Mechanistic insight in rhodium-mediated carbene polymerization

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Chapter 1

Carbene Insertion into Transition Metal-Carbon Bonds: A New Tool for Catalytic C–C Bond Formation*

1.1 Introduction

Polymers are widely applied in every day's life and it is hard to imagine a world without polymers. This is why polymerization processes have been a subject of research for many years in order to develop plastics with all tunable properties. Many mechanistic studies are focused on polymerization processes to gain more insight into the reaction and to obtain a broad variety of properties of the polymer. Polar functionalities in a polymer are essential to achieve important properties such as adhesion, paint/printability and other surface properties. Stereoregularity and control over the amount of polar functional groups are necessary to amplify these properties, but are a challenge to obtain.

Large scale polymer industries are based on olefin polymerization, every monomer contains a C=C (C2) unit which can be polymerized in 3 ways; radical polymerization, early transition metal (ETM) polymerization and late transition metal (LTM) polymerization reactions. Radical polymerization reactions have poor control over the tacticity and do not lead to stereocontrolled polymers. ETM polymerization gives control over the tacticity, but monomers with polar functionalities are not suitable for this polymerization. Polar groups tend to coordinate easily to ETM's and poisons the catalyst, leading to inactivity of the catalyst and no polymerization will occur. LTM polymerization reactions allow polar-groups, but when di-functionalized C2 units are used in the polymerization reaction, no polymers are obtained due to steric hindrance. To obtain these highly stereoregular polar functionalized polymers, carbene (C1) polymerization is used. This C1 polymerization reactions tolerates polar functionalities and can provide functional groups on every C-atom of the polymer chain in a stereocontrolled way.

These highly stereoregular polar functionalized polymers can be the core of new types of materials, such as plastic batteries, conducting materials or devices like polymeric organic LEDs would also belong to one of the possibilities. This carbene polymerization is a new type of C-C bond formation reaction. To gain more insight into this novel reaction, mechanistic elucidation is of great importance. However, before we go deeper into the details of the reaction mechanism of this unique polymerization reaction, an overview is given in the field of transition metal (TM), where the catalytic insertion of carbenes into metal-carbon bonds creates new C–C bonds.
C-C bond formation by carbene insertion reactions

First, the essential migratory insertion step in the mechanistic stoichiometric model reactions will be discussed, after which further catalytic developments are described. The elementary step of migratory carbene insertion offers interesting new opportunities to enlarge the substrate scope in Pd-catalyzed cross coupling reactions and polymerization reactions. These reactions are likely to have an important role in heterogeneous catalysis, such as in Fischer-Tropsch reaction and some related C1 polymerization reactions catalyzed by metallic surfaces. At the end of this Chapter we describe the key carbene insertion steps relevant for the synthesis of the above-mentioned highly functionalized polycarbenes using homogeneous, molecular rhodium-catalysts.

1.2. Carbene insertions

Migratory insertion reactions are important bond forming elementary steps, in particular the reactions involving CO and alkene insertions into transition metal-carbon bonds (TM–C). These reactions are ubiquitous tools in organometallic catalysis for C–C bond formation. The reaction generally involves the migration of an anionic alkyl- or aryl ligand to a cisoidal π-coordinated neutral ligand, thus forming a new anionic ligand (figure 1). Alkene and CO migratory insertions into TM–C bonds are key elementary steps in among others the Monsanto process, olefin oligomerization and (co)polymerization, olefin/CO copolymerization, hydroformylation and Heck-type reactions.

Migratory insertion of an alkene fragment leads to introduction of two additional carbons (C2 unit) to organic fragments, while insertion of CO has been widely exploited as a valuable and powerful method for the introduction of C1 fragments.

![Figure 1](image-url)

**Figure 1.** Migratory insertion of alkenes, carbonyls and carbenes into transition metal-carbon bonds.

Metal-carbene species can be easily generated from diazo compounds and other carbene precursors (e.g. sulfoxonium ylides and α,ω-dihalocarbons). Diazocarbonyl compounds are excellent and widely applied carbene precursors due to their ease of preparation and their relative ‘green’ character: the only byproduct upon carbene generation is dinitrogen, while other carbene precursors form byproducts that are...
not so easily removed from the reaction mixture (e.g. DMSO).\textsuperscript{6,7} The large scale applicability of carbene precursors is somewhat limited in substrate scope due to some potential safety hazards associated with some diazo compounds. Many diazo compounds are toxic, and some of them are even potentially explosive under certain conditions.\textsuperscript{8} Especially aliphatic diazoalkanes are very unstable and require handling at low temperatures and low concentrations. To avoid this pitfall, much more stable precursors can be used such as diazocarbonyl compounds (diazoketones or diazoesters). Hence they are frequently applied as carbene precursors in several organic transformations, even in large scale industrial reactions. They are excellent substrates for the introduction of highly-functionalized carbon units, since a wide variety of substituted diazocarbonyl compounds is readily available via well-defined synthesis routes developed in the past decades.\textsuperscript{9} Much effort has been put into the development of safer alternative methods to handle aliphatic carbene precursors, using either in-situ generation of the inherently unstable aliphatic diazo compounds (for a review see Fulton et al.\textsuperscript{10}) or avoid the use of diazo compounds entirely (for a review see e.g. Müller\textsuperscript{11}). The availability of these alternative methods to generate (aliphatic) carbenes at transition metals will certainly stimulate further research into the use of carbenes in (catalytic) organic transformations in general. In this light, migratory carbene insertion reactions into TM–C bonds offer valuable new tools to make new C–C bonds, and nowadays large potential substrate scope of several carbene precursors available to develop such new reactivity.

\subsection*{1.2.1. Mechanistic insights from stoichiometric model reactions}

Migratory carbene insertions play an essential role in several catalytic processes ranging from a variety of Pd-mediated cross-coupling reactions involving diazo compounds, C1 polymerization and Fischer-Tropsch synthesis. This elementary step is at the same time difficult to study. The reaction is often very fast, and hence the cis-carbene-alkyl intermediate is difficult to detect and characterise. However, some model studies focused on slowing-down the reaction in order to detect the carbene intermediate and in the next section we will discuss the mechanistic information available from experimental model studies. The insertion of carbenes into M–H bonds will not be considered here. Migratory insertions into metal-hydride bonds are generally easier than insertions into metal-carbon bonds, and we consider this beyond the scope of the current perspective.\textsuperscript{12} Noteworthy, Thorn and co-workers studied the mechanism of the formation of Rh\textsuperscript{III} and Ir\textsuperscript{III} cis-carbene-allyl species (generated by alcohol elimination from M–CH$_2$–OR species) in the presence of pyridine (2 in Scheme 2).\textsuperscript{13,14}
C-C bond formation by carbene insertion reactions

\[
\begin{align*}
\text{CH}_3 \text{Ir} & \quad \text{L} \quad \text{CH}_2 \text{OCH}_3 \text{Br} \quad \text{L} \quad \text{HPF}_6 \quad \text{py} \\
\text{CH}_3 \text{Ir} & \quad \text{L} \quad \text{CH}_2 \text{py} \text{Br} \quad \text{L} \quad \text{PF}_6 - \text{C}_2 \text{H}_4 \\
\text{Br}_2 \text{Ir} & \quad \text{L} \quad \text{CH}_2 \text{py} \text{Br} \quad \text{L} \quad \text{PF}_6 \\
\text{Br}_2 \text{Ir} & \quad \text{L} \quad \text{CH}_2 \text{CH}_3 \text{Br} \quad \text{L} \quad \text{PF}_6 - \text{py} \quad \Delta \\
\end{align*}
\]

Scheme 2. Migratory insertion of a ‘hidden carbene’ into an Ir–C bond (py = pyridine).

