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Rh-Mediated Carbene Polymerization: from Multistep Catalyst Activation to Alcohol-Mediated Chain-Transfer

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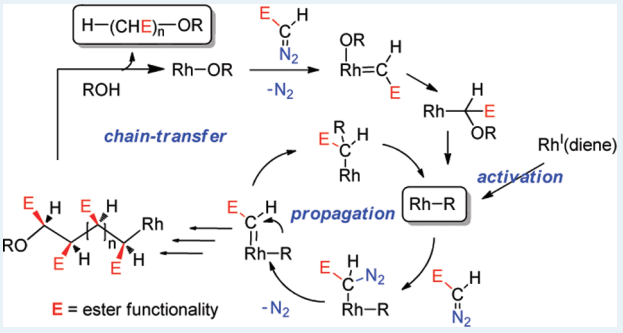
Supporting Information

ABSTRACT: Rh-mediated polymerization of carbenes gives access to new highly substituted and stereoregular polymers. While this reaction is of interest for the synthesis of syndiotactic polymers that are functionalized at every carbon atom of the polymer backbone, the catalyst activation, chain-initiation, and chain-termination processes were so far poorly understood. In this publication we present new information about these processes on the basis of detailed end-group analyses, dilution-kinetic studies, and a comparison of the activity of well-defined catalysts containing a preformed Rh−C bond. All data point toward complex catalyst activation processes under the applied reaction conditions. The use of well-defined Rh^{I}(cod)-alkyl, aryl, and allyl complexes does *not* lead to better initiation efficiencies or higher polymer yields. MALDI-ToF MS of the oligomeric fractions indicates that during the incubation time of the reaction, the precatalysts are first transformed into oligomer forming species with a suppressed tendency toward β-hydrogen elimination, and accordingly a shift to saturated oligomeric chains that are terminated by protonolysis. Further catalyst modifications lead to a shift from atactic oligomerization to stereoregular high molecular weight polymerization activity. Dilution-kinetic studies reveal that under diluted conditions two different active species operate that differ largely in their chain-termination behavior. Analysis of the reaction products by MALDI-ToF MS also allows conclusions about chain-initiation and chain-termination. Chain-initiation can occur by insertion of a preformed carbene into a Rh-ligand or Rh-hydride bond or by (internal or external) nucleophilic attack of water and/or alcohol on a Rh-carbene moiety. Chain-termination takes place mainly by (nucleophilic) protonolysis involving water or alcohols, while β-H elimination plays only a minor role and is only observed for the shorter oligomers. The detection of ethoxy and hydroxyl end-groups demonstrates the importance of trace amounts of water and ethanol toward chain-initiation. Alcohols further function as a chain-transfer agent, and increasing the alcohol concentration accelerates the chain-transfer process (which remains however relatively slow compared to chain-propagation). On the basis of the chemical properties of the alcohols, we propose a chain-transfer mechanism involving nucleophilic attack of the alcohol (nucleophilic, σ-bond metathesis type, protonolysis). This further allows us to draw some (careful) new conclusions about the oxidation state of the actual polymerization species.



KEYWORDS: *C1 polymerization, rhodium, carbene, diazo compounds, MALDI-ToF MS, chain-initiation, chain-termination, alcohols, chain-transfer*

INTRODUCTION

Polymers bearing polar functionalities are important within the vast field of polymer chemistry, 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 relatively poor control over the stereochemistry of the resulting polymers.[3] Promising routes toward *stereoregular and polar functionalized polymers* are living "group transfer" polymerization techniques developed by Chen, allowing the controlled synthesis of both syndiotactic and isotactic (rich) polymers from (methyl)methacrylates, acrylates, (meth)acrylamides, acrylonitriles, and vinylketones.[4−9] However, to the best of our knowledge, there are no catalysts known that can polymerize difunctionalized olefins, such as fumarates or maleates, in a stereocontrolled manner (even controlled radical

