Mechanistic insight in rhodium-mediated carbene polymerization

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Chapter 5

DFT Calculated Propagation and Termination Steps in [(allyl)Rh$^{III}$(alkyl)]$^{+}$ Mediated Carbene Polymerization
Chapter 5

5.1 Introduction

The synthesis of stereoregular, high molecular weight, densely functionalized sp$^3$-carbon chain polymers that contain a polar substituent at every carbon of the polymer backbone is currently restricted only to the Rh-mediated carbene polymerization techniques developed in our group (C1 polymerization). These polymerization reactions involve a chain growth process in which the polymer chain is built up by a sequence of migratory insertion steps involving carbene units generated at chain-bearing Rh complexes (Scheme 1). Typically, syndiotactic polymers are produced, which for a C1 polymerization reaction means that the substituents all point to the same side when the polymer chain is projected in a regular zig-zag conformation. This contrasts with syndiotactic olefin polymerization, which leads to a polymer having its substituents in an alternating front-back orientation along the zig-zag projected chain. This difference is a direct result of inserting C1 monomers versus C2 monomers.

Scheme 1. Rh-mediated carbene polymerization leading to fully functionalized, high molecular weight and syndiotactic carbon-chain polymers.

While the basic carbene-insertion mechanism shown in Scheme 1 was quickly established for the Rh-mediated carbene polymerization, several details of the polymerization mechanism have remained unclear for a long time. In particular, it has proved to be quite challenging to determine the structure of the active Rh-species as well as establishing certain details about the initiation, termination and chain-transfer mechanisms. However, recent mechanistic investigations have shed much more light on these matters, providing important information. In the previous chapters details were provided explaining three crucial steps of the polymerization reaction, all based on experimental observations: (a) Initiation of the reaction involves participation of water or a nucleophilic alcohol moiety; (b) the termination process involves water or alcohol present in the reaction medium, leading to protonation of the Rh-alkyl chain; (c) cationic [(allyl-cod)Rh(alkyl)${}^+$] species mediate the reaction rather than neutral [(diene)Rh(alkyl)] species. Still, the particular specifics of the propagation and termination steps of carbene polymerization with [(allyl-cod)Rh(alkyl)]${}^+$ species are unclear. To get a better insight into these processes, DFT calculations were performed to answer the following four main questions:
1. Why does the polymerization reaction proceed with a high syndio-specificity?
2. Why are high molecular weight polymers obtained?
3. Why are saturated polymers formed rather than unsaturated ones?
4. What is the reason for the low initiation efficiency of the catalyst (<10%)?

The above questions were previously explored with DFT calculations by examining neutral [(diene)Rh(alkyl)] species, which were at that time believed to be the active polymer forming species. Based on then available experimental data, assuming polymerization activity for neutral (diene)Rh(alkyl) species was initially believed to be most plausible. However, in follow-up studies this assumption was contradicted by several experimental observations (explored in Chapters 3 and 4). Furthermore, DFT studies using neutral (diene)Rh(alkyl) species failed to explain some important experimental observations and did not provide satisfying answers to the four above-mentioned questions. Most importantly, the formation of long polymers could not be explained by these initial DFT calculations, which predicted a low energy pathway for \( \beta \)-H elimination, comparable to the energy barrier for propagation, and thus predicted formation of only short unsaturated polymers in the polymerization reactions using neutral (diene)Rh(alkyl) species. However, such \( \beta \)-H elimination products are not observed experimentally in the polymerization reactions (see Chapter 3). Hence, the initially proposed (diene)Rh(alkyl) species simply cannot be the active species. This is confirmed by our studies in Chapter 4 wherein we describe the identification of the actual active polymerization species on the basis of HR-ESI-MS experiments. With this fundamental new insight in mind, we set out to perform new DFT calculations in order to unravel further mechanistic details and answer the key mechanistic question.

5.2 Results and Discussion
5.2.1 Applied DFT methods
To get a better insight into the propagation of the polymerization we performed DFT calculations to estimate the energies and the differences in energies of the different steps in the propagation. We used the hybrid B3-lyp functional as defined in the Turbomole libraries, and the large Ahlrichs def2-TZVP basis set, which is a commonly used combination with proven accuracy for DFT calculations on Rh complexes. To get the best reflection of the reaction mechanism, we optimized all geometries using Grimme’s dispersion (disp3) corrections to the DFT calculations in order to account for van der Waals interactions between the ligand/substrate fragments. Without these corrections we obtained unrealistically high energies for all calculated molecules as well as the calculated transition states in the energy pathway. The primary effect of the dispersion corrections is its effect on the binding energies of the diazo compound as well as its influence on the position of the oxygen atoms of the ester moieties, making the units more compact. The large
number of oxygen atoms present in the molecule explain the quite large observed 
energy differences with and without dispersion corrections (initial calculations 
showed energy difference between species A, B and TS1 without dispersion 
correction of 17 and 31 kcal mol\(^{-1}\) and with dispersion correction respectively of 1.1 
and 11.7 kcal mol\(^{-1}\)). To confirm that these calculated energies are reliable, the 
calculated energy barrier for TS1 (versus A + MDA; see Figure 2) with dispersion 
corrections were compared to the calculated energy barrier for TS1 with correlated 
Møller–Plesset (MP2) perturbation theory calculations. The relative values of TS1 
are nearly the same (11.0 kcal mol\(^{-1}\) with MP2 (def2-TZVP) versus 10.9 kcal mol\(^{-1}\) 
for the energies with b3-lyp DFT-D3). Therefore we performed all further 
calculations with DFT-D3 using the b3-lyp functional and the def2-TZVP basis set 
rather than time-consuming MP2 calculations.

