Angewandte Chemie
International Edition

DOI: 10.1002/anie.201200069

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

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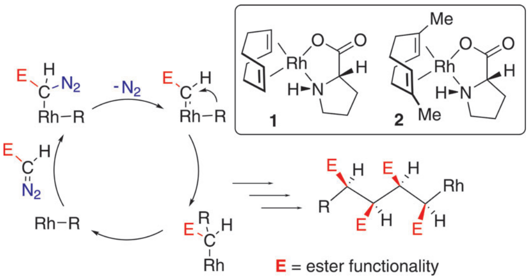
Polymers bearing polar functionalities are important materials, since they exhibit beneficial properties with respect to adhesion, paint/printability, and other surface properties.[1] The commercial synthesis of these materials is mainly based on radical processes, for which stereocontrol is difficult to achieve.[2] Stereocontrolled polymerization generally requires (transition-)metal catalysis. However, to the best of our knowledge there are no catalysts known that can polymerize 1,2-difunctionalized olefins such as fumarates or maleates in a stereocontrolled manner. Therefore, the synthesis of high molecular weight and stereoregular densely functionalized sp^3-carbon chain (co)polymers containing a polar substituent at every carbon atom of the polymer backbone is currently restricted to the Rh-mediated carbene polymerization techniques recently developed in our group (C1 polymerization; Scheme 1).[3] 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.[3g] Such polymers are not accessible from (1,2-difunctionalized) olefins,[4] and application of these new materials[5,6] therefore relies on increasing the efficiency of the carbene polymerization reaction.[3a]



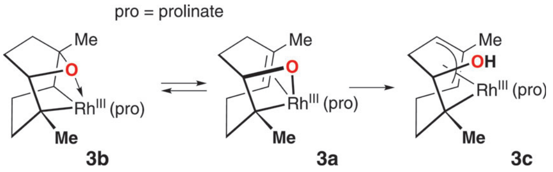
Scheme 1. Rh-catalyzed carbene polymerization.

The reaction mechanism of this intriguing carbene polymerization reaction has been the subject of intensive investigations in our group, but the exact nature of the polymer forming Rh-species remained elusive thus far. Recently, we discovered that partial oxidation of precatalyst **2** (Scheme 1) leads to markedly improved polymer yields and a higher amount of active Rh-species,[7] but the underlying reason was poorly understood.

As is 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 polymerization reaction, requires identification of the active species. Faced with seemingly contrasting observations in our initial studies,[8] we now report the nature of the active polymer-forming growing-chain rhodium species during carbene polymerization, which are formed after oxidation of the catalyst precursor with O_2.

Complex **2** reacts sluggishly with air or O_2, and hence it takes a long time to convert the solid starting material to the fully oxidized solid (**3**).[7,9,10] NMR spectra of this material are complicated, which is indicative of the presence of multiple species with overlapping signals, and are therefore not very informative (Figure S12 in the Supporting Information). They are, however, suggestive of the presence of (different geometrical isomers of) monooxygenated $[Rh(Me_2cod)]$ species (**3**) (Scheme 2; $Me_2cod = 1,5$-dimethylcycloocta-1,5-diene).[11]

This hypothesis was confirmed by ESI-MS; the clear and clean mass spectra revealed only monooxygenated species $[\mathbf{3}H]^+$. The high-resolution mass spectrometric measurements and isotopic distribution of $[\mathbf{3}H]^+$ fit exactly to the mass of the starting material plus one oxygen atom, and a proton functions as the charge carrier: $[\mathbf{2}+O+H]^+=[\mathbf{3}H]^+$ (Fig-



Scheme 2. Likely structures of **3** formed by oxidation of **2**.

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[**] Financial support from the European Research Council (ERC, grant agreement 202886-CatCIR), the Netherlands Organization for Scientific Research (NWO-CW), the Dutch Polymer Institute (DPI projects no. 646/647), the University of Amsterdam, the DFG (SFB-583 and Major Research Instrumentation Program) and MICINN/FEDER (Projects CTQ2008-03860 and CTQ2011-22516) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200069.

ure S1 in the Supporting Information). On the basis of our previous work in the field of Rh^I(olefin) oxygenation reactions,[11] the most likely monooxygenated species in this mixture (NMR) are (different isomers of) the 2-metalla-oxetane[12] species **3a**, its ring-closed analogue **3b**, and the allyl-β-alkyl-hydroxide species **3c** (Scheme 2).