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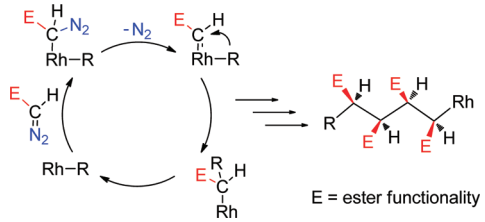
polymerization of difunctionalized polar vinyl monomers is not trivial and an unsolved problem to date). The synthesis of high molecular weight *stereoregular* densely functionalized sp^3-carbon chain polymers containing a polar substituent *at every carbon* of the polymer backbone is therefore currently restricted to the Rh-mediated carbene polymerization techniques developed in our group (C1 polymerization).[10−17] These new, highly functionalized sp^3-carbon backbone polymers reveal interesting and unexpected material properties, such as thermotropic and lyotropic liquid crystallinity, a broad thermal stability range, and a high storage modulus up to high temperatures.[16] The substrates, diazoalkanes bearing electron-withdrawing substituents (such as diazoacetates, N_2CHCO_2R), are reasonably stable,[18−21] easy to prepare and relatively cheap carbene precursors, and therefore extensively used in organic synthesis. Related Cu and Pd catalyzed oligomerization/polymerization reactions of diazoesters and diazoketones have been reported by Li and Ihara, which yield rather low molecular weight and atactic materials.[22−31]

The highest polymer yields in Rh-mediated carbene polymerization were achieved by using Rh^I(diene) complexes bearing N,O-type ligands. By variation of the ligands, we were able to show that the molecular weight and mass distribution of the obtained polymer is strongly dependent on the applied diene ligand while the anionic N,O-ligand largely influences the polymer yield. Previous investigations suggested that the high syndiotacticity of the polymerization can be explained by chain-propagation proceeding via chain-end controlled migratory carbene insertion (see Scheme 1).[17] A further remarkable

Scheme 1. Rh-Mediated Carbene Polymerization Leading to Fully Functionalized, High Molecular Weight and Stereoregular (Syndiotactic) Carbon-Chain Polymers



feature of the Rh(cod)-based system is that the reaction is associated with a rather low amount of active polymer forming Rh-species (~5%) and an incubation time. During this incubation time the selectivity of the catalyst drastically changes from predominant dimerization and oligomerization activity to almost fully selective polymerization.[17] We also investigated the importance of β-hydride elimination as a possible chain-transfer mechanism. While this process is competing with chain-propagation according to our computational studies,[32] we found so far no experimental evidence for its occurrence during carbene oligomerization or polymerization using the Rh(cod) systems. Hence, it is clear that the processes leading to catalysts activation, chain-initiation, chain-termination and/or chain-transfer associated with this reaction are not well understood, and require more attention. In this paper, we provide more information about these processes by means of catalyst variation, end-group analysis, dilution-kinetic studies, and polymerization reactions in the presence of alcohols.

RESULTS AND DISCUSSION

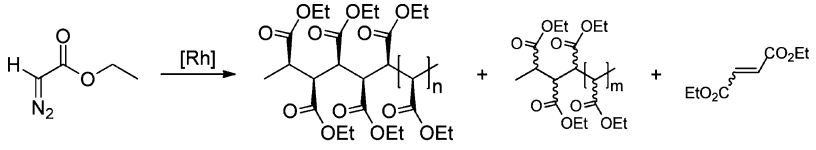
Characterization of the Oligomeric Fraction by MALDI-ToF MS End-Group Analysis. In an attempt to obtain more information about the nature of the initiation and chain-termination processes, we performed MALDI-ToF MS analyses of the oligomeric fraction. Polymer end-group analysis generally provides valuable information about the initiation and termination processes of a polymerization reaction. However, the high molecular weight and broad molecular weight distribution of poly(ethyl 2-ylidene-acetate) (PEA) hampers end-group analysis by NMR spectroscopy or mass spectrometry. Hence, we resorted to analyzing the oligomeric fractions, which are always formed as side products in varying amounts depending on the reaction conditions and the applied precatalyst (Scheme 2).

The oligomeric fraction is separated from the polymer by evaporation of the solvent from the reaction mixture and subsequently washing of the polymer with methanol, leading to a solid polymer fraction and a MeOH-soluble oligomeric fraction. The methanol and the dimers are then distilled off from the oligomeric fraction, leaving the oligomeric products as an orange to dark brown viscous oil. Their molecular weight (M_w ~1.2 kDa, PDI ~3.5) corresponds to 5−15 carbene units.