The intermediate methylene complex is trapped by pyridine. The pyridine adduct is stable at room temperature, but if the temperature is raised to 60°C a Ir–hydride complex is formed by pyridine loss, methyl migration to the Ir-carbene and subsequent β-hydride elimination with liberation of ethene. A similar reaction occurred when BrCH₂OMe reacted with the Ir–starting material, and the ethyl intermediate formed before β-hydride elimination was isolated in this case. The same end-products were obtained for the analogous RhIII complex, but no intermediates could be detected.¹⁴

Mechanistic insight into the carbene insertion process was also gained by studying various Pt–alkyl/Pt–aryl complexes¹⁵,¹⁶,¹⁷,¹⁸ and mixed Pt–(alkyl)X (X = halide) complexes. Exposing various Pt complexes bearing chiral diphosphine ligands [(chiral diphosphine)PtX(Me)] to different diazo compounds in polar solvents lead mainly to the Pt–C inserted products, although for these complexes there is a competition between Pt–C and Pt–X insertion (Scheme 3). The chemoselectivity can be tuned towards Pt–C insertion by increasing the polarity of the solvent and by varying the halides towards better leaving halides (chemoselectivity I < Br < Cl). These observations led to a proposed mechanism involving cationic Pt intermediates, which are formed by dissociation of the halide from the inner sphere of the metal center. The vacant site is then occupied by the carbene, followed by rapid insertion into the Pt–C bond. Afterwards, the halide binds again to the metal, forming Pt–(alkyl)X complexes in which the alkyl fragment is extended by one carbon unit. Polar solvents stabilize the cationic intermediates, thereby facilitating carbene insertion into the Pt–C bond. Insertion into the Pt–X bond follows a different pathway that does not involve these cationic species and is therefore not affected by the polarity of the solvent.

Involvement of cationic Pt complexes in carbene insertions is further emphasized by McCrindle et al. who prepared cationic [(cod)Pt(Me)]⁺ complexes on purpose by abstraction of the halide in (cod)Pt(Me)X complexes (cod = 1,5-cyclooctadiene).¹⁹ When these complexes were added to a solution of diazomethane the formation of large amounts of polymethylene were observed, indicating that multiple carbene
insertions take place for these species. When phosphine ligands were applied instead of the cod ligand, the intermediate carbene species are stabilized (slowing down carbene insertions) and in that case Pt-(CH$_2$)$_n$-Me (n ~ 8) species were observed, indicating that indeed the cationic Pt complexes are involved in the catalysis.

**Scheme 3.** Carbene insertions into Pt–X or Pt–C bonds.

Cooper et al. reported the insertion of carbenes into W$^+$–alkyl bonds, indicating that these reactions also take place for electrophilic (cationic) metal-alkylidene fragments.$^{20,21}$ The resulting cationic insertion product is rapidly converted to the coordinated olefin complex via β-hydride elimination. This strategy was further developed towards W$^+$–aryl insertions, which do not undergo further reactions due to the lack of β-hydrogens.$^{22}$ Winter and co-workers showed that insertion in neutral W–benzoyl complexes is also possible, although this reaction required harsher reaction conditions (reflux in THF, yield ~16%) while the analogous Mo complexes readily undergo insertion at room temperature in good yield (53%).$^{23}$ Later they reported formation of W–benzyl complexes that undergo carbene migrations, although the actual insertion products were never observed.$^{24}$ Instead, W–alkyl complexes and η$^3$-benzyl complexes were formed, which are proposed to be formed upon rapid β-hydride elimination/reinsertion after carbene migration (Scheme 4). Similar results were obtained with Mo, although here the starting benzyl–Mo–carbene complexes could not be isolated since the insertion takes place more rapidly than is the case for W.

**Scheme 4.** Observed products upon insertion of carbenes into W–benzyl or Mo–benzyl bonds.
C-C bond formation by carbene insertion reactions

Metallacyclopentene-iron complexes bearing a Cp ligand undergo migratory insertion to form cyclobutyl-iron complexes, which undergo rapid β-hydride elimination to the corresponding olefin complexes (Scheme 5). Remarkably this reaction is also reversible, i.e. forming a Fe-carbene complex from a Fe-alkyl complex. This is most probably due to a relief of ring strain in the Fe-cyclobutyl complex upon formation of the five-membered metallacycle-carbene complex and has also been predicted (but never observed) for cyclopropyl-iron complexes. This concept has been applied to the synthesis of metal-stabilized bridgehead olefins in situ, while they are normally very unstable and undergo rapid dimerization.

Scheme 5. Carbene insertion/formation in ring-strained iron complexes.

Carbene insertions for other metals have also been studied, but to a much lesser extent. Competitive CO and carbene migratory insertion of alkyl fragments has been studied for osmium complexes and it turned out that these insertions favor the carbene ligand. Schrock and co-workers prepared a tantalum carbene complex by alkylidene transfer from phosphoranes. The resulting complexes decompose readily to the corresponding olefin complexes via carbene insertion and sequential β-hydride elimination (Scheme 6).

Scheme 6. Carbene insertion formation for Ta–CH₃ complexes followed by β-hydride elimination.

Albeniz and co-workers were able to spectroscopically observe aryl–Pd–carbene species and the subsequent insertion products of the carbenes into the Pd–aryl bonds by applying highly fluorinated aryls. Solé and co-workers demonstrated insertions of trimethylsilyldiazomethane (TMSDM) and ethyl diazoacetate (EDA) in Pd–aryl bonds, giving rise to the formation of azapalladacycles (Scheme 7).

Scheme 7. Formation of azapalladacycles upon insertion of carbenes into Pd–aryl bonds.
1.3. Catalytic reactions

1.3.1 Single carbene insertions: Cross-coupling reactions

Insertions of carbenes have recently been used as starting point for various cross-coupling reactions. The interest in cross-coupling reactions as a tool for C–C bond formation has increased rapidly over the last decades, since these reactions contribute to facile synthesis of many biologically active building blocks and functional materials. Pd is often used as catalyst for these reactions, although Ni and Cu catalyzed cross-couplings have also been developed. Although a wide variety of products can be synthesized via traditional Heck reactions based on coupling of aryl halides with acrylates, the use of carbenes in this reaction can lead to wider substrate scope. As stated above, many carbene precursors are commercially available or can easily be made according to known procedures, giving rise to easy synthesis of a wide range of compounds extended by one carbon unit.

Recently, Van Vranken et al. developed C–C coupling reactions based on insertions of TMSDM into Pd–C bonds generated by oxidative addition of benzyl halides, leading to the synthesis of styrene derivatives in low to moderate yields (scheme 8).32 The SiMe₃ functionalities introduced in the product were easily lost by desilylation while ester functionalities introduced via reaction with EDA remained in the product, resulting in the synthesis of ethyl cinnamates with various substituents on the phenyl ring in good yields (up to 74%).33 This reaction was further extended to the synthesis of α,β-diarylacrylates by reaction of α-aryldiazoesters with various benzyl halides.34 Both benzyl bromides and chlorides were converted in good yields and stereoselectivities (up to 85% and 81% respectively with stereoselectivities >20:1). The reaction is tolerant towards many functional groups on the benzyl halide as well as the aromatic ring of the diazo compound, making this reaction a versatile pathway for the synthesis of many biologically active substrates.

