Stereospecific Carbene Polymerisation with Oxygenated Rh(diene) Species**

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Polymers bearing polar functionalities are important materials, since they exhibit beneficial properties with respect to adhesion, paint/printability and surface properties.[1][2] Commercial synthesis of these materials is mainly based on radical processes, which (so far) only allow poor control over the stereochemistry of the resulting polymers.[1][2] Stereo-controlled polymerisation generally requires (transition) metal catalysis. However, to the best of our knowledge there are no catalysts known that can polymerise 1,2-di-functionalized olefins such as fumarates or maleates, certainly not in a stereoregulated manner (even controlled radical polymerisation of di-functionalized polar vinyl monomers is not trivial and an unsolved problem to date). Therefore, the synthesis of high molecular weight and stereoregular densely functionalized sp²-carbon chain (co)polymers containing a polar substituent at every carbon atom of the polymer backbone is currently restricted to the Rh-mediated carbene polymerisation techniques recently developed in our group (C1 polymerisation; see Scheme 1).[3][4] These (co)polymers reveal interesting and unexpected material properties, such as thermotropic and lyotropic liquid crystallinity, gel-formation, a broad thermal stability range, and a high storage modulus up to high temperatures.[1][5][6] Such polymers are not accessible from (1,2-di-functionalised) olefins.[4][7] and any future application of these new materials[5][7] therefore relies on increasing the efficiency of the carbene polymerisation reaction.[6][4]

The reaction mechanism of this intriguing carbene polymerisation reaction has been the subject of intensive investigations in our group, but the exact nature of the polymer forming Rh-species remained thus far elusive.

Recently we discovered that partial oxidation of pre-catalyst 2 (Scheme 1) leads to markedly improved polymer yields and a higher amount of active Rh species,[6][4] but the underlying reason was poorly understood.

As commonly encountered in transition metal catalysis, the catalyst precursor is (partly) transformed in situ into the active species and a detailed understanding of the reaction, which is needed for further exploration of the potential of this promising unique polymerisation reaction, requires identification of the active species. Faced with seemingly contrasting observations in our initial studies,[7][4] we now report the nature of the active polymer-forming growing-chain rhodium species during carbene polymerisation that are formed after oxidation of the catalyst precursor with O₂.

Complex 2 reacts sluggishly with air or O₂, and hence it takes a long time to convert the solid starting material to the fully oxidized solid (3)[6][8][9]. NMR spectra of this material are complicated, indicative for the presence of multiple species with overlapping signals, and are therefore not very informative (see Supporting Information, Figure S12). They are however suggestive of the presence of (different geometrical isomers of) mono-oxygenated Rh(Me₂cod) species (3).[10] See Scheme 2.

This was confirmed by ESI-MS spectrometry; the clear and clean mass spectra revealed only mono-oxygenated species [3H⁺]: The high resolution mass spectrometric measurements and isotopic distribution of [3H⁺] fits exactly to

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the mass of the starting material plus one oxygen atom, and a proton functions as the charge carrier: \(2 + O + H^+ = [3H]^+\) (see Supporting Information, Figure S1). Based on our previous work in the field of Rh\(^{\text{III}}\)(olefin) oxygenation reactions,\(^{[10]}\) the most likely mono-oxgenated species in this mixture (NMR) are (different isomers of) the 2-rhodaoxetane 3a, its ring-closed analogue 3b and the allyl-\(\beta\)-alkyl-hydroxide species 3c (Scheme 2). Interestingly, the fully oxidized samples (3) in which no starting material (2) is present anymore according to NMR\(^{[8]}\) gives excellent yields in the carbene polymerisation reaction. In fact, even higher polymer yields are obtained with fully oxidized samples (3) than previously with partly oxidized 2. Furthermore, the percentage of active species is higher for the oxygenated species 3 (Table 1).\(^{[6]}\)

Next we monitored the polymerisation reaction with ESI-MS using complex (2 and) 3 as the catalyst. These experiments revealed the exact nature of the active propagating Rh-species and allowed us to draw several additional valuable conclusions about the carbene polymerisation process. The assignment of all detected species is described below and is based on high resolution mass determinations (deviations between measured and simulated m/z isotopic pattern masses are consistently smaller than 0.002 Da).

