the resulting catalyst showed lower activity than its H$_2$IMES analogue. Mol et al. reported on the synthesis of the asymmetrical NHC 1.13 with mesityl on one side and the sterically demanding adamantyl group on the other side. The substituted catalyst is inactive for CM though a fast initiator for ethyl vinyl ether and norbornene. Blechert et al. and Verpoort et al. reported concurrently on the synthesis of a series asymmetrical saturated NHC ligands with mesityl on one side of the ring and an alkyl group on the other side. Blechert concluded that the asymmetry of the catalyst substituted with 1.14 reflects on the E:Z ratio of the product. Furthermore, Verpoort et al. showed through a series of catalysts with ligands analogous to 1.14, that 1.14 is a superior ligand than H$_2$IMES for the RCM of DEDAM due to a diminished steric interaction. In a subsequent publication Verpoort et al. tried to optimize the ligands to 1.15 and analogues by the incorporation of an $^{i}$Pr group instead of the mesityl group, however, the catalytic activity of the resulting catalyst was lower than in the mesityl analogues.

![Figure 1.17: Various saturated NHC ligands substituted on the Grubbs catalyst.](image-url)
Recently, Grubbs et al. synthesized the fluorinated NHC 1.16 and substituted it on 1.3. The resulting complex displays an increased activity upon 1.4 for the RCM of DEDAM, which is rationalised by the assistance of fluoride coordination trans to the benzylidene. This favours phosphine dissociation and consequently increases the amount of active species. The asymmetrical analogue catalyst of 1.17 was also prepared. A mixture of two rotamers was obtained and the activity was intermediate to 1.4 and the 1.16 substituted catalyst. Hoveyda et al. prepared 1.18 of which the resulting catalyst unfortunately showed low stability. Grubbs et al. prepared the resulting catalysts form 1.19-1.20 but no catalytic data on the resulting complexes was presented. Furthermore, modifications of the backbone were performed by Grubbs et al. and Köhler et al. The catalytic activity of the 1.21 supported catalyst was not reported, but the catalyst substituted with 1.22 proved to be as efficient as 1.4 for RCM (at 5 mol%). Köhler et al. showed that the Hoveyda catalyst supported with 1.23 is also highly efficient for RCM, though if the catalyst equiv is decreased (0.005 mol%) it shows clearly lower stability than the standard second generation Hoveyda catalyst 1.36. Further modifications of the NHC ligand, concerning the enantioselectivity of the catalyst will be discussed in the next sub-chapter.

Grubbs et al. also prepared the disubstituted H$_2$IMES catalyst and the mixed IMES-H$_2$IMES substituted catalyst, however, both complexes lacked sufficient activity and stability. Fürstner et al. prepared a series of unsaturated imidazoles (1.24-1.30) to make a comparative activity study. The 1.27 substituted catalyst is a trigonal bipyramid unlike the other complexes (which are square pyramidal) and decomposes rapidly in chlorinated solvents. Its initial high activity is attributed to the fast decomposition of the catalyst. Remarkably, the IMES substituted 1.3 is more active for the RCM of the tetra substituted DEDAM than the H$_2$IMES substituted catalyst. Furthermore, the optimal ligand is substrate specific. The authors postulate a π-π interaction between the benzylidene and a phenyl ring of the imidazole, which causes these catalysts to be more active in toluene than in dichloromethane. This effect is less pronounced with IPr due to the steric crowding of t-Pr groups.

![Figure 1.18: Types of unsaturated NHC ligands substituted on the Grubbs catalyst: A.](image-url)
In 2004 Fürstner et al. continued with a publication on the asymmetrical mesityl imidazoles 1.31-1.32.\textsuperscript{109} 1.32 proved to be a better ligand than IMES for the RCM of tetra substituted DEDAM.\textsuperscript{109} The Grubbs catalyst substituted with 1.31 shows the phosphor ligand trans to 1.31 and can be transformed into the cis-isomer in the presence of silica gel.\textsuperscript{109} This is probably caused by the interaction with a polar medium and the absence of steric bulk on one side of the NHC (vide infra).\textsuperscript{110} The cis-isomer is more stable and less reactive than the trans isomer but can be reconverted to the trans form by heating.\textsuperscript{109} The cis-isomer can thus be considered a latent isomer capable of being stored with monomer without concomitant polymerization, with the ability of being activated by a trigger (here isomerization through heating).\textsuperscript{109} The cationic complex 1.33 is formed spontaneously upon reaction of the 1.31 substituted 1.3 and pyridine, however the complex shows no activity for metathesis.\textsuperscript{109}

\textbf{Figure 19:} Types of unsaturated NHC ligands substituted on the Grubbs catalyst: B.

Ignoring the hysterics of imidazole ligands as substitutes for PCy\textsubscript{3}, Forman et al. reported on the incorporation of phosphabicyclononanes (Phoban) on a Grubbs catalyst to yield 1.34, called Phobcat.\textsuperscript{111} This catalyst shows remarkable characteristics surpassing its parent catalyst on several essential features.\textsuperscript{111} 1.34 is stable in solvents such as acetonitrile, can be submitted to column chromatography and shows improved stability at higher temperatures.\textsuperscript{111} The reactivity and selectivity for self metathesis surpasses that of 1.3 and even 1.4 while the performance for RCM and ROMP is well in the realm of 1.4.\textsuperscript{111} The high activity in RCM, CM and SM stems from the lack of 1\textsuperscript{st} order decomposition of the methylidene which is a major drawback for applications with 1.3.\textsuperscript{111} 1.34 does not have the ability to rotate freely around the Ru-P bond and as a consequence different rotational isomers can be detected.\textsuperscript{112} The small energy difference between the different rotational isomers and the absence of 3-fold symmetry enable the catalyst (unlike 1.3; see chapter 3) to perform a metathesis cycle without rotation around the Ru-P bond and can be accounted as an important reason for the increased activity.\textsuperscript{112}

\textbf{Figure 1.20:} Phoban catalyst
1.5 Development of Grubbs-Hoveyda catalysts and the introduction of chirality

The second most important improvement of the Grubbs catalysts is definitely the incorporation of a chelating carbene ligand. In 1999 Hoveyda et al. reported on the reaction of (2-isopropoxyphenyl)-diazomethane and PCy$_3$ with Cl$_2$Ru(PPh)$_3$. The resulting complex 1.35 was found to offer excellent stability to air and moisture and can be recycled in high yield by basic silica gel chromatography. Similar catalysts with a chelating carbene ligand are often referred to as Grubbs-Hoveyda catalysts.

Figure 1.21: Grubbs-Hoveyda catalysts.

One year later both Blechert$^{114}$ and Hoveyda$^{115}$ reported on the 2nd generation Grubbs catalyst analogue 1.36. The extra stability of this catalyst is obtained through the chelating character of the carbene that assists the bad oxygen donor in its recoordination to form the 16 electron complex. Their superior architecture compared to the normal Grubbs systems for RCM or CM catalysis stems from the formation of a dormant methylidene species, while in the normal Grubbs systems the unstable methylidene carbene is persistently present even after full conversion has been obtained. Unfortunately, the methylidene species is responsible for the lion’s share of the deactivation of the catalyst.

In the Grubbs-Hoveyda catalysts the methylidene intermediate can be trapped by the isopropoxystyrene fragment (present after initiation) which transforms it in the very stable initiating species. The same process is responsible for the elimination of methylidene at the end of the reaction causing the auto-recycling of the catalyst.
Due to the slow initiation rate of 1.36, the challenge remained to implement variations on the chelating ligand to improve stability and reaction rate. Blechert et al. were the first to have spectacular results in catalytic improvement for RCM upon changing the chelating ligand to obtain 1.37 and 1.38, the latter being the fastest initiator.\textsuperscript{116,117} Both 1.37 and 1.38 outperform 1.4 kinetically for RCM while the catalyst’s stability is retained.\textsuperscript{116,117} Furthermore, a mechanistic study revealed that 1.38 initiates much faster than 1.36\textsuperscript{118}.

Figure 1.22: Mechanism for the Grubbs-Hoveyda catalyst.

Figure 1.23: Fast initiating Grubbs-Hoveyda catalysts.
At the same time Grela et al. were exploring electronic changes in the chelating ligand. Complex 1.39 exhibits similar activity to 1.4 and much higher activity than 1.36\textsuperscript{119} due to the electron withdrawing nitro group. Introduction of methoxy groups on the styrene fragment showed little rate improvement.\textsuperscript{120} Changes in the substitution pattern of 1.36, placing the nitro group on different positions could not improve activity of 1.39 and upon applying steric bulk together with an electron withdrawing group the catalysts loses structural integrity.\textsuperscript{121}

Introduction of a sulfonyl group between two isopropoxystyrene groups gives an increased activity upon 1.35 due to the electron withdrawing capacity of the sulfonyl group.\textsuperscript{122} Grela et al. synthesized a three dentate ligated catalyst 1.40 which exhibits higher activity than 1.36.\textsuperscript{123} This is highly unexpected since extra ligation should make the ligand less prone to dissociation. Fürstner et al. incorporated a coordinating carbonyl ester on 1.3 and the IMES substituted 1.3.\textsuperscript{124} Slugovc et al. implemented the coordinating carbonyl ester on 1.4 to obtain 1.41.\textsuperscript{125} It is remarkably that the PCy\textsubscript{3} and IMES substituted catalysts show the carbonyl trans to that ligand while in the H\textsubscript{2}IMES substituted 1.41 the carbonyl adopts cis coordination.\textsuperscript{124,125} Unfortunately no relevant RCM data were given for 1.41.

Van der Schaaf et al. found that with a bidentate carbene-pyridine on 1.3 the polymerization of dicyclopentadiene (DCPD) could be achieved\textsuperscript{126}. This idea was extended by Grubbs et al. on the second generation catalyst.\textsuperscript{127} The phosphine catalyst\textsuperscript{126} yields a product with the pyridine trans to the phosphine. For the second generation analogue the product with pyridine trans to H\textsubscript{2}IMES (1.42) is first created, after which an equilibrium is formed with the two isomers 1.42-1.43.\textsuperscript{127} Complexes 1.42-1.43 initiate much slower than 1.4. Furthermore, 1.42 is a faster initiator than 1.43 due to the trans effect of H\textsubscript{2}IMES.\textsuperscript{127} 1.42 is 6.8 kcal/mol more stable than 1.43 in the gas phase though in a polar medium this energy difference is greatly diminished.\textsuperscript{110} The cancelling polarity of the Cl-Ru-Cl bonds in 1.42 renders it more stable in apolar solvents.\textsuperscript{110}

Grela et al. synthesized a quinoline 1.44 and quinoxaline chelating catalysts.\textsuperscript{128} Both catalysts formed first the isomer with the nitrogen trans to the NHC which equilibrated with the cis isomer over time.\textsuperscript{128} The catalysts show low activity for the RCM of DEDAM and the trans isomer is, as expected, more active than the cis isomer.\textsuperscript{128} Mereiter et al. synthesized a five ring chelate and six ring chelate 1.45 imine complexes, both exhibiting trans geometry.\textsuperscript{129} Both complexes showed activity for a substituted norbornene only at elevated temperature with the six ring chelate 1.45 being the more active catalyst.\textsuperscript{129}
Grubbs et al. synthesized a series of 6-ring chelate exocyclic imine 1.46, 6-ring chelate endocyclic imine 1.47 and tridentate chelating imine 1.48 catalysts, which all show the trans configuration.\(^{130}\) 1.46 has improved activity upon 1.36 for the RCM of DEDAM. The endocyclic 1.47 exhibits some latent character for RCM and the ROMP of DCPD\(^{130}\) while increased activity is obtained with an aromatic substituent as R-group.\(^{130}\) 1.48 shows an increased latent character for RCM due to the extra chelation.\(^{130,\,IX}\)

Actually the first chelated carbene was synthesized by Snapper et al. in 1997.\(^{131}\) A chelating olefin complex 1.49 representing the catalyst caught in the act of metathesis was isolated.\(^{131}\) 1.49 acts as an initiator for ROMP, RCM and CM.\(^{131}\) In 2006 Grubbs et al. were able to isolate a second generation

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\(^{IX}\) Grubbs et al. performed the RCM of DEDAM at a catalyst ratio of 2.5 mol% which makes it unable to judge the stability of the catalysts. Furthermore, in the same year they presented ‘A standard system of characterization for olefin metathesis Catalysts’[(88)](Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* 2006, 25, 5740-5745.] in which they use the 1 mol% ratio (yet even that is objectively a high ratio knowing that 1.4 is able to give full conversion at 0.05 mol%)
chelating alkene species 1.50-1.51 with the chelating olefine cis to the NHC. Piers et al. and Grubbs et al. have showed that with a second generation system the actual cyclobutane can be caught in the act as in 1.52, with the cyclobutane trans to H₂IMES.

Figure 1.26: Chelating olefin catalysts.

One of the major challenges in RCM and CM is the introduction of chirality in the ligand framework of olefin metathesis catalysts. This allows for transformations of prochiral substrates into enantiomeric pure compounds which would answer the high demands of the pharmaceutical industry. Blechert et al. showed that without the introduction of chiral groups on catalysts of type 1.3, 1.4, 1.14 and 1.36 diastereoselectivity can be induced in some amount in RCM and RRM (Ring-Rearrangement Metathesis).

The first attempt was already realized in 1998 through the introduction of a chiral NHC in 1.53 by Herrmann et al. This methodology is up to now the only strategic route employed for these type of catalysts. Grubbs et al. introduced a vast amount of complexes 1.54, of which 1.55 and 1.56 proved to be very potent catalysts showing enantiomeric selectivity for the RCM of a prochiral compound. The introduction of an excess of NaI which should lead to fast exchange of a chlorine with a iodine at the Ru-centre was found to increase the enantioselectivity. In 2006, a more comprehensive study was published in which the iododerivates were isolated and found to increase the enantioselectivity. Substitution trans to the i-Pr group in 1.56 does not enhance stereoselectivity, however, extra substitution on the same side of the phenyl ring does induce a extra chiral resolution.

Figure 1.27: Chiral NHC-catalysts: A.

Hoveyda et al. reported on 1.57 with high chiral selectivity, however, the steric bulk does not allow recoordination of the isopropoxystyrene fragment. The introduction of other chelating carbenes or

\[ \text{X However, no relevant chiral data were presented.} \]
the substitution on the binaphtyl rings with an electron withdrawing group successfully increased the initiation of 1.57.\textsuperscript{140} Furthermore, an increase in both activity and selectivity was achieved applying 1.58.\textsuperscript{143} Recently, Collins et al. have prepared catalyst 1.59, which shows the unusual feature of having the benzylidene group located under the alkyl (methyl) group.\textsuperscript{144} 1.59 shows similar enantioselective control as its competitor 1.56,\textsuperscript{144} though through the induction of the steric backbone a much higher reaction rate is obtained.\textsuperscript{144,145} These chiral adjustments brought ruthenium metathesis for organic synthesis in the realm of molybdenum catalysts and ready for practical applications.

![Figure 1.28: Chiral NHC-catalysts: B](image)

### 1.6 Additional adjustments on Grubbs type catalysts

One of the first modifications of the Grubbs 1\textsuperscript{st} generation catalyst was the incorporation of a bidentate Schiff base.\textsuperscript{146} The complexes show high thermal stability, high tolerance to polar protic solvents and activity for metathesis at elevated temperatures (latent catalyst), however, they are poor initiators.\textsuperscript{146,147} Verpoort et al. reported on the second generation analogues 1.60,\textsuperscript{148,149} followed by another publication of Verpoort et al. on the same transformations for an indenylidene catalyst.\textsuperscript{150}\textsuperscript{XI} We later reported on the correct synthesis of 1.60 and its catalytic activity,\textsuperscript{151} moreover, upon addition of HSiCl\textsubscript{3} the catalyst proved extremely efficient for the polymerization of COD.\textsuperscript{152} Raines et al. confirmed that our compounds instead of the previous reported ones\textsuperscript{149} were 1.60, and found them highly active for metathesis in protic solvents.\textsuperscript{153} Jensen et al. tried to synthesize the amine analogues of 1.60 but was unsuccessful, however, they were able to synthesize the tridentate 1.61 which showed low activity and stability for metathesis.\textsuperscript{154} Herrmann et al. reported on catalyst 1.62 which bears a bidentate pyridinyl-alcololate ligand for the ROMP at elevated temperatures.\textsuperscript{155} Vosloo et al. prepared 1.63 and showed it was highly efficient for the SM of 1-octene.\textsuperscript{156}

\textsuperscript{XI} This technology was the basis of this entire current project and a full discussion of the validity of it will be presented in the experimental section.
The effect of the substitution of the ligand trans to H$_2$IMES was investigated extensively. Grubbs et al. reported in 2001 on the synthesis of a pyridine functionalized 2$^{nd}$ generation catalyst 1.64$^{157}$ which proved to be an excellent initiator$^{158}$. Its 1$^{st}$ generation analogue and the serendipitous discovery of 1-imidazole trisubstituted cationic complex 1.65 was reported later; however, both decomposed fast in the RCM of DEDAM.$^{159, \, \text{XII}}$

The application of 3-bromo-pyridine on catalyst 1.66 even accelerates initiation and low polydispersity polymers of norbornene and norbornene derivatives could be obtained.$^{158, \, 161}$ In a subsequent study, Grubbs et al. showed that the initiating speed of different phosphine substituted 2$^{nd}$ generation catalyst 1.67 is faster with electron withdrawing phosphines regardless of their steric size and concluded that the normal 2$^{nd}$ generation catalyst 1.4 is the slowest initiator due to the electron rich cyclohexyl groups.$^{162}$

Other interesting candidates for substitution are the chlorine ligands. Grubbs et al. showed that for 1.3 and 1.4 the replacement of the chlorine by a bromine or the larger iodine increases the phosphine exchange rate of the catalyst.$^{163}$ Surprisingly olefin metathesis activity of these complexes follows the inverse trend leaving the chlorine substituted 1.4 as the most active catalyst.$^{163}$ The lower $k_1/k_2$ ratio for the chlorine catalyst should be responsible for this selectivity$^{163}$. However, this is difficult to rationalize from steric considerations since PCy$_3$ is a very sterical encumbering ligand and can hardly

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The pyridine functionalised first generation indenylidene was recently reported by Nolan et al.$^{(160)}$ Clavier, H.; Petersen, J. L.; Nolan, S. P. *Journal of Organometallic Chemistry* **2006**, *691*, 5444-5447. and the second generation analogue has been prepared in our labs.
be considered less demanding than an olefin.\footnote{We were not able to find data about this. The olefins as ligands consist of 2 atoms which possess substituents all in the same plane, while the phosphorous ligands have one atom (P) in the free coordination space and the three substituents point away from the catalytic centre.} Also, steric strain is proposed to be a positive influence on catalytic activity.\footnote{Grubbs et al. reported on full conversion of DEDAM using 1.4 up to 2000 equiv but negligible conversion with 10 000 equiv of catalyst. Mol et al. however reported on a TON of 200 000 for the RCM of DEDAM with 1.4.}

It had been long assumed that, like in Mo or W systems, deactivations occurred with assistance of halides. In Ru-chemistry, there was support from dimeric catalysts with bidentate chlorines for such catalyst deactivation, presented by Fogg et al.\footnote{Grubbs et al. clearly showed the deactivation of the methylidene variant of 1.4. Both phosphine assistance and dimeric species with bridging chlorines are present in the proposed mechanism. This creates opportunities for the replacement of the halides (and phosphines) with other functional groups in order to suppress deactivation. (Chapter 4: bidentate Schiff base catalysts)} Grubbs et al. clearly showed the deactivation of the methylidene variant of 1.4.\footnote{Grubbs et al. reported on the substitution of the chlorines with alkoxide groups to form a 14 electron four coordinate species 1.68. While this \textit{-O-}t-Bu group substituted complex is a very poor catalyst, incorporation of more electron withdrawing groups increases activity. However, low thermal stability accompanies the low activity of 1.69A. Upon activation with HCl 1.69B becomes more active than 1.3 which is ascribed to the formation of free alcohol.} Both phosphine assistance and dimeric species with bridging chlorines are present in the proposed mechanism. This creates opportunities for the replacement of the halides (and phosphines) with other functional groups in order to suppress deactivation. (Chapter 4: bidentate Schiff base catalysts)

\begin{figure}
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\includegraphics[width=\textwidth]{fig1.31.png}
\caption{Decomposition of 2\textsuperscript{nd} generation methylidene.}
\end{figure}

Grubbs et al. reported on the substitution of the chlorines with alkoxide groups to form a 14 electron four coordinate species 1.68.\footnote{Inspired by these results and the report of Caulton et al. on the substitution of 1.3 with 1 equiv of NaOPh leading to a carbyn, Fogg et al. reported in 2002 on the reaction of 1.64 with 2 equiv of TIOC\textsubscript{6}F\textsubscript{5} to yield 1.70. This catalyst does not only exceed the activity of 1.68-1.69 but even obtains \textit{equal to superior} activity to 1.4 for the RCM of DEDAM with turnover numbers up to 40000 (with} While this \textit{-O-}t-Bu group substituted complex is a very poor catalyst, incorporation of more electron withdrawing groups increases activity. However, low thermal stability accompanies the low activity of 1.69A. Upon activation with HCl 1.69B becomes more active than 1.3 which is ascribed to the formation of free alcohol.\footnote{Grubbs et al. reported on full conversion of DEDAM using 1.4 up to 2000 equiv but negligible conversion with 10 000 equiv of catalyst. Mol et al. however reported on a TON of 200 000 for the RCM of DEDAM with 1.4.}

\begin{figure}
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\includegraphics[width=\textwidth]{fig1.32.png}
\caption{substitution.}
\end{figure}

Inspired by these results and the report of Caulton et al. on the substitution of 1.3 with 1 equiv of NaOPh leading to a carbyn, Fogg et al. reported in 2002 on the reaction of 1.64 with 2 equiv of TIOC\textsubscript{6}F\textsubscript{5} to yield 1.70. This catalyst does not only exceed the activity of 1.68-1.69 but even obtains \textit{equal to superior} activity to 1.4 for the RCM of DEDAM with turnover numbers up to 40000 (with
200 000 equiv used) and full conversion with 0.05 mol% catalyst.\textsuperscript{xV} In 2004, Fogg et al. reported on the mixed ligand systems with one ‘phenoxy’ and one halide. The showpiece of this series is 1.71, which exhibits activity exceeding those for 1.4, 1.38 and 1.39.\textsuperscript{170} The substitution of pyridine in 1.71 by the more labile 3-bromopyridine to achieve 1.72 leads to even higher activity for the ROMP of CO and substituted norbornenes.\textsuperscript{171} A lower $k_p/k_i$ ratio than 1.71 leads to more quantitative initiation and lower PDI’s of polymers.\textsuperscript{171} Fogg et al. recently reported on the incorporation of bidentate pseudohalides in the catalysts 1.73-1.74.\textsuperscript{172} The substitution lead to a decrease in activity compared to 1.71. The less electron deficient chelate 5-ring in 1.74 proved to be more active than the chelate 6-ring in 1.73.\textsuperscript{172} Spek et al. reported in 1999 on the substitution of the chloride ligands of 1.3 with trifluoroacetic acid groups into a dimer structure with a H$_2$O molecule encapsulated.\textsuperscript{173} In a subsequent publication some variations were made on the acetate group, however, in all cases the activity dropped compared to the parent 1.3 for the RCM of diethyl diallylmalonate.\textsuperscript{174} Buchmeiser et al. picked up the research exchanging the chlorines of the Grubbs-Hoveyda catalyst 1.36 with trifluoroacetic acid and triflic acid groups. 1.75 is the best of the examined catalysts with TONs in the range of 1.4 and 1.36.\textsuperscript{175} Furthermore, 1.76 exhibits almost twice as high TOFs than its chloride analogue.\textsuperscript{92}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure133.png}
\caption{Active substituted catalysts.}
\end{figure}

Buchmeiser et al. examined the influence of the length of the fluoroalkyl chain in complexes analogue to 1.75 observing an increase in TON for an increase in chain length.\textsuperscript{176} Unfortunately, TONs remained under those of the 2\textsuperscript{nd} generation Grubbs-Hoveyda catalyst 1.36.\textsuperscript{176} Rather contradictory to Fogg’s results\textsuperscript{169}, the substitution with -OC$_6$F$_5$ in complexes of type 1.75 led to a 10 fold decrease of TONs for the RCM of DEDAM (Diethyl diallylmalonate) compared to the parent 1.36 and 1.4. Actually the isopropoxystyrene fragment should even increase stability, but on the other hand Grubbs

\textsuperscript{xV} Conversion of RCM is generally followed as a function of time with 1-5 mol% catalyst and the activities of the catalysts are compared to the speed of full conversion (or incomplete conversion). This is in most cases irrelevant information. However, a test where the total turnover capacity of the catalyst is depicted or a kinetic plot with low catalyst loading, seem more objective criteria since a catalyst - especially those used here - is an expensive material and kinetic tests for TONs of 20 have little value for practical applications. The same holds for kinetic ROMP tests of COD (300-1000 equiv) compared to practical applications where DCPD is to be used in at least 20 000 equiv.
et al. have reported on the decrease in TON of 1.36 compared to 1.4 for the RCM of tetrasubstituted DEDAM.\textsuperscript{88,176} Fröhlich et al. substituted 1.4 with 2 equivalents of silver 2-pyridine-carboxylate. The resulting catalyst is only active for RCM after HCl activation.\textsuperscript{177} An ingenious, innovative approach was presented by Piers et al. resulting in the 14 electron species 1.77 that is the fastest initiating species synthesized up to now for the RCM of DEDAM.\textsuperscript{178} The introduction of steric bulk through the carbene in the 4 coordinative 1.77 as a Hoveyda-mimic has proven superior to the introduction of sterical alkoxy-ligands (1.68-1.70) onto a 14 electron species.

![Figure 1.34: 14 electron Grubbs complex.](image)

### 1.7 Solvent tolerant catalysis

Since functional group tolerance is one of the paramount advantages of ruthenium catalysts compared to their tungsten and molybdenum counterparts, the adoption of these catalysts to challenging solvents such as methanol, water, ionic liquids or fluorous solvents\textsuperscript{179} has been of great interest for practical applications. This causes advantages as environment-friendly solvents, high recyclability and low ruthenium residues. In 1996, Grubbs et al. synthesized a series of water soluble phosphine salts\textsuperscript{180} for substitution on Ru(Cl)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}CHPh to obtain 1.78-1.79. These catalysts show good activity for the ROMP of water-soluble norbornenes.\textsuperscript{181} Since hydroxide ions rapidly decompose the catalysts in aqueous media, small amounts of acid were added which accelerate the reaction due to phosphine scavenging.\textsuperscript{182} Unexpectedly, the propagating species are stable for months in solution, in contrast to the initiators 1.78-1.79, which decompose over several days in acid solution and even slowly in the solid state.\textsuperscript{182,181} Grubbs et al. propose that H\textsubscript{2}O, generally seen as a hazard for Grubbs catalysts, stabilizes the active species after the addition of acid which causes phosphine dissociation. This coordination effect in 1.80 disables bimolecular decomposition.\textsuperscript{182} RCM and CM should be the main target for applications in protic solvents, however, RCM of \(\alpha,\omega\)-dienes as DEDAM in methanol cannot be performed due to fast decomposition of the methyldiene species, and CM may be anticipated to fail.

\textsuperscript{xvi} Furthermore, it is interesting to note that reaction conditions play an important role in the comparison of catalysts and that straightforward comparison is not always evident. In the last example Buchmeiser et al. first reported on the similar TON’s for 1.36 and 1.75 (1500 and 1400) for a 2 hours reaction with 0.05 mol% of catalyst (75% and 70%) conversion\textsuperscript{(175)} Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. Chemistry-\textit{a} European Journal \textbf{2004}, \textit{10}, 777-784. In the subsequent publication, they compare the catalysts for an 18 hour reaction with 0.02 mol% of catalyst to find that respective TON’s are 4550 and 2150 with conversions of 91% and 43% \textsuperscript{(176)} Halbach, T. S.; Mix, S.; Fischer, D.; Maechling, S.; Krause, J. O.; Sievers, C.; Blechert, S.; Nuyken, O.; Buchmeiser, M. R. \textit{Journal of Organic Chemistry} \textbf{2005}, \textit{70}, 4687-4694. Data as such are rather hard to handle if one does not even standardize tests within the research group.
for the same reason. RCM with a substrate that has at least one internal olefin leads to moderate yields due to the inhibition of this methyldiene formation.

![Chemical structures](image)

**Figure 1.35:** Grubbs catalysts with ionic phosphine.

Blechert et al. reported in 2002 on the efficient RCM and CM of various substrates using 1.36 in methanol. Unlike 1.3 and 1.4, 1.36 dissolves substantially in methanol after which the reaction can proceed. Furthermore, a PEG resin was inserted to the isopropoxystyrene fragment in 1.81, similar to an earlier immobilisation of Yao et al., which performs well for the RCM in aqueous media. Grubbs et al. incorporated a PEG tail on IMES to produce 1.82. This catalyst shows only moderate activity for RCM in methanol, yet the ROMP in water shows fair conversion after the addition of HCl. Introduction of PEG into the backbone of H$_2$IMES leads to 1.83 which is a highly potent catalyst for ROMP, RCM and CM in aqueous media, superior to both 1.81-1.82.

![Chemical structures](image)

**Figure 1.36:** PEG substituted catalysts.

Beside methanol and water, ionic liquids are favourable solvents for practical applications in homogeneous catalysis because they present excellent properties such as good stability, nonvolatility and most importantly easy separation and recycling of the catalyst. Initial attempts consisted of using 1.3 and 1.91 in BMI-PF$_6$ (1-butyl-3-methyl-imidazolium hexafluorophosphate) but proved to be inefficient due to catalyst extraction in the organic phase or catalyst decomposition. The use of ionic liquids as additives for the metathesis of 1-octene gives good results. Mauduit et al. prepared 1.84 which performs the RCM of several substrates in BMI-PF$_6$ in good yields and can easily be
recycled and used in subsequent runs.\textsuperscript{189} The H\textsubscript{2}IMES analogue \textbf{1.85} even outperforms \textbf{1.84} and the average ruthenium residue over 8 runs is only 7.3 ppm.\textsuperscript{193} Optimal results are obtained with mixtures of BMI-PF\textsubscript{6} and toluene.\textsuperscript{194} A very similar catalyst \textbf{1.86} was developed leading to comparable results in BMI-PF\textsubscript{6}-CH\textsubscript{2}Cl\textsubscript{2} mixtures.\textsuperscript{195} Furthermore 2 pyridinium complexes like \textbf{1.87} were synthesized by Mauduit et al. and evaluated for RCM.\textsuperscript{196} However they are not able to match the activity of the parent \textbf{1.85}.\textsuperscript{196}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{catalysts.png}
\caption{Catalysts for usage in ionic liquids.}
\end{figure}

In Chapter 4 we will introduce, very successfully, our Schiff base catalysts for the RCM of DEDAM in methanol.

\section{1.8 Alternative homogeneous ruthenium catalysts}

One major sidetrack in ruthenium metathesis catalysts consists of bidentate phosphines. In 1999 Hofmann et al. reported on the synthesis of \textbf{1.88}\textsuperscript{197} and \textbf{1.89}\textsuperscript{198}. While \textbf{1.88} shows modest activity for the ROMP of CO, \textbf{1.89} clearly outperforms \textbf{1.3}, the best Ru catalyst at that time.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{biphosphine.png}
\caption{Biphosphine catalysts.}
\end{figure}

Hereby inspired Fogg et al. replaced the dtbpm (bis(di-tert-butylphsophino)methane) in \textbf{1.88} by BINAP (2,2’-bis(diphenyolphosphino)-1,1’-binaphtyl), dppb (1,4-Bis(diphenyolphosphino)butane) and dcybp (1,4-bis(dicyclohexylphosphino)butane) for several in situ experiments.\textsuperscript{199} All of these ligands outperformed the dtbpm from Hofmann et al. and low polydispersity polymers were achieved. The activity increases from dcybp to dppb to BINAP.\textsuperscript{199}
Hofmann et al. concluded that increasing the bite angle to dbpe and the introduction of weak coordinating ligands like CF$_3$COO$^-$/OTf$^-$ in 1.89 decreases activity. While 1.89 is much more active for the ROMP of CO compared to 1.4, the ROMP of COD has a similar rate compared to 1.4. Another important development is the synthesis of catalysts derived from the [RuCl$_2$(p-cymene)]$_2$ dimer. Noels et al. reported in 1992 on Ru(p-cymene)Cl$_3$PCy$_3$ (1.90) for the polymerization of norbornene and the same was done by Hafner et al. for DCPD in 1997. Noels et al. reported in 1997 on the ROMP promoted by in situ systems of [RuCl$_2$(arene)]$_2$, PR$_3$ and trimethyl silyl diazomethane (TMSD). The polymerization rate is increased spectacular by the introduction of TMSD. Fürstner et al. found that radiation under neon light in refluxing CH$_2$Cl$_2$ can also initiate the reaction. The first isolated carbenes of this catalyst type (1.91) were prepared by Fürstner et al. in 1998. Further optimization showed that PCy$_3$ is the most suitable phosphine and OTf$^-$ the best counterion.

Nolan et al. introduced IMES and IPr as alternatives for the PCy$_3$ in complexes 1.92 and 1.93 (compared to 1.90-1.91). 1.92 exhibits better activity for the RCM of DEDAM than 1.90 and 1.93 is even a better promoter for that reaction. Syntheses of the saturated NHC substituted analogues of 1.90 were already reported by Dixneuf et al. in 1996, however no metathesis experiments were then performed. In 2003 Dixneuf et al. also reported on the syntheses of chelating saturated imidazole complexes such as 1.94, which were tested for RCM. It was found that the species with an allenylidene is more active than its precursor 1.94. Interestingly, the H$_2$IMES substituted 1.95, a logical next step, has never been reported and many attempts of our group, and probably others, to obtain it have failed. Dixneuf et al. reported on the in situ ROMP with [RuCl$_2$(p-cymene)]$_2$, H$_2$IMES-HCl and Cs$_2$CO$_3$. Furthermore, Delaude et al. anticipated that the release of chloroform or alcohol, using the classical NHC-activation methods renders them unsuitable for in situ catalytic applications and introduced the CO$_2$-adducts developed by Louie et al.

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**Figure 1.39:** Special biphosphines.

XIX This line of technology has been under appreciated in academic research and many new approaches are still available such as the preparation of the dimeric cationic species from Fogg’s biphosphine catalyst and especially the introduction of bidentate carbene ligands (regarding the huge improvements they were able to induce in the classical Grubbs catalysts).

XX Yet their in situ techniques are performed without confirmation if their in situ catalysts – which are unambiguously depicted (1.95) – are actually formed. With the know-how we have developed in our lab, and especially by the work of N. Ledoux, it is safe to say that this logic is merely wishful thinking and that the in situ catalyst must have a different structure.
Olefin metathesis

In 2003 Dixneuf et al. were able to transform the allenylidene 1.91 into the indenylidene 1.96. This catalyst outperforms 1.4 for the polymerization of CO and is very promising for ROMP, RCM and ADMET.\textsuperscript{215} In a mechanistical study, it was shown that the indenylidene cannot be formed with 1.93 due to the high donor capacity of IMES which causes a disfavour of an aromatic electrophilic substitution. On the other hand a strong electron donor is favourable for fast polymerization.\textsuperscript{216} The methyl-phenyl allenylidene analogue of 1.91 could not be transformed into an indenylidene.\textsuperscript{216} Furthermore Dixneuf et al. postulate that full decooordination of the p-cymene unit is necessary to generate the active species.\textsuperscript{216}

The reaction of [RuCl\textsubscript{2}(p-cymene)]\textsubscript{2} with 1.3 affords a bimetallic species 1.97, which reacts faster than 1.3 for the polymerization of CO. Similar bimetallic Grubbs catalysts were formed with [OsCl\textsubscript{2}(p-cymene)]\textsubscript{2} and [Rh(\textsuperscript{t}Bu\textsubscript{2}Cp)Cl\textsubscript{2}], showing even higher reactivities.\textsuperscript{217} A major drawback in respect to practical applications is the use of a second metal atom for only one catalytic centre. However, this technology was later further extrapolated with Ru=CHPh(PC\textsubscript{y}3)(Cl)(IC\textsubscript{y})\textsuperscript{77} to form 1.98. Moreover, it was claimed that Schiff base substituted Grubbs catalysts which form the complexes like 1.99\textsuperscript{218} were also prepared (For further comment, see Chapter 4).

\begin{figure}
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\includegraphics[width=\textwidth]{figure1.40}
\caption{p-cymene substituted catalysts.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.41}
\caption{Bimetallic p-cymene catalysts.}
\end{figure}
Many other approaches have been described for the ruthenium catalyzed metathesis\textsuperscript{173,174,211,219-221,167}. However none of these were so effective as the Grubbs catalysts and the other reviewed systems. Furthermore, the immobilization of the catalysts for practical applications in RCM and CM has received great attention, however, a detailed discussion falls beyond the scope of this work.

1.9 Outlook

Metathesis has made enormous progress during the last decades resulting in complex organometallic ruthenium and molybdenum catalysts. This chapter has illustrated the great variety of Ru-catalysts which have already been developed.

The challenge still remains in extrapolating the mechanistical insights of these catalysts on to cheaper 3\textsuperscript{rd} period transition metals. On the other hand this challenge might remain unanswered since the smaller 3\textsuperscript{rd} period orbitals might not be able to produce the desired energetical and geometrical conformations for a metathesis reaction. The task might be hard and long because for the ruthenium systems, for which RuCl\textsubscript{3} was found to be an initiator 40 years ago, hundreds of Ru-carbenes were synthesized before an active catalyst was engineered.

The third chapter will deal with the mechanistic understanding of the metathesis reaction, especially from the Grubbs-type catalyst viewpoint. It will become clear that this task is not straightforward and arithmetic. In order to obtain such conceptual understanding, one must first understand the nature of the metal-ligand bond. Therefore, we shall first discuss contemporary insights into the metal-ligand bond in chapter 2.

1. Appendix 1: Subtleties in olefin metathesis: An alkenyl-ruthenium complex

Dixneuf et al. presented in 2006\textsuperscript{222} a good example on the subtlety of what a carbene really is and synthesized 1.100 which shows a vinylic \textsuperscript{13}C NMR resonance at $\delta = 154.71$ ppm. Although the vinylic carbon possesses a $\pi$-orbital, that orbital cannot conjugate with Ru, since the orbital already forms a double bond with the adjacent carbon.

![Figure 1.42: Alkenyl vs. carbene species](image)

In 1.101 (allylidene) and 1.3 (benzylidene), the vinyl and phenyl moieties stand as separate $\pi$-units. However, in both 1.101 and 1.3 some stabilisation of the electrophilic carbene $\pi$-orbital through conjugation with the $\pi$-system is possible and \textsuperscript{13}C NMR spectra show resonances at respectively $\delta =$
296 ppm and $\delta = 294.7$ ppm. Whereas in 1.102 (vinylidene) no conjugation of the carbene is possible and the carbene resonates at $\delta = 327.4$ ppm in $^{13}$C NMR.

1. Appendix 2: Subtleties in olefin metathesis: ROMP vs. RCM and CM in the Mol-catalyst

Mol et al. published in 2003 on the synthesis of $\text{H}_2\text{IAd}$ (1,3-di(1-adamantyl)-4,5-dihydroimidazol-2-ylidene) and the mixed ligand $\text{H}_2\text{IAdMes}$ (1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene$)^{99}$. Although it was not possible to substitute $\text{H}_2\text{IAd}$ on the Grubbs catalyst due to steric crowding, the incorporation of $\text{H}_2\text{IAdMes}$ forming 1.103 was successful. The resulting complex is extremely crowded and an ORTEP plot of a single crystal shows an adamantyl carbon trans to the benzylidene, 2.883 Å away from ruthenium centre with the rest of the adamantyl group crowding the space trans to the benzylidene.

Figure 1.43: Proposed mechanism of the adamantyl-Mol catalyst.

The complex exhibits absolutely no activity for the self metathesis of 1-octene and the RCM of DEDAM. However, it shows activity for the ROMP of 2-norbornene and even surpasses the initiation rate (reaction with ethyl vinyl ether) of 1.4. The authors suggest that the steric bulk of the adamantyl is responsible for the lack of reactivity and propose mechanism B for productive metathesis since only in that mechanism the steric blocking of the adamantyl group seems to hinder one of the conformations in the cycle. Mol et al. continue with ‘the poor catalytic activity of complex $\text{7}^{\text{XXI}}$ would tentatively suggest that B may be the most important intermediate, since only this possibility requires the position trans to the benzylidene to be unobstructed for the rearrangement required for the coordination of the olefin’. However the argument shows inaccuracies since the NHC-ligand cannot rotate due to steric influence of the chlorines, in order to have successful metathesis the position trans to the original carbene also has to be unobstructed for path C.

$^{\text{XXI}}$ Here 1.103
Yet this mechanism does not require rearrangements with concomitant high energy barriers. The activity can however easily be explained as follows; due to the steric crowding of the adamantyl group after cyclobutane formation the reaction cannot proceed to product formation but degenerates. However, when a substantial energy gain can be obtained by the formation of an ethyl vinyl ether carbene or by the release of ring strain, some more exotic pathways may become accessible. The energetically premium of a carbene not perpendicular to the Cl-Cl-NHC plane can be overcome or some other rearrangement like a cyclobutane rotation with subsequent chlorine migration may be possible.\(^{XXII}\) Furthermore, the 1\(^{st}\) order decomposition of methylidene species is well documented and the absence of RCM, CM and SM activity may stem from enhanced decomposition of the methylidene in contact with the adamantyl group.

References


\(^{XXII}\) Chen et al. showed that for strong exothermic reactions (like ethyl vinyl ether) with 1,3, the rotation of the PCy\(_3\) ligand i.e. normally the Rate Limiting Stap (RLS), can occur at a later point in the cycle and consequently avoid being the RLS in the reaction. (107) Adlhart, C.; Chen, P. *Journal of the American Chemical Society* 2004, *126*, 3496-3510.)


Olefin metathesis

(94) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *Journal of the American Chemical Society* 2001, 123, 749-750.
(102) G.C., V.; Grubbs, R. H. *Organometallics* 2007, 26, 2469-2472.
Olefin metathesis


Olefin metathesis


Olefin metathesis


Olefin metathesis
Chapter 2

Contemporary organometallic chemistry:
The metal-carbene, metal-phosphine
and metal-olefin bond

The goal of this second chapter is to present an overview of the various ligands in organometallic chemistry as well as their effect in organometallic complexes. In this task we will focus our attention on those ligands relevant for olefin metathesis.

For several reasons, most part of our overview and discussion concerns carbenes. Two carbenes of a different nature are present in the most efficient ruthenium catalysts for metathesis. One of the carbenes is the active site of the catalyst. The other one plays a quintessential role in the activity and stability of the catalyst. Carbenes have also been reported to be excellent ligands or key-intermediates in many other important homogeneous catalytic transformations such as Buchwald-Hartwig couplings, Suzuki-Miyaura couplings, asymmetric hydrogenation\(^1\), cyclopropanation and many others.

The carbene represents a highly unusual form of the carbon atom. Furthermore, the development of practical syntheses and fundamental understanding of the stabilization and the role in organometallic complexes of these species has made enormous progress in recent years and has been in the very centre of organometallic chemistry and catalysis.

Before the “NHC-revolution”, phosphines had been widely applied in organometallic chemistry and catalysis. This has spurred the development in the understanding of the metal-phosphine bond. Olefin transformations represent the lions share of catalytic processes and a thorough description of the metal-olefin bond is of crucial importance for the understanding of the metathesis process.

As starting knowledge for this chapter, one should have knowledge of the DCD (Dewar-Chatt-Duncanson) model (also called donor-acceptor model) for ligands such as CN\(^-\), NO\(^+\), CO, CS, olefins, phosphines, alkynes and carbenes. In this model, the metal-ligand bond is postulated to be the result of a 2-electron donation from the ligand with \(\sigma\)-symmetry and a 2-electron backbond from the metal to the ligand with \(\pi\)-symmetry. We will show that the classical DCD bond description is both limited and
Contemporary organometallic chemistry

outdated and should be complemented with more recent methodologies based on DFT (Density Functional Theory). EDA (Energy Decomposition Analysis) developed by Morokuma\textsuperscript{2,3} and by Ziegler\textsuperscript{4-6} and CDA\textsuperscript{7} (Charge Decomposition Analysis) are more complete descriptors of the metal-ligand bond realm. These tools have been widely applied by Frenking et al. in an attempt to redefine the organometallic bond. Furthermore, NBO\textsuperscript{8,9} (Natural Bond Orbital) is often used in the description of organometallic complexes.

2.1  Introduction to stable free carbenes

The first carbenes in organometallic species were reported in the 60’s by Fischer. Only in 1988, Bertrand et al. presented the synthesis of the first free stable (nucleophilic) carbene ([Bis(diisopropylamino)phosphine]trimethyl-silylcarbene \textsuperscript{2.1}10,11. This is highly unrecognized and the dawn of free stable (nucleophilic) carbenes is mostly credited to the landmark publication of Arduengo et al. in 1991 on the first stable N-heterocyclic carbene (NHC) 1,3-di-adamantyl-imidazol-2-ylidene \textsuperscript{2.2} which the crystal structure was reported.\textsuperscript{12} The lack of recognition for the Bertrand discovery stems from the fact that all practical applications in organometallic chemistry and catalysis have been performed with NHC-ligands, which were pioneered by Arduengo. Arduengo et al. published in 1992 on the synthesis of a series (unsaturated) NHCs such as IMES\textsuperscript{13} (\textsuperscript{2.3}) and in 1995 on the first saturated NHC\textsuperscript{14} 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (H\textsubscript{2}IMES; \textsuperscript{2.4}) which would later become the standard NHC on the Grubbs 2\textsuperscript{nd} generation catalyst. The preparation of NHC-ligands with aromatic substituents had been pioneered by Wanzlick et al., who synthesized some metal-NHC complexes a few decades before. However, the preparation of free carbenes was not successful at that time.\textsuperscript{15}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure21.png}
\caption{The first stable singlet carbenes.}
\end{figure}

By definition, a carbene is a carbon with 2 substituents and 6 electrons in the valence scale. Consequently two conformations are possible. The carbene can be either sp or sp\textsuperscript{2} hybridized, though the latter is the only practical important hybridization. A singlet carbene is a carbene in which the two non-bonded electrons occupy the same orbital (typically sp\textsuperscript{2} orbital and also called $\sigma$) while another orbital (typically p and also called $\pi$ orbital) remains unoccupied. This conformation is dominant if the difference between both orbitals is 2 eV or higher. A triplet conformation becomes the ground state when the energy difference falls below 1.5 eV.\textsuperscript{16} The triplet carbene is characterized by two orbitals occupied with a single electron; It generally shows higher reactivity than a singlet carbene due to its radical character. This has lead to far lesser reports on stable species. \textsuperscript{2.1-2.4} as well as most of

\textsuperscript{1}Evidence for fast equilibration between singlet and triplet carbenes has been reported as for fluorenylidene with a singlet ground state of only 1.1 kcal/mol above the triplet ground state.((17) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. \textit{Journal of the American Chemical Society} \textbf{1983}, \textit{105}, 6833-6845.)
the other carbenes (unless mentioned otherwise) in this chapter are all singlet carbenes. These singlet carbenes are characterized by smaller bond angles than their triplet counterparts.\textsuperscript{\textsuperscript{8}}

Harrison et al. showed that the electronegativity of the substituents \( X \) in \( :CX_2 \) play a major role and state ‘that in particular we find that very electronegative substituents (e.g. F) favor a singlet ground state while very electropositive (EP) substituents (e.g. Li) favor the triplet’.\textsuperscript{\textsuperscript{20}} This is applicable on the inductive effects for which electronegative (EN) substituents will cause a decrease in the energy level of the \( \sigma \)-orbital due to the lower lying \( p \)-orbitals of the EN element. An additional argument is that according to Bent’s rule\textsuperscript{\textsuperscript{21}} the atomic s-character of C should concentrate on electropositive substituents (for which a free electron pair is considered an electropositive substituent). With increasing EN of the substituents, the interaction of the carbon-\( p \)-orbitals with the substituents should increase, leaving a higher s character with lower energy to the \( \sigma \)-lone pair.

\[
\begin{align*}
\text{C} & \quad b_1 \quad \text{p-pi} \\
\sigma & \quad a_1 \quad \text{Energy gap} \\
\quad & \quad b_2 \\
\quad & \quad a_1 \\
\quad & \quad X \\
\quad & \quad \text{X} = \text{EN}
\end{align*}
\]

\textbf{Figure 2.2:} Carbene with EN and EP substituent.\textsuperscript{\textsuperscript{22}}

Mesomeric effects also play a major role in the carbene stabilization and can either be donating, withdrawing or mixed. The donating mesomeric group increases the energy level of the \( p_x \) and hence increases the S-T (Singlet-Triplet) gap. The nitrogen substituents on the NHC ligands clearly exhibit \( \sigma \)-withdrawing and \( \pi \)-donating character, moreover, the carbene is forced in a bent structure. These effects are highly compatible and are responsible for the high S-T gaps of NHCs. The donation-backdonation is also reminiscent of the organometallic dative bond.\textsuperscript{\textsuperscript{23}} A carbene with mesomeric withdrawing groups (e.g. Li-C-Li) is mostly predicted to be linear and the mixed systems are quasi linear. (see appendix 1)\textsuperscript{\textsuperscript{22}}

Besides electronic stabilization, steric effects play a crucial effect in the (mostly kinetic) stabilization. Excessive steric bulk around the carbene as in 2.2 protects the carbene from attacks of electrophiles and especially against dimerization.

\footnote{The \( \text{CH}_2 \) triplet has a predicted bond angle of 138°, while the singlet has a predicted bond angle of 102°. It can be postulated that factors decreasing the bond angle should increase the tendency for a singlet ground state. Steric interactions in 2.2 and \( :C(-\text{t-Bu})_2 \) are believed to open the bond angle and consequently raise the singlet state energy above the triplet state. (18) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. \textit{Ibid.}1982, 104, 2526-2327 (19) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M. \textit{Journal of the American Chemical Society} 1986, 108, 4232-4233.)}
A study on the basicity of NHCs has shown that substitution on the nitrogen of an alkyl group by a phenyl group significantly reduces basicity, which is likely due to the electron withdrawing effect of the phenyl rings. The saturation of the carbene and substitution on the backbone induce a slightly increased basicity, while the transformation to a 6-ring carbene or an acyclic carbene significantly increases basicity.

An experimental criterion to separate singlet from triplet carbenes can be put as followed: Triplet carbenes perform hydrogen abstraction and non-stereospecific cyclopropanation. Singlet carbenes on the other hand show ylide formation, stereospecific cyclopropanation and react with alcohols to yield ethers.

### 2.2 Synthetic tricks for the synthesis and application of diaminocarbenes

Of all the carbenes, only NHCs have been widely used as ligands in catalytic applications so far. A review of the applications and a full overview of all the NHCs (of which much were handled in chapter 1) will not be discussed here. However, in the interest of the synthetic chemist we will focus on an overview of synthetic tricks for practical applications.

In diaminocarbenes, the carbene shows a double bond character with the nitrogen leading to a decreased C-N bond length (1.33-1.38 Å). In mixed systems with an oxygen or sulfur substituent only the C-N bond shows considerable double bond character. The C-N-C angle is predicted in the range of 98°-105° for NHCs and 111°-113° for acyclic diamino carbenes.

The 13C NMR shift for the unsaturated carbenes is approximately 205-220 ppm and 15-25 ppm more downfield for the saturated analogues. The 13C NMR shifts for acyclic carbenes are found in the range of 235-300 ppm. The estimated S-T gap (singlet-triplet gap) for saturated model systems is 69 kcal/mol, 85 kcal/mol for the unsaturated and 59 kcal/mol for the acyclic carbenes. The preparation of unsaturated carbene precursors can be accomplished by different methodologies, which are depicted below. It should be noted that the coupling of readily available 1-substituted imidazoles into bidentate or tridentate ligands has become an easy procedure to attain a wide spectrum of reactions.

---

**Figure 2.3: Mesomeric effects in carbenes.**

[X = mesomere donating]

[X = mesomere withdrawing]

[X = mesomere withdrawing + mesomere donating]

---

[III] The basicity in H2O of the NHCs is on average almost 20 pKa units higher than for PCy3.

[IV] S-T gap for 2.2 = 79.6 kcal/mol; S-T gap for (tBu-C-N(iPr)2 = 26.7 kcal/mol
of multidentate ligands.\textsuperscript{27,28} The free carbenes can be obtained by reaction with NaH in THF or NH\textsubscript{3} \textsuperscript{12,26}, or more practically by reaction with M-O-t-Bu\textsuperscript{1}.

The preparation of symmetrical saturated 5-ring NHCs is classically accomplished by formation of a di-imine, followed by a reduction to the di-amine salt and ring closing of the intermediate, mostly performed by triethylortoformiate.\textsuperscript{29} The six ring symmetrical analogues were synthesized using two different methods.\textsuperscript{30,31} The synthesis of seven membered NHCs were reported by Stahl et al.\textsuperscript{32,33}, who were not able to synthesize the mesitylene analogues. Bertrand et al. showed that via an easy synthetic trick these compounds are readily available (vide infra).\textsuperscript{34} Mol et al., Grubbs et al., Blechert et al., Hahn et al.\textsuperscript{35} and Collins et al.\textsuperscript{36} published on methods for the preparation of asymmetrical saturated NHCs.\textsuperscript{35,37-40} Furthermore, a method to develop asymmetrical precursors for saturated NHC-salt was described.\textsuperscript{41}

\textbf{Figure 2.4:} Preparation of unsaturated carbenes.
Preparation of TM (Transition Metal) substituted saturated carbenes can be obtained by heating the precursor with KO-t-Bu. However, preferential methods are deprotonation with KHMDS (potassium hexamethyl disilylamide) or LiHMDS which directly provide the free carbene. An alternative method involves deprotection of thiones. Furthermore, there has been a great deal of interest in
preparative methods for carbene transfer without the involvement of a base. This has led to the development of chloroform adducts\textsuperscript{43,44,46}, pentafluorophenyl adducts\textsuperscript{47}, CO\textsubscript{2}\textsuperscript{48-50}-adducts and triethylborane adducts\textsuperscript{51}. On the other hand, the strategy of transmetallation via AgO\textsubscript{2} is probably the most applied alternative mode of coordination.\textsuperscript{27,52} Oxidative addition to zero-valent metal complexes is also well documented.\textsuperscript{53-57}

\textbf{Figure 2.6:} Preparation of carbene complexes.
Recently, Bertrand et al. reported on a versatile route for preparing NHCs adopted from their earlier work on CAACs (Cyclic Alkyl Amino Carbenes). The method consists of the preparation of a Li-salt which then reacts with dibromine. This procedure was then heavily extrapolated to the syntheses of various carbenes.

It should be noted that some very peculiar members of the NHC-family have already been synthesized. First, the use of bis-hydrazones in 2.5 has led to an increase of the donor capacity of the NHC compared to other imidazole-2-ylidenes. Grubbs et al. prepared an atypical four membered NHC 2.6. Roesler et al. published on a N-Heterocyclic carbene 2.7 with a diboron backbone, which shows increased donor capacity compared to classical NHCs. Bertrand et al. prepared a series of six-membered boron-NHCs 2.8 which also show an increased donor capacity compared to classical NHCs. Roesler et al. prepared a six membered anionic boron-NHC 2.9 which should provide higher $\sigma$-donor capacity and lower $\pi$-accepting capacity than normal NHCs.
Alder et al. pioneered the work on acyclic carbenes synthesizing the bis(diisopropylamino)carbene.\textsuperscript{63,64} Herrmann et al. reported on the synthesis of asymmetrical carbenes\textsuperscript{65,66} and the development of an easy method to obtain a library of symmetrical acyclic carbenes\textsuperscript{67}. Although the synthetic procedures presented cover a whole range of the acyclic diaminocarbene spectrum, no complexes with aryl substitutes have been reported while these would present a possible target as ligands for olefin metathesis.

\begin{center}
\includegraphics[width=\textwidth]{figure2.9.png}
\end{center}

\textbf{Figure 2.9:} Preparation of acyclic carbene precursors.

### 2.3 Bertrand carbenes

A tremendous explosion in the applications of NHCs over the last decade has led to a high visibility of these ligands. In the shadows of these developments, the Bertrand group has almost single-handedly developed a wide variety of stable atypical (non-diamino) carbenes and substituted those on metal complexes. Through these series of ingenious syntheses the scope on the nature of stable carbenes has been expanded to a higher level. We assume that the low applicability of these ligands has been caused by their much later development, the more difficult synthetic procedures, paradoxically the high diversity concomitant with the lack of a standard causing less visibility and lower S-T gaps, which should render these ligands more reactive and less suitable as stable ligands (cf. acyclic diaminocarbenes as ligands for the Grubbs catalyst).

In 2000, over a decade after the first publication on a stable carbene 2.1, Bertrand et al. reported on the first single crystal of a (phosphino)(silyl) push-pull carbene 2.10.\textsuperscript{68} In 2.10, the phosphor atom is in a planar environment and it shows a small (1.532 Å) C-P distance.\textsuperscript{68} The structure of 2.10 is best described as a phosphorous vinyl ylide.\textsuperscript{68,69} That same year, their group also reported on the synthesis of a (phosphino)(alkyl)carbene 2.11 and a stable (phosphino)(aryl)carbene 2.12.\textsuperscript{70} In 2.11, the phosphor atom shows a weak +I and +M character while the CF\textsubscript{3} group displays a −I character. The carbene is a transient singlet with a nucleophilic character, which is stabilized by introducing a −I, -M aromatic group in 2.12.\textsuperscript{70} The aromatic group in 2.12 is oriented perpendicular to the CPNN plane allowing maximal delocalization of the carbene lone pair into the phenyl ring.\textsuperscript{70}

One year later, Bertrand et al. reported on (aryl)(amino)carbenes of which 2.13 is a stable variant.\textsuperscript{71} 2.13 shows a shorter C-N distance (1.283 Å) than the diaminocarbenes (1.32-1.37 Å) which indicates the increased double bond character.\textsuperscript{71} The aryl ring acts, in contrast to the earlier published 2.12, as a spectator substituent.\textsuperscript{71} The lack of interaction is also evidenced by the dramatically shortened carbene angle in 2.13 (121°) compared to 2.12 (162°).\textsuperscript{71} In 2.12, the wide angle facilitates delocalization of the carbene lone pair, which almost orientates coplanar to the aryl ring.\textsuperscript{72} Furthermore, the size of this angle is determined by steric strain and when the N(i-Pr)\textsubscript{2} groups are replaced with NH\textsubscript{2} groups in 2.12,
the NCC angle decreases and the \( C_{\text{carb}}-C_{\text{ipso}} \) bond distance increases. However, this is not sufficient because electronic activation of the aryl ring seems to play a major factor for structure determination. \( \textbf{2.14} \), the mesityl analogue of \( \textbf{2.12} \), shows excellent stability but no evidence for conjugation with the mesityl group is observed since the carbene shows an angle of 148° (compared to 162° in \( \textbf{2.12} \)) and the \( C_{\text{carb}}-C_{\text{ipso}} \) bond length of \( \textbf{2.14} \) is 1.438 Å (compared to 1.390 Å in \( \textbf{2.12} \)).\(^7\) It was noted that the aryl conjugation through an electron withdrawing group can import some extra stability upon the carbene centre.\(^7\) The pentafluorophenyl analogue of \( \textbf{2.12} \), where the fluorine groups have potential \( \pi \)-donor capacities, shows no conjugation with the vacant carbene orbital.\(^7\)

Bertrand et al. investigated diphosphinocarbocations. These structures are more difficult to synthesize since P has a decreased \( \pi \)-donor capacity (the inversion barrier for \( \text{PH}_3 \) is 37 kcal/mol compared to 5.8 for \( \text{kcal/mol NH}_3 \)). When a second phosphor donor is added to the carbocation there is only a stabilization of 12 kcal/mol compared to 44 kcal/mol for the addition of a second nitrogen donor. This difference is also visible in the inability to obtain a planar structure with increased \( \pi \)-delocalization. This lack in conjugation can additionally be rationalized by the contra-productivity of the simultaneous \( \sigma \)-donation from the phosphor.\(^7\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.10.png}
\caption{Bertrand carbenes: A.}
\end{figure}

Bertrand et al. showed that in contrast to the (phosphino)(silyl)carbenes which show no complexation with metal species, \( \textbf{2.12} \) shows special characteristics in organometallic chemistry.\(^7\) The strong phosphor donating capacity facilitates three bonding modes; phosphor coordination, carbene coordination or both in a metallacyclopropane.\(^7\)

The low sterically constrained (aryl)(amino)carbene \( \textbf{2.15} \) was developed by the Bertrand group and inserts, in contrast to \( \textbf{2.13} \), into the OH bond of \( \text{t-ButOH} \).\(^7\) \( \textbf{2.15} \) shows the ability of coordination with...
metal centres. The complexes have typical dianinocarbene metal compound characteristics but the $^{13}$C NMR resonance lies significantly downfield from those of diamino-carbene-rhodium complexes.\textsuperscript{VI} In 2002, Bertrand et al. reported on the (amino)(phosphino)carbene \textit{2.16}.\textsuperscript{77} The high pyramidalization and the long P-C bond (1.856 Å) length suggest that the phosphor substituent is merely a spectator ligand.\textsuperscript{77} Furthermore, in contrast to phosphinocarbenes, the carbene bond angle is acute, similar to aminocarbenes.\textsuperscript{77} The versatile \textit{2.16} coordinates to BF\textsubscript{3} through the carbene and to BH\textsubscript{3} through the phosphor.\textsuperscript{77} \textit{2.16} has proven to be an excellent precursor for substitution at the carbene centre.\textsuperscript{78} After methylation of the phosphor in \textit{2.16}, the phosphorous group becomes an excellent leaving group ideal for substitution.\textsuperscript{78} This can lead to new types of (amino)(sulfur)carbenes, (amino)(oxygen)carbenes and different types of (amino)(phosphino)carbenes.\textsuperscript{78}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure211.pdf}
\caption{Substitution on P,N-carbenes.}
\end{figure}

Bertrand showed that both \textit{2.16} and \textit{2.17} act as bidentate carbene-phosphino ligands in Rh-complexes displaying Rh-carbene and Rh-phosphine bond lengths in the typical range of normal Rh-NHC and Rh-P bond lengths.\textsuperscript{79} The Bertrand group used this substitution pathway to synthesize a relatively stable (amino)(silyl)carbene \textit{2.18}, which shows a small carbene angle (116°), a low S-T gap (20.9 kcal/mol)\textsuperscript{VII} and a very weak interaction of the carbene with the silicon.\textsuperscript{80} This is in agreement with the earlier observations that stabilization of the carbene with one nitrogen is sufficient.\textsuperscript{80} In a further expansion of the carbene technology, the Bertrand group investigated (amino)(alkyl)carbenes. \textit{2.19} was the first relatively stable member of this class.\textsuperscript{81} It shows stereospecific cyclopropanation analogous to (phosphino)(silyl)carbenes and in contrast to diamino-carbenes which show no cyclopropanation activity.\textsuperscript{81} Upon complexation, the carbene displays a shift very downfield in the $^{13}$C NMR spectrum but the Rh-C\textsubscript{carbene} distance lies well within the range of typical NHCs.\textsuperscript{81} The CO stretching frequencies suggest a donor capacity intermediary to NHCs and

\textsuperscript{VI} Bertrand et al. argued ‘This chemical shift is 50 ppm downfield [sic] from that of the free carbene, but still significantly upfield [sic] from those of the diamino-carbene-rhodium complexes (180-234 ppm)’ (65)

\textsuperscript{VII} Though this is still larger than the S-T gap for the analogue (phosphino)(silyl)carbene (4.2 kcal/mol).
acyclic diaminocarbenes.\textsuperscript{81} However, the S-T gap (26.7 kcal/mol) and the HOMO (-4.3 eV) seem very low and high respectively, compared to NHCs (79.6 kcal/mol and -6.4 eV) and acyclic carbenes.\textsuperscript{81, VIII}

A series of a Cyclic Alkyl Amino Carbene (CAAC) were prepared.\textsuperscript{82} These are expected to be more stable than their acyclic analogues in correspondence to diaminocarbenes.\textsuperscript{82} \textbf{2.20} is an excellent example of a CAAC which exhibits good steric congestion.\textsuperscript{82} Upon complexation, CO stretching frequencies suggest that \textbf{2.20} exhibits increased donor capacity compared to NHCs. Furthermore, complexes substituted with \textbf{2.20} were applied with great success in the α-arylation of carbonyls with arylchlorides.\textsuperscript{82}

![Figure 2.12: Bertrand carbenes: B.](image)

\textbf{2.20} has shown to coordinate in low coordinate transition metal complexes due to the high electron donor capacity and the generation of efficient steric bulk.\textsuperscript{83} Moreover, an increase in nucleophilicity and electrophilicity causes the (amino)(alkyl)carbenes to react with CO to form the corresponding ketenes with an amino substituent.\textsuperscript{84}

In 2005, Bertrand et al. prepared the first P-heterocyclic carbene \textbf{2.21}.\textsuperscript{85} Although the π-donor capacities of heavier elements can be expected to be at least as high as their second period siblings, the phosphor generally acts as a weaker donor than nitrogen due to its preference for pyramidalization in spite of planar environment.\textsuperscript{86} Bertrand et al. circumvented this problem by cyclizing the phosphorous carbene and by introducing highly sterical demanding ligands which resulted in a nearly planar environment (353° and 348° as combined P-angles) for phosphor and consequently high π-donation and short C-P bond distances (1.67 Å and 1.71 Å compared to a P-C single bond of > 1.80 Å).\textsuperscript{85} Furthermore, the CO stretching frequencies in metal-complexes suggest \textbf{2.21} is almost as electron donating as the acyclic bis(diisopropylamino)carbene.\textsuperscript{85}

In 2006, Bertrand et al. showed that with the cleavage of the P-C bond in C-amino phosphorous ylides, easy access is obtained to bidentate carbene-phosphor ligands.\textsuperscript{87}

### 2.4 Studies on the nature of carbenes

#### 2.4.1 Free carbenes

In this part we will discuss the theoretical investigations on carbenes in detail, starting with the stability of the free carbenes. In 1992, Goddard III et al. calculated the S-T gaps of different simple carbenes.\textsuperscript{23} The singlet stability increases with the incorporation of EN groups able to participate in the

\footnote{VIII The NCC angle of 120° is in the typical range for aminocarbenes.}
σ-withdrawing, π-donating process. For example CF₂, CH₂ and CSi₂ were respectively calculated to have a S-T gap of 56 kcal/mol, -10 kcal/mol and -20 kcal/mol (positive value for more stable singlet carbenes). The bond angle of the singlet carbene is always smaller than for the triplet carbene and the tendency for EN atoms to prefer the smaller bond angles (singlet) is in accordance with Bent’s rule, which states that with increasing EN of the substituents (increased p-character in the bond) the bond angle decreases. However, among the singlet carbenes separately the trend is more ambiguous (:CHCl (101.4°) vs. :CF₂ (104°)).

In 1994, Arduengo et al. calculated and analyzed the single crystal of 2.22. It was concluded that NHCs display no delocalization of π-electrons in the pπ orbital of the carbene and that the ylide resonance structures show relatively low contributions. According to the authors, the lack of electrophilic character of the carbene would then stem from the repulsion of an incoming electron pair with the nitrogen lone pairs. We consider this a very weak reasoning since e.g. the free electron pairs on the oxygen do not prevent the nucleophilic attack on the carbon in the polarized C=O bond. The issue was readdressed in 1996 by two independent publications. Schwarz et al. calculated an energy gap of 66 kcal/mol in favor of the planar conformation of C(NH₂)₂ compared to the perpendicular orientation. In the former delocalization of the nitrogen lone pairs into the pπ orbital is possible. Furthermore, a shortening of the C-N distance with 0.1 Å appears when the planar conformation is adopted. This should provide evidence for sufficient interaction between the nitrogen lone pairs and the carbene pπ orbital.

Analysis of the structures of 2.23-2.26 reveals the dramatic shortening (11 pm) of the C-carbene-N bond upon carbenization (not in table). In the saturated case (2.25→2.26), not much of additional structural change upon carbene formation is present. On the contrary, in the unsaturated case (2.23→2.24) a significant shortening of the C Backbone-N distance (5 pm) and the elongation of the C₄=C₅ bond distance upon carbenization point to the delocalization of the π-electrons. Furthermore, the decline in the NCN bond angle in 2.24 leads to an increase of the other bond angles. By this, more homogeneous bond angles in an aromatic compound and a decrease in pyramidalization of the nitrogen are obtained.

<table>
<thead>
<tr>
<th></th>
<th>2.23</th>
<th>2.24</th>
<th>2.25</th>
<th>2.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(N₃₁-C₄₃) (pm)</td>
<td>143.4</td>
<td>138.5</td>
<td>147.6</td>
<td>147.2</td>
</tr>
<tr>
<td>d(C₄-C₅) (pm)</td>
<td>134.3</td>
<td>136.4</td>
<td>155.4</td>
<td>153</td>
</tr>
<tr>
<td>angle (N₁-C₂-N₃) (°)</td>
<td>105.4</td>
<td>99.4</td>
<td>104.4</td>
<td>103.4</td>
</tr>
</tbody>
</table>

![Figure 2.13: Model NHCs: Data from.](image)

Inspection of the magnetic susceptibility of 2.24 shows that more than 80% of the contribution is due to the fluxes of the magnetically induced current through the interatomic surfaces of the ring atoms. Moreover, the magnetic susceptibility in 2.24 obtains four times the value of that in 2.26. The authors

IX Planar and perpendicular refer to the orientation of the nitrogen lone pairs compared to the pπ carbene orbital.
also observed the trend that electrostatic interactions via localized charge distributions are less important in 2.24 than in 2.26 and found that this is an indication of a (small) degree of cyclic electron delocalization in 2.24.\textsuperscript{89}

A second study by Frenking et al. showed that 2.24 is stabilized by 20 kcal/mol more compared to 2.26.\textsuperscript{90} This can explain the increase in stability of unsaturated compared to saturated carbenes.\textsuperscript{90} The difference in behavior is explained as follows: The $p_\pi$-occupancy of the carbene in 2.24 is 0.67 e and 0.53 e for 2.26 indicating a 25\% increase for the unsaturated carbene.\textsuperscript{90} \textsuperscript{X} This $p_\pi$ density evidences the importance of the ylide structure in the carbene.\textsuperscript{90} Furthermore, these densities correlate with a 39.8 \% delocalization of the $p_\pi$ electrons in 2.26 and 55.8 \% delocalization in 2.24, while the polarity of the C-N $\sigma$-bonds remains the same; This can easily be explained by aromatic character.\textsuperscript{90} Frenking et al. concluded that the difference in $\sigma$-electron distribution between 2.24 and 2.26 is negligible, while the $\pi$-electron distribution of 2.24 has obtained a clearly higher weight at the carbene carbon compared to the carbene carbon of 2.26.\textsuperscript{90} This line of argumentation is clearly in contrast to main-stream metathesis thinking and we have used this analysis to model new NHC-ligands in this work. The lack of $\pi$-density at the carbene in 2.26 is not so dramatic that the carbene will destabilize and obtain electrophilic reactivity.\textsuperscript{90}

Frenking et al. challenged the aromaticity calculations of Arduengo et al. and showed that calculations of the magnetic susceptibilities hint that strong ring currents are present in 2.24.\textsuperscript{90}

In 2000, Schoeller presented an investigation on Phosphanylcarbenes (P-C-P). The S-T gap increases upon substitution on the phosphor with an alkyl group and even more with $(N(PH_3)_2)$. Additional stabilization of the singlet state can be obtained by the incorporation of the carbene into a ring structure.\textsuperscript{92} The increased pyramidalization leads to more p-character of P in the P-C bond and consequently renders the phosphor ligand more electropositive.\textsuperscript{92} According to Bent’s rule this should lead to an increase in the bond angle which means an increased preference for the triplet state.\textsuperscript{92} Consequently, phosphanylcarbenes show lower S-T gaps than aminocarbenes.\textsuperscript{92}

\subsection*{2.4.2 The Fischer-Schrock formalism for carbenes in organometallic compounds}

The first organometallic carbene species were observed by Fischer et al. and are polarized having $\delta^+$ on the carbene and $\delta^-$ on the metal. Later, R.R. Schrock was able to isolate organometallic carbenes with reversed polarization. Consequently, historically the classification Fischer carbene and Schrock carbene (also called alkylidene) was made upon this phenomenological character: electrophile or nucleophile carbene.

An excellent classical description can be found on the internet.\textsuperscript{93} The Fischer carbene 2.27 shows a metal-carbene bond distance in the realm of single bonds.\textsuperscript{93} Furthermore, the carbene substituents can stabilize the structure through 2 resonance structures.\textsuperscript{93} The negative charge on the metal can be delocalized through electron withdrawing ligands as CO.\textsuperscript{93} \textsuperscript{XI}This $\pi$-donation of the substituents causes shorter C-N and C-O distances.\textsuperscript{93} The carbon acts as a singlet carbene donating two electrons to the metal.\textsuperscript{93} \textsuperscript{XI}Note that the CO ligands are $\sigma$-donors but $\pi$-acceptors, and hence a more accurate formulation would be that the carbene bond is stabilized through $\pi$-acidic ligands on the metal. In fact, CO is mostly a net donor.
metal, which can return the favor with backdonation. However, this backdonation is very limited due to the donation of the two substituents in the carbene π-orbital and due the lack of electron density on the metal caused by the electron withdrawing substituents (note again that π-acidic substituents would be the better term). This effectuates in the polarization of δ⁺ on the carbon.