Scheme 8. Proposed mechanism for Heck-type C–C bond formation from benzyl halides and carbenes with Pd catalysts.
C-C bond formation by carbene insertion reactions

The proposed mechanism of these reactions is outlined in Scheme 8. The catalytic cycle starts by oxidative addition of the benzyl halide, followed by coordination of the diazo compound. Subsequent nitrogen loss leads to the formation of a benzyl–Pd–carbene species, which undergoes migratory insertion. The final products are formed by β-hydride elimination and the initial catalyst is recovered by treatment with a base.

Insertions into Pd–aryl bonds have also been developed and this concept was exploited as a tool for the synthesis of a variety of products. Van Vranken et al. demonstrated the synthesis of various indenylsilanes via insertions of TMSDM into Pd–aryl bonds, followed by a carboxypalladative cyclisation reaction (Scheme 9).[35]

![Scheme 9. Mechanism for the formation of indenylsilanes.](image)

Due to their instability, the use of diazo compounds without electron-withdrawing substituents in this reaction is rather limited. However, Barluenga and co-workers demonstrated that these substrates can be used in Pd-catalyzed cross-coupling reactions by generating them in situ from tosylhydrazones. The conditions for hydrolysis of the tosylhydrazones turned out to be compatible with cross-coupling catalysis. In this way both diazoaryls and diazoalkanes can be generated and coupled to aryl halides in a catalytic fashion, allowing the synthesis of polysubstituted olefins[36] and even 4-aryltetrahydropyridines,[37] which are valuable building blocks in medicinal chemistry (Scheme 10). Similarly, Wang et al. demonstrated the synthesis of di- and tri-substituted olefins under mild conditions in good yields (> 67%) by using these in situ generated diazo compounds directly in Pd-catalyzed cross-coupling reactions with benzyl halides as depicted in scheme 8.[38]
Scheme 10. Synthesis of polysubstituted olefins via insertion of in-situ generated carbenes (left) and structure of 4-aryltetrahydropyridines (right).

Pd–catalyzed cross-coupling of α-diazocarbonyl compounds with arylboronic acids affords 2-phenylacrylates (Scheme 11). This concept was extended to stereoselective synthesis of α,β-diarylacrylates by applying bulky bidentate N-donor ligands around the Pd center. In all cases the reaction was selective towards the formation of the E-isomer and mechanistic studies to account for this selectivity are ongoing. Remarkable about this reaction is that it requires solely molecular oxygen to reoxidise the catalyst, while most other processes based on boronic acids require external oxidants (e.g. benzoquinone) to initiate a new catalytic cycle.

Recently, Wang and co-workers have shown that aryl boronic acids can also be coupled to tosylhydrazones, which are assumed to generate aryl diazomethane compounds in situ (Scheme 11). This reaction further demonstrates the generality of coupling reactions based on carbene insertions. Tosylhydrazones have also been used as carbene precursors in a three-component coupling reaction involving carbenes, aryl halides and terminal alkynes (Scheme 12). After insertion of the carbene into the Pd–aryl bond the terminal alkyne is introduced on the Pd center via transmetallation from copper. Reductive elimination of both alkyne and alkyl groups yields benzhydryl acetylene derivatives from easily available starting compounds.
C-C bond formation by carbene insertion reactions

Scheme 12 Proposed mechanism for three-component coupling of carbenes, aryl halides and terminal alkynes.

The yields of the competing Sonogashira reaction between aryl halides and terminal alkynes could be reduced by carefully tuning the reaction conditions. This reaction is an elegant example in which two separate C–C bonds are formed on the same carbene carbon atom and it clearly shows that carbene insertions can be applied in combination with transmetallation from various metal-organic complexes.

Recently, Van Vranken and co-workers prepared vinyl silanes by reacting vinyl halides with TMSDM in presence of a Pd catalyst and a nucleophile (amines or stabilized carbon nucleophiles) (Scheme 13). The resulting vinylsilanes are excellent functional groups for nucleophilic substitution reactions and are therefore useful intermediates for stereospecific organic transformations. This concept was extended to the synthesis of α,β unsaturated γ-amino esters by insertion of EDA into Pd–vinyl bonds, followed by attack of the nucleophile. This route allows for a one-step synthesis of various γ-amino esters bearing both natural and non-natural side chains.

Scheme 13 Preparation of vinylsilanes via carbene insertion followed by nucleophilic attack (left) and structure of α,β unsaturated γ-amino esters (right).

Carbene insertion has been proposed as a possible pathway in the reaction of allyl halides with α-diazocabonyl compounds leading to functionalized 1,3-diene compounds (Scheme 14). However, different pathways involving non-carbenoid species can lead to the formation of similar products and mechanistic studies of this reaction are ongoing.
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Scheme 14 Synthesis of functionalized 1,3-diene compounds via carbene insertion into Pd–allyl bonds.

Wang et al. have exploited the similarities between CO insertions and carbene insertions to develop a tandem catalytic insertion reaction using both CO and carbenes (scheme 15). The catalytic cycle starts with insertion of CO into a Pd–aryl bond and the key step is believed to be migratory insertion of a carbene unit into the newly formed Pd–acyl bond. In presence of a base, the product formed is an enone, while the saturated counterparts (ketones) are formed in presence of Et₃SiH as external hydrogen source. The reaction is applicable for both carbenes with and without stabilizing carbonyl fragment, thereby giving rise to a large substrate scope. This reaction opens up new possibilities for Pd-catalyzed carbene transfer reactions.

Scheme 15. Pd–catalyzed tandem insertion reactions of CO and carbenes.

1.3.2. Multiple carbene insertions

Besides single carbene insertion reactions, also multiple catalytic carbene insertion reactions are known. If the rate constant for carbene insertion is significantly larger than the rate constant for elimination/termination or other follow-up reactivity, multiple carbene insertions will occur, leading to the formation of oligomers or polymers (provided an excess of the carbene precursor is available in the reaction mixture). As such, this process has gained much attention since it provides a valuable alternative to conventional olefin polymerization based on the coupling of C=C bond containing

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monomers, allowing the synthesis of densely functionalized polymers that (so far) cannot be synthesized in any other way. In the next sections we will highlight transition-metal catalysts that allow multiple insertions of both functionalized and non-functionalized carbenes and we will show recent advances in this field. Aside from transition metals several Lewis acids and main group metals are suitable for catalyzing this process and the whole field of the so-called ‘C1 polymerization’ has recently been reviewed.\textsuperscript{49,50} The reactions can be performed in a heterogeneous way, both in polymerization reactions and in the related Fischer-Tropsch synthesis, or in a homogenous way to obtain polymers with polar- and/or apolar side-groups. First the heterogeneously catalyzed carbene polymerization reactions will be described, followed by a more detailed overview of the homogeneously catalyzed carbene polymerization reactions (involving either or both polar and non-polar ‘carbenes’) known to date, which are most relevant for the topics discussed in this Thesis.