Our combined experimental evidence shows that the polymers and oligomers are formed by different active species. First of all, the oligomers have different stereochemical properties, and show broad signals in the ^{1}H and ^{13}C NMR spectra (Figure 1) indicative for ill-defined, atactic (and possibly branched) oligomers. In contrast, the polymers exhibit sharp signals in the ^{1}H and ^{13}C NMR spectra characteristic for syndiotactic chains.[17]

SEC-analysis of the reaction products further confirms that the oligomers must be formed by different Rh-species than those producing the polymer. The SEC traces of the reaction mixtures produced by precatalysts **1** and **2**, for example, show that the molecular weight distributions of the oligomer and the polymer fractions are well-separated (Figure 2). The same is

Scheme 2. Polymerization of Ethyl Diazoacetate (EDA) to Form High Molecular Weight, Stereoregular Poly(ethyl 2-ylidene-acetate) (PEA)[a]



[a]As side products, atactic oligomers of low molecular weight and the *cis* and *trans* dimers are formed.

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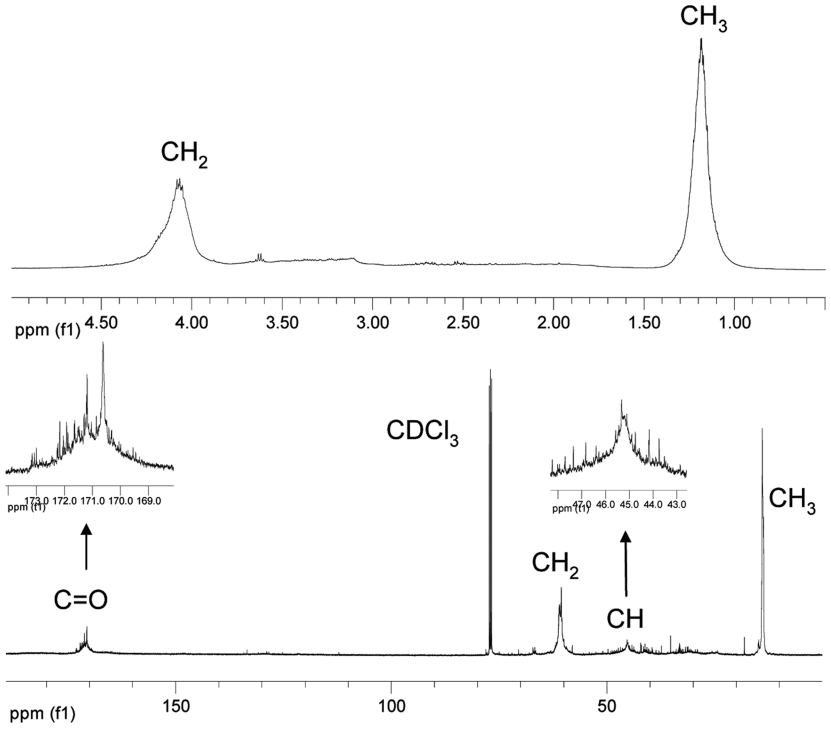

Figure 1. NMR spectra (top: ^{1}H NMR, 500 MHz, $CDCl_3$; bottom: ^{13}C NMR, 125 MHz, $CDCl_3$) of the poorly defined MeOH soluble oligomers obtained during workup of PEA. Typically, there are no signals of possible end-groups and the backbone in the ^{1}H NMR spectra while the signals of the carbonyl and backbone carbons in the ^{13}C NMR spectra reveal the atactic structure of the chain.