Interestingly, the fully oxidized samples (**3**), in which no starting material (**2**) is present anymore according to NMR spectroscopy,[9] give excellent yields in the carbene polymerization 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).[7]

Table 1: Carbene polymerization with precatalysts **1–6**.[a]

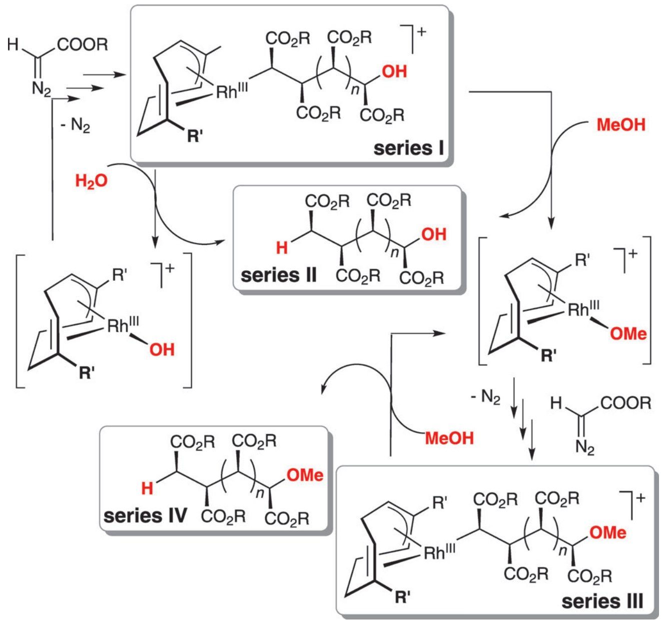
Catalyst	Polymer yield [%][b]	Oligomer yield [%][c]	M_w [kDa][d]	M_w/M_n	IE [%][e]
1[3d,g]	50	30	150	3.6	4
2	45	30	590	4.2	1.6
3[9]	**85**	15	311	2.4	2.4
4	25	38	117	3.4	3.2
5	66	19	357	4.5	3.6
6	**80**	12	111	2.4	**7.4**

[a] Conditions: 0.04 mmol catalyst; 2 mmol EDA, 5 mL chloroform, room temperature, 14 h. [b] Isolated by precipitation and washing with methanol. [c] Low molecular weight ($M_w < 2$ kDa) material.[d] Size-exclusion chromatography (SEC) (polystyrene standards). [e] Initiation efficiency: Number of polymer chains per Rh center in % (mol/mol × 100%).

Next, we monitored the polymerization reaction by 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 polymerization 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 precatalyst **2** in CH_2Cl_2 reveals only $[\mathbf{2}H]^+$, and these peaks do not visibly decrease over a period of more than an hour. Similar experiments with the oxidized precatalyst **3**, however, led to an immediate decrease of the signals of $[\mathbf{3}H]^+$ and the appearance of a clear repeating pattern of a $[(Me_2C_8H_9)Rh\text{-}(CHCO_2Et)_n\text{-}OH]^+$ propagating species that builds in :CHCOOEt carbene units ($\Delta M = 86$ Da; see series **I**, Scheme 3). The organometallic "$(Me_2C_8H_9)Rh$" fragment corresponds with the cationic $[(allyl)Rh^{III}\text{-}alkyl]^+$ species depicted in Scheme 3, which is supported by additional experiments (see below).

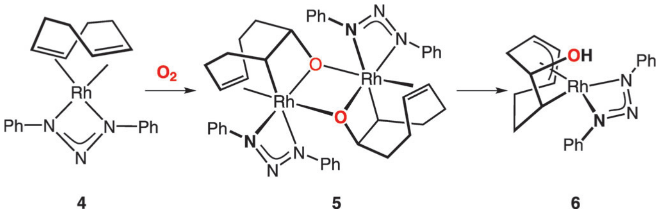
Most interestingly, the MS spectra further show the appearance of $[H\text{-}(CHCOOEt)_n\text{-}OH + Na]^+$ chains (series **II**, Scheme 3). Hence, chain growth starts on a hydroxide fragment. Furthermore, addition of MeOH results in the appearance of a clear pattern corresponding to $[(Me_2C_8H_9)Rh\text{-}(CHCOOEt)_n\text{-}OMe]^+$ growing chains (series **III**, Scheme 3) as well as terminated $[H\text{-}(CHCOOEt)_n\text{-}OMe + Na]^+$ 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 precatalyst **3**. The chains terminate by protonation, either involving H_2O or an alcohol.[3k] In the presence of MeOH, the alcohol clearly functions as a chain-transfer agent,[3k] thus generating $H\text{-}(CHCOOR)_n\text{-}OMe$ terminated polymer chains and allylic $[(Me_2C_8H_9)Rh^{III}\text{-}OMe]^+$ 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).