5.2.2 Identifying the most stable start geometries

The experimental data of Chapter 4 indicated that the active species for the 
polymerization is a cationic [(allyl-cod)Rh\(^{III}\)-polymeryl]\(^+\) species. For the DFT 
calculations this species was simplified to a [(allyl-cod)Rh\(^{III}\)(CH(COOMe))\(_3\)CH\(_3\)]\(^+\) 
species containing a short, three-carbon syndiotactic chain to reduce the calculation 
time. We argued that no less than three consecutive carbene insertion steps were needed 
to model the growing polymer chain in a realistic manner. Two of the ester carbonyl 
moieties tend to coordinate to the Rh\(^{III}\) center. A smaller model of EDA was used: 
methyl diazoacetate (MDA). All calculated pathways start from the [(allyl-
cod)Rh\(^{III}\)(CH(COOMe))\(_3\)CH\(_3\)]\(^+\) species (species, A). Before calculating the energetic 
pathway of the propagation of the polymerization, we optimized different geometrical 
isolomers of species A to find out which geometry is lowest in energy. The (allyl-cod)-
ligand is chiral, as is the syndiotactic growing chain, which leads to diastereomeric 
combinations. Furthermore, several different geometrical isomers are possible as a result 
of different mutual trans-arrangements of the alkyl, carbonyl, alkene and allyl moieties. 
Moreover, we had to explore several conformational positions of the ester-moieties of 
the syndiotactic growing chain, which can rotate in several different orientations. The 
lowest energy configurations of all species investigated are shown in Figure 1. It is 
worth noting that two carbonyl oxygen atoms of the growing chain coordinate to the 
Rh\(^{III}\) center in all of the geometrical isomers shown. Coordination of only one carbonyl 
oxigen atom or ester methoxy oxygen atom is also possible, but these structures are 
substantially higher in energy (~13 kcal mol\(^{-1}\)) and were therefore not considered in 
subsequent calculations.
Figure 1. Various geometrical and conformational isomers of species A. Diastereomers A1 and A2 (alkyl trans to the olefinic double bond of the cod-allyl ligand), and their higher energy rotameric forms A1R and A2R (alkyl trans to the allyl moiety of the allyl-cod ligand). A1' has a different orientation of the $\alpha$-ester unit than A1. Relative free energies ($\Delta G^\circ$ \textit{298K}) in kcal mol$^{-1}$ (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).

All of the calculated structures A have a 5-membered chelate ring in the equatorial plane of the overall distorted octahedral geometries around Rh. This ring consists of the Rh center, the carbon atoms of the last two inserted ester units and the $\beta$-carbonyl fragment. The carbonyl oxygen of the third-to-last inserted ester unit also coordinates to Rh$^{\text{III}}$, further stabilizing the complex (see for example geometry A1 in Figure 1). Rotation of the non-coordinated ester moiety attached to the last inserted carbene moiety quite strongly affects the relative energy of the species (for example, A1' is ~2.3 kcal mol$^{-1}$ higher in energy than A1, see Figure 1). This difference can be explained by the electronic effects of the carbonyl groups and the steric effects of the alkyl in the ester unit. In solution this ester-group is expected to rotate into the lowest energy conformation.

The alkyl carbon of the growing polymer can be coordinated to the Rh(allyl-cod) moiety either \textit{trans} to the olefinic double bond of the allyl-cod ligand (isomers A1 and A2) or \textit{trans} to the allylic unit (isomers A1R and A2R). The isomers A1 and A2 are about 3.7 kcal mol$^{-1}$ more stable than isomers A1R and A2R due to the strong \textit{trans} influence of the negatively charged alkyl-moiety favoring its \textit{trans}-position with respect to the olefinic moiety rather than the allylic moiety of the allyl-cod ligand.
While species $A_1$ and $A_2$ are diastereomers of each other, species $A_{1R}$ is a rotamer of diastereomer $A_1$, in which the chiral allyl-cod ligand has simply rotated in a different orientation with respect to the alkyl and carbonyl donors of the syndiotactic growing chain. Similarly, $A_{2R}$ is a rotamer of diastereomer $A_2$. The diastereomers $A_1$ and $A_2$ (like the diastereomers $A_{1R}$ and $A_{2R}$) differ only in the arrangement of the $-\text{CH}_2-$ and the $-\text{CH}_2-\text{CH}_2-$ fragments of the chiral allyl-cod ligand. This has only a marginal effect on the relative energy of these species (~0.1 kcal mol$^{-1}$). However, in the isomers $A_1$ and $A_{2R}$ the substrate binding site (i.e. the position trans to the coordinated ester carbonyl moiety bound to carbon 3, see Figure 1) is sterically somewhat less hindered than in the isomers $A_2$ and $A_{1R}$ (see section 5.2.3). This affects the MDA substrate binding event to some extent, which is the next step in the polymerization mechanism.