\subsection*{1.3.2.1 Carbene polymerization: Catalysis on heterogeneous metal surfaces}

Heterogeneous metal surfaces catalyze the polymerization of carbenes. Encouraged by the findings that colloidal gold particles catalyze polymerization of diazoalkanes \textit{(vide supra)} Nasini and co-workers found that polymers can as well be obtained by applying thin films of gold as catalysts in the reaction of various diazoalkanes.\textsuperscript{71} When diazoethane was used as carbene precursor, small amounts of stereoregular polyethylidene were formed, although the exact tacticity was not assigned (Scheme 16). Many other metal surfaces have also been explored in their catalytic activity towards diazomethane polymerization and most of them showed activity (Cu, Ti, Fe, Mg, W, Ni, V, Mn, Ta, Pt, Co, Zn, Cd, Cr, Al, Mo; listed in order of decreasing yield). No activity was obtained for metallic Pd, Rh, Zr and Ag, although a clear reason for this lack of activity could not be found. Remarkably, none of the other active surfaces gave rise to the formation of stereoregular polyethylidene.

The catalytic activity of gold surfaces in the polymerization of diazomethane (DM) has been used to obtain ultra-thin films of polymethylene on gold surfaces, since these films can be applied in areas as microelectronics and packaging.\textsuperscript{51} The films start to grow as nanometer-scale polymethylene assemblies on defect sites at the gold surface but in later stages these assemblies coalesce to uniformly cover the whole surface. Jennings \textit{et al.} have exploited this fact and modified the gold surface with either copper or silver, thereby enabling polymer growth uniformly on the whole surface.\textsuperscript{52} More recently, the same group found that EDA can act as co-catalyst for DM polymerization on gold surfaces.\textsuperscript{53} Although homopolymerization of EDA was not possible, small amounts (1-4\%) of esters were incorporated in copolymerization attempts. The thickness of the films could be tuned by changing the EDA concentration and films up to several hundreds of nanometers could be obtained. The effect of EDA on the polymerization of DM is thought to be caused by the removal of electron density from the gold surface by adsorbed ethyl ester...
carbene species and these electron-deficient gold sites are believed to be the active sites for polymerization. This effect is similar to that of copper-modified surfaces, in which the electropositive copper atoms remove electron density from gold.

**Scheme 16.** Proposed mechanism of propagation steps for the polymerization of diazomethane on gold surfaces.

Although the mechanism of these reactions is still elusive, most evidence points to the direction of carbene insertions involving \( \text{M}=\text{CH}_2 \) (or \( \text{M} \|=\text{CH} \)) species, which are similar to intermediates in the Fischer-Tropsch synthesis (for an overview of similar C–C bond forming reactions on surfaces see reference 54 and 55).

### 1.3.2.2. Fischer-Tropsch Synthesis

In the Fischer-Tropsch synthesis (FTS), reduction of carbon monoxide takes place in the presence of a heterogeneous transition metal catalyst and hydrogen. This leads to carbon-carbon formation and produces higher molecular weight (Mₘ) hydrocarbons. The reaction exists already for more than 75 years and much research was devoted to reveal the reaction mechanism behind this catalytic ‘fuel production’ reaction. Since the identification of the elementary steps is difficult for heterogeneous surface reactions, several reports deal with contradictory reaction paths, either based on insertion of carbenes or direct insertion of CO (see Scheme 17; for reviews on the mechanism see e.g. Hindermann and Dry).

Key intermediates in the carbene mechanism are oxygen-free C₁.species, generated by hydrogenation of CO followed by the cleavage of the C–O bond. Chain propagation occurs via insertion of the carbene-like CH₂ units into metal–alkyl bonds, giving rise to the formation of surface alkyl species. The CO insertion mechanism is based on the direct insertion of CO into metal-alkyl bonds. The resulting acyl species are reduced by \( \text{H}_2 \) to form a new metal-alkyl species that can undergo further insertions of CO. A third mechanism based on oxymethylidene species is known under many different names, e.g. the formyl mechanism or the hydroxycarbene mechanism. In this mechanism CO is partially hydrogenated to hydroxy-carbenes in which the C–O bond is not cleaved. Chain growth occurs in this case via condensation of two surface-bound hydroxycarbene species with elimination of water. This mechanism was once proposed as the main pathway, although more
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recent papers clearly disfavor this mechanism. More recent papers have indicated that a single reaction pathway cannot be responsible for the observed product distributions and therefore the FTS is presumed to be a combination of at least two parallel reactions, likely involving both carbene insertion and CO insertion steps.

Scheme 17. Different mechanisms proposed for the Fischer-Tropsch synthesis on heterogeneous catalysts.

However, there is still much debate on the mechanism, and research will be continued until direct observation of the active species will lead to conclusive evidence for one of the above-described mechanisms.

In principle all group VIII metals show some activity towards C–C bond formation in the FTS process, although the most active catalysts are found to be iron, cobalt, nickel and ruthenium. Of these catalysts only (the cheapest) iron and cobalt are used in industrial processes. Ruthenium is the most active metal, but is not economical for FTS due to its high price. The problem with nickel is that it produces mainly methane instead of higher olefins under industrial conditions. Most of the above-described mechanistic studies are performed with industrially relevant iron or cobalt systems, and thereby possible alternative pathways for other metals are mostly being neglected. Some homogeneous multinuclear complexes proved to be good models for the catalytically active multinuclear metal sites at heterogeneous surfaces in the Fischer-Tropsch process. Curtis et al. reported in 1980 the reaction of diazoalkanes with binuclear compounds containing a metal-metal bond. The reaction led to binuclear \( \mu \)-alkyldiene complexes with a bridging alkylidene-ligand. The formation of alkylidene species from diazoalkanes at multinuclear complexes is non-trivial, and can follow several pathways and can lead to several alkylidene coordination modes.
Cowie et al. studied binuclear Rh,Os species as synthetic homogeneous models for the active heterogeneous surfaces in the FTS process. They focused on the relevance of the bridging methylene groups and the role of the two different metals (Rh and Os). Mixing [RhOs(CO)₄(dppm)₂](BF₄) compound 5 with diazomethane led to the formation of complex 8, which is likely formed by a series of consecutive carbene insertions (Scheme 18). In order to get a better insight in the mechanism of this methylene-coupling reaction, the reaction was performed at different temperatures. This allowed them to obtain more information about the intermediates.

By increasing the temperature from −60°C to 0°C compound 6 transformed into the butanediyl species 7. Compound 4 can be observed at higher temperatures between −40°C and room temperature. Compound 6 can be converted to 7 and 8 by raising the temperature, but 7 and 8 do not interconvert. The mechanism likely proceeds via discrete Rh=CH₂ intermediates at the coordinatively unsaturated Rh site, and after diazomethane activation at this metal, methylene insertion into the Rh–C bond of the bridging methylene follows. The Os-hydrocarbyl bond strength increases by this process, and this is crucial for the chain growth. If otherwise, loss of ethene would stop the methylene coupling sequence. This underlines the importance of the bridging binding modes. The group of Dry described a similar type of methylene coupling sequence to support the carbon-carbon coupling in the Fischer-Tropsch process.

To gain more information about these insertion reactions, ¹³C and ²H labelled diazomethane was used. This, however did not provide much more information.
C-C bond formation by carbene insertion reactions regarding the formation of 7 and 8. Further information was however obtained by adding diazomethane to vinylidene-bridged species (Scheme 19). This leads to similar types of carbene insertion reactions with a comparable temperature dependency, and shows that carbene insertion into bridging positions is possible. Alkyl ligand migration between the two metals apparently plays an important role. The properties of the metals, the lability, the coordinative unsaturation of the Rh atom and the strong coordination of the hydrocarbyl ligands to Os make these homogeneous hetero-binuclear Rh,Os systems quite suitable to model Fischer-Tropsch-like C–C bond formations.