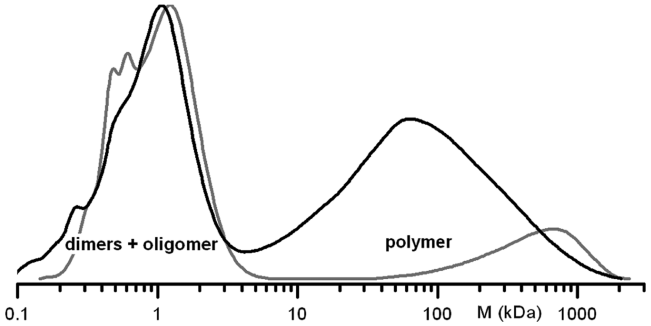

Figure 2. SEC-traces of the products produced by **1** (black line) and **2** (gray line) in the polymerization of EDA.

true for the other precatalysts; the molecular weight of both fractions differs too strongly to be formed by the same rhodium species.[33]

As the broad NMR spectra of the oligomeric products do not allow us to draw conclusions about the mechanism of their formation, we decided to analyze them by MALDI-ToF mass spectrometry. The oligomers formed by the reactions of catalyst precursors **1**−**10** (Figure 3) with EDA were used for this purpose. The synthesis of the complexes **1**−**3**,[13,17] **5**−**7**,[17,15,34] and **9**, **10**[35,36] has been described previously, while complexes **4** and **8** are reported for the first time. The molecular structures of **4** and **8** determined by X-ray diffraction are included in the Supporting Information.

Important to note at this point is that the oligomers used to obtain the MALDI-ToF mass spectra described below were obtained by similar carbene polymerization reactions, employing the different catalyst precursors **1**−**10**, but otherwise identical reaction conditions (reactions in (EtOH stabilized) $CHCl_3$ at room temperature using the same concentrations for all reactions).

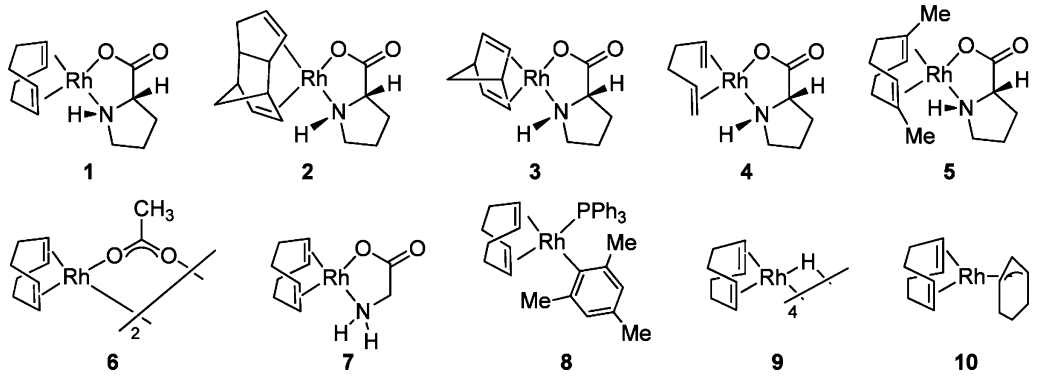

Figure 3. Catalyst precursors used for the polymerization of EDA.

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The oligomeric chains are detected in the typical range between 500 and 1300 Da, and the peaks with the highest intensity are between 600 and 900 Da, corresponding with 6–10 carbene units. For most experiments two or more series of signals are detected because of a combination of different oligomer end-groups and charge carrier cations.[37] However, addition of different metal-salts and variation of the applied catalysts allow conclusive assignments of the oligomer end-groups.

Quite remarkably, in most cases *saturated chains* $H-\{CHC(O)OEt\}_n-Y$ with different "−Y" chain-ends are dominating species in the MALDI-ToF MS spectra (see Figure 4). For example, with precatalyst **3** we obtained one series of