![Diagram](image_url)

**Figure 2.14:** Fischer carbene: Data from 93.

Most Fischer carbene complexes have high d populations (mostly d⁶ and 18 electron system with the carbene counted as a 2 electron donor). A strong carbene formation can be obtained by weak π-donating substituents on the carbene and in the absence of π-acidic ligands on the metal, however this causes kinetical liability analogue to the stronger C=C double bond vs. the C-C bond. The Schrock carbenes on the other hand always show a very strong M=C double bond character which comes to expression in the short bond distance. The carbene is δ-polarized on the carbon while mesomere donating groups destabilize the carbene. The metal is generally an early TM being electron deficient (d⁰ or d²) with a low electron count (14 or 16 electrons). The Schrock carbene (alkylidene) is also best represented by a classical double bond which is heavily polarized to the carbon. In this work we will refer to Schrock carbenes only with compounds which show a specific covalent double bond character and to Fischer carbenes only when the bond is specifically donor-acceptor.

![Diagram](image_url)

**Figure 2.15:** Fischer-Schrock carbenes.

Our main interest goes to the Grubbs carbene, which is traditionally considered to be a Fischer carbene on grounds of being a metal d⁶ compound and being a late transition metal. Schrock carbene classification can be rationalized through the 16 electron count (14 electrons in the active species), the
absence of π-acidic ligands and its high activity for metathesis (in competition with
cyclopropanation)\textsuperscript{XIII}, which is normally only seen with Schrock carbenes. The carbene can have alkyl
or hetero-substituents, however, the methylene carbene is very unstable while the ethoxycarbene shows increased stability which should point to a Fischer carbene. On the other hand, Jensen et al. have recently claimed that the methylene has more Schrock than Fischer character due to a negative charge on the carbon (which we will discuss in depth in chapter 3).\textsuperscript{96} As can be seen, the Grubbs carbene can not easily be positioned as formal Fischer or Schrock and a further investigation is necessary.

Goddard et al. already addressed the issue in 1986.\textsuperscript{97, XIII} A Fischer carbene is generally preferred with low valent metal fragments surrounded by closed shell ligands. This forces the metal fragment into low spin. The combination with a carbene that has a high preference for the singlet state (thus stabilized with heteroatoms) leads to a Fischer carbene.\textsuperscript{97} Schrock carbenes are generally formed with high valent metal species in the absence of closed shell ligands. This causes the metal to adopt the more energetically favored high spin configuration.\textsuperscript{97} This metal has to be coupled with a carbene having a relatively stable triplet state.\textsuperscript{97} Goddard et al. tried to set up some meaningful selection criteria for carbene or alkylidene formation.\textsuperscript{97} First, it is noted that the exchange energy of the metal unpaired electrons is of paramount importance.\textsuperscript{97} The formation of an alkylidene which should normally yield more orbital overlap and stabilization, is often concomitant with a loss of exchange energy of the unpaired electrons.\textsuperscript{97, XIV} This effect is expected to be bigger for 1\textsuperscript{st} period transition metals due to a higher exchange energy and there it is generally expected that the early transition metals systematically prefer alkylidene formation while late transition metals (for which the exchange energy is bigger) prefer carbene formation.\textsuperscript{97} For the late TMs, the carbene formation is also enhanced by the actual availability of an electron pair for backdonation.\textsuperscript{97} Moreover, the introduction of closed shell ligands can effectively induce carbene formation due to energy splitting and hence the increased preference of the metal to pair the electrons.\textsuperscript{97}

The preference of 18 electron systems for Fischer carbenes is difficult to rationalize because an 18 electron complex implies that no spin pairing is lost for the Fischer-Schrock transition and hence the alkylidene should be favored. We can only assume that this Fischer preference originates in energy splitting of the orbitals, which should increase the singlet stability. Introduction of qualitative VB (Valence Bond) theory ( vide infra for a detailed discussion) with 3-centre 4 electron bonds and unoccupied metal-p orbitals does however make the Fischer preference more logical.\textsuperscript{99}

\textit{We think that Fischer carbenes should transform in Schrock carbenes (which show higher bond
energies) when the σ-bond does not have to be subjected to resonance structure stabilization and the

\textsuperscript{XIII} Although cyclopropanation is reported for the Grubbs complex it is only accomplished through the addition of ethyldiazoacetate, which should effectively destabilize the Fischer carbene. However, there is up to now no evidence that the complex responsible for the cyclopropanation is effectively a Grubbs type system.\textsuperscript{(95) Hodgson, D. M.; Angrish, D. Chemical Communications 2005, 4902-4904.}

\textsuperscript{XIII} The dative carbene bond and covalent representation for the Fischer and Schrock carbenes respectively was first represented in 1984.\textsuperscript{(98) Taylor, T. E.; Hall, M. B. Journal of the American Chemical Society 1984, 106, 1576-1584.}

\textsuperscript{XIV} Technically, the Fischer carbene can bind to a higher unoccupied orbital, without the necessity of pairing the unpaired electrons. Furthermore, preferential bonding to s orbitals occurs when the loss of exchange energy is minimal.
\[ \pi \text{-bond also can be exclusively directed to the carbene in the VB theory.} \]

We explain this as follows: By default of other interactions, the double bond should be transformed in the most stable structure, which is the Schrock carbene. A ligand in trans position needs the use of resonance structures for stabilization in the sd-space. However, resonance structures which involve one electron in the metal orbital (Schrock carbene) and 0 electrons in the metal orbital (trans ligand) are incompatible.

The Schrock carbene is a strong bond and cannot be destabilized by the use of one of its orbitals in another resonance structure. The \( \pi \)-bond also needs one electron into the metal orbital; This orbital, which is now occupied in a covalent bond with the carbon atom cannot participate in backbonding to other parts of the ligand sphere. However, if such backbonding is necessary, Fischer-carbene formation should be preferred. With the installation of \( \pi \)-donor-substituents and internal resonance structures into the carbene it becomes less double bonded to the metal because the \( p_\pi \) orbital is no longer fully available for the double bond. This leads to the inability to make the strong double bond in the Schrock carbene and causes Fischer-carbene preference. This is extremely expressed in the NHCs which show exclusively Fischer-carbene character. So in fact a selection rule for Schrock carbene formation should be simple: If the necessary orbitals are exclusively available in the VB-space, then the Schrock carbene is formed. It is important to remind this selection rule in the rest of this discussion on carbenes.

Goddard et al. showed that the actual alkylidene bond strength should increase upon saturation of the metal complex, due to a reduction in exchange energies. Competitive alkylidene and carbene bonding should occur when \( \pi \)-backbonding is possible and when there is an intermediate loss of exchange energy in forming covalent bonds. RuCH\(_2\)+ is an example in which \( d_\pi-p_\pi \) backbonding is high enough and the exchange energy is large enough to allow competition between the carbene/alkylidene states.

It is evident that the isolated carbene fragment also plays an important role in the nature of the organometallic carbene bond. As expected, when the singlet ground state of the carbene is preferred, Fischer-carbenes are favored, and vice versa for Schrock carbenes. As an example one should note that replacing CH\(_2\) by CF\(_3\) leads to a preference of 66 kcal/mol in favor of the singlet carbene.

Furthermore, for ether and amino-substituents the existence of formal resonance structures even increases the stability of the Fischer bond-singlet carbene state. Excellent alkylidene substituents are \( \sigma \)-donating ligands without \( p_\pi \) lone pairs for backdonation such as hydrogen, alkyl and aryl ligands.

The difference in bonding should be visible in bond lengths. Goddard et al. calculated a 5 pm elongation for the RuCH\(_2\)+ Fischer carbene complex compared to the Schrock configuration. A similar bond elongation was found for the Roper complexes 2.29→2.28, for which in 2.28 the triplet state is 46 kcal/mol higher than the singlet state. It should be noted that typical 5-coordinated Grubbs complexes show Ru=CHPh bond lengths of 1.82-1.84 Å while 6 coordinated complexes (with a ligand trans to the carbene) show bond lengths of 1.88-1.89 Å. Off course, a trans effect should

\[ ^{15} \text{Goddard et al. show an example of dramatic change in chemistry and bond character due to ligand surrounds. MnCH}_2^+ \text{ undergoes metathesis reactions and (CO)}_3\text{MnCH}_2^+ \text{ yields only cyclopropanation products. This would imply Schrock and Fischer carbene respectively, the latter induced by the CO ligands. However, we must add that metathesis is established by the existence of a free coordination function on which an olefin can bond while in cyclopropanation the olefin directly adds on the carbene. These arguments would imply that the cyclopropanation is favored over the metathesis reaction on steric grounds. A similar conclusion can be drawn for the Grubbs catalyst which is exclusively active for metathesis whereas Ru-porphirine complexes are selectively active for cyclopropanation. In the latter, no physical cis-olefin bond to the carbene is possible, which evidences the absence of metathesis. In the former, either the carbene is sterically protected in the 16e species or a free cis-coordination site is available in the 14e species.} \]
cause an elongation of the bond length, but this might imply an even more drastic change in the carbene bond.

\[
\begin{align*}
\text{Figure 2.16: Roper carbene.}
\end{align*}
\]

In the late 90’s, the subject was revisited more efficiently thanks to the increase in calculation power. Wang et al. showed that Cr Fischer carbenes with an oxygen or amino substituent to the carbene bond are best represented as Cr-C-X three centre four electron bonds with the \( \pi \)-electron density concentrated on the Cr-d orbital and the X-p\( _z \) orbital.\(^{101}\) This produces a carbene which is electrophile in the p\( _\pi \) direction.\(^{101}\) Frenking et al. presented an insightful discussion on W-carbene complexes in 1998.\(^{102}\)

An increase in the W-C\( _{\text{carbene}} \) bond lengths (and bond energies) and a decrease in the W-C\( _{\text{(CO-trans)}} \) for the CO complexes in the series CH\(_2 \)< CHF < CF\(_2 \)< CHOH indicates the decrease in \( \pi \)-backbonding for the series 2.30-2.33.\(^{102, \text{XVI}}\) The Schrock complexes 2.34-2.39 show an average decrease of 15 pm in W-C\( _{\text{carbene}} \) bond distance compared to the Fischer complexes 2.30-2.33.\(^{102}\) The Schrock carbenes 2.34-2.39 also show a distinctly increased bond energy compared to 2.30-2.33.\(^{102}\) Furthermore, the strength of the alkylidene bond increases with increasing electronegativity of the W-substituents in the Schrock carbenes.\(^{102}\) The Fischer carbenes 2.30-2.33 show in contrast to the alkylidenes a distinct hole in the \( \pi \)-density at the carbene atom leaving it vulnerable for nucleophilic attack.\(^{102}\) The energy density at the bond critical point for 2.34-2.39 is in average three times the value of 2.30-2.33; both being negative.\(^{102}\) A negative value of the energy density at the bond critical point is generally associated

\[^{\text{XVI}}\text{It is interesting to note here that the (CO)}_5\text{WCPH}_3 \text{W-C carbene distance is 2.15Å compared to 2.128 for the CH(OH) carbene. This indicates that the phenyl group is a good stabilizer for a Fischer carbene (although it is often thought phenyl groups, such as in 1.3, should prefer Schrock carbenes). Steric effects could also play a role.}\]
with covalent bonds and a positive or close to zero value with closed shell interactions as ionic bonds or Van der Waals interactions. Furthermore, the bond elepticity for 2.34-2.39 has on average five times the value of 2.30-2.33. The bond elepticity represents a measure for the double bond character. The bond order in 2.30-2.33 is calculated to be only in the range of 0.93-1.18, while for 2.34-2.39 it was calculated in the range of 1.54-1.87.

The Fischer carbenes show σ-bonds with an average polarization of 75% towards the carbon. The typical (experimental) Fischer carbenes 2.31 and 2.33 only have a σ-bond in the NBO analysis, while the Fischer carbenes with less stabilization on the carbene from the carbene substituents show a W-carbene π-bond, which is on average 65% polarized on W. Very interestingly, the p-π occupancy among the Fischer carbenes is very similar (−0.67 e), and much lower than for the Schrock carbenes (1.10-1.20 e). The authors introduce a very interesting explanation for the difference in reactivity of the CH(OH) carbene 2.33 and CH₂ carbene 2.30, for which the latter is much less stable although thermodynamics suggest a similar stability. The stabilization is kinetic in origin and not thermodynamic: Breaking (stretching) the W-C bond in 2.30 induces a contraction of the π-electron density at the carbene (in contrast to 2.33), which makes the carbon extremely vulnerable against nucleophilic attack.

The Schrock carbenes 2.34-2.39 all show σ and π bonds polarized to the carbon and have a p-π occupancy higher than 1. Furthermore, this induces a formal negative charge on the carbene group (−0.24 e → -0.40 e) in contrast to the relative electroneutrality on the Fischer carbene (−0.13 e → 0.13 e). W mostly holds a strong positive charge in the alkylidene complexes and a negative charge in the Fischer complexes, which translates into a higher d orbital occupancy for the Fischer carbenes. The complexes were also investigated with CDA (Charge Decomposition Analysis). The Fischer complexes show no residue term, which indicates closed shell interactions. The σ-donating term is higher than the backdonation term, and the latter decreases with the introduction of stabilizing substituents on the carbene. The higher σ-donation compared to backdonation does not mean that the energy contribution has increased because the donating lone pair can also interact repulsively with filled d-orbitals.

A special interest goes to the anionic complexes 2.40-2.41, which show a high p-π density, negative charge on the carbene, polarized π-bonds to the carbene, a high bond order (1.48-1.58), high bond elepticity and a low d-orbital density at W. These factors all point to a Schrock carbene character. The energy at the bond critical point and the W-C distances take intermediate values between 2.30-2.33 and 2.34-2.39. However, the CDA analysis shows a distinctive donor-acceptor bond. No explanation on the origin of this phenomenon was added. However, understanding of this ambiguity could hold a key to fundamental understanding of the carbene-alkylidene issue. It is interesting to note that 2.40 and 2.41 both show octahedral geometry similar to the Fischer complexes 2.30-2.33, while 2.34-2.39 show distorted square pyramidal geometry. The calculation on square pyramidal W(CO)₄ carbenes might have solved some issues such as the influence of a ligand trans to the carbene. Furthermore, 2.30-2.33 are 18 electron complexes, 2.34-2.39 14 electron complexes and 2.40-2.41 12 electron complexes. Note that the closed shell complexes 2.40-2.41 and Schrock-complexes 2.34-2.39 are well in agreement with our Schrock carbene formalism. Similar conclusions were obtained for carbyne complexes.

XVII The quantity of the bond elepticity gives a measure of the deviation of the charge distribution from cylindrical symmetry and is thus correlated with the amount of π-character of a bond.
Frenking et al. published in 2002 on the bond characterization of Cr(CO)$_5$ carbene complexes. The shortest Cr-C$_{\text{carbene}}$ bond length was found for the CH$_2$ carbene. This was assigned to the enhanced $\pi$ donation from the metal to the carbene (and accordingly the longest Cr-C$_{\text{carbene}}$ bond length for amino substituents). The shortest Cr-C$_{\text{carbene}}$ distances also correlate with the longer Cr-CO$_{\text{trans}}$, shorter C-O$_{\text{trans}}$ distances and larger C-O$_{\text{trans}}$ stretching frequencies (as expected from the DCD mechanism). We expect the general explanation to be like this: The short M-carbene distance is caused by an increase in backdonation from the metal. This leads to less backdonation to the M-CO$_{\text{trans}}$ bond, concomitant with a longer bond distance. The lack of backdonation in the antibonding CO-orbital decreases the CO bond length and increases the energy of the CO stretching frequencies. Unfortunately, such reasoning is lacking in the analysis of NHC-M(L)-(CO)$_x$ complexes. The CO stretching frequencies in these complexes are mostly correlated with the $\sigma$-bonding strength of the carbene (because $\pi$-backdonation is incorrectly assigned to be negligible) (vide infra).

Interestingly, there is no direct relationship between the bond dissociation energies and the Cr-C$_{\text{carbene}}$ bond lengths (though a tendency exists). CDA analysis shows little difference in $\sigma$-donation between the different complexes, though backdonation varies more significantly and the lowest values for backdonation are obtained for carbenes with $\pi$-donor substituents as NHCH$_3$. Furthermore, carbens with more $\pi$-donating substituents (e.g. C(NMe$_2$)$_2$) and thus less metal-$\rightarrow$carbene backdonation, correspond to higher Cr-C$_{\text{carbene}}$, shorter Cr-CO$_{\text{trans}}$ and higher C-O$_{\text{trans}}$ bond lengths. On the contrary, the energies of the HOMO and LUMO of the carbene show a very poor correlation with the charge donation and backdonation respectively. EDA (Energy Decomposition Analysis) shows that the energy contribution of the orbital interactions of $\sigma$-donation is large and rather constant, while contributions from backdonation are smaller but divers. Furthermore, backdonation energies correlate well with structural parameters such as d(Cr-CO$_{\text{trans}}$) as concluded with CDA. A correlation with $\sigma$-contributions would be absurd since they are rather constant.

2.4.3 NHC ligands in organometallic compounds

Formally, NHCs (or Arduengo carbenes) in organometallic compounds are to be subdivided as Fischer carbenes due to their exclusive singlet character. The original agreement on absence of backbonding from the metal in these compounds has led to the division into a separate class. However, the evidence for backbonding from the metal has strongly increased over the last years. Therefore, the best way to classify the NHC ligands is as Fischer carbenes, which show increased stability of the singlet carbene due to two nitrogen substituents, a ring constraint on the carbene angle in favor of a singlet carbene and a kinetic protection facilitated by bulky substituents on the nitrogen atoms.

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XVIII It is also noted that for Fischer complexes rotation should be free of barrier (in contrast to Schrock carbenes).

XIX In absolute values $\sigma$-donation has on average twice the value of $\pi$-backdonation, a reverse trend from CO and CN ligands where $\pi$-donation is twice as important as $\sigma$-donation.

XX We also want to point out that in case the $\sigma$-donation would determine these parameters, the reasoning would have to go as follows: The nitrogen donors to the carbene increase the carbon $p$-character in the carbene-X bond and hence increase the $s$ character in the lone pair. This increased $s$-character from the carbene in the M-carbene bond should decrease the bond distance. This is the opposite of the observed trend which discredits the $\sigma$-involvement.

XXI The complexes with the most donating carbene substituents show the lowest electrophilicity.
Nolan et al. presented a series of experimental studies on the stereo-electronic effects of NHC ligands. The bond dissociation energies (BDE) of several NHCs were examined for the reaction \([\text{CpRuCl}]_4 + 4 \text{ L} \rightarrow 4 \text{ CpRu(L)Cl}\).\(^{105}\)

**Table 2.1:** BDE for L in CpRu(L)Cl. (kcal/mol)

<table>
<thead>
<tr>
<th>L</th>
<th>ICy</th>
<th>ITol</th>
<th>IpCl</th>
<th>IAd</th>
<th>IC12Mes</th>
<th>IMes</th>
<th>IPr</th>
<th>PCy3</th>
<th>P(‘Pr)3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE (kcal/mol)</td>
<td>21.2</td>
<td>18.8</td>
<td>18.6</td>
<td>6.8</td>
<td>12.1</td>
<td>15.6</td>
<td>11.1</td>
<td>10.5</td>
<td>9.4</td>
</tr>
<tr>
<td>L</td>
<td>H1MES</td>
<td>H1IPr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE (kcal/mol)</td>
<td>16.8</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from\(^{105}\). Cy = Cyclohexyl; Tol = 4-methylphenyl; pCl = 4-chlorophenyl; IC12Mes; Ad = adamantyl.

The BDE of ICy, ITol, IMes and IAd show that steric demand is important for the bond strength. Furthermore, a significant decrease in bond strength is witnessed when chlorines are introduced on the backbone.\(^{105}\) Unexpectedly, the saturated carbenes only show a minor increase in BDE and a minor shortening of the Ru-C\(_{\text{carbene}}\) bond compared to their unsaturated analogues.\(^{106}\) The authors were able to show a significant correlation between an increase in steric demand of the ligand and a decrease in BDE. This should alert against the use of BDEs as indications for orbital interactions.\(^{106}\) Furthermore, the NHC ligands seem to outperform the phosphines in BDEs.\(^{105}\)

Nolan et al. investigated the BDEs for the same series of ligands for substitution on a Ni(CO)\(_2\)(NHC) complex and found no significant difference between saturated and unsaturated NHCS.\(^{107}\) Though, with extreme steric bulk, a significant correlation between steric demand and a decrease in BDE can be observed. Furthermore, the CO stretching frequencies of complexes indicate that the unsaturated carbenes are even marginally more (net) electron donating than the saturated carbenes, which is in sharp contrast to conventional reasoning on carbene donor capacity.\(^{107}\) Note that the BDEs for CO in the carbene complexes Ni(CO)\(_3\)L are lower than those in the phosphine complexes (which is in contrast to the metathesis phosphine dissociation energies for 1.3-1.4). Thus, the BDE of PCy3 in 1.3-1.4 must be determined by another parameter than the BDE of CO in Ni(CO)\(_3\)L.

Furthermore, the higher \(\nu(\text{CO})\) frequencies for the phosphine complexes are associated with a stronger CO bond and with weaker M-C\(_{\text{CO}}\) bonds. This is in contrast to the BDEs of the M-CO bonds which are higher (in correspondence with the lower M-P bond strengths). This hints that the \(\nu(\text{CO})\) frequencies and thus CO bond strengths are determined by a different parameter (\(\pi\)-backdonation) than the BDEs which can be dominated by other factors (such as electrostatic repulsions, attractions or \(\sigma\)-donation; vide infra). The same trend will be shown on the analysis made by Hu et al.\(^{108}\). Crabtree et al. investigated the \(\nu(\text{CO})\) stretching frequencies of Ni(CO)\(_3\)(NHC) complexes with DFT and calculated that the saturated carbenes display lower frequencies than the unsaturated carbenes, which suggests them to be the better (net) donors.\(^{109}\)

Frenking et al. analyzed the NHC metal complexes 2.42-2.44 and found through CDA that the back donation to the NHCs is far less (10-20%) than in classical Fischer carbenes (30-45%) for Cr(CO)\(_3\)L complexes.\(^{110}\) The NHC ligands show high \(p_x\) populations (~0.85) and high C-N bond orders, which explain the high \(p_z\) population and the decrease in C-N bond length of 1 pm upon complexation.\(^{110}\) Furthermore, aromaticity is calculated to be slightly higher in the metal carbenes compared to the free carbenes (and in the range of cyclopentadienyl) due to the increased \(\pi\)-donation of the nitrogen atoms to the carbene.\(^{110}\) The carbene bond is dominantly ionic, though the covalent character is established as a result of an overlap of the free carbene lone pair with the partly occupied s orbital (due to M-Cl bonding).\(^{110}\) Repulsion with the \(d_{z^2}\) electrons induces the energy of the \(d_{z^2}\) orbital to increase and
enhances mixing with the s orbital. Furthermore, the Cl-M-NHC interaction is best represented by a 4 electron 3 centre bond.\textsuperscript{110}

![Figure 2.18: Model NHC-metal complexes.](image_url)

Cavell et al. also showed that upon complexation of an NHC to Pd, the occupancy in the p\textsubscript{x} orbital increases from 0.66 to 0.83.\textsuperscript{111} However, the p\textsubscript{x} orbital, a metal d-orbital and a cis-bonded alkyl group were found to interact and facilitate reductive elimination of the carbene ligand.\textsuperscript{111}

Herrmann et al. investigated the complexation of \textbf{2.48} and \textbf{2.49} with Cr(CO)\textsubscript{5}.\textsuperscript{112} CO frequencies suggest that \textbf{2.48} is somewhat more electron donating than \textbf{2.49}, despite of the single nitrogen \pi-donor to the carbene.\textsuperscript{112} The p\textsubscript{x} density at the carbene carbon is also not affected in \textbf{2.48} and shows a similar value as for \textbf{2.49} as well for the free carbene (~0.65) and the complexed species (~0.85).\textsuperscript{112} Herrmann et al. observed a constant C\textsubscript{carbene}-N distance upon coordination for \textbf{2.49}, which is supposed to be inconsistent with pure \sigma-donation of the carbene to Cr.\textsuperscript{112, XXII} However, \textbf{2.48} shows a shortening of 2 pm of the C-N distance.\textsuperscript{112}

The cation of \textbf{2.49} shows a great depletion of localized electron pairs compared to the free carbene and the Cr-complex, which should indicate that little electron delocalization exists in both the latter complexes.\textsuperscript{112} Electron delocalization along the C\textsubscript{carbene} bond in \textbf{2.48} seems less hindered than for the C\textsubscript{carbene}-N bond. This causes a small contribution of the ylide structure because the carbene centre is well integrated in a delocalized \pi-system via the C\textsubscript{carbene}-C bond.\textsuperscript{112} The authors conclude in accordance with Arduengo (and in contrast to Frenking) that stabilization at the carbene seems to primarily arise from –I effect of the N atoms while the lone pairs on N are localized and form a kinetic shield of protection.\textsuperscript{112}

The Cr(CO)\textsubscript{5} complexes of acyclic carbenes, saturated carbenes and free \textbf{2.49} show distinct holes of the local charge concentration in the p\textsubscript{x} plane. This is in contrast to the Cr(CO)\textsubscript{5} complex of \textbf{2.49}, which explains the increased kinetic stability of this complex.\textsuperscript{112}

An EDA study by Lammertsa et al. on Ir complexes shows that the NHC obtains a 20% \pi-stabilization (compared to 25% for the CH\textsubscript{2} carbene), however the stabilization through the difference in \Delta E\textsubscript{elst.} - \Delta E\textsubscript{pauli} is increased by 30 kcal/mol for NHCs compared to the classical CH\textsubscript{2} carbene.\textsuperscript{113} Deubel found a similar stabilization due to \Delta E\textsubscript{elst.} -\Delta E\textsubscript{pauli} in rhodium complexes and a lower contribution of \pi-stabilization in the NHC (16%) compared to CH\textsubscript{2} (43%).\textsuperscript{114} It should be noted that the non-orbital interaction term (\Delta E\textsubscript{elst.} - \Delta E\textsubscript{pauli}) has a negative influence on the stability of the Ir and Rh complexes.

\textsuperscript{XXII} Higher bond orders between C-N and shorter C-N bond distances led Frenking et al. to reason that this was caused by a strong \sigma-donation of the carbene to the metal, which induces stronger \pi-backdonation from N and consequently higher bond orders and shorter bond distances.

A constant distance on the other hand implies that there is little backdonation from the nitrogen to the carbene, and the backdonation should thus occur from the metal centre.
Evidence for extensive $\pi$-backbonding was already presented in 2001 for a Ag cluster with a tetradentate ligand\textsuperscript{115} and a bidentate carbene Cu complex\textsuperscript{116}. Furthermore, visual inspection by Meyer et al. showed interactions for the carbene $p_x$ orbital with the metal $d$ orbital for a Ag tripodal NHC complex\textsuperscript{117}. In 2004, Meyer et al. continued by showing that the $\pi$-energy stabilization of a biscardene Pd complex is calculated to be 35\% of the total orbital stabilization and CDA shows that the actual backdonation is 45\% of the $\sigma$-donation. This reveals that $\pi$-backdonation should not be considered negligible for NHC complexes.\textsuperscript{118}

2004 became the turnover point for the appreciation of $\pi$-backbonding from the metal. $\Pi$-backdonation had previously been accounted for as negligible or at best responsible for 20\% of the stabilization. Frenking et al. performed an EDA analysis on complexes 2.42-2.47 and found that $\sim$20\% of the energy stabilization of orbital interactions is caused by $\Delta E(\pi_\perp)$ out of plane $\pi$-interactions.\textsuperscript{119} Additionally, almost 10\% of energy stabilization is caused by in plane $\pi$ interactions. However, these cannot be considered to be caused by backdonation.\textsuperscript{119} It is also important to note that in contrast to the Ir and Rh complexes previously described, the non-orbital interaction term facilitates a stabilizing effect of 10-18 kcal per NHC.\textsuperscript{119}

![In plane interaction](image1.png) ![Out of plane interaction](image2.png)

**Figure 2.19:** In plane and out of plane $\pi$-interaction.

Herrmann et al. concluded that the similarity of the $\pi$-contribution of the NHC-M bond to the classical Fischer complexes (CO)$_3$CrC(OH)$_2$ indicates that there is little difference introduced by the *magically* stable NHC ligand compared to Fischer carbenes with two donor substituents.\textsuperscript{119}

Hu et al. investigated some interesting carbenes in the (CO)$_5$Cr(carbene) environment.\textsuperscript{108} In general, the NHCs and the acyclic diamino carbenes have longer Cr-$C_{\text{carbene}}$, shorter Cr-C$_{\text{CO trans}}$ and longer C-O$_{\text{trans}}$ distances than their Fischer-carbene siblings.\textsuperscript{108, XXIII} Upon introducing electron donating groups in the series 2.50$\rightarrow$2.51-2.52$\rightarrow$2.53-2.54, the Cr-$C_{\text{Carbene}}$ distance elongates. However, saturation has little influence on this parameter and indicates a small increase in backbonding to the saturated carbene (smaller bond length).\textsuperscript{108} The $\upsilon$(CO) values and proton affinities predict a small decrease in donor strength (or more correctly, an increase in backdonation) of the saturated carbenes.\textsuperscript{108} The unsaturated carbenes also display an increase of 10 kcal/mol in the S-T gap compared to their saturated analogues.\textsuperscript{108}

The increase in Cr-$C_{\text{carbene}}$ distance correlates with an increase in $\pi$-backdonation to the CO and lower $\upsilon$(CO) values.\textsuperscript{108} These lower $\upsilon$(CO) values can be assigned to a decrease in $\pi$-back bonding or an increase in $\sigma$-donation.\textsuperscript{108} It should be noted that Hu et al. add the restriction that ‘The difference in k(C-O)$_{\text{trans}}$ should not be attributed to $\pi$-back-donation alone.’\textsuperscript{108} Unfortunately, the $\sigma$-donation reasoning is the only approach used by practical chemists for the correlation of $\upsilon$(CO) values with the electronic parameters of the NHCs. It must be noted that Hu et al. conclude that the

\textsuperscript{XXIII} The decreased backdonation of the metal should cause a longer M-carbene distance and consequently a shorter M-carbonyl distance.
backdonation to NHCs is negligible on grounds of them having lower $\pi$-accepting abilities than the other carbenes and the apparent lack of variation in backbonding upon saturation of the carbene. However, it has been shown that this backdonation is not negligible.

Figure 2.20: Model NHC-complexes.

It is interesting to note from the metathesis perspective that the only acyclic carbene ever used as a substituent on the Grubbs catalyst (but failed), C(N(i-Pr)$_2$)$_2$, shows an extreme elongated Cr-C$_{\text{carbene}}$ distance which was explained by the high steric hindrance of the carbene. The bond energies of the NHCs are in the range of the other Fischer-carbenes, while acyclic diaminocarbenes show the lowest bond energies among the carbenes (expected due to the nitrogen stabilization of the carbene). It seems that the cyclization of the carbene might have an important effect after all.

Furthermore, the M-CO bond energies of the Cr complexes show a strong decrease for the acyclic diamino carbene complexes compared to the rest of the Fischer carbenes (including the NHCs). This is in sharp contrast with the short Cr-C$_{\text{CO}}$ bond lengths and other structural parameters which indicate a stronger Cr-(CO) bond due to the decreased backbonding to the carbene. Consequently, this evidences the error of correlating bond strengths with bond lengths.

The CO bond energies decline constantly with increasing bulk of the NHC which leads us to conclude that this steric influence is probably the main reason for the decreased bond strength. Hu et al. suggest that paradoxically the $k(\text{C-O})_{\text{trans}}$ decrease with decreasing Cr-(CO) bond energies from :CH$_2$ to :C(Me)(NMe$_2$) is explained by the ability of the carbene to stabilize the Cr(CO)$_4$ complex. We think that the $k(\text{CO})_{\text{trans}}$ value is dominated by the orbital interactions of the M-NHC bond (especially $\pi$-interactions) where the bond dissociation energies are more prone to other factors. It is important to note that the $\nu(\text{CO})$ frequencies cannot be correlated as a thumb rule to the strength of the M-CO bond. (vide infra-supra) Cavallo et al. published in 2005 on the ability of an NHC to act, not exclusively as a $\sigma$-donor – $\pi$-acceptor but as a $\pi$-donor in the [Ir(i'Bu)$_2$]PF$_6$ complex. This only complicates the prediction of NHC behavior and catalytic effects.

Figure 2.21: Out of plane $\pi$-backdonation and $\pi$-donation.
In 2006, Cavallo et al. studied a series of metal fragments complexed with 2.51. An increase of positive charge on the metal increases the non-orbital electrostatic energy stabilization ($\Delta E_{\text{elst.}} - \Delta E_{\text{pauli}}$) and the orbital interactions are generally higher with a higher d-electron count on the metal. While introducing a lesser $\pi$-acidic ligand trans to the carbene, the orbital interaction term in the M-carbene bond increases and the non orbital interactions become more destabilizing: Both effects are probably caused by an increased backdonation to the NHC. The $\pi$-contribution to the orbital energy stabilization varies from 10% to ~27% and the higher values are calculated for the complexes with a high d electron count. Analysis of the $\pi$-bonding energy stabilizations revealed that 60%-95% of the $\pi$-stabilization is caused by classical $\pi$-backbonding from the metal. Higher d-electron count metals correspond with a higher percentage of $\pi$-backbonding stabilization.

Bielawski et al. synthesized in 2006 a quinone-annulated N-Heterocyclic carbene 2.55. Annulated NHCs had previously been synthesized and their lack in stability was ascribed to the electron withdrawing capacity of the annulated rings which, extract electron density from the $p$ orbital of the carbene.

Figure 2.22: Quinone annulated NHC.

Bielawski showed through the CO (quinone and M-CO) stretching frequencies in IR that in the complexes 2.56-2.57, 2.55 acts as a stronger $\pi$-acidic ligand (lower $v_{\text{CO}}$) than COD and a weaker $\pi$-acidic ligand than CO (high $v_{\text{CO}}$). This stresses the ambivalent $\pi$-character of the NHC-ligand.

In 2006 Jensen et al. investigated the Grubbs complex and calculated the backdonation/donation (b/d) ratio of IMES and $H_2$IMES to be 1/3, which is extremely high and exceeding the 1/6 ratio of PCy$_3$. It seems that the backdonation in NHC complexes is not so ‘negligible’ at all. Furthermore, although the NHC donors are far better $\sigma$-donors in the Grubbs complex, their net donation only marginally exceeds the net donation of PCy$_3$. This can only suggest that a qualitative change in the bond is responsible for the difference in activity (see chapter 3).

Due to the obvious similarities of PHCs to NHCs, the former have also been under extensive investigation. Schoeller et al. showed that the wide carbene bond angles in acyclic phosphanylcarbenes provide a barrier for complexation, because the bond angle needs to decrease after complexation. Upon complexation, an elongation of the C-P bond is induced due to the competitive backbonding from the metal to the carbene in spite of the phosphor donation. This is correlated with an increased pyramidalization of the phosphor and a decrease of the S-T gap. The S-T gap is known to increase with increasing EN of the substituents on the carbene. The low S-T gaps for asymmetric

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This can be rationalized as follows: increased pyramidalization phosphor $\rightarrow$ more $p$-character of P in P-carbene bond $\rightarrow$ P acts as a more electropositive substituent $\rightarrow$ more $s$ character of C in the P-C bond $\rightarrow$ more $p$-character in the lone pair $\rightarrow$ higher HOMO energy $\rightarrow$ lower S-T gap. And: increased pyramidalization phosphor $\rightarrow$ less P $\rightarrow$C $\pi$-donation $\rightarrow$ less electron density at the C$_{\text{pt}}$ $\rightarrow$lower energy LUMO $\rightarrow$ lower S-T gap.
phosphanyl carbenes renders them excellent candidates for Schrock carbene formation in contrast to
diaminocarbenes, which are not compatible for the task.\textsuperscript{126}
P-heterocyclic carbenes are more likely to undergo stronger $\pi$-bonding with the metal than NHCs.\textsuperscript{127}
In fact, the PHCs, which are expected to have similar bond strengths as their NHC siblings are predicted to show a $\pi$-interaction contribution of 45\% in the orbital interaction energy compared to 25-35\% for NHC complexes.\textsuperscript{127, XXV}

\section*{2.5 General concepts in the metal-ligand bond}

\subsection*{2.5.1 EDA and CDA}

In 2000, Frenking et al. published an excellent review on the organometallic bond.\textsuperscript{128} Frenking et al. noted that the biggest accomplishment of the last decade in understanding the metal-ligand bond was the introduction of EDA as a more detailed analysis compared to the textbook DCD analysis. DCD analysis calculates the strength of the bond through the interactions of the filled ligand orbitals with the empty metal ligands (donation) and of the empty ligand orbitals with the filled metal orbitals.\textsuperscript{129} EDA on the other hand, also takes account of the steric interaction terms $\Delta E^{\mathrm{Elst}}$ (positive electrostatic interaction term) and $\Delta E^{\mathrm{Pauli}}$ (negative steric electronic interaction term), which provides a more complete view of the bond strength.\textsuperscript{129} Furthermore, the preparation energies ($\Delta E^{\mathrm{prep}}$); the energies necessary to excite the parts from their separate optimal geometries into their bonded geometries are taken into account.\textsuperscript{129} CDA (Charge Decomposition Analysis) enables the decomposition of the charge transfers in the bond in $\sigma$-bond and $\pi$-back-bonding.

\subsection*{2.5.2 M(CO)$_5$L complexes}

Frenking et al. investigated in 1996 the general properties of ligands in an 18 electron complex M(CO)$_5$L.\textsuperscript{130} The general bond strength decreases in the order NO$^+$ > CN$^-$ > CH$_2$ > CF$_2$ > CO > HCCH $\geq$ N$_2$ $\geq$ H$_2$.\textsuperscript{130} The ionic ligands outperform the neutral ones. The more stable (free) carbenes with extra stabilization from the substituent show lower bond energies than their more transient siblings (vide supra).\textsuperscript{130} The backdonation/donation ratio (computed with CDA) decreases in the order N$_2$ (3.96; weak donation) > NO$^+$ (3.17) > CH$_2$ (0.90) > CO (0.79) > HCCH (0.67) > CF$_2$ (0.59) > H$_2$ (0.37) > CN$^-$ (0.05).\textsuperscript{130} However, the absolute values or the ratios cannot be taken as a direct correlation for bond strengths.\textsuperscript{130} More importantly, the M-CO$_\text{trans}$ bond distances (normally in direct correlation with the CO stretching frequencies) show no relationship with the absolute value of the donation of the ligand.\textsuperscript{130} However, a direct link between the M-CO$_\text{trans}$ bond distance and the absolute value of M$\rightarrow$L backdonation can be observed. Strong acceptor L’s tend to increase the M-CO$_\text{trans}$ bond.\textsuperscript{130} This is – again - in complete contrast with the paradigm in

\textsuperscript{XXV} Jacobsen argues 'Stronger pyramidalization around the P causes a larger singlet-triplet gap as well as an increase of the HOMO orbital energies.' (With a reference to the experimental results on PHCs of Bertrand et al.). However this is in contrast to the previous reasoning mentioned by Frenking et al., furthermore Bertrand et al. claim in the referred article:‘…whereas the phosphorous centres of the corresponding PHC Ap are strongly pyramidalized, as expected. Consequently, the singlet-triplet gap drops from 79 kcal/mol for An to 21 kcal/mol for Ap’ and ‘As a consequence of the enforced planarization of the phosphorous center, the singlet-triplet energy gap increases strongly as does the energy of the HOMOs…’. A personal communication with Heiko Jacobson finally cleared that this was a blunder from their part.
practical NHC-chemistry, which correlates the (net) donation of the NHC with the $\nu_{\text{CO}}$ values. Deubel et al. calculated with EDA the relative stabilization of $\Delta E_{\text{orb}}(\sigma)/\Delta E_{\text{orb}}(\pi)$ for a tetrakis(carboxylato)dirhodium(II) complex and found that the values decrease in the order; NHC (5.2) $>$ benzene (2.6) $>$ CH$_2$ (1.3) = C$_2$H$_4$ (1.3).$^{114, \text{XXVI}}$

### 2.5.3 CO

The CO molecule is of great importance in organometallic chemistry and the $\nu$(CO) is – unfortunately- the standard tool for the determination of the $\sigma$-donation characteristics of NHC bonds by synthetic chemists. Frenking et al. made a remarkable publication on the nature of CO and claimed in the introduction that special nature of CO is ‘an isolated embarrassment for introductory chemistry teachers’.$^{132, \text{XXVII}}$ First, the electronic charge is depicted, from which follows that the carbon has an anisotropical charge distribution with a large portion of the electron density in a $\sigma$-orbital pointing away from the oxygen.$^{132}$ This qualitative difference in the charge distribution (with the carbon dominated $\sigma$-bond, located far away from the oxygen while oxygen shows a more spherical electron distribution) causes the small dipole (0.11D) with the negative end at the more electropositive carbon atom.$^{132}$ Paradoxically, this syndrome is accompanied by a partial positive charge ($\delta^+ \approx +1.33 \text{ e}$) on the carbon (since this parameter is not correlated to a distance of the charge to the center of the molecule).$^{132}$ This $\delta^+$ on the carbon would generally be considered as an indication for electrophilicity, however, the carbon is nucleophile.$^{132}$ It is the energy and the shape of the frontier orbitals which determine how a molecule interacts in orbital-controlled reactions and not the partial charges of the atoms.$^{132, \text{XXVIII}}$ Therefore, the HOMO ($7\sigma$) orbital with a high electron density at the far end of the carbon determines the nucleophilicity.$^{132, \text{XXIX}}$ Furthermore, Frenking et al. showed in a lengthy exposition that the $7\sigma$-orbital is slightly bonding and not anti-bonding (as generally assumed).$^{132}$ The unusual strength of the CO bond compared to N$_2$ was explained by the sharp decrease in negative interactions $\Delta E_{\text{Pauli}}$ which overcompensate for the decrease in electrostatic attraction (!) and the decrease in orbital interactions.$^{132}$ The decrease in (stabilizing) electrostatic interactions for CO is also extremely counter-intuitively but can easily be explained by the assertion of the qualitative three dimensional electron distribution compared to the analysis of point attraction of partial charges.$^{132}$ Furthermore, it should be noted that the bond is best described as two covalent $\pi$-bonds and a donor(-acceptor) $\sigma$-bond.$^{132}$

### 2.5.4 The M-CO bond

$^{\text{XXVI}}$ Recently, the $\sigma$-donor capacity of ligands has been accounted with Natural Orbitals for Chemical Valence (NOCV) to be decreasing in the series PH$_3 > C_2H_4 >$ CO. The $\pi$-backdonating to the ligand decreased in the series CO $>$ C$_2$H$_4$ $>$ PH$_3$ in a noncompetitive $\pi$-backdonating environment and C$_2$H$_4$ $\approx$ CO $\approx$ PH$_3$ for a competitive $\pi$-backdonating environment.$^{(131)}$ Mitoraj, M.; Michalak, A. Organometallics 2007, Published online 10/26/2007.

$^{\text{XXVII}}$ Due to A) the triple bond of oxygen, B) a dipole moment with the negative end on the carbon and C) a higher bond energy than N$_2$.

$^{\text{XXVIII}}$ The nature of orbital controlled reactions can also be controlled by the orbital relaxation, as can be determined by the Fukui functions.$^{(133)}$ Bartolotti, L. J.; Ayers, P. W. Journal of Physical Chemistry A 2005, 109, 1146-1151.

$^{\text{XXIX}}$ However, it should be noted that the inadequacy of the frontier-controlled versus charge-controlled dichotomy for describing chemical reactivity has been challenged by using Fukui functions to show the importance of orbital relaxation to chemical reactivity.$^{(133)}$ Ibid.
An inspection of M(CO)$_x$ complexes may also be very helpful to the organometallic understanding. Classically, the Cr(CO)$_6$ bonding shows a standard textbook explanation as sd$^2$p$^3$ hybridized complex with σ stabilization through the $e_g$ ($d_{x^2}$ and $d_{y^2}$) and $t_{1u}$ level (p-orbitals) and π stabilization through the $t_{2g}$ level ($d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals). The orbital interactions seem to be more than 3 times as important for π-bonding than for the $e_g$-caused stabilization. The lions share of the σ-stabilization is attributed to the electrostatic interactions of the deeply penetrating σ-lone pairs with the Cr-core. The π-interactions on the other hand show much less electrostatic contributions (vide infra; perpendicular orientation of π-orbital CO on M-CO bond) but do show high orbital interactions. It is concluded that ‘the physical origin of the metal-CO bonds in Cr(CO)$_6$ is different from the common bonding model’. Frenking et al. showed that in M(CO)$_6$ complexes the dominance of the orbital-π-interactions becomes even more important if the metals are negatively charged. The $e_g$ (σ-bond) energy becomes highly dominant over the π-orbital interactions for positively charged metals. The $t_{1u}$ interactions (associated with M-p-orbitals; σ and π L→M) emerge from negligibility in the neutral complexes to substantial (upto 1/4 of $e_g$ in M$^{13+}$) factors in the positively charged metals. One can easily associate this increase with the high increase of donation from L→M. It is however remarkably counter-intuitive that the electrostatic and Pauli interactions remain relatively constant for neutral, positive and negatively charged metal complexes. This is explained by the contraction and shielding of the cationic valence orbitals, which leads to higher repulsion with the incoming σ orbitals, causes a longer bond distance and consequently leads to a lower electrostatic attraction! An interesting observation is that in the neutral W(CO)$_6$ complex, the energy contributions to the orbitals from the CO→W donations for the d, s, p percentages are respectively 77%, 15% and 8%, which should strongly question the sd$^2$p$^3$ hybridization (vide infra). It seems the stabilization through the 3 p-orbitals only attributes for 8% of the stabilization (or less than 3% per orbital) and Frenking et al. comment that ‘The energy values associated with the p functions are clearly smaller than those for the s functions but are not negligible.’

2.5.5 π-trans influence in organometallic compounds

It has been shown that for the $\nu_{CO}$ stretching frequency, the influence of M(π) → CO(π*) backdonation is much more dominant than the CO(σ) → M(σ*) transfer. The previous and following analysis shows that the π-backdonation in the M-L bond, rather than the σ-donation from the ligand, is responsible for this M(π) → CO(π*) transfer. However, the question remains why the σ-donation of the ligand is less responsible for the M(π) → CO(π*) backdonation on a conceptual level? We propose that the symmetry of the orbitals and the competition for electrons is responsible for this. First, the σ-donation of L is evidently of σ-symmetry and this orbital cannot be considered a candidate for direct M→L π-backdonation trans to the ligand. Furthermore, we expect that a strong σ donation should destabilize the σ-trans bond due to a competition for the mixing with the metal orbital, for which the strong σ-donor should be dominant (destabilization through resonance structures; vide infra). This is the fountainhead of the commonly known trans influence combined with a similar influence for π-back-bonding. This π-trans-influence is responsible for the decrease in IR stretching frequency (weak π-acceptor L causes an increase of the π* electron density of CO). We think that the lack of a pure σ-influence on $\nu_{CO}$ can easily be explained by the marginality in bonding character of the bonding σ-orbital which can be evidenced by the controversy on the actual bonding or anti-bonding character. Of course, an increase in σ-bonding should increase the overall electron density at the metal and hence promote backdonation, however, in a non-stereospecific manner. Also, a lengthening
of the M-L bonds can provide better interactions for the M-L\textsubscript{trans} (M-CO) bond and hence increase backdonation.\textsuperscript{108} We point out that the \(\pi\)-interactions should have more influence on the bond distance than \(\sigma\)-interactions for ligands with \(\pi\)-bond orbitals perpendicular to the \(\sigma\)-bond direction (like CO or NHCs and not olefins). These perpendicular interactions should be more sensitive to bond elongation since these non-linear interactions provide less-orbital overlap.

![Diagram of sigma bonding and pi back bonding](image)

\textbf{Figure 2.23:} Competition for metal orbitals; sd resonance model and the difference of geometrical linear and non-linear overlap.

The reasoning is less straightforward for ligands which are not oriented in the trans position, and all calculations show that it is precisely the CO in trans position which shows the most pronounced influence. For ligands in cis position in an octahedral environment only two of the potentially 4 ligands possess the ability to compete for the backbonding with one \(\pi\)-orbital of the L-ligand.

For the \(\nu\text{(CO)}\) frequencies, the \(\pi\)-influence should be taken into account since the \(\sigma\)-trans effect is only marginal due to the low CO bonding character of the metal-bonding \(\sigma\)-orbital and the more pronounced anti-bonding character of the \(\pi^*\) orbital. For the analysis of NHCs, the standard analytic tool is the comparison of \(\nu\text{(CO)}\) frequencies of square planar LRhCl(CO)\(_2\) complexes. Tetrahedral complexes present a more difficult analysis. Unfortunately, also tetrahedral LNi(CO)\(_3\) complexes,
for which both $\sigma$ and $\pi$ influences of the ligand may affect the $\pi$-backbonding to the CO are evaluated in the same way, and hence the individual aspects remain more unresolved. Applying this knowledge obtained for tetrahedral complexes in a conceptual analysis of the square pyramidal Grubbs complex is not straightforward and can only lead to contradictions. We suggest that the coordination of the NHC to square planar, pyramidal or octahedral complexes can lead to better information, since then both $\sigma$ and $\pi$ characteristics are better separated. An octahedral environment would provide straightforward information on the $\pi$-backbonding through the $\nu$(CO)$_\text{cis}$ and $\nu$(CO)$_\text{trans}$ and the differential of the M-CO$_\text{trans}$ and M-CO$_\text{cis}$ bond length would provide information on the $\sigma$-donating character.

2.5.6 Evidence for $\pi$-backbonding competition in (CO)$_5$CrCH$_2$

Our reasoning for backbonding competition shows some explicit precedents in literature. First, Jacobsen and Ziegler analyzed the (CO)$_5$CrCH$_2$ complex, where the Cr-(CO) distances decrease in the following order: axial (189.2 pm) $>$ eq. perpendicular (187.6 pm) $>$ eq. parallel (185.4 pm) compared to a 186.6 pm bond distance for Cr(CO)$_6$. This shows that only a shortening takes place for the CO$_\text{eq}$ parallel. The authors comment that "The (CO)$_\text{eq \parallel}$ ligand shows for all systems a relatively short M-C bond around 185 pm. This ligand does not compete with the EH$_2$ group for bonding orbitals of the metal center. In contrast, the (CO)$_\text{eq \perp}$ shares the back-bonding donation of the metal with the EH$_2$ ligand. Consequently this EH$_2$ bond is slightly elongated." This nicely demonstrates the influence of $\pi$-backdonation to the ligands.

We think the CO$_\text{ax}$ should be expected to have less influence from the backdonation competition (1 x carbene; 4 x CO) than the CO$_\text{eq \perp}$ (1 x carbene; 5 x CO). The CO$_\text{ax}$ is also prone to a ($\sigma$)-trans effect which explains the longer Cr-CO$_\text{ax}$ distance. This is in contrast to our view that predominantly $\pi$-backbonding effects should determine bond lengths. However, the (C-O) distances should not (or less) be prone to the ($\sigma$)-trans effect and this is observed in the decrease in the C-O distance from eq. parallel (115.0 pm) $>$ ax (114.6 pm) $>$ eq. perpendicular (114.5) (which is not noted by the authors). This suggests that the backboning to CO is mainly dictated through $\pi$-backbonding competition.

Figure 2.24: Competition for backbonding in Cr(CO)$_5$CH$_2$. 

The authors argue that "The CH$_2$ contribution to the HOMO, 1b$_1$, is an occupied C-H bonding orbital, which undergoes a repulsive interaction with the metal 3d$_{ax}$ orbital. In this irreducible representation, the carbene ligand does not possess any empty orbitals suitable for back donation from the metal fragment. On the other hand, the axial CO group has an empty $\pi^*$ orbital, which can accept electron density from the Cr-3d$_{ax}$ orbital. The axial CO ligand competes with two of the equatorial CO groups,
namely the (CO)$_{eq}$, for back-bonding from the metal center. To compensate for the lack of π bonding of the axial CO group with the metal center, the (CO)$_{eq}$ ligands bent [sic] slightly toward the CH$_2$ group.

We would like to suggest a formal designation for this phenomenon. **Σ-trans influence of a strong σ-L –donor tends to weaken (and lengthen) the bond trans to L due to an increased competition for the mixing with the same metal orbital. Π-influence has both a cis and trans character and holds a qualitative factor for the direction of the π-orbitals. Π-trans influence of a strong π-acceptor tends to weaken and lengthen the bond of possible π-acceptors with the π-accepting-orbitals in aligned geometry in the trans position. Π-cis influence of a strong π-acceptor tends to weaken and lengthen the bond of possible π-acceptors with the π-accepting-orbitals in aligned geometry in the cis position. Furthermore, the influence on the M-L bond-distance due to π-effects should be higher if the L$_\pi$ orbitals are perpendicular to the M-L bond direction.** It is possible that these cis bonds bend away from the strong acceptor. Furthermore, we suggest that the energetic influences are environment specific: This holds for the geometry of the metal complex and the nature of the bonded ligands.

A second precedent in literature is the competition effect for backbonding (between CO, phosphines and amines) directly$^{138}$ and indirectly$^{139}$ calculated by Harvey et al. in two recent publications, which we will discuss in section 2.6. Furthermore, also Frenking et al. coin the issue in the phosphine analysis.$^{140}$ (vide infra).

### 2.5.7 Evidence for π-backbonding competition in the VB theory

A third precedent in literature is a theoretical base and concerns the Qualitative VB (Valence Bond) theory which is a refutation of the classically VSEPR (Valence Shell Electron Pair Repulsion) theory. The VB perspective on organometallic complexes$^{99}$ has been elaborately described in recent reviews on chemical bonding$^{128,141}$ and thoroughly critically analyzed$^{128}$. The TM Valence bond theory is dominated by the theorem that p-orbitals do not participate in the metal-hybridization with M-L bonds which are covalent in character.$^{99}$ Consequently, all metal complexes increasing the 12 electron count are hyper-valent complexes.$^{99}$ The theory is less applicable for ionic ligands (or ligands with high difference between the EN between M-L) and was originally developed for metal-hydrides and metal-alkyl complexes.$^{99}$

The theory is formalized in three rules.$^{99}$

1. The s-block and p-block elements form sp$^n$ hybrids, whereas d-block elements form sd$^n$ hybrids.$^{99}$ n is the number of orbitals minus one.$^{99}$

2. For molecules with mixed ligands, lone pairs, radicals, and/or multiple bonds, the distribution of p or d-character among the hybrid orbitals depends on the relative electronegativities of the ligands (Bent’s rule) and the bond orders.$^{99}$

_Lone pairs of p-block elements prefer s-orbitals$^{XXX}$, and singly occupied orbitals prefer p-character.$^{99}$ Lone pairs and singly occupied orbitals for d-block metals prefer purely d-character.$^{99}$ By this_
definition, the bond angles of singlet and triplet :CH\textsubscript{2} can be accurately calculated through orthogonality of the hybrid orbitals.\textsuperscript{99} The increased bond angle in triplet carbene is then caused by the higher s-character in the C-H bonds.\textsuperscript{99}

By symmetry restriction, no s-character can be used in \textpi-bonds. Therefore \textpi-bonds are purely p-character in main group elements and purely d-character in transition metals.\textsuperscript{99}

3. Strong ionic-covalent resonance rationalizes hypervalent bonding; such resonance commonly maximizes at a linear arrangement of the electron pair bond and the ligand localized electron pair.\textsuperscript{99} (In a way the ligands compete for the interaction with the metal sd\textsuperscript{n} orbital).

Normal and hypovalent (less than 12 electrons) structures will adopt normal sd\textsuperscript{n} configurations with n+1 ligands. sd and sd\textsuperscript{2} configurations adopt square bond angles.\textsuperscript{99} sd\textsuperscript{3}, sd\textsuperscript{4} and sd\textsuperscript{5} configurations can adopt several structures with the respective bond angles (71°, 109°); (66°, 114°); (63°, 117°).\textsuperscript{99}

Hypervalent species are constructed with the excess of ligands in normal valent bonding, trans to a already present ligand, to maximize the resonance structures with an ionic character: L-M\textsuperscript{+}L\textsuperscript{-}L\textsuperscript{-}M\textsuperscript{+}L.\textsuperscript{99} By this definition, if expanded to donor-acceptor bonds, the Cr(CO)\textsubscript{6} or W(CO)\textsubscript{6} complex is sd\textsuperscript{2} hybridized with three excess ligands trans to the 3 already present orthogonal ligands.\textsuperscript{99} Note that Frenking et al. calculated only an 8% p-orbital stabilization of the total orbital CO\rightarrow W stabilization, which hints more to a sd\textsuperscript{2} hybridization than a sd\textsuperscript{2}p\textsuperscript{3} hybridization.\textsuperscript{135} Qualitative VB theory has also been extended to include \textpi-effects.\textsuperscript{143}

The main reason for the high credibility of the VB theory is its highly accurate prediction of TM-complex configurations compared to the VSEPR-theory. However, its theoretical basis of non-p hybrid orbitals for the TM series has been under great attack.\textsuperscript{128,144, XXXII} Morokuma et al. presented a critical discussion on NBO for TMs.\textsuperscript{144} The authors calculated an increase (0.04e \rightarrow 0.20e) in p-electron density for linear Ni(H)\textsubscript{2} when the p-orbitals were introduced in the valence space instead of the ‘Rydberg’ space in the NBO analysis.\textsuperscript{144} The authors also calculated the partial charges on (PH\textsubscript{3})\textsubscript{4}Os(H\textsubscript{2})H\textsuperscript{+} (18e), for which Os shows a negative charge of -1.98 e in the p-orbital extended valence space.\textsuperscript{144} Morokuma et al. found that such a value is quite unreasonable for a metal which is in a formal oxidation state of +II.\textsuperscript{144} However, we want to point out that the formal assignment of oxidation states combined with metal-p orbitals which have a big radius and a very low density at the metal centre is also unreasonable. If these electrons show a higher density at the ligands than at the metal, maybe they should be assigned to as ionized p electrons and not be counted to the metal charge (vide infra).

Hall et al. have presented ORSAM (Orbitally Ranked Symmetry Analysis Method) as an alternative method for the VB theory.\textsuperscript{145} In their article, the theoretical basis for an exclusive sd valence space with NBO (Natural Bond Orbital) analysis is attacked because the NBO analysis does not include metal p-orbitals in the valence space.\textsuperscript{145} Using a modified version of NBO, the authors also assigned significant p-population (0.27) to the NiH\textsubscript{2} complex.\textsuperscript{145} The authors propose that contrast of the maximize in the bonds to the least EN atom, which would here be hydrogen and is also not consistent. The absolute s-occupancy in the orbitals is respectively 0.35 e, 0.35 e and 0.37 e, and is also in bad accordance with the VB theory.

\textsuperscript{XXXII} From semantic viewpoint, it should be noted that the combination of defining metals with higher than 12 electrons as hypervalent (more than normal valent) with the fact that most (normal) TM complexes are consequently hypervalent (have more than 12 electron-count) leads to a pure unfortunate contradictio in terminis.
involvement of p-orbitals in TM ‘hypervalent’ complexes compared to the lack of involvement of d-orbitals in p-block elements is caused because the first excited state containing a d orbital in the latter is 2-9 times higher than the first excited state to a state containing a p orbital of the former.\textsuperscript{145}

ORSAM validates the VB theory in normal and hypovalent complexes with the preferential sd hybridization in spite of p-orbital involvement.\textsuperscript{145} Hypervalent structures are represented in ORSAM as being stabilized by the extra hybridization through p-orbitals.\textsuperscript{145} However, ORSAM gives a wide variety of possible geometries for certain complexes, and this is one of the reasons why it is more difficult to predict a wrong complex geometry for a TM complex with this theory.\textsuperscript{145}

According to Frenking et al., neither the work of Hall et al. or Landis et al. gives a definite answer on the importance of the valence (n)p functions of TMs for chemical bonding.\textsuperscript{128} The only way to make definite judgments on both systems is through quantum mechanical (QM) calculations, which are not biased in the evaluation algorithm.\textsuperscript{128} This was performed for [PdH\textsubscript{3}]-, where the Pd-p-contribution of the two equatorial hydrogens almost equals the s- or d-contributions (27\% of the metal contribution to the bond).\textsuperscript{145} Frenking et al. calculated the orbital energy contributions (EDA) of the populations of s,d,p orbitals for W(CO)\textsubscript{6} and found only 8\% contribution for the p-population.\textsuperscript{135} We want to point out that the d-population energy contribution gradually decreases (77\%→66\%) and the s,p-contributions increase (15\%→20\%, 8\%→14\%) upon introduction of a positive charge on the M(CO)\textsubscript{6} complex going to Ir(CO)\textsubscript{6}\textsuperscript{3+}. Off course, the cationic complexes show a longer bond distance and less ‘short-distance’ π-bond interactions.\textsuperscript{135} To our opinion these are integrated events: The positive charge induces the decrease in backbonding. The decrease in the ‘short distance interaction’ backdonation should facilitate an elongation of the bond, which should manifest itself in more population in the orbitals with a higher radius. These are the s and p orbitals (more voluminous due to a higher principal quantum number). Furthermore, in analogy, a more ionic bond (high ∆EN) should show higher sp character for TMs due to the increased electron delocalization of the metal electron to distances further from the centre of the metal. In this respect it is interesting to inspect the analogy to the Frenking-Bent rule for TM complexes which states that ‘The energetically lower lying valence orbital concentrates in bonds directed toward electropositive elements’\textsuperscript{128} which means that s (and p even more if there are enough electrons for them to be used) character is centered to the EN elements which is clearly evident in Me\textsubscript{2}MCl\textsubscript{2} complexes.\textsuperscript{128}

It should also be noted that the p-character in the series Me\textsubscript{2}TiCl\textsubscript{2}, Me\textsubscript{2}ZrCl\textsubscript{2}, Me\textsubscript{2}HfCl\textsubscript{2} only starts to contribute to the bond in the Hf complex (5\% and 11\% of the M-orbital contribution for respectively C and Cl).\textsuperscript{128} However, this increase in p-character does not significantly change the bond angles, which points to a lack of interference of the p-bonds in the hybridization.\textsuperscript{128,146} However, no explanation of this phenomenon was added.\textsuperscript{146}

[PdH\textsubscript{3}]\textsuperscript{-} which was correctly handled for p-population analysis shows a higher bond distance (1.702 Å) for the equatorial hydrogens than for the axial hydrogen (1.518 Å).\textsuperscript{145} According to us, this higher bond distance can be assigned to an increased mixing of the sd (H\textsubscript{equatorial}) orbital with the p-orbitals, instead of the resonance structures in VB theory. This higher p-character should increase the bond length. However, this does not eliminate the trans-competition criterion, since the two equatorial ligands now compete for the low lying d-orbital, which is else replaced by p-character. This is obvious in the axial hydrogen which only has a minimal p-character. Furthermore, the lack of p-character in the M(CO)\textsubscript{6} bonds can be rationalized by a tight and close bonding through π-back-bonding, which disables involvement of the p-orbitals.
Very recently, Landis and Weinhold presented a discussion on whether the expansion of the valence space for TMs with p-orbitals is chemically and mathematically more reasonable.\cite{147} All complexes investigated are hydride complexes.\cite{147} First, it was shown that the hypovalent and normal valent (12 e) complexes show typically well localized bonds with low p-populations in both the standard (6s5d) NAO\textsubscript{s} (Natural Atomic Orbital) and the extended (6s5d6p) NAO\textsubscript{x} analysis.\cite{147} However, the hypervalent structures (>12 e) show strong 3-centre 4-electron (3c/4e) resonance delocalization, especially for the NAO\textsubscript{x} analysis.\cite{147} In the NAO\textsubscript{s} description, the p-occupation increases significantly (0.1→1 e) and the charge on the metal is much more negative compared to the NAO\textsubscript{s} method. Furthermore, these two values are strongly connected to each other.\cite{147} For some complexes ([PtH4]\textsuperscript{2-} and [AuH4]), the ‘6p’ orbitals are unrelated to the physical 6p-orbitals, but instead correspond to 7p-like energy and diffuse character.\cite{147} ‘The peculiar nodal structure confirms that “7p” gains superficial importance only because of the diffuse sprawl of its middle lobe over neighboring hydride centers, not because of any real physical connection to the 7p atomic orbital of the metal.’\cite{147} ‘The diffuse, high-energy “7p” is concentrated directly atop the hydride ion, from which it acquires spurious “partial occupancy”.’\cite{147}

The accuracy of the sd-localized and sd-resonance structures was compared and it was found that for the hypervalent structures the localized description shows a much higher RMSD (Root Mean Square Deviation) error and can hence be classified as an inferior method.\cite{147} Furthermore, the sd-resonance method is compared to the localized spd method.\cite{147} The RMSD error shows increased values for the localized spd description, which leads the authors to conclude that the sd-resonance method is superior.\cite{147} However, we wonder why no resonance structures of the spd-method were evaluated? It is not because the spd-orbital space can fully describe the valence space, that no resonance should be taken into account. Furthermore, as shown here, the p-orbital occupancy generally presents the increased negative charge measured with the spd-method. This means only that physically the metal-p-electrons are far away from the metal centre and should not be formally counted as metal electrons in the oxidation state (OS) count since their occupancy near the ligands is higher. This shows that the spd-localized and sd-resonance methods are highly resonant explanations for the same physical phenomenon and should hence be integrated in a sd-resonance-spd-localized method.

### 2.6 Phosphine and amine ligands

Phosphine ligands have been widely used in organometallic chemistry and catalysis. Due to their high (but tunable) electron donation and tunable steric character, they have been perceived as unique ligands until the emergence of NHCs. Therefore, much attention has been spent on the description of such ligands. On the other hand, to the best of our knowledge, amines and even more imines have remained in a quasi black hole of organometallic-QM description.

The general textbook explanation on the properties of phosphines in organometallic complexes is provided by the Tolman steric and electronic parameters.\cite{148} In 1977, Tolman set the standard for the electronic parameter of the phosphines as the frequency of the A\textsubscript{1} carbonyl mode of (the tetrahedral) Ni(CO)\textsubscript{3}L in CH\textsubscript{2}Cl\textsubscript{2} as a general mode for the ‘electron donating’ character of the phosphine.\cite{148} It goes without saying that this can only be a measure for charge transfer and not for differentiation in σ-bonding and π-backbonding. Tolman also introduced a parameter for the steric influence. The steric parameter was defined as a cone angle with the P in the top of the cone and the cone touching the Van der Waals radii of the outermost atoms.\cite{148}
In 1985, Orpen et al. were able to establish a π-acceptor function besides the σ-donation function. The backbonding is supposed to go to the LUMOs of the phosphorous compound (PR₃), which are a mixture of phosphorous 3d and P-R σ* orbitals. At present only σ* character is assumed to contribute. This level becomes more stabilized with increased deviation of the planar structure. Hence, complexes with increased backbonding should exhibit higher P-R distances and smaller cone angles.

Pacchioni et al. investigated the role of the 3d orbitals with Constrained Space Orbital Variation (CSOV) and concluded that backdonation occurs to the σ٭ orbitals though the d functions reinforce the backbonding. The d orbitals act as polarization functions in the formation of hybridized π-orbitals on PR₃. Furthermore, the authors showed that through this function the d orbitals provide a shortening of the bond distance and that the effect on a CO in trans position is caused by the change in π-acidity of the phosphine.

Nolan et al. investigated the bond energies for CpRu(PR₃)₂Cl systems for which was concluded that in this crowded system mainly steric influences determine the phosphine bond energies. The data also show that the Ru-P bond lengths decrease with decreasing steric interactions and increasing bond enthalpies for the phosphine in the tetrahedral CpRu(PR₃)₂Cl species. It can therefore be concluded that this system is controlled by steric effects. Nolan showed that in contrast, (CO)Rh(PR₃)₂Cl acts similar to the Tolman complex Ni(CO)₃L in having mainly electronic influences on the bond enthalpies. There appears to be a good correlation between the increasing Ru-P bond enthalpy, the decrease in π-withdrawing capacity (concomitant with an increase in σ-donor capacity) and the decreasing υ(CO) values in the (CO)Rh(PR₃)₂Cl complexes. This can easily be explained by the competition for π-backbonding with CO which should disfavor the complexation of another π-acceptor. A similar trend was detected for the Ni(CO)₃L complexes. In the weak π-accepting complexes (R₂P--N--R₂P)Rh(PR₃), the Rh-PR₃ enthalpies increase with an increasing π-backbonding capacity of PR₃. We suggest this is also caused by the lack of competition for π-backbonding. Accordingly, Nolan et al. suggest that nitrogen is a good σ/π-donor (in this complex) and is expected to render rhodium relatively electron rich. Nolan et al. also acknowledge the dichotomy between the square pyramidal (CO)RhCl(PR₃)₂ and (R₂P--N--R₂P)Rh(PR₃) and explain that ‘In the case of [RPNP]Rh(PZ₃), substitution occurs trans to a good σ/π-donor and modest π-donor (Cl). In addition, RhCl(CO)(PZ₃) already contains a potent π-acceptor ligand, CO… Comparing the two sets of complexes it is concluded that the balance of σ-donor, π-donor, and π-acceptor ligands ultimately determines the position of a ligand exchange equilibrium … This is a

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XXXIII We should warn for the resemblance of bond enthalpies of L with the υ(CO) frequencies or bond distances and point out that the correlation between υ(CO) and the bond energy is probably due to the good correlation of the bond energy with the π-accepting function.
direct consequence of the synergistic bonding between these donor/acceptor ligands and shared metal orbitals.154!

Landis et al. demonstrated with DFT studies that the introduction of π-acceptor ligands, which are less σ-donating, in the Rh systems (2.59→2.60) reverse the bond energy sequence of PR₃, so that the weaker π-acceptors (and better σ-donors) show higher bond energies in 2.60.153 Trans influences, measured as the difference in cis/trans complexes of (CO)Rh(PR₃)₂Cl, do not seem to change the sequence.153 The Rh-PR₃ bond lengths become longer and the Rh-CO bonds shorten as increasingly σ-donating (concomitant with decreasing π-accepting; not accredited) PR₃ ligands are applied.153 The authors conclude from these results that ‘these behaviors are consistent with the expectation that increasing the donor ability of PR₃ will enhance the Rh→CO π-back-donation.’ We suggest this is also caused by the decreased π-backdonation to the phosphine as a π-influence in the square planar complex, and that the increased charge on the metal is only of secondary importance. Furthermore, the small effect of the nature of PR₃ on the variance of the charge on Rh for 2.59-2.61 does suggest that the charge on Rh has little to do with it and that qualitative orbital interactions should be held responsible. Moreover, the formal charge on the metal in 2.59 (which lacks potent π-acceptors and has high bond strengths for PR₃ ligands with good π-acceptors) is intermediate to 2.60-2.61.

![Figure 2.26: Rh-P complexes investigated by Landis et al.](image)

The CDA results on these complexes are quite remarkable.153 First, the 138 complexes show very different values for both donation and backdonation for the different phosphines.153 Somehow (through competition effects), this change in electron density is ventilated because the electron density at Rh shows a negligible variation for these complexes! The same trend is observed for a PCP ligand.153

| Table 2.2: CDA for donation and backdonation in Rh-P Landis complexes. |
|-----------------|-----------------|-----------------|-----------------|
| d(P→Rh) (e) | b(Rh→P) (e) | d(P→Rh) (e) | b(Rh→P) (e) |
| 2.59-PH₃ | 0.345 | 0.179 | 2.61-PH₃ | 0.35 | 0.121 |
| 2.59-PH₂F | 0.321 | 0.244 | 2.61-PH₂F | 0.263 | 0.157 |
| 2.59-PHF₂ | 0.199 | 0.268 | 2.61-PHF₂ | 0.145 | 0.16 |
| 2.59-PF₃ | 0.091 | 0.269 | 2.61-PF₃ | -0.02 | 0.126 |
| 2.60-PH₃ | 0.428 | 0.148 | 2.61-PH₃ | 0.474 | 0.36 |
| 2.60-PH₂F | 0.282 | 0.182 | 2.61-PH₂F | 0.369 | 0.305 |
| 2.60-PHPF₂ | 0.121 | 0.192 | 2.61-PHPF₂ | 0.33 | 0.3 |
| 2.60-PF₃ | -0.016 | 0.196 | 2.61-PF₃ | 0.288 | 0.245 |

Data from 153.
A decrease in average donation and backdonation can be observed in the transition form 2.59 to 2.60. The decrease in donation is paradoxical with the introduction of a more π-acidic and less σ-donating ligand environment and therefore we conclude that the change in σ-donation of PR₃ is mostly a secondary effect. We suggest that mainly the increased π-acidic capacity of the ligand environment going from 2.59→2.60 induces a decrease of the PR₃ π-accepting capacity and a decrease of the variance in this π-accepting capacity. This decreased average backdonation apparently gives rise to a decrease in average donation. The competition for backbonding with the PF₂—N—PF₂ ligand decreases the ability of PR₃ to backbond successfully (less and without differentiation). The decrease in donation of the phosphine could then be caused by the decrease in backdonation in an attempt to maintain some synergy in the donor-acceptor bond. Only the intrinsic more basic PH₃ ligand is able to donate more to the increased π-acidic environment. However, the σ-donation-variance remains mainly unclear. One could claim that, due to the decrease of potent σ-donors on the complex, less competition for efficient σ-donation occurs with the other ligands which increases the variance. Analysis of 2.61 should make things more clear on that.

Table 2.3: Change in donation, backdonation for the Rh-P Landis complexes.