### 5.2.3 MDA Substrate Binding to species $A$

To engage chain growth via a carbene polymerization mechanism, the diazo substrate (MDA) needs to coordinate to the Rh$^{III}$ center in a cis-position to the syndiotactic growing chain. The Rh centers of the various isomers of species $A$, however, are coordinatively and electronically saturated (18 valence electron, 6-coordinated species). Hence, MDA must substitute one of the coordinated carbonyl moieties attached to the syndiotactic growing chain to allow the coordination of a carbene moiety. The weaker bound ester attached to carbon 3 (numbering shown in Figure 1) is more likely to be substituted by MDA than the stronger bound ester moiety attached to carbon 2 (for the large Rh metal center, 5-membered chelate rings are typically more stable than 6-membered chelate rings). Ligand substitution processes at Rh$^{III}$ (like most other d$^6$ octahedral transition metal complexes having a filled t$_{2g}$ d-orbital configuration) commonly proceed via a dissociatively activated interchange mechanism (I$_d$ substitution mechanism). In this process, binding of the incoming ligand and dissociation of the leaving ligand proceed in a concerted manner (despite the fact that in the transition state of the I$_d$ substitution process bond formation with the incoming ligand/substrate somewhat lags behind the bond dissociation of the leaving ligand). A similar process should occur in the formation of the MDA adducts $B$ upon reaction of species $A$ with the diazo substrate. As such, simultaneously with elongation of Rh-O bond upon dissociation of the carbonyl moiety attached to carbon 3 (6-membered chelate ring) the incoming MDA substrate must approach the metal center at the least hindered site, which is the coordination site trans to the leaving carbonyl moiety (see Figure 2). An alternative sequential process in which the carbonyl group of the 6-membered ring chelate attached to carbon 3 first dissociates from $A_1$ or $A_2$, followed by MDA binding to this same position (dissociative D mechanism) is very unlikely according to our DFT calculations. Unsupported dissociation of this carbonyl group at species $A_1$ has a prohibitively high energy (19.0 kcal mol$^{-1}$ relative to $A_1$).
DFT Calculated Mechanistic Steps in [(allyl)Rh(III)(alkyl)]⁺ Mediated Carbene Polymerization

**Figure 2.** Interchange (I<sub>d</sub>) mechanism for MDA binding, for species A<sub>1</sub> and A<sub>2</sub>. Bottom picture shows the energy for dissociative mechanism in kcal/mol.

Hence the I<sub>d</sub> mechanism shown in Figure 2 is much more favorable than a D mechanism for ligand substitution at A<sub>1</sub> or A<sub>2</sub> to form the necessary MDA adducts B in carbene polymerization.

Since the carbene polymerization reaction produces syndiotactic polymer, the subsequent carbene insertion steps leads to alternating R- and S-configured α-carbon atoms (carbon 1 in Figure 2) of the syndiotactic growing chain. Hence, both diastereomers A<sub>1</sub> and A<sub>2</sub> must be involved in the polymerization mechanism of the same polymeric chain. The higher energy rotamers A<sub>1R</sub> and A<sub>2R</sub> may also play a role in the propagation mechanism, as they should be formed as intermediates directly after migratory carbene insertion at A<sub>1</sub> and A<sub>2</sub>, respectively. However, it makes sense to assume that propagation always proceeds from the lowest energy species and that the higher energy rotamers rearrange to their lowest energy analogs. For simplicity, we therefore concentrate on chain propagation from the lowest energy rotameric forms of the diastereomers A<sub>1</sub> and A<sub>2</sub>.
Binding of MDA to A1 to form adduct B1 is endergonic by 10.2 kcal mol⁻¹, and MDA binding to A2 to form adduct B2 is endergonic by 10.7 kcal mol⁻¹. This is a marginal energy difference, and should not significantly affect chain propagation from either A1 or A2 (as is required in a syndiotactic polymerization mechanism).

Below, we focus on the DFT calculated propagation and termination mechanisms (sections 5.2.4-5.2.5). Chain propagation and β-H elimination were explored from both diastereomers A1 and A2 (in their lowest energy rotameric forms). To simplify the analysis and to minimize computational time we restricted our calculations of the MeOH-based termination/chain-transfer mechanism to those from species A1. In addition we explored the effect of a chain error at the α-carbon of species A1 on the propagation mechanism (section 5.2.6).

5.2.4. Propagation via migratory carbene insertion polymerization; chain-end control of syndiotactity

Once MDA adduct B1 is formed, the carbene polymerization propagation steps essentially proceed via an expected migratory carbene insertion polymerization mechanism according to DFT. Propagation from B1 proceeds via rate-limiting N₂ loss via TS1_1 (19.0 kcal mol⁻¹) to produce carbene intermediate C1, which undergoes migratory insertion into the Rh-C bond via a low-barrier transition state TS2_1 to produce species D1 having a one-carbon elongated polymeryl chain (see Figures 3 and 4). We explored both the syndiotactic and isotactic insertion steps from C1 in order to find a mechanistic explanation for the experimentally observed high syndiotacticity of the reaction. Syndiotactic insertion involves attack of the re-face of carbene intermediate C by the S-configured α-carbon atom of the growing chain (or, equivalently, si-face attack by an R-configured α-carbon atom) while a tacticity error can be induced by an isotactic insertion step involves si-face attack of on carbene intermediate C1 by the S-configured α-carbon atom (see also Figure 5). The species C1_{syndio} (Figure 3 and 6) is pre-organized for syndiotactic insertion, while C1_{iso} (Figure 4 and 6) is pre-organized for isotactic insertion. N₂-loss from B1_{syndio} (via TS1_1_{syndio}) and B1_{iso} (via TS1_1_{iso}) produces directly C1_{syndio} and C1_{iso} respectively. Species B1_{syndio} is slightly (+1.1 kcal mol⁻¹) higher in energy than B1_{iso}, but the TS1_1 barrier on the syndiotactic pathway (referenced from species A1) is slightly higher (1.6 kcal mol⁻¹) than on the isotactic pathway. However, both these observations are hardly relevant because species C1_{iso} and C1_{syndio} are easily inter-convertible via rotation about the Rh=C bond (low-barrier rotation barrier of +0.2 kcal mol⁻¹ for syndio → iso and +4.9 kcal mol⁻¹ for iso → syndio, see Figure 7). The stereospecificity of the carbene polymerization reaction is therefore mainly determined by the relative barriers of the subsequent low-barrier carbene insertion steps (Curtin-Hammett principle¹).
Figure 3. Calculated pathway for syndiotactic carbene insertion steps associated with (rate determining) carbene formation steps from A1 and MDA. The (allyl-cod)-ligand is omitted for clarity. Relative free energies ($\Delta G^\circ_{298K}$) in kcal mol$^{-1}$ (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).