Scheme 3. Reaction mechanism showing series **I–IV** (R′ = H, Me, R = Et, Bn).

Similar results were obtained when using benzyl diazoacetate (BnDA) instead of EDA, thus confirming the above assignments (Scheme 3, R = Bn; see Figures S6 and S7 in the Supporting Information). The data therefore show that the oxidized species **3** are capable of generating the active allyl-Rh-alkyl species $[(Me_2C_8H_9)Rh^{III}\text{-}P]^+$ (P = polymeryl). Apparently, the hydroxide fragment of species **3c** can be transferred to the metal to start the chain-propagation process through carbene insertion into the thus formed Rh^{III}–OH bond.

We were intrigued by the possibility that the active allyl species $[(Me_2C_8H_9)Rh^{III}\text{-}OH]^+$ (and hence related allylic $[(C_8H_{11})Rh^{III}\text{-}OH]^+$ species derived from cycloocta-1,5-diene) could be generated from the 2-rhodaoxetane species **3a** or the allyl-β-hydroxy–alkyl species **3c**, and hence we looked for similar activity in related compounds. Previously reported $[(C_8H_{12}O)Rh(N_3\text{-}ligand)]^+$ species[11] turned out to be nonreactive towards EDA, which can be expected for these saturated 18-valence-electron Rh^{III} species. Hence, we decided to look at "unsaturated" analogues reported previously. The triazenide complexes **5** and **6** (Scheme 4)[13] seemed good candidates to test our hypothesis that active allylic $[(C_8H_{11})Rh^{III}\text{-}OH]^+$ species can be generated from



Scheme 4. $[(C_8H_{12})Rh(N_3Ph_2)]$ (**4**), the 2-rhodaoxetane complex **5**, and its isomer allyl-β-alkyl-hydroxide compound **6**.

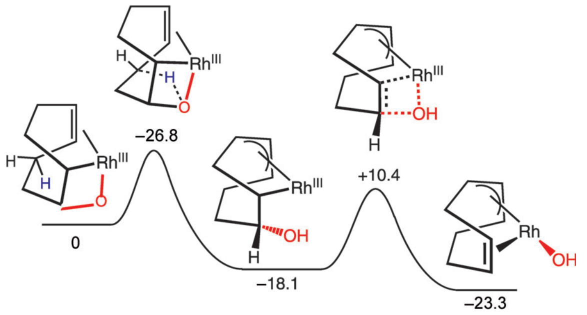
precursors containing a 2-rhodaoxetane fragment $(C_8H_{12}O)Rh^{III}$.

Complex **5** is formed in good yield and in good purity by oxidation of the triazenide precursor $[(C_8H_{12})Rh(N_3Ph_2)]$ (**4**) with O_2.[13] Complexes **4**–**6** were evaluated as catalyst precursors in the carbene polymerization of EDA (Table 1). As expected, [(triazenide)Rh^I(cod)] complex **4** is active, but it is less active than the non-oxidized $[(R'_2C_8H_{10})Rh^I(\text{prolinate})]$ complexes (R′ = H: **1**; R′ = Me: **2**). However, oxidation of **4** to **5** markedly improves the polymerization over oligomerization/dimerization selectivity, thus leading to substantially improved polymer yield (66 %). Conversion of **5** into **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 polymerization kinetics of complex **4**, **5**, and **6** under identical reaction conditions (Figures S16 and S17 in the Supporting Information). The reaction with complex **4** is very slow (full EDA conversion requires more than 10 h). Complex **5** converts EDA substantially faster than **4** (full conversion in ca. 5 h), 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 in shown in Table 1).