<table>
<thead>
<tr>
<th></th>
<th>d(MAX-MIN) (e)</th>
<th>b(MAX-MIN) (e)</th>
<th>d(average) (e)</th>
<th>b(average) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.59</td>
<td>0.254</td>
<td>0.09</td>
<td>0.239</td>
<td>0.24</td>
</tr>
<tr>
<td>2.6</td>
<td>0.444</td>
<td>0.048</td>
<td>0.2038</td>
<td>0.18</td>
</tr>
<tr>
<td>2.61</td>
<td>0.37</td>
<td>0.039</td>
<td>0.1845</td>
<td>0.141</td>
</tr>
</tbody>
</table>

Data calculated from 153.

An increase of the π-withdrawing ability in 2.61 further decreases the average backbonding to the phosphor. Again, this decrease in backbonding is concomitant with a decrease in average donation of the phosphine. This can be correlated with the tendency of the phosphine to hold its natural synergistically donor-acceptor character. Yet, this remains ambiguously and we suspect other reasons could be responsible for the phenomenon. For the backdonation, the decrease in average value consistently corresponds with a decrease in the variance of the backdonation (with a remarkable decrease in backdonation for PF₃). On the other hand, the variance in backdonation is well expressed with the more potent backdonator CO.

It is also interesting to analyze the bonding of CO in 2.61. As mentioned, the backbonding decreases with the introduction of more potent π-accepting PF₃ ligands. Furthermore, consistently contradictory to the expectation that upon introduction of decreased σ-donation and increased π-backdonation of the other ligands, CO should become more σ-donating, this does not occur. Instead the σ-donation declines consistently with the phosphine trend between 2.59→2.60, upon declining π-donation of CO. Apparently, the synergy in the donor-acceptor bond should not be taken lightly.

Landis et al. conclude that the ‘Rh-P bond strengths are not universal and not transferable.’ [italics original] 153 The calculations show that the Rh-PR₃ bond lengths shortened with increasing number of π-accepting F-substituted phosphines in all complexes. 153 Furthermore, ‘If a good π-acceptor ligand is present (such as CO), Rh-P bond strengths increase with phosphorus σ-donor strength. If there is not a good π-acceptor ligand, the Rh-P bond strengths increase with π-accepting capacity of the phosphorous.’ 153 We would like to add that the donating and backdonating values of a donor-acceptor ligand are, certainly for square pyramidal complexes, mainly determined by the π-accepting abilities of the ligand set around the metal. This should lead to a straightforward determination of ω(CO) frequencies based mainly on the π-accepting abilities of the ligand set.
However, all this says little about the actual nature of a phosphine. In the last 20 years, a theoretical development describing phosphine ligands called QALE (Quantitative Analysis of Ligand Effects) has evolved to the most used description for handling the phosphor-ligand realm.\textsuperscript{XXXIV} According to QALE, a ligand is determined by 4 factors: the $\sigma$-donor capacity described by $\chi_d$, the $E_{ar}$ effect (which is not only restricted to aryl groups), the $\pi$-acidity ($\pi_p$) and $\theta$; the steric parameter with a steric threshold $\theta_{st}$ exists and the switch function $\lambda$ for when the steric hindrance surpasses the steric threshold.\textsuperscript{155} (A high $\chi_d$ indicates a high $\sigma$-donating capacity.)

Each physiochemical property is then described by the equation:

$$\text{Property} = a \chi_d + b (\theta - \theta_{st}) \lambda + c E_{ar} + d \pi_p + e$$

The greatest accomplishment of QALE is the separation of the Tolman Electronic Parameter $\chi$ into a $\sigma$-component $\chi_d$ and a $\pi$ component.\textsuperscript{156} This has led to the clarification on the nature of ligands such as $\text{P(CH}_2\text{CH}_2\text{CN)}_3$, which was previously considered a good $\pi$-acceptor due to its high $\chi$.\textsuperscript{156} QALE analysis on the other hand, revealed that the ligand is a poor $\pi$-acceptor, and even a poorer $\sigma$-donor which causes the low $\chi$ value.\textsuperscript{156}

The QALE parameters of a few important phosphines are depicted below.\textsuperscript{XXXV}

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>$\chi_d$</th>
<th>$\theta$</th>
<th>$E_{ar}$</th>
<th>$\pi_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF$_3$</td>
<td>44</td>
<td>104</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>42</td>
<td>124</td>
<td>4.1</td>
<td>5.3</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>15.8</td>
<td>109</td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td>P(Ph)$_3$</td>
<td>13.25</td>
<td>145</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>17</td>
<td>87</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td>P(Me)$_3$</td>
<td>8.55</td>
<td>118</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P(i-Pr)$_3$</td>
<td>3.45</td>
<td>160</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCy$_3$</td>
<td>1.4</td>
<td>170</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Data from\textsuperscript{155}.

As for the link to metathesis, it is valuable to note that although PH$_3$ is often considered to show good resemblance with PMe$_3$ and PCy$_3$ (or PMe$_3$ with PCy$_3$), QALE definitely shows the opposite. Therefore, one should not make much conclusions from model calculations using PH$_3$ and PMe$_3$.

Nolan et al. investigated the complexes 2.61 with QALE and were able to conclude that the $\pi_p$ factor accounts for half of the variation in Rh-P bond length and $\nu$(CO).\textsuperscript{157} The $\chi_d$ and $\theta$ are equally responsible for the rest of the Rh-P bond distance, while the $\nu$(CO) variance is determined for one third by $\chi_d$.\textsuperscript{157} It is interesting to note that the $\sigma$-donor effect is here not considered negligible for the phosphines, as was previously suggested by us and others\textsuperscript{130} for carbenes.

The $\pi_p$ effect does not statistically effect the bond enthalpy calculated for the reaction $[(\text{CO})_2\text{RhCl}]_2 + 4 \text{PZ}_3 \rightarrow 2 \text{Rh}(\text{CO})(\text{Cl})(\text{PZ}_3)_2 + 2 \text{CO}$.\textsuperscript{157} This is rationalized by the competition for $\pi$-backbonding evidenced by the Rh-P bond length and $\nu$(CO) parameters.\textsuperscript{157} What is lost with CO is gained by PZ$_3$ and vice versa.\textsuperscript{157} We think that this characteristic points out an important principle in organometallic chemistry: A change in backdonation to the ligand can be masked in reaction enthalpies due to a change...
dissipation of the variation in backdonation to the rest of the ligand environment, thereby affecting the reactivity.

The reaction enthalpy of \( \text{Rh(acac)(CO)}_2 + \text{PZ}_3 \rightarrow \text{Rh(acac)(CO)(PZ}_3) + \text{CO} \) shows, in contradiction, a 50 % dependence of the \( \pi_p \) factor. This shows that upon the introduction of a \( \pi \)-donor the complex has not yet reached \( \pi \)-backdonation saturation. The results are also well in accordance with the conclusions from Landis et al. that Rh-P bond strengths only increase with increasing \( \sigma \)-bond strength when other potent \( \pi \)-acceptors are present in the ligand environment.\(^{153,157}\) From this, we can conclude that the high \( \pi \)-dependency of carbenes in \( \text{Cr(CO)}_5(\text{carbene}) \) complexes should indicate that the intrinsic capacity for backdonation of carbenes is at least in the realm and most probably higher than that for CO.

It should be noted that there still exists a controversy in the area. Koga et al. showed with Molecular Electrostatic Potential (MESP)\(^{XXXVI}\) that the \( \upsilon(\text{CO}) \) of \( \text{Ni(PR}_3)(\text{CO})_3 \) complexes is linearly correlated with the \( V_{\text{min}} \) of the phosphor lone pair, which implicitly suggests that the \( \upsilon(\text{CO}) \) frequencies of these complexes are not influenced by the \( \pi \)-acceptor capacity of the ligand!\(^{158}\) However, there can be no contradictions. We suggest that the MESP potential of the lone pair has implications on the rest of the orbitals:

1. Bulky and electron donating substituents should show a higher planarity of the PR\(_3\) structure. While these two factors increase the MESP and \( \sigma \)-donating ability, they surely also imply more difficult accessibility of the \( \sigma^* \) orbitals for backbonding.

2. Koga et al. state that ‘in general, when the \( d_{\text{C-P}} \) distance decreases, the \( V_{\text{min}} \) value becomes more negative.’\(^{158}\) When the \( d_{\text{C-P}} \) value decreases as in \( \text{P('Bu)}_3 \), this is due to an increase of s character in phosphor in the C-P bond and consequently an increase of p character in the lone pair. As the p character increases in the lone pair, it is located further from the nucleus and consequently is able to obtain a more negative MESP potential. However, this also implies less p-character in the \( \sigma \) and \( \sigma^*-\text{P-C} \) bond and hence the phosphor \( \sigma^* \) should be more concentrated close to the nucleus and be less available for backbonding.

3. When EN substituents are used, a dipole with the negative end towards the substituents is induced. This decrease in electron density activates the backbonding ability of the phosphor but also diminishes the MESP potential (due to lower electron density and/or closeness to the nucleus).

4. Pacchioni et al. calculated that the \( \sigma \)-donor capacity to a proton (and the polarization of PX\(_3\)) is fairly constant over the series \( \text{P(\text{CH}_3)}_3, \text{PH}_3, \text{P(\text{OCH}_3)}_3, \text{PF}_3 \), though the biggest difference in the proton affinity results from the purely electrostatic interaction.\(^{150}\) This purely electrostatic interaction is very limited in metal-phosphine complexes\(^{150}\) and from this one can conclude that it represents a rather poor analogy for the description of the organometallic bond. Since PA (Proton affinity) is determined by electrostatic interactions this also means that PA and MESP should be governed by the same force.\(^{150}\) Furthermore, while the \( \pi \)-accepting ability changes considerably in function of the PX\(_3\) ligand, the \( \sigma \)-donation is only slightly smaller in PF\(_3\) than in P(\text{CH}_3)\(_3\). Apparently, this conclusion contradicts the general belief that the trend in \( \sigma \)-basicity is, as measured by pK\(_a\) values, \( \text{PF}_3 < \text{P(\text{OCH}_3)}_3 < \text{P(\text{CH}_3)}_3 \). However pK\(_a\) values are not appropriate measures of basicity.\(^{150}\) The pK\(_a\) series nicely corresponds with the change in backbonding which is measured.

\(^{XXXVI}\) The aim of that work was to characterize the lone pair region of various substituted phosphine ligands using MESP. The MESP potential is as a quantity directly related to the interactive behavior of a molecule with a unit test charge. Lone pairs have negative values due to the higher contribution of the electronic term vs. the nucleus term. The global minimum potential \( (V_{\text{min}}) \) was used for the calculations.
This implies that the increasing dipole of the phosphine is responsible for the decreasing PA and MESP potential but also for the increasing electron-acceptance and decreasing electron-donation capacity of the phosphorus.

5. The Koga publication uses the Tolman complex Ni(PR\(_3\))(CO)\(_3\), in which the phosphor is not octahedral or square pyramidal but tetrahedral. This should increase the influence of the \(\sigma\)-orbital in the backbonding to CO due to symmetry considerations. In octahedral complexes the \(\sigma\)-donation and \(\pi\)-backdonation is performed by different types of orbitals. However, in this tetrahedral environment, the \(t_2\) orbitals (d\(_{xy}\), d\(_{xz}\), d\(_{yz}\)) act all as the orbitals accessible for \(\sigma\)-donation (after d/p hybridization) and for \(\pi\)-backdonation.\(^{130}\) This implies that in this tetrahedral environment the \(\sigma\)-donating P ligand directly interacts with the CO orbitals accessible for backbonding and that a correlation is to be expected. It is interesting to mark that the Grubbs complexes are not tetrahedral and that a similar reasoning cannot be applied.

Recently, a development called ‘Ligand Knowledge Base’ (LKB) has mapped the electronic properties with DFT calculated descriptors.\(^{159}\) Upon using this methodology, the authors were able to predict with high accuracy the TEP (Tolman Electronic Parameter), Rh-P distances in a Rh(I) complex and the enthalpies for the reaction \([(CO)\(_2\)RhCl]\(_2\) + 4 PZ\(_3\) \rightarrow 2 Rh(CO)(Cl)(PZ\(_3\))\(_2\) + 2 CO.\(^{159}\) Therefore, this method should be considered highly efficient in predicting properties of phosphine complexes. Furthermore, semi-empirical quantum mechanics (SEP) has also been applied with success to predict ligand geometries and \(\nu\)(CO) values. This method was found to give ‘a robust measure of ligand electronic effects that are fragment-independent.’\(^{160}\)

The resemblance of phosphorous ligands with NHCS or other ligands has been of great importance.\(^{161}\) Hu et al. discussed the difference of NHC complexation vs. phosphine complexation on the Cr(CO)\(_6\)L complexes via DFT calculations.\(^{108}\) We already discussed the NHC section in detail. The phosphine complexes all show an endothermic ligand exchange energy (\(\Delta E\)) for substitution in Cr(CO)\(_6\). This is in contrast to all the carbenes.\(^{108}\) The authors see this as a confirmation that phosphines are often used in an excess amount in catalytic processes.\(^{108}\) This endothermic reaction is caused by a sharp decline of the M-P bond energy (\(D_0\)) compared to the carbenes.\(^{108}\) No discussion is presented on the relative \(D_0\) energies. However, one can rationalize that they increase with a subtle correlation of increasing \(\sigma\) donating, \(\pi\) accepting capacity and decrease in steric strain. The authors suggest that ‘The steric effect of PCy\(_3\) is also seen in the longest d(Cr-P), shortest d(Cr-CO\(_{trans}\)), smallest \(\nu\)(CO) and k(C-O\(_{trans}\)) of its complex. The \(\pi\)-accepting ability is therefore the smallest among phosphines’\(^{108}\). This is a bold statement and an accreditation of the subtle interplay between the phosphine properties. In this context, it is useful to note that Jensen et al. calculated that the large PCy\(_3\) in the Grubbs complex, having a zero value for \(\pi_\pi\) in QALE, still receives one sixth of the charge lost from donation by backdonation.\(^{96}\) PPh\(_3\) shows a 1/5 ratio, PH\(_3\) a 1/4 ratio and PF\(_3\) almost a 1/1 ratio for the backdonation/donation in the Grubbs complex.\(^{96}\) This point out that there is no direct correlation between the QALE \(\pi_\pi\) value and the real \(\pi\)-backdonation in complexes, because the zero value still corresponds to residual backdonation.

Hu et al. suggest that ‘\(\nu\)(CO) and k(C-O)\(_{trans}\) are inversely proportional to cone angles, indicating that \(\pi\)-back-bonding of phosphine is hindered by steric strain.’\(^{108}\) We already noted that \(\pi\)-backbonding should be more dependant on bond length. This implies that a very steric environment can induce a sharper decrease of this type of bonding. The exception on this rule is PF\(_3\), which already has a strong intrinsic \(\pi\)-backdonating capacity.\(^{108}\) However, the lack of correspondence of \(D_0\) (M-L
bond energy) and $D_0$ (M-CO bond energy) with the cone angle suggest that this should not be taken as the criterion to assess the phosphine-metal total bond.\footnote{Hu et al. acknowledge some correlation between the proton affinity and the $k(C-O_{\text{trans}})$ with $R^2 = 0.916$ for the phosphines and $R^2 = 0.942$ for the carbenes.} They continue that ‘Since the PA is more of the $\sigma$ effect, the good correlation between PA and $k(C-O_{\text{trans}})$ [and $\nu$(CO)] suggest that $k(C-O_{\text{trans}})$ and $\nu$(CO) reveal information about the electron density induced by different ligands on the metal center and the carbonyl groups. They do not necessarily reveal $\pi$-back-bonding ability of the ligands, however.’\footnote{An ambiguous statement, which follows their previous assessment that ‘The difference in $k(C-O)$ should not be attributed to back-donation alone.’} Here, we want to refer to the reasoning we applied for MESP. (vide supra)

Furthermore, Hu et al. calculated the nucleophilicities and concluded that PCy$_3$ and PPh$_3$ are better nucleophiles than the NHCs (except for H$_2$IMES) and found that this correlates ‘fairly good’ [emphasis ours] with the $\nu$(CO) frequencies.\footnote{Crabtree et al. catalogued a series of ligands in the TEP space. It was calculated that IMe (2.49) is actually less electron donating than P(Me)$_3$ based on $\nu$(CO)’s of the Ni(CO)$_3$L complex.\footnote{Hu et al. reported the opposite result for the same complex.} Crabtree et al. found that the saturated analogue H$_2$IMe surpasses the donating ability of P(Me)$_3$ (as did Hu et al.). Quite remarkably, Crabtree et al. catalogued the ‘net donating ability’ of P(Me)$_3$ only marginally better than that of N(Me)$_3$ on the basis of TEP.\footnote{For the PF$_3$; NF$_3$ and PH$_3$; NH$_3$ couples the amines were even calculated to be the better ‘net donors’, which means the amines show lower $\nu$(CO)$_{\text{trans}}$ frequencies.}

In 2005 Harvey et al. investigated the influence of oxidation of the metal on the M-P bond in M(CO)$_5$L complexes for simple phosphines as PH$_3$ and PMe$_3$.\footnote{The calculated and crystallographic results show that upon oxidation ‘The lengthening of the M-P bond, shortening of the P-H or P-C bond, as well as the opening of the H-P-H or C-P-C angle, and the lengthening of the M-C bond and shortening of the C-O bond are well consistent with a decrease in back-bonding towards PH$_3$ (or PMe$_3$) and CO ligands upon ionization.’ In contrast, amines act differently and show a shortening of the M-N bond, a lengthening of the N-X bond and a shortening of the X-N-X angle.\footnote{The authors}} The authors

\begin{table}[h]
\centering
\begin{tabular}{|l|cccccccc|}
\hline
 & $\Delta E$ (kcal/mol) & $D_0$ (kcal/mol) & $D_0'$ (kcal/mol) & PA & $k(C-O)_{\text{trans}}$ (N/cm) & $\chi_d$ & $\theta$ & $E_{\text{ar}}$ & $\pi_p$ \\
\hline
PF$_3$ & 7.7 & 32.2 & 41.2 & 156.1 & 17981 & 44 & 104 & 0 & 14 \\
PH$_3$ & 15 & 24.9 & 39.6 & 185.1 & 17466 & 17 & 87 & 0 & 3.7 \\
PMe$_3$ & 3 & 36.9 & 39.4 & 227.2 & 17319 & 8.55 & 118 & 0 & 0 \\
PPh$_3$ & 9.8 & 30.1 & 33.2 & 236.8 & 17187 & 13.25 & 145 & 2.7 & 0 \\
PCy$_3$ & 12.4 & 27.4 & 26.4 & 247.2 & 17096 & 1.4 & 170 & 0 & 0 \\
\hline
\end{tabular}
\caption{Parameters of the Cr(CO)$_5$phosphine complex.}
\end{table}

Data from\footnote{However Hu et al. catalogue on the basis of TEP that IMe as a better donor than H$_2$IMe. This again contrasts with their conclusions that saturated carbenes are the better donors.}
state that 'The main change is a shortening of the M-N bond, which can readily be understood as being due to stronger metal-ligand σ interaction for the cationic complex. It can also be noted that the variations in the C-O and M-C bond lengths of the trans–CO ligand are more important for the amine complex than for PH₃ or PMe₃ complexes. This suggests that PH₃ and the trans-CO ligand compete for back-bonding from the same metal d orbital, thereby weakening the back-bonding to CO. [emphasis ours] As this competition is no longer present with the NH₃ ligand, stronger CO back-bonding effects are seen for the latter.' To understand this, one has to acknowledge the π-backbonding saturation of the complex. Upon oxidation, the decrease in backbonding can than be divided between the CO and the phosphine leading to slightly decreased effects. This effect is also seen with the CO₃cis ligands, which show less distortions due to the increased trans-π-acidic effect.

Harvey et al. also investigated the Fukui functions after ionization. The condensed Fukui functions (here f) show distinct substantial components from the HOMO and the relaxation. The positive charge is only 50% present on the metal ion and the rest is redistributed to the phosphor and CO ligands in a decrease in backbonding and an increase in σ-donation. A visual inspection of the Fukui functions shows a significant loss in backbonding to the phosphine P-R σ٭ orbitals.

Frenking et al. judge in the familiar condemning tone in 2002 'We wish to comment on the way the topic of π-acceptor strength of ligands is frequently addressed and discussed in literature. Many workers take the correlation between a measured quantity, such as a vibrational frequency or a force constant, NMR chemical shift components, or coupling constants, and selected theoretical data such as orbital populations as a measure of π-acceptor strength. While such procedures may be helpful to establish an ordering scheme of the ligands, they can be deceptive, because any observable quantity is the result of the total interactions between the ligand and the complex fragment. Without an explicit analysis of the actual changes of the σ and π charges and the associated effects on the observed properties, any statement about π-acceptor strength remains a speculation. For example the QALE (quantitative analysis of ligand effects) method has been developed as a mathematical tool to correlate the properties of phosphane ligands with so-called stereo-electronic parameters, which are then suggested as an indicator of π-acceptor strength. It is questionable whether a good correlation between different parameters is indicative of real change in the electronic structure. We also want to point out that the relative π-acceptor strength of the ligands can only be established with respect to a given complex fragment. Two ligands may have a reverse π-acceptor strength in combination with complex fragments of two different metals. Therefore, a description of the π-acceptor strength of ligands without a metal donor fragment as reference seems questionable. Finally, we want to mention that π-acceptor interactions may have different effects on experimental parameters. Vibrational spectra, NMR chemical shifts or coupling constants, and bond energies are affected to a different extent by π-acceptor interactions. Consequently, statements about the alleged strength or weakness of a ligand as a π-acceptor should be made with caution. However, such correct estimations are exactly what we need as organometallic and catalytic chemists in order to predict trends in the organometallic behavior. Furthermore, the central paradigm of science is to establish relations between experimental data and scientific concepts. It goes without saying that in chemistry qualitative environment changes can and will affect this `intrinsic nature’. Now the goal of organometallic chemistry and QM should be to establish these intrinsic natures and the possible variations caused by the environment. Frenking et al. note that in M(CO)₅PR₃, there is no tilting of the CO₃cis groups toward the COtrans or towards the PX₃ (in contrast to the analogous :CH₂ complex). The calculated and experimental metal-CO distances show that the CO ligands cis to the PX₃ group always have longer bonds than the
trans-CO group.\textsuperscript{140} From this, we conclude that the \(\pi\)-backdonation with PR\(_3\) ligands is less intense than for CO.

The M-PX\(_3\) bond distance increases in the order PF\(_3\) < PCl\(_3\) < PH\(_3\) < PMe\(_3\), which corresponds to the same sequence for the C-O\(_{\text{trans}}\) distance and to the reverse order in the M-CO\(_{\text{trans}}\) bond distance; PF\(_3\) > PCl\(_3\) > PMe\(_3\) > PH\(_3\).\textsuperscript{140} Frenking et al. argue that ‘This result supports the model of competitive M\(\rightarrow\)L back-bonding for ligands which are trans to each other.’\textsuperscript{140} [emphasis ours] ‘The axial M-CO bonds of M(CO)\(_5\) trans to the hole are significantly shorter than the equatorial bonds. They become clearly larger in (CO)\(_3\)MPX\(_3\) but remain shorter than the equatorial bonds.’\textsuperscript{140} This should stress again the decreased influence of phosphor compared to CO for CO in the trans position. Moreover, since phosphor is a better \(\sigma\)-donor than CO, the shortening of the M-CO\(_{\text{trans}}\) bond cannot be related to a \(\sigma\)-trans influence.

The P-X bonds in the complexes are always shorter than in the free PX\(_3\) ligands.\textsuperscript{140} XXXVIII Frenking et al. stress that there is no correlation between the M-PX\(_3\) bond lengths and their BDE which decrease in the following order; PMe\(_3\) > PF\(_3\) ≥ PH\(_3\) > PCl\(_3\).\textsuperscript{140} Furthermore, steric strain should not be taken as the cause for the bond distances.\textsuperscript{140} The paradoxical result of decreased bond energies with decreasing bond distances can be rationalized by the fact that the shorter bond should correspond to a higher \(s\) character in the \(\sigma\)-bond, though the higher \(s\) character leads to a decrease of the orbital energy of the donating orbital and consequently in a decrease in the interaction.\textsuperscript{140} However, other effects influence the interactions which makes it difficult to predict if a longer donor-acceptor bond is weaker or stronger.\textsuperscript{140}

Upon coordination, the \(s\) character of the lone pair decreases dramatically in the order of the sequence PCl\(_3\) > PH\(_3\) > PF\(_3\) > PMe\(_3\) (which is the reverse order of the bond energies!).\textsuperscript{140} The charges of the PX\(_3\) fragments (which equal their net donation strengths) decrease -unexpectedly - in the order PMe\(_3\) > PF\(_3\) > PH\(_3\) > PCl\(_3\) (again the BDE order).\textsuperscript{140} The \(\sigma\)-donation of the PX\(_3\) fragments shows the same sequence while the b/d shows the reverse ratio.\textsuperscript{140} The b/d ratio is about \(\frac{1}{4}\) (except for PCl\(_3\) which reaches 40\%) and hence the phosphines should be considered strong donors and weak acceptors.\textsuperscript{140}

The EDA analysis shows that the \(\Delta E_{\text{prep}}\) is minimal.\textsuperscript{140} The steric and electrostatic contributions (\(\Delta E_{\text{pauli}} + |\Delta E_{\text{elstat}}|\)) are on average three times the contribution of \(|\Delta E_{\text{orb}}|\) while the pauli repulsion is always the biggest term.\textsuperscript{140} There is no correlation between the bond energy and the \(\pi\) contributions to the orbital interactions. This is to be expected in such a \(\pi\)-backbonding competitive environment. Furthermore, Frenking et al. conclude that the strength of the metal-ligand bonds is not determined by a single contribution alone, although the best correlation is found with \(\Delta E_{\text{elstat}}\).\textsuperscript{140} Frenking et al. also claim that ‘The results shown in Table 3 suggest the order PF\(_3\) > PCl\(_3\) > PMe\(_3\) > PH\(_3\) for the \(\pi\)-bonding contributions to the M-PX\(_3\) bonds, which is given by the absolute values of \(\Delta E_{\text{el}}\) and by the relative strength given as percent \(\Delta E_{\text{el}}\).\textsuperscript{140} However, the data in table 3 of the Frenking publication shows a different order of PX\(_3\) (\(\Delta E_{\text{el}}\), percent \(\Delta E_{\text{el}}\); PF\(_3\) (-31.58; 49.2\%) > PCl\(_3\) (-26.16; 46.3\%) > PH\(_3\) (-15.69; 31.2\%) > PMe\(_3\) (-14.15; 25.7\%).\textsuperscript{140} XXXIX This is the same order for the M-CO\(_{\text{trans}}\) distance and the reverse order for the M-PX\(_3\) and C-O\(_{\text{trans}}\) distances which thus suggests the dominance of \(\pi\)-phosphine factors for these parameters!

\textsuperscript{XXXVIII} This could be taken as an argument that the M\(\rightarrow\)PX\(_3\) \(\pi\)-back-donation takes place in the empty d(\(\pi\)) orbital rather than in the antibonding \(\sigma^*\) orbital. Frenking et al. think no such conclusion can be made due to two arguments: Upon coordination, the \(s\) character of the P-X bond increases (due to a decrease of \(s\) character in the lone pair) which leads according to Bent’s rule to a shortening of the P-X bond. Furthermore, upon coordination the phosphor receives an increased positive charge which may lead to a decreased bond distance in the P-X bond.\textsuperscript{140} Frenking, G.; Wichmann, K.; Frohlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Lage, M. Organometallics 2002, 21, 2921-2930.

\textsuperscript{XXXIX} G. Frenking acknowledged this ‘unfortunate mistake’ in a personal communication.
In the conclusions, Frenking et al. assert that there is no correlation between the BDEs and the bond lengths of the phosphors. In fact, the order PMe₃ > PF₃ > PH₃ > PCl₃ is the sequence for BDE, p-character of the σ-bond, q(PX₃), q-σ-donation, ΔE_pauli (and almost for ΔE_elstat). This is all logic: The bond energy is dominated by the σ-donation of the phosphor which is much larger than the backdonation (not to mention the highly competitive π-backbonding environment). This charge transfer proceeds easy with high p-character of the σ-bond causing the high pauli repulsions, but also high electrostatic attractions. However, it is strange that PF₃ shows this much p-character in the σ-bond, since the P in the P-F bond is expected to show high p-character. The PMe₃ > PH₃ > PCl₃ > PF₃ sequence corresponds to the M-P distance, C-O trans distance, inverse of M-CO trans distance, percentage of σ-contribution in the covalent bond and inverse of ΔE. One can reason that the covalent bond with the π-character in particular, rather than electrostatic interactions, dominate the bond distances while the σ bond is obviously more capable of operating on long distances than the π-bond (although the P-π-bond orbitals are not completely perpendicular to the M-P bond direction).

<p>| Table 2.6: Bond distances and energies in the Cr(CO)₅phosphine complex. |</p>
<table>
<thead>
<tr>
<th>PMe₃</th>
<th>PH₃</th>
<th>PCl₃</th>
<th>PF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Cr-CO trans) (pm)</td>
<td>186.6 (186.4)</td>
<td>186.6</td>
<td>187.9</td>
</tr>
<tr>
<td>ΔEπ (kcal/mol)</td>
<td>-14.15</td>
<td>-15.69</td>
<td>-26.16</td>
</tr>
<tr>
<td>ΔEσ (kcal/mol)</td>
<td>-40.96</td>
<td>-34.64</td>
<td>-30.43</td>
</tr>
<tr>
<td>d(Cr-P) (pm)</td>
<td>239</td>
<td>235.6</td>
<td>230</td>
</tr>
<tr>
<td>d(C-O trans) (pm)</td>
<td>115.9</td>
<td>115.7</td>
<td>115.4</td>
</tr>
<tr>
<td>d(Cr-CO trans) (Hu et al.) (pm)</td>
<td>187.1</td>
<td>187.1</td>
<td>189.7</td>
</tr>
<tr>
<td>d(Cr-P) (Hu et al.) (pm)</td>
<td>241.6</td>
<td>239.9</td>
<td>225</td>
</tr>
<tr>
<td>d(C-O trans) (Hu et al.) (pm)</td>
<td>115.64</td>
<td>115.51</td>
<td>115.05</td>
</tr>
</tbody>
</table>

The relative changes of d(Cr-CO)trans correlate well with the ΔEπ values as we earlier proposed in a trans-π-influence model. The ΔEπ values also dominate the d(Cr-P). However, the change seems to be less proportional. We think this is due to the lack of orthogonality of the π-acceptor orbitals and the domination of the σ-character in the total orbital interactions. No other explanation can be found for the increase in d(Cr-P) from PH₃ → PMe₃ and the more than proportional decrease from PCl₃ → PF₃. We suggest that the lack of orthogonality induces an increased expression of other bond-parameters. A similar problem of proportionality presents itself with the d(C-O trans) for which we note that the CDA should be able to present the actual charge transfers and is a better concept for this than EDA. The ΔEπ on the other hand correspond better with the d(Cr-P) distances calculated by Hu et al. The problem of proportionality remains for d(C-O trans). However, we can safely say that if one needs to correlate the distances of Cr-PX₃, Cr-CO and C-O in Cr(CO)₅PX₃ for non-steric phosphines with an organometallic concept, it should be the energetical stabilization of π-interactions in the P-Cr bond. This is very reminiscent of the conclusions we had to draw from the analysis of the Cr(CO)₅carbene complexes. This can only let us propose that the π-backbonding of L is responsible for the d(C-O trans) and consequently for the νCO trans. There remain two issues that we wish to point out. Firstly, Frenking did not investigate steric encumbered complexes, and Hu’s conclusions that ‘ν(CO) and k(C-O)trans are inversely proportional to cone angles, indicating that π-back-bonding of phosphine is hindered by steric strain.’ cannot be neglected. Secondly, all this is very contradictory with the dominating cataloguing parameter in NHC-classification, which holds the ν(CO) of Rh(Cl)(CO)NHC complexes as a direct measure for the (net) donating capacity of the ligand. This might correlate quite reasonably.
for tetrahedral complexes. However, in complexes with geometries dominated by straight angles, different mechanisms operate. In these complexes, the donating and backdonating effects are well separated and result in more complex behaviors.

In a comparative study of amines and phosphines as ligands Frenking et al. showed that ‘the bond dissociation energy (BDE) is not a good measurement of the intrinsic donor-acceptor strength of the complexes.’ In the Cr(CO)$_5$L complex, amines show lower interactions for $\Delta E_{\text{pauli}}$, $\Delta E_{\text{elstat}}$ and $\Delta E_{\text{orb}}$. The overall bond energies are also much lower (except for PH$_3$-NH$_3$ where the difference is only marginal). The stronger M-P bond is mostly caused by an overall doubling of the orbital interaction term. The $\nu$(CO) and Cr-N distances show no relation to the $\Delta E_{\pi}$ values. Upon investigating this feature, we came up with the following question: The amine already has obtained the octet structure and technically no backdonation from the metal is possible since there are no d-orbitals (or it should be minimal)? Gernot Frenking replied with: ‘Concerning your first question, please note that there are always empty orbitals in a molecule even when all atoms have a completely filled octet shell. For example, CH$_4$ has empty antibonding C-H orbitals in addition to the occupied C-H orbitals. The vacant antibonding orbitals are rather high in energy and therefore, they do not yield very stable molecules, but they may yield weakly bonded complexes with transition metal fragments. NH$_3$ also has empty N-H antibonding orbitals and they are better acceptor orbitals than the vacant C-H antibonding orbitals of CH$_4$ because the electronegativity difference is larger. BH$_3$ has rather high lying occupied B-H orbitals which can mix in H$_3$B-NH$_3$ with the vacant N-H antibonding orbitals. There may also be a mixing of the occupied N-H bonding orbitals with the vacant B-H orbitals but the latter pi-interaction should be weaker than the former because of the larger energy difference between occupied and empty orbital. Such interactions are not considered as violating the octet rule. You can see from our EDA data that the $\pi$ interactions in H$_3$B-NH$_3$ are rather weak.’ Hence, we conclude that due to the small effect of the $\pi$-interaction (half to 1/4th of phosphine interactions), it becomes of minor importance for the $\nu$(CO) and Cr-N distances. Furthermore, one can easily envisage that the actual charge transfers will be minimal due to the nitrogen octet structure.

After writing this chapter, we came in contact with a specific paper on the backbonding of amines and phosphines. Harvey et al. performed their study using NBO (Natural Bond Orbital) expanded with the three-centre four-electron bond. The $\pi$-accepting ability (kcal/mol) of L in a PdL complex and CO in a Pd(CO)L complex respectively are presented by the series NMe$_3$ (2.50/54.98) < NH$_3$ (4.29/54.24) < C$_2$H$_5$N (8.29/54.03) < PH$_3$ (14.91/42.64) < PPh$_3$ (15.38/46.09) < PMe$_3$ (16.44/46.08) < P(OOMe)$_3$ (18.31/43.12) < NF$_3$ (21.93/46.86) < PF$_3$ (23.68/33.88) < PCl$_3$ (24.96/34.18) < CO (50.24/35.12). As can be seen, the backbonding to normal amines is negligible. It becomes small in pyridine due to the availability of the $\pi^*$ orbital for backbonding. For the phosphines the $\pi$-accepting ability double the value compared to pyridine. Furthermore, the halogenated species NF$_3$, PF$_3$ and PCl$_3$ show the highest values except for CO which is clearly even a much more potent backbonder. The authors showed that in the CO-Pd-L complex the backdonation of both CO and L diminish with the increasing ‘intrinsic’ $\pi$-accepting ability of the other ligand. It should be noted that for L= NMe$_3$, NH$_3$ and pyridine, the $\pi$-accepting ability of CO shows a value of 54→55 kcal/mol, which also hints that the increase of $\sigma$-bond (of the trans ligand) leads to a change in the backbond. However, this 10% increase in backbonding of the amines changes to a 10% decrease for the lowest phosphine $\pi$-acceptors. This is clear evidence that whenever non-negligible $\pi$-accepting ability is present in a ligand, this $\pi$-accepting ability and not the $\sigma$-donor strength will be responsible for
the change in the backbonding to a competing ligand $L'$ in a $L_2M-L'$ complex.\textsuperscript{138} The ligands $L$ that are stronger $\pi$ acceptors will lead to a weaker backbonding interaction with the CO ligand, consistent with the chemical idea of two trans ligands competing for the same metal $d$ orbitals.\textsuperscript{138, XLI}

The same overall trends are observed for Cr(CO)$_5$L and Mo(CO)$_5$L complexes.\textsuperscript{XLI} The backdonation in the Mo complexes is also 1.5 times the value than in the Cr complexes.\textsuperscript{138} This is caused by the higher energy of the donor orbitals on Mo and the bigger overlap term.\textsuperscript{138}

Harvey et al. make a comparison of their results obtained with NBO and those obtained with EDA (ETS = Extended Transition State) for PH$_3$ and NH$_3$.\textsuperscript{138} It is first of all clear that the ETS method attributes much higher [emphasis ours] absolute values to the $\pi$ back-bonding interaction than the NBO analysis does. It also suggests that this interaction is stronger in the Cr than in the Mo complexes. Substantial back-bonding is also indicated towards the NH$_3$ ligands, with a $\pi$ interaction close to half that obtained for the PH$_3$ ligand in some cases. In the NBO calculations, going from neutral to the cation leads to a significant decrease in the strength of the back-bonding interaction. This is because the loss of one electron from the donor orbital, and because the increased charge leads to a lowering of the energy of all the donor $d$ orbitals, and to their contraction and hence the overlap with the acceptor orbitals. Decreased back-bonding upon ionization is also shown by analysis of the Fukui function for these compounds. In contrast, the ETS analysis does not show a substantial change in the strength of back-bonding upon ionization. In fact, for the NH$_3$ ligand, there is even a predicted increase in back-bonding upon oxidation. These trends in the ETS analysis are surprising in all respects (Cr vs. Mo, N vs. P, cation vs. neutral), whereas the NBO analysis gives in each case the expected trend. This relatively less good behavior of the ETS scheme can amongst others be attributed to the fact that $\Delta E_{\text{orb}}$ not only contains covalent bonding effects, but also intra-fragment relaxation effects or polarization. This can be understood by examining the thermodynamic cycle used to determine $\Delta E_{\text{orb}}$. In this cycle, the $\Delta E_{\text{elstat}}$ term is determined using the charge distributions of the interacting fragments, and thereby does not account for electrostatic effects due to orbital relaxation (e.g. polarization and charge transfer), which are instead included in the $\Delta E_{\text{orb}}$ term. Also, $\Delta E_{\text{Pauli}}$ is computed by evaluating the energy of the Slater determinant obtained through simple antisymmetrization of the fragment wavefunctions. Orbital relaxation – which contributes to $\Delta E_{\text{orb}}$ – will occur within each fragment so as to relax the electron distribution towards this perturbation. For these reasons, $\Delta E_{\text{orb}}$ is expected to overestimate the importance of covalent bonding effects, and in particular can be seen to exaggerate the impact of $\pi$ backbonding in all the complexes considered in Table 6. Others have already noted the potential importance of these relaxation functions.\textsuperscript{138} The ETS analysis leads to minimum a doubling of the orbital interaction term.\textsuperscript{138} One can reason that this orbital relaxation is actually also due to the $\pi$ backbonding orbital interactions and that it is technically a secondary orbital interaction phenomenon. Frenking et al. might argue that they calculated an 8% contribution of p orbitals\textsuperscript{128} for the $\sigma$-bond so that the sd$^2$ hybridization Harvey et al. use is a wrong starting condition and that conclusions from it should not be taken so seriously. Anyway, this discussion is QM technically and further discussion is not relevant for this chapter and lies far beyond our expertise.

\textsuperscript{XLI} Harvey et al. show in a graph that the total $\pi$-backbonding stabilization of the combined ligands in the (CO)$_2$ML complex remains relatively constant 51-58 kcal/mol. However they omit the OC-M-CO combination for which the total stabilization is 70.24 kcal/mol.

\textsuperscript{XLI} The pyridine complex shows here slightly higher $\pi$-backbonding capacity than the normal phosphines.
Finally, we want to mention some special phosphines which have recently been developed. Firstly, the Verkade base \textbf{2.62} has proven to be the strongest phosphine base currently accessible.\textsuperscript{163,164} The high basicity stems from the high planarization of the phosphor induced by the ring structure and donation of the bridge-nitrogen lone pair to the phosphor.\textsuperscript{165} This leads to a \( pK_a \) of the conjugated acid of \textbf{2.62} in THF of ca. 16.\textsuperscript{165}

A second class are the pyrrolyl phosphines \textbf{2.63} and pyrrolidinyl phosphines \textbf{2.64}.\textsuperscript{165-167} \textbf{2.63} and \textbf{2.64} have almost identical cone angles, though for the \( \nu(CO) \) frequencies of the Rh(CO)(Cl)L\textsubscript{2} (square planar complex), \textbf{2.63} shows a frequency higher than that of P(OPh)\textsubscript{3} and \textbf{2.64} one lower than for P(\textsuperscript{\textpi}Bu)\textsubscript{3}.\textsuperscript{167} \textbf{2.64} is definitely the stronger bonded ligand and is able to displace \textbf{2.63} in the Rh(CO)(Cl)L\textsubscript{2} complex. On the other hand, the Rh-P bond distance is the shortest for the weakest bond \textbf{2.63} (and best \( \pi \)-acceptor).\textsuperscript{167} The main difference consists here of the nitrogen lone pair, which is embedded in the aromatic pyrrole structure in \textbf{2.63} though in \textbf{2.64} it can freely donate into empty P-orbitals. Moloy et al. suggest that this increasing donating power to the phosphor should increase the donating capacity significantly, causing the big difference in the \( \nu(CO) \) for both ligands.\textsuperscript{167} We actually think it is more straightforward to assume that ‘backbonding’ from nitrogen to phosphor should significantly affect the backbonding of a metal fragment to the phosphine. Yet, the lack of planarization of nitrogen (absence of backbonding) should increase the \( \sigma \)-character in the \( \sigma \)-bond. In fact, pyrrolidinyl phosphines (\textbf{2.64}) complexes show two planar nitrogens and one pyramidalized one.\textsuperscript{167} This explains the high difference in \( \nu(CO) \). Moloy et al. also evidenced the high \( \pi \)-accepting capacity of \textbf{2.63}, by studying the coordination chemistry of an anionic Rh complex with \textbf{2.63}.\textsuperscript{167, XLII}

\textbf{Figure 2.27:} Special phosphines.

## 2.7 The metal-olefin bond

The olefin bond is classically described through the DCD \( \sigma \)-bond-\( \pi \)-backbonding. A more correct analysis is made using contemporary QM theory such as CDA and EDA in the bond description. The donor acceptor bond can have the following contributions: the \( \sigma \) L\( \rightarrow \)M bond (1) and the M\( \rightarrow \)L \( \pi \| \) (2) bond which normally represent the lion’s share of the bond-interaction.\textsuperscript{168} There is also possibility for L\( \rightarrow \)M \( \pi \perp \) (3) interaction which is normally much weaker or negligible. However, this interaction can increase in some cases of triple bond-coordination.\textsuperscript{168} The last interaction is the long distance and negligible interaction M\( \rightarrow \)L of \( \delta \) symmetry (4).\textsuperscript{168}

\( \chi_d \) shows a big difference and E\textsubscript{ar} is high for \textbf{2.63}. However, as we mentioned before the QALE parameters show no direct reference to reality.
In 1996, Frenking et al. challenged the classical DCD bond concept for olefins by examining W(CO)$_5$C$_2$H$_4$ (2.65), W(Cl)$_4$C$_2$H$_4$ (2.66) and W(Cl)$_5$C$_2$H$_4$ (2.67) computationally.\textsuperscript{169,170} The bond distance of free ethene and a C-C single bond are respectively 1.336 Å and 1.54 Å. 2.65-2.67 show intermediate carbon-carbon bond distances with 2.65 having more double bond character and 2.66 more single bond character.\textsuperscript{170} This difference is also reflected by a shorter W-C$_2$H$_4$ distance in 2.66, for which a strong and short (π interaction) should increase the C$_2$H$_4$ bond length.\textsuperscript{170} 2.67 shows intermediate bond distance characteristics, though more similar to 2.66.\textsuperscript{170} CDA Classifies both 2.65 and 2.67 as donor acceptor complexes, while 2.66 shows no closed shell structure.\textsuperscript{170} This is analogous to the Fischer carbene - Schrock carbene classification for which only the Cl$_4$W(carbene) species shows a Schrock-type open shell structure!

However, recently a crystal structure of 2.65 has been obtained. The ethene bond distance shows a value of 1.339 Å and the average W-C bond distance was determined to be 2.43 Å.\textsuperscript{171} The shortest M-CO bond was the one trans to ethene in analogy with a decreased π acceptor capacities of ethene.\textsuperscript{171} It should be noted that the ethene bond distance between the calculated value and the experimental value is extremely large.\textsuperscript{170,171} The experimental ethene distance suggests that the backbonding to the ethene is actually to be neglected in 2.65! This means that the highly π-competitive environment is able to let the ethene function as a solely σ-donating ligand which explains the low stability of the complex.

Frenking et al. investigated the ethene bond in Ni(0), Pd(0) and Pt(0) complexes with two phosphine substituents PH$_3$, PMe$_3$ or a bidentate ligand.\textsuperscript{168} The ethene BDE in the PH$_3$ complexes is slightly more exothermic than for the PMe$_3$ complexes due to the lower ΔE$_{Pauli}$ and ΔE$_{Prep}$.\textsuperscript{168} The calculated data indicate that there is no correlation between the metal-bond energies and the geometries of the molecules.\textsuperscript{168} Frenking et al. propose that the larger ΔE$_{int}$ are responsible for the shorter bond distances with the PMe$_3$ complexes.\textsuperscript{168} We wish to add that the increase in ΔE$_{int}$ for the PMe$_3$ complexes is completely caused by an increase in ΔE$_{\pi}$-\textsuperscript{168} Furthermore, it is interesting to note that the ΔE$_{\pi}$ contributions attain values of 58-74% of the total ΔE$_{int}$, and even increase for alkyn substrates.\textsuperscript{168} Finally, the complexes with bidentate ligands show the highest M-ethene bond energies due to a further decrease of the ΔE$_{Prep}$.\textsuperscript{168}
Frenking et al. showed with EDA that the $\Delta E_{\pi}$ values of the cationic of Cu⁺, Ag⁺ and Au⁺ complexes show low contributions (20-30%) to the $\Delta E_{\text{int}}$ and show relatively small ethene C=C bond distances (1.374-1.411 Å). The Cr(CO)$_3$C$_2$H$_4$, Mo(CO)$_3$C$_2$H$_4$ and W(CO)$_3$C$_2$H$_4$ show similar (small) C-C bond distances and absolute values for $\Delta E_{\pi}$. This can be attributed to the high competition for backdonation with all the CO ligands. On the contrary, the Fe(CO)$_3$C$_2$H$_4$, Ru(CO)$_3$C$_2$H$_4$ and Os(CO)$_3$C$_2$H$_4$ complexes show almost a doubling of the $\Delta E_{\pi}$ interaction compared to the Cr, Mo and W complexes (with concomitant increasing ethene C=C bond distances). We figure this is caused by a decrease in competition for backdonation originated in an increase of d-electrons, a decrease of CO acceptors, and an important effect of no (π-accepting) ligand in the trans position. The same reasoning holds for the Ni, Pd and Pt phosphine complexes.

The W(Cl)$_3$C$_2$H$_4$ shows a **four to five fold increase** of all energy components compared to W(CO)$_3$C$_2$H$_4$. Frenking et al. argue concerning the $M$-C$_2$H$_4$ distance that ‘it is arbitrary to pick out one bonding component to be responsible for the short interatomic distance. A plausible reason for this is the fact that the interacting fragments in Cl$_2$TM-C$_2$H$_4$ are open shell species while the fragments in (CO)$_3$TM-C$_2$H$_4$ complexes are closed shell molecules. The influence of the ligand environment on the C-C bond distance, shows a different behavior for the Os(CO)$_3$C$_2$H$_4$, W(CO)$_3$C$_2$H$_4$, Pt(PMe$_3$)$_3$C$_2$H$_4$, AuC$_2$H$_4^+$ W(Cl)$_3$C$_2$H$_4$ and W(Cl)$_3$C$_2$H$_4$ complexes. The absence of a π-acceptor in the trans position increases backdonation (all but W(CO)$_3$C$_2$H$_4$). Furthermore, the charge on the complex is also very decisive; a positive charge cripples backdonation and hence induces longer C-C bonds (AuC$_2$H$_4^+$), while a negative charge should increase the donation strength (W(Cl)$_3$C$_2$H$_4$). Furthermore, the open shell structure increases the C-C bond length (WCl$_3$C$_2$H$_4$).

### Table 2.7: Bond distances and π-stabilization energies for [M]-C$_2$H$_4$ complexes.

<table>
<thead>
<tr>
<th></th>
<th>d(C-C) (Å)</th>
<th>$\Delta E_{\pi}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(CO)$_3$C$_2$H$_4$</td>
<td>1.438</td>
<td>-58.2</td>
</tr>
<tr>
<td>W(CO)$_3$C$_2$H$_4$</td>
<td>1.388 (1.402$^{(a)}$)</td>
<td>-26.2</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_3$C$_2$H$_4$</td>
<td>1.441$^{(b)}$</td>
<td>-73.9$^{(b)}$</td>
</tr>
<tr>
<td>W(Cl)$_3$C$_2$H$_4$</td>
<td>1.438$^{(a)}$</td>
<td></td>
</tr>
<tr>
<td>WCl$_3$C$_2$H$_4$</td>
<td>1.451 (1.459$^{(a)}$)</td>
<td>-97.5</td>
</tr>
<tr>
<td>AuC$_2$H$_4^+$</td>
<td>1.414</td>
<td>-26.5</td>
</tr>
</tbody>
</table>

Data from$^{172}$, (a)$^{169}$, (b)$^{168}$

Frenking et al. further point out that W(CO)$_3$C$_2$H$_4$ and W(Cl)$_3$C$_2$H$_4$ are two extremes of the bond model examples of donor-acceptor and metallacycles, for which most complexes will have borderline behavior.$^{172}$

Lin et al. have recently examined the bond energies and geometries of complexes $^{2.68-2.72}$ Complexes $^{2.68}$, $^{2.70-2.71}$ show higher bond dissociation energy values for olefins with more π-donating substituents (NMe$_3$ and OMe) compared to π-acidic substituents (CN). We shall assign them as **type 1 complexes**.$^{173}$ On the contrary, $^{2.69}$ and $^{2.72}$ show preference for ligands with π-acidic

$^{XLIII}$ The $\Delta E_{\pi}$ values in the (CO)$_3$CrL complexes show for the ligands C$_2$H$_4$, PMe$_3$, PH$_3$, PCl$_3$ and PF$_3$ respectively the values of -22kcal/mol; -14.5 kcal/mol; -15.65 kcal/mol; -26.16 kcal/mol; -31.58 kcal/mol, from which we can conclude that the intrinsic capacity for π-backbonding for ethene is intermediate between normal phosphines and halogenated phosphines.

$^{XLIV}$ The unfavorable energetic components $\Delta E_{\text{prep}}$ and $\Delta E_{\text{Pauli}}$ are most increased.
groups. We shall assign them as type 2 complexes. The BDEs of the olefins in type 1 complexes are clearly dominated by σ-donating effects. 2.69 displays an obvious domination of π-backbonding in the BDE. 2.72 shows a domination of the π-bond but the σ-donation is also important. This is in agreement with the EDA of 2.72-C₆H₄ by Frenking et al. who calculated a double energy stabilization by ΔEπ|| compared to ΔEm. An interesting feature for these species, is the bond distance for the ethene complexes. The type 1 complexes 2.68 (1.35 Å), 2.70 (1.37 Å) and 2.71 (1.37 Å) show (as expected) short distances while the typical type 2 complex 2.69, for which the bond is dominated by backdonation, shows a high bond distance (1.45 Å) for the C-C bond. The borderline complex 2.72 has an intermediate bond distance (1.39 Å). If one compares this with the values of the 5th period TMs of the Frenking papers for M (C-C bond distance [Å]; ΔEπ|| [kcal/mol]; % ΔEπ|| contribution) being; Pd(PH₃)₂C₂H₄ (1.401; -42.5; 64.4), AgC₂H₄⁺ (1.374; -8.8; 20.6), Ru(CO)₅C₂H₄ (1.415; -43.4; 55.5); Mo(CO)₅C₂H₄ (1.375; -19.4; 45.6), it becomes obvious that the absolute values of ΔEπ|| are a good measurement for the ethene bond distance. It goes without saying that absolute charge transfers into the pπ٭ orbital of ethene determine the real C-C distance. For instance in the AgC₂H₄⁺ the backdonation from the Ag⁺ may not be so energetically favorable and show a lower relative value compared to the actual transfer of electrons.

In the Pd complexes the Pd-C₂H₄ distance shortens as the bond gets dominated by π-interactions, which can also be concluded by the data on Pd complexes of Frenking et al..

Figure 2.30: σ-donating and π-backdonating dominated olefin complexes.

The asymmetry in both the M-C bond distances for CH₂CHR substrates is relatively small for the very potent π-backdonor 2.69 for π-acidic R’s as CN (Δd = 0.09 Å). The π-basic R’s as NMe₂ (Δd = 0.07 Å) also show a low variation, though in the latter both M-C bonds lengthen which evidences the π-competition. The type 1 complexes, which are dominated by σ-donation of the olefin, show a low asymmetry with the π-acceptor R substituents as CN (Δd = 0.02-0.04 Å), though a high asymmetric bond for π-basic R’s such as NMe₂ and Δd’s upto 0.81 Å are found. The very short bond distance at CH₂ (Δd = 2.18 Å) and extremely long distance at CHN(Me)₂ (Δd = 2.70 Å) has been suggested to evidence a rehybridization into a resonance structure C=(H)₂C(H)=N’(Me)₂. Most of the literature on [M]-olefin or [M]-carbene bonds has been presented (by Frenking et al.) on homoletic [M] fragments. It is interesting to note that 2.71, as a mixed, neutral 16 electron species, is definitely a more borderline complex and more importantly, a better mirror-image for the Grubbs catalyst. In this aspect it is important to note that 2.71 shows a donor-acceptor bond with the donor aspect as the dominant part. Furthermore, the π-dominated Pd complex 2.72 shows a lower Pd-ethene bond distance (2.22 Å) than the type 1 Pd complexes (2.31-2.32 Å).
Previous studies have shown that the bond of a cyclic olefin with a metal is dominated by sp\(^2\) → sp\(^3\) rehybridization which is caused by the σ-donation of the HOMO and π-backdonation in the LUMO.\(^{174}\) It was previously stated that the cyclic strain is directly proportional to the metal-olefin bond strength due to an increase in orbital overlap, however, Codeno et al. have shown that the reorganization energy may also be (negatively) very important for the smaller cyclic olefins such as cyclopropene and cyclobutene.\(^{174}\)

### 2.8 The M-halide bond

The halides F, Cl, Br and I go in the series F → I to bigger size, higher σ-donation, more trans effect and increased bond strengths to late/low oxidation state metals.\(^{175}\) In the reverse series I → F, the π-bond donation increases and bond strengths increase with early/high oxidation state metals.\(^{175}\) The π-donation in complexes is enhanced if potent π-acceptors are present to delocalize the charge in the d\(_xy\), d\(_xz\) and d\(_yz\) orbitals, which results in a preference for F (or Cl) compared to Br or I trans to a CO ligand.\(^{175}\) Furthermore, it should be noted that M-halide bonds generally extract electrons from the metal s-orbitals since these are best polarizable due to the higher energy.\(^{128}\) Although the covalent Sn-halide or Pb-halide bonds have been reported to have more p-character (in accordance to Bent’s rule, with the absence of free d-orbitals).\(^{128,170}\)

### 2.9 Conclusions

In this chapter, we have evaluated the metal-ligand bond. First, it should be noted that the former DCD analysis is replaced by more recent theoretical methods such as EDA, CDA and NBO analysis. EDA accounts next to bonding and backbonding interactions also electrostatic attractions and Pauli repulsions. Furthermore, it is expected that the nature of the [M]-L bond is extremely dependant on the specific metal environment.

*If the necessary orbitals are exclusively available in the VB-space, then a Schrock carbene is formed in favor of the weaker Fischer-carbene bond. A Fischer-carbene becomes evident when the necessary orbitals can be used in stabilizing resonance structures in the VB-space.*

*NHC ligands are in nature extremely strong σ-donor ligands with a considerable π-acceptor function in 1 direction perpendicular to the NHC plane. The in plane π-direction can be considered to be electron donating. This makes the NHC ligands even more unique because besides the extreme σ-donation for these ligands the important π-backbonding is not degenerated in the two directions.*

Concerning specific rules on the M-L bond we wish to formulate some guidelines:

1. The M-L bond distance does not correlate to bond strength.
2. The M-L bond distances of a class of ligands L correlate well with the inverse strength of π-backbonding, especially if the L\(_π\) orbitals for backbonding are perpendicular to the M-L bond direction.
3. The difference in ν(CO) frequencies in [M]CO complexes are caused by the variation in π-backbonding to CO.
Organometallic species with straight angle geometries show special features: Due to symmetry restrictions, the backbonding and bonding to ligands is facilitated by different sets of orbitals. This causes highly expressed effects between the donating ligand-orbitals in trans position. The same competition-communication is present for the \( \pi \)-acceptor orbitals which are linked with the same occupied metal-d orbital. In particular, the difference in \( \pi \)-backbonding of a ligand \( L \) in a complex is most influenced by the backbonding towards other ligands through competition for the same metal-d-orbital and hence in these complexes the \( \nu \)(CO) frequencies are determined by the backbonding to the communicating-competing ligands.

Characteristics of ligands in straight angle geometry environments should not be transferred to e.g. tetrahedral environments (and vice versa), since in the latter some of the metal donating orbitals also represent the metal accepting orbitals and consequently direct influence of a \( \sigma \)-donating ligand orbital is exerted on a \( \pi \)-acceptor orbital of another ligand.

More ambiguous trends have also been found:

Evidence has been found for \( \pi \)-bonding of phosphines to affect the amount of \( \sigma \)-bonding of the phosphines. This suggests that the \( \pi \)-bonding capacities of the ligand cage determine the \( \sigma \)-bonding capacity of the phosphine. Subtle interplay of the ligand characteristics can cause a highly steric environment to diminish \( \pi \)-interactions.

The olefin bond is very similar to the carbene bond as it is characterized by a \( \sigma \)-donor and \( \pi \)-acceptor interaction and can switch from open shell to closed shell structures.

In the next chapter we will analyze the QM descriptions of the Grubbs catalyst and use the conceptual organometallic knowledge of this chapter to evaluate the ligand environment.

### 2. Appendix 1: Linear singlet carbenes

In 1980, Schoeller calculated the bond angles of different singlet carbenes and concluded that the bent form is applicable to carbenes with substituents \( X \) having a larger EN than carbon and that with e.g. \( X=\text{Li} \) the linear conformation is adopted.\(^{176}\)

![Linear and bent carbenes](image)

**Figure 2.31:** Linear and bent carbenes.

Pauling explained this by the availability of orbitals being responsible for the structure and bond angles, while the relative ENs determine the stability of the corresponding structures.\(^{177}\) First, it should
be noted that when electron density is being imported in the carbene through $\sigma$-bonding, backbonding of the $p_a$ electrons can help to maintain electroneutrality. Furthermore, if mixing is possible this should only lead to lower energies. Pauling argues ‘the linear carbenes are linear because a double bond is formed with use of the carbon electron pair, leaving the carbon atom with the formal charge +1’. We think the structure can actually be predicted through available orbitals but in a simpler (more comprehensive) matter. If the bent structure is adopted, the empty $\sigma$-orbital will have a substantial $s$-character, and consequently the electrons will prefer this orbital. However, no stabilization through conjugation with the EP substituents is possible due to the energetically stabilization of the $s$-orbital in the $\sigma$-orbital. In the linear formation, all the positive energy stabilization of the $s$-orbital is used in the two $sp$ C-Li bonds leaving the two $p$-orbitals degenerated. This high $s$-character in the $\sigma$-bond is more favorable for EP substituents compared to EN substituents as N. This structure is then highly stabilized by the canceling of the degeneration through conjugation with the empty Li-orbitals. In this way the $s$-orbital stabilization and the conjugation with the Li-orbitals can both be accomplished. Furthermore, $\pi$-donation from an electronegative substituent (e.g. N) is synergistically with the $\sigma$-withdrawing bond. The reverse order can be witnessed with electropositive substituents; The $\sigma$-bond is polarized towards the carbene (and has necessarily high $s$-character) and this is synergistically with $\pi$-back-bonding from the carbene to the electropositive substituent.

2. Appendix 2: Triplet carbenes

Triplet carbenes are more difficult to prepare than singlet carbenes. Most examples have two aryl substituents with sufficient steric bulk to stabilize the carbene for attacks and to widen the bond angle which is favorable for a triplet carbene (vs. singlet). Halogenation of the aromates is a well used strategy. It is also interesting to have a criterion to test if the carbene is either triplet or singlet. Triplet carbenes react non-stereoselective with olefins in cyclopropanation, in contrast to singlet carbenes which perform stereoselective cyclopropanation. Singlet carbenes also react with alcohols to give the corresponding ethers. On the other hand, triplet carbenes are known for H-abstraction.

2. Appendix 3: Silylenes

Sylilenes can be expected to have similar chemistry than carbenes, however there are some big differences between both. First, the silicon 3p-orbitals are larger than the 2p-orbitals of carbon, which causes a decrease in electron-electron repulsion. Consequently for silylenes it is even more rare to find triplet species. However, the more electropositive silicon, which shows the propensity for hyperconjugation, has difficulty in bearing a positive charge with the concomitant undercoordination. The first example was synthesized in 1994 for which aromatic stabilization was calculated. Interestingly, the S-T gap of the unsaturated silylenes was calculated to be higher than for the saturated ones in contrast to the intuitive stabilization through aromatization. NHSis are expected to exhibit slightly more enhanced backbonding than NHCs.
It is interesting to note that attempts to isolate analogues of 2.73 bearing mesityl, phenyl or adamantyl groups have all failed and present evidence for the different nature of silylenes vs. carbenes.\footnote{181} Carbenes are accepted to react more exothermic with metal centres, however Herrmann et al. have observed the substitution of Pd(\textit{T}Bu)$_2$ by 3 equivalents of 2.73 to be fast.\footnote{182} This is possible due to the reduced steric requirements of silylenes vs. carbenes.\footnote{182}

\section*{2. Appendix 4: Abnormal binding of NHCs}

Crabtree et al. have shown that besides classical C$_2$ carbene substitution of NHCs on metals, an alternative mode of ligand donation is possible. In 2002, their group disclosed the abnormal C$_5$-bound NHC complexes at Iridium.\footnote{183} It was shown that the counter ion holds a special role in the type of coordination (C$_2$ vs. C$_3$). The C$_2$-coordination is quasi-irreversible, which is probably due to the assistance of the counter ion in abstraction of the C$_2$-hydrogen.\footnote{184} Furthermore, substitution on the 4-position of the NHC is beneficial for substitution of selective C$_5$ coordinated NHCs on complexes without steric crowding.\footnote{185} More fundamentally, it was shown that the C$_5$-coordinated NHCs show increased electron donation upon their C$_2$ coordinated siblings.\footnote{185}

Danopoulos et al. have shown that such abnormal coordination is also possible with pincer dicarbene species in a crowded Fe(II) complex.\footnote{186} Furthermore, Meyer et al. showed that in contrast to their previous tripodal NHC Cu(I) complexes,\footnote{187} an alternative tripodal ligand coordination mode is possible with 2 carbenes classically coordinated and the 3rd one with abnormal C$_5$ coordination (due to steric crowding in a dimmer formation).\footnote{188} They assign the abnormal binding as alkenyl and not as a carbene, supported by the upfield shift of 20 ppm in the $^{13}$C NMR spectrum to $\delta$ = 168.7 ppm.\footnote{188} This is also in accordance with our previous discussion (Chapter 1 Appendix 1). One can reason that the C$_5$ $\pi$-orbital is already formally occupied in a double bond with the C$_4$ carbon. However, this can not explain the higher (net) electron donation observed by Crabtree et al. since an alkenyl ligand should not drastically increase electron density but actually the polarized M-C bond should extract electron density from the metal. However, a closer look at the structure shows that the carbene construct is more likely than the alkenyl conformation!

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure233.png}
\caption{Alkenyl vs. carbene in abnormal binding of NHC.}
\end{figure}
The alkenyl structure 2.74 shows a double bond between C4-C5, however there are two destabilizing factors present in the structure. First, The C2 carbon is formally a radical and should show high reactivity. Off course, stabilization can occur through conjugation with the two nitrogens. However one can expect high reactivity and it does not comply to our rule that all normal XLV carbons should be formally conjugated in a real XLVI bond. Secondly, a ring system is created with 7 electrons in which no aromatic stabilization is possible.

In contrast, the carbene structure 2.75 shows aromatic stabilization. This also cancels out the problem with the radical C2 and provides some extra stabilization to the C5 π-orbital. Furthermore, Herrmann et al. have shown that delocalization of electrons is much more efficient through the carbon bond than through the nitrogen atom.112 The aromatization is probably not partial as observed in classical NHC-bonding because without aromatization, 3 deficient π-orbitals (C2, C4 and C5) would be created. This is probably the cause of the enhanced (net) electron donation of the ligand (σ-donation with strongly reduced π-backdonation from the metal).

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XLV “Normal” means not being a carbene.
XLVI “Real” means a bond with 2n atoms and 2n electrons with exceptions for aromatic structures.
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Chapter 3

Understanding olefin metathesis

This chapter contains a brief overview on a restricted collection of articles concerning the understanding of olefin metathesis combined with some personal comments. Herein some of the issues which were shortly handled in Chapter 1, are discussed in a more detailed description. Furthermore, we will apply a conceptually organometallic reasoning (Chapter 2) to evaluate the olefin metathesis analysis.

To the best of our knowledge, there is not yet a consensus on some of the major theoretical issues in metathesis such as energetic differences, ruthenium backbiting the polymer, the nature and the influence of the NHC ligand on catalyst activity and the cause for the bending of the NHC away from the carbene. Furthermore, essentials such as the nature of the carbene in the catalyst remain controversial and mainly unhandled in a systematic fashion. This causes the literature discussion on these issues to seem either contradictory or indirect. If things were to be briefly summarized in one final model, a great deal of subtleties would disappear. Therefore, it seems reasonable to provide the crude data, the interpretations of the researchers who performed the research and our own comments on topics where contradictions emerge. This will permit the reader to make a judgement of his own.

3.1 Experimental data on the ligand environment in the Grubbs catalysts

The first and most important experimental data on the comparison of 1.3, 1.4 and similar structures appeared in 2001 in two groundbreaking articles.\textsuperscript{1,2} \textsuperscript{31}P magnetization transfer studies were utilized to obtain exchange rate constants ($k_\text{B}$) for these catalysts. $k_\text{B}$ was determined at 80°C for 1.3 and 1.4 and found to be $9.6 \pm 0.2$ s\textsuperscript{-1} and $0.13 \pm 0.01$ s\textsuperscript{-1} respectively and independent of [PCy\textsubscript{3}] over a wide range.

\textsuperscript{1} \textsuperscript{31}P NMR spectroscopy indicated that phosphine exchange in 3 and 4 is relatively slow. In both cases no coalescence of the free and bound phosphine was observed up to 100 °C in toluene-d\textsubscript{8} [1. (1) Sanford, M. S.; Ulman, M.; Grubbs, R. H. \textit{Journal of the American Chemical Society} \textbf{2001}, \textit{123}, 749-750.]
of concentrations\textsuperscript{1}. The values for $\Delta H$ (kcal/mol), $\Delta S$ (cal/mol K) and $\Delta G$ (298K) (kcal/mol) in toluene for 1.3 are $23.6 \pm 0.5$; $12 \pm 2$; $19.88 \pm 0.06$ and $27 \pm 2$; $13 \pm 6$; $23.0 \pm 0.4$ for 1.4.\textsuperscript{1} These results are surprising since initial rationalizations attributed the higher olefin metathesis activity of 1.4 compared to 1.3 to the higher $\sigma$-donor capacity of the NHC ligand causing an increased trans influence on the phospine, which then improves decooordination and consequently increases metathesis activity.\textsuperscript{3,4} Furthermore, Grubbs et al. argued that H\textsubscript{2}IMES should show higher basicity due to the lack of stabilization caused by the absence of $\pi$-interactions.\textsuperscript{4}

![Figure 3.1: Reaction of 1.3 and 1.4 with ethyl vinyl ether.](image)

The fast and irreversible reaction of 1.3 and 1.4 with ethyl vinyl ether was followed by $^1$H NMR. The initiation constant ($k_{\text{obs}}$) of 1.4 was found to be independent of olefin concentration over a wide concentration range (5 equiv to 60 equiv) and in good agreement with the data from magnetization experiments\textsuperscript{1}. This indicates that the old model, which holds the dissociation of the phosphine as the rate determining step, remains intact. In contrast, $k_{\text{obs}}$ of 1.3 was found to be dependent on the olefin concentration over a range of 30 to 120 equiv.\textsuperscript{1} In order to avoid this dependence, experiments with saturation kinetics were performed using 5300 equiv of substrate. The $k_{\text{obs}}$ was found to be in agreement with $k_B$.\textsuperscript{1}

![Figure 3.2: Dissociative mechanism.](image)

Grubbs et al. concluded that in the dissociative pathway a steady state concentration of the 14 electron complex is formed.\textsuperscript{1} Under the assumption that all reaction steps succeeding olefin binding are fast, the following relation for the pseudo-first order conditions in olefin was proposed:

$$\frac{1}{k_{\text{obs}}} = (k_C [\text{PCy}_3] / k_1 k_2 [\text{olefin}]) + \frac{1}{k_1}$$
However, Chen et al. showed that in the reaction of 1.3 with ethyl vinyl ether the cyclobutane formation is the RLS (Rate Limiting Step), which is logical considering the olefin concentration dependence of the reaction.\(^5\) In normal CM and RCM with 1.3, phosphor dissociation becomes rate limiting.\(^5\) For catalyst 1.4, phosphor dissociation is rate limiting for all reactions\(^5\). Furthermore, the model shows little applicability for ROMP.

\(^1\)H NMR studies on the reaction of 1.3 and 1.4 with ethyl vinyl ether and various [PCy\(_3\)] concentrations provided the relationship of 1/k\(_{\text{obs}}\) with [PCy\(_3\)]/[olefin].\(^1\) The k\(_1\)/k\(_2\) ratio of 1.3 and 1.4 are respectively 15300 and 1.25.\(^1\) It was concluded that this 4 orders of magnitude higher preference of the fourteen electron species of 1.4 for olefin association is more important than the high energy barrier for phosphine dissociation. This represents the fountainhead for the high activity of the second generation Grubbs catalyst and was formalized in stating that the presence of H\(_2\)IMES in the fourteen electron species seems to improve the selectivity towards \(\pi\)-acidic substrates in the presence of \(\sigma\)-donating free phosphine.\(^1\) We wish to add that this is true for the activity as a TOF concept, though not as a TON concept since in the latter, which we consider more important, the focus is on stability rather than speed.

However, the assumption that all steps are fast after coordination of the olefin cannot be extrapolated to all types of olefins. In reactions with 1.3, this is more pronounced since even the easy metathesis substrate ethyl vinyl ether already shows an olefin concentration dependence.\(^2\) Another argument against the simple kinetic model holds that some challenging substrates only react with 1.4 and not with 1.3 for RCM and ROMP (see chapter 4).\(^4\) Furthermore, it should be noted that for the ROMP with 1.3 and 1.4 an induction period cannot be rationalized by these simple kinetics.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{catalysts.png}
\caption{Experimentally investigated catalysts for initiating and propagating constants.}
\end{figure}

Later that year, a full study was released using the same methodology for a wide range of catalysts\(^2\). Cavel et al. compared a series of Pd(0)-olefin complexes containing either N-heterocyclic carbenes or phosphines as ancillary ligands\(^2,6\) and concluded that NHCs promote and stabilize metal-to-olefin backbonding to a much greater extent than the phosphine ligands do in these systems\(^2,6\).\(^1\) Grubbs et al. argued that this olefin stabilizing effect is present in their own catalysts.\(^2\) Furthermore, the H\(_2\)IMES substituted catalyst 1.4 shows higher \textit{activity} for the polymerization of COD than the IMES substituted complex 3.6 and H\(_2\)IMES is claimed to be a better electron donor than IMES.\(^2\) However,

\(^{11}\) It is interesting to note a few details on the Cavel publication. As representative phosphine, PPh\(_3\) was taken, which is a much worse ligand for the Grubbs catalyst than PCy\(_3\). Moreover, the structure of the Pd complex was not revealed but a Pd(0) complex should not be very representative for the interactions in the Grubbs complex.
this last remark has been rebutted. The increased activity should also be attributed to steric factors and/or π-backbonding effects because the electron donating capacities of IMES and H₂IMES are actually quite similar (see Chapter 2). The data in the article show that \( k_B \) of 1.4 amounts 4 times the value of 3.6, which could explain the increase in activity on the basis of better phosphine dissociation with all other characteristics remaining unchanged.