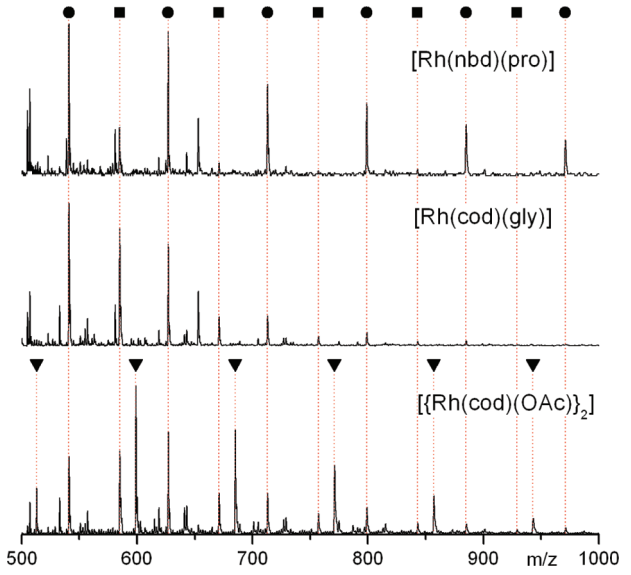

Figure 4. Part of the MALDI-ToF mass spectrum (reflectron mode) of the oligomers obtained with **3** (top), **7** (center), and **6** (bottom). The assigned series correspond to $Na^+\{H-(CHCO_2Et)_n-H\}$ (●), $Na^+[EtO-(CHCO_2Et)-H]$ (■), and $Na^+[AcO-(CHCO_2Et)-H]$ (▼).

strong signals with a repetitive pattern of 86 Da (the mass of one carbene unit), thus confirming a (migratory) carbene insertion mechanism (Scheme 1). The peaks correspond to $(86n + 25)$ Da (e.g., 799.37 Da with $n = 9$) which we interpret as saturated oligomeric chains with two hydrogen chain-ends and Na^+ as a charge carrier: $Na^+[H-(CHCO_2Et)_n-H]$ (●). This interpretation was confirmed by addition of CF_3CO_2Li: then the same oligomeric chains are detected, this time with Li^+ as charge-carrier, that is, $Li^+[H-(CHCO_2Et)_n-H]$.

Furthermore, saturated chains with hydroxyl and ethoxy "−Y" end-groups are observed, for example, $Na^+[HO-(CHCO_2Et)-H]$ (not marked in Figure 4)[38] and $Na^+[EtO-(CHCO_2Et)-H]$ (■). Interestingly, for the oligomers obtained with precatalysts **6** and **8**, the anionic ligand of the starting complex is detected as end-group of the chains, that is, acetate (▼) or mesityl groups respectively. Na^+, Rh^+, or even $Rh(diene)^+$ (diene = cod, dcp, nbd, hxd, dmcod) can possibly act as charge carrier, rendering the interpretation sometimes ambiguous. However, mass changes triggered by addition of sodium or lithium salts to the samples allow a detailed assignment of the charge carriers, and thereby the oligomer chain-ends in most cases. For example, the MALDI-ToF mass spectrum of the oligomeric fraction obtained with precatalyst **4** contains mainly chains with Rh^+ as charge carrier; by addition of CF_3CO_2Na and CF_3CO_2Li, the masses of the saturated chains are shifted accordingly (see Figure 5).

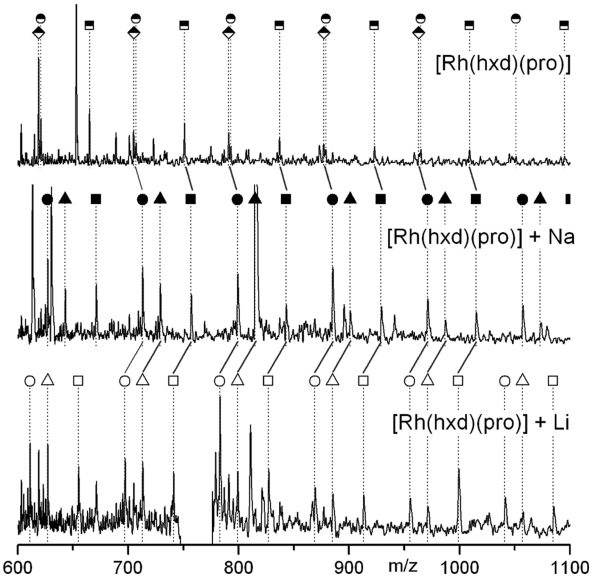

Figure 5. MALDI-ToF mass spectra (reflectron mode) of the oligomers obtained with **4**; without salt addition (top), addition of CF_3CO_2Na (center) and CF_3CO_2Li (bottom, for clarity a part of the spectrum is deleted). The series correspond to $Rh^+/Na^+/Li^+[H-(CHCO_2Et)_n-H]$ (circle); $Rh^+/Na^+/Li^+[EtO-(CHCO_2Et)_n-H]$ (square), $Na^+/Li^+[HO-(CHCO_2Et)-H]$ (triangle), and $Rh^+[H-(CHCO_2Et)_n-CCO_2Et{=}CHCO_2Et]$ (diamond).