Hence, it is clear that the allyl-β-alkyl-hydroxide 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 polymerization event (ca. 7 %), thus showing that complex **6** itself is still a precatalyst 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 [(cod)Rh^I] or [$(Me_2cod)Rh^I$] 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 previously.[14]

The carbene polymerization reaction using species **5** and **6** was further probed by high resolution ESIMS to obtain a detailed understanding of the reaction mechanism. The results are very similar to those obtained with **3** as the precatalyst in EDA and BnDA polymerization reactions. In absence of methanol, clear repeating patterns of $[(C_8H_{11})Rh^{III}\text{-}(CHCOOR)_n\text{-}OH]^+$ growing chains were detected (series **I**, R = Et, Scheme 3), as well as terminated $[H\text{-}(CHOOR)_n\text{-}OH + Na]^+$ chains (series **II**, R = Et). Again, in the presence of methanol patterns of $[(C_8H_{11})Rh^{III}\text{-}(CHCOOR)_n\text{-}OMe]^+$ growing chains (series **III**, R = Et) and patterns of terminated $[H\text{-}(CHCOOR)_n\text{-}OMe + Na]^+$ chains containing a methoxy end group (series **IV**, R = Et) appeared (Figures S8 and S9 in the Supporting Information). Similar results were obtained using BnDA instead of EDA (Scheme 3, R′ = H, R = Bn; Figure S10). Important to note here is that these series **I**–**IV** (R′ = H) were detected using pure samples of **5** and **6** as precatalysts, and hence the Rh^{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 $[(C_8H_{11})Rh^{III}\text{–}OH]^+$ 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-hydroxide ligand to generate the active allylic $[(C_8H_{11})Rh^{III}\text{–}OH]^+$ species. DFT calculations (b3lyp, def2-TZVP) confirm that this is an energetically favorable and kinetically accessible pathway (Scheme 5).



Scheme 5. DFT calculated pathway for activation of 2-rhoda^{III}oxetane precursors to form the active (allyl–cod)Rh^{III}–OH species.

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). This transformation is experimentally observed in the rearrangement from **5** to **6** and in related reported reactions.[11,13] More importantly, β-hydroxy elimination from the cationic allyl-β-alkyl-hydroxide rhodium(III) species is exergonic by approximately 5 $kcal\,mol^{-1}$ and has an accessible transition state barrier of 28 $kcal\,mol^{-1}$.[15] Clearly, oxidation of $[(R'_2C_8H_{10})Rh^I]$-type complexes to $[(R'_2C_8H_{10}O)Rh^{III}]$-type species, followed by rearrangement to $[(R'_2C_8H_9)Rh^{III}\text{–}OH]^+$ allyl compounds (R′ = H, Me) is an effective pathway to engage carbene polymerization activity.

Carbene polymerization is also observed for non-oxidized rhodium(I) diene complexes under strict anaerobic conditions. Hence, the active $[(R'_2C_8H_9)Rh^{III}\text{-}Y]^+$ allyl species can also be generated via a different pathway, directly from the non-oxidized rhodium(I) diene precursors (albeit less effectively). A plausible route for activation of the non-oxidized $[Rh^{I}(cod)]$ catalyst precursors is discussed in the Supporting Information (Scheme S1).

In conclusion, high-resolution ESI-MS measurements allowed us to characterize the polymer-forming growing-chain rhodium species that are active during Rh(diene)-catalyzed stereoregular carbene polymerization reactions. These turn out to be cationic $[(allyl)Rh^{III}\text{-polymeryl}]^+$ species. Unexpectedly, these species are most efficiently generated from oxygenated complexes $[(\text{“diene-O”})Rh^{III}]$, which produce higher polymer yields and allow better initiation efficiencies than their non-oxidized $[(diene)Rh^{I}]$ precursors. Rearrangement of 2-rhodaoxetanes to allyl-β-alkyl-hydroxide species followed by β-hydroxy elimination gives access to $[(allyl\text{–}diene)Rh^{III}\text{–}OH]^+$ species. To the best of our knowledge, this is the first unambiguous example of a concerted β-hydroxy *syn*-elimination reaction at a rhodium center,[16,17] which adds further diversity to the remarkable palette of 2-metallaoxetane reactivity.[12] The active $[(allyl)Rh^{III}\text{-polymeryl}]^+$ 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 polymerization 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 into active species, and remind us of the fact that the cod ligand (which is widely applied in $[\{M(\mu\text{-}Cl)(cod)\}_2]$ and $[(M(cod)_2]BF_4$ 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 or become a potent ancillary ligand during catalytic turnover.