Table 3.1: Rate constants for several Grubbs catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( k_1 / k_2 ) (50°C)</th>
<th>( k_B ) (s⁻¹) (80°C)</th>
<th>( K_{rel} ) for ROMP COD (300 equiv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>1.3 x 10⁴</td>
<td>9.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>8.2 x 10⁴</td>
<td>30 ± 2</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>2.6 x 10⁶</td>
<td>1660 ± 220</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>1.25</td>
<td>0.13 ± 0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td>0.52 ± 0.02</td>
<td>1.4</td>
</tr>
<tr>
<td>3.4</td>
<td>3.3 x 10²</td>
<td>29 ± 3</td>
<td>1.4</td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

Data from ²

The substitution of chlorine by iodine as the halide ligand has a positive effect on \( k_B \) which is ascribed to the increased steric bulk of the system. However, \( k_1 / k_2 \) increases in a proportional way resulting in an overall relatively small change of catalytic activity². In addition, it should be noted that the 14 electron species is responsible for deactivation of the catalyst.³ This deactivation is second order in the 14 electron species. Consequently, the high \( k_{init} \) (≈ \( k_B \)) of the bromine and iodine catalysts is expected to cause faster decomposition than their chlorine analogues. The same reasoning can be applied for 1.4 and 3.5 compared to 1.3. This explains the high robustness of 1.4 and even more for 3.5². For example, Nolan et al. demonstrated that 3.5 shows no signs of decomposition after 1h in toluene-d₈ at 100 °C.²,⁷

In an attempt to determine \( k_{init} \) of the methyldiene analogue of 1.4, insufficient reaction with ethyl vinyl ether was found due to faster catalyst decomposition.² The methyldiene species is the key intermediate in both RCM and CM. It shows very slow phosphine decoordination and decomposition is first order in the catalyst concentration while decomposition for the other carbene catalysts (e.g. benzylidene) is 2nd order in carbene.²

The ligand in the series PCy₃, PPh₃ and substituted PPh₃’s, trans to H₂IMES in 1.4 decoordinates faster with decreasing basicity.⁸ These phosphine catalysts and pyridine analogues create opportunities to produce catalysts of high activity with tailored initiation characteristics.⁸,⁹ We applied a similar strategy with Schiff base ligands to obtain a wide spectrum of initiation and propagation characteristics and to additionally obtain higher tolerance for water and oxygen (Chapter 4).¹¹

Grubbs et al. determined the relative reaction rates for catalysts 1.3, 1.4, 3.5 and 3.6 for the RCM of 20 equiv mono-methyl substituted DEDAM in C₆D₆ and the ROMP of 300 equiv 1,5-cyclooctadiene (COD) in CD₂Cl₂.¹²
Both for RCM and ROMP, a significant increase in the reaction ratio was found for the sequence 1.3 < 3.6 < 3.5 < 1.4. RCM shows an additional rate increase upon the introduction of an NHC. The lower activity of 3.6 could be explained by an increased electron withdrawing effect of the chlorines, which leads the nitrogens to become more electron withdrawing, leading to more p-character of the carbene in the C-N bonds. Consequently, the carbene σ-lone pair shows more s-character and lower energy, which induces a decreased electron donating ability. It should also be noted that the relative activities for 1.4 and 3.6 can easily be explained by their difference in $k_B$. Moreover, since the polymerization of 50 equiv COD with 1.4 is finished before 5% of the catalyst has initiated, this trend of catalyst activity might in fact be more a trend in catalyst initiation.

3.2 A detailed Quantum Mechanical (QM) study by L. Cavallo

Luigi Cavallo published in 2002 the first quantum mechanical study on different ruthenium metathesis systems concentrated on the actual catalysts and not only on model systems. Complexes 1.3, 1.4 and 3.5 are all show distorted square-pyramidal geometry with the alkylidene at the vertex and almost coplanar with the chlorine atoms. In 1.4 and 3.5 the N-C_ipso-C_para mesitylene angle is distorted from 180° to 173° and 175° respectively, in favour of a steric relaxation from the mesityl groups away from the chlorine and alkylidene ligands. Furthermore, in the absence of the mesityl group (Mes → H), the NHC can rotate considerably around the Ru-C axis.

Upon phosphine dissociation, the distances between Ru and the ligands shorten due to a reduced electron density at the metal. This causes a short contact (< 3Å) between the alkylidene carbon and the C_ipso mesityl carbon of 1.4 and 3.5. The N-C(ipso)-C_para mesitylene angles are relaxed to 178°. Ethene is bound stronger to 1.4 and 3.5 than to 1.3, while the ethene bond in all complexes is only slightly elongated (1.36-1.37 Å) compared to free ethene (1.34 Å). From the

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Table 3.2: Relative rates for ROMP and RCM.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$K_{rel}$ RCM</th>
<th>$K_{rel}$ ROMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.4</td>
<td>138</td>
<td>27</td>
</tr>
<tr>
<td>3.5</td>
<td>53</td>
<td>8</td>
</tr>
<tr>
<td>3.6</td>
<td>19</td>
<td>3</td>
</tr>
</tbody>
</table>

Data from 12

Reading this landmark publication on the understanding of olefin metathesis, one should realize there has been unfortunately one misconception on the activities concerning systems 1.4 and 3.5. Cavallo argues 'Experimentally, systems similar to 2 were shown to have slightly lower activation parameters for phosphine exchange, and to be more active for the polymerization of cyclooctadiene, than systems similar to 3.' (with 2 and 3 corresponding relatively to 3.5 and 1.4). However the opposite is true.
evidence of Chapter 2 we can now state that the Ru-ethene bond is dominated by a $\sigma$-donation interaction.

We want to point out that the distance between Ru and the $C_{\text{trans}}$ is large and relatively constant throughout the complexes (2.45-2.46 Å), while the Ru-C$_2$ distance is shorter and varies significantly between the NHC catalysts 1.4 and 3.5 (2.32 Å) and the phosphine catalyst 1.3 (2.37 Å). We think that the high trans effect of the NHC or phosphine induces a weak $C_{\text{trans}}$ bond with Ru, which should lead to facile cyclobutane formation in a next step. (vide infra). Furthermore, the asymmetrical olefin bondushers the $C_2$ in the vicinity of the $d_{xy}$ Ru orbital (with the $z$-axis in the Cl-Ru-Cl bond direction), from which backbonding can occur. The olefin shows an angle with the Ru-Cl-carbene plane, with the $C_{\text{trans}}$ pointing away from the plane. This causes a diminishing overlap of the $C_{\text{trans}}$ $\pi^*$ and the $d_{xy}$ orbital. Moreover, the long Ru-$C_{\text{trans}}$ also suggests a minimal $\pi$-bonding. Since backbonding is directed towards only one carbon of the ethene bond, the bond only shows moderate elongation (+ 0.02-0.03 Å).

In the transition state (TS) preceding cyclobutane formation the alkylidene bends 20° towards the ethene to form the new bond. The old Ru-C$_2$ is shortened to 2.11-2.15 Å and the alkene bond stretches to 1.42-1.44 Å. We assume this is evidence for a change from a donation dominated olefin bond to a backdonation dominated olefin bond. In catalyst 1.3, the Ru-P bond stretches 0.06 Å which is attributed to the trans effect of the hard Ru-C $\sigma$ bonds on the soft PCy$_3$. The increased backbonding to the ethene probably accounts for a decrease in backbonding to the phosphine and hence also for a decrease in bond length. This is supported by the limited bond elongation for the NHC ligands (+ 0.01-0.02 Å), which have no competing backbonding orbitals to the $d_{xy}$ orbital. In 1.4 and 3.5 the distance between the alkylidene carbon and the ipso mesitylene carbon has lengthened to more than 3.4 Å.$^{13}$

In the cyclobutane conformation the Ru-$C_{\text{cyclobutane}}$ distances are 2.00-2.02 Å and in 1.4 and 3.5 the N-$C_{\text{ipso}}$-$C_{\text{para}}$ mesitylene angles are relaxed to 180°.$^{13}$

![Complexes investigated by Cavallo.](image)
Variations in Binding Energies (BE) should explain the difference in activity of the catalysts. NHC ligands coordinate more strongly than phosphines, which in their turn have higher BEs than ethene. The higher BE of PC\textsubscript{3} in 3.9 compared to 3.11 is explained by the HOMO of IMES which is 0.15 eV more stable than for H\textsubscript{2}IMES. This should lead to a decrease in the trans effect. Off course, a more stable orbital is tended to donate less electrons to the metal and consequently results in a lower trans effect. This tendency of 3.11 to lose a phosphine more readily than 3.9 is experimentally observed (vide supra), but we have shown that the relative donor capacities of H\textsubscript{2}IMES and IMES are controversial (Chapter 2). The difference in NHC properties might even be more pronounced in the π backbonding capacity (Chapter 2). Furthermore, Cavallo’s explanation does not show why this tendency is only present with phosphine and absent with ethene.

A qualitative description in which no backbonding to the NHC is possible in the d\textsubscript{xy} orbital seems more appealing. The backbonding to the olefin in the active olefin conformation should only proceed through the d\textsubscript{xy} orbital. However, PC\textsubscript{3} can also accept backbonding from the d\textsubscript{yz} orbital (with the Ru-NHC as the y direction), which shows direct competition to the NHC-backbonding. Only the phosphine bond is affected by the backbonding to the NHC ligand. Off course, also the steric bulk of the NHC could be responsible, since in H\textsubscript{2}IMES the carbene angle is wider, which consequently leads to an increase in the steric interaction and a lower BE with the bulky phosphine. The low steric demanding ethene should not be influenced by this change of steric environment. Either way, it seems to us that the HOMO of the NHC is the least responsible for the change in the BE!

The differences in BEs of PC\textsubscript{3} compared to ethene for 3.7, 3.9 and 3.11 are respectively 10.0, 14.0 and 8.3 kcal/mol. Adding up the additional energy gap between the ethene coordinated intermediate and the transition state, being 8.2, 1.9 and 1.9 kcal/mol respectively, synchronizes the theoretical values (18.2; 15.9; 10.2 kcal/mol respectively) with the experimental catalyst rates, which increase from 1.3 over 3.5 to 1.4. According to Cavallo, the high activity of NHC systems stems thus not only from their selectivity towards olefins but is mainly caused by their ease of cyclobutane formation after olefin complexation. It is shown that this cyclobutane formation is not longer determining for methyldiene species (vide infra). We wish to add that the solution free energies in toluene (\(\epsilon = 2.72\))

<table>
<thead>
<tr>
<th>Complex</th>
<th>gas-phase (\Delta_{E_{g}})</th>
<th>(\Delta_{G_{s}}; \epsilon = 2.74)</th>
<th>(\Delta_{G_{s}}; \epsilon = 8.93)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7-IMES</td>
<td>39.5</td>
<td>39.0</td>
<td>26.7</td>
</tr>
<tr>
<td>3.7-H\textsubscript{2}IMES</td>
<td>34.6</td>
<td>29.5</td>
<td>21.1</td>
</tr>
<tr>
<td>3.7-PC\textsubscript{3}</td>
<td>16.2</td>
<td>14.1</td>
<td>13.3</td>
</tr>
<tr>
<td>3.7-C\textsubscript{2}H\textsubscript{4}</td>
<td>6.2</td>
<td>5.6</td>
<td>5.9</td>
</tr>
<tr>
<td>3.8-PC\textsubscript{3}</td>
<td>23.7</td>
<td>22.6</td>
<td>21.6</td>
</tr>
<tr>
<td>3.8-C\textsubscript{2}H\textsubscript{4}</td>
<td>11.5</td>
<td>11.0</td>
<td>10.7</td>
</tr>
<tr>
<td>3.9-PC\textsubscript{3}</td>
<td>28.2</td>
<td>26.3</td>
<td>25.2</td>
</tr>
<tr>
<td>3.9-C\textsubscript{2}H\textsubscript{4}</td>
<td>14.2</td>
<td>13.7</td>
<td>12.8</td>
</tr>
<tr>
<td>3.10-PC\textsubscript{3}</td>
<td>15.1</td>
<td>15.9</td>
<td>12.9</td>
</tr>
<tr>
<td>3.10-C\textsubscript{2}H\textsubscript{4}</td>
<td>11.9</td>
<td>10.6</td>
<td>11.7</td>
</tr>
<tr>
<td>3.11-PC\textsubscript{3}</td>
<td>23.0</td>
<td>21.5</td>
<td>20.6</td>
</tr>
<tr>
<td>3.11-PPh\textsubscript{3}</td>
<td>20.4</td>
<td>19.5</td>
<td>21.4</td>
</tr>
<tr>
<td>3.11-C\textsubscript{2}H\textsubscript{4}</td>
<td>14.7</td>
<td>14.4</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Data from\(^{13}\); Toluene: \(\epsilon = 2.74\); Dichloromethane: \(\epsilon = 8.93\).
for \(3.7\text{-PCy}_3\) (14.1 kcal/mol) and \(3.11\text{-PCy}_3\) (21.5 kcal/mol) of Cavallo are in poor agreement with the \(\Delta G\) values experimentally determined by Grubbs et al. for \(1.3\) (19.88 ± 0.06 kcal/mol) and \(1.4\) (23.0 ± 0.4 kcal/mol).\(^{1,13}\)

The larger BEs of ethene and \(\text{PCy}_3\) in \(3.8\) relative to \(3.7\) are ascribed to the lower basicity of \(\text{PH}_3\) compared to \(\text{PCy}_3\), causing a lower trans effect for \(3.8\).\(^{13}\) It also shows that the Ru-ethene bond energy cannot be dominated by \(\pi\)-interactions, since that would imply that ethene shows a higher bond energy with the \(\text{PCy}_3\) complex \(3.7\). Steric requirements also might be an issue.\(^{14}\) On the contrary, \(3.10\) shows lower dissociation energies for \(\text{PCy}_3\) and ethene than \(3.9\).\(^{13}\) This is ascribed to the contraction of the fourteen electron species, which causes an energetic unfavourable short distance between the alkylidene carbon and the \(C_{\text{ipso}}\) mesityl carbon.\(^{13}\) This tension is released upon coordination of a ligand and reflects in the higher dissociation energies for the \(\text{H}_2\text{IMES}\) complex \(3.9\).\(^{13}\) \(^{\text{IV}}\) Furthermore, the energy gap between the ethene coordinated intermediate and the metallacyclobutane transition state of 8.9 kcal/mol for \(3.10\) indicates that there is no energetic relaxation between the alkylidene carbon and the \(C_{\text{ipso}}\) mesityl carbon in the absence of the mesityl-group.\(^{V}\)

Cavallo made an excellent study on the energetic aspects of metathesis, especially explaining the role of the mesityl group in the NHC. However, one of the key issues was not tackled. What is responsible for the change in the difference between the phosphine and the ethene BEs between complexes \(3.7\) - \(3.11\) and especially between \(3.9\) and \(3.10\)? The decrease in binding energy of \(\text{PCy}_3\) going from \(3.9\) to \(3.10\) is explained by the improved (longer) \(C_{\text{ipso}}\) mesityl carbon-Carbene distance in \(3.9\) after the coordination of the phosphine compared to the 4 coordinate species. However, the absence of the same (proportional) principle in the ethene coordination implies that at least a more complex mechanism is at work. Moreover, the difference in behaviour of \(3.9\) and \(3.11\) is explained by the HOMO of IMES and \(\text{H}_2\text{IMES}\) which is probably a big oversimplification.

**Table 3.4: Ethene and \(\text{PCy}_3\) gas phase binding energies (kcal/mol).**

<table>
<thead>
<tr>
<th>complex</th>
<th>(\Delta E) (complex-(\text{PCy}_3) – complex-(\text{C}_2\text{H}_4))</th>
<th>(\Delta E_{\text{bond}}) complex-(\text{PCy}_3)</th>
<th>(\Delta E_{\text{bond}}) complex-(\text{C}_2\text{H}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
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<td>16.2</td>
<td>6.2</td>
</tr>
<tr>
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<td>8.9</td>
<td>23.7</td>
<td>11.5</td>
</tr>
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<td>3.11</td>
<td>8.3</td>
<td>23.0</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Data from \(^{13}\).

### 3.3 A detailed analysis by the Chen group

The Chen group has been a driving force in the mechanistic understanding for olefin metathesis during the last decade. Their work consists of electron-spray ionization experiments and quantum mechanical calculations.

\(^{\text{IV}}\) The NHC donor capacity can also be anticipated not to decrease as fast in \(3.9\rightarrow3.10\) as the P-donation capacity does in \(3.7\rightarrow3.8\).

\(^{\text{V}}\) However, the small energy difference between \(3.10\text{-PCy}_3\) and \(3.10\text{-C}_2\text{H}_4\) (3.2 kcal/mol) compensates for this by obtaining a higher amount of active species. Explanations for this phenomenon will be discussed later.
A first publication on electron ionization concerns experiments in the gas phase released by Grubbs et al. Addition of norbornene to the benzylidene proceeds 1.7 times faster than the addition on the propylidene species, probably due to electronic effects. Moreover, the second addition of norbornene to 3.12 proceeds 1500 times slower than the initial addition and 10 times slower than the second addition to the propylidene species. The authors ascribe this effect to the π-complexation of the chelated intermediate, which decreases the concentration of active species. The lower $k_2$ of the benzylidene species likely stems from the better donating abilities of the phenyl ring compared to the simple olefin. The rate constant for the second and third addition of norbornene on the propylidene species are equal and support this hypothesis. We think that these data imply that the faster initiating benzylidene might show an initial barrier for polymerization due to a less favourable pre-equilibrium for a second addition, and that this is partly responsible for the initiation period witnessed in polymerizations with 1.3. Chen et al. also propose that the higher reaction rate of norbornene compared to other substrates originates in the rigidity of the spacer, which causes more difficult intramolecular π-complexation, and not by the high ring strain release of the norbornene.

![Figure 3.5: Cationic complexes for ROMP of norbornene. (data from 15)](image)

Chen et al. found support for their analysis in a publication by Grubbs et al., wherein the $k_i/k_p$ ratio (initiation versus propagation ratio) was determined to be 9 for the polymerization of norbornene with a ruthenium-benzylidene-PPh$_3$ complex. Unfortunately, the relative rates of the Chen experiments correlate poorly with other experimental studies. From the Chen paper, one can conclude that propagation only starts after practically full initiation (first addition) for the Grubbs 1st generation catalyst since $k_1$ amounts to 1500 times the value of $k_2$ and presumably 150 times the value of $k_3$. Khosravi et al. reported that when 50 equivalents of 2-norbornene had reacted with 1.3, the benzylidene peak was still much larger than the propagating doublet at ~18.75 ppm in $^1$H NMR, while similar trends were observed for substituted norbornenes by Khosravi et al. and Gibson et al. Moreover, Khosravi et al. found no signs of a chelating propagating species in the polymerization of norbornene.
Chen et al. reported the benzylidene to be 1.67 times faster in the polymerization of a norbornene than the propylidene, though Sponsler et al. showed that the phosphine exchange rate for 1,4 is 10 times as low compared to the propylidene analogue.\(^{19}\) The two systems may not be identical, though the trend is obviously reversed and calls for caution with the use of model systems.

In a subsequent publication, Chen et al. showed that the introduction of electron withdrawing groups at the benzylidene fragment enhances the speed of initiation while electron rich groups decrease the initiation rate.\(^{20}\) This is attributed to the absence of conjugation of the phenyl group in the cyclobutane ring.\(^{20}\) The effect of an electron withdrawing group should be less destabilizing in the cyclobutane and therefore provide a smaller energy gap with the carbene. Furthermore, Chen et al. showed that the ROM of cyclopentene is reversible in contrast to the ROM of the highly strained norbornene.\(^{20}\)

In 2000, Chen et al. were able to prove that the resting state of 1,3 for ROMP is a monophosphine complex in contrast to the biphosphine resting state for acyclic metathesis. This was possible by introducing a cationic substituted norbornene to a propagating system of 1,3 with norbornene.\(^{21}\) The only complex observed in the MS (Mass Spectroscopy) spectrum was the monophosphine complex from which was concluded that the monophosphine complex is the actual resting state for the ROMP with 1,3.\(^{21}\)

However, as mentioned earlier, Khosravi et al. showed that the propagating species of the ROMP of norbornene with 1,3 in CDCl\(_3\) displays a resonance in the \(^1\)H NMR spectrum at \(\delta \approx 18.75\) ppm.\(^{17}\) This resonance is assigned to the biphosphine system, since it remains upon addition of PCy\(_3\) and disappears upon addition of CuCl.\(^{17}\) The relevance of the Chen paper was not discussed by Khosravi though the results are clearly irreconcilable. The absence of a monophosphine species in the Khosravi paper cannot be attributed to the low concentration of norbornene in the system ([norbornene] /[catalyst] = 50) because Chen et al. only used 5 equivalents of norbornene and 0.1 equivalents of the cationic norbornene. Chen et al. do argue that with their neutral catalyst and cationic ligand only those complexes which bind with the cationic substrate can be detected.\(^{21}\) Nevertheless, all complexes should be in equilibrium and after reaction, phosphine exchange should occur since phosphine exchange has been reported to be \(\sim 10^4\) times faster than the reaction rate for these systems.\(^{1,22}\) Of course, there is a 100-fold dilution before the reaction is sent to the MS (mass spectrometer). This is unfavorable for the bimolecular phosphine association which creates the biphosphine complex, but enhances intramolecular complexation with the propagating chain. This explains some of the discrepancy. However, in the Chen paper the biphosphine signal is not observed in a 100:1 noise ratio, where Khosravi et al. do not report any signal for the monophosphine system. Hence, further explanations should be attributed to differences in the catalyst characteristics \(k_1, k_{-1}\), barriers for phosphor association caused by the growing polymer, barriers for chelated olefin dissociation or influences by the positive charge.\(^{5,VI}\) It should also be noted that low detectability of the biphosphine complex with cationic phosphines can be attributed to the positive charge of the phosphines. However, when the carbene is positively charged, such argumentation no longer makes sense.

\(^{VI}\) The possibility that Khosravi et al. had mistaken the biphosphine system (18.75 ppm) for the monophosphine system is very unlikely, since Slugovc et al. showed for the reaction of 1,3 with norbornenes containing groups able to coordinate to the Ru-species that these groups do coordinate to the Ru giving a specific NMR-signal (and another attributed to the biphosphine system), where upon addition of PCy\(_3\) the former peaks disappear and the latter grow. Furthermore, they were able to pinpoint the former signal to the functional group coordination due to the high difference of signal intensity between the several monomers. [\(^{23}\) Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. *Macromolecular Rapid Communications* 2004, 25, 475-480.]
Chen et al. showed that the monophosphine complex of 3.12 is 40 times more active than that of the dissociated dimer species of 1.89. In a comparison between 1.3 and 1.89, it was concluded that the 40 times lower active species of catalyst 1.89 is overcome by its higher concentration in active species and its tendency not to engage in backbiting the polymer. Those qualities enable 1.89 to be a more potent catalyst than 1.3 for ROMP. However, this lack in backbiting renders the same complex unsuitable for RCM. In the same publication, Chen et al. were able to tune the Hoffmann catalyst in an elegant way using their Electronspray Ionization Tandem Mass Spectrometry.

In 2003, Chen et al. compared the first and the second generation Grubbs catalysts by testing the reactivity of the 14 electron species substituted with a cationic group on the benzylidene with ethyl vinyl ether. From the lack of reactivity of the first generation system and the high reactivity of the second generation system was concluded that in the former there is a high energy TS for the cyclobutane and in the latter a low energy barrier. This is in agreement with former experimental observations and theoretical calculations.

In conclusion, we propose that the well documented electron spray experiments of Chen et al. are to be considered with great caution as models for actual polymerizations due to their lack of correspondence with the real polymerization system.

The Chen group proceeded with two DFT studies examining in great detail the metathesis reaction with the Grubbs catalyst. First, it was shown that the first generation catalyst 1.3 needs to perform a phosphine rotation as the rate limiting step after cyclobutane formation in order to obtain productive metathesis. However, for strongly exothermic reactions the rotation can occur after the eclipsed product-carbene, stabilized by the exothermic reaction, has been formed. In these cases, it does not represent the RLS (Rate Limiting Step). An alternative pathway in which the carbene is eclipsed with a cyclohexyl group is energetically unfavorable. This conceptual investigation shows the important different steric implications between the 3-folded symmetry of L in the first generation catalyst and the 2-folded symmetry in the second generation catalyst. The electronic implications of the different symmetry which manifest in the π-backdonation will be discussed in a later section.

Figure 3.6: Rotation of PCy3 during the reaction path.

In the second generation catalyst 1.4, this problem does not occur due to the 2-folded symmetry. Furthermore, the H2IMES ligand cannot rotate over the chlorine atoms due to steric bulk and the RuCl2(H2IMES) fragment remains a rigid structure throughout the catalytic cycle. The Chen group experimentally explored this theory by synthesizing 3.13 with a phosphine which is fixed and unable to rotate. This catalyst is able to synthesize alternating polymers of cyclooctene and norbornene...
through the switching carbene mechanism.\textsuperscript{28,29} When the carbene is at the bulky \textsuperscript{t}Bu side, it reacts quickly with every monomer (here Cyclooctene which is used in excess).\textsuperscript{28,29} When the carbene is on the phenyl side, it reacts very difficult and reaction only proceeds with the highly ring strained norbornene.\textsuperscript{28,29}

\begin{equation}
\text{Figure 3.7: Rigid phosphine catalyst as prove for the necessity of phosphine rotation.}
\end{equation}

A subsequent publication consisted of a full detailed analysis of the metathesis cycle on several catalysts\textsuperscript{5} and the determination of the influence of the real ligand vs. model ligands.

In the series 3.14, 3.15 and 3.16 the dissociation energies from A → B amount to 21.1, 28.3 and 21.5 kcal/mol.\textsuperscript{5} Chen et al. argue that the stronger π-acidity and the weaker basicity for PH\textsubscript{3} compared to PCy\textsubscript{3} justifies the similar dissociation energy of 3.14 and 3.16.\textsuperscript{5} An explanation which includes the similarity on basis of the trans effect or the steric congestion of the system seems more appropriate. Note that the dissociation energy of H\textsubscript{2}IMES is 38.1 kcal/mol in 3.19, while the increase to 52.3 kcal/mol for H\textsubscript{2}IH in 3.22 can easily be explained by the lack of steric strain and decrease of trans influence. Furthermore, the authors suggest that ‘the strong sensitivity of ligand dissociation energies on π-acidity and σ-basicity and a dramatic trans effect are observed in the dissociation energies of the mixed complex (PMe\textsubscript{3})(PH\textsubscript{3})(Cl)\textsubscript{2}Ru=CH\textsubscript{2}.’ (3.17-3.18).\textsuperscript{5}
Chen et al. state that the increasing olefin affinity for the PCy₃ < PMe₃ < PH₃ systems (ΔE(B-C) for 3.14-3.16) is consistent with a reducing basicity and an increasing π-acidity and the assumption that electron-withdrawing groups destabilize the 14-electron species B more than the olefin coordinated species C. However, the increased π-acidity of L (e.g. in PH₃) should destabilize the Ru-olefin (back)bond, which does not occur, and thus the π-acidic effect apparently is not that important in this phase (for phosphine catalysts). We suggest the Ru-olefin bond strength in the olefin complex is mainly dominated by the σ-donating interaction (for phosphine-catalysts). This was also evident from the bond length calculations by Cavallo. The relative stability of the metallacyclobutanes D compared to the 14-electron species shows the opposite trend since the electron deficiency at the 14-electron species is partly stabilized by the carbene whereas in the metallacyclobutane no such conjugation is possible. Here, we think that the increasing π-acidity might be crucial in destabilizing the cyclobutane ring, since the cyclobutane M-C bonds are now aligned in the dₓᵧ orbital and consequently ‘compete’ for backbonding. Furthermore, the strong trans effect of PCy₃ should enhance cyclobutane formation by destabilizing the olefin complex. The only ligands able to reach an exothermic reaction from C to the metallacyclobutane D, are the steric congested 3.14, 3.19 and 3.22, indicating that besides the electronic factor also a steric relaxation should be taken in to consideration as noted by Cavallo. In the systems 3.19-3.20, the ΔE(C-B) are quite similar and the cyclobutane formation is 9.7 kcal exothermic for 3.19 compared to 1.4 kcal endothermic for 3.20. Cavallo’s argument that the destabilization of the 14 electron species 3.19B is due to the steric pressure of the carbene and the mesitylene is also confirmed by the higher PCy₃ dissociation energy of 3.19A compared to 3.14A. Since 3.19 bears the stronger σ donor and hence stronger trans effect compared to 3.14A, a lower dissociation energy of PCy₃ in the former should be expected. It should also be noted that the imidazole ring and the chlorines in complex 3.20 have an in plane orientation, which places the backbonding from the NHC in competition with the same orbital for cyclobutane formation. This can be held responsible for the decrease in stability of the cyclobutane complex (which will be later discussed in detail).

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### Table 3.5: Bond energies for the Grubbs systems investigated by Chen et al. (kcal/mol).

<table>
<thead>
<tr>
<th></th>
<th>3.14</th>
<th>3.15</th>
<th>3.16</th>
<th>3.17</th>
<th>3.18</th>
<th>3.19</th>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>21.1</td>
<td>28.3</td>
<td>21.5</td>
<td>32.8</td>
<td>17.2</td>
<td>26.1</td>
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<td>16.6</td>
<td>6.7</td>
<td>18.0</td>
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<td>14.5</td>
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<td>25.6</td>
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<td>45.1</td>
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<td>20.2</td>
<td>14.3</td>
<td>25.6</td>
<td>9.2</td>
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<td>1.4</td>
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<td>7.6</td>
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<td>ΔE (D-B)</td>
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<td>-7.2</td>
<td>-8.0</td>
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<td>-11.7</td>
<td>-11.7</td>
<td>-12.1</td>
<td>-7.2</td>
</tr>
</tbody>
</table>

Data from 5

---

VII It should be noted that if the carbene is considered to be a Fischer carbene, the 14 electron species B and the olefin bonded species C are both in OS +II where the metallacyclobutane species D is in OS +IV. The more electron donating ligands should than be more able to stabilize the high oxidation state.
Table 3.6: Comparison between the Chen and Cavallo results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>3.7 (Cavallo)</th>
<th>3.14 (Chen)</th>
<th>3.11 (Cavallo)</th>
<th>3.19 (Chen)</th>
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</thead>
<tbody>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>16.2 (20.8)</td>
<td>21.1</td>
<td>23 (28)</td>
<td>26.1</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>15.1</td>
<td>8.3</td>
<td>15.0</td>
</tr>
<tr>
<td>TS (CD)</td>
<td>18.2</td>
<td>18.5</td>
<td>10.2</td>
<td>17.3</td>
</tr>
<tr>
<td>D</td>
<td>15.4</td>
<td>8.9</td>
<td>7.1</td>
<td>5.3</td>
</tr>
<tr>
<td>ΔE (C-B)</td>
<td>-6.2</td>
<td>-6.0</td>
<td>-14.7</td>
<td>-11.1</td>
</tr>
<tr>
<td>ΔE (D-C)</td>
<td>5.4</td>
<td>-6.2</td>
<td>-1.2</td>
<td>-9.7</td>
</tr>
<tr>
<td>ΔE (D-B)</td>
<td>-0.8</td>
<td>-12.2</td>
<td>-15.9</td>
<td>-20.8</td>
</tr>
</tbody>
</table>

Data from \(^5\) for 3.14 and 3.19 and from \(^13\) for 3.7 and 3.11.

Between parentheses are the values calculated by Chen et al. for the benzylidene species using IMOMM (Integrated Molecular Orbital-Molecular Mechanics). \(^27\). The experimental values for 3.7 and 3.11 are respectively 23.6 ± 0.5 kcal/mol and 27 ± 2 kcal/mol. \(^1\)

3.7 and 3.11 correspond to the benzylidene species of the Grubbs 1\(^{st}\) and 2\(^{nd}\) generation complexes, while 3.14 and 3.19 correspond to the methylidene species. \(^5,13\) The higher bond energy between 3.14A→B compared to 3.7 is well in agreement with experimental data, as the phosphine is found to be less prone to dissociate in a methylidene species. \(^5,13\) Maughon et al. suggested that the difference is caused both by electronic and steric factors (determined from PMe\(_3\) energies). \(^30\) The highest discrepancy between the Chen and Cavallo calculations lies in the cyclobutane formation. Chen et al. calculated much more exothermic values for the olefin-metallacyclobutane transformation. This can be rationalized by conjugation through the benzylidene stabilizing the carbene which is lost in the cyclobutane D, assuming the carbene is a donor-acceptor bond. \(^5\) Yet, an energy gap of over 10 kcal/mol seems large to be justified only through a secondary electronic conjugation effect.

Some interesting conclusions can be drawn from this. The higher bond energy of PCy\(_3\) in the methylidene species renders PCy\(_3\) dissociation the RLS in RCM for the first generation catalyst, while the effect is even more dramatic for the second generation catalyst 3.19. This generates opportunities for the variation of ligands to increase the concentration of the active species in RCM. The same should not be necessary for ROMP because after the benzylidene has reacted, a latent polymer coordinated Ru-complex can become competitive to recoordination of the ligand, at least according to Chen et al. (vide supra).

From these data, it also seems possible for ROMP, at most for a second generation catalyst without a conjugated carbene and an unstrained monomer (vide infra), to have a cyclobutane intermediate Ru catalyst backbiting the polymer as the most abundant intermediate structure, since the energy of the cyclobutane intermediates 3.19D and 3.11D lie well below the olefin coordinated structure C. However, no such in situ cyclobutane intermediate has been reported in ROMP while it could be anticipated for the polymerisation of cyclopentene or COD. On the other hand, metallacyclobutane structures have been reported for H\(_2\)IMES substituted catalysts.

Fürstner et al. suggested that a π-π stacking \(^31\) is responsible for the increased reaction rate of aromatic NHC substituted catalysts in aromatic solvents, for which the solvent competes for the π-π interaction. However, the ΔE(D-C) for 3.14 - 3.7 (or the energy difference between the cyclobutane and the olefin-bonded species of the methylidene vs. the benzylidene for the first generation catalyst) is -11.6 kcal/mol. This accounts only for the conjugation effect, where ΔE(D-C) for 3.19 - 3.11 (for the
Understanding olefin metathesis

second generation system) amounts only to -8.5 kcal/mol and should account both for the conjugation effect and the π-π stacking but somehow is less. Alternative explanations would be that the higher σ-donation of the NHC reduces the need of the ruthenium-carbene for the extra stabilization through conjugation of the benzylidene or a negative steric mesityl-benzylidene interaction. Fürstner’s argument can also be attacked since it is not the cyclobutane formation - the step where the π-π stacking energy should be lost - which is the RLS in this process but phosphine dissociation is rate limiting here. Moreover, Fürstner et al. based their conclusions on the RCM experiments in which the phosphine dissociation becomes even more rate limiting and π-π stacking of the benzylidene only occurs in the first initiation step VIII.

Chen et al. also investigated the role of the substrate for the first and second generation Grubbs catalysts. It was shown that the metallacyclobutane is no local minimum for the reaction of the first generation catalyst with ethyl vinyl ether. In this case, it represents the RLS for the cycle. The high transition state and the strong exothermicity after cyclobutane formation make the reaction of the Ru-initiator with ethyl vinyl ether irreversible. This high TS explains the concentration dependence on ethyl vinyl ether when Grubbs et al. determined the rate for phosphine dissociation of 1.3 postulating that after phosphine dissociation all steps are fast. The metallacyclobutane ring is not a TS for the second generation catalyst and the TS to the metallacyclobutane is 5 kcal/mol lower than the 14 electron complex. This corresponds to the absence of concentration dependence of the phosphine exchange rate, observed by the addition of ethyl vinyl ether.²

Chen et al. reported that for the exothermic reaction with norbornene, the complexation of the sterically demanding norbornene to the 14 electron complex is unexpectedly more exothermic than with ethene. However, we think this is not so surprisingly since strained olefins are known to show higher metal-olefin bond energies. The first generation system shows an energy of the TS before cyclobutane formation somewhat higher than for ethene, though still lower (-1.1 kcal/mol) than for the 4-coordinate 14 electron species. Upon opening of the metallacyclobutane the energy of the norbornene strain (15 kcal/mol) is starting to be released and steric strain is thus not responsible for the fast polymerization since these events are happening after the RLS. The second generation catalyst can travel through a path with the highest energy 8 kcal/mol lower than the 14 electron species and here again the ring strain is only released after cyclobutane formation. Fomine et al. investigated the propagation of norbornene for a IPh substituted second generation catalyst. The authors found no TS in the metallacyclobutane formation and the reaction was completely exergonic from the norbornene coordination up to the decoordination of the ligated (metathesized) polymer chain! Furthermore, the most exergonic step in the reaction is the cyclobutane formation, which indicates that the ring strain is released before cyclobutane-cleavage. Consistently contradictory, Fomine et al. calculated the norbornene complexation to be less exergonic (-3.2 kcal/mol) than the ethene coordination (-4.1 kcal/mol). However, no reference to the discrepancy with the results by Chen et al. was mentioned.

VIII Since recoordination of the benzylidene in RCM or CM has not yet been reported.
IX The lower energy of the sterical more demanding complexation of norbornene vs. ethene is also an argument against conclusions that catalysts are less active due to steric NHC-ligands causing more difficult coordination of olefin compared to phosphine.
X IPh refers to the N-phenyl substituted unsaturated NHC.
3.4 Orbital analysis and qualitative comparison with model systems

Since 2005, an increased interest of theoretical chemists towards the metathesis reaction emerged. First, a contribution of Harvey et al. will be discussed. Harvey et al. computed the energies of model systems, real systems and intermediate systems. However, their relative energies of the real systems were in bad agreement with previous DFT studies and experimental values. More specifically, the phosphine dissociation values were calculated much too low and the 1st generation complex was calculated to have a stronger Ru-PCy3 bond than the second generation system. Strangely, the authors were not able to find a solution for their discrepancies with other values and hence a discussion of the absolute values of their complete systems makes little sense. However, Harvey et al. did make as the first a full orbital analysis and were able to conclude interesting qualitative judgements of which some were previously coined by Thiel et al.

Harvey et al. assert CH2 and CHPh to be neutral singlet ligands and the Ru species to be in the +II oxidation state. Furthermore, ‘the strong field character of the ligands means that all Ru complexes treated here adopt a low spin configuration’ and calculations supported that assertion. The Cl-Ru-Cl axis was taken as the z-axis and the Ru-carbene axis as the x-axis. The analysis was performed on 3.16B and 3.21B: the PH3 and H2IH substituted fourteen electron methylidene species.

It should be noted that the methylidene adopts a perpendicular orientation (hydrogens not in the plane with the chlorines) in contrast to the real systems. The HOMO-2, HOMO-1 and HOMO are respectively the dxy, dxz and dyz orbitals and can participate in backbonding. Bonding occurs by dative interactions from the σ lone pairs on the PR3, carbene and chlorine ligands into the dz2 and dx2-y2 orbitals.

The HOMO-2 dxy orbital undergoes a stabilizing interaction donating to the PH3 ligand. Also a small (donating) interaction from the chlorines due to non-orthogonality with the carbene is destabilizing this orbital. The HOMO-1 dxz orbital undergoes a destabilizing interaction with the filled orbitals on the chlorines and a stabilizing interaction with the empty orbital on the carbene. Finally, the HOMO dyz displays a stabilizing interaction due to donation to the phosphine and destabilization due to the interaction with the filled chlorine orbitals. The authors reason that the upright position of the carbene is adopted due to electronic reasons in order to maximize the interaction with the dxz orbital. This is very well put, as one can see that in this conformation the π-donation from the chlorine atoms is channelled by the carbene and the phosphine. In the alternative (real system) conformation, the dxz orbital cannot divert the donation from the chlorine atoms. Furthermore, the dxy orbital is then doubly
attacked for backdonation, which could render the backdonation inefficient (beyond saturation) as was
evidenced for phosphorous systems (Chapter 2).

When backdonation to a ligand is only
accomplished through a decrease of backdonation to the competing ligand sphere, it leads to absence
of any enthalpic effect due to backdonation of this ligand. This is in accordance with the lack of \(\pi\)-
acidity influence in the bond energies of different phosphines in the olefin substituted complexes
calculated by Chen et al.\(^7\) The steric effect is expected to prevent the upright position of the carbene in
the real catalyst systems which leads to a decreased interaction.\(^35\)

'It should also be noticed that backbonding from the \(d_{xy}\) and \(d_{yz}\) orbitals to the \(\sigma^*\) orbitals of
alkylphosphines is expected to be fairly weak, and doesn’t depend on the orientation of the
phosphine.'\(^35\) 'The situation is different for the diaminocarbene-based “second-generation”
catalyst systems, for which the \(p\) orbital on the ligating carbon is at fairly low energy, but is only
able to overlap with one of the two ruthenium \(d\) orbitals of \(\pi\)-symmetry with respect to the Ru-C
bond.'\(^35\) [emphasis ours]. In the model system this backbonding originates from the \(d_{xy}\) (HOMO-2)
orbital for which no competition is present, however, the \(d_{yz}\) HOMO remains unhampered by
backdonation (see figure 3.10; Ru \(d_{yz}\) in the NHPhosphine-Ru-Cl plane). The authors reason that this
geometry is preferred due to a H\(_{\text{III}}\)-Cl bond which fixes the NHC fragment.\(^35\) (These geometries were
previously suggested by Thiel et al.)\(^36\) Both the ethene and PH\(_3\) bond energies are higher in the PH\(_3\)
based system, which can be attributed to the relatively low basicity of PH\(_3\) destabilizing the 14
electron species and the cyclobutane species.\(^35,36\)

For intermediate systems with PMe\(_3\) as the only phosphine and benzylidene as the carbene ligand the
Ru-P bond energy increases due to an increased bonding in the \(\sigma\)-bond of PMe\(_3\).\(^35\) However, the ethene
bond energy decreases and Harvey et al. note that ‘although the reason why bonding of alkene is less
dependent on the trans influence than bonding of the phosphine is unclear.’\(^35\) A straightforward
explanation consists in the use of the same olefin while a different phosphine was taken. We assume
that backbonding to the ethene should be more efficient with PMe\(_3\)\(^\text{XI}\) as the trans ligand, so we can
again only conclude that the ethene bond energy is mainly \(\sigma\)-donor based! Moreover, Harvey et al.
(and Chen et al.) calculated the PMe\(_3\) bond energy to be higher for the Ru-PMe\(_3\) system than for the
Ru-H\(_{\text{II}}\) system while the reverse trend exists for the ethene bond in these sterical unhindered
systems.\(^35\) This evidences that the ligand effect cannot be simply evaluated as more or less electron
donating but that qualitative differences in the bond are of paramount importance. Jensen et al. showed
that the Ru-NHC bond is differentiated from the Ru-P bond by an increased \(\sigma\)-donation and increased
\(\pi\)-backdonation in the Grubbs complex.\(^39\) However, this NHC \(\pi\)-backdonation does not directly
compete with the ethene backdonation in the Ru-H\(_{\text{II}}\) system. We think this may cause the relative
increase in Ru-ethene bond energy (vide infra).

The metallacyclobutane system is even more stabilized in the H\(_{\text{II}}\) system compared to the PMe\(_3\)
system for which the \(\pi\)-trans influence of the NHC should be substantial. However, a potential change
in hybridization in the metallacyclobutane should be able to account for different competition effects.
\(\text{(sd}^2 \rightarrow \text{sd}^3)\)

We want to point out that the metallacyclobutane is positioned as in Thiel’s publication where before
formation of the cyclobutane (TS), the competition for backdonation from the \(d_{xy}\) orbital (HOMO-2)
seems extreme: The ethene, NHC and carbene receive backdonation from the same orbital, while the

\(^{\text{XI}}\) Harvey et al. also have shown for CO-Pd-phosphine complexes that PMe\(_3\) is a lesser \(\pi\)-backdonation
competitor than PH\(_3\); the same conclusion can be made indirectly from other phosphine investigations.
chlorine donation into the $d_{xz}$ (HOMO-1) and $d_{yz}$ (HOMO) orbitals has no way to be ventilated and hence this seems the worst combination possible. Thiel et al. predict a lower energy (3.7 kcal/mol) for the metallacyclobutane compared to the ethene coordinated complex for IH with a methylidene species. Chen et al. calculate a reverse equilibrium of 1.5 kcal/mol for the similar transition with $H_2$IH in a methylidene species.\textsuperscript{5} With $H_2$IH as primary ligand, Harvey et al. calculated a lower energy of 3.9 kcal/mol for the cyclobutane compared to the ethene coordinated methylidene and a 2.2 kcal endothermic cyclobutane ring formation for the benzylidene carbene.\textsuperscript{15} This is intuitively correct since the benzylidene carbene is thought to be more stabilized than the methylidene and hence cyclobutane formation should go more smoothly in the latter. The same trend was observed when we compared the results of Chen et al. with those of Cavallo on the $H_2$IMES substituted catalyst. However, the Cavallo-Chen analysis ($H_2$IMES) shows a more exothermic ethene addition for the benzylidene vs. methylidene while the Harvey analysis ($H_2$IH) shows a more exothermic reaction for ethene addition with the methylidene species.

Harvey et al. continue with ‘The origin of the lower TS energies in the “second-generation” carbene-based catalyst systems is hard to identify. As mentioned above, the stronger $\sigma$-donating carbene ligand might stabilize the incipient +IV oxidation state of the forming ruthenacycle. If this were correct, the barrier heights relative to the corresponding alkene $\pi$-complexes 5b, 6b, 5b' and 6b', in which the metal is clearly in the +II level, should also show stabilization by the carbene. In fact, they do not, so that much of the difference in barrier height simply reflects the larger binding energy of the alkene to the carbene-derived 14-electron species.’\textsuperscript{35} (with 5b, 6b, 5b' and 6b' the ethene coordinated complexes to a PMe$_3$ and $H_2$IH substituted catalyst) Later Straub showed that the TS for the IMe catalyst (with the IMe plane perpendicular to the Cl-Ru-Cl direction), lies very close in energy with the active olefin complex.\textsuperscript{14}

Harvey et al. also described the real catalyst systems 1.3 and 1.4.\textsuperscript{35} Concerning the absolute values of the energy differences, it should suffice to say that the BDE for PCy$_3$ in 1.3 and 1.4 are calculated to be 17.3 kcal/mol and 15.9 kcal/mol respectively.\textsuperscript{35} The experimental enthalpy values are 23.6 ± 0.5 kcal/mol and 27 ± 2 kcal/mol respectively. Previous calculated values were 16.2 kcal/mol and 23 kcal/mol by Cavallo\textsuperscript{13} and 20.8 kcal/mol and 28.0 kcal/mol by Chen et al.\textsuperscript{27} (vide supra). The values obtained by Harvey et al. do not only show a huge underestimation of the BDE, the difference in error between the calculated values for 1.3 (6.3 ± 0.5) and 1.4 (11.1 ± 2) is so large that even the relative bond strength switches in both complexes.\textsuperscript{35} The values calculated by Cavallo represent an underestimation (7.4 ± 0.5 for 1.3 and 4 ± 2 for 1.4)\textsuperscript{13}, however, the underestimation is lower and it does not violate the only boundary condition being the relative phosphine dissociation energies. The calculated values by Chen et al. are even more in synchronization with the experimental values.\textsuperscript{27} We
choose not to discuss the absolute values calculated by Harvey et al. though we will critically analyze the organometallic reasoning they apply.

'This larger stabilization in the real system is probably due to a stereoelectronic effect. Ru-C bonding in the ruthenacycle is best described in a covalent framework, with chemical bonding due to overlap between carbon based sp³ orbitals and metal-based d orbitals, especially d_xy as this has the correct symmetry to interact with the terminal carbon atoms of the 1,3-propylidene ligand. However, as shown in Figs. 2 and 3, this orbital is also involved in back-bonding to the phosphine or diaminocarbene ligand, at least in the model systems. This back-bonding will compete with and weaken the Ru-C bonding in the metallacycle. As discussed in the context of Fig. 3(b), backbonding of this type to the phosphine is independent of rotation around the Ru-P bond, but very sensitive to rotation around the Ru-C bond in the diaminocarbene systems. The heterocyclic carbene only has one vacant orbital suitable for back-bonding. In intermediate model ruthenacycle 8b, the diaminocarbene ligand is rotated in such a way as to facilitate this form of back-bonding as shown in Fig. 7(a) (compare with Figure 3(b)). In contrast, in the real system, 8c (Fig 7(b)) the ligand is rotated by 90°, so that this back-bonding does not occur from the d_xy orbital, and the absence of this interaction means that the latter is better able to engage in bonding in the four-membered ring, thereby stabilizing the latter. The differing orientation of the ligand in the two cases is due to the formation of an intramolecular hydrogen bond between NH and Cl in 8b, which is impossible in 8c, and to steric hindrance which would occur between the mesityl side-chains and the chlorine atoms in 8c if it adopted the same geometry as 8b.35 (Figures referring to the original publication; 8: metallacyclobutane conformation; b: H₂IH substituted; c: H₂IMES substituted)

This type of reasoning is extremely close to our position on the matter, at least concerning the olefin coordination to the second generation complex preceding the transition state and the metallacyclobutane formation. It seems that this 2-fold symmetry backbonding can only lead to preference of the Ru-ethene bond in the active position. However in the cyclobutane, a rehybridization of the ruthenium should occur after the oxidation from Ru(II) to Ru(IV). In fact according to Landis' valence bond theory for TMs (of which Harvey is a clear proponent!) the ruthenium precursor is sd² hybridized. However, we think that in this sd² hybridization a clear interaction with two p-orbitals is not to be neglected going to a sd²-(p²) hybridization. Upon oxidation, the Ru is in the Valence Bond theory formally sd¹ hybridized! The most logical Valence Bond structure for this is a tetraeder.40 However, in the hypervalent structure, one ligand (here chlorine) has to be placed trans to an other ligand with corresponding resonance structures. This leads to two non-degenerated Lewis structures for bonding of the two chlorines. After combining those structures, the complex should adopt the trigonal bipyramidal structure as is experimentally observed for the cyclobutane species. Hall et al. also place the trigonal bipyramidal structure (D₃h) among the d⁴ structures for MH₅ complexes (in the sd³p hybridization).41 We assume that the 4 d electrons should then be localized in the d_xz and d_yz orbitals with the Cl-Ru-Cl as the z-axis. Furthermore, we assume that there is some involvement of the p orbital into a sd¹-(p) hybridization. However, the d_xy orbital should not show any electron density in our scheme since it is used in the sd³ hybridization! Backbonding to the NHC ligand is then not affected because the rehybridization only consumes the d_xy orbital.
Upon formation of the cyclobutane ring, a rehybridization is necessary. This rehybridization is promoted by a strong L-σ-ligand which destabilizes the trans C-ethene bond. The σ-L ligand, which highly donates to the ruthenium, destabilizes the Ru(II) and stabilizes the Ru(IV) oxidation state. The π-accepting function of the NHC ligand can only play a secondary effect: It turns itself away from the highly competitive d\textsubscript{xy} orbital, facilitating easier rehybridization. Furthermore, this easier backdonation from the less competitive d orbital should provide a better synergy in the donation-backdonation interaction from the NHC and hence increase the σ-donating effect.

Previously, we expected that the π-accepting ability of the NHC would influence the cyclobutane-ring by not competing with the d\textsubscript{xy} orbital. However, upon rehybridization, this orbital formally doesn’t exist anymore, thus the absence of the NHC-influence in this orbital also promotes this rehybridization. However, the d\textsubscript{xy} orbital should have a primary effect on the TS, and a high electron density in the orbital, without interactions to the rest of the coordination sphere of ruthenium should facilitate an easier TS. Sd\textsuperscript{2} or sd\textsuperscript{3}, the NHC-π-orbital for backdonation never meddles with the direct bond to the metallacyclobutane.

The extreme ligand optimization of the NHC in metathesis stems thus from steric effects favoring the cyclobutane, the active σ-donation destabilization of the olefin σ-bond, extra donation stabilizing the +IV oxidation state and the orientation of the NHC into an inactive spectator π-orbital orientation!

With the installation of a pure Fischer carbene CH(OEt), the carbene π\textsubscript{a} orbital shows a strong interaction with the oxygen to stabilize the electron density. However, this means that the interaction of the carbene with the metal-d\textsubscript{xy} orbital decreases. Now, it is this highly populated interaction which attacks the olefin π\textsuperscript{*} orbital, so the attack should not be favorable in the case of ethyl vinyl ether carbene due to the necessity of extra electron reorganizations. In this context it should be noted that Frenking et al. found 2 NBOs between the Fischer carbene fragments Cr(CO)\textsubscript{5} and :CH\textsubscript{2}, though if the typical Fischer carbene fragment :CH(OEt) was used with the same Cr fragment only one NBO, the σ-orbital, was found.\textsuperscript{42} This illustrates the possible lack of a π orbital between Ru and the ethyl vinyl ether carbene and hence the difficulty of the carbene to interact with the π\textsuperscript{*} orbital of the olefin.
Harvey et al. investigated the discrepancies of their computational results with the practical and theoretical results. Expansion of the basis sets and implementation of the BP86 functional instead of the B3LYP functional could not improve results. Application of the IMOMM, in analogy with Chen et al. showed an increase in the phosphine dissociation values. However the 1st generation complex still showed a higher BDE than the 2nd generation complex.

3.5 Active carbene orientation and intrafragment polarization

Straub presented in 2005 his first analysis on the Grubbs complexes. It should first be noted that all energy values presented in his studies concern Gibbs free energies and not bonding energies. Straub showed that the energy values of 3.24-3.25(A-C) are very similar. 3.24 is slightly more stable than 3.25 and the stability decreases in the series C > B > A. However, transition from 3.25 to complex 3.26 imposes a high barrier (5-6 kcal/mol) for A-B. On the contrary, the NHC complex C shows no worsening of the energy level upon rotating the carbene. Steric congestion which would disfavor the carbene orientation in 3.24-3.25 with the methyl ligand could explain such a difference. No local minimum for 3.27 was found but the energies of 3.26 were close to the TS values before cyclobutane formation.
Figure 3.13: Different olefin coordination on the Grubbs complex.

Straub proposed that intrafragment polarization (mixing of 5p and 4d orbitals) of the ruthenium towards the halide ligands and the NHC cause a bending of these ligands away from the carbene.\textsuperscript{14} This causes the non-bonding interactions of the chlorine and NHC ligand separately to become increasingly anti-bonding and increases the overlap of the carbene and the Ru-d orbital.\textsuperscript{14} The bending of the chlorines stabilizes the inactive carbene conformation while the active conformation is stabilized by the bending of the NHC ligand.\textsuperscript{14} The olefin is supposed to be a weak donor and should not lead to a pronounced anti-bonding character, however, Cavallo predicted the olefin to be bonded asymmetrical.\textsuperscript{14} Straub calculated the carbene angles for the carbene, halides and phosphine ligands and observed that the phosphine ligand does not show significant bending.\textsuperscript{43} Since a phosphine ligand is both a $\sigma$-donor as well as a $\pi$-acceptor, an increase in the phosphine-ruthenium carbene angle would lead both to an anti-bonding interaction $\sigma$(P) to d(Ru) as well as a loss of back-bonding d(Ru) to $\sigma^*$(P-C).\textsuperscript{43}

Figure 3.14: Intrafragment polarization.

 Straub proposed that the low dissociation energy for 1.3 compared to 1.4 is caused by the steric interaction between the $\beta$-hydrogen atoms of the cyclohexyl rings in 3 with the chlorine ligands.\textsuperscript{14} Straub also proposed that the mesityl substituents on 1.4 contribute to the active carbene orientation.\textsuperscript{14} Straub investigated the influence of the anionic X-ligands in Grubbs type catalysts\textsuperscript{43} and concluded that the in-plane d-orbital which is used for backdonation to the carbene should be stabilized in the order alkyl > aryl > NR$_3$ > OR > SR ≈ F ≈ NHC > I > Br > Cl > O$_2$SR > R$_3$P > NR$_3$/NH$_3$ ≈ OR$_2$/OH$_2$ ≈ alkene or alkene >> free coordination site.\textsuperscript{43} The H$_2$CSO$_3^-$ (mesylate) group was calculated to be the most productive anionic ligand. This is due to the weak donating character of the oxygen substituent which causes little intrafragment polarization.\textsuperscript{43} Furthermore, dissociation of phosphine is assisted by biscoordination of one of the mesylate ligands and the TS for cyclobutane formation shows a lower energy than the chlorine analogue.\textsuperscript{43} We agree that rehybridization to the sd$^3$-(p) state is indeed less energetical demanding if the chlorines are already in the full trans position. If the NHC shows some \textit{intrafragment polarization}, then the angle with the carbene is already widened (90°→108°\textsuperscript{43}; 98°\textsuperscript{13}).
The angle between the NHC and the closest olefin carbon (C₂) is closed (→148°) due to asymmetrical bonding so that these values are already closer to the angle of the cyclobutane-NHC (138°). Note that an angle of 138° in the metallacycle is not really the envisaged 120° of the trigonal bipyramide, so that alternative bonding modes such as the agostic interaction should also determine the electronic reality (vide infra). However, the transition, state which is the RLS after phosphine decoordination shows an angle of 118° between H₂IMES and the C(Initial carbene)-cyclobutane carbon and to the best of our knowledge no agostic interactions for this TS have yet been reported.

3.6 The metallacyclobutane ring

Koga and Suresh calculated the cyclobutane formation in the PH₃ substituted Grubbs catalyst. The π-orbital of the carbene is directed towards the olefin and therefore the formation of the new C-C bond proceeds easy. When the cyclobutane is formed, the ring shows an unusual CCRu angle (77°), CCC angle (119°) and a long C-C bond distance (1.587 Å). The authors first suggested that these unusual features were evidence of two α-CC agostic interactions. In a subsequent publication, Suresh and Baik revised this statement and concluded that the cyclobutane exhibits a 4-centre-2-electron α,β-(C-C-C) agostic bond, involving the donation of the σ-electron density from the propylene moiety to the ruthenium-centre which increases the electron count by 2, to formally reach a 16-electron complex! The authors considered this an explanation for the high stabilities of the – formerly 14 electron – cyclobutane intermediates, which they calculated to be 7.4 and 9.2 kcal/mol more stable than the olefin adducts for the first and second generation Grubbs catalysts respectively. This is in analogy with the results calculated by van Rensburg et al.

A reconstruction is presented applying a neutral (PH₃)RuCl₂ fragment (dₓᵧ, dₓz and dₓz occupied) and a neutral propylene fragment. Baik et al. suggest that the bonding MO of the propylene adduct donates its electron density to the - formally full - Ru dₓᵧ orbital in an agostic interaction. Agostic interaction through a Ru p orbital cannot occur due to symmetry restrictions. We think that the agostic bond, which donates the electron density of the bonding propylene orbital to the Ru-dₓᵧ orbital, can be considered the resultant of two resonance structures of methylene and ethene coordinated species (see Figure 3.15). When the agostic bond is taken into account, the dₓᵧ orbital comes to the centre of the catalytic transformation, playing a crucial role in the olefin species, cyclobutane species and the TS. The agostic interaction is calculated to account for a bonding order between Ru and C₂ of 0.213 and 0.199 in 1.3 and respectively 1.4. This should result in approximately a double bond order for the total interaction.

Baik et al. construct 3 bonding interactions: The agostic (occupied) bonding orbital interaction which is the lowest in energy (-11 eV) and interacts with the (occupied) dₓᵧ orbital. The LUMO of the propylene results in the second lowest interaction of the three (-9.5 eV) through an interacts with the dₓᵧ orbital. Thirdly, the HOMO propylidene interacts with a combination of the dₓz, dₓz and dₓ² and increases the energy of these orbitals. The propylidene bonding orbital donates electrons into the dₓᵧ orbital through the agostic interaction and lowers in energy. This dₓᵧ orbital mixes with the propylidene LUMO to delocalize the charge and redistribute it in a backbonding interaction to the two

[^XII]: 108° calculated by Straub for the H₂Ime ligand and 98° calculated by Cavallo for H₂IMES!
[^XIII]: The authors state that during the cyclobutane formation the Ru atom is oxidized to Ru(IV) implying that the Ru-carbene-alkylidene is formally a Fischer carbene.
end-carbons (note the analogy with the olefin description). Furthermore, the HOMO delocalizes its charge into the \(d_{xz}, d_{yz}\) and \(d_z^2\).  

![Propylene interacting orbitals](image)

**Figure 3.15:** The metallocyclobutane interactions.

Baik et al. also investigated the influence of the saturated vs. unsaturated carbene in the metallocyclobutane ring.\(^{47}\) The Ru-NHC bond lengths indicate that NHCs with an electron withdrawing substituent (F in \(\text{H}_2\text{IF}\)) are ‘the most tightly binding’ ligands which Baik et al. attribute to a **stronger \(\pi\)-interaction**.\(^{47}\) This is manifested in a decrease of orthogonality in the Cl-Ru-C\(_{\text{carbene}}\)-N bonding orbital: responsible for agostic interaction.\(^{47}\) This is manifested in a decrease of orthogonality in the Cl-Ru-C\(_{\text{carbene}}\)-N dihedral angle for the methyl-N (in \(\text{H}_2\text{IMe}\)) substituents compared to F-N substituents.\(^{47}\) Backbonding could be considered optimal when the dihedral angle is orthogonal, which leads to a chlorine-NHC interaction.\(^{47}\)

As stated by Thiel et al.\(^{36}\), the IH and \(\text{H}_2\text{IH}\) prefer a position orthogonal to the cyclobutane ring and with the NHC plane parallel to the Cl-Ru-Cl, with which the IH forms a hydrogen bond.\(^{47}\) (Baik et al. depict both for the perpendicular and parallel orientation the Cl-Ru-Cl perpendicular to the cyclobutane ring)

Baik et al. note that with \(\text{H}_2\text{IH}\) in the orthogonal cyclobutane-NHC orientation, there is an interaction between the agostic cyclobutane bond and the \(d_{xy}\) orbital in which a coupling can occur to the backdonation in the NHC. Baik et al. concede that ‘this is not a classical \(\pi\)-back-donation type interaction, as it is not the \(\pi^*\)-orbital of the NHC-ligand that is involved, but rather the \(\pi\)-orbital with one node. Thus, MO-42 contributes to delocalizing the \(\alpha,\beta-(\text{C-C-C})\) agostic bond, which weakens the agostic interaction within the metallocyclobutane fragment as electron density is removed from the metallocycle.’\(^{47}\)

As Baik et al. depict the situation, the NHC orbital which interacts with the \(d_{xy}\) orbital is in fact the \(\text{H}_2\text{IH HOMO-1}\) orbital (-8.9 eV). However, it is rather strange to assume that this type of interaction is formally backbonding altogether since in Baik’s interpretation, all three orbitals, \(d_{xy}\), NHC HOMO-1 and bonding agostic orbital are all filled! Baik et al. conclude that this extra interaction leads to a weakening of the metallocyclobutane interaction.\(^{47}\)

This coupling (cyclobutane-Ru-NHC) of the orbitals is not possible in the cyclobutane-NHC equatorial position.\(^{47}\) Surprisingly, the NHC \(\pi\)-interaction is only present in the perpendicular NHC orientation because in the equatorial position, the \(\text{H}_2\text{IH}\) \(\pi\)-orbitals do not interact with the \(d_{xz}\) orbital!\(^{47}\)
On the other hand, for the IH substituted complex in the equatorial orientation (with the Cl-Ru-Cl axis perpendicular to the NHC-Ru-cyclobutane plane), the IH $\pi$-HOMO shows a strong interaction with the $d_{xz}$ and the coupled Cl$^-$ ions. Baik et al. reason that the HOMO in H$_2$IH is not of the appropriate symmetry for this interaction and that the HOMO-1 is too low in energy to interact with it.

![Figure 3.16: $\pi$-orbitals in IH and H$_2$IH. (Data from 47)](image)

In the metathesis reaction ([Ru]-olefin $\to$ TS $\to$ [Ru]-cyclobutane) with saturated carbenes, the cyclobutane stability shows little dependence on the N-substituents (H,CH$_3$, F) but the TS shows a significant decrease for the F substituent. On the contrary, with the unsaturated NHC ligands, there is a systematic energetic gain for CH$_3$ > H > F for both the TS and the cyclobutane conformation. This dramatic dependence of the reaction energy profiles is attributed to a higher degree of electronic communication introduced by the extended $\pi$-system. (All reaction profiles were constructed for an equatorial NHC-cyclobutane orientation.)

From these studies, we want to emphasize that the $\pi$-orbitals play a crucial role in the metathesis cycle. Furthermore, the role of these orbitals may be very complex which would be a serious downfall of the simplified $\pi$-interactions presented by us and even much more by Jensen et al. (vide infra). However, the studies suffer from idealized models and the lack of obvious backbonding (which is here portrayed as a donating $\pi$-interaction) from the metal to the NHC. This backbonding has been shown by CDA, EDA and NBO analysis (Chapter 2) and is logical through the synergistically donation-backdonation mechanism.

It is interesting to note that from the synthetic perspective, Piers and Romero were able to synthesize the second generation metallacyclobutane (without substituents) at low temperatures. Grubbs et al. presented the first examples of substituted metallacyclobutanes at low temperatures. None of these researchers were able to obtain a first generation metallacyclobutane ring. Grubbs et al. determined that interchange of the C$_2$ with the C$_1$ and C$_3$ carbons occurs in the metallacyclobutane ring and is caused by fast switching between the cyclobutane conformation and the carbene-olefin conformation and subsequent fast rotation without detection of any carbene conformation. Furthermore, Piers and Romero showed that the change of the olefin bond in the unsubstituted metallacyclobutane ring occurs in an associative reaction mechanism.
Understanding olefin metathesis

From this, the high discrepancies between theoretical and practical chemistry are obvious. Where theoretical chemists preach the stability of the metallacyclobutane, practical chemists are barely able to synthesize a complex which is then only stable at low temperatures. This should indicate firstly that the metallacyclobutane is actually not so stable thermodynamically. Furthermore, a thermodynamic stability refers to the whole Ru-complex, while the formation of the cyclobutane could imply the introduction of kinetically weak points in the propyldiene species readily available for attack. In this context, a short overview on the degradation of the catalysts will be presented.

Grubbs et al. reported in 1999 on the degradation of first generation complexes. The benzylidene, propyldiene and methylidene analogues of show a half-life of respectively 8 days, 8 hours and 40 minutes (0.023M in C6D6 at 55°C). Maughon et al. at The Dow Chemical Company have reported on a 10 fold longer lifetime for the methylidene at 30°C compared to an extrapolation of the Grubbs values. The methylidene species decomposes in first order kinetics, probably with assistance of the phosphine ligand. The propyldiene complex stability shows high dependence on the phosphine concentration. Decomposition occurs through the coupling of the carbene fragments of two phosphine-dissociated complexes and is consequently much slower. The deactivation of several catalysts in process of RCM of the mono methyl substituted DEDAM was monitored. The first generation Schiff base catalyst shows excellent activity, being the only catalyst reaching 100% conversion. With the Schiff base catalyst, the reaction only proceeded at higher temperatures (55°C). However, no methylidene species could ever be detected and the corresponding benzylidene species was still present at the end of the reaction. The IMES substituted catalyst also shows good stability and is the only catalyst for which methylidene species was detected after the reaction had ended. Surprisingly, a bis-NHC complex shows very poor activity, and counter-intuitively methylidene decomposition is very competitive with RCM for this catalyst.

Grubbs et al. proposed that the dissociation of the second generation catalyst proceeds in a dissociative mechanism through the assistance of migration of the phosphine into the carbene. This leads to which reacts with a phosphine dissociated complex in a cascade reaction into a well characterized product (chapter 1). Here again, the negative involvement of the phosphine into the carbene decomposition is proposed.

Forman et al. experimentally and computationally investigated the substrate-induced deactivation of the catalyst. The degradation is supposed to occur in the cyclobutane formation after which a β-hydrogen transfer can occur with the formation of an allyl hydride species. Subsequently, reductive elimination results in a propene coordinated, inactive complex. The activation barrier (ΔG for cyclobutane → hydride formation) for the second generation catalyst (24.3 kcal/mol) is calculated to be 7.4 kcal/mol higher than for the first generation analogue (16.9 kcal/mol). This provides excellent theoretical evidence for the increased stability of the second generation catalyst in action. Experimental observations in which propene was detected suggest this is a valuable mechanism, however, with the second generation system an excess of propene to the stoichiometrical decomposed catalyst was observed. However, Grubbs et al. countered these findings. They recently showed that the methylidene of in progress of metathesis shows the same phosphine decomposition products as without substrate involvement and concluded that this pointed to the same deactivation mechanism in both cases.
3.7 Gibbs energies for the metathesis reaction and solvent effects

Van Rensburg et al. of Sasol Technology presented in 2006 a mechanistic comparison of ruthenium olefin catalysts.\(^{46}\) In their introduction, they state that ‘Despite the large theoretical interest in the mechanism of first- and second-generation catalyzed metathesis the studies focus, to the best of our knowledge, either to strip-down models, both with and without \(\Delta G\) corrections, or relevant complete models without \(\Delta G\) corrections. In a small number of metathesis related theoretical studies \(\Delta G\) corrections are included for complete model systems, but these studies are not focused on the basic metathesis mechanistic comparison between first- and second generation catalysts.’\(^{46}\) Or to summarize, the previous complete system descriptions by Cavallo\(^{13}\), Chen et al.\(^{5,27}\) and Harvey et al.\(^{35}\) do not include \(\Delta G\) corrections. However, it should be noted that Cavallo presented \(\Delta G_s\) (solution free energies)\(^{13}\), which could be considered more relevant for practical applications than the gas phase free energies. Furthermore, Chen et al. presented Gibbs free energies in which only translational components of entropy were incorporated.\(^{5}\)

Van Rensburg et al. performed their study on the methylidene species of \(1.3, 1.4\) and on the Phoban catalyst \(1.34\) (Phobcat; see Chapter I).\(^{46}\) In the first generation methylidene complex, the carbene is oriented with the hydrogens in the phosphor-Ru-carbene plane (perpendicular orientation) and no stationary point could be found for the methylidene with the hydrogens in-plane with the Cl-Ru-Cl (parallel orientation).\(^{46}\) Van Rensburg et al. note that Chen et al. wrongly used the parallel orientation in the construction of the potential energy surface which lies ~6 kcal/mol (\(\Delta E\)) higher in energy than the perpendicular orientation.\(^{46, XIV}\) For the second generation catalyst and Phobcat, the equatorial orientation is the most favorable.\(^{46}\) Upon decoordination of the phosphate, all complexes show the perpendicular configuration as the most stable one.\(^{46, XV}\)

The coordination of ethene to the 14 electron complexes can occur in 4 ways as described in the Straub discussion (3.24-3.27) (for which 3.27 is the interesting cyclobutane-precursor with the parallel carbene and the olefin parallel to the carbene). The relative \(\Delta G\) values (298.15 K; 1 atm) for the first generation system are 3.24 (0 kcal/mol) < 3.25 (1.3 kcal/mol) < 3.27 (4.6 kcal/mol) < 3.26 (7.7 kcal/mol).\(^{46}\) The conformation with the olefin parallel to the carbene, and the carbene in the perpendicular position (3.24) is energetically most stable.\(^{46}\) Note that Straub calculated for the model systems the same conformation at lowest energy, however, no local minimum was found for conformation 3.27, which is the precursor for the cyclobutane TS.\(^{14}\) Van Rensburg et al. noted that Chen et al. used the highly energetical 3.26 as the standard ethene complex in their calculations of their potential energy surface.\(^{5,46}\)

For the second generation catalyst, no local minimum was found for the cyclobutane precursor 3.27, because all attempts to optimize a structure led to the formation of the cyclobutane ring.\(^{46, XVI}\) The following energy trend was calculated: 3.27 (0 kcal/mol) < 3.26 (0.9 kcal/mol) < 3.25 (4.0 kcal/mol) < 3.24 (5.3 kcal/mol).\(^{46}\) It should be noted that, upon coordination of ethene the complex spontaneously degenerates into the cyclobutane species.\(^{46}\)

\(^{XIV}\) The energy was determined by a flattening of the potential energy surface (PES).

\(^{XV}\) We want to point out that the Ru-carbene distance in the perpendicular orientation of 1.3 (1.952 Å) is much larger than all the values of the other complexes calculated by van Rensburg et al. and Chen et al. (1.82-1.83Å) including the parallel orientation. However, our suspicion of a typo was confirmed in a personal communication with W.J. van Rensburg.

\(^{XVI}\) The authors obtained a value for 3.27 form the flattening of the potential energy surface for 3.27 \(\rightarrow\) metallacyclobutane optimization prior to the formation of the metallacyclobutane ring.
The Phobcat system has the parallel orientation of the carbene as the most stable for the bisphosphine system. The olefin coordinated systems shows another trend than the previously discussed ones. However, the values lie energetically close together and there is again no local minimum for 3.27, which transforms spontaneously to the metallacyclobutane.46

The geometries of the most stable olefin complexes were depicted.46 The second generation system with 3.27 as the ground state shows a clear asymmetrical olefin bond, similar to the Cavallo structure. The ethene H2IMES–trans carbon (C\text{trans}) shows in both publications a long distance to Ru (2.46 Å).13,46 The second carbon (C2) shows a short Ru-C distance of 2.32 Å in the Cavallo calculation and 2.26 Å in the van Rensburg calculation.13,46 Furthermore, the ethene distance in these papers is 1.36 Å and 1.38 Å respectively.13,46 In the Cavallo paper, all complexes show the 3.27 orientation and the asymmetrical bond.13 Chen et al.5 and van Rensburg et al.46 depict conformations 3.24-3.26 to be rather symmetrical bonds with differences of 0.01 Å in the Ru-C bond distances (in one complex), yet the discrepancy of the 3.27 bonding mode with 3.24-3.26 was not noticed by any of these authors. It seems clear to us that the asymmetrical bond in structures 3.27 evidences that this structure (local minimum for Cavallo)13 is already an intermediate cyclobutane characterized by an elongated Ru-C\text{trans} bond, an alkyl-like Ru-C2 bond and some rehybridization of the Ru in the plane perpendicular to the Cl-Ru-Cl bond.