![Scheme 19. Products obtained by reacting of diazomethane with vinylidene bridged heterodinuclear Rh–Os compounds.](image)

**1.3.2.3. Carbene polymerization: Homogeneous & colloidal catalytic systems**

**Polymers from diazoalkanes**

Although many different metals have been attempted as catalysts for the polymerization of diazoalkanes, most of the earlier reports deal with the activity of copper and gold and have been reviewed (Scheme 16). In 1909 polymerization of diazoalkanes was attempted with Cu-bronze. Unfortunately this reaction produced only dimers (dialkyl maleate and dialkyl fumerate) and short oligomers. Later on a broad range of copper reagents (copper metal, Cu and Cu salts) has been applied for the polymerization of carbenes from diazo compounds. The molecular weights ($M_w$) of polymethylene obtained from diazomethane with these copper reagents are up to 20,000 Da. The active catalyst is a Cu species. If the reaction is starting with a Cu catalyst (e.g. copper sulfate, copper stearate) it is thought to be reduced *in situ* to Cu during the reaction. Several mechanistic proposals for the Cu-mediated polymerization have been postulated: rapid growth of a cationic chain, step-growth *via* repetitive migratory insertion steps of carbene units (generated from the diazo compound) into a Cu–alkyl growing chain, and radical polymerization by a stabilized Cu radical have all been proposed. Colloidal gold particles were later found to be highly active catalysts for the polymerization of diazomethane. The active colloidal gold species were formed...
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upon immediate reduction of the AuCl₃ precursor upon reaction with the diazo compound, resulting in almost quantitative formation of polymethylene with Mₙ up to 50 kDa. After complete reduction of all AuCl₃, new polymer chains with similar lengths were obtained upon addition of fresh diazomethane, indicating that metallic gold is the catalytic active center. Higher diazaalkanes could also be polymerized by this system with some indications of the formation of stereoregular (syndiotactic) polymer, albeit with lower reaction rates and lower yields (< 35%).

Scheme 20. General mechanism for polymerization of diazomethane by TM catalysts.

The activity of other metals is less extensively studied, but there are some reports mentioning the activity of nickel and palladium towards polymerization of diazaalkanes. Nickel carbene complexes are mainly used as catalysts for cyclopropanation reactions and insertion of carbenes into TM–C bonds with these complexes is rare. Nevertheless, Werner and co-workers found a highly selective nickelocene complex that is able to polymerize diazomethane to polymethylene in almost quantitative yield. The reaction is much faster than reactions carried out by copper powder and ferric chelates and in all cases the catalyst is recovered unchanged after the reaction. The unique feature of this catalyst is that it produces exclusively polymers without the formation of byproducts such as ethene or low-Mₙ oligomeric material. These results do not change when the reaction is performed in the presence of alkenes or aromatic hydrocarbons, emphasizing the high selectivity of this reaction towards polymerization over e.g. addition to double bonds. This suggests that no free carbenes are formed during the reaction. The high selectivity is likely the result of extremely fast propagation rates of the polymerization. The intermediacy of radicals could also be ruled out since addition of radicals does not influence the reaction.

The reactivity of the [Ni(Cp)₂] complex towards other diazaalkanes and diazoesters diminishes with increasing steric bulk of the carbon bearing the diazo group, thereby limiting its use. Reaction of phenyldiazomethane yields only a small amount of polymer while diphenyldiazomethane or diazofluorene shows no reaction at all. Ethyl diazoacetate was not polymerized and the main products were the dimers diethyl fumarate and diethyl maleate. In the presence of double bonds, the cyclopropanation product was formed as a third reaction product due to the lack of polymerization activity.

Polymethylene was also produced by the iridium chloro-carbonyl-bis(triphenylphosphine) complex [IrCl(CO)(PPh₃)₂] upon reaction with diazomethane. By electrophilic attack of the Ir-species on the carbon of the
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diazomethane a methylene (:CH\textsubscript{2}) moiety coordinates as a fifth ligand and the resulting complex is stable in air. In contrast with the above-described nickel catalyst, the iridium complex decomposes in solution and the only products obtained after reaction with diazomethane are polymethylene and decomposition products.

More recently Ihara and co-workers showed that phenyl diazomethane can be converted to small amounts of low-M\textsubscript{w} oligomers (M\textsubscript{w} \textasciitilde 1500 Da, yield < 20%) in presence of Pd\textsubscript{2}(dba)\textsubscript{3}(CHCl\textsubscript{3}) and pyridine. The \textsuperscript{1}H NMR spectrum of the resulting polymers shows broad resonances for both the aromatic protons and the proton attached to the carbon atom of the polymer backbone, indicating the formation of atactic material. Elemental analysis showed the incorporation of a large amount of azo groups in the polymer (\textasciitilde one per four monomer insertions), which indicates that the reaction is not fully selective towards carbene insertion (Scheme 21). This, in combination with the low yields and the lack of stereoregularity of the reaction, shows that the reaction needs to be optimized to exploit its full potential.

Scheme 21. Polymerization of phenyl diazomethane by Pd\textsubscript{2}(dba)\textsubscript{3}(CHCl\textsubscript{3}).

Polymers from carbenes bearing polar functionalities

C\textsubscript{1} polymerization of carbenes bearing polar functionalities is much more challenging due to the increased stability of the corresponding carbene precursors and most metal catalysts form only the corresponding dimers upon the decomposition of these precursors.

From 2003 on Ihara and co-workers investigated the polymerization of diazo compounds bearing polar functionalities catalyzed by a variety of Pd\textsuperscript{II} catalysts. They were able to obtain a variety of highly-functionalized oligomers/polymer/\textsuperscript{poly(substituted methylene) synthesis via so-called 'poly(substituted methylene) synthesis' by both homo- and copolymerization of different diazo monomers. Amongst these were mainly diazoesters,\textsuperscript{77,80,81} diazoketones,\textsuperscript{77,82} cyclic diazoketones\textsuperscript{83} and diazoacetamides\textsuperscript{84} and all could be converted to oligomeric or low M\textsubscript{w} atactic polymeric material. In 2003 they reported that PdCl\textsubscript{2} reacts with methyl diazoacetate (MDA) and ethyl diazoacetate (EDA) in the presence of an amine with formation of low-M\textsubscript{w} oligomers (up to 700 Da) that could be isolated as viscous oils in good yields (50-100\%).\textsuperscript{80} NMR analysis showed broad resonances indicative for atactic material and the spectra looked similar to those of the product obtained by radical polymerization of fumarates. However, MALDI-ToF analysis of the resulting materials confirmed
that the polymers consisted of repeating carbene units, thereby excluding participation of olefin polymerization. From the $m/z$ values it could be deduced that polymers bear amine functionalities at both chain ends of the polymer. Since then, several Pd salts have been applied as catalysts for this reaction and it turned out that the results are quite similar in all cases.\(^8\) Surprisingly, Pd\(^0\) sources such as Pd\(_2\)(dba)\(_3\)(CHCl\(_3\)) show similar activity towards polymerization. The authors proposed that in this case the active species are formed by in-situ oxidation of Pd\(^0\) to Pd\(^{II}\). Later reports deal mainly with the use of PdCl\(_2\)(MeCN)\(_2\) as the catalyst, because this catalyst has a better solubility in organic solvents.