Received: January 4, 2012
Revised: March 9, 2012

Keywords: diazo compounds · oxidation · polymerization · rhodium

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[1] a) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, *109*, 5215; b) L. S. Boffa, B. Novak, *Chem. Rev.* **2000**, *100*, 1479.

[2] Tacticities in radical polymerization (RP) are generally expressed as triad percentages, and are typically low (< 70%). Some exceptions are reported for RP reactions at low temperatures or for RP reactions with bulky monomers: K. Satoh, M. Kamigaito, *Chem. Rev.* **2009**, *109*, 5120. Much higher tacticities (pentad selectivities > 99%) can be achieved with (transition) metal-catalyzed processes.

[3] a) A. F. Noels, *Angew. Chem.* **2007**, *119*, 1228; *Angew. Chem. Int. Ed.* **2007**, *46*, 1208; b) E. Jellema, A. L. Jongerius, J. N. H. Reek, B. de Bruin, *Chem. Soc. Rev.* **2010**, *39*, 1706–1723; c) N. M. G. Franssen, A. J. C. Walters, J. N. H. Reek, B. de Bruin, *Catal. Sci. Technol.* **2011**, *1*, 153–165; d) D. G. H. Hetterscheid, C. Hendriksen, W. I. Dzik, J. M. M. Smits, E. R. H. van Eck, A. E. Rowan, V. Busico, M. Vacatello, V. Van Axel Castelli, A. Segre, E. Jellema, T. G. Bloemberg, B. de Bruin, *J. Am. Chem. Soc.* **2006**, *128*, 9746–9752; e) E. Jellema, P. H. M. Budzelaar, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2007**, *129*, 11631–11641; f) M. Rubio, E. Jellema, M. A. Siegler, A. L. Spek, J. N. H. Reek, B. de Bruin, *Dalton Trans.* **2009**, 8970–8976; g) E. Jellema, A. L. Jongerius, G. A. van Ekenstein, S. D. Mookhoek, T. J. Dingemans, E. M. Reingruber, A. Chojnacka, P. J. Schoenmakers, R. Sprenkels, E. R. H. van Eck, J. N. H. Reek, B. de Bruin, *Macromolecules* **2010**, *43*, 8892–8903; h) N. M. G. Franssen, J. N. H. Reek, B. de Bruin, *Polym. Chem.* **2011**, *2*, 422–431; i) M. Finger, J. N. H. Reek, B. de Bruin, *Organometallics* **2011**, *30*, 1094–1101; j) M. Finger, M. Lutz, J. N. H. Reek, B. de Bruin, *Eur. J. Inorg. Chem.* **2012**, *9*, 1437–1444; k) A. J. C. Walters, E. Jellema, M. Finger, P. Aarnoutse, J. M. M. Smits, J. N. H. Reek, B. de Bruin, *ACS Catal.* **2012**, *2*, 246–260.

[4] Nonstereospecific synthesis of shorter (atactic) polymers by Cu- and Pd-catalyzed carbene polymerization was reported by Li and Ihara and co-workers: a) L. Liu, Y. Song, H. Li, *Polym. Int.* **2002**, *51*, 1047–1049; b) E. Ihara, H. Takahashi, M. Akazawa, T. Itoh, K. Inoue, *Macromolecules* **2011**, *44*, 3287–3292; c) E. Ihara, Y. Ishiguro, N. Yoshida, T. Hiraren, Y. Itoh, K. Inoue, *Macromolecules* **2009**, *42*, 8608–8610; d) E. Ihara, Y. Goto, T. Itoh, K. Inoue, *Polym. J.* **2009**, *41*, 1117–1123; e) E. Ihara, T. Hiraren, T. Itoh, K. Inoue, *Polym. J.* **2008**, *40*, 1094–1098; f) E. Ihara, T. Hiraren, K. Itoh, K. Inoue, *J. Polym. Sci. Part A* **2008**, *46*, 1638–1648; g) E. Ihara, A. Nakada, T. Itoh, K. Inoue, *Macromolecules* **2006**, *39*, 6440–6444; h) E. Ihara, M. Fujioka, N. Haida, T. Itoh, K. Inoue, *Macromolecules* **2005**, *38*, 2101–2108; i) E. Ihara, N. Haida, M. Iio, K. Inoue, *Macromolecules* **2003**, *36*, 36–41.