Addition of ethyl diazoacetate (EDA) to a solution of pre-catalyst 2 in CH\(_2\)Cl\(_2\) simply reveals [2H]+, and these peaks do not visibly decrease in time over a period of more than an hour. Similar experiments with the oxidized pre-catalyst 3, however, led to an immediate decrease of the signals of [3H]+, and appearance of a clear repeating pattern of a \([(\text{Me}_2\text{C}_5\text{H}_5)\text{Rh}(\text{HCHO})\text{Et})_{\text{y}}\text{OH}^+\] propagating species that builds in CHCOEt carbene units (\(\Delta M = 86\) Da), (see series I, Scheme 3). The organometallic ‘\([(\text{Me}_2\text{C}_5\text{H}_5)\text{Rh}^\text{III}]\text{H}^+\) fragment corresponds with the cationic [[allyl]Rh\(^{\text{III}}\)-alkyl] species depicted in Scheme 3, which is supported by additional experiments (see below).

Most interestingly, the MS spectra further show the appearance of \([\text{H}] \cdot (\text{CHCOEt})_n \text{OH}^+ + \text{Na}^+\] chains (series II, Scheme 3). Hence chain-growth starts on a hydroxide fragment. Furthermore, addition of MeOH results in the appearance of a clear pattern corresponding to \([(\text{Me}_2\text{C}_5\text{H}_5)\text{Rh}(\text{HCHO})\text{Et})_{\text{y}}\text{OMe}^+\] growing chains (series III, Scheme 3) as well as terminated \([\text{H}] \cdot (\text{CHCOEt})_n\text{OMe} + \text{Na}^+\) chains containing a methoxy chain-end (series IV, Scheme 3). These observations clearly show that the polymer initiates at a hydroxide fragment generated from the oxidized pre-catalyst 3. The chains terminate by protonation, either involving H\(_2\)O or an alcohol.\(^{[30]}\) In the presence of MeOH, the alcohol clearly functions as a chain-transfer agent\(^{[30]}\) thus generating H-\((\text{CHCOOR})_{\text{y}}\text{OMe}\) terminated polymer chains and allylic \([\text{Me}_2\text{C}_5\text{H}_5]_{\text{Rh}^\text{III}}\text{OMe}^+\) species from which a new chain starts growing (Scheme 3). Representative MS spectra showing series I-IV are shown in Figures S2-S5 (Supporting Information).

Similar results were obtained when using benzyl diazoacetate (BnEDA) instead of EDA, thus confirming the above assignments (Scheme 3, R= Bn; see Figures S6, S7, Supporting Information). The data therefore show that the oxidized species 3 are capable of generating the active allyl-Rh-alkyl species \(\text{[(Me}_2\text{C}_5\text{H}_5)\text{Rh}^\text{III}](\text{P}^+)\) \((P = \text{polymer})\). Apparently, the hydroxide fragment of species 3c can be transferred to the metal in order to start the chain-propagation process through carbene insertion into the thus formed Rh\(^{\text{III}}\)–OH bond.