A comparison of the electronic energy (\(\Delta E\)) with the Gibbs free energy \(\Delta G\) (at 298.15K and 1 atm) was presented (all energies are relative to the lowest energy in the 16 electron precatalyst).46 The first generation catalyst shows the RLS for phosphine dissociation in the \(\Delta E\) surface, with a value of 19.3 kcal/mol!XVII.46 In the \(\Delta G\) surface this conformation is the second most stable with a value of 2.1 kcal/mol.46 The formation of structure 3.27 (12.7 kcal/mol) and the TS for metallacyclobutane formation (13.8 kcal/mol and here the RLS) are much more energetically demanding on the \(\Delta G\) surface.46

It should be noted that for the first generation system on the \(\Delta E\) scale, the active olefin coordinated species 3.27 (18.6 kcal/mol) does not need activation for the TS before metallacyclobutane formation (18.4 kcal/mol), while the metallacyclobutane complex energy (10.9 kcal/mol) is even far below those conformations.46 Furthermore, the cyclobutane intermediate is lower in energy than all the olefin coordinated complexes.46 Hence, metallacyclobutane species rather than olefin coordinated species are here the stable intermediates.

The RLS on the \(\Delta E\) surface for the second generation system is also phosphine dissociation (23.8 kcal/mol).46 However, the \(\Delta G\) surface reveals that the phosphine dissociated complex (4.6 kcal/mol) is energetically less demanding than the olefin complex 3.27 and the TS before metallacyclobutane formation (both 6.3 kcal/mol) which become the rate limiting steps.46 It is important to note that here phosphine dissociation is not rate limiting. Furthermore, the cyclobutane conformation shows the most negative point on the \(\Delta G\) surface (-0.8 kcal/mol). The metallacyclobutane ring should thus not only be the most abundant species in the absence of phosphine, as experimentally shown by Piers et al.48,49 It should be readily detectable in mixtures using the methylidene complex in the presence of phosphine! However, there has not been reported detection of cyclobutane complexes in any real propagating system, which degrades this theoretical description. Furthermore, addition of the phosphine scavenger CuCl does not lead to cyclobutane formations but to destruction of the catalysts. In fact, a \(\Delta G\) description using only the incorporation of translational entropy and norbornene as substrate leads to a

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XVII In general, \(\Delta E\) is calculated to have the RLS for the first generation system at the TS before metallacyclobutane formation.
more satisfactory result.\textsuperscript{5} Then, the olefin and cyclobutane conformations show much higher energies than the phosphine coordinated complexes.\textsuperscript{5}

It should also be noted that van Rensburg et al. calculated in all cases the olefin coordination to be energetically favorable in the $\Delta E$ surface, though the negative entropy factor leads the addition to be exergonic on the $\Delta G$ surface.\textsuperscript{46}

Since the study mainly concentrated on the deactivation of the catalyst via the degeneration of the metallacyclobutane, it should be mentioned that the PhoCat system shows an intermediate value for metallacyclobutane activation (into hydride) compared to the first and second generation Grubbs catalysts.\textsuperscript{46}

The synthesis of side bonded chelating olefin complexes by Grubbs et al.\textsuperscript{55}, led Cavallo et al. to a reevaluation of the side-bonded mechanism for olefin metathesis. This was done on the basis of a solvent-dependent analysis which had previously been coined by Grubbs et al.\textsuperscript{56} and Goddard et al.\textsuperscript{57}

The conformations with chlorines in the cis-position were found to be favored in solvents with high dielectric constants (such as CH$_2$Cl$_2$).\textsuperscript{57}

![Figure 3.17: trans and cis coordinated olefin and cyclobutane.](image)

Calculations showed that the chelating olefin complex of Grubbs et al. especially showed a good preference for the cis chelated conformer in CH$_2$Cl$_2$ compared to an indifference for the gas phase $\Delta G$.\textsuperscript{58} The addition of ethene to the second generation methylidene was calculated to be preferential in the trans position for the gas phase, though the cis conformation is preferred in CH$_2$Cl$_2$.\textsuperscript{58} The transition state for cyclobutane formation, however, shows a preference for the trans geometry in solution (CH$_2$Cl$_2$) and even more in the gas phase.\textsuperscript{58} Introduction of a more sterical and more realistic substrate leads to an indifference for the olefin coordination in CH$_2$Cl$_2$ and strong preferences for the TS in the trans position.\textsuperscript{58} These cis bonded structures should be considered in the conformation-distributions. However, in real-steric systems productive metathesis through the cis-conformation is negligible, due to high barriers in the cyclobutane formation. Cavallo et al. suggested that mainly a steric effect is responsible for the lack of stability in the cis-cyclobutane ring.\textsuperscript{58} However, we think that also the strong trans effect of the NHC orients the olefin in the trans conformation in a a-typical olefin-bond; which is more an intermediate olefin-cyclobutane conformation and thus energetically close to the cyclobutane conformation. Hence, little activation in the TS is needed.
3.8 Quantitative structure-activity relationship (QSAR) of 2nd generation Grubbs catalysts

In 2006, Jensen et al. presented a study which relates the catalyst activity to quantitative structural parameters determined by DFT calculations. First, we will focus on the determination of the backbonding in the complexes. Jensen et al. used as the value for backbonding the difference in population of the $d_{xz}$ and $d_{yz}$ orbitals (with L in the z-direction) of the naked complex $\text{Cl}_2\text{RuCH}_2$ (3.96) and the complex $\text{Cl}_2\text{Ru(L)CH}_2$ determined by NBO analysis. The authors claim that the approximation of donation and backdonation by differences in orbital populations and atomic partial charges is based on the assumption that effects from geometry relaxation and intrafragment polarization remain essentially constant between the different ligands.

However, the assumption that the effects from intrafragment polarization remain constant between the different ligands may be less straightforward. Straub suggested that bending of the ligands is caused by intrafragment polarization. Furthermore, the bending with H$_2$IMES is substantial while the phosphines do not bend significantly. Straub also argued that the loss of backbonding for phosphines with the Ru-d orbital upon intrafragment polarization is the reason why no such bending occurs. Yet, the carbene orientation in $\text{Cl}_2\text{Ru(L)CH}_2$ is perpendicular, thus no intrafragment polarization is necessary. However, the backdonation should be affected by intrafragment polarization in (Cl)$_2$RuLL’CH$_2$ and the active ethene coordinated complex. The latter is considered to be the RLS in the $\Delta G$ profile of the second generation catalyst systems by van Rensburg et al.

Another objection should be made concerning the backbonding in the analysis made by Jensen et al. The authors quantify the total backbonding to L for all ligands and use it as a parameter for their activity description. However, backbonding is not symmetrical for all ligands. NHC-ligands show highly asymmetrical backbonding with all the backbonding occurring in the plane perpendicular to the NHC ring. Furthermore, the $d_{xz}$ and $d_{yz}$ orbitals might be rather degenerate in the $\text{Cl}_2\text{Ru(L)CH}_2$ complexes due to a carbene which is oriented perpendicular. But along the reaction path of productive metathesis, this orientation has to be parallel which uplifts the degeneration. Moreover, upon coordination of olefin and cyclobutane formation an extra differentiation is introduced. The backbonding to the NHC does not interfere with this orbital, while the phosphine backbonding is degenerate and meddles with both the metal d-orbitals. Jensen et al. calculated a relatively low backdonation value for $\text{Cl}_2\text{Ru(L)CH}_2$.

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XVIII We thought that the transformation from the planar $\text{Cl}_2\text{RuCH}_2$ to $\text{Cl}_2\text{Ru(L)CH}_2$ should lead to a difference in electronic distributions. As evidenced by EDA, Pauli repulsion contributions are important factors in the bond strength and for that matter the electron distribution. It should be noted that in a planar configuration, the energy of the free electron pairs should be very low in orbitals which do not occupy this plane. However, the introduction of an extra ligand which disrupts the planar conformation, should lead to the transfer of the free electron density from out-of-plane into the plane. This effect would then lead to an overestimation of the backbonding in the complexes. This can be evidenced by the extreme values calculated for the backbonding of H$_2$IMES and IMES being one third of the donation and in absolute values 0.17 e and 0.16 e respectively. However, the backdonation value for H$_2$O and NEt$_3$ is estimated to be 0.01 e and 0.02 e respectively, with donation values of 0.18 e and 0.34 e. These backdonation values are almost negligible, as expected, and hint that the overestimation due to the geometry effect is negligible. Furthermore, imidazoles and pyridine show higher values for backdonation (0.06-0.09 e) than amines in accordance to results obtained by Harvey et al. (39) Occhipinti, G.; Bjorsvik, H. R.; Jensen, V. R. Journal of the American Chemical Society 2006, 128, 6952-6964 (39) Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. N. Organometallics 2007, 26, 2637-2645. The phosphines in the Jensen publication show similar backdonation to the imidazoles and pyridine. It should be noted that ligands which bind mainly through $\sigma$-bonding such as amines and ethers do not readily coordinate trans to L in the Grubbs complex, while imidazoles and pyridines which show considerable backdonation do.
regression coefficient for the backbonding (-0.290). This can be attributed to the lack of regression of the backbonding in their analysis of the complex. We can easily concede that backdonation from the competing d-orbital should diminish reactivity through a decreased interference of the d-orbital into the catalytic process. This is either through diminished backbonding to the rest of the ligands, diminished synergistic effects or reluctance to rehybridization. However, backdonation from the d-orbital perpendicular to the metallacyclobutane ring (as in NHCs) should not directly interfere with the reactive orbitals. Secondary effects should decrease electron density at the Ru atom (showing increased reluctance for oxidation) and increase electron density at the NHC-carbene π-orbital, which can cause synergistically more σ-bonding. This σ-donation is a positive descriptor (0.757) in the QSAR model and should thus lead to an increase in the activity. Moreover, Chapter 2 has shown that high backdonation leads to shorter bonds, which would lead to a decrease in the Ru-L bond and an increase in steric strain. Jensen et al. found the steric repulsion (L-alkylidene) to be a positive descriptor (0.976) for the metathesis activity.

Furthermore, the necessity for PCy₃ rotation to obtain productive metathesis, which represents the highest barrier in the cycle is not addressed in the publication.

The criterion for productivity is defined as follows: Productivity = - (ΔH₃.29 - ΔH₃.28) with both ΔH₃.28 and ΔH₃.29 referring to the change from the 14 electron complex and both being negative. Thus a high (negative) value for ΔH₃.29 and a low (negative) value for ΔH₃.28 are good for a high productivity.

As we mentioned before, it might be more straightforward to take the active olefin coordinated complex instead of 3.29 for the NHC catalysts due to its higher energy.

![Figure 3.18: Productivity criterion of Jensen et al.](image)

The phosphine catalysts are generally predicted to have lower productivity than the NHC substituted catalysts. The productivity of PCy₃, P’Pr₃ and PPh₃ complexes are predicted to be respectively -3.5 kcal/mol, -5.5 kcal/mol and -10.7 kcal/mol in accordance with practical chemistry. However, P(C₅H₁₁)₃ is calculated to have a productivity of -3.2 kcal/mol where in reality it only shows productivity comparable with P’Pr₃. The authors suggest that ‘this discrepancy probably reflects a minor inaccuracy in the multivariate model.’

The productivities of Cl₂IMES, IMES and H₂IMES are predicted to be respectively 1.1 kcal/mol, 2.3 kcal/mol and 2.4 kcal/mol. This was suggested to be in accordance to the experimental results in the RCM of mono-methylated DEDAM and ROMP of COD. However, Fürstner et al. showed that metathesis is very substrate dependent and that the previous reaction rate sequence changes with

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XIX If the backbonding to the carbene does not lead to an increase in p-occupancy, it must lead to a decrease in N → carbene π-donation → Nitrogen gets more electrons and becomes less electron affectuous → N is less electron withdrawing in the N-carbene σ-bond → the carbene uses more s character in the C-N σ-bonds → more p-character in the carbene lone pair and a higher energy → the NHC becomes a better σ-donor.
different RCM substrates.\textsuperscript{31} Furthermore, \( \text{H}_2\text{IPh}('\text{Pr})_2 \) was shown to be a far superior ligand than \( \text{H}_2\text{IMES} \) for CM and RCM upon the comparison of TONs.\textsuperscript{60} However, these values are correlated to \textit{total productivity} and consequently include deactivation of the catalyst, while the \textit{productivity} values calculated by Jensen et al. resemble \textit{kinetics} in non-deactivation conditions. Furthermore, Jensen et al. acknowledge that the \( '\text{Bu} \) ligand is calculated to be far more effective than \( \text{H}_2\text{IMES} \). However, the low stability of similar catalysts indicates that the \textit{positive molecular descriptor} \textquote{steric exchange repulsion} might be \textit{too big} here and results in catalyst decomposition.\textsuperscript{39}

Both electronic and steric factors are important for the productivity.\textsuperscript{39} The most important electronic descriptors are the Wiberg bond index for the Ru=CH\(_2\) bond (1.389) and the Ru=CH\(_2\) bond distance (-1.419).\textsuperscript{39} Jensen et al. explain that \textquote{both descriptors show that a strong ruthenium-alkylidene bond is important for catalytic activity and the highest productivities are obtained for catalysts displaying a Ru=CH\(_2\) Wiberg bond order well above 1.6.}\textsuperscript{39} We wish to add here that the high Wiberg bond order and the short bond distance directly imply an important \( \pi \)-backbond interaction (Chapter 2). However, as Frenking et al. pointed out many times, \textit{a shorter bond distance does not correlate to a stronger bond} because also other factors are important for the bond energy and the \( \Delta E_{\text{Pauli}} \) repulsion term becomes increasingly more important with shortening bond distance. So, we suppose that the important \( \pi \)-bond certainly induces a positive kinetic effect due to the high electron density which can readily be donated to the olefin anti-bonding orbitals in the transition state. Furthermore, the high backbond character of the carbene suggests a high ability of the Ru to donate from that particular d-orbital which is also necessary to stabilize the cyclobutane. \textbf{This also implies little interaction of this orbital with L.} From this reasoning the (anticipated) lower bond order with Ru=CH(OEt) clearly explains the lack of reactivity.

Jensen et al. continue as follows \textquote{The best Lewis structures obtained in resonance structure analysis performed with the NBO program contained a Ru=CH\(_2\) double bond, and two natural bonding orbitals are always found between ruthenium and the alkylidene carbon which carries a partial negative charge (CHELPG) in the range -0.1 e to -0.5 e. The bulk of the present carbenes can thus be characterized as having more Schrock than Fischer character. This furthermore indicates that they should rather be considered as complexes of ruthenium (+4) although they are usually referred to as ruthenium (+2) complexes, i.e., carbene complexes of ruthenium in oxidation state +2. In the metallacyclobutane intermediate, however, ruthenium has oxidation state +4. Thus, the strong correlation between Ru=CH\(_2\) bond strength and productivity indicates that the 14 electron complexes which are effectively in a high oxidation state should form comparably stable metallacyclobutane intermediates; i.e., these complexes need less activation in order to increase their oxidation state.}\textsuperscript{39} Concerning this, it should first be noted that Frenking et al. calculated that W(CO)\(_4\)CH\(_2\), a \textit{Fischer carbene complex (donor acceptor)}, has according to NBO a \( \sigma \) bond and a \( \pi \) bond while the CH\(_2\) fragment carries a partial charge of \(-0.13\) electrons.\textsuperscript{42} Furthermore, the charge at the hydrogen, calculated by Jensen et al., is positive (\( 2 \times 0.1-0.2\) e) which really synchronizes the charge values of the CH\(_2\) groups in both cases.\textsuperscript{39,42} The charge at the \textquote{alkylidene} carbon calculated by Jensen et al. for L = CO and \( \text{H}_2\text{IMES} \) are respectively -0.40 e and -0.21 e, with the general trend of increased productivity for lower charge at the \textquote{alkylidene}.\textsuperscript{39} It should be noted that the higher productivity with higher carbene bond order and lower bond distance (more backbonding) contradicts the high productivity with small (negative) charge at the alkylidene. Yet this could be reconciled if the \( \pi \)-bond would be mainly concentrated on the Ru: This implies a Fischer carbene.

Moreover, the charge of the CH\(_2\) group of all the complexes presented in a table by Jensen et al. show a charge (after calculation) of only \(-0.08 \rightarrow 0.01\), which is very low.\textsuperscript{39} In the complexes investigated
by Frenking et al., the CH2 groups showed a charge of -0.13 e for the Fischer complex, -0.40 e → -0.24 e for the Schrock complexes and -0.63 for the hybrid complex [W(F)5CH2]. The high charge on the Schrock carbene complexes and the hybrid Fischer-Schrock complex in the Frenking analysis is the result of the polarization of both the σ bond and π bond towards the carbon. From this, we think it is more evident to conclude that the Grubbs carbene is actually a Fischer carbene as a doubled polarization should lead to a negative charge on the CH2 carbene group. Unfortunately, we regret that due to explicit concept definitions, discussions on this topic degenerate quickly from being scientific to being semantic.

The σ-donor strength of L is also an important molecular descriptor; The higher the donor strength, the better the productivity. This descriptor also shows covariance with other descriptors such as a reduction of the Fukui atomic electrophilic reactivity index for Ru and moderate covariance with the more important R=CH2 bond order (and negative bond distance). According to Jensen et al., the π-backdonation only shows a weak correlation with the productivity, but we previously discussed the fallacy of their treatment on that issue.

Jensen et al. also made an extensive investigation into the steric interactions. The steric exchange repulsion between L and the alkylidene was found to be beneficial for the productivity. First, it should be noted that this is very substrate dependent, since for the RCM of DEDAM-2 a steric NHC will definitely lower the catalyst activity.

The authors assigned the wider angles between the carbene and L to `the increased steric repulsion toward the alkylidene group.` This is sharply in contrast to the suggestion of Straub that the bending is caused by the intrafragment polarization, and that the reason why it does not occur with phosphines is due to concomitant backbonding loss. Moreover, the calculations of Jensen et al. do not show the differentiated bending between NHC and phosphine ligands calculated by Straub.

The steric interaction was calculated for four important methylidene complexes with PMe3 as L’ (decoordination ligand). L was taken to be PPh3, PCy3, IMES and H2IMES. The steric interaction term is bigger in all the L’ complexes than in their corresponding cyclobutane conformations in the order PPh3 (-2.1 kcal/mol) < PCy3 (-3.3 kcal/mol) < IMES (-6.4 kcal/mol) < H2IMES (-7.0 kcal/mol). In the phosphine complexes, the fourteen electron species shows a slightly higher steric energy than the L’ coordinated complex, in accordance with Cavallo. For the NHC complexes, however, the steric energy of the 14 electron complex is intermediate to the L’ complex and the cyclobutane conformation, in contrast to the Cavallo’s assumption that upon contraction of the bonds in the fourteen electron species the steric interaction should increase. Cavallo calculated the parallel orientation for the benzylidene in the 14 electron species, while Jensen et al. reported the perpendicular orientation of the methylidene, which could cause the discrepancy. Jensen et al. did not note the similar change in carbene orientation: In the phosphine complexes, the carbene remains perpendicular, while in the NHC complexes a rotation occurs from the planar conformation in the L’ complex to the perpendicular orientation in the 14 electron complex. To us, this seems the only

Note that IUPAC classifies the Grubbs carbene as an alkylidene, though they do not implement Fischer carbenes in their section on ‘Organometallic compounds’ (61) IUPAC http://www.iupac.org/reports/provisional/abstract04/RB-prs310804/Chap10-3.04.pdf.

However, piperidine and THF show higher Ru=CH2 bond orders than the NHC ligands but lower σ-donation and definitely lower productivity.
explanation why the steric energy would increase in the phosphor complexes by 0.6-0.7 kcal/mol but
decrease by 2.1-2.6 kcal/mol when L’ dissociates in the NHC complexes.

We were puzzled by the fact that the perpendicular orientation of the carbene would decrease the steric
strain, since it certainly brings the carbene hydrogen closer to the mesityl ring. Moreover, the steric
strain in the H_{2}IMES-cyclobutane conformation (4.6 kcal/mol) is calculated higher than the steric
strain for the PPh_{3},L’-methylidene complex, which is highly contradictory! It seems only reasonable
that when PPh_{3} shows an angle of 93° with the carbene in the perpendicular position (hydrogen
pointing to PPh_{3}), the steric strain should be higher than in any cyclobutane conformation with an
angle of 137° between L and the cyclobutane carbon. In the H_{2}IMES cyclobutane conformation, the
distance between the C_{Mesityl-ipso} and the metallacyclobutane carbon (for the benzylidene) was
calculated to be 3.97Å.

To account for these paradoxes, a closer investigation of the premises is necessary. Jensen et al.
footnote on the natural steric analysis that ‘The CH_{2} moiety employed in the calculations of steric
exchange repulsion in Ru alkylidene complexes include the occupied valence orbitals of the carbene
acceptor atom, the C-H bonds, and the metal-carbon σ- and π-bonds. In the metallacyclobutane
intermediate, the corresponding σ-bonded CH_{2} group was used in addition to the second Ru-CH_{2} σ-
bond in the metallacycle, resulting in a fragment including the same number of electrons as the CH_{2}
moiety defined for the Ru alkylidene complexes. For the ligand L, all the valence electrons were used
including those of the Ru-L bond.’

The first paradox, of the decreasing steric strain in the perpendicular carbene orientation compared to
the planar conformation can be explained as follows: In the parallel orientation, there is a close contact
between the M-carbene π-bond (which should be polarized towards Ru) and the deeply penetrating
σ-donating orbital of the NHC. This means that actually the bonding orbitals would explain for the
difference in steric strain.

The second paradox can only be solved in the same way. When the void between the mesityl rings and
the cyclobutane indicates that no steric interaction is present, little possibilities remain to obtain a
close contact. The closest contacts we can think of are the three σ-bonding interactions with the Ru.
This would again render the bonding orbitals with ruthenium to be the main cause for the ‘steric’
interaction.

In organometallic chemistry (or chemistry in general), the concept of ‘steric bulk’ is to be associated
with the negative chemical interaction of chemical atoms (A,B) which are remotely bonded (X_{A}-(X-
)_{B} with n>1). Cavallo assigns the C_{carbene}-Ru-C_{H_{2}IMES-N-C_{ipso}} interaction as the steric interaction on
this conceptual basis. Such interactions are normally low in energy. 1st order steric interactions, e.g.
the ΔE_{Pauli} repulsion term in N_{2} (791.7 kcal/mol) can be extremely high. It goes without saying that the
2nd order interaction between the bonding orbitals in C-Ru-C will also show considerable
contributions. However, we think that Cavallo was not referring to that phenomenon when he
discussed the steric interactions. Furthermore, from the NBO viewpoint, the trans influence could be
addressed as a steric interaction, because with the NBO sd-resonance method, both ligands are
competing for the same orbital (their bonding electrons are competing for the same orbital space). 1st
order steric interactions and 2nd order steric interactions of the bonding orbitals to the central atom are
best not included into the steric interactions but assigned to as electronic factors. Off course, all
interactions in molecules are of electronic nature. We think that therefore it should only be remotely
bonded atoms which are addressed to have steric interactions. Due to the lack of such a division in the Jensen paper, conclusions from the data can thus only lead to oversimplifications.\textsuperscript{XXII} Jensen et al. suggest that the difference between the IMES and H\textsubscript{2}IMES catalysts can be explained by the better \(\sigma\)-donating and \(\pi\)-accepting ability of H\textsubscript{2}IMES, which insures a shorter bond and increases the steric bulk with the alkyldiene.\textsuperscript{39} Jensen et al. predict that PHC ligands should be poorer ligands in metathesis than the corresponding NHC ligands in contrast to recent reports.\textsuperscript{39} This was attributed to the increased backdonation from Ru to the PHC. It goes without saying that we don’t agree with such statements.

Also new target NHC ligands were evaluated as potential substitutes for H\textsubscript{2}IMES.\textsuperscript{39} All the NHCs which provide an increase in productivity, show a substituted back-bone. This implies that for new target NHC ligands the \textit{steric design} should be most important. These ligands are also more donating than the classical H\textsubscript{2}IMES ligand.\textsuperscript{39} Recently Collins et al. synthesized a catalyst with 'Bu groups on the backbone for asymmetrical catalysis, and showed that while their catalyst obtained similar selectivity upon previous enantioselective catalysts, its activity was greatly improved.\textsuperscript{64}

### 3.9 Schiff base catalysts

The Schiff base ligand has not received much attention in computational chemistry. However, Jensen et al. calculated the bond enthalpies in complexes (Cl)\textsubscript{2}Ru(PC\textsubscript{y}\textsubscript{3})(CH\textsubscript{2})L and discovered that for the ligands imidazole, piperidine and PC\textsubscript{y}\textsubscript{3} the bond enthalpy for L was very similar (18.9-19.2 kcal/mol), though the bond enthalpy for PC\textsubscript{y}\textsubscript{3} in the amine and imine complexes is much higher (29.0-30.5 kcal/mol). The authors suggest that ‘The similar dissociation enthalpies calculated for the two cyclic ligands, imidazole (\(\Delta H = 19.1\) kcal/mol) and piperidine (\(\Delta H = 19.2\) kcal/mol), suggest that imines and amines should form equally strong bonds to the metal in Grubbs-type ruthenium complexes. Moreover, these bond enthalpies are also very similar to those of PC\textsubscript{y}\textsubscript{3}…’ However, later in the article, the authors calculated the bond enthalpies for 3.30-3.33 to be 21.5, 8.6, 17.8 and 16.0 kcal/mol respectively. The difference in bond enthalpy between 3.30 and 3.31 was attributed to amines being more capable of sterically influencing the complex than imine complexes. Although we must agree with that statement, it should be noted that the backbonding and bonding interactions also should contribute to this difference. The model-molecule for an imine as piperidine and imidazole also might not be ideal. Since in imidazole the donating \textit{imine} is part of an aromatic structure, this should heavily influence backbonding, moreover, in piperidine the amine \(\sigma^*\) is much less capable for backdonation than the \(\pi^*\) in the imine.\textsuperscript{59} 3.30 is very similar to the complexes we synthesized. The bond enthalpy of the imine bond is higher than that of PC\textsubscript{y}\textsubscript{3} in 1.3 though lower than that of PC\textsubscript{y}\textsubscript{3} in 1.4 (which is higher due to the decrease of steric interactions). This might indicate the difficult substitution with a Schiff base which was encountered when the substitution was started from 1.4 or 3.30, although the substitution can be

\textsuperscript{XXII} It should be noted, however, that IH shows very low values for the steric interaction in both the L’ complex (2.8 kcal/mol) and the cyclobutane complex (2.0 kcal/mol) and that the decrease in ‘steric strain’ for L=CO in the same transition only accounts to 1.5 kcal/mol. However, we think that 2\textsuperscript{nd} order steric \(\sigma\)-interactions should be minimized when the orbitals are orthogonal. Furthermore, the carbene is oriented perpendicular which excludes interactions of the carbene \(p^*_z\) orbital. Also, it should be noted that in the IH-cyclobutane conformation, the chlorine atoms shield all \textit{steric} influence (Cl’s in plane with NHC) from the IH, so that the calculated \textit{steric strain} (2 kcal/mol) can only originate from 2\textsuperscript{nd} order binding electron interactions. Still, it remains difficult to assign all the calculated steric strain of the H\textsubscript{2}IMES-cyclobutane species (4.6 kcal/mol) to binding electron interactions since the difference is too high compared to the IH-cyclobutane complex (2 kcal/mol). Only the increased \(\sigma\)-donation of H\textsubscript{2}IMES can here be used as an argument for our exposition.
obtained readily with 1.3 (Chapter 4). Furthermore, the higher bond energy of PCy$_3$ in 3.30 compared to the imine explains why we found that 3.30 does not react with [RuCl$_2$(p-cymene)]$_2$ to form a bimetallic complex (Chapter 4), though formation of a trimetallic complex is more logical through nitrogen dissociation.$^{65}$ Jensen et al. explain that the increased bond enthalpy for the imine in 3.30 compared to the phosphine in 1.3 is the cause of the higher reaction temperatures needed in metathesis. We think that the bidentate nature of the ligand should also decrease the entropical gain upon decoordination, and hence also strongly influence the population of the imine-coordinated complex and create an additional barrier.

In a Ru catalyst system (Cl)$_2$Ru(L)(L’)CHR, the ligand L which remains through the cycle, should be sufficiently sterical encumbering. This will lead to the easier formation of a metallacyclobutane ring from the 14 electron species or the olefin coordinated complex. Yet, in the case of sterical substrates, this should be avoided, since it will deactivate the catalyst.

Electronic influences are more complex. The reactions proceeds from the fourteen electron complex through the correctly oriented olefin complex, through a transition state to the metallacyclobutane species. First, it should be noted that the NHC ligands show, in contrast to the phosphine ligands, no interaction with the d$_{xy}$ orbital. (with Cl-Ru-Cl as the z-axis)

In the fourteen electron species, the carbene shows a perpendicular orientation, which means that it does not interact with the L-backdonation. Increase of net-donation from the ligand should favor this configuration. However, the concentration of this species should not be too high since it is a key intermediate in bimolecular decomposition. Introduction of a bidentate Schiff base ligand – as in our
complexes - can also prevent bimolecular decomposition through the inhibition of dimer structures (Chapter 4).

Next, olefin coordination should occur. Four possible coordinations of olefin and carbene are possible, though only the parallel carbene and parallel olefin is of interest, since only this is a necessary intermediate before cyclobutane formation. In the most efficient catalysts, this conformation represents no local minimum, but only a passage way to the metallacyclobutane conformation. This is caused by two effects: Destabilization of the olefin complex and stabilization of the metallacyclobutane intermediate.

Only in the active conformation, the olefin is asymmetrically coordinated and should show a donation and backdonation effect. In analogy with backdonation saturation, it has been shown that the bond strength is dominated by σ-donor interactions. Thus in the first place, a strong donor trans to the olefin destabilizes every olefin coordinated complex. Also backdonation to L from the d\textsubscript{xy} orbital (as with phosphines) could decrease the backbonding with the olefin, but have little effect on the bond energy.

The metallacyclobutane (and TS) conformation should be sd\textsuperscript{3} hybridized with concomitant consumption of the d\textsubscript{xy} orbital and consequently any interaction with this orbital (as for phosphines) is very destabilizing for the metallacyclobutane structure. In alternative hybridizations, the d\textsubscript{xy} orbital should also be occupied by the metallacyclobutane ring and thus interference of L with this orbital cannot benefit efficient cyclobutane formation. Furthermore, the high σ-donation of L should facilitate easier oxidation of the complex into the +IV OS.

Thus, the ideal L should show sufficient steric bulkiness, high σ-donating character and low π-accepting character in the xy plane. It should be noted that design of NHC ligands as substitutes to increase activity has mainly focused on the increase in σ-donating character. However, as we have shown in chapter 2, the experimental and theoretical methods for the determination of σ-donating capacity of NHCs are highly ambiguously.

We suggest that a very straightforward idea to enhance activity would be to activate the π-acceptor function of the NHC ligand in the z-direction (Chapter 5). First, an increased π-acceptor function might increase dissociation of the competing phosphine. Secondly, upon olefin coordination the increased backdonation to the NHC should lead to less interaction for the olefin bond in perpendicular (inactive) orientation and hence lead to less inactive intermediate species, which might participate in deactivation mechanisms. Thirdly, and most importantly, the increased π-accepting function should lead to increased σ-donation synergy and hence promote metallacyclobutane formation. Fourthly, the increased π-interaction should decrease the Ru-NHC bond length, so increase the steric interaction and hence increase activity.

As evidence for our reasoning, we want to point to the high controversy on whether IMES or H\textsubscript{2}IMES is the better net donor and the controversy on which one would be the more productive ligand. Either way, H\textsubscript{2}IMES provides faster decoordination of the phosphine ligand and thereby faster reaction. Moreover, Frenking et al. calculated the difference in σ-electron distribution between free H\textsubscript{2}IH and IH to be negligible.\textsuperscript{66} However, they also calculated the p\textsubscript{π}-occupancy of the carbene for H\textsubscript{2}IH (0.53 e) substantially less than in IH (0.67 e).\textsuperscript{66} This should have implications on the backbonding and thereby on the bond distance and steric effects of the ligand.

Moreover, other variations of the H\textsubscript{2}IMES ligand (focusing on the σ-donation strength) have shown to have little or bad effects on the catalyst activity.
3.11 Conclusions

Recently, there has been a huge interest from computational chemists to capture the essence of the Grubbs catalyst. However, after all this intensive research, core issues such as the Ru(II) or Ru(IV) debacle, the importance of the steric and electronic influences, the cause of bending by the NHC either due to steric interactions or intrafragment polarization, remain unsettled. Furthermore, Harvey et al. could not reproduce the experimental and previously calculated trends using the same methods as their colleagues. Also, the non-degenerated NHC backbonding is fairly underappreciated in conceptual analysis.

However, also much has been accomplished in this field. Chen et al. showed that the necessity of the first generation catalyst for a ligand rotation was the RLS in productive metathesis. Furthermore, there is a general consensus on the increased stability of the cyclobutane ring compared to the olefin species for the second generation catalyst. Cavallo showed that subtle steric interactions might be very influential and that solvent choice can effect the reaction pathway. Furthermore, Jensen et al. have made a first attempt in the prediction for efficient NHC ligands in the Grubbs catalyst. We also developed some easy criteria for the design of ligands. However, as Baik et al. showed, the role of ligands might surpass that simplicity.

We are convinced that closely monitoring to extreme vigilance of the computational efforts in catalyst prediction and the interpretation of such results from an organometallic concept base is of the highest importance for the catalyst designer. We think that through the help of such investigations the coming years will be very fruitful in development of superb catalysts for metathesis.

References

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Chapter 4

Schiff base Grubbs catalysts

4.1 Introduction

In 1998 Grubbs et al. published on the synthesis of a series of complexes 4.1A. The complexes proved to be stable to air and moisture. Furthermore, heating of the complexes to 80°C over several hours showed no decomposition. The complexes 4.1A show low activity at room temperature for RCM, but at elevated temperatures the catalyst activity increases dramatically for the RCM of DEDAM. In addition, the complexes showed excellent stability towards protic solvents and the RCM of the diallylamine-HCl salt was easily accomplished in MeOH.

![Chemical structures](image)

**Figure 4.1:** Different type of Schiff base Ruthenium carbene systems previously synthesized.

The Verpoort group acknowledged the potential of the Schiff base ligands, which add increased temperature and solvent tolerance. A series of analogues was explored. Upon the H$_2$IMES revolution in Ru-metathesis, De Clercq et al. reported on the synthesis of complexes 4.1B and their activity for various reactions. The catalysts 4.1B were also evaluated for metathesis and proved to be ‘highly efficient catalysts for promoting ring-closing metathesis and ring-opening metathesis polymerization reactions under mild conditions.’
They also reported on the synthesis and metathesis activity of complexes of type 4.3, which were described as a ‘new class of homobimetallic ruthenium olefin metathesis catalysts exhibiting the best combination of stability and activity known so far for this type of catalyst.’

Opstal and Verpoort published on the ATRP with the indenylidene and ethylether carbene complexes 4.3-4.4. Also efficient metathesis experiments were performed with catalysts 4.3. Unfortunately no synthesis was reported for all complexes and only NMR data of 4.3A were presented.

The current thesis is the result of a project aiming to optimize the patented catalysts 4.1B, 4.2 and 4.3B and to search for innovative applications for these catalysts. We preliminary want to note that especially the complexes 4.1B should be excellent targets for catalysts due to the increased stability of a Schiff base ligand combined with the increased activity and stability of a NHC substituted catalyst. This makes the resulting catalysts superior to both the classical second generation complex and the 1st generation Schiff base substituted catalysts 4.1A. Furthermore, complexes of type 4.2 had been proved to be active for tandem RCM and dehydrogenation resulting in pyrroles.

In our research we focused on the optimization of catalysts 4.1B. We also attempted to synthesize catalysts 4.2 and obtained interesting results concerning a Ru-O,Ru-Cl exchange. However, no extensive research was performed on the resulting species, since they were previously reported and only showed moderate activity. Catalysts 4.3 have been the focal point of Viacatt N.V. and to avoid conflicts of interest, it was chosen not to explore this pathway. From scientific viewpoint catalysts 4.1B can be easier compared to other reported catalysts since the benzylidene is the standard alkylidene. Complexes of type 4.4 were also not prepared since the economics of the procedure, i.e. multiple synthesis steps, the use of Ru, the use of an NHC and the use and destruction of an alkylidene seems far inferior to the commonly used Cu amine species in ATRP and ATRA. During our catalytic experiments of the catalysts, a strange phenomenon was observed in the COD polymerization, which was further investigated and led to better understandings in the secondary metathesis of Grubbs type catalysts (Section 4.5).

Catalysts 4.1B all have the H$_2$IMES ligand in common, and in chapter 5 we focused on improving this part of the catalyst (on the model 2nd generation catalyst 1.4).

### 4.2. Synthesis and initial screening of second generation Grubbs benzylidene complexes with bidentate Schiff base substituents 4.1B

#### 4.2.1. Synthesis and structural analysis of the complexes 4.1B

The preparation of complexes 4.1B (4.5-4.10) was previously reported by our group. The synthesis was described as the reaction of the tert-butoxy adduct of H$_2$IMES with the first generation Schiff base catalysts 4.1A. The reaction is performed at elevated temperatures in order to obtain the free carbene needed for substitution. Surprisingly all our attempts to synthesize complex 4.10 using this methodology failed. No shift in the carbene proton in $^1$H NMR from $\delta = 19.77$ ppm to 19.66 ppm could be observed. Variation in the Schiff base precursor, reaction temperature, solvent, H$_2$IMES-salt

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1 Spinoff company of Ugent.
and base for H$_2$IMES deprotection (KHMDS; Potassium hexamethyldisilyl amide) did not lead to the predicted product with a $^1$H NMR resonance at 19.66 ppm. At best, a complex mixture of carbene species with the precursor as the dominating peak could be observed in $^1$H NMR. Figure 4.2B shows an example of this (with H$_2$IMES-HCl and KHMDS). Most of the carbene-species is of the starting complex and considerable amounts of 1.3 and 1.4 are formed. Also two new peaks are formed of which one will later prove to be associated with 4.10.

**Figure 4.2A:** Previously reported synthesis of complexes 4.1B.

**Figure 4.2B:** Complex carbene mixture when the previously reported method was applied.
In one of our attempts we tried to reverse the order of substitution on the Grubbs catalyst. First, we synthesized the classical Grubbs 2nd generation catalyst 1.4 by substitution of PCy₃ on the first generation complex 1.3 with the H₂IMES carbene ligand. Thereafter, we added the Schiff base Tl-salt 4.11 to the complex. We used the toxic thallium since Grubbs et al. reported this to be the most efficient in the substitution of 4.13 to obtain 4.1A.

After a long reaction time, a peak in ¹H NMR was obtained at δ = 18.95 ppm. This resonance is 0.82 ppm more upfield than the first generation analogue 4.1A, which is exactly the same shift as between the classical Grubbs 1st and 2nd generation catalysts 1.3 and 1.4. This led us to seriously consider that this new resonance in ¹H NMR at δ = 18.95 ppm (CDCl₃) was to be attributed to 4.10 in contrast to the previously reported resonance at δ = 19.66 ppm (CDCl₃).

The classical 2nd generation catalyst 1.4 is known for its high PCy₃ bond energy with concomitant slow initiation in metathesis. This consequently leads to slow reaction rates in substitution reactions. To avoid the sluggish substitution of 4.11 on 1.4, the more reactive complex 4.12 was first prepared. Grubbs et al. published on the easy synthesis of 4.12 by the reaction of an excess of pyridine to 1.4. 4.12 dissociates pyridine readily and is well known as ‘a versatile precursor for the synthesis of new ruthenium olefin metathesis catalysts.’ As expected, the reaction of 4.12 with 4.11 leads to a colour change from green(4.12)-yellow(4.11) to red brownish within minutes at room temperature while a white precipitate (TlCl) is formed. The product 4.10 can be obtained in reasonable yield (74%).

Figure 4.3: 1st preparation of catalysts of type 1B.
The $^1$H NMR spectrum of 4.10 shows no phenolic proton at $\delta = 14.35$ ppm and the resonances at $\delta = 8.11$ and 8.07 ppm can be ascribed to the Schiff base fragment. Most remarkably, three of the $^1$Pr protons in 4.10 are shifted upfield up to 0.19 ppm. The CH$_2$CH$_2$ bridge protons of the H$_2$IMES are shifted to 4.12-3.86 ppm.

The $^{13}$C NMR is even more conclusive showing a resonance of the benzylidene carbene of 4.10 at $\delta = 299.6$ ppm, the H$_2$IMES carbene resonance at $\delta = 219.6$ ppm and the CH$_2$CH$_2$ bridge carbons of H$_2$IMES at $\delta = 51.7$ and 50.3 ppm. Furthermore, the peak sequence at $\delta = 174.3$, 167.5, 151.4, 148.5 and 141.5 ppm for 4.10 corresponds to the peak sequence respectively at $\delta = 174.9$, 167.5, 153.1, 148.8 and 140.1 ppm for the first generation Schiff base substituted analogue 4.10A.

Our synthesis of 4.10 was confirmed by single-crystal X-ray analysis. The crystals were grown in a solution of a minimum of chloroform in pentane.
The ORTEP diagram of 4.10 is shown in figure 4.5 and the selected bond angles and bond distances are shown in the table 4.1. 4.10 has a longer Ru-N bond (2.125 (2) Å) than the first generation analogue 4.10A (2.106 (4) Å) and a shorter Ru-C(NN) bond (2.035 (3) Å) than the second generation catalyst 1.4 (2.085 (2) Å). This can be ascribed to the bigger trans influence from H$_2$IMES compared to PCy$_3$, the smaller trans influence of the Schiff base compared to PCy$_3$ and a decrease in steric strain.\textsuperscript{1,9} Moreover, as we pointed out in Chapter 2, the $\pi$-backbonding should influence the bond distance considerably. In 4.10, the $\pi$-acceptor orbitals of H$_2$IMES and the Schiff base interact with two different metal d-orbitals. Hence, from this point of view, the bond distance should decrease for both bonds. However, these complexes are not suitable for unambiguous analysis, since they are governed by high steric interactions and a strong $\sigma$-donors. Moreover, sp$^2$ hybridized nitrogens were predicted to show only half the backbonding capacity of the already weak backbonder PMe$_3$.\textsuperscript{10} Consequently, changes in the backbonding to this ligand should be even less expressed in the rest of its bond characteristics.\textsuperscript{11}

The intramolecular $\pi$-$\pi$ stacking does not only seem to be present in the mesitylene-benzylidene fragments\textsuperscript{11-13}, but also in the mesitylene-phenoxy fragments. Indeed, the large N-Ru=C$_{\text{benzylidene}}$ angle of 106.3° places the phenoxy fragment more parallel to the mesitylene substituent.

\textsuperscript{11} Furthermore, since the backbonding to the imine is very little even at maximum, the changes in this backbonding have difficulty to affect the backbonding to the rest of the ligand sphere.
Table 4.1: Selected bond lengths and bond angles for Grubbs type catalysts:

<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>4.10A (a)</th>
<th>1.4 (b)</th>
<th>4.10</th>
<th>4.13 (c)</th>
<th>4.7 (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru=C</td>
<td>1.850 (6)</td>
<td>1.835 (2)</td>
<td>1.846 (3)</td>
<td>1.840 (4)</td>
<td>1.838 (2)</td>
</tr>
<tr>
<td>Ru=CNN</td>
<td>2.085 (2)</td>
<td>2.035 (3)</td>
<td>2.037 (4)</td>
<td>2.032 (2)</td>
<td></td>
</tr>
<tr>
<td>Ru-P</td>
<td>2.345 (2)</td>
<td>2.4245 (5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-N</td>
<td>2.106 (4)</td>
<td>2.125 (2)</td>
<td>2.124 (3)</td>
<td>2.108</td>
<td></td>
</tr>
<tr>
<td>RuX(1) (Cl)</td>
<td>2.382 (2)</td>
<td>2.3912 (5)</td>
<td>2.3834 (7)</td>
<td>2.397 (1)</td>
<td>2.398</td>
</tr>
<tr>
<td>RuX(2)</td>
<td>2.055 (4)</td>
<td>2.4245 (5)</td>
<td>2.067 (2)</td>
<td>2.044 (3)</td>
<td>2.053</td>
</tr>
<tr>
<td>N1(benzyliden side))=CNN</td>
<td>1.348 (2)</td>
<td>1.341 (4)</td>
<td>1.340 (5)</td>
<td>1.346 (3)</td>
<td></td>
</tr>
<tr>
<td>N2=C</td>
<td>1.347 (2)</td>
<td>1.352 (4)</td>
<td>1.337 (5)</td>
<td>1.346 (3)</td>
<td></td>
</tr>
<tr>
<td>N1-C (mesityl)</td>
<td>1.432 (2)</td>
<td>1.432 (4)</td>
<td>1.438 (5)</td>
<td>1.441</td>
<td></td>
</tr>
<tr>
<td>N2-C (mesityl)</td>
<td>1.440 (2)</td>
<td>1.434 (4)</td>
<td>1.440 (5)</td>
<td>1.442</td>
<td></td>
</tr>
<tr>
<td>X(1)-Ru-X(2)</td>
<td>173.0 (1)</td>
<td>167.71 (2)</td>
<td>175.17 (6)</td>
<td>171.11 (8)</td>
<td>172.50 (4)</td>
</tr>
<tr>
<td>L(1)-Ru-L(2)</td>
<td>159.8 (1)</td>
<td>163.73 (6)</td>
<td>157.2 (1)</td>
<td>160.2 (1)</td>
<td>158.34 (8)</td>
</tr>
<tr>
<td>L(1)-Ru=C</td>
<td>96.8 (2)</td>
<td>100.24 (8)</td>
<td>96.5 (1)</td>
<td>97.8 (2)</td>
<td>98.28 (9)</td>
</tr>
<tr>
<td>L(2)-Ru=Cl</td>
<td>103.5 (2)</td>
<td>95.98 (6)</td>
<td>106.3 (1)</td>
<td>102.0 (2)</td>
<td>103.07 (8)</td>
</tr>
<tr>
<td>L(1)-Ru-Cl(1)</td>
<td>89.0 (1)</td>
<td>83.26 (5)</td>
<td>90.43 (8)</td>
<td>88.9 (1)</td>
<td>94.73 (6)</td>
</tr>
<tr>
<td>L(1)-Ru-X(2)</td>
<td>88.4 (1)</td>
<td>94.55 (5)</td>
<td>90.6 (1)</td>
<td>88.0 (1)</td>
<td>83.79 (7)</td>
</tr>
<tr>
<td>Ru-C=N1(benzylidene side)</td>
<td>128.08 (14)</td>
<td>135.5 (2)</td>
<td>132.0 (3)</td>
<td>132.82</td>
<td></td>
</tr>
<tr>
<td>Ru-C=N2</td>
<td>123.90 (14)</td>
<td>117.1 (2)</td>
<td>120.3 (3)</td>
<td>119.08</td>
<td></td>
</tr>
<tr>
<td>C=N1-C (mesityl)</td>
<td>128.39 (16)</td>
<td>127.6 (2)</td>
<td>126.7 (3)</td>
<td>126.95</td>
<td></td>
</tr>
<tr>
<td>C-N2-C (mesityl)</td>
<td>127.74 (16)</td>
<td>122.4 (2)</td>
<td>124.7 (3)</td>
<td>126.32</td>
<td></td>
</tr>
</tbody>
</table>

Priority to X is given by Cl>O. Priority to L is given by H$_2$IMES > P > N. N$_1$ is on the benzylidene side of H$_2$IMES (a); Data from 1, (b); Data from 6, (c) 4.13 represents the 4.1B catalyst with R$_1$= H and R$_2$ = mesitylene (see Figures 4.1 and 4.17), (d) Data from 14 and data from CCDC (Cambridge Crystallographic Data Centre). The data for Ru-N, Ru-O and Ru-Cl showed incorrect values in the article 14 (2.3976 Å, 2.1080 and 2.0530 Å respectively) but analysis of the cif-file resulted in the correct data. Bond lengths in Å.

Furthermore, an asymmetrical distortion of the H$_2$IMES ligand in 4.10 compared to 1.4 was found. An angle of 9.3° is present between the H$_2$IMES and Ru-C(H$_2$IMES) direction which is to the best of our knowledge the second biggest torsion angle reported for a saturated imidazole ligand on a Grubbs catalyst. Moreover, the Ru-C(H$_2$IMES)-N$_1$ (117.1°) and C(H$_2$IMES)-N$_1$-C(mesityl) (122.4°) angles are the second smallest and smallest ones reported for saturated imidazole ligands on a Grubbs catalyst. We suggest this is to be assigned to the π-π stacking of the mesityl-phenoxy fragments, even though an angle of 16° is still present between the two planes due to the steric bulk of the 'i-Pr group. We want to stress that π-π stacking should not be assigned too lightly, because the stacking of benzyl rings quasi parallel to each other in congested metal centres can easily be the result of efficient ordering in order to minimize the steric interactions. In 4.10 this phenomenon is definitely present. Actually, the benzylidene and mesitylene ring are not oriented above each other, but next to each other, which is clear when 4.10 is projected in the plane perpendicular to the H$_2$IMES imidazole ring (figure 4.6). Cavallo attributes the sterical strain of the classical second generation catalyst 1.4 to a close contact between the C$_{carbene}$ and C$_{ipso-mesityl}$ of 2.99 Å (3.04 Å for the IMES catalyst). A contraction in the fourteen electron species of this distance to 2.97 Å leads to a preference for the cyclobutane species (note that Cavallo also calculated a 3.01 Å distance for the ethene coordinated complex). The crystal structure of 1.4 shows a distance of 3.04 Å for the C$_{carbene}$ and C$_{ipso-mesityl}$ contact supporting info of 9. The crystal structure of 4.10 shows a C$_{carbene}$-C$_{ipso-mesityl}$ contact of 3.11 Å, which is considerably less than for 1.4. Furthermore, the benzylidene and mesitylene ring in 1.4 are better
stacked above each other. This could indicate that the high decrease of steric interactions leads to a decrease in the formation of the 14e active species (which is observed).

**Figure 4.6:** Projections of the benzylidene-mesitylene interaction in 4.10. Left: space filled; right: projection in the plane perpendicular to the imidazole plane (bottom left: phenyl ring of benzylidene; bottom right: phenyl ring of mesitylene; both phenyl rings are positioned next to each other and not above each other)

The ORTEP structure also provides interesting information about the bonding of the imine ligand. The di-isopropyl phenyl group (Ph(‘Pr)₂) is oriented perpendicular on the Ru-N-C plane, which should make conjugation of the Ph‘Pr system possible into the N-Ru σ-bond. However, the wide Ru-N-\text{C}_{\text{Ph}(‘\text{Pr})_2} angle (123.9°) suggests that no such conjugation is present. It should be noted that the Ph(‘Pr)₂ cannot freely position itself, since one of the ‘Pr groups is in very close contact with the benzylidene. Reducing the angle would create a steric interaction between the ortho-methyl mesitylene and one of the ‘Pr methyl groups. Previously Bertrand et al. have shown that similar conjugation of a phenyl ring with the σ-orbital of a phosphino-aryl carbene is possible, but is concomitant with a widening of the carbene angle.²²

**Figure 4.7:** Left: perpendicular orientation of the Ru-N-C plane to the Ph(‘Pr)₂ plane (Ph(‘Pr)₂ plane shows right in the figure); right: space filled representation of the steric interaction of one of the ‘Pr groups with the mesitylene.
Schiff base Grubbs catalysts

The phenoxy-group is positioned almost parallel with the quasi planar chelate ring. This facilitates a conjugated π-system of the phenoxy-ring with the Schiff base. It is expected that the nitro-group withdraws electrons from the nitrogen π-orbital (even though it is oriented in the meta position) and consequently enhances backbonding. Harvey et al. have shown that imines are relative weak to receive backdonation compared to classical phosphine ligands as PCy₃, but still much better to accept backdonation than amines, due to the use of the π* orbital instead of a σ* orbital. Jensen et al. have shown that the bond enthalpy of the Ru-N bond in 4.10A (21.5 kcal/mol) decreases sharply when the corresponding amine is applied with a hydrogen in the new site (8.6 kcal/mol). Jensen et al. attributed the huge difference to the increased steric demand of the amine. This can definitely be confirmed by the concomitant decrease in Ru-PCy₃ bond enthalpy (31.9 → 23.9 kcal/mol). However, a less steric demanding tridentate amine ligand also shows a substantial decrease in the Ru-N bond enthalpy (21.5 → 16.0 kcal/mol), while the Ru-P bond enthalpy only decreases marginally (31.9 → 31.1 kcal/mol). This indicates that other factors might be present in the case of the Schiff base coordinated 4.10A. Yet, we must stress that the Schiff base intrinsically has a low π-backbonding capacity. Furthermore, the Schiff base is here competing for backdonation in the xy plane with the benzylidene and hence backdonation occurs in a competitive environment (Chapter 2). Overall, we suggest that the π-backbonding to nitrogen contributes poorly to the complex stability, because what is gained in the Ru-N backbond can also be lost in the Ru-benzylidene backbond.

![ORTEP plot of 4.13](image)

Figure 4.8: ORTEP plot of 4.13. (For schematic structure of 4.13, see figure 4.17)

We were also able to obtain a crystal of the 4.1B catalyst with R₁ = H and R₂ = mesitylene: 4.13. The bond distances and bond angles are quite similar to those of 4.10 and mostly somewhat milder. The biggest differences of 4.10 → 4.13 are the contracted Ru-O bond (2.067 Å → 2.044 Å), the tighter N-Ru-C(benzylidene) angle (106.3° → 102.0°) and the more acute Ru-C(H₂IMES)N(benzylidene)-side angle (135.5° → 132.0°). The contraction of the Ru-O bond is expected since upon the absence of the NO₂ group, a stronger electrostatic attraction (Ru⁵⁺O⁻⁶; O more negative) can be expected with a concomitant shorter bond distance in a bond which is dominated by electrostatic interactions. Although this should decrease σ-donation (which experimentally has been shown to result in a weaker bond), mesomere
backdonation should increase and lower the bond-distance. Similar contractions of the Cu-O bond are observed in salicylaldimine-Cu complexes upon removing a NO₂ ligand in the same position.²⁵ The Ru-N-Cₘeso₃ angle in 4.13 shows a similar value (122.6°) as found for the Ru-N-C angle of 4.10 (123.9°), although the mesitylene ring now has more freedom to rotate. This leads us to conclude that no conjugation of the mesityl π-system to the Ru-N σ bond is present.

Surprisingly, the C_carbene and C_ipso-mesityl contact in 4.13 is reduced to 2.99 Å which is even 0.05 Å closer than in the classic second generation catalyst 1.4. The small differences of bond angles (C_carbene-Ru-C_H₂IMES; +1.3°; Ru-C_H₂IMES-N; -3.5°; C_H₂IMES-N-Cₘeso₃; -0.9°) are responsible for this 0.12 Å closer contact in 4.13 compared with 4.10. According to Cavallo, this structural feature should lead to a lower amount of 14 electron species and higher preference for the cyclobutane species.²¹ Moreover, the benzylidene and mesitylene moieties considerably overlap. This changed preference compared to 4.10 is accomplished by the difference in dihedral angle C_benzylidene-Ru-C_H₂IMES-N_benzylidene-side, which is in opposite direction. In 4.10 the torsion directs the mesitylene away from the benzylidene where for 4.13 the mesitylene is directed towards the benzylidene. Furthermore, in 4.13 the N_benzylidene-side-C_ipso-mesityl shows a bending away from the planar NHC-framework to position the mesitylene group above the benzylidene! This shows that small structural differences act synergistically to obtain overall structurally different characteristics, which result in the clear π-π stacking of the mesitylene with the benzylidene in 4.13!

![Figure 4.9: π-π stacking of the mesitylene with the benzylidene in 4.13.](image)

The discrepancies about the two structures continue. While 4.10 shows quasi parallel mesitylene and phenoxy rings, this feature is not present in 4.13. 4.13 shows quite the normal configuration. In 4.10 the torsion in the chelate ring and the excessive C_carbene-Ru-N angle (106.3°) are able to usher the two rings in quasi-parallel orientation. Of course, as we mentioned before, the extreme bending of the NHC angles towards the phenoxy group also contributes. This is another example of the addition of minor structural differences which lead to very distinct stereo-electronic features of the complex.
It should be noted that our synthesis method and NMR data for catalysts of type 4.1B have been validated by a publication of Raines et al. shortly after our own publication.\textsuperscript{6,14} Raines et al. concurred with our statement that the previously published synthesis of our group does not lead to the desired products and that the NMR data reported by De Clercq et al. did not match the ones of the actual products.\textsuperscript{7,14} The authors also confirmed their synthesis by the ORTEP structure of a crystal from 4.7. Furthermore, Raines et al. also showed that the direct synthesis of complexes 4.1B from 4.1A is possible by the use of the base potassium tert-amylate in hexane.\textsuperscript{14} Raines et al. did not investigate the crystal of 4.7 extensively.\textsuperscript{III} We want to note that the distance between the \(C_{\text{carbene}}\) and \(C_{\text{ipso-mesityl}}\) of 4.7 is 3.06 Å and that the mesitylene group is directed well above the benzylidene group.

\textsuperscript{III} It should be noted that the data in the crystallographic analysis by Raines et al. are not depicted correct in the article. To obtain the correct data one can submit a request to CCDC.
Most structural characteristics of 4.7 are similar to those of 4.13, except for the NHC-Ru-X angles which are very asymmetrical. For 4.7 the NHC-Ru-Cl angle and the NHC-Ru-O amount to 94.73° and 83.79° respectively. This feature is highly unexpected, although it is present in the classical second generation catalyst 1.4.9

In 1.4 the Ru-benzylidene is also twisted by an angle of 12.45° to the Cl-Ru-Cl bond. The same measurement for all the Schiff base catalysts is meaningless since the phenyl(benzylidene) ring, the carbene and the Ru are not positioned coplanar (vide infra). Therefore, the angle between the benzene and the O-Cl-Ru-carbene plane was calculated.

An angle of 8.83° was found between the Ru-carbene-C_ipso-benzene and both the O-Ru-carbene and Cl-Ru-carbene planes for 4.7. Angles of 11.86° and 11.43° respectively were measured for 4.13 and 14.10° and 15.55° respectively for 4.10. The small differences between the angles illustrates (as expected) the coplanarity of the O, Cl, Ru and the carbene. The angle itself reflects on the twisting of the phenyl(benzylidene) with the Cl-O-Ru-carbene plane. The angle in 4.13 is the biggest, but this is not exceptionally since recently a Grubbs type complex was reported which shows an angle of 20.22°.26
An illustration on the orientation of the phenyl(benzylidene) ring and the Ru-carbene is shown below. The classical second generation catalyst 1.4 shows a flat benzylidene ring and the Ru-carbene bond is almost parallel to the phenyl plane. The steric catalyst 4.10 is the only catalyst which shows no coplanarity of the carbene-phenyl bond with the phenyl (not visible in figure). It is also the only catalyst for which the phenyl bends towards the mesitylene group. This is possible due to the long C_{carbene}-C_{ipso-mesityl} contact of 3.11 Å, the lack of π-stacking with the mesitylene and the pushing of one of the i-Pr groups on the other side of the plane. 4.7 and 4.13 are here also structurally quite similar.\textsuperscript{IV} The carbene-phenyl bond is coplanar with the phenyl ring and is bent away from the mesitylene.

\textbf{Figure 4.13}: Orientation of the phenyl(benzylidene) ring and the Ru-carbene bond for 1.4 (top left), 4.10 (top right), 4.13 (bottom left) and 4.7 (bottom right). Plots for 1.4 and 4.7 were constructed with Mercury 1.4.1 from supplementary info from \textsuperscript{9} and \textsuperscript{14} respectively.

In conclusion, it has been shown that small changes in the Schiff bases lead to small changes in the bond lengths and bond angles which act synergistically to obtain very distinct overall steric-electronic structures. It would be interesting if the activity studies in the next subchapters could lead to activity-structure relations. Moreover, if an increased amount of crystal structures were available, patterns in structure-activity relations would evolve.

\textbf{4.2.2 Catalytic screening}\textsuperscript{6}

Besides 4.10 and 4.13, also 4.8 and 4.9 were synthesized in our initial attempts to produce catalysts of type 4.1B. We were very much interested in their activity for Ring Opening Metathesis Polymerization (ROMP). As reported for the first generation analogues 4.1A, our initial catalysts 4.1B showed very poor activity at room temperature.\textsuperscript{1} Moreover, the catalysts 4.1B can be considered to be practically

\textsuperscript{IV} It should be noted that the bending of the benzylidene towards the mesitylene in 4.10 is not facilitated by a wide carbene-Ru-NHC angle since this angle is acuter in 4.10 compared to 4.7 and 4.13.
inactive at room temperature for (COD, DCPD, Norbornene, DEDAM,...). As an example, the ROMP of 20 000 equiv of DCPD (dicyclopentadiene)\(^V\) with catalyst 4.10 dissolved in a minimum amount of \(\text{CH}_2\text{Cl}_2\) is unsuccessful even after a week and no gelated polymer was obtained.

The catalysts 4.1B show no signs of decomposition during several years when stored as solids under normal atmosphere and temperatures. Moreover, when the catalysts are left in a solution of \(\text{CDCl}_3\) under normal atmosphere for 1 month, no decomposition is observed! This illustrates the high robustness of these complexes. Furthermore, when the catalysts are added to certain monomers no polymerization occurs, but the catalysts remain intact and can later be activated by several methods (vide infra).

These features facilitate the mixing and storing of catalysts with certain monomers without undesirable polymerizations.\(^17\) The catalysts can then be activated at the appropriate time. This type of catalysts are also called latent catalyst. They are extremely valuable for RIM (Reaction Injection Molding) in which two feed stocks, one with catalyst and one with activator, are used. It should be noted that the most important application of metathesis catalysts is the RIM of DCPD. For these reasons, latency in our catalysts and high activity towards the polymerization of DCPD are desirable. Unfortunately, the testing of catalysts for reaction with DCPD is not included in the standard metathesis tests proposed by Grubbs et al.\(^27\)

The Ru catalysts are superior for practical applications due to their high tolerance towards oxygen and towards impurities in the monomer feeds. However, the high cost of Ru for the catalysts is its worst enemy. The average price in July (US $) per troy ounce (31.10g) at Johnson Matthey NY climbed from 33 (2003) to 60 (2004) to 80 (2005) to 171 (2006) to 390 (2007) (565 in November 2007) with a peak of 852 in February 2007.\(^28\) The Molybdenum (a competitive metal for metathesis) price (US $ / troy ounce) has risen form ~5 in October 2002 (over a peak of ~46 in July 2005) to ~35 in the beginning of August, November 2007 and most of the price rise was obtained in 2004.\(^29\) So, as the Ru price was approximately only double of the price of Mo in July 2004, it now is over 10 times as expensive. The gold price (US $ / troy ounce) has risen from 400 (2003) to 780 (November 2007) which shows that Ru will soon be more expensive than gold. Hence, we strongly discourage the development of bimetallic catalysts (Section 4.4).

\(\text{DCPD}: \text{Dicyclopentadiene}\) \hspace{1cm} \(\text{Norbornene}\) \hspace{1cm} \(\text{COD}: \text{1,5-cyclooctadiene}\)

Figure 4.14: Monomers for ROMP.

\(^V\) A liquid formulation of DCPD which is also applied in industry was used.
The polymerization of COD (1,5-Cyclooctadiene) can be followed relatively easily by $^1$H NMR. Furthermore, the in situ polymerization of COD in CDCl$_3$ was recently proposed to be one of the standard analysis methods for mapping the catalyst activity and is widely applied in literature.$^{27}$ For our catalysts, higher temperatures were necessary and therefore the polymerization of COD was monitored at 90°C in toluene-d$_8$. The catalysts compared are 4.8, 4.9, 4.10, 4.13 and 4.10A, the first generation analogue of 4.10.

![Figure 4.15: Monitoring of the COD polymerization in 600 µl toluene-d8; 2.717 µmol catalyst and 8.15 mmol (100 µl; 300 equiv) of COD.](image)

All Schiff-base substituted catalysts 4.8-4.10, 4.13 and 4.10A are less active than their phosphine analogues, which are active at room temperature. Comparing the 1$^\text{st}$ and 2$^\text{nd}$ generation analogues 4.10A and 4.10, the latter is showing higher activity. The 2,6-‘i-Pr-C$_6$H$_3$ Schiff base substituted catalysts 4.9-4.10 exhibit the highest reaction rates, which can be ascribed to the sterical hindrance of the iso-propyl groups. This is increasing the energy of the coordinated Schiff base complex leading to a marginal favoring of the decoordinated form and consequently increasing activity according to a dissociative mechanism. Also, the lack of a benzylidene-mesitylene $\pi-\pi$ interaction could boost activity.

The activity of the nitro-substituted 4.10 is not significantly different compared to its analogue 4.9. This is in sharp contrast to our reasoning that the nitro group should withdraw electron density from the imine-nitrogen, making it a less donating ligand with smoother decoordination and an increased activity. Furthermore, nitro-substitution on a random place of the phenyl group on the Grubbs-Hoveyda catalyst improves catalyst activity, which shows that it also influences on the meta position.$^{30}$
However, the increase in activity of the Hoveyda catalysts may also stem from the withdrawal of electron density from the carbene.

An induction period is clearly visible with 4.13, in contrast to the other Schiff base catalysts. We previously attributed this effect to a slow initiation or a competitive associative mechanism which gains in importance with a decrease in steric congestion as in 4.13. However, after obtaining the ORTEP structure, this more difficult initiation of 4.13 compared to 4.10 could be attributed to the π-π stacking of the benzylidene. Cavallo’s argument would suggest slower initiation due to the lower C_{ipso_mesitylene}-C_{benzylidene} distance (assuming that this bond distance contracts by the same amount for the fourteen electron species in 4.10 and 4.13).

Table 4.2: Polymer characteristics after full polymerization (25 h, at 90°C):

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>conversion [%]</th>
<th>trans [%]</th>
<th>M_n</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8</td>
<td>100</td>
<td>87</td>
<td>58700</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
<td>100</td>
<td>84</td>
<td>38400</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>4.10</td>
<td>100</td>
<td>84</td>
<td>34300</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>4.13</td>
<td>100</td>
<td>60</td>
<td>119300</td>
<td>1.6</td>
</tr>
<tr>
<td>5</td>
<td>4.10A</td>
<td>100</td>
<td>47</td>
<td>45800</td>
<td>1.7</td>
</tr>
</tbody>
</table>

As displayed, trans percentages of the polymers of 4.8-4.10 and 4.13 are higher than the one found for 4.10A. This is a trend also observed for the classic second and first generation catalyst. The PDI’s of the obtained polymers are lower than those of 1.4. At first, we suggested that the low M_n values (34 300 for 4.10) and low PDI’s (1.5 for 4.10) imply high initiation and relative control, in contrast with the suggestion that less than 5% of 4.10 initiates. However, in subsequent investigations we have shown that information about M_n, PDIs and especially cis/trans ratios are very ambiguous and that a simple analysis lacks the necessary context to provide accurate information (vide infra; equilibrations play an important role).

Despite the above mentioned problems we encountered with DCPD, we consider testing DCPD quintessential due to the industrial importance of this monomer. Furthermore, in our tests performed with COD and all the standard testing proposed by Grubbs et al., only information about the initiation kinetics can be obtained but the longlivety or decomposition of the catalyst remain unhandled.

The activity of a few catalysts was monitored for the polymerization of 20 000 equivalents of DCPD by a thermocouple. Due to the latent character of the catalysts, the polymerization vessel was placed in a thermoblock and heated to 150°C. The appearance of an exotherm is evidence for a fast exothermic polymerization. With this experiment, we were able to test the industrially relevant DCPD monomer, using high monomer concentrations to evaluate the catalyst TON (Turn Over Number) and mimicking the RIM environment of a heated mould (although in RIM the mould is only heated to 60 °C-80 °C).
Figure 4.16: Polymerization of 20 000 equiv of DCPD in a heated (150 °C) mould.

For the polymerization using 4.10, an exotherm starts at 129 °C (to 179 °C), while for the phosphine analogue 4.10A only a small shoulder at 90°C is present. From the latter only a gelated polymer was obtained. We suggest that the NHC substitution leads to a higher stability and activity of the catalyst as observed for the NHC substitution of the classical Grubbs systems. Furthermore, this test proves the applicability of the catalyst for high loadings of DCPD which can be mixed and stored without concomitant polymerizations while the catalyst can be activated by a heated mould in a RIM process.

4.3 Expanding the scope and applicability of the Schiff base catalysts 4.1B

4.3.1 Expanding the scope of the catalysts

The catalysts described above showed only small differences in design and catalytic activity. As we were interested in tuning the Schiff base ligand to provide a whole spectrum of catalysts which could be applied at different temperatures, a broader range of catalysts was prepared which are all shown below.
**Figure 4.17:** All Schiff base catalysts of type 4.1B prepared.

4.14 was found to be a very potent precursor due to the extreme steric hindrance exerted by the \( t \)-Bu groups. The catalyst showed very high activity. At that time, we had not been able to make crystals of any of the complexes and were interested in whether the increased activity was caused by the \( t \)-Bu groups in the ortho or para position. Hence catalyst 4.15 was a very logical next step.

With increasing electron withdrawing capacity of N-substituent, the ligand should dissociate more readily. To investigate this, 4.16 was synthesized.

Also aliphatic Schiff bases are a very interesting alternative. The installation of a carbon sp\(^3\) centre gives rise to interesting steric possibilities. To this purpose, the sterically unencumbered 4.17 was synthesized. Due to the lack of steric bulk, this catalyst can also be expected to be sensitive for associative olefin coordination reactions. Unfortunately, the catalyst quickly decomposed in solution which inhibited the collection of \(^{13}\)C NMR data.

With 4.18, a very steric aliphatic catalyst was prepared, which we wanted to compare with the steric aromatic catalyst 4.14. The sterical intermediate 4.19 was also prepared. The aliphatic catalysts posses an intriguing property. Aliphatic Schiff bases are known to be less stable than their aromatic siblings. Therefore, these catalysts might not show the envisaged high stability of their aromatic analogues. However, lack of stability of the imine bond can be exploited when monomer impurities such as water could decondensate the bond and replace it with an aldehyde functionality.
4.3.2 Catalytic activity of the catalysts 4.1B for the COD polymerization

We were interested in a good test for the initiation kinetics of the catalyst. As mentioned, the polymerization of COD is considered a good reaction for this purpose.

Since catalysts 4.8-4.10 and 4.13 were already tested for this polymerization, only catalysts 4.14-4.19 were evaluated and catalyst 4.10 was added as reference. Due to the increased activity of the catalysts, a lower temperature (40°C) was applied. This made it possible to use the more economical CDCl₃ as solvent which was dried and degassed. Consistent with the former tests, a 300 equiv of monomer to catalyst ratio was employed. It should be noted some problems with the reproducibility of catalyst 4.15 occurred. We presume that 4.15 is prone to some activation mechanism for which the impurities in the used solvents and monomers were too high, despite the prior drying and degassing process.

The comparison of the catalysts shows very distinct trends. As being Schiff base catalysts, the sterically encumbered catalysts 4.14 and 4.18 show extremely fast polymerizations. After 15 minutes both polymerizations have reached 100%. Our reference catalyst 4.10 and catalyst 4.16 show the slowest kinetics. The slow polymerization of 4.16 is very surprising since the pentafluorophenyl group should decrease the donating ability of the amine and hence promote the activity. However, the lack of electronic influence on the activity is in accordance with the activities measured for 4.9 and 4.10, which did not show any influence upon the introduction of a nitro-group on the phenoxy-fragment (vide supra).

The relative fast polymerization of 4.15 is also very unexpected. 4.15 clearly surpasses the initiation kinetics of 4.10, yet in our initial results we thought that the higher activity of 4.10 should be attributed to the steric strain which is considered to be higher than for 4.15. In retrospect, 4.15 was actually a bad design, since the crystals we were able to prepare showed that the N-phenyl para substituent is directed completely outwards and hence cannot exert any steric influence. It is very tricky to propose explanations for this phenomenon, since catalysts 4.14 and 4.18 show that the steric influence is in fact very important. We suggest that maybe through the absence of substituents in the

Figure 4.18: Polymerization of COD (8.15 mmol (100 µl; 300 equiv) in 500µl CDCl₃ at 40°C.
ortho-phenyl position, this catalyst is more prone for an associative reaction mechanism than the others which reflects on the faster initiation kinetics. In fact, the ortho-positions of the phenyl ring both shield the benzyldiene and the free coordination site trans to the benzyldiene. The methyl and cyclohexyl substituted catalysts 1.17 and 1.19 also show intermediate activity, though lower than 1.15. An associative mechanism can also be the reason for the higher activity in this case. The steric influence of the cyclohexyl group seems to exert little effect on the kinetics of the catalyst. However, the stability of the complex increases much upon the introduction of a cyclohexyl group compared to a methyl group (vide infra).

4.3.3 Catalytic activity of complexes 4.1B for the DCPD polymerization

In literature, the activity determination of catalysts is mainly directed to the description of the initiation kinetics of RCM. RCM, which acts with the methyldiene as intermediate, is very different from ROMP reactions. Furthermore, the activity tests in literature for RCM show only the kinetics of the reaction and not the more interesting property being the stability of the catalyst throughout the reaction.

The usage of ROMP to describe the activity of the catalysts is less applied. The description of the ROMP of catalysts in literature focuses on the kinetics of COD polymerization. Unfortunately, little contributions concern the stability towards high monomer feeds (high TON), industrially important and unpurified monomers (DCPD) and applications (RIM) or the use of unpurified (not H₂O, O₂ free) and challenging solvents.