This reaction could be extended to oligomerization of saturated and unsaturated diazoketones. A clear relation between the structure of the monomer and the ease of polymerization was observed.\(^7,8\) For example, diazo compounds with a double bond next to the carbonyl functionality could be polymerized in good yields (e.g. $M_w \sim 2500$ Da, yield $\sim 50\%$) while the corresponding saturated diazoketones gave only low yields and lower molecular weights under the same conditions with the same catalyst ($M_w \sim 900$ Da, yield $\sim 13\%)$.\(^8\) This indicates that the presence of a double bond adjacent to the ketone functionality is beneficial for polymerization, although it is not exactly clear why this is the case.\(^6\) Polymerization is hampered by steric hindrance around the metal center during polymerization, as is emphasized by very low reactivity of Pd systems towards bulky diazoketones and a variety of cyclic diazoketones (scheme 22).\(^8\) Unsaturated cyclic diazoketones can be polymerized, albeit in low yields (9-24%, $M_w = 900-1400$ Da), while saturated cyclic diazoketones do not undergo polymerization reactions.

![Scheme 22. Structure of some diazoketones attempted as monomers in the Pd-catalyzed polymerization.](image)

Depending on the structure of the diazoketone various amounts of azo functionalities were incorporated in the polymer main chain, sometimes giving rise to rather ill-defined copolymeric structures. Cyclic diazoketones gave rise to higher amounts of azo groups ($\sim 25\%$) than acyclic diazoketones ($\sim 10\%$), although in the latter case the amounts varied significantly for the different monomers.

Oligomers functionalized with N-substituted carbamoyl groups were available via polymerization of certain diazoacetamides, although they were obtained in low
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yield (~10%) and with higher azo contents (~20%) than the oligomers described above. These results indicate that the catalyst system is not sensitive to the presence of functional groups in the monomer, emphasizing the wide range of applicability of this technique towards the synthesis of functional materials.

Recently the authors have shown that higher-Mₚ polymers of EDA (up to 24 kDa) could be obtained in reasonable yields by applying a Pd⁰(NHC)/BPh₄⁻ systems as catalysts. NMR analysis of the polymeric material showed that the material is atactic, although variations in the structure of the NHC ligand seem to have a slight effect on the tacticity, thereby creating possibilities for stereocontrol. Activation of the Pd⁰(NHC) catalyst by BPh₄⁻ is required to obtain higher-Mₚ polymers. For all catalysts, the authors propose a Pd¹⁻-based mechanism that does not involve discrete carbene intermediates, thereby formally excluding these systems from the scope of this perspective. According to Ihara and co-workers the initiation takes place via nucleophilic attack on the α-carbon atom of the diazo compound, which leads via nitrogen extrusion to the formation of a Pd²⁺–carbon bond. Amines are proposed as initiating species but, since the reaction also proceeds in absence of amines, this could well involve the attack of weak nucleophiles such as water, MeCN or the monomer. The observation of amines at both chain-ends suggests that two polymer chains might grow simultaneously from one Pd center and the final polymer could well be formed by reductive elimination of both chains.

Propagation was proposed to involve direct migration of the growing polymer chain onto the coordinated diazo monomer, followed by nitrogen extrusion (Scheme 23). A true carbene polymerization mechanism involving discrete Pd-carbene intermediates can however not be excluded.

Scheme 23. Proposed chain propagation in Pd-mediated ‘carbene’ polymerization from diazo compounds.
The proposed mechanism (Scheme 23) contrasts with other reports suggesting that carbenoid species are intermediates in insertion reactions with diazo compounds catalyzed by Pd,\textsuperscript{32,33} and since there is no direct evidence for direct attack on the diazo compounds, the intermediacy of carbene species in Pd-catalyzed oligomerization reactions cannot be ruled out. Since these reports contribute for a large part to the development and understanding of carbene polymerization (and C1 polymerization in general) we decided to include them in this perspective, despite the ambiguity about the mechanism.

Recently, we have shown in our group that most likely low valent Pd species (probably Pd\textsuperscript{0}) are involved as catalytically active species in this reaction.\textsuperscript{86} Several Pd\textsuperscript{0} complexes, including heterogeneous Pd\textsuperscript{0} on carbon, catalyzed the formation of oligomers from EDA in good yields (up to 80\%) and higher $M_w$ (up to 2000 Da) than the previously reported Pd\textsuperscript{II} salts. Furthermore, these systems do not incorporate olefins in the growing carbene polymer chain, which would have been expected if Pd\textsuperscript{II}–alkyl intermediates were involved. This, in combination with the known reducing power of diazo compounds, makes the involvement of low valent Pd more likely. These results might contribute to a more strategic reaction design, directed to the development of highly active and (stereo)selective Pd-based C1-polymerization catalysts.

In 2006, we reported that polar functionalized carbenes generated from diazo compounds were polymerized in a stereoregular manner by transition metal catalysts.\textsuperscript{87} By reacting EDA and other diazoesters with Rh\textsuperscript{I}(diene) catalysts, syndiotactic (co)polymers are produced with high molecular weights and in high yields ($M_w$ up to 150,000 Da, yields up to 85\%) (scheme 24). The remaining products are atactic oligomer ($M_w \sim 1200$ Da, $M_w/M_n \sim 3$) and diethyl maleate and fumarate.\textsuperscript{88,90,91} The syndiotactic polymers are highly crystalline, and reveal thermotropic and lyotropic liquid crystalline (LC) properties.\textsuperscript{87,91}

\begin{tikzpicture}
  \node at (0,0) {\textbf{Scheme 24.} Formation of syndiotactic poly-carbenes from diazo-esters mediated by Rh(diene) catalysts.}
  \begin{scope}[xshift=3cm]
    \draw[->,thick] (0,0) -- (0,0.5) node[above] {$E$};
    \draw (0,0) -- (0.5,0) node[above] {$R_1$};
    \draw (0,0) -- (0,-0.5) node[below] {$R_2$};
    \draw[->,thick] (0.5,0) -- (1,0) node[above] {$E$};
    \draw (1,0) -- (1.5,0) node[above] {$R_1$};
    \draw (1,0) -- (1,-0.5) node[below] {$R_2$};
    \draw[->,thick] (2,0) -- (2,0.5) node[above] {$E$};
    \draw (2,0) -- (2.5,0) node[above] {$R_1$};
    \draw (2,0) -- (2,-0.5) node[below] {$R_2$};
  \end{scope}
\end{tikzpicture}

The observed LC behavior of these materials is unexpected for flexible sp\textsuperscript{3}-carbon backbone polymers. Recently, our group disclosed that these polymers reveal a liquid crystalline thermotropic phase for a special reason. A combined set of experimental measurements, supported by molecular mechanics-based molecular...
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dynamic studies, suggests that the LC behavior is due to self-aggregation of the polymer chains into triple helix aggregates (see Figure 2). This triple helix is stabilized mostly by inter-chain van der Waals interactions. Helix formation renders the polymer-chains much more stiff than individual chains, thus explaining the LC properties of these materials. Cross-linking of different triple helices can also take place (involving the same self-assembly process but involving interconnecting triple helices). This explains why these polymers are quite difficult to melt, as well as their gel-forming abilities at higher concentrations in solution. The intriguing supramolecular self-assembling behavior of these polymers is an additional interesting aspect of these new materials.

Figure 2. Liquid-crystalline behavior of poly-carbenes explained by supramolecular self-aggregation, reflecting the importance of the ‘tertiary structure’ of synthetic polymers on their material properties.