[5] Functionalized materials by catalyzed carbene copolymerization, E. Jellema, A. L. Jongerius, N. M. G. Fransen, B. de Bruin, WO-2011-157444A1, **2011**; PCT-EP2011–003016, **2011**.

[6] Atactic poly(dialkyl fumarate)s find application as materials for O_2 permeable membranes, optical and contact lenses, and as biocompatible scaffolds for bone tissue engineering: a) T. Kawagushi, US patent US-4868260; b) A. Matsumoto, T. Otsu, *Macromol. Symp.* **1995**, *98*, 139–152; c) M. S. Cortizo, M. S. Molinuevo, A. M. Cortizo, *J. Tissue Eng. Regener. Med.* **2008**, *2*, 33–42; d) J. M. Fernandez, M. S. Molinuevo, A. M. Cortizo, A. D. McCarthy, M. S. Cortizo, *J. Biomat. Sci.* **2010**, *21*, 1297–1312.

[7] E. Jellema, A. L. Jongerius, A. J. C. Walters, J. M. M. Smits, J. N. H. Reek, B. de Bruin, *Organometallics* **2010**, *29*, 2823–2826.

[8] For example, the non-oxidized precatalysts **1** and **2** (complex **1** does not even react with air) give clear access to carbene polymerization under strict anaerobic and dry conditions, whereas partial oxidation of **2** leads to higher activities (see Refs. [3] and [6]). All tested pre-formed Rh^{I}–allyl and Rh^{III}–alkyl species have very poor (if any) activity (see Ref. [3i–k]).

[9] The oxidation process can be accelerated by crushing the microcrystalline solid **2** before exposing it to a small amount of water and pure O_2. After several weeks, the less-soluble oxidized material (**3**) was separated from starting material **2** by adding $CHCl_3$, followed by filtration and thorough washing of the solid residue (**3**) with $CHCl_3$ (see the Supporting Information).

[10] Reactions of **2** with air or with O_2 in solution proceed differently (NMR spectroscopic evidence). Such samples give incomplete conversion in carbene polymerization.

[11] a) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236–4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142–4157; b) B. de Bruin, J. A. Brands, J. J. J. M. Donners, M. P. J. Donners, R. de Gelder, J. M. M. Smits, A. W. Gal, A. L. Spek, *Chem. Eur. J.* **1999**, *5*, 2921–2936; c) B. de Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schle-

bos, R. de Gelder, J. M. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem.* **1997**, *109*, 2153 – 2157; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064 – 2067; d) C. Tejel, M. A. Ciriano, *Top. Organomet. Chem.* **2007**, *22*, 97 – 124.

[12] For a recent overview of 2-metallaoxetane synthesis and reactivity, see: A. Dauth, J. A. Love, *Chem. Rev.* **2011**, *111*, 2010 – 2047.

[13] a) C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos-Moreno, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2005**, *117*, 3331 – 3335; *Angew. Chem. Int. Ed.* **2005**, *44*, 3267 – 3271; b) M. P. del Río, M. A. Ciriano, C. Tejel, *Angew. Chem.* **2008**, *120*, 2536 – 2539; *Angew. Chem. Int. Ed.* **2008**, *47*, 2502 – 2505.

[14] No stereo-errors are detectable with ^{13}C NMR spectroscopy; see Ref. [3] for details.

[15] Note that these reactions are strongly exothermic.

[16] Examples of (non-concerted) β-hydroxy anti-elimination reactions: a) R. S. Pryadun, J. D. Atwood, *Organometallics* **2007**, *26*, 4830 – 4834; b) X. Fu, S. Li, B. B. Wayland, *J. Am. Chem. Soc.* **2006**, *128*, 8947 – 8954.

[17] Concerted β-hydroxy-elimination also explains the outcome of the reaction of complex **6** with carbon monoxide: C. Tejel, M. P. del Río, J. A. López, M. A. Ciriano, *Chem. Eur. J.* **2010**, *16*, 11261 – 11265.