Figure 4. Calculated pathway for isotactic carbene insertion associated with (rate determining) carbene formation steps from A1 and MDA. The (allyl-cod)-ligand is omitted for clarity. Relative free energies ($\Delta G^\circ_{298K}$) in kcal mol$^{-1}$ (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).
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Figure 5. Newman projections of Rh-mediated carbene coordination before insertion into the polymer chain showing sterically preferred syndiotactic insertion (chain-end control). P=polymer chain R=Me. Attack on the carbene re-face always produces an R-configured α-carbon atom of the elongated growing chain, while attack on the carbene si-face always produces an S-configured α-carbon atom of the elongated growing chain.

Due to the presence of a chiral (allyl-cod)-ligand on the catalyst, the tacticity of the polymer can in principle be controlled by the catalyst (site-control) and does not necessarily have to be chain-end controlled (see also Figure 5) as assumed in previous studies.¹

Figure 6. Structures of species C1, left the syndiotactic geometry, the ester unit is pointing to the front with the proton pointing backwards. Right picture: isotactic geometry, proton pointing to the front, and the ester unit pointing backwards.

Site control may indeed play a role, as the DFT calculations show that the chiral allyl-cod ligand affects the relative energy of C1iso versus C1syndio due to stabilizing interactions of the ester groups in the lower energy species C1iso. Notably, this leads to a substantially higher TS2_1iso barrier compared to TS2_1syndio. The energy difference between the TS2_1syndio and TS2_1iso barriers (6.5 kcal mol⁻¹) for the cationic [(allyl-cod)Rh⁺(alkyl)]⁺ is actually much higher than previously calculated for carbene insertion at the neutral [(diene)Rh(alkyl)] species (~1 kcal mol⁻¹).² However, since carbene rotation is a low-barrier process, the ratio of syndiotactic versus isotactic chain propagation steps depends mostly on the relative barriers TS2_1syndio versus TS2_1iso relative to C1iso (see Figure 7). This leads to a preference for syndiotactic propagation based on steric repulsion between the ester moieties of the carbene monomer and the last inserted monomer of the chain. Hence, despite the chirality of the catalyst, the stereospecificity of the carbene polymerization reaction is still largely chain-end
controlled. On this basis, the DFT calculations predict a moderate syndiospecificity ($k_{\text{syndio}}/k_{\text{iso}} \approx 21$). A steady state kinetic model including all calculated kinetic parameters ($k_1, k_1', k_2, k_2', k_3$ and $k_3'$, see Figure 8) and a kinetic model neglecting the influence of $k_1$ and $k_1'$ lead to similar results (Table 1). The experimental stereospecificity is higher (stereo-errors are hardly detectable in the obtained polymers), but the predicted trend is correct. Since the transition state energy differences are small, slight errors in the calculations easily lead to large deviations in predictions of the stereospecificity compared to experimental values. In that sense, predicting the stereospecificity of a polymerization reactions with DFT is associated with similar problems as predicting ee%’s in enantioselective catalysis. The correctly predicted syndiospecific propagation is an important feature, answering the first mechanistic question posed in the introduction.

![Figure 7](image1.png)  
Figure 7. Chain-end control leading to syndiospecific propagation. Selectivity determining transition states TS2ₜₚ.syndio and TS2ₜₚ.iso preceded by carbenes C₁ₜₚ.syndio and C₁ₜₚ.iso in a rapid pre-equilibrium. The (allyl-cod)-ligand is omitted for clarity. Relative free energies ($\Delta G^\circ$) in kcal mol⁻¹ (B3-LYP, def2-TZVP, corrected for van der Waals interactions (disp3)).

![Figure 8](image2.png)  
Figure 8. Selectivity of the syndiotactic over isotactic carbene insertion ($k_{\text{syndio}}/k_{\text{iso}}$) depending on rate constants $k_1, k_1', k_2, k_2', k_3,$ and $k_3'$.

| Table 1. Predicted stereoselectivity $k_{\text{syndio}}/k_{\text{iso}}$ and limiting values, based on calculated barriers. |
|---|---|
| Steady state model | C $\rightarrow$ D limiting |
| $\Delta G^f$ | 20.8 | 20.9 |
Species D1, formed after migratory insertion of the carbene moiety in C1\textsubscript{syn} (via TS2\_1\textsubscript{syn}), is in fact a (one-carbon elongated) version of rotamer A2\textsubscript{R} and hence a rotamer of diastereomer A2 rather than A1 (See Figure 7).

This is logical, because after each migratory insertion the configuration of the chiral α-carbon attached to Rh changes from S to R or vice versa. The next propagation step might proceed directly from D1, but the species is perhaps more likely to rearrange first to its more stable rotameric form A2 (or rather its one-carbon elongated version).*  

Figure 9. Species D, with the alkyl of the polymer-chain trans to the allyl moiety of the (allyl-cod)-ligand.

*While A2 formed from D1 should in fact have one extra carbene unit inserted into the polymer chain, this extra moiety is positioned more than 4.90 Å away from the active site and hence will not affect the propagation barriers at all. Hence the simplified [(allyl-cod)Rh\textsubscript{III}(\text{CH(COOMe)}\textsubscript{3}CH\textsubscript{3})]+ version of species A2 functions as a simplified model to study the next carbene insertion step.