Rh-mediated stereoselective polymerization is also applicable to other polar functionalized C1 monomers, such as n-butyl diazoacetate, 3-butenyl diazoacetate, benzyl diazoacetate and t-Bu-diazaacetate. This reaction allows the synthesis of random and [homo-A]-[random-B>A]-type block copolymers (scheme 25). Both the homopolymers and the above block copolymers (Scheme 25) are rather long, and have a functional group on every carbon atom of the stereoregular polymer chain. This makes these highly crystalline polymers quite difficult to (melt) process. Hence, attempts were undertaken to incorporate non-functionalized monomers to improve the polymer processability. Additionally, copolymerization of functionalized carbenes with (cheap) non-functionalized olefins would be of industrial commercial interest to prepare polyolefins containing small amounts of surface-active polar-groups. Such polymers are of interest to improve the surface properties of polyethylene or polypropylene, so that paint and ink attach better in a durable manner to the surface-area of such modified polymers. Only a small amount of functionalized carbene monomers should be enough to achieve this effect.
Formation of copolymers of functionalized and non-functionalized monomers is further of interest to make compatibilizers for use in polymer blends. Such blending agents can act as glue between polymers with and without functionalities, and can be obtained by copolymerizing functionalized carbones with non-functionalized ones. Three ways were developed in our group to synthesize these type of block-polymer: copolymerization of diazomethane and EDA,\textsuperscript{95} copolymerization of ethene and EDA,\textsuperscript{96} and copolymerization of sulfur ylides and EDA.\textsuperscript{97} This last example uses an alternative carbene source in the carbene-polymerization reaction. Like diazo compounds, also sulfoxonium ylides can form a metal-bound carbenoid species upon reaction with transition metals (leading to loss of dimethyl sulfoxide; DMSO). Using Rh(diene) catalysts with a bulky group on the diene, this leads to polymerization activity producing linear polymethylene (nearly identical to linear polyethylene) in up to 80\% polymer yield.

When EDA is added to the catalyst/substrate mixture, the polymerization reaction yields linear diblock copolymers with a –\{(CH\textsubscript{2})\textsubscript{m}(CHCOOEt)\textsubscript{m}\} – structure. This method, as well as the ethene-EDA copolymerization technique is an interesting alternative for the relatively dangerous copolymerization of EDA with diazomethane (DM). Nonetheless, DM is potentially explosive and highly toxic.
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However, the ylide based copolymerization only allows the synthesis of linear diblock copolymers, and a limitation of the Rh-mediated ethene-EDA copolymerization is the fact that only a small amount of ethene (maximal 11%) can be incorporated in the polymer chain. The DM-EDA copolymerization allows random copolymerization reactions in which the \(-\text{CH}_2-\) to \(-\text{CHCOOR}-\) ratio in the final polymer chain can be controlled by changing the feed ratio of the monomers. This is an advantage of this polymerization technique.

**Previous mechanistic studies**

Mechanistically, the carbene polymerization reaction is still associated with many open questions. The initiation efficiency (IE) of this Rh-mediated carbene polymerization is low (< 5%). To understand this low IE number, catalyst screening and mechanistic studies have been performed.\(^9\) The conclusion from these studies was that the \(O,N\)-ligand and the diene ligand of the \([\{(O,N\text{-ligand})\text{Rh(diene)}\}]\) precatalysts have different effects on the polymerization reaction. The \(O,N\)-ligands have a strong influence on IE of the polymerization reaction, while the diene-ligand is important for stabilization of the active species during the propagation-steps.\(^9\)

The exact role of the anionic- and the diene-ligand during the polymerization process is, however, still unknown. Furthermore, the exact structure of the active species remains unidentified and has to be clarified by deeper mechanistic studies. In case Ir analogues of this Rh catalyst were used for the polymerization of EDA, only \([\{\text{N-benzyl-L-prolinate}\text{Ir}^i\text{(cod)}\}]\) proved active.\(^8\) In 2007, Buchmeiser et al. studied the reactivity of another Ir\(^i\)-complex, \([\{\text{N-acetyl-N,N-dipyrid-2-yl})\text{Cl}\text{Ir}^i\text{(cod)}\}]\), towards EDA. This did not polymerize EDA at all, while the analogous Rh complex proved quite active in the polymerization of EDA.\(^10\) Some attempts to use cobalt-based catalysts in our own group also failed to produce polymer from EDA. Hence, rhodium seems essential for these reactions.

**DFT calculation on the polymers bearing polar functionalities**

ADFT study was performed to explain the formation of stereoregular polymer with non-chiral catalysts, suggesting that the propagation steps are chain-end controlled.\(^8\) The diene ligand, or a ligand derived from the diene formed under the applied reaction conditions, must be stabilizing the active species for polymer formation. This can be derived from the large influence of the applied diene ligand on the obtained polymer lengths and molecular weight distributions.\(^8\) DFT calculations using unmodified \([\text{cod}\text{Rh(polymeryl)}]\) species as a simplified model of the catalyst suggest that the reaction proceeds via a migratory insertion mechanism (Scheme 27).\(^8\)
Scheme 27. Proposed mechanism of propagation steps of the Rh-mediated polymerization of polar functionalized carbenes (P = growing polymer chain, E = COOMe).

The termination steps of the polymerization reaction were also investigated computationally, again using unmodified [(cod)Rh(polymeryl)] species as a simplified model. Interestingly, these DFT calculations revealed a low energy pathway for $\beta$-H elimination compared to propagation. Hence, these studies revealed that unmodified [(cod)Rh(polymeryl)] species can actually not be responsible for polymer formation. Such species are expected to form only dimers or short, unsaturated and atactic oligomeric chains, which are the products of rapid $\beta$-H elimination. This is in marked contrast with the experimentally observed long isotactic polymers. Hence, catalyst modification must occur during the initiation-phase of the polymerization reaction. This is in agreement with the previously observed induction period during which the selectivity changes from predominant dimerization/oligomerization activity to almost exclusively polymerization activity. Ligand modification or other catalyst alteration steps occurring under the applied reaction conditions (e.g. ligand and/or metal oxidation by H$_2$O/O$_2$ in case of 1,5-dimethylcyclooctadiene) cannot be excluded. Additional DFT studies were performed to elucidate the potential nature of the active species. Calculations on the Rh(diene)-species showed that stabilization of the active species is achieved by the formation of a five-membered chelate ring which includes the $\beta$-ester group of the last inserted ester unit (see Figure 3). This, however, does not help in achieving higher propagation over termination rates in the calculations.

Figure 3. Calculated active species for the polymerization.

Experimental work confirmed that preformation of [(cod)Rh(polymeryl)] species as shown in Figure 1 (with an unmodified Rh(diene) moiety) does not lead to higher amounts of catalyst active in polymerization compared to regular [(prolinate)Rh(diene)] precatalysts normally used in carbene polymerization reactions. This further suggested that a modification of the diene-ligand is required to obtain active catalysts. However, it is also clear that much more research is needed to fully understand these systems. Considering the abovementioned
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interesting applications of the Rh-mediated carbene polymerization reaction could be in the synthesis of novel materials with potential ‘specialty’ applications (e.g. plastic electronics, conducting materials, batteries, polymeric organic LEDs, compatibilizers in polymeric blends, etc.). Also, the intriguing supramolecular self-aggregation of poly-carbenes into LC triple-helix assemblies can be beneficial. Our group has developed a strong drive to advance this interesting new polymerization protocol. Hence, in order to exploit the full potential of these new reactions, a detailed mechanistic understanding is crucial.