We found it relevant to evaluate the catalysts for the industrially important DCPD polymerization. Where standard COD polymerizations using various catalysts show monomer:catalyst ratios of 300-3000, in the following ratios of ≥ 30 000 of RIM monomer were applied to test the catalyst in a more industrial appealing fashion.

Research in our group has also shown that the catalysts of type 4.1B can be efficiently activated by HCl and silanes. It was suggested that in dry conditions the Schiff base is protonated by HCl and decoordinates to form an active species. Furthermore, if HCl is added in the presence of H₂O also the Ru-O bond cleaves to form a Ru-Cl bond. The mixing of one monomer portion with latent catalyst and one containing the activator also represents an excellent mimic for a RIM reaction.

![Figure 4.19: Acid activation of Schiff base catalysts.](image-url)
Most catalysts were screened for the DCPD polymerization with RIM monomer. However, due to disintegration of the monomer and the unavailability of new stock, not all catalysts and activation mechanisms were tested. The data presented are the best data of multiple runs, since thermocouple placing sometimes mismatched the screening and the RIM monomer was prone to oxidation which led to bad conversions. However, results were only used when they were at least twice obtained.

First, catalyst 4.10 was submitted to the polymerization of 30 000 equiv DCPD with HCl as activator. 10 equiv of HCl are not able to activate the catalyst enough. 30 equiv HCl is preferential and a temperature of 183 °C was obtained after 478 s. The polymerization with 60 000 equiv of monomer is less successful, and only gelated polymers and low temperature boosts were obtained.

![Figure 4.20](image-url)

**Figure 4.20:** Catalyst 4.10; 30 000 equiv DCPD.

![Figure 4.21](image-url)

**Figure 4.21:** Catalyst 4.10; 60 000 equiv DCPD.

Catalyst 4.13 shows excellent activity for the reaction of 30 000 equiv of DCPD reaching 196 °C after 65 seconds with 20 equiv of HCl. By decreasing the acid concentration (10 equiv), the temperature rise is delayed, which is concomitant with a lower maximum temperature (178 °C). A high temperature produces extra cross-linked polymer which are obtained through radical reactions. When 20 equiv of HCl are used for this catalyst, it shows a long induction period (~50 s) and a high maximum temperature (191 °C).

4.13 is also able to polymerize 60 000 equiv of polymer, for which a temperature of 166 °C was obtained when PhSiCl₃ was used as the initiator.

It should be noted that for the acid catalyzed DCPD polymerization, this catalyst shows better characteristics than 4.10, which is evident by the higher temperatures obtained.
Catalyst 4.8 shows the highest temperature rise to 187 °C after 300 s for 90 equiv of HCl for the polymerization of 30 000 equiv of DCPD. Unfortunately, the polymerization of 60 000 equiv only results in a gelated polymer and a maximum temperature of 69 °C (1100 s).

Catalyst 4.15 shows the best profile of all catalysts for the polymerization of 30 000 equiv of DCPD. First, there is a small initiation period, which could be used in RIM processes for the mixing of the two components and the filling of the mold. Thereafter, the mixture polymerizes fast and reaches a temperature of 198 °C for both 10 or 20 equiv of HCl added.

Here again, the polymerization of 60 000 equiv is more problematic and only a temperature of 82 °C is obtained after a much longer polymerization for 10 equiv of HCl activation.
Figure 4.25: Catalyst 4.15; 30 000 equiv DCPD.

Figure 4.26: Catalyst 4.15; 60 000 equiv DCPD.

The pentafluorophenyl catalyst 4.16 shows an optimum at 30 equiv HCl for the ROMP of 30 000 equiv of DCPD, for which it reaches a maximum of 179 °C after 300 s. The production of big objects (boat fuselage) which need longer to fill the mold could benefit from such a long initiation period. Interestingly, this catalyst is like 4.13 also very potent at 60 000 equiv of DCPD, reaching a temperature of 160 °C at 465 s.

It is interesting to note that the maximum temperature for the polymerization of 60 000 equiv of DCPD is established somewhat later than for 30 000 equiv but the time frames are still comparable. For the other catalysts the $t_{T_{\text{MAX}}}$ for 60 000 equiv of DCPD is much longer than for 30 000 equiv.

Figure 4.27: Catalyst 4.16; 30 000 equiv DCPD (and one entry of 60 000 equiv).
The above mentioned lack of stability of the methyl Schiff base catalyst 4.17 is also expressed in the polymerization of 30 000 equiv of DCPD. This is the only second generation Schiff base catalyst which just results in a gelated polymer when 30 000 equiv are used. The optimum of HCl was established at 10 equiv, where a maximum of 80 °C was reached. However, for 4.17 this amount of acid hampers efficient mixing which is displayed by the lack of initiation period.

![Figure 4.28: Catalyst 4.17; 30 000 equiv DCPD.](image)

The sterically encumbered catalysts 4.14 and 4.18 need very small amounts of acid to activate, since these catalysts already show good activity without activation (see COD polymerization). For the polymerization of 30 000 equiv of DCPD 4.18 shows the biggest exotherm (179 °C at 122 s) for 3 equiv of HCl. PhSiCl$_3$ is also a potent activator but only 163 °C was reached as maximum temperature. The combination of PhSiCl$_3$ with 1-propanol was also investigated, as it produces HCl in situ. The addition of 1-propanol to the PhSiCl$_3$ results in an increase of the temperature to 171 °C.

Also, the activation of 4.18 using a weak acid was monitored. An optimum at 20 equiv of acid was reached for acetic acid, wherefore the polymerization mixture reaches a temperature of 114 °C. This is still very low compared to the addition of HCl or PhSiCl$_3$. However, a side reaction is possible in this activation method. Generally HCl activation can either protonate the imine or facilitate the decoordination of the Schiff base by cleavage of the Ru-O bond. In the latter, the classical second generation catalyst active species is formed, which should propagate fast. In this second activation mechanism, the introduction of acetic acid will produce a new catalyst with a Ru-OC(O)Et bond which shows different activity than the classical second generation catalyst. The results we obtained are in agreement with this activation through the cleavage of the Ru-O bond.

At 60 000 equiv of DCPD to 4.18, the polymerization shows a maximum temperature of only 71 °C (350 s).
Catalyst **4.14** is the only Schiff base catalyst which shows a clear exotherm in the polymerization of 30 000 equiv of DCPD without any activation. This is clear evidence that the Schiff base fragment can be tuned to obtain special initiation characteristics. The $T_{\text{MAX}}$ without activation is 146 °C at 480 s. The activation with HCl shows an optimum at 1-2 equiv of HCl, for which a temperature of 188 °C is obtained after 86 s. The decrease of the acid concentration (0.4 equiv) establishes a longer initiation period with a relative small $T_{\text{MAX}}$ decrease (7 °C).

The polymerization of 60 000 equiv of DCPD shows a maximum at 134 °C which is relatively high. Only **4.13** and **4.16** are able to produce similar results at this low catalyst ratio.
These results clearly show that the Schiff base catalysts of type 4.1B are found efficient for the polymerization of up to 30 000 equiv of DCPD when activated with acid. The optimum of acid concentration is different for each catalyst, as is the induction period and the maximum temperature achieved. Catalyst 4.15 is considered to be the best performing catalyst of the ones investigated, since this catalyst reaches the highest temperature (198 °C) with a clear initiation period (10-20 s) and a fast polymerization. Surprisingly, this catalyst shows bad characteristics for the polymerization of 60 000 equiv of DCPD. Apparently, the polymerization of 60 000 equiv shows even greater demands on the stability (TON) vs. speed (TOF). It is interesting to note that the instability of 4.17 is reflected in the DCPD polymerization, since this is the only catalyst which just reaches gelated polymers without any high temperature boost.

There also appears to be a double activation present. The acid activates the catalyst at room temperature, but when a temperature of 85-105 °C is reached an additional acceleration is present. Often, the temperature boost is proceeded by a decrease in temperature rise. The boost is only not visible with 4.14 (when activated) and with 4.15. These catalysts show very fast polymerizations, so the boost can easily be masked since both catalysts also show no retardation.

The retardation and boost are present in the polymerization using 4.14 without acid. Hence we suggest that both phenomena are not related to the acid. Yet, the phenomena can not be easily pinpointed to a physical process.

Possibly a reorganization of the catalyst or a change in catalyst transport (viscosity) could be responsible for this. In this context, it should be noted that the $T_g$ of linear poly-DCPD is 53 °C and that the decrease of temperature rise could be associated to a similar process with the non-linear DCPD in our system.

Moreover, linear poly-DCPD has been shown to crosslink in a thermally induced polymerization at 150 °C. This is also the reason why it is important to achieve high temperatures in the DCPD polymerization, so that additional cross-linking can be achieved.

The polymerization of 60 000 equiv of DCPD is only efficient with 4.13, 4.14 and 4.16. It is impossible to connect this to some stereoelectronic properties, since these three catalysts are very different; a classical catalyst without a nitro group (4.13), the most sterical catalyst (4.14) and the pentafluorophenyl catalyst (4.16), which both have a nitro group on the bidentate ligand.

In conclusion, it is evident that the Schiff base catalysts are very suitable for the polymerization of 30 000 equiv of DCPD. They all show a very distinct profile, with a different optimum of acid activator quantity for each catalyst. The steric catalysts need the least activation, but this is the only structure-activity relation which can be obtained form these results. Moreover, only three catalysts (4.13, 4.14 and 4.16) are efficient for the polymerization of 60 000 equiv of DCPD.

**4.3.4 RCM of DEDAM with catalysts 4.1B in aprotic solvents**

As stated before, RCM is the most widely used technique to evaluate the metathesis activity of a catalyst. Moreover, the high cost of Ru will reduce the applications in polymer science, but high added value in pharmaceuticals or chemical research (RCM and CM) could still justify the use of expensive catalysts.

However, most of the data published involve a relatively high catalyst loading of 5 mol% in purified CD$_2$Cl$_2$. Unfortunately, in these tests *increased activity* of a catalyst is then assigned to a *faster initiating* species and faster reaction. No information on the longlivety of the catalyst by TON
determination is possible since only 20 equiv of substrate is used and all catalysts comfortly perform the metathesis of 20 equiv of easily convertible substrates. The most common monomers used for the reaction are N-tosyl-diallylamine (NTDAА), DEDAM (diethyl diallylmalonate), monosubstituted-DDEAM (4,4-dicarbethoxy-2-methyl-1,6-heptadiene; DEDAM-1) and disubstituted DEDAM (4,4-dicarbethoxy-1,2-dimethyl-1,6-heptadiene; DEDAM-2). NTDAA and DEDAM are easily convertible monomers (and most common in use) while the increasing steric bulk in DEDAM-1 and DEDAM-2 hinders the ring-closing substantially, e.g. DEDAM-2 can only be ring-closed by the second generation catalyst 1.4 and not by the phosphine substituted catalyst 1.3.

![Monomers](image)

**Figure 4.31:** Most used monomers in RCM test reactions.

Frequently, a complete series of monomers are screened by organ(ometal)ic chemists, affording rings with different sizes. We chose not to screen a whole library due to the time-consuming effect and because we prefer to focus on the catalysts and not on RCM in particular. Moreover, the RCM of DEDAM was screened at 0.5 mol% instead of the widely used 5 mol%, since the latter custom can provide only marginal information on the catalyst decomposition.

![Conversion vs Time](image)

**Figure 4.32:** RCM of DEDAM with 4.1B in CDCl₃ at 40 °C; 0.5 mol% catalyst.

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VI This can also be achieved more easily when GC-MS is very easy accessible.
Most of the catalysts show very slow initiation. Only the sterically activated catalysts 4.14 and 4.18 show relative fast reaction. Unfortunately, the fastest initiating catalyst 4.14 had almost decomposed completely after 2 hours reaction. It is also interesting to note that 4.17 shows absolutely no activity which can be ascribed to the extremely low stability of the methyldiene species in this case. Activation of 4.16 with PhSiCl₃ yields an increase in activity compared to the non-activated catalyst. It is interesting to note that for example catalyst 4.8 shows only 2 % conversion after 120 hours reaction, while ¹H NMR still shows a very high resonance of the α-benzylidene proton of the unreacted initiator. Grubbs et al. proposed a standard activation determination test for DEDAM at 30 °C, but these results show that a specific catalyst needs specific reaction conditions, and that the temperature of 40 °C is even too low to measure the reactivity of most of the Schiff base complexes. In a next set of experiments, the activity of the catalyst was measured in toluene at 100 °C at 0.01 mol% of catalyst. Unfortunately, most catalysts show bad conversion, especially compared to the results obtained with the classical Grubbs catalyst under the same reaction conditions. Only 4.13 shows unexpectedly a high conversion of 68 %. Note that 4.13 also shows good characteristics for the polymerization of DCPD both at 30 000 and 60 000 equiv.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>1</td>
<td>4.15</td>
<td>5</td>
</tr>
<tr>
<td>4.9</td>
<td>1</td>
<td>4.16</td>
<td>1</td>
</tr>
<tr>
<td>4.10</td>
<td>1</td>
<td>4.18</td>
<td>11</td>
</tr>
<tr>
<td>4.13</td>
<td>68</td>
<td>4.19</td>
<td>8</td>
</tr>
<tr>
<td>4.14</td>
<td>4</td>
<td>1.4</td>
<td>74</td>
</tr>
</tbody>
</table>

In summary, it can be stated that the Schiff base catalysts 4.1B perform poorly for the RCM of DEDAM under standard conditions and at elevated temperatures. Sterical activation of the catalyst enhances fast initiation but is concomitant with a faster deactivation of the catalyst. Moreover, this reaction confirms the high instability of catalyst 4.17.

### 4.3.5 RCM of DEDAM-2 with catalysts 4.1B

DEDAM-2 has been shown to be the most challenging substrate for RCM with Grubbs type catalysts due its high steric nature. This leads to TONs in RCM nowhere near commercial applicable requirements. Grubbs et al. published on the standard system of characterization for olefin metathesis catalysts. All standard tests (RCM, CM and ROMP of several monomers) concern kinetic data where the same TON is obtained for all catalysts, except the test for the RCM of DEDAM-2. DEDAM-2 is applied in a reaction using 5 mol % of catalyst in CD₂Cl₂ at 30°C. The conversion is determined after 4 days. As an illustration of the poor conversions obtained, a table is added with the conversions for the several catalysts. The catalysts tested were the standard first generation catalyst (1.3), the first generation Hoveyda catalyst (1.35), the standard second generation catalyst (1.4), the second generation Hoveyda catalyst (1.36), the IMES substituted second generation catalyst (3.5), the second generation pyridine catalyst (4.12) and the second generation catalyst (4.20A) substituted with H₃IPr (1.7).
Table 4.4: RCM of DEDAM-2 in CD$_2$Cl$_2$ at 30°C after 4 days using 5 mol% catalyst. (Data from$^{27}$)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.36</td>
<td>6</td>
<td>1.2</td>
</tr>
<tr>
<td>4.20A</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>1.4</td>
<td>17</td>
<td>3.4</td>
</tr>
<tr>
<td>3.5</td>
<td>31</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The first generation catalysts show no activity towards DEDAM-2. Even the standard second generation catalyst 1.4 only shows 17 % conversion after 4 days, which represents a TON of 3.4!! The best performing catalyst tested is 3.5, which still only reaches the very poor TON of 6.2. It should be concluded that all these catalysts show disastrous activity for sterically encumbered substrates, which Grubbs et al. translate more elegantly into ‘Given the long reaction times and poor yields, this reaction represents a major challenge for the design of new, more efficient catalysts in the future.’$^{27}$

Initial attempts to use this substrate with catalysts 4.1B were unsuccessful. However, catalysts 4.1B show a slow initiation and strong stability towards high temperatures. Moreover, DEDAM-2 is a difficult monomer to initiate. Therefore, the reaction was performed at 100 °C and monitored over a long period of time. Only the stable catalysts were tested for this reaction, due to the high temperatures and long reaction times which had to be enforced. The data obtained are presented in Table 4.5.

Table 4.5: RCM of DEDAM-2 at 100 °C in toluene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst loading (mol%)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>4.8</td>
<td>0.5</td>
<td>40</td>
<td>22</td>
<td>44</td>
</tr>
<tr>
<td>4.9</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>4.9</td>
<td>0.5</td>
<td>40</td>
<td>32</td>
<td>64</td>
</tr>
<tr>
<td>4.10</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>4.10</td>
<td>0.5</td>
<td>40</td>
<td>68</td>
<td>136</td>
</tr>
<tr>
<td>4.13</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>4.13</td>
<td>0.5</td>
<td>40</td>
<td>55</td>
<td>110</td>
</tr>
<tr>
<td>4.15</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>4.15</td>
<td>0.5</td>
<td>40</td>
<td>35</td>
<td>70</td>
</tr>
<tr>
<td>4.16</td>
<td>5</td>
<td>15</td>
<td>78</td>
<td>15.6</td>
</tr>
<tr>
<td>4.16</td>
<td>0.5</td>
<td>40</td>
<td>18.3</td>
<td>36.6</td>
</tr>
<tr>
<td>4.19</td>
<td>5</td>
<td>15</td>
<td>87</td>
<td>17.4</td>
</tr>
<tr>
<td>1.4</td>
<td>5</td>
<td>15</td>
<td>33</td>
<td>6.6</td>
</tr>
</tbody>
</table>

At first, the catalysts were tested at a 5 mol% catalyst loading. Under these conditions, 4.8-4.10, 4.13 and 4.15 achieve full conversion. 4.19 only reaches 87 % conversion and 4.16 yields 78% conversion. However, 4.16 still shows signals of the initiator α-benzylidene proton after this long period of reaction, as do both 4.10 and 4.13. 1.4 shows a conversion of 33% under the same circumstances, which is considerably lower than all Schiff base catalysts. We do note that this is almost double the
value than under ‘the standard testing’ method which certainly doesn’t imply optimal reaction conditions for that method.

Since full conversions were obtained for most catalysts, the tests were repeated under 0.5 mol% of catalyst loading. 4.10 shows an exceptional conversion of 68% corresponding to a TON of 136. 4.13 also performs well with a TON of 110. These results are very extraordinary: **The incorporation of the Schiff base in 1.4 to 4.10 results into more than a 20-fold increase of the TON.**

Recently, a publication of Schrodi et al. (Materia) have shown that complex 4.20B is able to obtain a TON of 38 in the RCM of DEDAM-2.37 Although the performance of the phosphine analogue is much poorer. Our and Schrodi’s results clearly show that the presence of phosphines for the RCM of DEDAM-2 leads to deactivation of the catalyst. Moreover, a valuable alternative to 4.10 would be to substitute H2IMES with the NHC ligand from 4.20B.

![Figure 4.33: Alternative catalyst for the RCM of DEDAM-2.](image)

Schiff base catalysts tend to initiate slowly, but then propagate fast. Because of this, it was until this point not possible to in situ detect the propagating carbene species, as this carbene is always present in a very low ratio. However, when 4.10 was used in 5 mol% to DEDAM-2, also a second carbene resonance besides the initiator carbene was detected after 12h reaction at 100°C. This detection of a carbene proton in 1H NMR at 18.16 ppm is to be assigned to the methyldene species, which is an intermediate in RCM.

![Figure 4.34: In situ generation of a new carbene peak. RCM of DEDAM-2 with 5 mol% of catalyst 4.10, 15 hours of reaction, 100°C in toluene. 1H NMR in CDCl3 after evaporation of the solvent.](image)

In conclusion, the Schiff base catalysts 4.1B and especially 4.10, are an excellent answer to ‘a major challenge for the design of new, more efficient catalysts in the future’37 for the RCM of sterically encumbered substrates such as DEDAM-2 with Grubbs type catalysts. 4.10 shows more than
a 20-fold increase of TON-based activity than the standard second generation catalyst 1.4. Therefore, this should be considered one of the greatest benefits that catalysts of type 4.1B can offer.

4.3.6 RCM with catalysts 4.1B in methanol

It is interesting to expand the scope of catalysts to environmentally more friendly solvents, such as methanol or water. Due to price issues, the testing of catalysts is more preferable in CD$_3$OD than in CD$_3$CD$_2$OD, although ethanol is also an excellent candidate as a green solvent.

The Grubbs catalysts, which are well-known for their high functional group tolerance, only show relatively low stability in these protic solvents.$^{38}$ This has led to the extensive research on efficient adaptations of the Grubbs catalyst to obtain an applicable Grubbs type catalyst for the use in green solvents.$^{14,39,40}$

Grubbs et al. concentrated on the variation of the H$_2$IMES ligand on catalysts 1.82 and 1.83 to increase their solubility in protic solvents.$^{39,40}$ 1.82 converts 40% of DEDAM using a 5 mol% catalyst ratio in MeOH-$d_4$ and polymerizes 30 equiv of endo-4.22 in D$_2$O.$^{39}$ 1.83 shows to be effective for the RCM of amine salt substrates at a 5 mol% ratio and the polymerization of 30 equiv of endo-4.22 in D$_2$O.$^{40}$ During our experiments with catalysts of type 4.1B in methanol, Raines et al. published on the RCM of various substrates in methanol and water with catalysts 4.8 and 4.21.$^{14}$ Conversions of $>$ 95% were obtained for the RCM of DEDAM in methanol-$d_4$ and up to 36% in 2:1 CD$_3$OD:D$_2$O mixtures at 5 mol% substrate ratios.$^{14}$

All RCM reactions in these articles were at best performed at a 20 equiv of substrate ratio$^{14,39,40}$. In our experiments, the catalytic tests were performed at 200 equiv of substrate in order to obtain the higher TONs which are possible with catalysts 4.1B. Moreover, in contrast to all the previous reports of RCM in methanol, we monitored the catalysts throughout the reaction. Our catalysts 4.1B are not soluble in D$_2$O and therefore only methanol-solvated reactions were investigated. Moreover, due to the low solubility of the non-nitro substituted catalysts 4.9, 4.13 and 4.19, only 4.18 (which is the fastest catalyst in CD$_2$Cl$_2$) of this type was investigated for this reaction.
The catalysts show faster decomposition in CD$_3$OD than in CD$_2$Cl$_2$. The sterical demanding catalysts 4.14 and 4.18 decompose almost immediately. 4.18, the best performing catalyst in CD$_2$Cl$_2$, has almost completely decomposed after 15 minutes of reaction in MeOH-$_d4$. At that time, already 36.8 equiv of substrate has been converted. Unexpectedly, 4.15 shows relatively fast decomposition. The highly polar and soluble catalyst 4.16 initiates fast, although the conversion halts at 94%. After decoordination, the pentafluorophenyl group should be better stabilized in the more polar methanol. 4.10, which affords less than 20% conversion in CD$_2$Cl$_2$ after 70 hours, initiates faster but controllable in CD$_3$OD and over 95% conversion is obtained after 70 hours. Methanol, which is known as a catalyst destructor, behaves as a catalyst initiator for 4.10. The TONs of the catalyst are impressive: The fast decomposing 4.18 reaches a TON of 36.8 after 15 minutes reaction compared to a previous maximum TON of 19 as the best ever reported. Moreover, the most efficient catalyst 4.10 reaches a TON of 190 with almost quantitative conversion. This shows the high efficiency of the Schiff base substitution in 4.10 (TON = 190) compared to the NHC modification in 1.82 (TON = 8).

In conclusion, it can be stated that stability and slow initiation is important for catalysts of type 4.1B to obtain high TONs for RCM in CD$_3$OD. Methanol proves to increase the initiation compared to dichloromethane as a solvent. Furthermore, 4.10 outperforms all former reported catalysts by a factor

**Figure 4.36**: RCM of DEDAM in MeOH-$_d4$ with 0.5 mol% of 4.1B at 50°C. Top: full RCM; bottom: first 4.5 hours.
10 in the RCM of DEDAM in methanol-\textsubscript{d$_4$}. This niche-reaction is again a very good example of how the substitution with a Schiff base can effect highly increased TONs for a reaction which requires high catalyst stability instead of a ‘highly active’ speedy reaction. This increased tolerance for protic solvents is also one of the greatest benefits the substitution of a Schiff base ligand can offer.

### 4.3.7 Polymerization with catalysts 4.1B in methanol

Encouraged by our RCM success in methanol, we were eager to extend this solvent tolerance to ROMP. Grubbs et al. already explored the ROMP of Grubbs catalysts in water, though no report has been made on the ROMP in methanol. Several monomers were screened though most of them did not show enough solubility in methanol or destroyed the Schiff base catalysts (which is quite remarkable for these stable catalysts) without polymerization.

![Figure 4.37: Monomer for polymerization in methanol.](image)

**Exo-4.23** was prepared and shows relative good solubility in MeOH. The resulting polymer, on the other hand, is completely insoluble in methanol. A compromise could be achieved by performing the polymerizations in 50:50 chloroform-\textsubscript{d$_1$}:methanol-\textsubscript{d$_4$} solutions. This enabled the monitoring of the polymerization in the presence of high amounts of methanol, which can be considered a mimic for substrates in RCM or ROMP that contain an alcohol function. Moreover, since a chloroform: methanol mixture was used, also 1.4 could be tested. 1.4 is at present the standard catalyst for olefin metathesis. Hence, a model reaction which can incorporate this catalyst shows a high added value.

![Figure 4.38: Polymerization of 50 equiv 4.23 in 50:50 chloroform-\textsubscript{d$_1$}:methanol-\textsubscript{d$_4$} at 50 °C.](image)
The polymerization of 50 equiv of 4.23 was monitored in a chloroform-\textit{d1}:methanol-\textit{d4} solution. The polymerization data reveal little of the catalyst stability. Only 4.14 shows insufficient stability to reach 100% conversion. The classical Schiff base catalysts 4.8-4.10 and 4.13 show the slowest rates. It is interesting to note that the classical second generation catalyst 1.4 performs well in the presence of methanol and reaches 100% conversion after 15 minutes. All catalysts show during the polymerization and at 100% conversion a 36.5±1 \textit{trans} content. The only exception is 4.18, which already shows 49 \% \textit{trans} double bonds after 15 minutes (first measurement; 100% conversion).

As for the polymerization of COD and CO (vide infra), also for this polymerization the catalyst activity can be monitored beyond 100% conversion through secondary metathesis events. During these secondary metathesis events, the polymerization mixture shifts to thermodynamical equilibrium, which in this case corresponds to the transformation of \textit{cis}-polymer into \textit{trans}-polymer. In order to assess the full activity of the catalyst, the \textit{cis}:\textit{trans} content was monitored until this ratio remained constant over half of the total polymerization-isomerization time. Using this guideline, it can be stated that 4.18 is the fastest catalyst for this reaction, with a reaction rate far beyond that of 1.4.

However, as hydride formation with Grubbs catalysts (not incorporated with Schiff bases) in alcohols is a well documented phenomenon\textsuperscript{41,42} and such hydride catalysts are active in olefin-isomerization reactions, we were unable to pinpoint the full isomerization event to metathesis activity. Moreover, observation of active hydrides is very difficult since low concentrations can already show a big impact on the \textit{cis}:\textit{trans} content and the observation of the active carbene during the process has also shown unexpectedly to be very troublesome (vide infra).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Trans polymer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>4.9</td>
<td>24</td>
<td>39</td>
</tr>
<tr>
<td>4.10</td>
<td>96</td>
<td>41</td>
</tr>
<tr>
<td>4.13</td>
<td>24</td>
<td>39</td>
</tr>
<tr>
<td>4.14</td>
<td>0.25</td>
<td>36</td>
</tr>
<tr>
<td>4.15</td>
<td>4</td>
<td>42</td>
</tr>
<tr>
<td>4.16</td>
<td>22</td>
<td>42</td>
</tr>
<tr>
<td>4.18</td>
<td>0.25</td>
<td>49</td>
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<tr>
<td>4.19</td>
<td>24</td>
<td>41</td>
</tr>
<tr>
<td>1.4</td>
<td>24</td>
<td>47</td>
</tr>
</tbody>
</table>

Another interesting phenomenon was observed. Catalysts 4.9 and 4.13 show a very fast disappearance of the \textit{\alpha}-benzylidene proton signal in \textsuperscript{1}H NMR, although the polymerization continues and even secondary metathesis occurs. To investigate this, catalyst 4.9 was monitored in higher concentration (2.8 \times 10^6 \text{ mol in 500\mu l solvent}). Integration of the aliphatic and olefinic polymer protons in \textsuperscript{1}H NMR shows that no addition polymerization takes place.
Figure 4.39: Carbene peak for 4.9 after additional forcings; from left to right: a) in chloroform-\textit{d}_{1}: methanol-\textit{d}_{4}; b) 15 minutes at 50 °C; c) next, 5 equiv of 4.23 was added and the mixture was placed for 15 minutes at 50 °C; d) after an additional 2 hours at 50 °C.

As presented in Figure 4.39, the carbene peak disappears after additional forcings were applied. It should be noted that after 15 minutes exposure of 4.9 to 5 equiv of 4.23 (Figure 4.39 c), no polymerization was observed. Total polymerization was observed with 36\% trans content after the additional 2 hours of reaction. 76\% trans content was obtained after 24 hours reaction. Thus, the polymerization occurred after most of the carbene had disappeared in the $^1$H NMR spectrum. Moreover, the more troublesome secondary-metathesis-isomerization was facilitated after the disappearance of the $\alpha$-benzylidene proton resonance in $^1$H NMR. Yet, the initial trans content of 36\% proves that the polymer was produced by an NHC substituted second generation catalyst (vide infra and polymerization of 4.23 using 1.3 results in a cis:trans ratio of 47:53 throughout the total polymerization [to 100\%]).

One of the samples after 2 hours of degradation at 50 °C (Figure 4.39 d), was submitted to the RCM of 200 equiv of DEDAM to Ru, yielding 11\% conversion (TON = 22) after 17 hours reaction at 50 °C. That confirmed that the catalyst mixture was still active (more active than the normal catalyst in CD$_2$Cl$_2$) after the $\alpha$-benzylidene proton observance had disappeared in $^1$H NMR.

The disappearance of the $\alpha$-benzylidene proton resonance in $^1$H NMR could also be stimulated by the multiple resonances possible for the polymerization of a monomer like 4.23. The polymer can coordinate to the catalyst with one of the oxygens or backbite with the olefin bond. This would decrease the intensities since the propagating carbones show multiple conformations. Therefore, a test was performed without 4.23 in chloroform-\textit{d}: methanol-\textit{d}_{4} for 2 hours at 50 °C. This reaction showed approximately the same spectrum as for the similar experiment in the presence of 4.23.

Figure 4.40 shows the monitoring of the iso-propyl protons (of the Schiff base ligand) during the same reaction. The phenolic proton cannot be monitored since it is not visible in $^1$H NMR in CDCl$_3$:CD$_3$OD. Also the aromatic protons show no distinct pattern.
Figure 4.40: Methyl-isopropyl peaks for 4.9 after additional forcings; a) in chloroform-\textit{d}_1::methanol-\textit{d}_4; b) 15 minutes at 50 °C; c) after 5 equiv of 4.23 were added, additional 15 minute at 50 °C; d) additional 2 hours at 50 °C; e) additional 22 hours at 50 °C.

Four of the iso-propyl group methyl groups are present in the spectrum of 4.9 in chloroform-\textit{d}_1::methanol-\textit{d}_4 (Figure 4.40 a). The second doublet on the left (\(\delta = 1.19\) ppm) represents the decoordinated Schiff base ligand. When 4.9 was dissolved, 14 % of the Schiff base corresponds to decoordinated species and after the forcing of 2 hours at 50 °C in the presence of 5 equiv of 4.23 (Figure 4.40 d) 34 % of the Schiff base corresponds to the decoordinated species. However, at that point, the complete \(\alpha\)-benzylidene proton signal had disappeared in \(^1\text{H}\) NMR (vide supra), though the mixture still remained catalytically active for RCM. This indicated that a species with Schiff base and
without carbene (probably 14 e species) was formed which was still active for olefin metathesis. A new carbene would have to be formed in situ.\textsuperscript{vII}

Also an other possibility emerged: The \textsuperscript{1}H NMR signals of the Schiff base remained unchanged by this ‘disappearance of the carbene’ which indicated that the catalyst structure was intact. If this were true, the α-benzylidene proton should be masked. An exchange of the α-benzylidene proton with the deuterated solvent could be an easy explanation for such a phenomenon. Such an α-benzylidene-solvent proton-deuteron exchange is unprecedented, but then again also the in situ monitoring of α-benzylidene protons in methanol is unprecedented. To investigate this, we aimed to re-exchange the deuterated-benzylidene (after evaporation) in a CDCl\textsubscript{3}:CH\textsubscript{3}OH mixture. First, the mixture was degenerated during twice the time it took the α-benzylidene proton to disappear in the \textsuperscript{1}H NMR spectrum, whereupon the mixture was evaporated. Next, the resulting solid was redissolved in a small amount of CDCl\textsubscript{3} which caused, to our surprise, the reappearance of the α-benzylidene proton in \textsuperscript{1}H NMR.

This result indicated that the initial catalyst was chemically unchanged during the whole process even when the α-benzylidene proton disappeared in \textsuperscript{1}H NMR. \textit{Somehow}, through solvation with methanol, the α-benzylidene proton becomes masked in \textsuperscript{1}H NMR.

After 24 hours (Figure 4.40 e) no species that resembles the initial catalyst was detected. Most of the Schiff base had decoordinated and during the process a small amount of new species had been formed (0.62 ppm; 0.54 ppm; 0.22 ppm and one masked signal). Two samples of this mixture were subjected to metathesis investigation: the first to 50 equiv of 4.23 and the second to 200 equiv of DEDAM. The sample with 4.23 polymerizes to 100% conversion with 36% \textit{trans} content after 15 hours at 50°C. The sample with DEDAM shows no conversion after 15 hours at 50°C. The 36% \textit{trans} olefins of the poly-4.23 indicates that the NHC ligand is still present in this catalyst. Consequently, we suggest that it is difficult to assess the polymerizations of highly ring-strained monomers like 4.23 to the original catalyst species, since decomposition products can also contribute seriously to the polymerization when the reaction times are considerably long. The same reasoning should also hold for 4.22, which was polymerized by Grubbs et al.\textsuperscript{39}

1) Initial \textit{cis:trans} ratio =>
H\textsubscript{2}IMES is still present

2) Isopropyl protons =>
Schiff base decoordinated

3) No alfa-carbene proton =>
No carbene present?

\[
\begin{array}{c}
\text{H}_2\text{IMES} \\
\text{Ru}
\end{array}
\] DEDAM 4.23

\textit{no in situ carbene formation}
\textit{in situ carbene formation due to highly ring strained monomer}

\textbf{Figure 4.41A:} Schematic representation of the degradation process of 4.9 in CDCl\textsubscript{3}:CD\textsubscript{3}COD and the regeneration of a carbene in the presence of 4.23.

The general mechanism for a carbene generation form an olefin and a metal is presented in Figure 4.41B.\textsuperscript{43} In fact it represents the \textit{retro-deactivation} based on the deactivation mechanism proposed by van Rensgurg et al.\textsuperscript{44}

\textsuperscript{vII} The transformation into a carbene showing no α-carbene proton was improbable due to the reaction mixture.
The influence of the changes in the Schiff base ligand for catalysts of type 4.1B was evaluated. The introduction of a sterical Schiff base in 4.14 and 4.18 is very effective in speeding up the catalyst to levels of the classical second generation catalyst 1.4. This acceleration is concomitant with loss of extra stability and these catalysts show difficulties to outperform 1.4 in activity. However, 4.18 is at least as effective as 1.4 for RCM and ROMP in the presence of methanol.

The installation of the non-sterical Schiff base in 4.17 is ineffective since catalyst integrity is seriously compromised without any compensation in activity. Most probably, the carbene in 4.17 is no longer shielded by the Schiff base fragment and is consequently easily available for attacks. Unfortunately, no structure-reactivity relation can be established through the obtained crystal structures.

The classical Schiff base catalysts show the best characteristics. Although these show negligible activity under the standard tests proposed by Grubbs et al.\textsuperscript{27}, their benefits are numerous. They can be stored together with monomers without any concomitant polymerizations, and polymerized when needed. This activation can be established either by a simple temperature rise or by acid activators. The polymerization of DCPD at very low catalyst loadings using these methods is one of the most important practical applications for metathesis catalysts. All catalysts need a different amount of acid for the activation. In this context, it is interesting to note that 4.13, 4.14 and 4.16 should be recommended for the polymerization of 60 000 equiv of DCPD.

The Schiff base catalysts show big advantages for niche-domains in academic metathesis such as the use of sterical substrates and tolerance for alcohol functionalities in substrates or alcohols as solvents. Moreover, real-production systems for RCM do not generally show easy reaction conditions.
These niche-domains in academic science represent excellent methods to test the catalyst activity for these more straining conditions which may occur in commercial applications. More specific, the TON for RCM of DEDAM-2 with 4.10 is increased by a factor of 20 compared to the classical second generation catalyst 1.4. 4.10 also shows more than 10 times the TON compared to the best systems for the RCM of DEDAM in MeOH up to date.

For the first time, the ROMP of Grubbs catalysts in methanol was performed. Also, the regeneration of a carbene species was evidenced during this reaction. These results show that the Schiff base catalysts 4.1B show far superior activity for specific applications compared to their standard second generation catalyst 1.4, when these are used in the appropriate reaction conditions. The ‘standard system for characterization for olefin metathesis catalysts’ proposed by Grubbs et al. cannot provide these subtleties but is very efficient in showing the benefits of catalyst 1.4 under these standard reaction conditions.

### 4.4 Synthesis of a bimetallic catalyst

#### 4.4.1 Introduction

The synthesis and activity of the bimetallic catalysts 4.2 have been reported by our group in 2002. The catalysts were presented to be ‘the best combination of stability and activity known so far for this type of catalysts.’

We want to point out that all catalysts using two Ru atoms instead of one are the result of poor catalyst design from practical point of view since Ru is by far the biggest cost in the production of such catalysts. Yet, catalysts of type 4.2 represent a unique class of catalysts showing a nitrogen substituted complex as the active species. All other Grubbs type complexes show a phosphine or NHC substituted active species. Moreover, the excellent catalytic results obtained with these catalysts should then later spur developments in the monometallic catalysts with a Schiff base coordinated active species.

![Nitrogen coordinated active species in the bimetallic catalysts 4.2.](image-url)
4.4.2 Synthesis

At first, a species we thought was 4.2, was synthesized using the protocol shown in Figure 4.42 (vide infra) and provided at Dr. Dieltiens for pyrrole synthesis\(^5\). However, now we have to revise the final structure of the compound investigated. For the synthesis of compounds 4.2, 4.24 was taken as model complex, since with this standard Schiff base most crystals of carbene complexes are available. This makes it possible to perform a crystal structure comparison.

Unfortunately, the synthesis of 4.24 proved to be troublesome. The article\(^3\) reporting on its synthesis describes 2 different practical procedures. The published procedure consists of a reaction in toluene or benzene at room temperature followed by washing with benzene, which is similar to the procedure of Grubbs et al.\(^{45}\) However, mixing both compounds in toluene of benzene at room temperature yields no reaction, which is evidenced through monitoring by \(^{31}\)P NMR. In order to obtain new products we adapted the procedure, refluxing the reagents in THF.\(^VIII\)

\[
\begin{align*}
\text{RuCl} & \text{CH} & \text{Cl} \\
\text{Ph} & \text{O} & \text{N} \\
\text{PCy} & \text{3} \\
\text{RuCl} & \text{O} & \text{Ph} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{RuCl} + \\
\text{4h, reflux} & \text{THF} \\
\end{align*}
\]

Figure 4.43: Proposed synthesis of 4.24.

The synthesis was monitored by \(^{31}\)P NMR and was completed after 4 hours. At that point, the phosphorous resonance has shifted 4~5 ppm upfield\(^IX\). The reaction was also followed by \(^1\)H NMR (Figure 4.44). Complex 4.10A shows a \(^1\)H NMR resonance at \(\delta = 19.77\) ppm as reported by Grubbs et al.\(^1\) The new complex shows a \(^1\)H NMR resonance upfield at \(\delta = 19.63\) ppm. The previously reported complex 4.24 shows a resonance in \(^1\)H NMR at \(\delta = 19.81\) ppm, a shift downfield to the mother complex.

\[^{VIII}\] Synthesis in benzene at room temperature shows no conversion after 7 hours, after refluxing the mixture for 7 hours, only partial reaction was obtained.

\[^{IX}\] No internal standard was used, so the absolute values shift.
Schiff base Grubbs catalysts

Figure 4.44: $^1$H NMR spectra during the reaction of 4.10A with [Ru(p-cymene)Cl$_2$]$_2$: a) reaction in progress; b) final product.

The signal in $^1$H NMR for the carbene proton for the new compound and previously reported complex appears as a doublet. This is in accordance to the doublet reported by Grubbs et al. for the PCy$_3$ substituted catalyst 1.97.$^{45}$ Herrmann et al. reported a singlet for the NHC substituted bimetallic catalyst 1.98.$^{46,47}$ The doublet in Grubbs catalysts stems from a coupling of the benzylidene proton with the phosphor, in case of non-orthogonality between the Ru-P bond and the benzylidene plane.$^{45}$ A similar coupling cannot occur for complex 4.24, since $^{14}$N is not an NMR active nucleus. A singlet should be observed similar to the report by Herrmann et al.$^{46}$

Figure 4.45: $\alpha$-carbene proton coupling in $^1$H NMR.

During our first synthetic attempts, several purification steps were undertaken. Upon recrystallizations, the resonance in the $^{31}$P NMR remained, the complex decomposed upon performing column
chromatography and no crystals could be obtained. Previous reports of De Clercq et al. stated that ‘Although we have purified the bimetallic catalytic systems (see experimental section), it should be mentioned that the stoichiometrically generated piano-stool-type complexes [Ru(p-cymene)PCy$_3$Cl$_2$] (see scheme 1) do not affect catalyst activity and, in fact, do not need to be separated for routine usage.’ Yet, upon analyzing the NMR data in more detail, we found it necessary to assign the $^{31}$P NMR peak at $\delta = 48.9$ ppm. NMR data on 4.25 could not be obtained easily from literature, so 4.25 was synthesized and shows a $^{31}$P NMR resonance at $\delta = 26.4$ ppm and not at 48.9 ppm. This further evidences that the previously suggested mechanism$^3$ (Figure 4.42) is not correct since 4.25 is not formed during the reaction.

The coupling constant for the carbene proton in our obtained product is $J_{HP} = 9.9$ Hz while Grubbs et al. reported a coupling constant for the PCy$_3$ substituted bimetallic catalyst of $J_{HP} = 10$ Hz in 1.97. Moreover, the $^{31}$P NMR for 1.97 shows a resonance at 48.7 ppm. These data suggest that the newly synthesized complex should structurally be very similar to 1.97.

An explanation was sought from mechanistical viewpoint. 4.10A initiates in metathesis either by dissociation of phosphine or dissociation of the Schiff base nitrogen, whereupon olefin addition occurs. De Clercq et al. made an elaborate exposition on why 4.10A should initiate by nitrogen dissociation.$^3$ Furthermore, Jensen et al. presented calculations on 4.10A, which show that the nitrogen shows a bond dissociation enthalpy 10 kcal/mol lower than PCy$_3$. Moreover, our reinvestigation of the complex begun after significant evidence was found from initial polymerization fingerprints in the ROMP of CO and COD that both 4.10A and the new complex synthesized show the profile of a PCy$_3$ substituted active species (vide infra). Hence, a nitrogen dissociation mechanism is to be expected for 4.10A.

The substitution of [Ru(p-cymene)Cl$_2$]$_2$ to 4.10A should be accomplished in a similar fashion as the olefin substitution. Therefore, [Ru(p-cymene)Cl$_2$]$_2$ should react with the nitrogen dissociated active species as presented in Figure 4.46.

![Figure 4.46: Synthesis an mechanism for formation of trimetallic catalyst 4.26](image)

The $^{31}$P NMR similarities between 1.97 and 4.26 are described above. In addition, 4.26 shows substantial structural similarity with 4.27. 4.27 represents a part of 4.26 where the only difference is one oxygen substituent instead of a chlorine. 1.97 represents the other part of the puzzle, though here
the oxygen is replaced by a chlorine ligand. The resemblance of the $^1$H NMR data of these three complexes leaves little to the imagination. All the $^1$H NMR peaks of 4.27 can be found in the spectrum obtained from 4.26. The correspondence of 1.97 with 4.26 is somewhat less straightforward, although the comparison of the $^1$H NMR of 1.97 adequately complements the rest of the $^1$H NMR spectrum of 4.26. The doublet, which is observed for the α-benzylidene proton is also compatible with the structure of 4.26.

![Structural similarities of 4.26 with 4.27 and 1.97.](image)

**Figure 4.47:** Structural similarities of 4.26 with 4.27 and 1.97.

**Table 4.7:** Comparison of $^1$H NMR data (δ in ppm) of 4.26 with 1.97 and 4.27.

<table>
<thead>
<tr>
<th></th>
<th>1.97 (a)</th>
<th>4.26</th>
<th>4.27 (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.58 (d)</td>
<td>19.65 (d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.47 (d, 2H)</td>
<td>8.53 (d, 2H)</td>
<td>8.03 (dd, 1H)</td>
<td>8.02 (dd, 1H)</td>
</tr>
<tr>
<td>7.92 (d, 1H)</td>
<td>7.91 (d, 1H)</td>
<td>7.76 (t, 1H)</td>
<td>7.72 (t, 1H)</td>
</tr>
<tr>
<td>7.45 (t, 2H)</td>
<td>7.45 (t, 2H)</td>
<td>7.55 (s, 1H)</td>
<td>7.55 (s, 1H)</td>
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<tr>
<td>5.57 (d, 1H)</td>
<td>5.55 (1H)</td>
<td>5.46 (1 H)</td>
<td>5.46 (d, 1H)</td>
</tr>
<tr>
<td>5.41 (d, 1H)</td>
<td>5.35 (t, 2H)</td>
<td>5.33 (d, 1H)</td>
<td></td>
</tr>
<tr>
<td>5.28 (d, 1H)</td>
<td>5.27 (d,1H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.17 (d, 1H)</td>
<td>5.16 (d, 1H)</td>
<td>5.00 (d, 1H)</td>
<td>5.00 (d, 1H)</td>
</tr>
<tr>
<td>4.27 (d, 1H)</td>
<td>4.28 (d, 1H)</td>
<td>4.03 (sept, 1H)</td>
<td>4.02 (sept, 1H)</td>
</tr>
<tr>
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<td>3.12 (sept, 1H)</td>
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<td></td>
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<td>2.91 (sept, 1H)</td>
<td>2.95 (sept, 1H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.79 (sept, 1H)</td>
<td>2.79 (sept, 1H)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) data from $^{35}$ (performed in CD$_2$Cl$_2$); (b) data obtained from Hans Van der Mierde (unpublished results; PhD in progress).

Despite these unsuccessful attempts, we were still interested in the synthesis of 4.24. The application of a longer synthesis period was unsuccessful. In an attempt to synthesize 4.24, 0.5 equiv of [Ru(p-
cymene)Cl₂, was added to 1 equiv of 4.10A in THF, and the resulting mixture was refluxed for 16 hours. A dark-ocher powder was obtained which to our surprise showed no carbene in ¹H NMR. After performing column chromatography, NMR analysis of one of the products suggested it to be 4.27.

![Figure 4.48A: Alternative method for the preparation of the bimetallic catalyst 4.2 with result 4.27B.](image)

The formation of 4.27 in this decomposition process brought about additional uncertainty upon the catalyst structure 4.26. Since 4.27 is formed by a Ru-Cl, Ru-O exchange and exchanges of anionic ligands in Grubbs catalysts have been reported⁴⁸, the possibility emerged that 4.26 was not the correct structure, but instead the products were a mixture of 1.97 and 4.27, since both products precipitate in benzene-pentane solutions and NMR data resemble dangerously close. Grubbs et al. had performed ¹H NMR of 1.97 in CD₂Cl₂ (which we first had overlooked), so the resonances can fluctuate when a spectrum is performed in CDCl₃. 1.97 was synthesized and ¹H NMR was performed in CDCl₃ δ (ppm): 19.65 (d, 1H), 8.53 (d, 2H), 7.71 (t, 1H), 7.45 (t, 2H), 5.55 (d, 1H), 5.35 (d, 1H), 5.26 (d, 1H), 5.16 (d, 1H), 2.95 (sept, 1H), 2.20 (s, 3H), 2.05 (q, 3H), 1.83-1.17 (m, 36H).

![Figure 4.48B: Reorganization of 4.26 into 1.97 and 4.27.](image)

An additional experiment was performed using the same starting products, from which 4.27 was obtained as a pure precipitate and a mixture of 1.97 and 4.27 as filtrate. 4.27 appears as an ocher solid similar to the previously complex mixture. A possible reaction mechanism is depicted below. Yet, involvement of a trimetallic catalyst has not been evidenced by ¹H NMR of the reaction in process.
In summary, bimetallic catalysts of type 4.2 could not be prepared using the previously described synthesis. Adapting the synthesis led to the reaction of the starting products. Unfortunately, 4.2 was not the end product, but a Ru-Cl, Ru-O exchange resulted in the formation of 1.97 and 4.27. Catalyst kinetics suggest this occurs through decoordination of the Schiff base in 4.10A. Decoordination of the phosphine in 4.10A would result in direct formation of the bimetallic catalysts 4.24.

### 4.4.3 Catalytic data

The COD polymerization of 300 equiv with (1.97 + 4.27) can be obtained at room temperature. Under these conditions the trans % for t → all catalyst destroyed, is only 50% which is an expression of the limited stability of the catalyst (vide infra).

**Figure 4.48C:** Possible reaction mechanism for the formation of 1.97 and 4.27

**Figure 4.49:** ROMP of 300 equiv of COD with 1.97 + 4.27 at 23 °C.
The thermal monitoring of the polymerization of 30 000 equiv of DCDP with 1.97 + 4.27 in the presence of 20 equiv of HCl only shows a minimal temperature rise (24 °C → 27 °C). This further illustrates the inefficiency of 1.97.

The reaction of 200 equiv of DEDAM with 1.97 + 4.27 in CD$_2$Cl$_2$ at 40 °C reached 68 % conversion after 2 hours of reaction. After this, all the catalyst had decomposed.

In conclusion, 1.97 shows low to moderate activity for a Grubbs type catalyst and is prone to fast activation and fast destruction. The necessity for 2 Ru-atoms in one catalyst handicaps the catalyst for any practical application.

### 4.5 Secondary metathesis in ROMP: case study on COD and CO (cis-Cyclooctene)

#### 4.5.1 Introduction

In our initial screening (Figure 4.15, Table 4.2) of Schiff base catalysts for the ROMP of COD, the cis-trans ratio was not determined in situ. To mimic the NMR polymerization the 3-fold of monomer and a 3-fold of un-deuterated toluene (for economic reasons) was used and polymerization was performed at 90° for 25 hours. Thereupon, a sample of the product was taken to determine the PDI and cis-trans distribution.

In our second COD-polymerization tests (Figure 4.18), the cis-trans ratio was chosen to be analyzed in situ using $^{13}$C NMR. Furthermore, it was found possible to determine the polymerization conversion in situ using $^{13}$C NMR ($\delta$ (ppm)) by integrating the signals of poly-COD-cis (27.41), poly-COD-trans (32.74) and COD (28.18). Normally, $^{13}$C NMR is time consuming due to the high number of scans which have to be applied. However, due to the high concentration of repetitive units in the polymerization, $^{13}$C NMR spectra could be obtained in less than 2 minutes. For these reasons, the activity was sometimes measured with $^{13}$C NMR instead of $^1$H NMR. Upon doing this, the interesting feature was found that the cis-trans content of the polymer is highly dependent on the time of measurement, or better, the degree of polymerization.

Previous notions of similar phenomena were reported. Grubbs et al. argued in 2000 concerning 1.4 that ‘In general, $^1$H NMR spectroscopy indicated a predominantly (75-95%) trans-olefin microstructure in these polymers. As expected for an equilibrium-controlled polymerization in which chain transfer occurs, longer polymerization times resulted in higher trans-olefin values.’ which explains our observations. Furthermore, the authors suggested that the relatively high PDIs of the polymers and the gradually increasing trans percentage in them, indicates that secondary metathesis also occurs. Moreover, when 50 equiv of COD were polymerized by 1.4, less than 5% of the catalyst had initiated when full polymerization was obtained. Yet after 15 minutes, all the initial carbene had been transferred to propagating species through a chain transfer mechanism. Grubbs et al. reported in Science that 4.27 produces cyclic polymers with cyclooctene (CO). The polymers obtained show a PDI of 2.0. Cyclic polymers are obtained due to the lack of end groups in both catalyst and monomer. Grubbs et al. also mentioned that catalyst 3.5 produces linear polymers. However, it should be noted that technically the amount of linear polymer is limited to the amount of catalyst precursor (when no chain transfer reagent is used). In the same fashion as 4.27 cuts
(backbites) the polymer to produce a PDI of 2.0, 3.5 will cut the polymer into cyclic oligomers and linear polymer.

\[
\begin{align*}
&\text{4.27} \\
&\text{3.5}
\end{align*}
\]

**Figure 4.50:** Catalysts for cyclic and linear poly-CO and secondary metathesis on a CO polymer.

The next and last account on secondary metathesis with Grubbs catalysts is a paper of Fogg et al. who showed that RCM of rings of at least 6 atoms is accomplished in 2 steps.\(^{26}\) First, cyclooligomers are formed and in a second step the backbiting reaction affords the thermodynamical stable smaller rings.\(^{26}\) Only for DEDAM a direct formation of the product is observed.\(^{26}\)

### 4.5.2 Secondary metathesis path for COD with second generation Grubbs catalysts

Upon investigating our measurements, a remarkable observation was made. All catalysts of type 4.1B afford the same \textit{trans} percentage in polymer at the same polymer conversion. The \textit{trans} percentage can be determined more accurately at higher conversion rates due to the increase in the intensity of the concerning signals. Therefore, an arbitrary point for the comparison of the initial \textit{cis}:\textit{trans} ratio was taken at 50 % conversion. Since the secondary metathesis is a much slower process than the polymerization (vide infra), the cumulative secondary metathesis can be considered negligible at this point.

The Schiff base catalysts 4.1B are excellent candidates for the investigation of the \textit{cis}:\textit{trans} ratio during the polymerization since the catalysts are not active at room temperature for this polymerization. Hence, the polymerization can be performed at high temperatures while at specified times the polymer \textit{cis}:\textit{trans} ratio of the in situ polymerization can be determined by long \(^{13}\text{C} \) NMR measurements at room temperature. The same luxury is not present in the classical second generation catalyst 1.4 which is very active at room temperature and causes fast polymerization.

All catalysts 4.1B show an initial \textit{cis}:\textit{trans} ratio of \(~75:25\) (The \textit{trans} % only varies between 23-27 % from 40 % to 70 % conversion).\(^X\) This implies that the polymerization of COD is initially not stereoselective. Since only one double bond is opened of \textit{cis}-COD, a 75:25 \textit{cis}:\textit{trans} ratio represents the theoretical predicted non-selective polymerization. Upon 95 % polymerization of 300 equiv of COD only \(~31 \%\) \textit{trans} content is obtained. This is much lower than the \textit{trans} % values reported for the ROMP of COD with 1.4 by Grubbs et al. (75-95 %).\(^{32}\)

\(^X\) Since conversions below 40% showed to be very inaccurate, we decided not to use these data.
Figure 4.51: Initial secondary metathesis for the COD polymerization with catalysts 4.1B.

Further reaction leads slowly to a lower cis:trans ratio with a maximum of 84-85 % trans percentage. At this point, a slow decrease of the initial trans-peak can be observed. One new signal in the $^{13}$C NMR spectra ($\delta = 32.5$ ppm) appears near the initial trans resonance. As we assumed this was associated to trans olefin, the signal was integrated in the trans percentage. This is visualized in Figure 4.51 where the '90 % conversion time’ is taken arbitrary as end point of the polymerization (so the x-value at 2 is twice the time necessary to obtain 90% conversion), since determination of the exact time for the 100 % conversion is more difficult.

Figure 4.52: Secondary metathesis for the COD polymerization with catalysts 4.1B

The slow catalysts show excellent characteristics for the determination of the cis:trans ratio in the beginning of the reaction, while the faster catalysts prove to be more potent for the determination of the cis:trans isomerizations. To investigate the occurrence of the new peak in $^{13}$C NMR, the classical second generation Grubbs catalyst 1.4, which is a fast initiator, was chosen to react at room temperature. In this way, experiments were performed in the time range of 1 hour instead of weeks. 1.4 is less suitable for the evaluation of the cis:trans ratio on strict conversion-time as previously was
performed using catalysts 4.1B, since due to its initiation period, the determination of the starting point cannot be determined as accurately. Moreover, due to the fast polymerization, the low concentration of polymer and the limited scans in the $^{13}$C NMR spectra, the cis:trans ratios and conversions could not be obtained as accurate as for catalysts 4.1B.

**Figure 4.53:** Secondary metathesis of 100µl (300 equiv) COD in 500 µl CDCl$_3$ with 1.4.

As can be seen from Figure 4.53, the cis:trans ratio of the polymer shows the same shape in function of the conversion (~25 % trans at low conversion and 29 % trans at 91 % conversion) as the curve for the catalysts 4.1B. It should be noted that the first new signal fit for integration ($\delta = 32.5$ ppm) appears at a 79 % trans percentage (1.4 % new signal) and the new peak reaches a maximum at 5.4 % of the C$_4$H$_6$ mixture in this time-frame (for 100µl COD in 500µl CDCl$_3$). The new resonance in $^{13}$C NMR at $\delta = 32.50$ ppm is associated with another resonance at $\delta = 131.64$ ppm. Moreover, $^1$H NMR of the final product shows a new signal at 5.01 ppm, which has the same integration (among the olefinic protons) as the resonance at $\delta = 32.50$ ppm in the aliphatic carbon region. Upon screening SDBS$^{11}$, a possible match was found in trans,trans,trans-1,5,9-cyclododecatriene (t,t,t-CDT) with $^{13}$C NMR signals at $\delta = 32.34$ ppm and 131.43 ppm. The product was purchased and a complete match was found with our NMR data.

**Figure 4.54:** t,t,t-cyclododecatriene (t,t,t-CDT)

The literature was screened for relevant publications, however –initially- no relevant papers were found. Thereupon, focus was placed on whether the values obtained were the equilibrium values for the polymerization. Figure 4.55 shows the polymerization of 300 equiv (100µl monomer in 500µl CDCl$_3$) COD and 200 equiv of t,t,t-CDT (which corresponds to the same C$_4$H$_6$ amount). For both polymerizations the same product distributions were obtained at the end of the polymerization (5000

$^{11}$ [http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi](http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi): spectral database
min). This proves that equilibrium conditions were reached: trans-poly-COD: 79.4 %; cis-poly-COD: 14.7 %; t,t,t-CDT: 5.9 %. Figure 4.56 shows the equilibrium at 100 equiv COD (3µl in 500 µl CDCl₃) and an equal C₄H₆ amount of t,t,t-CDT. Here also, the polymerizations reach equilibrium values: trans-poly-COD: 61.0 %; cis-poly-COD: 11.5 %; t,t,t-CDT: 27.5 %. The trans percentage of the polymer fraction is in both cases 85 %. The theoretical cis:trans ratio in toluene at equilibrium for a poly-butadiene chain at 25°C is 17:83. The most important difference between the two polymerizations is that the t,t,t-CDT fraction sharply increases in the polymerization when a lower concentration of C₄H₆ units is used (5.9% → 27.5%).

In the 300 equiv polymerization of COD, a maximum of the cis-poly-COD concentration is observed at 64 % of the C₄H₆ mixture. At this point, the secondary metathesis consumes more cis-polymer than the amount of newly formed cis-polymer, which is created from the COD polymerization. The same maximum cannot be detected at 100 equiv of monomer, because the fast polymerization causes the first measurement to be beyond this maximum. The 100 equiv polymerization of COD shows an obvious maximum in the trans-poly-COD concentration due to the higher end value of t,t,t-CDT.

These data prove that 1.4 is a potent catalyst to transform 100 equiv and 300 equiv of COD into thermodynamical equilibrium. Moreover, 1.4 is also a potent catalyst for the ROMP of t,t,t-CDT, which is also transferred into thermodynamical equilibrium.

![Graph](image-url)

**Figure 4.55:** Polymerization of 0.088 g (300 equiv of COD; 200 equiv of CDT) of (C₄H₆)ₙ rings in 500 µl CDCl₃ using 1.4. Starting product in parentheses: (COD) of (CDT). Bottom: enlargement of the first 100 minutes.
Figure 4.56: Polymerization of 0.029g (100 equiv of COD; 67 equiv of CDT) of (C₄H₆)ₙ rings in 500 µl CDCl₃ using 1.4. Starting product in parentheses: (COD) of (CDT)

In summary, it can be stated that the second generation catalysts show no preference for the trans-orientation in the initial stage of the COD-polymerization. However, a secondary metathesis event transforms the polymer mixture into a polymer with high trans content. Moreover, when sufficient trans polymer has been produced by secondary metathesis, a tertiary metathesis event occurs, which transform trans-1,4-polybutadiene into t,t,t-CDT. The amount of this t,t,t-CDT in the thermodynamical equilibrium is dependant on the C₄H₆-fraction concentration. Moreover, t,t,t-CDT can also be polymerized with second generation Grubbs catalysts.

### 4.5.3 Determination of the equilibrium concentrations of t,t,t-CDT

In a next step, the t,t,t-CDT equilibrium ratio for lower concentrations of COD was investigated. The concentration of COD in 500 µl CDCl₃ was varied. For the lower concentrations, no accurate $^{13}$C NMR was possible, so the concentration of t,t,t-CDT was determined via $^1$H NMR. However, in this case no determination of the cis and trans orientation of the polymer was possible. The t,t,t-CDT percentage of the C₄H₆ mixture increases with lower concentrations of C₄H₆.
Figure 4.57: Percentage of t,t,t-CDT at equilibrium conditions for several concentrations of C₄H₆ in 500µl of CDCl₃. Metathesis performed with 1.4.

After doing this study, we came in contact with three publications of Thorn-Csányi et al. who describe the metathesis polymerization/depolymerization equilibrium of the 1,4-polybutadiene system (= poly-ROMP-COD) using Schrock catalysts.⁵¹⁻⁵³ Thorn-Csányi et al. state that ‘At a low feed concentration, the formation of small rings without ring strain is strongly preferred for entropical reasons in comparison to polymer chains’⁵¹ (Small rings are small rings compared to normal polymer size and refers 12, 16, 20 and 24 atom rings, respectively 3-6 unit rings). Our measurements between 0.044 g → 0.0035 g fall into the concentration profile of Thorn-Csányi et al.⁵¹ The authors investigated the concentrations for the 3 to 6 unit rings (the 2-unit ring COD was not investigated because it does not appear at equilibrium).⁵¹ The three-unit rings (12 atoms) hold 75% of the small ring fraction and more than 90% of the three-unit rings is represented by t,t,t-CDT.⁵¹

The Thorn-Csányi measurements were performed at 25°C while our experiments were conducted at 20°C. Hence, a small deviation may occur in the t,t,t-CDT concentration. The influence of the solvent toluene compared to chloroform is within the error margin of the measurements by Thorn-Csányi et al.⁵³ As can be seen in Figure 4.57, a small deviation of our values was obtained compared to the Thorn-Csányi measurements at low concentrations.
Grubbs et al. recently proposed standard tests for olefin metathesis catalysts\textsuperscript{27}, however, the obtained data show little information on the longlivety of the catalyst. At that concentration of $\text{C}_4\text{H}_6\text{n}$, the t,t,t-CDT equilibrium concentration should contain 30\% of the $\text{C}_4\text{H}_6$ mixture. Prolonged measurement of the polymerization mixture could extend the activity measurement throughout secondary and tertiary metathesis. Consequently, the deactivation process of the catalyst could be monitored more accurately.

4.5.4 Secondary metathesis in the 1,4-polybutadiene system using various catalysts

The examination of the initial cis:trans ratio of the polymers was extended to a broader range of catalysts. The catalysts with a phosphine in the active species (1.3, 4.10A and 1.97 + 4.26) show very similar initial cis:trans ratios. The initial cis:trans ratio (determined at 50\% conversion) for these catalysts is 27.5 \% compared to 25\% for the 2nd generation catalysts 1.4 and 4.1B. The catalysts with a phosphine in the active species are thus selective for a 55\% conversion into trans-bonds for the COD-polymerization. This only represents a small preference. Throughout the polymerization up to 100 \% conversion, the trans ratio in the polymers for the phosphine substituted catalysts remains \sim 3 \% higher than for the 2nd generation catalysts. This suggests that the relative rate for secondary metathesis-cis-trans-isomerization of the 1,4 polybutadiene chain (= poly-ROMP-COD polymer) and the primary metathesis of COD are similar for phosphine and NHC substituted active species.

Although in general, higher trans percentages in polymers are found for second generation catalysts, this does not stem from the actual polymerization of COD. The secondary metathesis and the higher stability of these catalysts beyond the end of the polymerization are responsible for these higher trans amounts, which are closer to thermodynamical equilibrium. Moreover, it should be noted that COD polymerizations with Grubbs type catalysts are sometimes described in literature to have trans percentages \leq 20 \% or \geq 90 \%, for which the former values do not correspond to the initial cis:trans ratio limits here determined and for which the latter are thermodynamical impossible.
Figure 4.59: Comparison of the initial trans percentage for the COD polymerization using the classical 1st generation catalyst 1.3, the Schiff base substituted 1st generation catalyst 4.10A, 1.97 + 4.27, the standard 2nd generation catalyst 1.4 and the Schiff base substituted 2nd generation catalysts 4.1B.

Also the complete development of the polymerization of 100 equiv of COD with 1.3 was monitored (Figure 4.59).\textsuperscript{XII} No detectable amount of CDT could be observed after 15 hours. Upon the addition of 3 extra portions of Grubbs 1st generation catalyst (in total 25 equiv COD to catalyst) 4 % of CDT was detected after all the catalyst had decomposed. However, the equilibrium concentration for 0.029 g of COD in 500 µl CDCl$_3$ is 27.5 %. Therefore, it can be stated that although the relative rate for secondary metathesis cis:trans-isomerization of the 1,4 polybutadiene chain and the primary metathesis of COD are similar for phosphine and NHC substituted active species, the formation of t,t,t-CDT is substantially hindered for phosphine substituted catalysts.

Figure 4.60: Polymerization of 0.029 g (100 equiv) of COD in 500 µl undegassed CDCl$_3$ with 1.3.

\textsuperscript{XII} The initial measurements are limited to very few scans which leads to increased errors in the data. This is illustrated by the trans\% of the polymer of ~30% in the beginning of the polymerization and 40% after 90% polymerization.
Since the transformation of the 1,4 polybutadiene chain into t,t,t-CDT with 1.3 is inefficient, the polymerization of t,t,t-CDT with 1.3 was investigated. The polymerization of 66 equiv of COD (0.029 g) in CDCl₃ does not result in any polymer after 10 hours reaction. The polymerization of 16.5 equiv of t,t,t-CDT (0.029 g) with 1.3 also does not afford polymerization after 4 hours. A huge initial carbene resonance at $\delta = 19.99$ ppm was still present and no propagating carbene species could be detected. After 15 hours, the mixture had reached 4% of polymer (TON = 0.66) while some carbene was still left (Note that paradoxically 1.3 is a much faster initiator than 1.4). At this point, an additional portion of 1.3 was added, which decreased the t,t,t-CDT to 8.25 equiv. After the polymerization had ended (50 hours) 35 % of polymer was formed (TON = 2.9).

When 4.10A and 1.97 + 4.27 were subjected to 33 equiv of t,t,t-CDT, the former lead to 0 % polymer and the latter to 4 % after all catalyst had decomposed. Hence, all catalysts with a phosphine active species are highly inefficient for the polymerization of t,t,t-CDT. However, 2nd generation catalysts are potent catalysts for t,t,t-transformations. T,t,t-CDT can thus be as considered a challenging monomer for ROMP, such as DEDAM-2 is a challenging substrate for RCM. The advantage of t,t,t-CDT over DEDAM-2 consists that it does not need to be synthesized since it is commercially available. The advantages of t,t,t-CDT over cis,cis-cycloocta-1,5-diene are that the product distinguishes between different types of catalysts, doesn’t smell as bad as COD (because it is a solid material) and does not need distillation or degassing before usage.

### 4.5.5 Secondary metathesis in the CO polymerization

Also CO (Cyclooctene) is a very widely used monomer for test reactions in ROMP. Since CO does not show a second olefin bond in the monomer which is not polymerized, the preference for a cis:trans orientation of the catalyst should be more expressed in the initial cis:trans distributions.

The initial $trans$-ratio for the phosphine-active-species-catalysts 1.3, 4.10A and (1.97 + 4.27) is ~36 %. The second generation catalysts show a $trans$ ratio of ~62 %, although the Schiff base substituted 4.10 shows a slightly lower $trans$ ratio than the classical second generation catalyst. With the phosphine-active-species-catalysts, the secondary metathesis event can be detected before the end of the CO polymerization. This is caused by the higher $cis$ ratio in the initially formed polymer and hence the increased difference between the initially formed polymer and the thermodynamical equilibrium.
The second generation catalysts show a trans preference while the phosphine-active-species-catalysts show a distinct cis preference. This is the opposite trend compared with the COD polymerization where the phosphine-active-species-catalysts show a small cis preference and where the second generation catalysts show no preference. Note that for the polymerization of 4.23, a small preference for the trans-configuration (53%) was found for the 1st generation catalysts and a distinct preference for the cis-configuration (64%) for the 2nd generation catalysts. Thus a catalyst can show either cis or trans preference, dependant on the monomer polymerized. This means that the thermodynamical equilibrium for the polymer cis:trans ratio is incapable of determining the initial cis:trans ratio of the polymer. Quite expectedly, the cis:trans ratio in the beginning is not thermodynamically, but kinetically controlled. Moreover, the specific catalyst-active-species interaction with the monomer leads to this specific ratio. Consequently, the active species leaves its fingerprint on the polymer in the beginning of the polymerization and from these data information on the active species can be collected through the observation of the polymer microstructure in the initial stages of the polymerization (vide supra; polymerization of 4.23).

From the collected data, a clear difference between two types of the examined catalysts can be observed: The NHC catalysts and the phosphine-active-species-catalysts 1.3, 4.10A and 1.97. For 4.10A this phosphine-active-species mechanism was not yet proved a certitude. However, only shear coincidence could lead the initial cis:trans ratios for the polymers of 4.10A to be the same as for 1.3 and 1.97. Hence, these data further support the claim that catalyst 4.10A performs metathesis through an active species 4.29 similar to the active species 4.28 of the classical first generation catalyst.
The *cis:trans* data also contain a paradoxical feature: The catalyst fingerprint on the polymer seems to be mostly determined by the ligand in *trans* position to the coordinated olefin and only minimally by the *cis*-coordinated chlorine or oxygen. Common sense would suspect the ligands closest to the substrate to determine the energy of the different conformations. However, the minimal differences between the polymer-microstructures obtained by the active species 4.28-4.29 and 4.31-4.32 separately suggest the opposite. Cavallo et al. have presented a study on the origin of enantioselectivity in the asymmetric Ru-catalyzed metathesis of olefins in which a communication of a chiral site through other groups to the catalytic centre was proposed. A computational analysis would also be necessary to provide an unambiguous reasoning for the absolute selectivities and the difference of selectivity observed for the similar substrates CO and COD.

**4.5.6 Conclusions**

The COD polymerization with Grubbs type catalysts shows some special features:

1. The polymerization of COD with Grubbs catalysts is quasi non-selective, but a slower secondary metathesis event enables the *cis:trans* ratio to establish thermodynamic equilibrium.
2. The activity measurement of the catalyst via the ROMP of COD to 100% conversion can lead to initiation kinetics with a normal polymerization observation. However, the catalytic activity measurement can be extended. The slower catalytically induced thermodynamical equilibration of the polymer can provide information on the longlivety of the catalyst.
3. A third event which takes place is the formation of t,t,t-CDT from *trans*-poly-COD. This event can even prolong the activity measurement of the experiment. Moreover, the t,t,t-CDT equilibrium concentration holds 30% of the C₄H₆ mixture in the standard polymerization of COD proposed by Grubbs et al.²⁷ The prolonged activity investigation can provide stability data combined with the kinetic initiation data.
4. This third event is only marginally present for catalysts which perform metathesis through a phosphine-substituted-active-species.
5. Although the relative rates of primary and secondary metathesis show no distinguishable difference between the phosphine and the NHC substituted active species, tertiary metathesis does, because it is negligible for the former.

T,t,t-CDT can easily be polymerized by second generation catalysts, while first generation catalysts only show negligible polymerization activity. The t,t,t-CDT polymerization can thus be used to
evaluate the potency of the active species of the catalyst and provide additional confirmation on the
structure of the active species. T,t,t-CDT can be tested for ROMP in the same fashion as DEDAM-2
acts as a challenging substrate in RCM, with the extra benefit that t,t,t-CDT is commercially available
while DEDAM-2 has to be synthesized. Moreover, t,t,t-CDT can be used as a more suitable alternative
for ROMP test reactions compared to COD since the former does not show the annoying smell of
COD and does not need distillation or degassing.

The initial cis:trans conformation of polymers from the ROMP of CO produced by Grubbs catalysts
shows a distinct fingerprint of the catalytic active species. This can help to determine the active
species of the catalysts used. By this, we have provided additional evidence that the active species of
catalysts of type 4.1A is substituted by a phosphine and not by a Schiff base.
Furthermore, it should be noted that unexpectedly the ligand trans to the coordinated olefin shows a
greater impact on the polymer microstructure than the ligands in cis-position.