Figure 10. Calculated pathway for syndiotactic and isotactic carbene insertion associated with (rate determining) carbene formation steps from A2 and MDA. The (allyl-cod)-ligand is omitted for clarity. Relative free energies (ΔG°298K) in kcal mol\textsuperscript{-1} (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).
To streamline the discussion and simplify the calculations, we therefore calculated the propagation steps for the next carbene insertion step to proceed from diastereomer A2. The subsequent propagation steps from diastereomer A2 (to which MDA can only coordinate on the side of the –CH₂– fragment of the cod-allyl) proceed in a very similar manner as from A1, with comparable energy barriers as well, albeit with absolute barriers that are somewhat higher than for the pathways from A2. The relative barrier of TS2_{2iso} compared to TS2_{2syndio} (Figure 10) is comparable to TS2_{1iso} versus TS2_{1syndio} (Figure 7), again predicting a preference for syndiotactic propagation. This is to be expected, and in fact a prerequisite for an insertion mechanism leading to syndiotactic carbene polymers.

The somewhat higher absolute transition state barriers observed for the propagation pathways from species A2 are due to the increased steric hindrance of the –CH₂– fragment in species A2 being close to the substrate binding site as compared to the more open –C₂H₄– moiety in A1.

Overall, the above DFT calculations show that propagation involving a migratory carbene insertion mechanism is certainly feasible for a cationic [(allyl-cod)Rh^{III}(alkyl)]⁺ species, and the computations are in agreement with the experimentally observed syndiotacticity of these polymerization reactions. However, the question why polymers with a high Mₘ are obtained is not yet clarified. To answer this question we investigated the likely termination steps of the polymerization reaction, as discussed in the next sections.

5.2.5 Termination processes

The last step in the polymerization process is termination, in which the active polymer chains are capped, preventing further chain growth. Typically, if termination is close (or even lower) in energy than propagation, short (low molecular weight) polymers (or dimers) are obtained. In chapters 2 and 3, detailed analysis of the experimental polymers obtained revealed that the polymers most likely terminate by protonation of the Rh–C bond of the active polymeryl chain by alcohols, thus leading to saturated polymer chain-ends (polymeryl–CH(COOR)–CH₂(COOR)). Chain termination by β-H elimination leading to unsaturated chain-ends (polymeryl–C(COOR)=CH(COOR)) does not seem to play an important role in the mechanism. Previous DFT calculations on neutral [(diene)Rh{alkyl}] species demonstrated a low energy pathway for β-H elimination, and could not explain the experimentally observed long polymers. Neutral [(diene)Rh{alkyl}] species are thus predicted to produce dimers and short, unsaturated oligomers as product (see Figure 11). This may explain the formation of the minor side-

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To be precise, ligand rotation in D1 to produce its most stable rotameric form produces the enantiomer of A2 as drawn in Figure 1. Obviously, enantiomers of A2 (and A1) have the same reactivity towards the non-chiral MDA substrate. Hence there is no point at all in investigating the influence of using different enantiomers of A1 or A2 on the polymerization mechanism. For consistency, however, we nonetheless used the correct enantiomer of A2 as formed upon ligand rotation in D1 to calculate the next carbene insertion step.
products obtained in these reactions, but not the main polymeric products. Rapid $\beta$-H elimination and reinsertion might occur for these species, but this remained an unsatisfying explanation of the experimental results.

Figure 11. Unsaturated polymer obtained by $\beta$-H elimination

We decided to perform new calculations on the termination steps using cationic [(allyl-cod)Rh(alkyl)]$^+$ species A1 as a model for the active species (based on the results described in Chapter 4). We will first describe the calculated pathway for $\beta$-H elimination to compare the energy barrier with those of the propagation steps (section 5.2.5.1). In section 5.2.5.2 we will describe the calculated pathway for alcohol mediated protonation of the active polymer chain, again to compare the barriers for termination and propagation.

5.2.5.1 Termination by $\beta$-H elimination

The calculated pathway for $\beta$-H elimination at cationic [(allyl-cod)Rh(alkyl)]$^+$ species A1 and A2 is shown in Figure 12.

Figure 12. Calculated pathway for $\beta$-H elimination at cationic [(allyl-cod)Rh(alkyl)]$^+$ species A1 (top) and A2 (bottom). The (allyl-cod)-ligand is omitted for clarity. Relative free energies ($\Delta G^{298K}$) in kcal mol$^{-1}$, relative ($\Delta H^{298K}$) entropy in brackets (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).
The transition state barriers \( \text{TS4}_{\beta-H} \) \( +22.1 \text{ kcal mol}^{-1} \) and \( \text{TS4}_{\beta-H} \) \( +25.1 \text{ kcal mol}^{-1} \) are much higher than the highest barriers on the propagation pathways from \( \text{A1} \) and \( \text{A2} \), respectively (see Figures 3 and 4). These energy barriers are likely too high to represent a reasonable termination pathway. Furthermore, formation of the hydride species \( \text{E}_{\beta-H} \) is highly endergonic in both cases \( +21.6 \text{ kcal mol}^{-1} \) from \( \text{A1} \), \( +24.8 \text{ kcal mol}^{-1} \) from \( \text{A2} \), and these species have their unsaturated ‘terminated’ polymer chain coordinated in a chelating fashion with both an ester carbonyl and the olefinic double bond in cis-position to the hydride. This makes olefin re-insertion into the Rh–H bond (to regenerate \( \text{A1} \) or \( \text{A2} \)) a facile process, which is more likely to occur than dissociation of an unsaturated polymeryl–C(COOR)=CH(COOR) chain. This high energy pathway for chain-transfer or chain-termination via \( \beta-H \) elimination helps to explain why unsaturated polymer chains are not obtained experimentally.

5.2.5.2 Alcohol mediated chain transfer

Another way to terminate polymer growth is through protonation of the polymer chain by an alcohol. In chapters 3 and 4 experimental proof was given for this mechanism. DFT calculations support these experimental data (see Figure 13). To minimize computation time we evaluated this pathway only from species \( \text{A1} \).