We were intrigued by the possibility that the active allyl species \(\text{[(Me}_2\text{C}_5\text{H}_5)\text{Rh}^\text{III}](\text{P}^+)\) (and hence related allylic \(\text{[(C}_3\text{H}_7\text{H})\text{Rh}^\text{III}](\text{P}^+)\) species derived from 1.5-cyclooctadiene) can apparently be generated from the 2-rhodaoxetane species 3a or the allyl-\(\beta\)-hydroxyl-alkyl species 3c, and hence we looked for similar activity of related compounds. Previously reported \(\text{[(C}_3\text{H}_7\text{H})\text{O}]\text{Rh}(\text{N}_2\text{ligand})^+\) species\(^{[12]}\) turned out to be non-reactive towards EDA, which can be expected for these saturated 18 VE Rh\(^{\text{III}}\) species. Hence we decided to look at ‘unsaturated’ analogues reported previously. The triazenide complexes 5 and 6 (see Scheme 4)\(^{[11]}\) seemed good candidates to test our hypothesis that active allylic \(\text{[(C}_3\text{H}_7\text{H})\text{Rh}^\text{III}](\text{P}^+)\) species can be generated from precursors containing a 2-rhodaoxetane fragment (\(\text{C}_8\text{H}_{12}\text{O})\text{Rh}^\text{III}\).
Complex 5 is formed in good yield and in good purity by oxidation of the triazenide precursor \([\text{[(C}_3\text{H}_5)_3\text{Rh(N}_2\text{P}_3\text{H}_2))]\) (4) with O\(_2\).\(^{[11]}\) Complexes 4-6 were evaluated as catalyst precursors in the carbene polymerisation of EDA (Table 1). As expected, \([\text{[(triazenide)Rh]}(\text{cod})])\) complex 4 is active, but it is less active than the non-oxidized \([\text{[(R'}\text{3}C\text{H}_5)_3\text{Rh}}(\text{prolinate})]\) complexes \((R' = \text{H}; 1; \text{R' = Me}; 2)\). However, oxidation of 4 to 5 markedly improves the polymerisation over oligomerisation/dimerisation selectivity, thus leading to a substantially improved polymer yield (66%). Conversion of 5 to 6 further increases the selectivity towards polymer formation (80%), while at the same time the initiation efficiency (percentage of active Rh species) increases (see Table 1).

The above data are in excellent agreement with the markedly different polymerisation kinetics of complex 4, 5 and 6 under identical reaction conditions (Figure S16-S17, Supporting Information). The reaction with complex 4 is very slow (full EDA conversion requires >10 hrs). Complex 5 converts EDA substantially faster than 4 (full conversion in ~5 hrs), but much slower than 6 (full conversion in only a few minutes). These kinetic data are best explained by a progressively easy catalyst activation process on going from 4 via 5 to 6 under the applied reaction conditions, thus leading to a higher amount of active polymer forming Rh-species (in good agreement with the data shown in Table 1).

Hence, it is clear that the allyl-β-alkyl-hydroxy complex 6 more easily converts into the active polymer forming species than 2-rhodaoxetane 5. Yet, still only a minor amount of species 6 becomes active in the polymerisation event (~7%), thus showing that complex 6 itself is still a pre-catalyst that requires further activation under the applied reaction conditions (i.e., loss of the triazenide ligand and ligand rearrangement). The low efficiency of this process is likely due to competing and unwanted side-reactions with EDA during the incubation time of the reaction, possibly related to sluggish displacement of the bidentate triazenide N-ligand from rhodium(III). However, complex 6 does give easier access to the polymer forming growing-chain species than non-oxidized \((\text{cod})\text{Rh}^\circ\) or \((\text{Me}_2\text{cod})\text{Rh}^\circ\) complexes such as 1, 2 and 4. In fact, complex 6 shows the highest initiation activity of all Rh-compounds studied so far. The (oxygenated) Rh-species 3, 5 and 6 produce polymers of the same high syndiotacticity as reported before.\(^{[9]}\)