References

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Chapter 5

Substitution of PCy$_3$ in the first generation Grubbs catalyst

5.1 Introduction

This research project consisted of enhancing the activity of Schiff base substituted Ru catalysts for olefin metathesis and the exploration of new applications for these species. In chapter 4, the synthesis of complexes 4.1B was described. These catalysts showed good characteristics for several applications. Unfortunately, catalysts of type 4.2 could not be prepared. As we previously mentioned, complexes of type 4.3B were extensively investigated by Viacatt NV. This only left complexes 4.1B to be further optimized. The Schiff base fragment was considerably varied in order to obtain different catalyst properties. Moreover, activation mechanisms were extensively investigated in our research group. The most obvious site to enhance the activity of catalysts 4.1B represents the NHC ligand H$_2$IMES. The variation of this ligand can first be examined by the substitution of it on the standard Grubbs catalyst 1.3. The results are then best compared with the standard second generation catalyst 1.4. When the ligand substitution shows positive effects in this system, the procedure can be transferred to the Schiff base substituted catalysts 4.1B and 4.3B.

The substitution of PCy$_3$ in the classical Grubbs first generation complex 1.3 for a ligand which would cause an increase in activity upon 1.4 has been the interest of many chemists and was widely described in Chapter 1. Moreover, a vast amount of theoretical investigations describing the essence of the effects of H$_2$IMES compared to PCy$_3$ in the Grubbs catalyst have been published and discussed in detail in Chapter 3. We have coupled these data with an investigation on the contemporary organometallic thinking and especially the inner workings of carbenes and phosphines in organometallic chemistry. This was discussed in great detail in Chapter 2.
Most of our design focused on a publication of Frenking et al. in 1996, which evidenced that the major difference between saturated and unsaturated carbenes was an increased electron density in the \( p_e \) carbene orbital of the unsaturated carbene.\(^1\) As a result, a strategy for this widely attempted substitution on the Grubbs catalyst has been proposed.

The ideal ligand \( L \) should show sufficient steric bulkiness, high \( \sigma \)-donating character and a low \( \pi \)-accepting character in the \( xy \) plane (with the Ru-Cl bond as the \( z \)-direction). It should be noted that previous design of NHC ligands has mainly focused on the increase in \( \sigma \)-donating character. More specifically, we suggested that a very straightforward idea to enhance the catalyst activity is to activate the \( \pi \)-acceptor function of the NHC ligand (in the \( z \)-direction). First, an increased \( \pi \)-acceptor function should increase dissociation of the competing phosphine ligand. Second, upon olefin coordination, the increased backdonation to the NHC should lead to a decreased interaction with the olefin bond in perpendicular (inactive) orientation and hence lead to less inactive intermediate species. This inactive species for olefin metathesis might participate in deactivation mechanisms of the catalyst. Third, the increased \( \pi \)-accepting function should lead to an increased \( \sigma \)-donation synergy and hence promote metallacyclobutane formation. Fourth, the increased \( \pi \)-interaction should decrease the Ru-NHC bond length, increase the steric interaction and consequently show increased activity. This shows that multiple positive effects might arise from the installation of a \( \pi \)-acceptor function on a spectator-site in the NHC ligand due to indirect effects. One negative effect consists of the increase of the total \( \pi \)-backbonding. This should increase the positive charge on the Ru and make it less prone to the +IV oxidation state in the metallacyclobutane ring.

Further evidence for our reasoning has recently been provided by Nolan et al. who showed that \( \text{H}_2\text{IMES} \) is both a stronger \( \sigma \)-donor and \( \pi \)-acceptor than IMES: 'The synergistic effect between \( \pi \)-backdonation and \( \sigma \) donation present in the saturated NHC systems results in increased electron density at the platinum center compared to the bonding situation in the unsaturated carbenes.'\(^2\)

Excellent candidates for such ligands would be PHC-ligands, which have been theoretically investigated to show the envisaged properties.\(^3\) However, the synthesis of such carbenes proves to be challenging and only one successful attempt has been published by Bertrand et al.\(^4\) We have chosen other strategies to accomplish our goals, though the PHC substitution still remains a valuable alternative.

In our work, we concentrated on the syntheses of carbenes 5.1, 5.2, 5.3 and 2.55 which are depicted in Figure 5.1. 5.3 and 2.55 were eventually used, since the attempts to produce carbenes 5.1 and 5.2 were troublesome. The synthesis of 2.55 had already been reported.\(^5\)

![Figure 5.1: Possible targets for an NHCs with a considerable \( \pi \)-acidic function.](image)

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\(^1\) The steric bulkiness is not an absolute, since for steric substrates as DEDAM-2 is will definitely be contraproducive.
It should be noted that the synthesis of NHC ligands bearing these π-acceptor functions exceeds the interest of metathesis chemists but even benefits the understanding of organometallic chemistry in general (Chapter 2). For example, Bielawski et al. were able to show with Rh-complexes of 2.55 the considerable π-accepting function of this NHC, which resulted in a JACS\textsuperscript{II} publication. Carbenes 5.1-5.3 should show an even greater π-acceptor function due to the proximity of the π-acceptor orbital compared to 2.55. However, this excessive function is probably the reason why the synthesis of carbene 5.1 was not successful. Until this research, only 6 types of 5-membered NHC ligands had been reported. Type I and Type II represent the classical saturated and unsaturated NHCs, which show many applications in organometallic chemistry and catalysis due to their relatively easy synthesis, easy variability and their good ability to coordinate to metal complexes. Types III-V, only led to a small amount of reports due to their more difficult preparation. Moreover, for Type IV the inability to install the mesitylene and 2,6-diisopropylphenyl groups to obtain a rigid steric umbrella limits the applicability. The preparation of Type VI carbenes (CAACs) has only been reported very recently.\textsuperscript{6} They show rather difficult preparation, but this might be compensated by the sterical tuning possible with R1 and R2.

To comment on the scientific relevance of this, it should be noted that the first reports on these types of 5 membered NHC ligands were all published in high impact journals.\textsuperscript{6-11, iii} All our attempts to prepare 5.1 or a metal complex substituted with 5.1 ultimately failed. However, with the preparation of 5.3 substituted metal complexes, we were able to introduce a 5 membered (amino)(amido)NHC ligand as the first example of a new class of NHC-ligands.

In addition, a few other targets were investigated. A catalyst substituted with 5.4 was our first attempt to modify H$_2$IMES. Yet this was performed before the extensive literature screening was performed. It showed the merit of introducing a small variation in the H$_2$IMES structure, since many attempts to introduce significantly different structures have often led to a decrease in the catalyst activity. 2.15 was also used as a target ligand. 2.15 is a Bertrand carbene which has previously been substituted on other metal centres, such as Rh. Bertrand et al. conceded that ‘These results as a whole demonstrate that despite the presence of a single amino substituent, the amino-anthryl-carbene 2 behaves as a

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\textsuperscript{II} Journal of the American Chemical Society

\textsuperscript{iii} High impact journal: JACS (Impact factor of 7.7 in 2006) and Angewandte Chemie International edition (Impact factor of 10.2 in 2006).
strong σ-donor/weak π-acceptor ligand. Monoamino-carbenes might therefore be considered as valuable alternatives to diaminocarbenes.\textsuperscript{12} The Verkade base \textbf{2.62} has proven to be the strongest phosphine base currently accessible.\textsuperscript{13,14} The high basicity stems from the high planarization of the phosphor induced by the ring structure and donation of the bridge-nitrogen lone pair to the phosphor.\textsuperscript{15} This should also lead to a decrease in backbonding to the ligand. Since the development of the Phoban catalyst has shown that the substitution of PCy\textsubscript{3} with another phosphine can be quite successful, also \textbf{2.62} seemed to be a suitable candidate for substitution on the Grubbs catalyst.\textsuperscript{16,17}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/other_targets.png}
\caption{Other targets for substitution on the Grubbs catalyst.}
\end{figure}

\section*{5.2 Preparation of ligands and complexes}

\subsection*{5.2.1 Ligand and ligand precursor synthesis}

\textbf{2.62} was purchased from Aldrich, the triflate precursor salt \textbf{5.5} of \textbf{2.15} was prepared according to literature procedure\textsuperscript{12}, as was the chlorine salt of \textbf{2.55}.\textsuperscript{5} Attempts to prepare the CO\textsubscript{2} adduct\textsuperscript{18-20} or the silver salt\textsuperscript{21} of \textbf{2.15} (using \textbf{5.5}) according to standard procedures\textsuperscript{18} used for other carbenes were unsuccessful. These products were expected to be valuable precursors for the reaction with the Grubbs catalyst.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/failed_preparations.png}
\caption{Attempts of the preparation of Ag salt or CO\textsubscript{2} adduct of \textbf{5.4}.}
\end{figure}

The synthesis of the chlorine salt \textbf{5.6} was performed in a similar way as the normal H\textsubscript{2}IMES ligand, and is depicted in Figure 5.5.
The preparation of 5.8 was performed analogous to literature procedures for a similar phenyl substituted compound. The reaction also worked smoother in THF than the previously reported synthesis in CHCl₃.²²

The proton on the chlorine substituted carbon in 5.8 shows a resonance at $\delta = 7.13$ ppm in the $^1$H NMR spectrum. This is considerably upfield to the normal NHC salts which show their proton resonance at $\sim \delta = 9$ ppm and even more upfield compared to the salt of the π-acidic precursor 2.55, which shows a resonance at $\delta = 12.88$ ppm or the triflate precursor of 2.15 showing a resonance at $\delta = 10.19$ ppm. Moreover, the phenyl substituted analogue is no salt.²² It should be noted that a salt formation is illogical due to the presence of two amide functions. 5.8 is extremely hygroscopic and even reacts in the solid state with water from the atmosphere. The hydroxide and ethoxide adducts 5.9 and 5.10 can easily be prepared. Although the preparation of carbenes from a chlorine adduct which is not a salt (as 5.8) has not yet been reported, the thermal substitution via chloroform adducts or ether-adducts on Grubbs type complexes has been shown to be effective. Unfortunately, the standard $^t$BuO ether could not be prepared either through simple reaction with $^t$BuOH or reaction with K$^t$BuO. Moreover, attempts to synthesize the Ag-salts, CO₂-adducts or to prepare the stable free carbene 5.1 with different procedures were unsuccessful.
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The difficult preparation of the free carbene 5.1 from 5.8 can be anticipated. Although 5.1 represents a unique possibility to form a carbene with a high π-acidic character, the inability to prepare the carbene clearly stems from insufficient stabilization of the carbene through mesomere donation of the substituents. Bertrand et al. have shown that the stabilization by only one substituent⁶,²³ is sufficient to obtain stable carbenes. Hence, we suggest that in 5.1 the nitrogen atoms show negligible ability in mesomere donation to the carbene. The π-orbital of the amide nitrogen is not free for bonding with the carbene, since it is already occupied in the amide bond! 5.1 can even expected to be a triplet carbene due to this lack of stabilization. The adaptation to 5.2 should provide one nitrogen substituent which is capable of mesomere backbonding and another (the amide) which is not. This should provide sufficient stability to the carbene.

Unfortunately, the synthesis of 5.2 proved to be very troublesome. The synthesis of 5.11B, which already shows great structural resemblance with the target carbene precursor is very straightforward. However, the chlorine salt of 5.11B does not react with (EtO)₃CH to form the corresponding carbene precursor. Also, the reaction of 5.11B with dimethoxy-N,N-dimethylmethanamine ((CH₃)₂N-C(OMe)₂) and NH₄BF₄ or the reaction of 5.11B with (EtO)₅CH and NH₄BF₄ did not afford ring closing.

In an alternative method, 5.11B was ring closed to 5.12A.²⁴ With this procedure the salt needs to be generated in a next step and additional problems come about. The oxidation is performed using NBS (N-Bromosuccinimide).²⁴ Brominating can occur on both the carbons adjacent to the nitrogen. This also occurs and reveals a weakness in the precursor design 5.13. In order to prepare the free carbene, a strong base needs to be added, however, the α-carbonyl protons also show considerable acidity.

We were able to isolate the bromine salt while further reaction led to the BF₄ salt 5.13. Unfortunately, the reaction with NBS remained troublesome. In a first series of attempts, we were able to isolate the
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bromine salt in THF and in 1,2-dimethoxyethane, although several times the reaction failed for unexplainable reasons. The obtained quantity of product was insufficient for a full analysis of carben formation and substitution on the Grubbs catalyst. After revisiting the reaction, this step could no longer be reproduced in either solvent at different temperatures using fresh NBS, old NBS or recrystallized NBS in different solvents in multiple experiments. Also, the reaction of 5.12A with iodine$^{25}$ showed no salt formation.

Figure 5.9: Synthesis of 5.13.

An alternative method to provide a precursor for 5.2 consists of the reaction of 5.7 with chloroacetyl chloride which would result in a fast synthesis. Unfortunately, this reaction resulted in indefinable products. Also the reaction of 5.7 with bromoacetyl chloride resulted in reaction mixtures of indefinable products. This was unexpected, since we anticipated at least a straightforward reaction of the acid chorine with the amine.

Figure 5.10: Synthesis of 5.10

Since we suspected that the problems in this reaction were caused by the $\alpha$-carbonyl protons, eventually, a synthesis reacting 5.7 with 2-chloro-2,2-diphenylacetyl chloride was attempted. The
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The synthesis smoothly yielded 5.14 at room temperature in THF while the ring closure of this product to 5.15 was very straightforward in CH$_3$CN at 90 °C. With this synthesis of 5.15, a very easy procedure was established to obtain precursors of (amino)(amido)NHCs. The synthesis can easily be adapted to obtain a whole series of precursors. Also, when a base is introduced to 5.15, no α-carbonyl protons are available for abstraction, which makes this design far superior to our previous suggestion of 5.13. Moreover, for metathesis-specific purposes, the introduction of two phenyl groups on the NHC backbone introduces some steric crowding to the complex. This is considered to have a positive effect on the metathesis activity. It should be noted that direct reaction of 5.7 with 2-chloro-2,2-diphenylacetyl chloride in CH$_3$CN at 90 °C in an attempt to establish a one-step reaction was unexpectedly inefficient.

![Figure 5.11: Synthesis of 5.15.](image)

Since 5.15 represents a unique carbene precursor, this makes it necessary to explore the characteristics of the corresponding carbene 5.3 and more specific its general coordination behavior. 5.3 shows a $^{13}$C NMR (benzene-$d_6$) shift at $\delta = 263.0$ ppm. For H$_2$IMES, 2.55 and IMES the carbene resonances have been found at $\delta = 243.8$ ppm (benzene-$d_6$)$^{26}$, 231.7 ppm (benzene-$d_6$)$^3$ and 219.7 ppm (thf-$d_8$)$^{27}$ respectively. It seems that the more electron-deficient the $p_\pi$ orbital, the more downfield the $^{13}$C NMR carbene shift.$^{IV}$ Moreover, Frenking’s claim that the biggest difference between the electronic

$^{IV}$ The carbene resonance at $\delta = 255.5$ ppm (benzene-$d_6$) of the acyclic carbene :C(N/i-Pr)$_2$ is somewhat more difficult to rationalize. It can be expected that the carbene-nitrogen bonds can rotate in solution. In the heterocyclic carbenes, the N-$p_\pi$ orbitals are physically forced in conjugation-orientation due to the ring structure, which could lead to the difference in the $^{13}$C NMR spectrum.

Grubbs et al. have presented a 4-membered NHC 2.6 showing the $^{13}$C NMR resonance is at 285 ppm, yet in the four membered NHC the nitrogens show no planar environment and hence have difficulty to donate mesomerically into the carbene $p_\sigma$ orbital. Bertrand’s PHC carbene 2.21 shows a $^{13}$C NMR resonance upfield at 184.4 ppm, and the authors suggested ‘a very weak $p_\pi$-donation from the metal to the carbene’ in complexes with it, which can suggest a high electron density at the $p_\sigma$ orbital of the carbene. The reasoning can also be applied to the CAACs of Bertrand et al. which display $^{13}$C NMR resonances in the range of $\delta = 300-320$ ppm, where only a single nitrogen donor is present for mesomeric donation.(4) Martin, D.; Bareiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. Angewandte Chemie-International Edition 2005, 44, 1700-1703(6) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. Angewandte Chemie-International Edition 2005, 44, 5705-5709(28) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. Angewandte Chemie-International Edition 1996, 35, 1121-1123(29) Despagnet-Ayoub, E.; Grubbs, R. H. Journal of the American Chemical Society 2004, 126, 10198-10199.

Yet, the reasoning is difficult to rationalize in Rh-carbene complexes, since the carbene $^{13}$C NMR resonances for (CO)$_2$RhCl(Carbene) are in general upfield to that of (COD)RhCl(Carbene). However, it should be noted that the
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structure of the carbene carbon form IH and H₂IH is the occupancy of the pₓ orbital is consistent with this statement.¹ It should be noted that Herrmann et al. have argued that the chemical shift of the carbene in rhodium complexes does not correlate with the donor strength of the Rh-carbene complexes.³¹

5.2.2 Ligand-metal complex preparation and analysis

The Verkade base 2.62 does not show substitution on the 1ˢᵗ generation Grubbs catalyst 1.3. Also 5.5 could not be transferred to the standard Grubbs catalyst through in situ reaction of 5.5, 1.3 and LiHMDS at -40°C. Modification of 5.5 into more useful precursors was unsuccessful. Reaction of 5.8 with 1.3 in the presence of LiHMDS or K-O’Bu also did not yield substitution. The substitution of 5.13 on 1.3 using LiHMDS was troublesome. A very small amount of unpurified product showing ¹H NMR resonance at 19.05 ppm was obtained. However, the difficulties in the synthesis of the precursor 5.13, the troublesome low yield in the substitution on 1.3, and the success obtained with the substitute 5.15 resulted in the ceasing of this practical implementation. The substitution of 5.3, 2.55 and 5.4 on 1.3 proceeds easily. The resulting complexes 5.16-5.18 were obtained by the one pot reactions of 1.3, the NHC-HCl salts and LiHMDS.

Figure 5.12: Schematic representation of the synthesized 2ⁿᵈ generation Grubbs complexes.

Since the new carbene 5.3 is interesting from purely organometallic viewpoint, the RhCl(COD)(5.3) complex 5.19 and RhCl(CO)₂(5.3) complex 5.21 were prepared. Bielawski et al. prepared the similar complexes 5.20 and 5.22 and evidenced the considerable backdonation function in the NHC through the CO stretching frequencies in IR.⁵ We aimed to do the same for 5.3. Comparison of CO stretching frequencies with the complexes 5.17 and 5.18 can also provide information on the backbonding in the Grubbs catalyst. Furthermore, with the synthesis of 5.18-5.19, we hoped to obtain crystals of the complex. These could show the asymmetrical N-C-N bonds, in which the amide C-N bond should be considerably longer and evidence the absence of mesomere N→C donation. The shortening of this bond in non-competitive π-backdonation environments could also evidence the Ru→CO charge transfer.

backbonding to C₂H₄ has been accounted to be similar to CO in a competitive π-backdonating environment. Also other effects can gain importance in organometallic compounds.(30) Mitoraj, M.; Michalak, A. Organometallics 2007, Published online 10/26/2007.
IR frequencies of the backbone CO stretching frequencies were obtained from 5.15, 5.17-5.19 and 5.21 and are depicted with the values obtained from the Bielawski publication in Table 5.1. Bielawski et al. argued that the high frequency of 2.55-HCl is caused by a strong N→C donation, draining electron density from the CO. Also, the higher frequency of 5.22 compared to 5.20 was assigned to Rh being a better backdonator in 5.20, leading to a higher electron density in the CO. This was presented as experimental proof for the backdonation to NHCs. The same effects are found with ligand 5.3 in 5.15, 5.19 and 5.21.

2.55 receives backdonation from the Ru in the Grubbs catalyst 5.17, intermediate to 5.22 and 5.20. Backdonation to 5.3 in the Grubbs complex 5.18 even exceeds the backdonation to the RhCl(COD)(NHC) complex 5.19! This seems very ambiguously, but in fact this is further evidence that ‘the influence of the metal can be substantial, changing not only the magnitude of electron transfer but also the relative donor-acceptor characteristics of the different ligands’30. Moreover, as previously mentioned, (Chapter 2) Frenking et al. pointed out that ‘the relative π-acceptor strength of ligands can only be established with respect to a given complex fragment.’32

Nevertheless, the backbonding in the Grubbs complexes (5.17 and 5.18) is somewhere in the range of the RhCl(COD)(NHC) complexes. This means that, as expected, the π-backdonation to a ligand L in the L-Ru-Cl plane is quite substantial. The opposite is to be expected in the L-Ru-benzylidene plane. Furthermore, the new ligand 5.3 shows π-backbonding to the NHC in the Grubbs complex, even exceeding that from RhCl(COD)(5.3). This means that the objective of making an NHC ligand with high π-backbonding in the Grubbs catalyst has been obtained. Moreover, with these results we have experimentally shown that extrapolation of ligand characteristics in the Rh(COD)Cl(NHC) and Rh(CO)₂Cl(NHC) complexes to other complexes, such as the Grubbs catalysts is not very straightforward and should only be done with great caution! This supports Baik reasoning (Chapter 3) that the backbonding to the NHC in Grubbs complexes is indeed extremely difficult to understand and shows a very different behavior for saturated and unsaturated NHCs.13
Table 5.1: IR frequencies of the backbone CO.

<table>
<thead>
<tr>
<th>Complex with 2.55</th>
<th>IR CO (cm⁻¹)</th>
<th>Complex with 5.3</th>
<th>IR CO (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55-HCl</td>
<td>1685(a)</td>
<td>5.15</td>
<td>1773</td>
</tr>
<tr>
<td>5.22 ([RhCO])</td>
<td>1680(a)</td>
<td>5.21 ([RhCO])</td>
<td>1764</td>
</tr>
<tr>
<td>5.17 (Grubbs)</td>
<td>1674</td>
<td>5.19 ([RhCOD])</td>
<td>1754</td>
</tr>
<tr>
<td>5.20 ([RhCOD])</td>
<td>1670(a)</td>
<td>5.18 (Grubbs)</td>
<td>1749</td>
</tr>
</tbody>
</table>

(a) data from ³.

Table 5.2: IR CO stretching frequencies ν (cm⁻¹) for Rh(CO)₂Cl(L).

<table>
<thead>
<tr>
<th>L</th>
<th>ν(CO) I</th>
<th>ν(CO) II</th>
<th>L</th>
<th>ν(CO) I</th>
<th>ν(CO) II</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="#" alt="Structure" /></td>
<td>2057(a)</td>
<td>1984(a)</td>
<td><img src="#" alt="Structure" /></td>
<td>2089</td>
<td>2000</td>
</tr>
<tr>
<td><img src="#" alt="Structure" /></td>
<td>2062(b)</td>
<td>1976(b)</td>
<td><img src="#" alt="Structure" /></td>
<td>2089(c)</td>
<td>2003(c)</td>
</tr>
<tr>
<td><img src="#" alt="Structure" /></td>
<td>2059(c)</td>
<td>1985(c)</td>
<td><img src="#" alt="Structure" /></td>
<td>2089(d)</td>
<td>2009(d)</td>
</tr>
<tr>
<td><img src="#" alt="Structure" /></td>
<td>2081(d)</td>
<td>1996(d)</td>
<td><img src="#" alt="Structure" /></td>
<td>2074(d)</td>
<td>1958(d)</td>
</tr>
<tr>
<td><img src="#" alt="Structure" /></td>
<td>2076(e)</td>
<td>2006(e)</td>
<td><img src="#" alt="Structure" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a): 34, (b): 24, (c): 4, (d): 35, (e): 5. ³⁴ is the standard reference for Rh(CO)₂Cl(H₂IMES). In ³⁵ Cetinkaya et al. did not mention the previous report on Rh(CO)₂Cl(H₂IMES) by Herrmann et al.³⁴ Yet in a subsequent publication Cetinkaya et al.³⁶ use the values obtained by Herrmann et al. and the reference of the article³⁴?? In the same article³⁶ Rh(CO)₂Cl(IMES) is mistaken for Rh(CO)₂Cl(IcHex).

Mes* = 2,4,6-tri-i-butylaniline.
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General reasoning for this $\nu$(CO) frequencies goes as follows: The more electron donating the ligand $\rightarrow$ the more electron rich metal $\rightarrow$ the more backbonding to CO $\rightarrow$ the more electron density in the antibonding $\pi^*$ orbital $\rightarrow$ the weaker the bond $\rightarrow$ lower $\nu$(CO) frequencies. Using this reasoning, it must be stated that the new (amido)(amino)NHC 5.3 shows weak electron donating ability, weaker than H$_2$IMES. This means that the aim for synergy in backbond-bond has not led to an increased net-donating ability.

Yet we concluded from Chapter 2 that ‘the difference in $\pi$-backbonding of a ligand L in a complex is most influenced by the backbonding towards other ligands through competition for the same metal-d-orbital and hence in these complexes the $\nu$(CO) frequencies are determined by the backbonding to the communicating-competing ligands.’, moreover ‘The M-L bond distances of a class of ligands L correlate well with the inverse strength of $\pi$-backbonding, especially if the L $\pi$ orbitals for backbonding are perpendicular to the M-L bond direction.’

As can be seen in Table 5.2, three ligands (acyclic, six-membered and PHC) clearly outperform the rest in net electron donation to Rh. For the six-membered NHC this is highly unexpected, since one would expect similar character to H$_2$IMES on the basis of pure electronics. Yet, for the six-membered NHC the N-C-N angle is 115.3° in a Rh(COD)Cl(NHC) complex, which is considerably wider than the ~106° of 5 membered NHC’s. A wider carbene angle increases the steric strain in the Rh(CO)$_2$Cl(L) complex $\rightarrow$ increase in the bond distance $\rightarrow$ decrease in the backbonding to the NHC $\rightarrow$ this decrease in backbond is the most important factor for the decrease in backbonding to the CO ligands $\rightarrow$ lower $\nu$(CO) frequencies.

The N-C-N angle of :C(N(\text{-}i\text{Pr})$_2$)$_2$ is 121°.\textsuperscript{28} Moreover, Hu et al. have shown that :C(N(\text{-}i\text{Pr})$_2$)$_2$ has an extremely elongated Cr-carbene bond compared to normal NHCs and Fischer carbenes in Cr(CO)$_5$L complexes.\textsuperscript{37} Clearly a much higher steric strain is induced by :C(N(\text{-}i\text{Pr})$_2$)$_2$ compared to normal 5-membered NHCs $\rightarrow$ lower backdonation to :C(N(\text{-}i\text{Pr})$_2$)$_2$ $\rightarrow$ lower $\nu$(CO) frequencies.

Also Bertrand’s PHC carbene 2.21 shows a high net-donating ability. Bertrand et al. mentioned in their report the seminal paper of Schleyer et al. who concluded that the inherent $\pi$-donor capabilities of the heavier elements (as phosphor) show an intrinsic equal or higher $\pi$-donor capability than their second period analogues.\textsuperscript{4,38} The problem with phosphor is the lack of planarization, yet Bertrand et al. were able to solve this issue and used this intrinsic $\pi$-donor capacity to its full extent.\textsuperscript{4} This implies a high population of the carbene $p_\pi$ orbital. Moreover, the extremely low $^{13}$C NMR resonance ($\delta = 184$ ppm) also hints that the $p_\pi$ density of the carbene is very high (vide supra). Even the authors suggest ‘a very weak $\pi$-donation from the metal to the carbene ligand’ in the Rh(COD)Cl(2.21) complex.\textsuperscript{4} The P-C-P angle is only 100.7°, though the Mes* (2,4,6-tri-\text{-}butylaniline) substituents probably overcompensate this in the steric balance. This should all lead to a lower backbonding to 2.21 $\rightarrow$ lower $\nu$(CO) frequencies.

It has been shown that the three carbenes showing the most distinct (net-donating) profile in the Rh(CO)$_2$Cl(L) complexes have clearly hindered backdonation from Rh either through steric constraints or due to a high occupancy of the $p_\pi$ orbital in the free carbene. Therefore, we conclude that the $\nu$(CO) frequencies of the Rh(CO)$_2$Cl(L) complexes show better the characteristics for the $\pi$-backbonding character of the carbene than for the net-electron-donating ability. However, it should be noted that the $\pi$-backbonding obviously is a part of the net-electron-donating ability. Hence, the high $\nu$(CO) values obtained for Rh(CO)$_2$Cl(5.3) are completely expected, since a high backbonding to 5.3 was in fact the aim.
5.3 Catalytic activity

Complexes 5.16-5.18 were evaluated for metathesis and their reactivity was compared to the standard second generation catalyst 1.4. First, the polymerization of 300 equiv of COD was monitored. 1.4 and 5.18 polymerize to 100 % conversion before the first measurement at 2 minutes. The Bromo-catalyst 5.17 reacts somewhat slower and the Bielawski-Grubbs catalyst shows the slowest kinetics.

![Conversion vs Time](image)

**Figure 5.14:** ROMP of 300 equiv of COD (100 µl COD, 22 °C).

For the 300 equiv polymerization of COD all catalysts reached thermodynamical CDT equilibrium. The catalyst loading was decreased to 1 over 3000, to obtain a better overview on the catalyst stability and to show the difference in initiation kinetics between 1.4 and 5.18. Here again, 5.17 is the slowest catalyst followed by 5.16. The new catalyst 5.18 shows faster polymerization kinetics than the standard second generation catalyst. Hence, under contemporary semantics, this catalyst should be assigned to be the most active catalyst (TOF). Yet, we consider the total activity an additional and better descriptor for catalysts, hence also secondary metathesis isomerizations and CDT formation were monitored. All four catalysts also show complete secondary metathesis and CDT formation. Consequently no differentiation on the total activity could be presented by this test.

![Conversion vs Time](image)

**Figure 5.15:** ROMP of 3 000 equiv of COD (100 µl COD, 22 °C).
Since the previous tests showed little information on the variation of the ‘total activity’ of the catalyst, the catalysts were tested for the ROMP of 30 000 and 300 000 equiv of COD. For the polymerization of 30 000 equiv of COD, all catalysts reached 100 % conversion after 40 hours. However, the cis:trans conformation of the obtained polymers suggests the following total activity: 1.4 > 5.18 > 5.17 > 5.16. The polymerization of 300 000 equiv is very inefficient, but a similar catalyst total activity (here also TON) trend; 1.4 > 5.18 > 5.17 = 5.16 was obtained.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cat./COD</th>
<th>Conversion (%)</th>
<th>trans%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1/30 000</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>5.16</td>
<td>1/30 000</td>
<td>100</td>
<td>59</td>
</tr>
<tr>
<td>5.17</td>
<td>1/30 000</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>5.18</td>
<td>1/30 000</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>1.4</td>
<td>1/300 000</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>5.16</td>
<td>1/300 000</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>5.17</td>
<td>1/300 000</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>5.18</td>
<td>1/300 000</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>

It should be noted that in the COD polymerization the newly formed catalysts 5.16-5.18 show comparable activity upon the standard second generation catalyst 1.4. The activity (polymerization kinetics; TOF) decreases in the order 5.18 > 1.4 > 5.16 >> 5.17. The total activity (TON) decreases in the order 1.4 > 5.18 > 5.17 > 5.16. Since 5.16-5.17 perform on both accounts worse than the standard second generation catalyst 1.4, these should not be considered valuable substitutes. 5.18 on the other hand, shows competitive characteristics to 1.4 for the ROMP of COD.

The polymerization of 2 000 equiv of CDT was also monitored. For this polymerization 5.18 and 5.17 again clearly show relatively the fastest and slowest polymerization. 1.4 and 5.16 show very similar reaction profiles, which should be expected due to the big catalyst similarities.

Since the RCM of DEDAM is the most performed activity test for metathesis catalyst, the activity of 5.16-5.18 compared to the standard 1.4 was also investigated for this reaction (0.5 mol%). The standard second generation catalyst 1.4 clearly shows the fastest kinetics followed by 5.16. 5.17 is again the slowest catalyst. Very surprisingly, 5.18 shows very bad stability and only 63 % conversion could be reached, after which all catalyst had decomposed! It must be noted that 5.18 is synthesized as
a mixture of two isomers, one with the benzylidene on the amido side and one with the benzylidene on the amino side. One isomer crystallizes, but left in solution equilibrium is reached within 12 hours, which means that 5.18 shows a slow rotation of the H$_2$IMES ligand. When RCM is in progress, the methylidene always switches sides after a substrate is converted. Moreover, the methylidene shows in general easier decomposition than all other carbene species. Here a deactivation by one of the 2 isomers in solution could occur. Since both necessarily need to exist, instability of one would be sufficient. We suggest that, if such a mechanism would be working here, the amino-side would be most vulnerable since there the carbene-N bond is expected to be the shortest and give rise to closer contacts.

Figure 5.17: RCM of 200 equiv of DEDAM (110 µl DEDAM, 400 µl CD$_2$Cl$_2$, 22 °C).

Figure 5.18: Change of the methylidene upon RCM.

The RCM of 10 000 equiv of DEDAM shows decreasing TONs in the order 1.4 > 5.16 > 5.17 > 5.18. This shows that on the basis of TOF and total activity none of the new catalysts can compete with the second generation catalyst 1.4 for the RCM of DEDAM.
Substitution of PCy₃ in the first generation Grubbs catalyst

Table 5.4: RCM of 10 000 equiv of DEDAM
(100°C, 15 hours, 40 µl DEDAM in 1 ml of toluene).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>74</td>
</tr>
<tr>
<td>5.16</td>
<td>49</td>
</tr>
<tr>
<td>5.17</td>
<td>39</td>
</tr>
<tr>
<td>5.18</td>
<td>8</td>
</tr>
</tbody>
</table>

The RCM of 20 equiv of DEDAM-2 with these catalysts shows the same TON profile (1.4 > 5.16 > 5.17 > 5.18) as for the RCM of DEDAM. Also for this reaction the new catalysts cannot outperform the standard second generation Grubbs catalyst 1.4.

Table 5.5: RCM of 20 equiv of DEDAM-2 (15 hours, 40 µl DEDAM-2 in 1 ml of toluene).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>33</td>
<td>100 °C</td>
</tr>
<tr>
<td>5.16</td>
<td>24</td>
<td>60 °C</td>
</tr>
<tr>
<td>5.17</td>
<td>19</td>
<td>60 °C</td>
</tr>
<tr>
<td>5.18</td>
<td>5</td>
<td>100 °C</td>
</tr>
</tbody>
</table>

5.4 Conclusions

The objective of the new catalysts incorporated with π-deficient carbenes in this chapter was to establish higher ‘total activity’ but also higher ‘activity’ for metathesis reactions. The latter would be obtained by higher steric strain and increased competition for backbonding to the phosphine. The former and latter would be obtained by a synergy in σ-bonding-π-backbonding which would increase the metallacyclobutane stability.

First, it should be noted that the elaborate search for establishing a direct π-accepting function on the backbone of the carbene has been fruitful. The inability to perform carbenes or carbene substituted species with 5.1 clearly shows both the necessity for mesomeric donation in the NHC and the lack of the mesomeric effect when an amido nitrogen is used instead of an amino nitrogen. The greatest achievement in this chapter was the preparation of an (amino)(amido)NHC 5.3. This NHC type provides the ability to install analogous steric environments (mesityl groups) as for saturated carbenes, but leaves the carbene only mesomerically stabilized by one nitrogen. This NHC should therefore show an increased π-acceptor function.

Unfortunately much ambiguity has risen during the research. This begins with the assignment of the organometallic character of the new carbene vs. the other ones. We have shown through the IR stretching frequencies of the backbone CO, as Bielawski et al. did for 2.55, that the NHC clearly receives backdonation. But where for 2.55 the backdonation from Rh(CO)₂Cl(NHC) exceeds that form the corresponding Grubbs complex by this criterion, the opposite was found for 5.3. Hence we can only confirm sporadic statements of theoretical chemists that ‘the relative π-acceptor strength of ligands can only be established with respect to a given complex fragment.’

Moreover, Baik et al. have shown that backbonding to the NHC in Grubbs complexes might in fact be a very, very complicated issue and differ completely between saturated and unsaturated carbenes.

Taking this into account we still performed the standard characterizing method for NHCs, being the analysis of the ν(CO) frequencies of Rh(CO)₂Cl(L). Using the general interpretation of this analysis,
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\(\text{5.3}\) is a low net electron-donator compared to the other carbenes. However, using the conclusions from Chapter 2 and an evaluation of some of the most outspoken net-donating carbenes in \(\text{Rh(CO)}_2\text{Cl}(\text{L})\), we think it is more straightforward to see the \(v(\text{CO})\) frequencies as a measure for \(\pi\)-withdrawing character, than net-donating character. Although both are clearly related. However, using the \(\pi\)-withdrawing character criterion, it is only logical that \(\text{5.3}\) scores high, since in fact this was what we aimed for.

We have also shown that with the current data available, the idea that the free NHCs or related free carbenes show more downfield shifts in \(^{13}\text{C} \text{NMR}\) can be explained solely on them having a lower occupancy of the \(p_\pi\) orbital, cannot be dismissed.

The kinetic data from COD polymerizations show that \(\text{5.18}\) (substituted with \(\text{5.3}\)) reacts faster than \(\text{1.4}\) and much faster than \(\text{5.17}\) (substituted with \(\text{2.55}\)). Although, for both \(\text{5.3}\) and \(\text{2.55}\) the backbonding to the NHC has been shown, backbonding to the NHC in the Grubbs complex compared to a Rh complex has been shown to be much more efficient for \(\text{5.3}\) than for \(\text{2.55}\). Hence, the reasoning that faster initiation (‘activity’) should be established by the higher \(\pi\)-accepting function still stands tall.

Unfortunately, none of the new catalysts can outperform \(\text{1.4}\) on the basis of ‘total activity’ both in the ROMP (of COD and CDT) or RCM (DEDAM and DEDAM-2). Hence, assuming that the change in initiation (‘activity’) between \(\text{1.4, 5.17}\) and \(\text{5.18}\) was caused by the difference in \(\pi\)-backbonding to the NHC, it can be stated that the ‘total activity’ is not determined by the difference in \(\pi\)-backbonding. It is more difficult to tackle this issue at the origin, since it concerns not metathesis but everything else the catalyst can be subjected to.

Kinetic activity plots for RCM are even more difficult to interpret, since here \(\text{1.4}\) seems to be the most active catalyst and \(\text{5.18}\) deactivates really fast. This shows that reasoning concerning activity and total activity are, unfortunately, even substrate dependant.

Finally, the catalytic results for metathesis are only unambiguously on one point: No distinct improvement was obtained upon the standard second generation catalyst \(\text{1.4}\).

References

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Chapter 6

Experimental

6.1 General

NMR spectra were obtained on a Varian Unity 300 MHz spectrometer. SEC analysis was performed on a Shimadzu 10 ADVP system with three polystyrene-divinylbenzene columns in serie (100 nm, 1000 nm and 10 000 nm). X-Ray analyses on single crystals were performed by Anthony Linden at the University of Zürich on a Nonius KappaCCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Elemental analysis was performed by Dr. Marc Proot and Olivier Genelle at Chevron (Zwijnaarde). IR spectra were obtained in an FT-IR Galaxy spectrometer by Danny Vandeput. All solvents were dried under argon using standard techniques: THF (Na; Benzophenone), Toluene (Na), toluene-d₈ (Na), benzene-d₆ (Na), CH₂Cl₂ (CaH₂). The monomer COD (1,5-cis,cis-cyclooctadiene) was distilled over CaH₂. All reactions using Ru were performed under argon atmosphere unless stated otherwise. Argon was dried over a column of Drierite®.

1.3 and 2.62 were purchased from Sigma-Aldrich. 1.4¹ and 4.12² were be prepared using well established procedures. The H₂IMES-HCl was prepared using a previously reported method.³ For the synthesis of 1.4 a small adaptation of a literature procedure was applied: KHMDS (potassium bis(trimethylsilyl)amide) or LiHMDS was applied as base to deprotonate the H₂IMES-HCl salt. This was performed separately and in situ in a one pot synthesis. 1.4 can be obtained by precipitation in MeOH after which it is washed with hexane and dried in vacuo.

4.10A⁴ and [Ru(p-cymene)Cl₂]₂⁵, 5.5⁶, 5.6⁷, 5.7⁸ and 5.16⁹, were prepared using well established procedures.

6.2 Preparation of Complexes 4.1B
6.2.1 Preparation of Schiff bases and Schiff base salts

6.1-6.3 and 6.10 were prepared as previously reported. The Tl-salts 6.1-10(B) were prepared from the reaction of the Schiff bases 6.1-10(A) in dry THF with an equimolar amount of TiOEt. The solvent was evaporated until much of the reaction product precipitated. The resulting solids were filtered off and dried in vacuo. The obtained products were yellow solids except 6.7B, which precipitated as an orange-red product.

![Schiff bases and Schiff base Tl salts](image)

Figure 6.1: Schiff bases and Schiff base Tl salts.

6.2.1.1 Synthesis of 6.4A

To a solution of 10.0 g salicylaldehyde (82 mmol) in 20 ml of ethanol, 11.09 g of 2,4,6-trimethylaniline and one drop of HCOOH were added. The mixture was refluxed for 2 hours and cooled down in an ice bath. 6.4A was filtered off in 80% yield as a light yellow solid and dried in vacuo. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm): 13.21 (s, 1H, OH), 8.33 (s, 1H, N=CH), 7.41 - 7.31 (m, 3H, H$_{arom}$, phenoxy), 7.05 (d, 1H, H$_{arom}$, phenoxy), 6.92 (s, 2H, H$_{arom}$, mesityl), 2.30 (s, 3H, CH$_3$), 2.17 (s, 6H, CH$_3$).

$^{13}$C NMR (300 MHz, CDCl$_3$): δ (ppm): 167.0 (C=N), 161.5 (C-O), 145.9 (C$_{arom}$), 133.3 (C$_{arom}$), 132.4 (C$_{arom}$), 129.3 (C$_{arom}$), 119.2 (C$_{arom}$), 119.1 (C$_{arom}$), 117.6 (C$_{arom}$), 21.1 (CH$_3$), 18.7 (CH$_3$).

6.2.1.2 Synthesis of 6.5A
Experimental

To a solution of 2.0 g 2-hydroxy-5-nitrobenzaldehyde (12.0 mmol) in 10 ml of ethanol, 3.13 g of 2,4,6-tri-tert-butylaniline (12.0 mmol) and one drop of HCOOH were added. The mixture was refluxed for 2 hours and cooled down in an ice bath. 6.5A precipitated and was filtered in 87% yield as a bright yellow solid which was dried in vacuo. 1H NMR (300 MHz, CDCl3): δ (ppm): 14.64 (s, 1H, OH), 8.32-8.23 (m, 3H, CH aromatic, CHC(NO2) and C=NH), 7.42 (s, 2H, CH aromatic, tri-tert-butylphenyl), 7.13 (d, 1H, CH(OH)), 1.35 (s, 9H, CH3, ortho), 1.33 (s, 18H, CH3, para); 13C NMR (300 MHz, CDCl3): δ (ppm): 167.7 (C-O), 167.1 (C=N), 147.2 (C aromatic), 145.5 (C aromatic), 140.5 (C aromatic), 140.2 (C aromatic), 129.1 (C aromatic), 128.6 (C aromatic), 122.6 (C aromatic), 119.0 (C aromatic), 117.1 (C aromatic), 36.1 (C(CH3)3, ortho), 35.1 (C(CH3)3, para), 32.5 (CH3, ortho), 31.8 (CH3, para).

6.2.1.3 Synthesis of 6.6A

To a solution of 2.0 g 2-hydroxy-5-nitrobenzaldehyde (12.0 mmol) in 10 ml of ethanol, 1.79 g of 4-tert-butylaniline (12.0 mmol) and one drop of HCOOH were added. The mixture was refluxed for 2 hours and cooled down in an ice bath after which 6.6A precipitated. The product was filtered off in 77% yield as a sharp yellow solid and dried in vacuo. 1H NMR (300 MHz, CDCl3): δ (ppm): 14.64 (s, 1H, OH), 8.72 (s, 1H), 8.38 (s, 1H), 8.26 (d, 1H, CH(CH3)(NO2)), 7.49 (d, 2H, CH aromatic, tert-butylaniline), 7.29 (d, 2H, CH aromatic, tert-butylaniline), 7.08 (d, 1H, CH(OH)), 1.36 (s, 9H, CH3); 13C NMR (300 MHz, CDCl3): δ (ppm): 167.3 (C-O), 159.9 (C=N), 151.9 (C aromatic), 144.0 (C aromatic), 140.1 (C aromatic), 128.5 (C aromatic), 128.4 (C aromatic), 126.8 (C aromatic), 121.1 (C aromatic), 118.6 (C aromatic), 118.4 (C aromatic), 35.0 (C(CH3)3), 31.5 (CH3).

6.2.1.4 Synthesis of 6.7A

To a solution of 2.0 g 2-hydroxy-5-nitrobenzaldehyde (12.0 mmol) in 10 ml of ethanol, 2.20 g of pentafluoroaniline (12.0 mmol) and one drop of HCOOH were added. The mixture was refluxed for 4 hours and cooled down in an ice bath. 6.7A precipitated and was filtered off in 81% yield as a yellow-ocher solid and dried in vacuo. 1H NMR (300 MHz, CDCl3): δ (ppm): 13.15 (s, 1H, OH), 8.98 (s, 1H), 8.42 (s, 1H), 8.42 (s, 1H), 8.34 (s, 1H, CH(NO2)), 7.17 (d, 1H, CH(OH)); 13C NMR (300 MHz, CDCl3): δ (ppm): 168.9 (C=N), 166.6 (C-O), 143.1 (C aromatic), 141.8 (C aromatic), 140.1 (C aromatic), 128.5 (C aromatic), 128.4 (C aromatic), 126.8 (C aromatic), 121.1 (C aromatic), 118.6 (C aromatic), 118.4 (C aromatic), 35.0 (C(CH3)3), 31.5 (CH3).

6.2.1.5 Synthesis of 6.8A

To a solution of 2.0 g salicylaldehyde (16.4 mmol) in 5 ml of dry THF, 8.4 ml of a 2M methylamine solution (16.8 mmol) and one drop of HCOOH were added. The mixture was refluxed for 3 hours. Thereafter, the solvent and the remaining methylamine were evaporated in vacuo. 6.8A was obtained as a yellow oil in 95% yield. 1H NMR (300 MHz, CDCl3): δ (ppm): 13.17 (s, 1H, OH), 8.21 (s, 1H, N=CH), 7.25 (t, 1H, OH), 7.16 (d, 1H, H aromatic), 6.93 (d, 1H, H aromatic), 6.84 (t, 1H, H aromatic), 3.37 (s, 3H, CH3); 13C NMR (300 MHz, CDCl3): δ (ppm): 166.5 (C=N), 161.5 (C-O), 132.3 (C aromatic), 131.3 (C aromatic), 119.1 (C aromatic), 118.7 (C aromatic), 117.2 (C aromatic), 46.1 (CH3).

6.2.1.6 Synthesis of 6.9A

To 4.01 g of 1-adamantylamine hydrochloride (21.3 mmol) in 15 ml THF, 3.90 g of salicylaldehyde (1.5 equiv) was added. Over a period of two hours, 6.45g of NEt3 (63.9 mmol; 3 equiv) was added to
Experimental

the mixture and the reaction was filtered. Thereafter, the solvent of the filtrate was evaporated, ethanol was added and the mixture was placed in an ice bath. The yellow precipitate 6.9A was filtered off and dried in vacuo and obtained in 74 % yield. 1H NMR (300 MHz, CDCl3): δ (ppm): 14.51 (s, 1H, OH), 8.32 (s, 1H, N=CH), 7.33-7.20 (m, 2H, C_arom), 6.93 (d, 1H, C_arom), 6.84 (t, 1H, C_arom); 13C NMR (300 MHz, CDCl3): δ (ppm): 162.6 (C-OH), 159.4 (C=N), 132.2 (C_arom), 131.5 (C_arom), 119.1 (C_arom), 118.2 (C_arom), 117.6 (C_arom), 57.3 (CNC3), 43.2 (C-C-N), 36.6 (CH2C3), 29.6 (CHC3).

6.2.2 Preparation of Schiff base-Ru complexes 4.1B

6.2.2.1 Synthesis of 4.8

0.276 g of the Tl salt 6.1B (0.501 mmol; 1.1 equiv) was added to a 15 ml THF solution of 0.330 g 4.12 (0.455 mmol; 1 equiv) and stirred for 2 hours at room temperature. The reaction mixture was evaporated, dissolved in toluene and the white precipitate TlCl was removed by filtration. The filtrate was evaporated and ~2 ml of CH2Cl2 was added to redissolve the product. Then, 40 ml of hexane was added after which the dispersion was placed in an ultrasonic bath for 10 minutes and a solid was obtained by filtration. The red-brown precipitate 4.8 was washed with 10 ml of hexane and dried in vacuo. Yield: 76%.

1H NMR (CDCl3): δ (ppm): 18.50 (s,1H, Ru=C-H-Ph), 8.07 (d, 1H), 8.04 (s, 1H), 7.58-6.75 (br m, 11H), 6.43 (s, 1H), 6.36 (s, 1H), 4.12 (m, 2H), 4.01 (m, 2H), 2.57 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H), 1.48 (s, 3H), 1.03 (s, 3H). 13C NMR (CDCl3) (spectrum obtained on a 300 MHz JEOL spectrometer at the faculty of bioscience engineering): δ (ppm): 301.4 (Ru=CH-Ph), 219.1 (Ru-CNN), 174.6 (C-O), 167.2 (C=N), 151.7, 150.0, 140.2, 139.3, 138.4, 137.7, 136.7, 136.3, 135.5, 133.8, 133.4, 131.4, 130.6, 130.5, 129.9, 129.5, 129.2, 129.1, 128.3, 128.2, 128.1, 123.9, 118.7, 117.9, 51.6 (CH2, H2IMES), 50.9 (CH2, H2IMES), 20.0, 18.8, 18.3, 18.2, 17.8, 17.7, 17.6. Elemental analysis calculated (%) for C43H34N4O3ClRu (881.27): C 58.60, H 5.03, N 6.36; found C 58.81, H 5.87, N 6.38.

6.2.2.2 Synthesis of 4.9

0.146 g of the Tl salt 6.2B (0.305 mmol; 1.2 equiv) was added to a 15 ml THF solution of 0.184 g 4.12 (0.254 mmol; 1 equiv) and stirred for 2 hours at room temperature. The solvent was evaporated and the mixture was dissolved in toluene after which the white precipitate TlCl was removed by filtration. The solution was evaporated and 5 ml of hexane was added. The mixture was placed in the ultrasonic bath for 10 minutes after which a solid precipitated. 4.9 was obtained as a red-pink powder in 45% yield. 1H NMR (CDCl3): δ (ppm): 18.85 (s, 1H, Ru=CH-Ph), 7.66 (s, 1H), 7.50-6.92 (br m, 9H), 6.80 (d, 1H), 6.67 (s, 1H), 6.55 (s, 1H), 6.48 (t, 1H), 6.10 (s, 1H), 4.19-4.13 (m, 1H, CH2, H2IMES), 4.10-4.00 (m, 2H, CH2, H2IMES), 3.89-3.83 (t, 1H, CH2, H2IMES), 3.71-3.65 (s, 1H, CH2, H2IMES), 2.71 (s, 3H), 2.51 (sept, 1H, CH(C2H3)), 2.42 (s,3H), 2.38 (s,3H), 2.21 (s, 3H), 2.06 (s, 6H), 1.69-1.63 (m, 1H), 1.34-1.31 (d, 3H), 0.83-0.81 (d, 3H), 0.39-0.37 (d, 3H), 0.22-0.20 (d, 3H). 13C NMR (CDCl3): δ (ppm) (spectrum obtained on a 300 MHz JEOL spectrometer at the faculty of bioscience engineering): 296.4 (Ru=CH-Ph), 221.6 (Ru-CNN), 169.3 (C-O), 168.0 (C=N), 154.9, 151.6, 149.8, 142.0, 140.5, 139.3, 138.3, 137.7, 137.0, 136.7-136.6 (m), 133.8, 133.4, 129.4-129.0 (m), 128.0, 127.9, 125.7, 123.4, 123.1, 122.0, 118.0, 113.3, 51.6 (CH2, H2IMES), 50.4 (CH2, H2IMES), 29.3, 26.3, 25.0, 24.9, 23.0, 22.2, 21.1, 21.0, 20.0, 18.7, 18.5, 17.8. Elemental analysis calculated (%) for C47H54N3ClRu (813.49): C 65.59, H 6.68, N 5.17; found C 65.59 H 6.02 N 5.11.
6.2.2.3 Synthesis of 4.10

0.338 g of the Tl salt 6.3B (0.637 mmol; 1.1 equiv) was added to a 15 ml THF solution of 0.420 g 4.12 (0.579 mmol; 1 equiv) and stirred for 2 hours. The reaction mixture was evaporated, dissolved in toluene and the white precipitate TlCl was removed by filtration. The filtrate was evaporated and ~1 ml of CH$_2$Cl$_2$ was added to redissolve the product. Then, 40 ml of hexane was added after which the dispersion was placed in an ultrasonic bath for 30 minutes and a solid was obtained by filtration. The red precipitate 4.10 was washed with 10 ml of hexane and dried in vacuo. Yield: 74%.

$^1$H NMR (CDCl$_3$): $\delta$ (ppm): 18.95 (s, 1H), 8.13-8.09 (dd, 1H), 8.01 (d, 1H), 7.70 (s, 1H), 7.41 (t, 2H), 7.38 (s, 1H), 7.06-7.01 (br m, 5H), 6.91-6.88 (d, 1H), 6.82-6.79 (br m, 1H), 6.63 (s, 1H), 6.55 (s, 1H), 6.16 (s, 1H), 4.21-4.16 (t, 1H), 4.12-4.00 (m, 2H), 3.92-3.86 (t, 1H), 2.68 (s, 3H), 2.43-2.32 (br m, 7H), 2.22 (s, 3H), 2.07 (s, 6H), 1.62-1.54 (m, 1H), 1.37-1.35 (d, 3H), 0.87-0.85 (d, 3H), 0.39-0.36 (d, 3H), 0.19-0.18 (d, 3H).

$^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) (spectrum obtained on a 300 MHz JEOL spectrometer at the faculty of bioscience engineering): 299.6 (Ru=C-Ph), 219.6 (Ru-CNN), 174.3 (C-O), 167.5 (C=N), 151.4, 148.5, 141.5, 139.9, 139.5, 138.9, 138.8, 138.2, 137.7, 136.6, 136.2, 135.2, 134.8, 132.8, 129.3-128.1 (br m), 126.4, 125.3, 123.6, 123.2, 122.3, 117.2, 51.7 (CH$_2$, H$_2$IMES), 50.3 (CH$_2$, H$_2$IMES), 29.5, 26.5, 25.1, 25.0, 23.1, 21.9, 21.1, 21.0, 19.9, 18.7, 18.4, 17.8. Elemental analysis calculated (%) for C$_{47}$H$_{43}$N$_4$O$_3$ClRu (858.48): C 65.76, H 6.22, N 6.53; found C 65.48, H 6.20, N 6.53.

Crystals suitable for X-ray analysis were grown from a saturated solution of chloroform added with pentane, which was placed in the refrigerator with a balloon of argon for several weeks. The crystals are black and show crimson solutions when redissolved.

6.2.2.4 Synthesis of 4.13

A solution of 0.215 g Tl-salt 6.4B (0.485 mmol; 1.1 equiv) in 10 ml of THF was added to a solution of 0.320 g complex 4.12 (0.441 mmol) in 10 ml of THF and stirred at room temperature for 2 hours. The solution was evaporated and dissolved in 10 ml of toluene, cooled to -20°C and the TlCl was removed by filtration. The filtrate was evaporated and 10 ml of hexane was added. The dispersion was placed in an ultrasonic bath for 10 minutes and then cooled to -20°C for 1 hour after which a red-orange powder was obtained and dried in vacuo. 4.13 was isolated in 30 % yield. $^1$H NMR (CDCl$_3$): $\delta$ (ppm): 18.62 (s, 1H, Ru=C), 7.60 (s, 1H, N=C), 7.44-6.50 (br m, 14H, H$_{arom}$), 6.25 (s, 1H, H$_{arom}$), 4.10 (br m, 2H, CH$_2$, H$_2$IMES), 3.97 (br m, 2H, CH$_2$, H$_2$IMES). 2.61-1.05 (br m, 27H, H$_{aliph}$). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm): 297.9 (Ru=C-Ph), 221.3 (Ru-CNN), 169.6, 167.6, 167.5, 152.0, 149.9, 140.2, 139.2, 138.9, 138.1, 137.7, 137.3, 136.9, 136.6, 134.3, 134.1, 133.8, 131.9, 130.4, 130.1,129.5, 129.3, 129.1, 128.7, 128.0, 127.7, 123.7, 123.4, 119.2, 113.7, 113.5, 51.5 (C$_{CH2, H2IMES}$). 51.0 (C$_{CH2, H2IMES}$), 21.3, 21.1, 21.0, 19.0, 18.5, 18.3, 18.0, 17.8. Elemental analysis calculated (%) for C$_{47}$H$_{43}$N$_4$O$_3$ClORu (770.39): C 68.59, H 6.28, N 5.46; found C 68.59, H 6.20, N 6.53. Crystals suitable for X-ray analysis were grown from a saturated solution of chloroform added with pentane, which was placed in the refrigerator with a balloon of argon for several weeks. The crystals are black and when redissolved, a reddish solution is formed.

6.2.2.5 Synthesis of 4.14

0.3727 g of the Tl salt 6.5B (0.637 mmol; 1.1 equiv) was added to a 15 ml THF solution containing 0.440 g of 4.12 (0.607 mmol; 1 equiv) and the resulting mixture was stirred for 2 hours at room
temperature. The solvent was evaporated, the residue redissolved in toluene, and the white precipitate TlCl was removed by filtration. The filtrate was evaporated and ~1 ml of CH₂Cl₂ was added to redissolve the product. Then, 20 ml of hexane was added after which the dispersion was placed in an ultrasonic bath for 2 minutes. A solid was obtained by filtration. The dark green precipitate 4.14 was washed with 10 ml of hexane and dried en vacuo. Yield: 74 %. 

1H NMR (CDCl₃): δ (ppm): 18.82 (s, 1H, Ru=C₃H₇Ph), 8.78 (s, 1H), 8.37 (s, 1H), 7.54-6.61 (m, 11H), 6.29 (s, 1H), 5.69 (d, 1H), 4.20 (s, 2H, CH₂, H2IMES), 3.86 (d, 2H, CH₂, H2IMES), 2.85 (d, 6H, CH₃, MesCH₃), 2.47 (s, 6H, CH₃, MesCH₃), 1.90 (s, 6H, CH₃, MesCH₃), 1.39 (s, 27H, C₆H₁₃, tert-butyl); 13C NMR (CDCl₃): δ (ppm) (spectrum obtained on a 300 MHz JEOL spectrometer at the faculty of bioscience engineering): 308.6 (Ru=C₃H₇-Ph), 217 (Ru-C NN), 176.4 (C-O), 167 (C=N), 158.4, 155.0, 152.1, 151.9, 143.4, 140.3, 139.9, 139.3, 139.1, 138.8, 137.6, 136.9, 136.2, 134.7, 133.1, 131.1, 130.8, 130.2, 129.6, 129.3, 128.9, 128.5, 128.0, 127.2, 126.6, 124.7, 123.9, 123.7, 122.5, 121.8, 119.0, 52.8 (CH₂, H2IMES), 50.7 (CH₂, H2IMES), 36.2, 36.0, 35.0, 34.9, 32.3, 32.0, 31.6, 21.3, 21.0, 20.4, 20.2, 18.0, 17.3 (While the 13C NMR was in progress a considerable amount of decomposed product was already formed).

6.2.2.6 Synthesis of 4.15

0.405 g of 1.4 (0.478 mmol; 1 equiv) was put in a flask together with 1 ml of pyridine. The reaction was placed in the ultrasonic bath for 2 minutes and 30 ml of hexane was added. The resulting green solid 4.12 precipitated, was filtered and washed with 2 ml of hexane. The solid was dried in vacuo. 10 ml of THF was added in the filter to transfer 4.12 in a new flask. 0.2645 g of 6.6B (0.526 mmol; 1.1 equiv) was added and the reaction was stirred for 2 hours at room temperature. The reaction mixture was evaporated, dissolved in toluene and the white precipitate TlCl was removed by filtration. The filtrate was evaporated and ~1 ml of CH₂Cl₂ was added to redissolve the product. Then, 40 ml of hexane was added after which the dispersion was placed in an ultrasonic bath for 10 minutes and a solid was obtained by filtration. The red precipitate 4.15 was washed with 10 ml of hexane and dried en vacuo. Yield: 67%. 1H NMR (CDCl₃): δ (ppm): 17.89 (s, 1H, Ru-C₃H₇Ph), 7.98 (dd, 1H), 7.91 (d, 1H), 7.62 (s, 1H), 7.46 (t, 1H), 7.54 (s, 1H), 7.33 (s, 1H), 7.21 (s, 1H), 7.18 (m, 1H), 7.15 (m, 1H), 7.06 (t, 2H), 6.83-6.73 (m, 3H), 6.60 (s, 1H), 6.46 (s, 1H), 6.43 (s, 1H), 4.21 (s, 1H, CH₂_H2IMES), 4.18 (s, 1H, CH₂_H2IMES), 4.08 (m, 2H, CH₂, H2IMES), 2.53 (m, 3H), 2.50 (m, 3H), 2.46 (s, 3H), 2.31 (s, 3H), 2.22 (s, 3H), 1.30 (s, 3H). 13C NMR (CDCl₃): δ (ppm) (spectrum obtained on a 300 MHz JEOL spectrometer at the faculty of bioscience engineering): 304.9 (Ru-C₃H₇-Ph), 219.0 (Ru-CN), 174.0 (C-O), 164.8 (C-N), 151.2, 150.5, 148.7, 140.4, 139.2, 139.1, 138.1, 137.8, 136.6, 136.3, 135.3, 134.1, 132.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.2, 127.8, 127.3, 124.6, 123.3, 118.6, 51.8 (CH₂_H2IMES), 50.4 (CH₂_H2IMES), 34.4, 31.6, 31.4, 31.3, 31.2, 21.1, 21.0, 20.3, 18.7, 18.0.

6.2.2.7 Synthesis of 4.16

0.298g of 1.4 (0.362 mmol; 1 equiv) was put in a flask together with 1 ml of pyridine. The reaction was placed in the ultrasonic bath for 2 minutes after which 30 ml of hexane was added. The resulting green precipitate 4.12 was filtered, was washed with 2 ml of hexane. The solid was dried in vacuo and 8 ml of THF was put in the filter to transfer 4.12 in a new flask. 0.2134 g of 6.7B (0.398 mmol; 1.1 equiv) was added and the reaction was stirred for 2 hours at room temperature. The reaction mixture was evaporated, dissolved in toluene and the white precipitate TlCl was removed by filtration. The filtrate was evaporated and ~1 ml of THF was added to redissolve the product. Then, 30 ml of hexane was added after which the dispersion was placed in an ultrasonic bath for 10 minutes and a solid was...
obtained by filtration. The red precipitate 4.16 was washed with 10 ml of hexane and dried in vacuo. Yield: 60%. $^1$H NMR (CDCl$_3$): $\delta$ (ppm): 18.09 (s, 1H, Ru=CHPh), 8.07-8.00 (m, 2H), 7.69 (s, 1H), 7.44-7.38 (m, 3H), 7.09-7.04 (m, 3H), 6.90-6.87 (d, 1H), 6.62 (s, 1H), 6.55 (s, 1H), 6.51 (s, 1H), 4.25-4.00 (m, 4H, CH$_2$, H$_2$IMES), 2.52 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm): 305.6 (Ru=C-Ph), 218.0 (Ru-CNN, 175.2, 169.7, 151.5, 139.7, 139.5, 138.5 (d), 137.9, 136.6, 136.2, 135.9, 135.3, 132.5, 130.3 (d), 129.8, 129.5, 129.4, 129.2, 128.6, 128.1, 124.5, 117.5, 51.9 (CH$_2$, H$_2$IMES), 50.8 (CH$_2$, H$_2$IMES), 21.2, 21.1, 20.1, 18.9, 18.3, 18.2.

6.2.2.8 Synthesis of 4.17

0.1 g of 6.8A (0.734 mmol; 1.1 equiv) was put in flask with 5 ml of THF. Next, 0.184 g of thallium ethoxide (0.734 mmol; 1.1 equiv) was added. The mixture was stirred for 2 hours at room temperature after which the solvent was removed in vacuo. 0.484 g of 4.12 (0.667 mmol; 1 equiv) and 10 ml of THF were added. The mixture was stirred for 1 hour at room temperature after which the solvent was evaporated. The resulting product mixture was dissolved in 5 ml of toluene and the white precipitate TlCl was removed by filtration. The filtrate was evaporated again and 5 ml of hexane was added. The mixture was placed in the ultrasonic bath for 5 minutes after which a solid appeared which was filtered and dried in vacuo. 4.17 was obtained as a green to dark-green solid in 55% yield. 4.17 decomposes fast in solution which disabled us to acquire a $^{13}$C NMR spectrum. $^1$H NMR (CDCl$_3$): $\delta$ (ppm): 18.00 (s, 1H, Ru=CH-Ph), 8.63 (s, 1H), 7.55 (s, 1H), 7.42-7.39 (m, 2H), 7.13 (1H), 7.05-6.99 (m, 2H), 6.87-6.84 (m, 3H), 6.62 (s, 2H), 6.39 (1H), 5.59 (1H), 4.08 (s, 4H, CH$_2$, H$_2$IMES), 3.42 (s, 3H, CH$_3$, NMe), 2.51 (s, 9H), 2.16 (s, 9H).

6.2.2.9 Synthesis of 4.18

0.2715 g of the Tl salt 6.9B (0.541 mmol; 1.1 equiv) was added to a 15 ml THF solution with 0.416 g 4.12 (0.491 mmol; 1 equiv) and stirred for 2 hours at room temperature. The solvent was evaporated and the mixture was dissolved in toluene after which the white precipitate TlCl was removed by filtration. The solution was again evaporated and 6 ml of hexane was added. The mixture was placed in the ultrasonic bath until a precipitate was formed which was filtered and dried in vacuo. 4.19 was obtained as a green solid in 65% yield. 1H NMR (CDCl$_3$): $\delta$ (ppm): 17.72 (s, 1H, Ru=CH-Ph), 7.45 (s, 1H), 7.42 (s, 1H), 7.38 (1H), 7.20 (s, 1H), 7.03-6.95 (m, 4H), 6.89 (d, 2H), 6.78 (d, 1H), 6.56 (d, 1H), 6.42 (s, 1H), 6.25 (1H), 4.16 (s, 1H, CH$_2$, H$_2$IMES), 4.13 (s, 1H, CH$_2$, H$_2$IMES), 4.10-3.92 (m, 2H, CH$_2$, H$_2$IMES), 2.70 (s, 3H), 2.63 (s, 3H), 2.58 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 2.04 (s, 6H), 1.98-1.83 (m, 6H), 1.63 (m, 6H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm): 301.5 (Ru=C-Ph), 220.3 (RuCNN), 170.3 (C-O), 159.3 (C=N), 151.2, 134.7, 131.6, 129.9, 129.8, 129.6, 129.0, 128.7, 127.5, 113.7, 98.8, 65.0, 51.9 (CH$_2$, H$_2$IMES), 50.7 (CH$_2$, H$_2$IMES), 43.2, 38.4, 36.5, 30.7, 21.2 (d), 20.5, 19.3, 18.4, 18.1.

6.2.2.10 Synthesis of 4.19

0.3582 g of the Tl salt 6.10B (0.883 mmol; 1.2 equiv) was added to a 15 ml THF solution of 0.533 g 4.12 (0.736 mmol; 1 equiv) and stirred for 2 hours at room temperature. The solvent was evaporated and the mixture was redissolved in toluene after which the white precipitate TlCl was removed by filtration. The solution was again evaporated and 6 ml of hexane was added. The mixture was placed
in the ultrasonic bath for 10 minutes after which a green precipitate appeared which was filtered off and dried in vacuo. **4.19** was obtained as a bright green solid in 68% yield. $^1$H NMR (CDCl$_3$): δ (ppm): 17.66 (s, 1H, Ru=CH-Ph), 7.47 (s, 1H), 7.38-7.30 (m, 3H), 7.09-6.97 (m, 4H), 6.87 (s, 1H), 6.84 (s, 1H), 6.78-6.75 (d, 1H), 6.69 (s, 1H), 6.57 (s, 1H), 6.34 (t, 1H), 5.09 (t, 1H), 4.24-3.94 (m, 4H, CH$_2$, H$_2$IMES), 2.55 (s, 9H), 2.22 (s, 6H), 1.93 (s, 3H), 1.70-1.32 (m, 8H), 1.0 (m, 1H), 0.57 (q, 1H); $^{13}$C NMR (CDCl$_3$): δ (ppm): 301.1 (Ru=C-Ph), 221.1 (Ru-CNN), 168.5 (C-O), 159.2 (C=N), 151.6, 135.2, 131.9, 129.8, 129.3, 129.2, 128.7, 127.7, 122.5, 120.8, 113.3, 62.9 (C-N), 51.9 (CH$_2$, H$_2$IMES), 50.7 (CH$_2$, H$_2$IMES), 37.0, 32.3, 26.2, 26.0, 25.8, 21.2, 20.5, 18.9, 18.1. No crystals suitable for X-ray analysis could be obtained using CH$_2$Cl$_2$/pentane, CHCl$_3$/pentane and CH$_2$Cl$_2$/hexane mixtures.

### 6.3 Attempts at the reparation of bimetallic catalysts 4.2

#### 6.3.1 Synthesis of the catalyst mixture 1.97 + 4.27

A 50 ml flask was charged with 0.25 g (0.3 mmol) of **4.10A** and 0.202 g (0.33 mmol) of [Ru(p-cymene)Cl$_2$]$_2$. 25 ml THF was added and the reaction mixture was refluxed. The reaction was monitored with $^{31}$P NMR which showed that after 4 hours the reaction was finished. Thereupon, the reaction was cooled down and the remaining [Ru(p-cymene)Cl$_2$]$_2$ was filtered off. The reaction was evaporated, and 5 ml of benzene was added. Since no precipitation was formed, 5 ml pentane was added to precipitate the complex, which was washed twice with 10 ml of a 1:1 benzene:pentane solution and dried in vacuo. The yellow-ocher solid 1.97 + 4.27 was obtained in 58% yield.

$^1$H NMR (CDCl$_3$): δ (ppm): 19.65 (d, J$_{HP}$ = 9.9 Hz, 1 H, Ru=CH-Ph), 8.53 (d, 2 H, H$_2$IMES fragment 1.97), 5.84 (d, 1H, H$_2$IMES fragment 4.27), 5.35 (t, 2 H, H$_2$IMES fragment 1.97), 5.26 (d, 1H, H$_2$IMES fragment 4.27), 5.16 (d, 1H, H$_2$IMES fragment 1.97), 5.00 (d, 1H, H$_2$IMES fragment 4.27), 4.27 (d, 1H, CH$_2$, H$_2$IMES fragment 1.97), 2.95 (sept, 1 H, CH(CH$_3$)$_2$, 4.27 fragment), 2.79 (sept, 1 H, CH(CH$_3$)$_2$, 4.27 fragment), 2.20-0.88 (m, 63 H); $^{31}$P NMR (CDCl$_3$): δ (ppm): 48.9. $^{13}$C NMR could not be obtained due to the instability of the catalyst.

#### 6.3.2 $^1$H NMR of 1.97 in CDCl$_3$

1.97 was prepared analogously to literature$^{11}$, though THF was used as solvent instead of benzene.$^1$H NMR (CDCl$_3$): δ (ppm): 19.65 (d, 1H), 8.53 (d, 2H), 7.71 (t, 1H), 7.45 (t, 2H), 5.55 (d, 1H), 5.35 (d, 1H), 5.26 (d, 1H), 5.16 (d, 1H), 2.95 (sept, 1H), 2.20 (s, 3H), 2.05 (q, 3H), 1.83-1.17 (m, 36H).

#### 6.3.3 Synthesis of complex 4.27

0.1026 g of **4.10A** (0.123 mmol; 1 equiv) was added to 0.038 g of [Ru(p-cymene)Cl$_2$]$_2$ (0.062 mmol; 0.5 equiv) in a 50 ml flask. The products were dissolved in 10 ml of THF and refluxed for 16 hours. The solvent was evaporated and the product was precipitated in a benzene:pentane 1:3 mixture and washed with pentane. **4.27** was obtained in 55 % yield as a dark(black)-ocher powder which showed yellowish in diluted solution. Column chromatography was performed using hexanes with a gradient addition of ethyl acetate fraction from 0 to 1/3. $^1$H NMR (CDCl$_3$): δ (ppm): 8.02 (dd, 1H), 7.91 (d, 1
Experimental

H), 7.55 (s, 1H), 7.36-7.29 (m, 4 H), 6.89 (d, 1 H), 5.46 (d, 1 H), 5.33 (d, 1 H), 5.00 (d, 1 H), 4.28 (d, 1 H), 4.02 (sept, 1 H), 2.79 (sept, 1 H), 1.95 (s, 3 H), 1.49 (d, 3H), 1.38 (dd, 6 H), 1.29 (d, 3 H), 1.03 (dd, 6 H); 13C NMR (CDCl3): δ (ppm): 173.1, 166.6, 152.0, 142.2, 141.0, 136.3, 132.9, 129.9, 128.6, 128.4, 124.8, 123.8, 122.8, 119.2, 105.6, 94.8, 88.2, 84.9, 82.2, 31.0, 28.3, 27.7, 26.9, 26.3, 23.4, 22.9, 22.5, 22.1, 18. The NMR data completely match the NMR data of 4.27 which is a red powder and red in solution.