In agreement with the experimental observations showing that the nucleophilicity of the alcohol plays a role (see Chapter 2), the calculated alcohol-mediated chain-transfer process proceeds via initial coordination of the alcohol moiety to the Rh center. The catalyst has a similar affinity for \( \text{MeOH} \) as for \( \text{MDA} \), although coordination of methanol to the Rh\(^{III} \) center of the cationic \([\text{allyl-cod}][\text{Rh}^{III}(\text{alkyl})]\)^{+} species \( \text{A1} \) is slightly less endergonic \( 5.1 \text{ kcal mol}^{-1} \).

![Figure 13. Calculated pathway for inner-sphere proton transfer from a coordinated alcohol moiety to the polymer chain leading to chain termination via protonation of the Rh–C bond. The (allyl-cod)-ligand is omitted for clarity. Relative enthalpy \( \Delta G^\circ \) in kcal mol\(^{-1} \), relative \( \Delta H^\circ \) entropy in brackets (b3-lp, def2-TZVP, corrected for van der Waals interactions (disp3)).](image-url)
The transition state for direct proton transfer from the coordinated alcohol moiety in MeOH adduct F to the Rh–C bond is very high ($\Delta G^\ddagger = 54 \text{ kcal mol}^{-1}$; $\Delta H^\ddagger = 31 \text{ kcal mol}^{-1}$), and clearly out of range for reactions at room temperature. Therefore, the molecule has to rearrange to species G having an O-coordinated enolate moiety to allow efficient proton transfer from MeOH to terminate the polymer chain. Formation of isomer G from F is endergonic by 11 kcal mol$^{-1}$. We have thus far not located the transition state $\text{TS}_5$ for rearrangement of F to G. Proton transfer from MeOH to the enolate carbon in G proceeds via transition state $\text{TS}_6$, (+ 5 kcal mol$^{-1}$ higher than G), representing an overall free energy barrier of ~25 kcal mol$^{-1}$. This barrier is higher than the barrier for $\beta$-H elimination from A1 (22.1 kcal mol$^{-1}$). However, the entropy contributions to the DFT calculated free energy barrier $\text{TS}_6$ in the gas phase are overestimated. In the actual solution mixtures, the reactions are performed with a large excess of alcohol. Hence, the translational entropy contributions to the free-energy barrier of the experimental alcohol-mediated chain-transfer pathway are much lower. The actual free energy barrier for MeOH mediated chain-transfer in solution under non-standard conditions ($\Delta G^\ddagger = \Delta G^\ddagger + \text{RTlnQ}$ is the correct value to be compared with $\beta$-H elimination) should therefore be somewhere in between +25 ($\Delta G^\ddagger$) and +13 kcal mol$^{-1}$ ($\Delta H^\ddagger$), hence lower than $\beta$-H elimination ($\Delta H^\ddagger = 22.7 \text{ kcal mol}^{-1}$). Furthermore, $\beta$-H elimination is, overall, a strongly endothermic ($\Delta H^\ddagger = 21.6 \text{ kcal mol}^{-1}$ from A1) and endergonic ($\Delta G^\ddagger = +21.6 \text{ kcal mol}^{-1}$ from A1) process with a low-barrier transition state for the reverse reaction (see Figure 12), while alcohol mediated chain-transfer is exothermic ($\Delta H^\ddagger = -2.7 \text{ kcal mol}^{-1}$). Taken together, the computed alcohol-mediated chain-transfer pathway is both kinetically and thermodynamically preferred over $\beta$-H elimination, in good agreement with the experimental observations described in Chapter 2.

The free-energy barrier for alcohol-mediated chain-transfer is higher than the barrier for chain-propagation. These barriers can be directly compared because the alcohol and the diazo substrate are both used in a large excess compared to the (active) catalyst (similar deviations in the translational entropy contributions). Hence, in agreement with the experimental observations (see Chapter 2), chain-propagation is much faster than alcohol-mediated chain-transfer. Experimentally, alcohol-mediated chain-transfer starts to compete significantly with chain-propagation only when using relatively high alcohol concentrations. This is in agreement with a large entropy contribution to the computed standard free energy barrier ($\Delta G^\ddagger$) for alcohol-mediated chain-transfer in combination with a lower translational entropy contribution when increasing the alcohol concentration ($\Delta G^\ddagger = \Delta G^\ddagger + \text{RTlnQ}$).

The pathway shown in Figure 13 leaves a Rh-OMe fragment in species H, from which a new polymer-chain can start growing in a later stage. The terminated polymer chain having a saturated chain-end (RO–polymeryl–CH(COOR)–CH$_2$(COOR)) is initially still coordinated to Rh, but only with one of its carbonyl moieties. This
DFT Calculated Mechanistic Steps in [(allyl)Rh III(alkyl)]+ Mediated Carbene Polymerization

fragment should thus be easily displaceable from H once a new chain starts growing. The calculated pathway therefore readily explains the experimentally observed chain-transfer role of alcohols.

5.2.6 The effect of stereo-errors on the propagation mechanism and the stereo-error repair mechanism

We further investigated chain propagation from an analog of A1 containing a stereo-error at the α-carbon atom of the [(CH(COOMe))₃]⁺ moiety with DFT. This [(allyl-cod)Rh III(CH(COOMe))₃Me]⁺ species A3 has an RSR configured chain instead of the SSR configuration in A1. MDA binding at syndiotactic A1 leads to formation of adduct B1, which upon N₂-loss produces the discrete carbene intermediate C1 (Figure 14, left). Exploring the same reaction at the non-syndiotactic analog A3 containing an RSR configuration of the –{CH(COOMe)}₃Y moiety gives markedly different results. First of all, MDA has to bind to a sterically more encumbered position from which the substrate is sterically isolated from the ester moiety attached to the α-carbon of the RSR configured –{CH(COOMe)}₃Y moiety (B3). More importantly, the carbene species C3 generated from this intermediate tends to be unstable, and easily converges (in a virtual barrier-less process) to an oxygen-ylide-structure C3’ in which the ester attached to the α-carbon of the RSR configured –{CH(COOMe)}₃Y moiety has attacked the carbene unit (Figure 14).