The carbene polymerisation reaction using species 5 and 6 was further probed by high resolution ESI-MS spectrometry to obtain detailed understanding of the reaction mechanism. The results are very similar to those obtained with 3 as the pre-catalyst in EDA and BnDA polymerisation reactions. In absence of methanol, clear repeating patterns of \([\text{[(C}_3\text{H}_5)_3\text{Rh}}(\text{HOOCOR})\text{–OH}^-]\) growing chains are detected (series I, \(R = \text{Et}\), Scheme 3), as well as terminated \([\text{H}}(\text{HOOCOR})\text{–OH}^- + \text{Na}^+\) chains (series II, \(R = \text{Et}\)). Again, in the presence of methanol clear patterns of \([\text{[(C}_3\text{H}_5)_3\text{Rh}}(\text{HOOCOR})\text{–OMe}^-]\) growing chains (series III, \(R = \text{Et}\)) and patterns of terminated \([\text{H}}(\text{HOOCOR})\text{–OMe}^- + \text{Na}^+\) chains containing a methoxy end-group (series IV, \(R = \text{Et}\)) appeared (See Figures S8-S9, Supporting Information). Similar results were obtained using BnDA instead of EDA (Scheme 3, \(R' = \text{H}, \text{R' = Bn}\); see Figure S10). Important to note here is that these series I-IV \((R' = \text{H})\) were detected using pure samples of 5 and 6 as pre-catalysts, and hence the Rh\text{III-OH} fragments (at which chain-growth starts) must be formed from these complexes. Therefore 5 and 6 must liberate a hydroxide fragment from their oxidized cod moiety to form the observed active cationic allylic \([\text{[(C}_3\text{H}_5)_3\text{Rh}}\text{III-OH}^-]\) species. A straightforward explanation is that 5 rearranges to 6 under the catalytic conditions, after which the complex loses the triazenide ligand and undergoes a β-hydroxy elimination from the allyl-β-alkyl-hydroxy ligand to generate the active allylic \([\text{[(C}_3\text{H}_5)_3\text{Rh}}\text{III-OH}^-]\) species. DFT calculations (b3lyp, def2-TZVP) confirm that this is an energetically favourable and kinetically accessible pathway (see Scheme 5, top).

Proton transfer from an allylic position to the 2-rhodaoxetane oxygen atom is exergonic by ~18 kcal mol\(^{-1}\) and has a barrier of ~27 kcal mol\(^{-1}\) (simplified cationic model in the gas phase; Scheme 5, top). This transformation is experimentally observed in the rearrangement from 5 to 6 and in related reactions reported.\(^{[10,11]}\) More importantly, β-hydroxy elimination from the cationic allyl-β-alkyl-hydroxy rhodium(III) species is exergonic by ~5 kcal mol\(^{-1}\) and has an accessible transition state barrier of ~28 kcal mol\(^{-1}\).\(^{[12]}\) Clearly, oxidation of \([\text{[(R'}\text{3}C\text{H}_5)_3\text{Rh}}\text{III}]^\circ\)-type complexes to \([\text{[(R'}\text{3}C\text{H}_5)_2\text{O}])\text{Rh}^\circ\)-type species, followed by rearrangement to \([\text{[(R'}\text{3}C\text{H}_5)_2\text{Rh}}\text{III-OH}^-]\) allyl-compounds \((R' = \text{H}, \text{Me})\) is an effective pathway to engage carbene polymerisation activity.
Carbene polymerisation is also observed for non-oxidized rhodium(I)-diene complexes under strict anaerobic conditions. Hence the active ([R₂C₃H₅]RhH-OH)⁺ allyl-species can also be generated via a different pathway, directly from the non-oxidized rhodium(I)-diene precursors (albeit less effectively). Oxidative addition of an allylic C-H bond to form an allyl-hydride intermediate ([R₂C₃H₅]Rh-H) seems to be a likely possibility. Such reactions are experimentally investigated for 1,5-cyclooctadiene-iridium(I)-cod complexes,¹ ¹³ but are unreported for rhodium(I)-cod.¹ ¹⁴ This suggests that this pathway is not very effective, which correlates with the very low initiation efficiencies of non-oxidized Rh⁺(diene) species in the carbene polymerisation reaction (see also Table 1).¹⁰