6.3.4 Alternative procedure for the preparation of 4.27 in stead of 4.24

A 25 ml Schlenk flask was charged with 0.0775 g 4.10A (0.091 mmol), 0.0650 g [Ru(p-cymene)Cl2]2 (0.106 mmol) and 10 ml of THF. The reaction was stirred at 70°C for 6 hours. The solvent was removed in vacuo and the residue was redissolved in 4 ml of THF and 4 ml of pentane. The remaining [Ru(p-cymene)Cl2] was filtered and washed with a THF/pentane 1:1 mixture. The filtrate was evaporated after which 2 ml of benzene and 2 ml of pentane were added. The precipitate was filtered and washed with a 1:1 benzene:pentane mixture (the filtrate was removed). In an attempt to isolate 1.97, the precipitate was washed with a 25:1 acetone/benzene mixture, similar to the purification by Grubbs et al.11 No colour change of the precipitate occurred (ocher) and all the precipitate was washed away, disabling us to separate 1.97. The filtrate was evaporated and again 2 ml of benzene and 2 ml of pentane were added. The precipitate was filtered and washed with 4 ml of a benzene/pentane 1:1 solution and subsequently with 5 ml of pentane. The yellow/ocher solid which was obtained was pure 4.27 and the filtrate showed a mixture of both 1.97 and 4.27. Both NMR analysis and elemental analysis were performed on the obtained 4.27 to validate its structure.

6.4 Synthesis of NHC-precursors and metal-NHC complexes

6.4.1 Synthesis of NHC-precursors

6.4.1.1 Synthesis of precursors for 5.1

6.4.1.1.1 Synthesis of 5.8

A slightly modified preparation of the of O2IPh-HCl synthesis12 was performed. A 100 ml flask was charged with 4.107 g (0.0164 mol) 1,3-dimesitylformamidine (5.7), 40 ml of THF and placed in an ice bath whereupon 1,3-dimesitylformamidine precipitated. 1.239 ml (0.0164 mol) of oxalyl chloride was added upon which the precipitation disappeared. The reaction was stirred for 2 hours, evaporated under reduced pressure and dried in vacuo. 5.8 was obtained in quantitative yield and hydrolyzed slowly in the presence of small amounts of H2O in solution and even in the solid state into 5.9. 1H NMR (300 MHz, CDCl3): δ (ppm): 7.14 (s, 1H, ClC6H5), 7.06 (s, 2H, Harom), 7.00 (s, 2H, Harom), 2.37 (s, 6H, ClC6H5), 2.33 (s, 6H, ClC6H5), 2.26 (s, 6 H, CH3); 1H NMR (300 MHz, DMSO): δ (ppm): 7.88 (s, 1H, ClC6H5), 7.01 (s, 4H, CCl5), 2.26 (s, 6H, CH3, para), 2.19 (s, 12H, CH3 ortho); 13C NMR (300 MHz, CDCl3): δ (ppm): 155.7 (C=O), 140.5, 138.0, 134.6, 130.6, 130.0, 127.7, 84.5 (CCI), 21.3, 19.3, 18.8, 18.24, 18.19.

1Received from Hans Van Der Mierde (PhD student COMOC, Ghent University)
6.4.1.1.2 Synthesis of 5.9

A 50 ml flask was charged with 0.505 g (1.41 mmol) of 5.8, 5 ml of CHCl₃ and 1 ml of H₂O. The reaction was stirred for 1 hour, the CHCl₃ was removed under reduced pressure. The product was precipitated in H₂O and obtained in 94% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.97 (s, 2H, H-arom), 6.93 (s, 2H, H-arom), 6.40 (s, 1H; CNNH), between 4.30 and 3.10 (depending on the concentration and H₂O impurities, s, 1H: O-H), 2.29 (s, 6H, CH₃), 2.24 (s, 6H, CH₃), 2.16 (s, 6H, CH₃); ¹H NMR (300 MHz, CD₃OD): δ (ppm): 7.04 (s, 4H), 6.39 (d, 1H), 2.31-2.26 (18 H); ¹³C NMR (300 MHz, CDCl₃): δ (ppm): 156.7 (C=O), 139.8, 138.6, 135.5, 130.1, 129.7, 128.3, 88.4 (CNOH), 21.30, 21.27, 18.8, 18.7, 18.2, 18.1.

6.4.1.1.3 Synthesis of 5.10

A 50 ml flask was charged with 0.368 g (1.03 mmol) of 5.8 and 15 ml of EtOH. The resulting reaction mixture was refluxed for 5 minutes and then cooled down in an ice bath. 30 ml of water was added and the precipitate was collected in 96% yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.00 (s, 2H, H-arom), 6.96 (s, 2H, H-arom), 5.94 (s, 1H, CNNH), 3.17 (q, 2H, OCH₂CH₃), 2.32 (s, 12H, CH₃, ortho), 2.26 (s, 6H, CH₃, para), 0.79 (t, 3H, OCH₂CH₃); ¹³C NMR (300 MHz, CDCl₃): δ (ppm): 156.6 (C=O), 139.7, 138.4, 134.9, 130.1, 129.6, 129.3, 128.7, 95.3 (CNOH), 67.7 (OCH₂CH₃), 21.3, 18.7, 18.2, 15.1.

6.4.1.2 Synthesis of 5.13

6.4.1.2.1 Synthesis of 5.11A

A 500 ml flask was charged with 8.1 g (88 mmol) of glyoxalic acid monohydrate and 80 ml of THF. 24.72 ml (176.16 mmol) of 2,4,6-trimethyl aniline was added. After 10 minutes, 18.56 g (88.08 mmol) of DCC (N,N'-Dicyclocarbodiimide) was added whereupon the reaction mixture heated. 15 minutes later a white precipitate was filtered off. The filtrate was evaporated, n-propanol was added and the mixture was placed in an ice-bath. 5.11A was obtained as a yellow product in 58 % yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.64 (s, 1H), 7.74 (s, 1H), 6.96 (s, 2H, H-arom), 6.93 (s, 2H, H-arom), 6.96 (s, 2H, H-arom), 6.93 (s, 2H, H-arom), 2.30 (s, 6H, CH₃), 2.27 (s, 6H, CH₃), 2.16 (s, 6H, CH₃); ¹³C NMR (300 MHz, CDCl₃): δ (ppm): 161.6, 157.4, 145.2, 137.5, 135.3, 135.2, 130.5, 129.4, 129.3, 128.7, 95.3 (CNOH), 67.7 (OCH₂CH₃), 21.3, 18.7, 18.2, 15.1.

6.4.1.2.2 Synthesis of 5.11B

A 500 ml flask was charged with 13.7 g (44.4 mmol) of 5.11A and dissolved in 100 ml of dry THF. During 2 hours 2.2 equiv of NaBH₄ (97.7 mmol; 3.70 g) were added. The reaction was stirred for 15 hours at room temperature and subsequently heated for 2 hours under reflux. Thereupon, the mixture was placed in an ice-bath. 5.11B was obtained as a yellow product in 58 % yield. ¹H NMR (300 MHz, DMSO): δ (ppm): 9.93 (s, 1H, C(O)NH₂), 6.94 (s, 2H, C-arom), 6.85 (s, 2H, C-arom), 4.19 (s, 2H, NH-CH₂-C=O), 2.40 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 2.02 (s, 6H, CH₃).

A 250 ml flask was charged with 8 g of 5.11B·HCl and 50 ml of H₂O. Thereupon, 6 g of NaOH was added and the reaction was placed in the ultrasonic bath for 30 minutes. The resulting mixture was 4 times extracted with 50 ml of ethyl acetate. The combined organic fractions were extracted with 50 ml of H₂O. The ethyl acetate solution was dried with MgSO₄, the MgSO₄ was filtered off and the filtrate
was evaporated. Pentane was added and the resulting 5.11B was filtered off as a white solid in 84 % yield. 

1H NMR (300 MHz, CDCl3): δ (ppm) : 8.51 (s, 1H, C(O)N\textsubscript{H}), 6.92 (s, 2H, H\textsubscript{arom}), 6.87 (s, 2H, H\textsubscript{arom}), 3.79 (s, 2H, NH-CH\textsubscript{2}-C=O), 2.34 (s, 6H, CH\textsubscript{3}), 2.28 (s, 6H, CH\textsubscript{3}), 2.23 (s, 6H, CH\textsubscript{3}); 13C NMR (300 MHz, CDCl3): δ (ppm): 169.8 (C=O), 142.5, 137.3, 135.1, 133.0, 131.1, 130.2, 13.0, 129.6, 129.5, 129.3, 52.6 (N-CH\textsubscript{2}-C=O), 21.2, 20.8, 18.8, 18.6.

6.4.1.2.3 synthesis of 5.12A

A 50 ml Schlenk flask was charged with 2.2 g (7.1 mmol) of 5.11B, 30 ml of methanol and 1.264 g (15.6 mmol) of a 36 % CH\textsubscript{2}O solution in water. The flask was sealed and the mixture was stirred at 80 °C for 15 hours. The solvent was evaporated and Et\textsubscript{2}O was added upon which a precipitate appeared. The mixture was filtered, the filtrate was evaporated and the residue was precipitated in pentane in 45 % yield as a white solid. 1H NMR (300 MHz, CDCl3): δ (ppm) : 6.96 (s, 2H, H\textsubscript{arom}), 6.92 (s, 2H, H\textsubscript{arom}), 4.76 (s, 2H, N\textsubscript{2}CH\textsubscript{2}), 4.07 (s, NCH\textsubscript{2}-C=O), 2.35 (s, 6H, CH\textsubscript{3}), 2.29 (s, 12H, CH\textsubscript{3}); 13C NMR (300 MHz, CDCl3): δ (ppm): 171.0 (C=O), 138.8, 138.6, 137.0, 136.4, 130.0, 129.7, 129.3, 125.3, 68.8 (N-CH\textsubscript{2}-N), 53.3 (N-CH\textsubscript{2}-C=O), 21.2, 21.1, 18.7, 18.0.

6.4.1.2.4 Synthesis of 5.12B

5.12B was successfully synthesized by two different procedures reacting 5.12A with NBS (N-Bromosuccinimide), though both procedures were not reproducible.

Method A: In a 50 ml flask, 0.2078 g of 5.12A (0.644 mmol) and 0.1147 g of NBS (0.644 mmol; 1 equiv) were added. The mixture was dissolved in 10 ml of dry 1,2-dimethoxyethane and placed in the ultrasonic bath for 3 hours. Thereupon, 20 ml of Et\textsubscript{2}O was added after which no precipitation occurred. Then, 30 ml of pentane was added to the mixture, upon which a light yellow precipitate of the desired product formed which was filtered off. 5.12B was obtained as a yellow solid in 25 % yield.

Method B: A 50 ml flask was charged with 0.6033 g of 5.12A (1.87 mmol), 0.3330 g of NBS (1.87 mmol) and 30 ml of THF. After 3 hours of reaction, a white powder formed. The reaction was stirred for an additional 15 hours upon which a yellow powder 5.12B precipitated, which was filtered off in 24 % yield.

1H NMR (300 MHz, DMSO): δ (ppm) : 9.66 (s, 1H, BrC\textsubscript{H}NN), 6.95 (s, 2H, H\textsubscript{arom}), 6.87 (s, 2H, H\textsubscript{arom}), 4.15 (s, 2H, N-CH\textsubscript{2}-C=O), 2.36 (s, 6H, CH\textsubscript{3}), 2.21 (s, 6H, CH\textsubscript{3}), 2.04 (s, 6H, CH\textsubscript{3}); 13C NMR (300 MHz, DMSO): δ (ppm): 165.4, 137.3, 136.6, 135.3, 131.9, 131.6, 130.8, 129.1, 51.4, 21.2, 20.9, 18.6, 18.4.

6.4.1.2.5 Synthesis of 5.13

A 25 ml flask was charged with 0.209 g of AgBF\textsubscript{4} (1.08 mmol) and 0.4306 g of 5.12B (1.08 mmol). Dry ethanol was added and after stirring for a few minutes, AgBr was filtered off. The reaction mixture was evaporated and the residue was redissolved in a minimum of dichloromethane. Next, pentane was added until a precipitate appeared. 5.13 was filtered off as a yellow solid in 82 % yield. 1H NMR (300 MHz, DMSO): δ (ppm) : 9.62 (s, 1H, C\textsubscript{H}NN), 6.93 (s, 2H, H\textsubscript{arom}), 6.85 (s, 2H, H\textsubscript{arom}), 4.12 (s, 2H, N-CH\textsubscript{2}-C=O), 2.34 (s, 6H, CH\textsubscript{3}), 2.19 (s, 6H, CH\textsubscript{3}), 2.02 (s, 6H, CH\textsubscript{3}); 13C NMR (300 MHz, DMSO): δ (ppm): 165.4, 137.3, 136.6, 135.3, 131.9, 131.6, 130.8, 129.1, 51.4, 21.2, 20.9, 18.6, 18.4.
6.4.1.3 Synthesis of 5.15

6.4.1.3.1 Synthesis of 5.14

A 1 l flask was charged with 3.979 g (14.2 mmol) of 5.7 and 150 ml of dry THF. Then, 3.76 g 2-chloro-2,2-diphenylacetyl chloride (14.2 mmol) was added in three portions over 5 minutes. The reaction mixture was stirred for one hour after which 350 ml of saturated NaHCO₃ was added. The resulting mixture was 3 times extracted with ethyl acetate, the combined organic fractions were dried over MgSO₄ and the solvent was evaporated. 50 ml of Et₂O was added and the white precipitate was filtered.

5.14 was obtained as a white powder in 90 % yield. \(^1\)H NMR (300 MHz, CDCl₃): δ (ppm): 8.34 (s, 1H, N=CH), 7.36 (s, 10H, H\text{phenyl}), 6.97 (s, 2H, H\text{arom, mesityl}), 6.65 (s, 2H, H\text{arom, mesityl}), 2.32 (s, 6H, CH₃), 2.28 (s, 3H, CH₃), 2.16 (s, 3H, CH₃), 1.73 (s, 6H, CH₃); \(^{13}\)C NMR (300 MHz, CDCl₃): δ (ppm): 169.3 (C=O), 149.8, 145.4, 140.1, 138.4, 135.4, 133.3, 132.6, 129.8, 129.2, 128.8, 128.7, 128.6, 127.9, 21.4, 20.9, 18.6, 18.3.

6.4.1.3.2 Synthesis of 5.15

A 100 ml Schlenk flask was charged with 5.837 g of 5.14 (11.5 mmol) and 75 ml of dry acetonitrile. The flask was sealed and the reaction mixture was heated to 100 °C. Within 15 minutes, the solid was dissolved. The reaction was stirred at 100 °C for an additional 10 hours, upon which a white solid formed. The mixture was cooled down and the white precipitate was filtered off and washed with Et₂O.

5.15 was obtained in 90 % yield. Upon evaporation of the filtrate, precipitation of the residue in Et₂O and recrystallization in acetonitrile, additional 5.15 was obtained up to a combined yield of 97 %. If pinkish-orange impurities are generated in the product it can be purified by reprecipitations in acetone.

\(^1\)H NMR (300 MHz, CDCl₃): δ (ppm): 11.82 (s, 1H, H\text{CNN}), 7.53-7.40 (10H, H\text{arom, phenyl}), 7.04 (s, 2H, H\text{arom, mesityl}), 6.77 (s, 2H, H\text{arom, mesityl}), 2.47 (s, 6H, CH₃), 2.33 (s, 3H, CH₃), 2.23 (s, 3H, CH₃), 1.80 (s, 6H, CH₃); \(^{13}\)C NMR (300 MHz, CDCl₃): δ (ppm): 172.8 (C=O), 168.3 (CNN), 141.8, 137.5, 135.9, 131.1, 131.0, 130.8, 130.7, 130.0, 129.3, 126.0, 21.3, 21.1, 20.7, 19.6. IR (cm\(^{-1}\)): 1772 (KBr)

6.4.2 Synthesis of metal-NHC complexes

6.4.2.1 Synthesis of 5.17

A Schlenk flask was charged with 0.3467 g 2.55-HCl (0.737 mmol) and 0.303 g 1.3 (0.368 mmol) and dissolved in 20 ml of toluene. 736 µl of a 1 M LiHMDS solution in toluene (0.737 mmol) was added to the mixture. After 1.5 hours of reaction no 1.3 was present and the reaction mixture was evaporated. The product was precipitated in methanol. The precipitate was purified using flash column chromatography over silica with Et₂O/hexane 1/9 → 1/3 as the eluent gradient. A dark fraction appears where after a red fraction appears. Upon evaporation of the dark fraction, 5.17 was obtained as a grey-black solid was obtained in 58 % yield. \(^1\)H NMR (300 MHz, CDCl₃): δ (ppm): 19.27 (s, 1H, Ru=C\text{HPh}), 9.05 (br s, 1H, HC=CN), 7.68 (3H), 7.35 (s, 1H), 7.14 (4H), 5.95 (br s, 1H), 2.43-0.89 (51H); \(^{13}\)C NMR (300 MHz, CDCl₃): δ (ppm): 298.8 (d, J(P,C) = 24.6 Hz, Ru=\text{C-Ph}), 207.6 (d, J(P,C) = 85.2 Hz, Ru=\text{CNN}), 174.0 (C=O), 163.7 (CNN), 151.6, 140.2, 139.5, 137.9 (br), 136.0, 134.5 (d, J = 11 Hz), 133.0, 132.0, 130.1, 129.3, 129.0, 127.2, 127.1, 126.0, 35.2, 32.2, 31.9, 31.7, 30.4,
29.9, 29.6, 29.3 (br), 28.1, 27.9, 27.3, 27.1, 26.6 (d), 26.3, 22.9, 21.7, 21.5, 20.1, 18.8 (br), 14.4. \(^{31}\)P NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm): 30.05. IR (cm\(^{-1}\)): 1674 (KBr).

6.4.2.2 Synthesis of 5.18

A Schlenk flask was charged with 0.539 g of 1.3 (0.654 mmol) and 0.834 g of 5.15 (1.637 mmol, 2.5 equiv) and 15 ml of toluene were added. Thereupon, 1.637 ml of 1 M solution of LiHMDS in toluene (1.637 mmol) was added. After 2 hours of reaction at room temperature, all 1.3 had reacted whereupon the solvent was removed. The crude product was purified using flash column chromatography over silica with hexane \(\rightarrow\) Et\(_2\)O/hexane 1/14 as the eluent gradient. 5.18 was obtained in 84 % yield as a light brownish solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) (from crystal): 19.06 (s, 1H, Ru=C\(_{\text{Ph}}\)), 8.90 (br s, 1H), 7.67 (br s, 4H), 7.35-7.25 (7H), 7.07 (5H), 6.5 (br s, 1H), 5.48 (br s, 1H), 2.72-0.9 (51H). \(^1\)H NMR shows no isomers. However, \(^{31}\)P NMR and \(^{13}\)C NMR clearly show the existence of two isomers. \(^{31}\)P NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm): 28.74 (41 %), 27.87 (59 %). Upon crystallization in CH\(_2\)Cl\(_2\)/pentane, CH\(_2\)Cl\(_2\)/hexane and THF only the isomer with a resonance in \(^{31}\)P NMR at \(\delta = 27.87\) remains. The mixture returned to equilibrium before a \(^{13}\)C NMR could be obtained. The most reasonable equilibrium structures are depicted in Figure 6.2. \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm): 300.4 (Ru=C-Ph), 299.2 (Ru=C-Ph), 241.2 (RuCNN), 240.7 (RuCNN), 240.1 (RuCNN), 239.6 (RuCNN); possibly (241.2 and 240.1) and (240.7 and 239.6) are doublets based on the signal height (and the same coupling constant): 240.7 (d, \(J(P,C) = 82.0\) Hz, RuCNN), 240.2 (d, \(J(P,C) = 83.4\) Hz, RuCNN); based on signal heights 240.7 should be associated with 299.2); 173.2 (C=O), 151.2, 150.5, 140.1, 139.6, 139.5, 138.6, 136.5, 130.8, 130.5 (br), 130.1, 129.3, 129.1, 128.1, 127.3, 36.0, 35.1, 32.2, 31.8, 31.7, 31.6, 31.5, 31.4, 30.4, 29.9, 29.6, 29.5-29.0, 28.1, 27.9, 27.2, 27.1, 26.6, 26.5, 26.4, 26.3, 22.9, 22.3, 21.5, 21.2, 21.1, 20.8, 14.4. IR (cm\(^{-1}\)): 1749 (KBr)

Figure 6.2: Equilibrium of two isomers from 5.18

6.4.2.3 Synthesis of 5.19

A Schlenk flask was charged with 0.2488 g [Rh(COD)Cl]\(_2\) (0.505 mmol) and 0.5651 g 5.15 (1.11 mmol, 2.2 equiv) 5.15 and 10 ml THF. 1.11 ml of a 1 M LiHMDS solution (1.11 mmol) was added,
the reaction was stirred for 2 hours at room temperature after which the solvent was removed. The crude reaction product was purified using flash column chromatography over silica with hexane → Ethyl acetate/ hexane 1/1 as the eluent gradient. 5.19 was obtained in 75 % yield as a yellow solid. NMR data were collected from crystals grown in CH$_2$Cl$_2$/hexane.

\[ \delta (ppm): 7.72 (m, 2H, Ph), 7.38-7.32 (m, 4H, Ph), 7.24 (t, 2H, Ph), 7.14-7.10 (m, 3H, Ph and Mes), 7.05 (s, 1H, Mes), 6.92 (s, 1H, Mes), 6.61 (s, 1H, Mes), 4.83 (1H, cod CH), 4.60 (1H, cod CH), 3.39 (s, 2H, cod CH), 2.65 (s, 3H, Mes), 2.39 (s, 3H, Mes), 2.34 (s, 3H, Mes), 2.27 (s, 3H, Mes), 2.26 (s, 3H, Mes), 1.70-1.45 (m, 8H, cod CH$_2$), 1.03 (s, 3H, Mes); \]

\[ \text{IR (cm}^{-1}\text{): 1754 (KBr)} \]

6.4.2.4 Synthesis of 5.21

A flask was charged with 0.218g of 5.19 (0.292 mmol) and 10 ml of CH$_2$Cl$_2$. During 30 minutes, CO was purged through the mixture, after which the solvent had evaporated. 30 ml of pentane were added and the mixture was placed in an ultrasonic bath for 30 minutes whereupon a fine powder appeared. The light yellow suspension was filtered and washed twice with 5 ml of pentane. The precipitate was dried in vacuo. 5.21 was obtained as an off-white solid in 76 % yield. \[ \delta (ppm): 7.46-7.26 (m, 10H, Ph), 7.04 (s, 2H, Mes), (br s [6.85-6.65], 2H, Mes), 2.46 (s, 6H, CH$_3$Mes), 2.38 (s, 3H, CH$_3$Mes), 2.26 (s, 3H, CH$_3$Mes), 2.5-1.2 (plateau, 6H, CH$_3$Mes). In order to obtain more resolution of the plateau-hydrogens (\[ \delta = 2.5-1.2 \text{ ppm} \]) a $^1$H NMR spectrum was obtained just after the NMR tube was taken out from liquid nitrogen (warming solid CDCl$_3$): (300 MHz, CDCl$_3$): \[ \delta (ppm): 7.60 (2H), 7.55-7.24 (6H?), 7.22-7.04 (4H?), 6.87 (1H), 6.68 (1H), 2.55 (3H), 2.40 (6H), 2.28 (3H), 2.17 (3H), 1.30 (3H). The broad resonances at room temperature for 5.21 for 2 of the Mes-aromatic protons and for 6 Mes aliphatic protons suggests a rotation takes place on the NMR-time-scale. Either the Ru-C bond rotates or the mesityl group rotates around the N-C bond. \[ \text{IR (cm}^{-1}\text{): 1764.4 (KBr), 1999.6 (KBr), 2089.4 (KBr)}. \]

6.5 Catalytic tests

6.5.1 ROMP of COD with 4.8-4.10, 4.13 and 4.10A at 90 °C (Figure 4.15)

2.717 µmol of catalyst was transferred into an NMR tube and the tube was degassed while heating it. The NMR tube was brought under argon atmosphere using three argon-vacuum cycles. 600 µl of distilled toluene-$d_8$ and 0.81 mmol (100 µl) of COD were added. The tube was transferred into the preheated NMR spectrometer at 90°C and the spectra were obtained choosing reasonable time intervals. To determine the yield, the allylic protons were integrated in the $^1$H NMR spectrum. \[ \delta (ppm): \text{COD: 2.36; poly-COD 2.15-2.0.} \]
6.5.2 Polymer characteristics of poly-COD for the ROMP at 90 °C with 4.8-4.10, 4.13 and 4.10A (Table 4.2)

8.151 µmol of catalyst was transferred into a 15 ml vial. The tube was placed under argon and 1.8 ml of toluene was added. Next, 300 µl of COD (2.43 mmol) was added, the vial was sealed and placed in a thermoblock at 90 °C for 25 hours. Thereafter, the vials were taken out, a small amount of ethyl vinyl ether and 2,6-di-tert-butyl-4-methylphenol were added and the vials were poured into 40 ml of MeOH. The precipitate was dried under air. One small sample was used to determine the trans % by integrating the poly-cis-COD ($\delta = 27.41$ ppm) and poly-trans-COD ($\delta = 32.74$ ppm) resonances in $^{13}$C NMR. Another sample was used to perform GPC (Gel Permeation Chromatography) analysis in chloroform. The $M_n$ values are relative to PS (Polystyrene) standards.

6.5.3 Thermal activation of the DCPD polymerization with 4.10 and 4.10A (Figure 4.16)

A vial was degassed and flame dried. 10 mg catalyst was weighed into the 15 ml vial. The vial was brought under argon atmosphere applying three argon-vacuum cycles. 500 µl of toluene was added to obtain a stock solution. In a 15 ml vial, 2 g of DCPD and the appropriate amount of catalyst from the stock solution were added under argon atmosphere to obtain a 20 000:1 monomer:catalyst ratio. The vial was closed, a thermocouple was pierced through the septum into the reaction mixture and the vial was placed in a thermostat at 150°C.

6.5.4 ROMP of COD with catalysts 4.1B at 40 °C (Figure 4.18, Figure 4.51, Figure 4.52)

2.717 µmol of catalyst was transferred into an NMR tube. The tube was degassed while heating it and was brought under argon atmosphere applying three argon-vacuum cycles. 500 µl of dried, degassed CDCl$_3$ and 0.81 mmol (100 µl; 300 equiv) of COD were added. The stop was sealed with parafilm. The tube was transferred into a thermoblock filled with water at 40 °C. At the appropriate time, the tubes were taken out and the spectra were obtained quickly, whereupon the tubes were returned to the thermoblock. To determine the yield, the allylic protons were integrated in the $^1$H NMR spectrum. $^{13}$C NMR spectra were only obtained when the time needed to collect the $^{13}$C NMR data could be neglected upon the total polymerization time (~4 hours) or after full polymerization. The cis:trans ratios and the conversions were determined by integrating the poly-COD-cis (27.41 ppm), poly-COD-trans (32.74 ppm) and COD (28.18 ppm) $^{13}$C NMR resonances. This led us also to detect the signal at $\delta = 32.5$ ppm of t.t.t-CDT, which can be integrated more difficult due to interference with the poly-COD-trans peak. However, the CDT olefinic proton ($\delta = 5.01$ ppm) showed no interference with the polymer olefinic protons in $^1$H NMR and was more easily integrated that way.

6.5.5 Catalytic activity of complexes 4.1B for the DCPD polymerization with RIM monomer and activator (Figures 4.20-4.30)

As DCPD source a RIM monomer (liquefied formulation of CPD) as used in industrial applications was obtained by Noveon Inc. This RIM monomer consists mainly of DCPD, containing small amounts
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of additives. The detailed description is not available. Catalyst and activator solutions were prepared so that 200-250 µl of undistilled CH\textsubscript{2}Cl\textsubscript{2} was used in all samples. 10 ml of RIM monomer was used in each polymerization. 5 ml of the RIM monomer was transferred in a vial (15 ml vials) together with the activator. Another vial was filled with 5 ml of RIM monomer and the catalyst solution. The activator vial was poured into the catalyst vial after which the thermocouple was immediately pierced into it and was used to stir for 2 s. The temperature measurement was started. The thermocouple was placed at approximately the same place for each measurement (middle of the vial, 2 cm from the bottom of the vial). The vial was placed in a semi-isotherm environment and the temperature measurement was ceased after a maximum in temperature was reached.

6.5.6 Assignment of \textsuperscript{1}H NMR for DEDAM, DEDAM-2 and the corresponding ringclosed products

It should be noted that the reporting of \textsuperscript{1}H NMR data on the DEDAM and DEDAM-2 ringclosred products has been a scientific disaster. For ringclosed-DEDAM we calculated the yield by the integration of the allylic protons in \textsuperscript{1}H NMR at $\delta = 2.97$ (s) ppm compared to those of the starting product at $\delta = 2.59$ ppm. SDBS\textsuperscript{13} reports the DEDAM allylic protons in \textsuperscript{1}H NMR at $\delta = 2.64$ ppm and Nugent et al.\textsuperscript{14} reported the allylic protons in \textsuperscript{1}H NMR for the ringclosed-DEDAM at $\delta = 3.02$ ppm. The small deviation can be explained by the broad signals we obtained and by some inaccuracy in the assignment of the reference. Previous PhDs performed in our research group assigned the ringclosed DEDAM in \textsuperscript{1}H NMR at $\delta = 2.25$ ppm\textsuperscript{15} and 2.56 ppm\textsuperscript{16}.

![Diagram of DEDAM and DEDAM-2](image)

\textbf{Figure 6.2:} RCM of DEDAM and DEDAM-2

For DEDAM-2 the assignment is even more disastrous. The most popular source-reference\textsuperscript{11} for DEDAM-2 is a publication by Grubbs et al.\textsuperscript{17} in which DEDAM-2 is characterized by \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta$ (ppm): 4.88-4.85 (m, 4H), 3.95 (q, J = 7.1Hz, 4H), 3.01 (s, 4H), 1.68 (s, 6H), 0.91 (t, J = 7.1 Hz, 6H).\textsuperscript{17} Our DEDAM-2 was also characterized by \textsuperscript{1}H NMR and yielded a very different spectrum: \textsuperscript{1}H NMR: (300 MHz, CDCl\textsubscript{3}): $\delta$ (ppm): 4.84 (s, 2H, H\textsubscript{olefinic}), 4.73 (s, 2H, H\textsubscript{olefinic}), 4.15 (q, 4H, COOCH\textsubscript{2}CH\textsubscript{3}), 2.73 (s, 4H, H\textsubscript{allylic}), 1.68 (s, 6H, H\textsubscript{allylic}), 1.25 (t, 6H, COOCH\textsubscript{2}CH\textsubscript{3}). (Our result is

\textsuperscript{11} 159 references at 15/10/2007
more in agreement with a recent publication of Schrodi et al.\textsuperscript{18}. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ (ppm): 2.61 (H\textsubscript{allylic}) Yet, our DEDAM-2 resulted in ringclosed DEDAM-2 which was analyzed by \textsuperscript{1}H NMR [(300 MHz, CDCl\textsubscript{3}): δ (ppm): 4.18 (q, 4H), 2.93 (s, 4H), 1.59 (s, 6H), 1.25 (t, 6H)] and is in good agreement with the ringclosed product by Grubbs et al.\textsuperscript{17} (Grubbs reported values 0.02 ppm lower than ours\textsuperscript{17}). An argument in favor for our DEDAM-2 spectrum is that the ethoxy-protons, which are positioned far from the chemical transformation, don’t shift much in the \textsuperscript{1}H NMR when the product is ringclosed (δ = 4.15 ppm → 4.18 ppm and 1.25 ppm → 1.25 ppm) while the results by Grubbs et al. clearly show a big deviation (δ = 3.95 ppm → 4.16 ppm and 0.91 ppm → 1.22 ppm). Other researchers in our group also synthesized the starting product DEDAM-2. These previous results\textsuperscript{16} were in relative agreement with our data, while others\textsuperscript{19,20} deviated substantially.

6.5.7 RCM of DEDAM at 40 °C in CD\textsubscript{2}Cl\textsubscript{2} (Figure 4.32)

An NMR tube was charged with 2.28 \times 10^{-6} mol catalyst. Then, 500 µl CD\textsubscript{2}Cl\textsubscript{2} and 110 µl of DEDAM (4.56 \times 10^{-4} mol; 200 equiv) were added. The tube was closed and the stop was sealed with parafilm. The reaction was placed in a thermoblock at 40 °C and at the appropriate times the tube was taken out to collect a \textsuperscript{1}H NMR spectrum. Conversion was determined by integration of the allylic protons in the \textsuperscript{1}H NMR spectrum. \textsuperscript{1}H NMR; δ (ppm): DEDAM: 2.59 (d), ring-closed product: 2.97 (s).

6.5.8 RCM of 10 000 equiv of DEDAM in toluene at 100 °C (Table 4.3, Table 5.4)

A 15 ml vial was charged with 1 ml of dry, degassed toluene. 20 µl (1.667 \times 10^{-8} mol catalyst) of a diluted solution (3.33 \times 10^{-9} M) of catalyst in dry, degassed toluene and 40 µl of DEDAM (1.67 \times 10^{-4} mol; 10 000 equiv) were added. The vial was closed, sealed with parafilm and transferred into a thermoblock at 100°C. At the designated time (40 hours) the vial was taken out and the solvent was removed \textit{in vacuo}. The residue was redissolved in CDCl\textsubscript{3} and the conversion was determined by integrating the allylic protons in the \textsuperscript{1}H NMR spectrum.

6.5.9 RCM of DEDAM-2 in toluene (Table 4.5, Table 5.5 )

DEDAM-2 was prepared according to literature procedure.\textsuperscript{17} A 15 ml vial was charged with 7.45 \times 10^{-6} mol (or 7.45 \times 10^{-7} mol; 200 equiv) of catalyst after which 1 ml of dry, degassed toluene and 40 µl of DEDAM-2 (1.49 \times 10^{-4} mol; 20 equiv or 200 equiv) were added. The vial was closed, sealed with parafilm and transferred into a thermoblock at 100 °C (or 60 °C) for the designated time. Thereafter, the vial was taken out, the solvent was removed \textit{in vacuo} and the residue was redissolved in CDCl\textsubscript{3}. The conversion was determined by integrating the allylic protons in the \textsuperscript{1}H NMR spectrum. \textsuperscript{1}H NMR; δ (ppm): DEDAM-2: 2.74 (s), ring-closed product: 2.93 (s).

6.5.10 RCM of DEDAM at 50 °C in CD\textsubscript{3}OD (Figure 4.36)

An NMR tube was charged with 2.28 \times 10^{-6} mol of catalyst and 500 µl CD\textsubscript{3}OD. Next, 110 µl (4.56 \times 10^{-4} mol; 200 equiv) DEDAM was added, the tube was closed and the stop was sealed with parafilm. The reaction was placed in a thermoblock at 50 °C and at the appropriate times the tube was taken out to
obtain a $^1$H NMR spectrum. Conversion was determined by integrating the allylic protons in the $^1$H NMR spectrum.

6.5.11 ROMP of 4.23 (Figure 4.38, Table 4.6)

4.23 was prepared using a literature procedure which was slightly adapted.\textsuperscript{21} 2.5 g of exo-3,6-epoxy-1,2,3,6-tetrahydrophtalic anhydride (15 mmol) was dissolved in 120 ml of methanol and 2 ml of a 2M HCl solution in ether (4 mmol) was added. The reaction was heated at 60 °C for 3 hours after which the solvent was removed. 4.23 was precipitated and washed with Et₂O in 41% yield.

An NMR tube was charged with 0.0115 g of 4.23 (5.42 $10^{-5}$ mol; 50 equiv) and (1.08 $10^{-6}$ mol; 1 equiv) of catalyst. Thereafter, 250 µl of CDCl\textsubscript{3} and 250 µl of CD\textsubscript{3}OD were added under ambient atmosphere. The NMR tube was transferred in a thermoblock which was heated at 50°C. At the appropriate times, the NMR tube was taken out to collect $^1$H NMR data. Conversions and cis:trans ratios were determined by integration of the olefinic signals in $^1$H NMR; δ (ppm): 4.23: 6.48; cis-poly-4.23: 5.62; trans-poly-4.23: 5.89.

6.5.12 Carbene resonance experiment with catalyst 4.9 and monomer 4.23 (Figures 4.39 and 4.40)

Under ambient atmosphere, an NMR tube was charged with 0.0023 g of 4.9 (2.83 $10^{-6}$ mol; 1 equiv), 250 µl of CDCl\textsubscript{3} and 250 µl of CD\textsubscript{3}OD. A $^1$H NMR was collected (first spectrum). The tube was placed in a thermoblock at 50 °C for 15 minutes; a second $^1$H NMR spectrum was performed thereafter. Next, 0.0030 g of 4.23 (1.41 $10^{-5}$ mol; 5 equiv) was introduced and the tube was placed for 15 minutes at 50 °C in the thermoblock (a third NMR spectrum was taken). Then the NMR tube was placed for an additional 2 hours (4\textsuperscript{th} spectrum) and an additional 22 hours (5\textsuperscript{th} spectrum) in the thermoblock at 50 °C.

6.4.13 ROMP of COD at room temperature (Figure 4.49, Figure 4.53, Figure 4.55, Figure 4.56, Figure 4.60, Figure 5.14-5.15)

For 300 equiv of COD, 2.717 µmol of catalyst was transferred into an NMR tube. 500 µl of CDCl\textsubscript{3} (undegassed, stored on mol. sieves) and 0.81 mmol (100 µl; 0.0088 g) of COD were added. Except for Figure 5.14 (degassed, dried CDCl\textsubscript{3}). For 100 equiv of catalyst, 33 µl of COD was applied. For 3 000 equiv, an appropriate dilution of the catalyst was prepared and redissolved in the CDCl\textsubscript{3} (degassed and dried).

The tube was transferred into the NMR and the $^1$H NMR and $^{13}$C NMR spectra were obtained choosing reasonable time intervals. NMR integration, vide supra. Figure 4.49: T = 23° C. Figure 4.53, Figure 4.55, Figure 4.56: T = 21°C. Figure 4.60: T = 21°C. Figure 5.16-5.17 : T = 22 °C.

6.5.14 ROMP of t,t,t-CDT at room temperature (Figure 4.55, Figure 4.56, Figure 5.16)

For 200 equiv of monomer:catalyst ratio, 2.717 µmol of catalyst was transferred into an NMR tube. 500 µl of CDCl\textsubscript{3} (undegassed, stored on mol. sieves) and 0.0088 g (100 µl, 0.81 mmol) of t,t,t-CDT
Experimental

were added. For 67 equiv of catalyst, 0.0029 g of t,t,t-CDT was applied. For 2 000 equiv, a diluted solution of catalyst was prepared in CH₂Cl₂, which was evaporated and redissolved in the CDCl₃ (degassed, dried) and 0.0088 g was used.

The tube was transferred into the NMR spectrometer after which the ¹H NMR and ¹³C NMR spectra were obtained choosing reasonable time intervals. NMR integration, vide supra. Figure 4.55, Figure 4.56: T = 21°C. Figure 5.16: T = 22 °C.

6.5.15 Determination of the equilibrium concentrations of t,t,t-CDT for the 1,4-polybutadiene system in CDCl₃ at room temperature (Figure 4.57)

A 54.3 mM stock solution of 1.4 in CDCl₃ was prepared. An NMR tube was filled with the appropriate amount of CDCl₃. An appropriate amount of stock solution was added to give a combined volume of 500 µl. Then COD was added to the different NMR tubes: 0.044 g (0.41 mmol; 50 µl; 150 equiv to 1.4), 0.029 g (33 µl; 0.27 mmol; 100 equiv to 1.4), 0.018 g (20 µl; 0.17 mmol; 60 equiv to 1.4), 0.0132 g (15 µl; 0.12 mmol; 50 equiv to 1.4), 0.0088 g (10 µl; 81 µmol; 40 equiv to 1.4), 0.0035 g (4 µl; 32 µmol; 4 equiv to 1.4), 0.0018 g (2 µl; 16 µmol; 10 equiv to 1.4), 0.00088 g (1 µl; 8.1 µmol; 6 equiv to 1.4). The equilibration was monitored by ¹H NMR (vide supra). The final distribution value was obtained when no change occurred over half of the measured time. T = 20°C.

6.5.16 Determination of the initial cis:trans ratio for COD polymerizations (Figure 4.59)

Due to the fast reaction and initiation periods, the accurate initial cis:trans ratios for the COD polymerization with 1.3 and 1.4 were not be performed using the classical method used for 4.1B, 4.10A and 4.26 (6.4.4 and 6.4.12). Therefore, a 100 µl solution in 500 µl of CDCl₃ was prepared, and a very small amount of catalyst was introduced to the mixture with a spatula. The polymerization occurred with initiation periods of 15 minutes to 1 hour, but conversion was slow enough to obtain good ¹³C NMR spectra. When polymerization and isomerization ceased due to catalyst decomposition, new small amounts of catalyst were introduced. The cis:trans content is determined with ¹³C NMR (vide supra).

6.5.17 Determination of the initial cis:trans ratio for the CO polymerization (Figure 4.61)

Analogous reaction conditions were used as for the COD polymerization (6.4.15). The conversion and cis:trans ratios were determined using ¹³C NMR with the poly-cis-allylic resonance (δ = 27.45 ppm), the poly-trans-allylic resonance (δ = 32.86 ppm) and an aliphatic CO resonance (δ = 25.68 ppm).

6.5.18 RCM of DEDAM at rt in CD₂Cl₂ (Figure 5.17)

An NMR tube was charged with 2.28 10⁻⁶ mol catalyst. Then, 500 µl CD₂Cl₂ and 110 µl of DEDAM (4.56 10⁻⁴ mol; 200 equiv) were added. The tube was closed and the stop was sealed with parafilm. The reaction was placed in the NMR-spectrometer and at the appropriate time intervals a ¹H NMR
spectrum was collected. Conversion was determined by integration of the allylic protons in the $^1$H NMR spectrum.

References

(13) [http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi](http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi).
Chapter 7

Conclusions

This research project dealt with the follow-up of previously reported ruthenium Schiff base complexes that showed excellent activity for olefin metathesis and ATRP. In the current project, these catalysts needed to be optimized and new applications were to be explored. The previously described O,N Schiff base catalysts were monometallic benzylidene catalysts (4.1B), indenylidene Schiff base catalysts (4.3) and bimetallic benzylidene catalysts (4.2). Since the indenylidene catalysts 4.3 were investigated by Viacatt NV, our focus was directed to the monometallic and bimetallic Schiff base benzylidene catalysts.

The benefits of bidentate O,N-Schiff base catalysts compared to their phosphine analogues is twofold: First, phosphine, which is an important catalyst-destructor, is no longer present. Secondly, the substitution of a Ru-Cl by a Ru-O bond disables Ru to form bimetallic species which are known to be intermediate decomposition products.

First, it should be noted that all the syntheses of these catalysts using previously reported methods were unsuccessful. For the monometallic catalysts 4.1B the previously described method did not result in the correct product, moreover, NMR data of our monometallic Schiff base complex did not correspond to the previously reported species. As conclusive evidence for our results we were able to obtain crystals suitable for X-ray analysis.

Also, the synthesis of the bimetallic catalyst 4.2 was unsuccessful using the previously described method. Adapting the literature method led to a different catalyst. Our NMR data on this species did not correspond to the NMR data previously reported for 4.2. Although we first assumed this species to be the bimetallic catalyst 4.2, or trimetallic species 4.26, it turned out to be the bimetallic catalyst 1.97 with the byproduct 4.27. The formation of 1.97 is obtained by a Ru-Cl, Ru-O exchange. Catalytic activity determination of 1.97 seemed not essential, since it is a well known species and does not incorporate a Schiff base ligand.
The structure of catalysts 4.1B was intensively investigated. Although interesting features in the crystal structures were revealed, these could not be implemented into a structure-activity relationship.

The initially synthesized Schiff base catalysts (4.08-4.10, 4.13) showed negligible activity for metathesis reactions at room temperature for all reactions investigated. Several methods were investigated to activate these catalysts. It was shown that they can be activated by simply heating them. Other researchers in our group established an effective activation procedure which involves the addition of acid. Species which are inactive at room temperature but can be activated by external force are also called latent catalysts. Paradoxically, this means that their inability to perform metathesis at room temperature is not a disadvantage but is to be exploited as a special attribute. For example, in RIM technology, two monomer flows are brought together in the mold. One flow can be monomer mixed with the catalyst and the other flow can be monomer mixed with the activator. By bringing the flows together, the polymerization starts. A catalyst which is active at room temperature, cannot be used in such technology. Moreover, due to the latent character, the catalysts show better characteristics for storing.

Although several activation mechanisms were established, we also explored the extensive variation of the Schiff base fragment in order to obtain a catalyst spectrum with a wide variety of initiation kinetics (4.14-4.19). This strategy proved very effective, since two sterically encumbered species (4.14 and 4.18) were developed which show activity at lower temperatures. On the other hand, the reduction of steric crowding in 4.17 resulted in less protection of the benzylidene fragment, which caused catalyst instability.

Several applications for these catalysts were explored. With the COD polymerization, the low activity of the classical Schiff base catalysts (4.8-4.10, 4.13) at lower temperatures was shown. This is concomitant with a high catalyst stability. The sterically encumbered catalysts (4.14 and 4.18) already show high activity at lower temperatures. However, the higher activity of these catalysts is concomitant with faster decomposition. Unfortunately, due to this faster decomposition, the sterical complexes (4.14 and 4.18) show no special advantages compared with their mother complex 1.4.

The industrial relevant DCPD polymerization showed good results for both thermal and acid activation at 30 000 equiv, using all catalysts except 4.17. A different acid concentration had to be applied for each catalyst. Also the reaction profile and the maximum temperature achieved was different for each catalyst. The sterically encumbered catalyst 4.14 was the only Schiff base catalyst which polymerized 30 000 equiv of DCPD without any activation, and only 4.13, 4.14 and 4.16 were efficient for the acid-activated polymerization of 60 000 equiv of DCPD.

The Schiff base catalysts show big advantages for niche-domains in academic science. They allow the RCM of sterical substrates, and they are tolerant for alcohol functionalities in substrates or the use of alcohols as solvent in metathesis. Since real-production systems for RCM do not generally involve easy reaction conditions, these niche-domains in academic science represent excellent methods to test the catalyst activity for these more demanding conditions.

More specific, the TON for the RCM of DEDAM-2 with 4.10 is increased by a factor 20 compared with the classical second generation catalyst 1.4. 4.10 also shows more than 10 times the TON compared with the best systems for the RCM of DEDAM in MeOH up to date.

These results show that the Schiff base catalysts 4.1B have a far superior activity for specific applications compared to the standard second generation catalyst 1.4, when these are used in the appropriate reaction conditions. The ‘standard system for characterization for olefin metathesis
Conclusions

catalysts’ proposed by Grubbs et al. cannot provide these subtleties but is very efficient in showing the benefits of catalyst 1.4 under these *standard* reaction conditions.

The polymerization of 4.23 with 4.9 in a mixture of methanol-\textsubscript{d\textsubscript{4}} and chloroform-\textsubscript{d\textsubscript{1}} showed some interesting features concerning the catalyst decomposition. In a first step the α-benzylidene proton disappeared from the \textsuperscript{1}H NMR spectrum, although the initial catalyst was still present. In a next step, the Schiff base disappeared from the catalyst, and hence the original catalyst structure had disappeared. Yet, the Ru still contained the \textsubscript{H\textsubscript{2}}IMES ligand and remained active for the polymerization of 4.23. We concluded that it was difficult to asses the polymerization of easily convertible ROMP monomers such as 4.23 to the initial catalysts, since several decomposition products were also considerably active for this reaction.

During the ROMP of COD with the Schiff base catalysts, some unexpected events occurred, which were extensively investigated. This led to new insights concerning the COD polymerization with Grubbs catalysts:

1. The polymerization of COD with Grubbs catalysts is quasi non-selective, but a slower secondary metathesis event enables the *cis*:*trans* ratio to establish thermodynamic equilibrium.
2. The activity measurement of the catalyst via the ROMP of COD to 100% conversion can lead to initiation kinetics with a normal polymerization observation. However, the catalytic activity measurement can be extended. The slower catalytically induced thermodynamical equilibration of the polymer provides information on the longivety of the catalyst.
3. A third event is the formation of t,t,t-CDT from *trans*-poly-COD. This event can even prolong the activity measurement of the experiment. Moreover, the t,t,t-CDT equilibrium concentration holds 30 % of the C\textsubscript{4}H\textsubscript{6} mixture in the *standard polymerization* of COD proposed by Grubbs et al. The prolonged activity investigation provides stability data combined with the kinetic initiation data.
4. This third event is only marginally present for catalysts which perform metathesis through a phosphine substituted active species. Although the relative rates of primary and secondary metathesis show no distinguishable difference between the phosphine and the NHC substituted active species, tertiary metathesis does, because it is negligible for the former.

T,t,t-CDT can easily be polymerized by second generation catalysts, while first generation catalysts only show negligible polymerization activity. The t,t,t-CDT polymerization can thus be used to evaluate the potency of the active species of the catalyst and provide additional information on the structure of the active species. T,t,t-CDT can be tested for ROMP in the same fashion as DEDAM-2 acts as a challenging substrate for the RCM. T,t,t-CDT is commercially available while DEDAM-2 needs to be synthesized. Moreover, t,t,t-CDT can be used as a more suitable alternative for ROMP test reactions compared to COD, since the former does not show the annoying smell of COD and does not require distillation or degassing.

The initial *cis*:*trans* conformation of polymers from the ROMP of CO produced by Grubbs catalysts shows a distinct fingerprint of the catalytic active species. This can help to determine the active species of the catalysts used. By this, we have provided additional evidence that the active species of catalysts of type 4.1A is substituted with a phosphine and not by a Schiff base. Furthermore, it should be noted that unexpectedly the ligand *trans* to the coordinated olefin shows a greater impact on the polymer microstructure than the ligands in *cis*-position.
Next, we tried to further enhance the activity of the Schiff base catalysts. The obvious choice was to improve the already very potent catalysts 4.1B. The most important ligand in these catalysts, determining the catalyst stability and activity, is the H$_2$IMES ligand. Hence we aimed to find an improvement through the modification of the NHC ligand. During the last decade, the search for a ligand substitute for H$_2$IMES in 1.4 has been the focal point of many metathesis researchers. Therefore, preliminary, a thorough investigation was performed on all those previous attempts, all theoretical investigations concerning the issue, and recent ideas in organometallic chemistry concerning the concepts involving this substitution. As a result, we formulated that the ideal substitute should show sufficient steric bulkiness, high $\sigma$-donating character and a low $\pi$-accepting character in the xy plane (with the Ru-Cl bond as the z-direction).\footnote{It should be noted that previous design of NHC ligands has mainly focused on the increase in $\sigma$-donating character. Therefore, we proposed an innovative approach to implement the previous guideline. We suggested that a very straightforward idea to enhance the catalyst activity is to activate the $\pi$-acceptor function of the NHC ligand (in the z-direction). First, an increased $\pi$-acceptor function should increase dissociation of the competing phosphine ligand. Second, upon olefin coordination, the increased backdonation to the NHC should lead to a decreased interaction with the olefin bond in the perpendicular (inactive) orientation and hence lead to less inactive intermediate species. This inactive species for olefin metathesis might participate in deactivation mechanisms of the catalyst. Third, the increased $\pi$-accepting function should lead to an increased $\sigma$-donation synergy and consequently promote metallacyclobutane formation. Fourth, the increased $\pi$-interaction should decrease the Ru-NHC bond length, increase the steric interaction and therefore show increased activity. This shows that multiple positive effects might arise from the installation of a $\pi$-acceptor function. We chose to implement the ligand changes upon the non-Schiff base substituted standard catalyst 1.3. When these changes prove effective, they can easily be implemented on the Schiff base catalysts.} It should be noted that previous design of NHC ligands has mainly focused on the increase in $\sigma$-donating character. Therefore, we proposed an innovative approach to implement the previous guideline. We suggested that a very straightforward idea to enhance the catalyst activity is to activate the $\pi$-acceptor function of the NHC ligand (in the z-direction). First, an increased $\pi$-acceptor function should increase dissociation of the competing phosphine ligand. Second, upon olefin coordination, the increased backdonation to the NHC should lead to a decreased interaction with the olefin bond in the perpendicular (inactive) orientation and hence lead to less inactive intermediate species. This inactive species for olefin metathesis might participate in deactivation mechanisms of the catalyst. Third, the increased $\pi$-accepting function should lead to an increased $\sigma$-donation synergy and consequently promote metallacyclobutane formation. Fourth, the increased $\pi$-interaction should decrease the Ru-NHC bond length, increase the steric interaction and therefore show increased activity. This shows that multiple positive effects might arise from the installation of a $\pi$-acceptor function. We chose to implement the ligand changes upon the non-Schiff base substituted standard catalyst 1.3. When these changes prove effective, they can easily be implemented on the Schiff base catalysts.

This quest involved the development of pure organometallic chemistry and therefore, some interesting findings were made in that field. It was experimentally impossible to obtain a (amido)(amido)NHC, which was assigned to the lack of mesomere donation of the amido groups to the carbene. Therefore, the attempt was made to obtain a (amido)(amino)carbene. By succeeding at this, we have synthesized the first example of a new subclass of NHC ligands. This subclass could be very interesting, since these NHCs can be sterically tuned analogously to the popular saturated and unsaturated NHCs, although the electronic profile, especially the $\pi$-effect, should show pronounced difference. Moreover, we have shown a very easy way to synthesize these ligands.

The $\pi$-backdonation to the NHC in the Grubbs catalyst was experimentally proved. Comparing the $\nu$(CO) in IR, we have shown experimentally that ‘the relative $\pi$-acceptor strength of ligands can only be established with respect to a given fragment’\footnote{It should be noted that the bulkiness is context-dependent. With steric substrates as DEDAM-2, the incorporation of a steric NHC can certainly not be beneficial.} which some theoretical chemists have coined before. Moreover, we have shown that the standard method for evaluating the ‘net donating character’ of NHCs, being the $\nu$(CO) frequencies in IR of Rh(CO)$_2$Cl(NHC) complexes, is in fact a better measure for one of its components, being the $\pi$-backdonation.

With the synthesis of 5.18, the attempt at preparing a Grubbs catalyst containing an NHC ligand with a distinct $\pi$-acceptor function has been successful. 5.18 also shows an increased activity (TOF) upon 1.4 for the polymerizations of COD and CDT, as we anticipated. However, the RCM of DEDAM with 5.18 shows lower activity than for 1.4. Moreover, the more important characteristic of ‘total activity’
(TON) of 5.18 proved to be slightly lower for the ROMP of COD and dramatically lower for the RCM of DEDAM and DEDAM-2. Combining the data of TOF and TON, we were able to conclude that there was no straightforward relation between the π-backbonding to the NHC and the TON obtained for the evaluated catalyst-set. Improving the catalysts in terms of TON requires complete knowledge of all the deactivation mechanisms available. Much of this uncharted territory is one of the few challenges which remain for Grubbs-catalyst researchers.

In summary, we synthesized the previously claimed Schiff base catalysts 4.1B and showed that the previously reported 4.24 cannot be prepared, since a bimetallic catalyst 1.97 is formed instead. We showed that catalysts 4.1B show benefits upon their parent catalyst 1.4 in their latency. Moreover, exploration of catalytic applications showed that these catalysts also possess far superior activity compared to their parent catalyst for the RCM of DEDAM in methanol and the RCM of the sterically very challenging monomer DEDAM-2 due their high stability. Secondary metathesis was extensively investigated and we have shown that catalysts leave fingerprints on the initially formed polymers, which provide information on the catalytically active center. Moreover, the total metathesis event of the COD-1,4-polybutadiene-CDT system was mapped in great detail.

Olefine metathese is een reactie waarbij twee olefine substituents uitwisselen: \( C_A=C_B + C_C=C_D \rightarrow C_A=C_C + C_B=C_D \). Dit is een chemische reactie die niet spontaan doorgaat omwille van een te hoge activatie energie. Door toevoegen van een katalysator kan deze activatie energie verlaagd worden zodat de reactie doorgaat tot thermodynamisch evenwicht bereikt is.

8.1 Inleiding

De gekatalyseerde olefine metathese reactie gaat door via een metallacyclobutaan intermediair dat in evenwicht staat met een olefine gesubstitueerd metaal complex. Via dit mechanisme kunnen de dubbele bindingen substituents uitwisselen.

![Figure 8.1: Metallacyclobutaan intermediair in metaal gekatalyseerde olefine metathese.](image-url)
Door deze metallacyclobutaan formatie zijn verschillende transformaties van organische producten mogelijk. In RCM (Ring Closing Metathesis), CM (Cross Metathesis) en ADMET (Acyclic Diene METathesis polymerization) is de vorming van het vluchtige etheen de drijvende kracht van de reactie. Voor RCM worden lage concentraties substraat gebruikt om selectieve reactie te bekomen tegenover de competitieve ADMET reactie. De stabilisatie van de ring is ook van uiterst belang. Waar in RCM een nieuwe ring gevormd wordt, wordt in ROMP (Ring Opening Metathesis Polymerization) een ring geopend dankzij ringspanning die vrijkomt in de reactie.

\[ \text{Figure 8.2: Verschillende metathese reacties.} \]

Sinds 1992 werden een reeks Ru complexen ontwikkeld die efficiënte katalysatoren zijn voor de olefine metathese reacties. De belangrijkste Ru-katalysatoren zijn de Grubbs $1^{\text{e}}$ generatie katalysator (8.1), de Grubbs $2^{\text{e}}$ generatie katalysator (8.2) en de Hoveyda $2^{\text{e}}$ generatie katalysator (8.3).

\[ \text{Figure 8.3: Belangrijkste Grubbs type katalysatoren.} \]

### 8.2 Synthese van Schiffse base katalysatoren

Grubbs et al. introduceerden Schiffse basen in complexen van het type 8.4A en ondervonden dat de stabilititeit van deze complexen verhoogde ten opzichte van het moeder complex 8.1. Vorige researchers in onze onderzoeksgroep hadden complexen 8.4B-8.7 gesynthetiseerd en concludeerden dat deze katalysatoren heel efficiënt waren in katalyse. Het doel van het huidige onderzoeksproject bestond erin deze katalysatoren te optimaliseren en vernieuwende toepassingen te vinden. De focus van Viacatt NV (spin off bedrijf Ugent) was gericht op katalysatoren 8.6 en om belangenconflicten te vermijden werden deze katalysatoren in dit project niet onderzocht. Katalysatoren 8.7 kunnen enkel gebruikt worden voor radicale atoom transfer reacties maar vereisen een enorme kostprijs vergeleken met alternatieve systemen die gebaseerd zijn op koper. Daarom is er eveneens niet verder ingegaan op de synthese van deze katalysatoren.
De synthese van Schiffse base katalysatoren gebruik makende van eerder gepubliceerde reactie methodes van onze onderzoeksgroep was niet succesvol. De synthese van 8.4B via de gepubliceerde methode resulteerde niet in deze complexen en toen een aangepaste methode ontwikkeld werd om deze complexen te synthetiseren bleken de NMR data van onze complexen 8.4B niet overeen te stemmen met de eerder gepubliceerde resultaten. Door een kristal te analyseren van onze nieuwe katalysatoren 8.4B hebben we onze complexen kunnen valideren en zo kunnen aantonen dat zowel de eerder gepubliceerde synthese route als de eindproducten niet correct waren.
Daar de synthese van complexen 8.5 via de eerder gepubliceerde reactiemethode niet de gewenste producten opleverde, werd een kleine aanpassing aangebracht zodanig dat de reagentia effectief reageerden. De vorming van 8.9 en 8.10 uit de reactie van 8.8 met [Ru(p-cymene)Cl$_2$]$_2$ is niet logisch omdat 8.8 initieert via Schiffse base decoordinatie tot 8.11. Dit complex zou dan verder kunnen reageren met [Ru(p-cymene)Cl$_2$]$_2$ tot een trimetallische katalysator 8.12. Er bleek onverwachts een Ru-O, Ru-Cl uitwisseling op te treden waardoor de species 8.13 en 8.14 gevormd werden. Het is wel mogelijk dat 8.12 een kortlevend intermediair is tijdens de vorming van deze producten. Uiteindelijk bleek de synthese van complexen 8.5, gebruik makende van verschillende methoden niet mogelijk.

### 8.3 Activiteit van de Schiffse base katalysatoren

De structuur van katalysatoren 8.4B werd extensief onderzocht. Alhoewel er interessante eigenschappen zijn in de kristalstructuren van deze complexen zijn we er niet in geslaagd deze te implementeren in structuur-reactiviteit relaties.

De initiële gevormde Schiffse base katalysatoren vertoonden verwaarloosbare activiteit voor metathese reacties bij kamertemperatuur. De katalysatoren werden geactiveerd door ze simpelweg te verwarmen. Andere onderzoekers in onze groep hebben daarnaast goeie resultaten bekomen met zure activatie. Inactieve katalysatoren die later kunnen geactiveerd worden staan bekend als latente katalysatoren. Zo ontstaat de paradox dat de inactiviteit van de katalysatoren bij kamertemperatuur een voordeel is. In RIM (Reaction Injection Molding) kan één stroom monomeer met katalysator bevatten en een tweede stroom monomeer met activator. Door het samenbrengen van beide stromen wordt het mengsel reactief. Katalysatoren die reactief zijn bij kamertemperatuur kunnen niet gebruikt worden voor dergelijke applicaties.

Alhoewel verschillende activatie mechanismen ontwikkeld waren, werd verder nog extensief onderzoek verricht in de variatie van het Schiffse base fragment om zo een grote waaier aan katalysatoren te synthetiseren met verschillende initiatie profielen.

Er zijn verschillende metathese applicaties voor deze katalysatoren onderzocht. Met de COD polymerisatie werd aangetoond dat de klassieke Schiffse base complexen verwaarloosbare activiteit bezitten bij kamertemperatuur, doch gemakkelijk geactiveerd kunnen worden door de temperatuur te verhogen. Bij deze tests bleek ook dat de sterisch geactiveerde katalysatoren een snellere initiatie vertoonden. De snellere initiatie van deze katalysatoren gaat echter gepaard met een beperkte stabiliteit van de complexen. Daarom biedt de substitutie van sterische Schiffse basen basen op 8.2 weinig voordeel ten opzichte van het moeder complex 8.2.

De industrieel belangrijke DCPD polymerisatie vertoonde goede resultaten voor thermische activatie en zure activatie bij een monomeer:katalysator verhouding van 30 000 voor alle katalysatoren (behalve een erg onstabiele sterisch ongehinderde katalysator). Bij het opdrijven van de monomeer:katalysator verhouding tot 60 000 bleken slechts enkele katalysatoren efficiënt te zijn.

De interessantste applicaties voor de Schiffse base katalysatoren 8.4B zijn deze waar de stabiliteit van het complex kan uitgebruikt worden. Enkele van deze nichedomeinen zijn de RCM van sterische substraten en de RCM in methanol. Meer specifiek vertoont de RCM van DEDAM in methanol-$d_4$ met 8.15 een TON 10 keer zo hoog als het beste systeem tot nu toe bekend. De RCM van DEDAM-2 met 8.15 is met grote voorsprong het beste systeem tot nu toe beschikbaar en bereikt een TON meer dan 20 keer de waarde van de standaard tweede generatie katalysator (en moeder complex) 8.2.
\section*{8.4 Modificatie van het H$_2$IMES ligand}

In 1999 introduceerden Grubbs et al. het H$_2$IMES ligand in de tweede generatie katalysator 8.2 en omdat dit ligand nog altijd het best presterende is, prijkt het ook op onze katalysatoren 8.4B. Daar dit ligand de best aangewezen kandidaat is om de katalysatoren 8.4B te verbeteren hebben wij een poging ondernomen tot modificatie op deze site. Het laatste decennium zijn er al vele inspanningen geleverd om dit ligand te verbeteren maar helaas is er weinig vooruitgang geboekt. Daarom werd eerst een grondige studie gemaakt over alle eerder ondernomen pogingen, alle theoretische studies over de metathese katalysatoren en de recente ontwikkelingen in organometaalchemie die relevant zijn voor dit onderzoek. Daarna werd de volgende strategie geformuleerd: Het ideale substituut moet veel (doch niet excessieve) sterische bulk, hoge $\sigma$-donor capaciteit en lage $\pi$-backdonor capaciteit in het xy vlak (met Cl-Ru-Cl als $z$-richting) bezitten. De huidige trend in de katalysator ontwikkeling is om vooral op de $\sigma$-donor capaciteit te focussen terwijl er nog geen onderzoek verricht is naar NHC substitueerde
katalysatoren met een speciaal π-acceptor profiel. Daarom hebben we voor de innovatieve aanpak gekozen om NHC liganden te maken met een verhoogde π-backdonatie in de z-richting. Ten eerste zou de verhoogde π-backdonatie moeten leiden tot een verhoogde dissociatie van het fosfine in trans positie. Ten tweede, zou de hogere backdonatie in de z-richting moeten leiden tot een verlaagde interactie van Ru met olefines in de niet actieve oriëntatie en vervolgens tot een lagere populatie van dit species. Dit inactief metathese intermediair kan wel deelnemen in andere decompositiemechanismen. Ten derde kan de verhoogde π-backdonatie naar het NHC zorgen voor een verhoogde synergetische σ-donatie in de donor-acceptor binding. Deze σ-donatie bevordert de activiteit. Ten vierde zal de verhoogde backdonatie zorgen voor een kortere binding, wat ook de activiteit van het complex moet verhogen. Dit toont dat verschillende indirecte positieve effecten kunnen ontstaan door een verhoging van de π-acceptor functie in het NHC.

De zoektocht naar dergelijke liganden behoort tot de fundamentele ontwikkeling van de organometaalchemie en daarom is het belangrijk om de resultaten grondig te analyseren. Het bleek experimenteel onmogelijk om het (amido)(amido)NHC 8.18 te synthetiseren en metaalcomplexen te vormen gesubsSTITUTE met 8.18. Dit werd toegeschreven aan het gebrek aan mesomere π-donatie van stikstof aan het carbeen omdat beide stikstoffen geïncorporeerd zijn in een amide binding. Hieruit blijkt het belang van de mesomere donatie voor de stabilité van het NHC. Daarom werd de strategie aangepast tot de synthese van (amido)(amino)NHCs. Dit bleek succesvol te zijn en zo werd er met 8.19 het eerste species van een nieuwe subklasse NHC gesynthetiseerd. Deze subklasse kan bijzonder interessant zijn omdat ze gelijkaardige sterische modificaties (incorporatie mesityl groepen) biedt als de populaire verzadigde en onverzadigde NHC liganden, doch een duidelijk verschillend elektronisch profiel vertoont omdat slechts één stikstof geconjugueerd is met het carbeen en er zo versterkte π-backdonatie tot het carbeen kan optreden. We hebben ook een eenvoudige synthese ontwikkeld voor deze liganden wat de toepasbaarheid enkel kan bevoorvellen.

Door de analyse van de υ(CO) IR frequenties in 8.20-8.22 werd er voor de eerste keer experimenteel aangetoond dat er π-backdonatie naar het NHC is in een Grubbs-type complex. Met υ(CO) IR frequenties werd ook experimenteel aangetoond dat ‘de relatieve π-acceptor sterkte van liganden enkel kan bepaald worden ten opzichte van een bepaald complex’ wat al door sommige theoretische chemici gesuggereerd was. Verder is er ook aangetoond dat de standaard methode voor de evaluatie van de netto-donatie van NHC liganden, zijnde de analyse van de υ(CO) IR frequenties in Rh(CO)₂Cl(NHC) complexen, beter conceptueel en experimenteel correspondeert met een van zijn componenten, zijnde de π-backdonatie.

Met de synthese van 8.20 is de doelstelling een Grubbs complex te synthetiseren met een π-zure NHC groep bereikt. 8.20 vertoont ook de geanticipeerde verhoogde activiteit (TOF) ten opzichte van 8.2 voor de ROMP van COD en CDT. De RCM van DEDAM met 8.20 vertoont echter lagere activiteit (TOF) dan met 8.2. Ook de belangrijkere eigenschap ‘totale activiteit’ (TON) is lichtjes lager voor de

\[ R_1 \quad R_2 \quad R_3 \quad R_4 \quad R_5 \quad R_6 \]

**Figure 8.8:** NHC liganden.
ROMP van COD en dramatisch lager voor de RCM van DEDAM en DEDAM-2 wanneer het nieuwe complex 8.20 gebruikt wordt. Door de data van activiteit en totale activiteit te combineren kon er geen direct verband tussen de π-backdonatie naar het NHC en de totale activiteit van het complex bekomen worden. Om de katalysatoren te verbeteren op vlak van TON (ipv TOF) zal een beter begrip van alle deactivatie processen tot stand dienen te komen (ipv metathese processen) wat nog een van de weinige grote uitdagingen is voor de Grubbs-katalysatoren.

![Grubbs complex en Rh complexen gesubstitueerd met 8.19.](image)

**Figure 8.9:** Grubbs complex en Rh complexen gesubstitueerd met 8.19.

### 8.5 Secundaire metathese en katalysator vingerafdrukken

Tijdens de ROMP van COD met Schiffse base katalysatoren werd onverwachts een nieuw fenomeen ontdekt. Dit heeft geleid tot enkele interessante conclusies in verband met de COD polymerisatie met Grubbs katalysatoren:

1. De polymerisatie van COD met Grubbs katalysatoren is quasi niet cis:trans selectief, maar een trager secundair metathese proces brengt het mengsel in thermodynamisch cis:trans evenwicht.
2. De activiteit meting van de ROMP reactie van COD leidt tot de normale kinetische beschrijving. Door ook de thermodynamische cis:trans evenwichtsinstelling te volgen kan de katalysatoractiviteit veel langer gemeten worden.
3. Wanneer voldoende trans-polymeer gevormd is met secundaire metathese treedt een derde proces op waarin t,t,t-CDT gevormd wordt. In de standaard test voorgesteld door Grubbs et al. zou deze fractie 30% bedragen van het evenwichtsmengsel (dochter daar wordt de vorming niet besproken). Door ook deze evenwichtsinstelling te meten kan er naast een initiatiemeting ook veel informatie over de stabilité van de katalysator bekomen worden.
4. De primaire polymerisatie en secundaire cis:trans isomerisatie vertonen gelijke relatieve snelheden bij alle katalysatoren. De t,t,t-CDT vorming daarentegen is niet efficiënt bij fosfine gesubstitueerde actieve species.

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T,t,t-CDT kan gemakkelijk gepolymeriseerd worden met 2e generatie katalysatoren terwijl de 1e generatie katalysatoren slechts verwaarloosbare activiteit vertonen voor deze polymerisatie. De t,t,t-CDT polymerisatie kan dus gebruikt worden om confirmatie te krijgen over het actief species. Dit monomeer kan aangewend worden als een uitdagend substraat zoals DEDAM-2 in RCM. Ten opzichte van het ROMP monomeer COD bezit t,t,t-CDT ook de bijkomende voordelen dat het niet hoeft gedestilleerd te worden en niet tot geurhinder leidt.

De initiële cis:trans conformatie van de polymeren gevormd in de CO-polymerisatie vertonen een duidelijke vingerafdruk van het actieve species. Dit kan helpen in de determinatie van het actieve species van de katalysator. Zo werd er aangetoond dat katalysatoren 8.4A initiëren door Schiffse base decoördinatie en werd het carbeen deactivatie-regeneratie proces voor de polymerisatie van 8.17 met 8.16 beter in kaart gebracht.

![Figure 8.10: katalysator vingerafdrukken, secundaire en tertiaire metathese.](image)

### 8.6 Besluit

Er werd bewezen dat de eerdere rapportering over complexen van het type 8.4B incorrect was. De correcte complexen 8.4B werden succesvol gesynthetiseerd. Er werd daarnaast aangetoond dat de vorig gerapporteerde complexen 8.5 niet gesynthetiseerd kunnen worden. Katalysatoren 8.4B hebben een toegevoegde waarde ten opzichte van hun moeder complex 8.2 door hun latent karakter. Verder hebben deze katalysatoren door hun hogere stabiliteit een veel hogere activiteit dan hun moeder complex 8.2 voor de RCM van DEDAM in methanol en voor de RCM van DEDAM-2 (in toluene).

Het eerste (amino)(amido)NHC werd gesynthetiseerd en dit ligand werd gesubstitueerd op de klassieke Grubbs katalysator. Zo kon de π-backdonatie naar het NHC in de Grubbs katalysator experimenteel aangetoond worden. Alhoewel de nieuwe katalysator 8.20 verbeterde activiteit toont voor de ROMP van COD en CDT zijn de prestaties van deze katalysator voor RCM bijzonder slecht.

De secundaire metathese is extensief onderzocht en er werd aangetoond dat de katalysatoren een vingerafdruk van hun actief species achterlaten op de initieel gevormde polymeren. Ook het volledige metathese proces van het COD-1,4-polybutadiene-CDT systeem met Grubbs katalysatoren is volledig in kaart gebracht.
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SCIENTIFIC CAREER

a1  ARTICLES IN MAGAZINES SUBMITTED TO THE SCIENCE CITATION INDEX

Synthesis of 1,3-dioxo-hexahydropyrido[1,2-c][1,3] diazepine carboxylates, a new bicyclic skeleton formed by ring expansion-RCM methodology. Dieltiens, N.; Claeyes, D. D.; Allaert, B.; Verpoort, F.; Stevens, C. V. Chemical Communications 2005, 4477-4478.


Bis-coordination of N-(alkyl)-N’-(2,6-diisopropylphenyl) heterocyclic carbenes to Grubbs catalysts. Ledoux, N.; Allaert, B.; Linden, A.; Van Der Voort, P.; Verpoort, F. Organometallics 2007, 26, 1052-1056.


c2 PATENTS