1.4 Conclusions

Migratory carbene insertions into the TM–C bonds offer interesting opportunities in catalytic C–C bond formation and this reaction already has some exciting applications. Intriguing examples show the preparation of densely functionalized polymers from C1 monomers, and hence the synthesis of new (stereoregular) polymers that are functionalized with (polar) substituents at every carbon atom of the polymer backbone. Such polymers are not so easily obtained by conventional olefin polymerization techniques. Carbene insertions most likely also play an important role in the related Fischer-Tropsch synthesis, and therefore renewed mechanistic insights into this reaction based on (stoichiometric) studies of carbene insertion reactions may well contribute to further developments of this catalytic ‘fuel production’ reaction. Several of such model reactions reveal the feasibility of the migratory carbene insertion elementary step, and underline the importance of electronic and steric influences of ligands and (partial) charges on the outcome of the reaction, both in homogeneous systems as on heterogeneous metal-surfaces. This offers ample opportunities for catalyst development (catalysis by design). This will be important to gain control over the chain-growth and chain termination/transfer processes in (existing) Fischer-Tropsch and C1 polymerization reactions, but also holds the promise to develop completely new (catalytic) reactions based on migratory carbene insertions. In this respect, recent developments in Pd-catalyzed cross-coupling reactions show that transmetallation can be successfully combined with migratory carbene insertions, thus expanding the substrate scope substantially and allowing the efficient synthesis of new molecular compounds.

Another significant challenge in this field of research is to obtain a detailed mechanistic understanding of the Rh-mediated stereoregular carbene polymerization reactions. Important goals are to reveal the exact structure of the key polymer forming Rh-species, understanding the process of catalyst activation and how the (modified) ligands influence this process. Furthermore, revealing details about the propagation, termination and chain-transfer mechanisms is important to further develop this new polymerization reaction.
1.5 Outlook of the thesis

The importance of understanding the key elementary steps in the reaction mechanism of Rh-mediated stereoregular carbene insertion reactions has been illustrated by the previously described examples. The main focus of this thesis is to elucidate the mechanistic details of the Rh-mediated, stereocontrolled carbene polymerization. This reaction is currently the only tool to obtain highly functionalized syndiotactic polymers, and it allows the design and synthesis of special polymers with desirable properties. While some fragmented mechanistic information was obtained in previous studies, a detailed mechanistic picture was lacking thus far. Mechanistic understanding of this new reaction is important for several reasons. First of all the development of new and improved catalysts critically depends on a detailed understanding of catalyst activation process. Understanding this process should allow us to achieve higher initiation efficiencies towards the active catalyst, thus allowing us to synthesize polycarbenes in higher yields while using less of the expensive Rh-catalyst (in earlier studies a polymer yield of maximum 50% could be achieved using catalysts with a typical initiation efficiency lower than 5%). Understanding the process of stereoregulation is also important for the development of future catalysts, and may eventually allow us to steer the tacticity from syndiotactic to isotactic, and in-between. This, in turn, is expected to have a strong influence on the polymer properties. Understanding the mechanistic details of propagation, termination and chain-transfer is important to decrease the formation of dimeric and oligomeric side-products and to allow a better control over the molecular weight and weight distribution of the polymer obtained (e.g. through addition of specific chain-transfer agents). The latter is important to improve the (melt) processability of the new materials.

In this Thesis we study in detail the structure of the active species of the carbene polymerization reaction, how it is formed and why it produces polymer with a high syndiotacticity. We further focus on the factors influencing chain termination and chain transfer, and we performed supporting DFT calculations to rationalize the results in a detailed mechanistic picture. The obtained mechanistic information provided is further used to synthesize improved catalysts and to control the polymer molecular weights. Specific research questions that will be addressed include:

(a) Why is the initiation efficiency of the catalyst in the polymerization reaction low, and can we enhance the efficiency of catalyst activation?
(b) What is the structure of the polymer-forming active species?
(c) What are the propagation, termination and chain-transfer mechanisms?
(d) Does chain-transfer occur at all?
(e) Why are highly stereoregular polymers formed?
The answers to these questions should lead to a better understanding of the Rh-mediated carbene polymerization protocol, which in turn is important to fully exploit the potential of these intriguing new polymerization reactions.

In chapter 2 we report the mechanistic details of the carbene polymerization reaction using the originally reported Rh(I(cod)-based catalysts. These precatalysts are involved in a multistep activation process leading to several different active species, which are responsible for the formation of the different products obtained (dimers, atactic oligomer and syndiotactic polymer). The studies further expose important experimental details about the chain-termination and chain-transfer processes. Strikingly, the studies reveal an important role of added alcohols, which induce chain-transfer. This leads to protonation of the growing chain and alkoxide-transfer to the metal, thus producing saturated H-chain-OR polymers. A new polymer chain grows from the formed Rh-OR moiety.

In Chapter 3 and 4 we focus on identification of the active Rh-species responsible for formation of the stereoregular polymers. Detailed information was obtained by following an important lead from previous studies, showing that aerobic oxidation of the solid [(prolinate)Rh(Me₂cod)] precatalyst (containing two diastereomers) led to higher polymer yields, suppressed formation of unwanted dimers and oligomeric side-products, and resulted in improved catalyst activation efficiency. This observation was initially thought to be the result of selective decomposition of one of the two diastereomers of the (pre)catalysts, the one believed to be responsible for formation of the side-products (leaving only the desired activity of the diastereomer responsible for polymer formation). To shine more light on this hypothesis, we investigated the influence of the diastereomer-ratio of several related derivatives of [(prolinate)Rh(Me₂cod)] on the polymerization activity (Chapter 3). Since for some of these precatalysts the opposite effect was observed as initially hypothesized, we actually disproved the theory that the effect of aerobic oxidation of the precatalyst is only due to the removal of a side-product forming form of the (pre)catalyst. Hence, aerobic oxidation must play a more active role in catalyst activation. Hence, we next investigated the influence of aerobic oxidation of the solid precatalyst samples in more detail (Chapter 4).

In Chapter 4 we show that the Rh(I(diene) precatalysts are in fact oxidized to Rh(III)(allyl-hydroxide-diene)-species. These species are only one step away from forming the actual active Rh(III)(allyl-diene)(alkyl) species responsible for polymer formation. The active form of the catalyst could be identified by using ultra-high ESI-MS analysis and the important role of alcohol as a chain-transfer agent was confirmed by these studies as well. Hence, these studies led to an important modification of the mechanistic features of the reaction.

In Chapter 5 we further investigated the propagation, termination and chain-transfer steps of the polymerization reaction using DFT methods, and using a slightly
simplified model of the active Rh_{III}(allyl-diene)(alkyl) species. The details of the computational model are in excellent agreement with all experimental observations. Chapter 6 deviates from the general mechanistic topic of this Thesis, and here we describe two functionalizations of the new, highly functionalized, stereoregular polymeric materials towards potential new applications of these polymeric materials. First, we will show that we can generate amphiphilic block copolymers that form micelles by initiating the EDA polymerization on a preformed PEG polymeric chain containing an alcohol end-group. Secondly, we investigated the synthesis of polymers from several different diazo compounds expected to produce polymers with electron-conducting properties. Such polymers potentially find application in new polymeric solar cells.

1.6 References and Notes

1 Catalytic C–C bond formation can also be achieved by carbene insertions into C–H bonds\(^{19}\), but this is beyond the scope of this thesis.
7 Of course, if we include the energy load and the byproducts generated in their synthesis, diazo compounds are less ‘green’ in terms of atom and energy efficiency. Diazo compounds – Properties and Synthesis, M. Regitz, G. Maas, Academic Press, Orlando, 1986.
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Chapter 1