Indeed, DFT calculations indicate a very high barrier (~52 kcal mol⁻¹) for oxidative addition of an allylic C-H bond of the ([C₃H₆]Rh)⁺ moiety to form the [C₃H₇H]⁺-H allyl-hydride species (Scheme 5, bottom). Binuclear pathways were not computationally investigated, but may have lower barriers. More importantly, the equilibrium lays strongly at the ([C₃H₆]Rh)⁺ side. The allyl-hydride formation is endergonic by almost +20 kcal mol⁻¹, so there is a strong driving force for the back-reaction from the cationic hydride species (Scheme 5, bottom). Hydride migration to the double bond is a further complication that may prevent trapping of the hydride by a carbene-unit to form the active ([C₃H₇H]⁺-allyl)⁴⁺ species. The combination of these effects (high barrier, endergonic reaction and competing hydride migration pathway) provides a good explanation for the fact that catalyst activation is cumbersome when starting from non-oxidized Rh⁺(diene) species, but becomes more effective upon oxygenation.

In conclusion, high resolution ESI-MS measurements allowed us to characterise the polymer forming growing-chain rhodium species that are active during Rh(diene)-catalysed stereoregular carbene polymerisation reactions. These turn out to be cationic ([allyl]Rh⁺-polymeryl)⁺ species. Unexpectedly, these species are most efficiently generated from oxygenated complexes ([diene-O]Rh⁺), which produce higher polymer yields and allow better initiation efficiencies than their non-oxidized [dieneRh⁺] precursors. Rearrangement of 2-rhodaoxetanes to allyl-β-alkyl-hydroxide species followed by β-hydroxy elimination give access to ([allyl-diene]Rh⁺-OH)⁺ species. To our best knowledge, this is the first unambiguous example of a concerted β-hydroxy syn-elimination reaction at rhodium.¹⁵,¹⁶ The active ([allyl]Rh⁺-polymeryl)⁺ growing-chains are formed by carbene-insertion into the Rh–OH bond. These important new mechanistic insights will greatly aid the development of Rh-mediated stereoregular carbene polymerisation reactions in the near future, and hold the promise to make new polymeric materials from carbene precursors in a much more effective, selective and better controllable manner. The data further imply that catalyst oxidation can be crucial to convert catalyst precursors to active species, and remind us of the fact that the cod ligand (which is widely applied in [(M₂(C₅H₅)Cl)cod]₂ and [(Mcod)₂BF₄ precursors (M = Rh, Ir) for in situ catalyst generation in a variety of catalytic reactions) should not be inadvertently assumed to be labile or easily displaced, but can actually be(come) a potent ancillary ligand during catalytic turnover.

Keywords: Rhodium · Oxidation · 2-Metallaaoxetanes · Diazocompounds · Beta-hydroxy elimination · C1 Polymerisation

References


[7] Such as the fact that the non-oxidized pre-catalyst 1 and 2 (complex 1 does not even react with air) give clear access to carbene polymerisation under strict anaerobic and dry conditions, while partial oxidation of 2 leads to higher activities (see ref 3 and 6). All tested pre-formed Rh⁺-allyl and Rh⁺-alkyl species have very poor (if any) activity (see ref 3-i).

[8] The oxidation process can be accelerated by crushing the microcrystalline solid 2 before exposing it to a small amount of water and pure O₂. After several weeks the least soluble oxidized material (3) was separated from unreacted 2 by adding CHCl₃, filtration and thorough washing of the solid residue (3) with CHCl₃ (see Supporting Information).

[9] Reactions of 2 with air or O₂ in solution proceed differently (NMR evidence). Such samples give incomplete conversion in carbene polymerisation.


[12] Note that these reactions are strongly exothermic.


Breath-taking activation

Stereoregular carbene polymerisation turns out to proceed via cationic [(allyl)Rh\textsuperscript{III}–polymeryl\textsuperscript{+}] species. These are most efficiently generated by oxygenation of the [(diene)Rh\textsuperscript{I}] precatalysts, which involves an unusual rearrangement of 2-rhodaioxetane intermediates. This discovery gives detailed insight in the reaction mechanism, and increases the efficiency and selectivity of the reaction substantially.

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