Figure 14. Effect of tacticity-errors on the polymerization reaction. Left: The discrete carbene intermediate C1 is stable because the oxygen-ylide-formation is not possible in the syndiotactic SSR configuration of the –{CH(COOMe)}₃Me moiety. Right: In the non-syndiotactic analog carbene formation leads to spontaneous attack of the ester carbonyl attached to the α-carbon of the RSR configured –{CH(COOMe)}₃Y moiety producing the low-energy dead-end species C3’.

This bond formation (C-O bond distance 1.497 Å, see Figure 14) substantially stabilizes the species (C3’ is 22.0 kcal mol⁻¹ lower in energy than C1). This means that stereo-errors induced at the α-carbon atom should substantially slow down the subsequent propagation via carbene insertion compared to chain-propagation from [(allyl-cod)Rh III(CH(COOMe))₃P]⁺ species without such stereo-errors. While slowing down the reaction, ylide formation is reversible and allows for a repair mechanism involving syndiotactic carbene insertion in the Rh–C bond. The ksyndio/kiso ratio calculated in section 5.2.4 is high enough to correct for such ‘errors’ to result in mainly syndiotactic chain growth.

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Figure 15. Calculated pathway for syndiotactic carbene insertion associated with (rate determining) carbene formation steps from A3 and MDA. The (allyl-cod)-ligand is omitted for clarity. Relative free energies ($\Delta G_{298K}$) in kcal mol$^{-1}$ (b3-lyp, def2-TZVP, corrected for van der Waals interactions (disp3)).

5.2.7 Possible explanations for the experimentally observed low initiation efficiencies

Chain-errors generated during carbene polymerization should have a similar effect on all active syndiotactic growing polymer chains (although it may potentially affect the molecular weight distribution over time, as observed in the experimental polymerization reactions). However, chain-errors such as those in species A3 likely have a strong influence on the initiation efficiency of the reaction, because they should clearly slow-down chain propagation from non-syndiotactic chains. In the experimental polymerization reactions we consistently observed that only a minor amount of the Rh species become active as a polymerization catalyst (initiation efficiencies typically < 10% neglecting chain transfer effects). Experimental data could thus far not provide a satisfying explanation for this behavior. While highly syndiotactic polymers are obtained in the experimental reactions, ill-defined atactic oligomers are also formed in the beginning of the reaction. Hence, the initial cationic [(allyl-cod)Rh$^{III}$($\text{CH(COOMe)}$)$_3$Y]$^+$ species (Y = H, OH, OR) formed during the catalyst activation process, which are required to initiate chain-growth, do not necessarily all contain a syndiotactic –$\text{CH(COOMe)}$$_3$Y moiety. In fact, it is very unlikely that the first three carbene insertion reactions during the catalyst activation process generate only syndiotactic –$\text{CH(COOMe)}$$_3$Y moieties, because at this stage of the reaction the initiating chain is yet too short to benefit from the same protecting chelating properties of the carbonyl moieties as in A1 or A2. The carbonyl moieties of the initiating growing chain fragment either do not or only partially coordinate to Rh$^{III}$.
and any chelating properties of the chain at this stage are different and weaker than those in species A1 or A2. This short initiating growing chain fragment has much more flexibility to rotate around the Rh–C bond, in addition to the openness of the metal site (at this stage) compared to A1 or A2, which leaves room for MDA to bind at more positions. The formation of a syndiotactic –{CH(COOMe)}₃Y moiety in the first three insertion steps must therefore be (at least in part) based on chance, leading to a more or less statistical distribution of –{CH(COOMe)}₃Y chain configurations (RRR, RRS, RSS, SSR, SRS, of which only SSR and RRS are syndiotactic). In itself, the \( k_{\text{synd}}/k_{\text{iso}} \) ratio calculated in section 5.2.4 should be high enough to correct for these initial ‘errors’ to produce syndiotactic chain growth later-on in the reaction. However, chain-growth from already syndiotactic chains should start and proceed much faster than from non-syndiotactic chains, so that much of the MDA substrate may already be consumed before chain-growth from the initial non-syndiotactic species even starts. If we assume that the initial catalyst activation steps are purely statistical (RRR, RRS, RSS, SSR, SRS), only 33% of syndiotactic SSR and RRS species are generated initially. This may well contribute to the experimentally observed low initiation efficiencies of these catalyst in carbene polymerization reactions. Ineffective formation of the cationic \([(\text{allyl-cod})\text{Rh}^{\text{III}}(\text{CH(COOMe)}_3)\text{Y}]^+\) species from the catalyst precursors used likely reduces the overall initiation efficiency further.

5.3 Conclusions

The DFT computed pathways for chain-propagation and chain-transfer reveal important details about carbene polymerization using cationic \([(\text{allyl-cod})\text{Rh}^{\text{III}}(\text{alkyl})]^+\) species and with this new insight we were able to answer the four questions mentioned in the introduction.

Chain-propagation at these species is clearly competitive with \(\beta\)-H elimination, explaining the formation of high molecular weight polymers. These results are in good agreement with experimental observations, and clearly in contrast with previously reported DFT calculations using neutral \([(\text{diene})\text{Rh}(\text{alkyl})]\) species which failed to explain the formation of long polymers. In analogy with previous calculations using neutral \([(\text{diene})\text{Rh}(\text{alkyl})]\) species, chain-propagation at cationic \([(\text{allyl-cod})\text{Rh}^{\text{III}}(\text{alkyl})]^+\) species is still chain-end controlled, leading to a clear preference for syndiotactic polymerization.

Chain-transfer involving alcohol-mediated protonolysis is computed to be a more favorable pathway than \(\beta\)-H elimination, which answers question 3 from the introduction. This explains the formation of saturated, alcohol-terminated RO–polymeryl–CH(COOR)–CH₂(COOR) chains rather than unsaturated (H-polymeryl–CH(COOR)=CH(COOR) chains. Furthermore, in good agreement with the experimental observations showing that the nucleophilicity of the alcohol plays a role (see Chapter 2), the calculated alcohol-mediated chain-transfer process proceeds via initial coordination.
of the alcohol moiety to the Rh center. Protonolysis of the growing chain requires rearrangement of the Rh-polymethyl chain to an O-bound Rh-enolate, followed by rapid proton-transfer from the coordinated alcohol moiety to the enolate carbon-moiety. This process has a higher barrier than chain-propagation, but a lower barrier than β-H elimination.

Chain-propagation from species with a stereo-error at the alpha-carbon atom of the growing chain is substantially slowed-down compared to propagation from syndiotactic species without stereo-errors. This effect arises from attack of the carbonyl group of the alpha-ester moiety on the carbene-unit, stabilizing the propagating species in an unfavorable off-cycle equilibrium. This process is reversible, allowing a stereo-repair mechanism. Similar effects may play a role in explaining the low initiation efficiency of the catalyst. Statistically, only 33% of the initially formed triad-chains are formed in a syndiotactic manner during the activation process of the catalyst. Much faster propagation from these syndiotactic chains compared to non-syndiotactic chains may well contribute to the experimentally observed low initiation efficiencies of these catalysts in carbene polymerization reactions.

With these new computational insights, in combination with the experimental results described in Chapters 2-4, the mechanism of the polymerization reaction is largely clarified.

5.4 Computational Details

DFT geometry optimizations. All geometry optimizations were carried out with the Turbomole program\(^{15,16,17,18}\) coupled to the PQS Baker optimizer\(^{19,20}\) via the BOpt package.\(^{21}\) Geometries were fully optimized as minima at the b3-lyp level\(^{22,23,24,25}\) using the Turbomole polarized triple-\(\zeta\) def2-TZVP basis\(^{26, 27, 28,29}\) (small-core pseudo-potential at Rh\(^{30}\)). We further employed Grimme’s dispersion corrections (disp3 version).\(^{31}\) All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The relative (free) energies obtained from these calculations are reported in the main text of this Chapter. The nature of the transition states was confirmed by IRC calculations. Optimized geometries are visualized with the PLATON\(^{32}\) program (rendered with POVRAY). By calculation of the partition function of the molecules in the gas phase, the entropy of dissociation or coordination for reactions in solution is overestimated. For reactions in ‘solution’ we therefore corrected the Gibbs free energies for all steps involving a change in the number of species (except the N\(_2\) loss step following TS1) by 2.5 kcal mol\(^{-1}\) (correction for the condensed-phase reference volume\(^{33}\)).

5.5 Acknowledgements

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Appendix: Calculation of syndio/iso insertion preference

The kinetic model used for this system, consisting of 5 different species, is schematically represented as:

Where 1 corresponds to complex A, 2 and 2’ to Cs and Ciso and 3 and 3’ to Ds and Diso. This models allows us to calculate the ratio between the syndio- and isotactic insertions from the rate equations describing the formation of species 3 and 3’:

\[
\frac{d[3]}{dt} = k_{23}[2] \quad \frac{d[3']}{{dt}} = k_{23'}[2']
\]

After integration, the syndio/iso ratio is expressed by:

\[
\frac{[3]}{[3']} = \frac{k_{23}[2]}{k_{23'}[2']}
\]

which can be calculated from the kinetic equations below:

\[
\frac{d[2]}{dt} = k_{12}[1] + k_{22}[2''] - k_{22}[2] - k_{23}[2]
\]

\[
\frac{d[2']}{dt} = k_{12}[1] + k_{22}[2] - k_{22}[2'] - k_{23}[2']
\]

Steady-state assumption on [2] and [2’] (d[2]/dt = 0 and d[2’]/dt = 0) gives:

\[
[1] = \frac{k_{22}[2] + k_{23}[2'] - k_{23}[2]}{k_{12}} \quad \text{and} \quad [1] = \frac{k_{22}[2'] + k_{23}[2'] - k_{23}[2]}{k_{12}}
\]

which gives combined and rearranged the following equation:

\[
[2] = \frac{(k_{12}k_{22} + k_{12}k_{23} + k_{12}k_{12})}{(k_{12}k_{22} + k_{12}k_{23} + k_{12}k_{22})} = \frac{k_{12}(k_{22} + k_{23}) + k_{12}k_{22}}{k_{12}(k_{22} + k_{23}) + k_{12}k_{22}}
\]

As a result we approach the syndio/iso ratio by the following kinetic expression:

\[
\frac{[3]}{[3']} = \frac{k_{23}}{k_{23'}} \frac{k_{12}(k_{22} + k_{23}) + k_{12}k_{22}}{k_{12}(k_{22} + k_{23}) + k_{12}k_{22}}
\]

The rate constants were calculated from the DFT free energies of activation. The thus obtained syndio/iso selectivities are presented in Table 1 (steady-state model).
5.6 References and notes

4  Syndiotactic polymers arise if the last inserted monomers have alternating R and S configurations (IUPAC definition).
19  PQS version 2.4, 2001, Parallel Quantum Solutions, Fayetteville, Arkansas, USA (the Baker optimizer is available separately from PQS upon request).
25  Calculations were performed using the Turbomole functional ‘b3-lyp’, which is not completely identical to the Gaussian “B3LYP” functional.