Previous density functional theory (DFT) calculations already suggested that β-H elimination plays a minor role as a chain-transfer process.[32] The above observations are in good agreement with these results. *Only rarely can unsaturated chains be detected*, likely containing a vinylic end-group generated by β-H elimination, that is, $H-(CHCO_2Et)_n-CCO_2Et{=}CHCO_2Et$. An illustrative example is shown in the MALDI-ToF mass spectrum measured in the absence of salts (Figure 5, top). These unsaturated oligomers are mainly detected with Rh^+ and $Rh(diene)^+$ as charge carrier; addition of Na^+ or Li^+ salts mostly suppresses them.[39] There are no unsaturated equivalents of the chains with ethoxy or hydroxyl end-groups. The ratio between saturated and unsaturated chains seems to be dependent on the applied catalyst, the reaction conditions,[40] and the reaction time.

The MS-data reveal that oligomer chain-growth can be initiated from several nucleophiles or nucleophilic ligands (OH^-, OEt^-, H^-, Mes^- and AcO^-). The observation of −OH and −OEt chain-ends suggests further that water and the ethanol stabilizer in chloroform may play an important role. Only in some cases, the actual anionic ligands of the precatalysts act as chain-initiator. Chain-termination occurs via two distinct pathways: β-H elimination and protonolysis. Whereas β-H elimination is a minor pathway,[32] protonation of the chain by water, ethanol (present in the solvent as a stabilizer), or possibly the weakly acidic diazo ester is the dominating chain-termination route that explains the formation of saturated chains.[41,42] These results are quite remarkable, considering the fact that β-H elimination is generally an easy and fast reaction for rhodium complexes.

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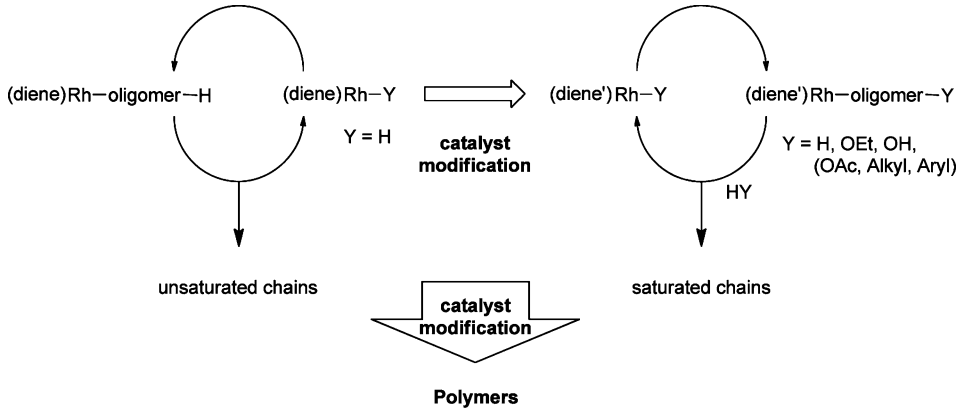
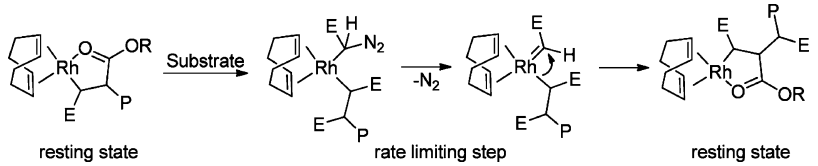
Scheme 3. Proposed Product Formation in the Reaction of the Rh-Catalyst Precursor with EDA



Scheme 4. DFT Calculated Propagation Steps in the Rh-Mediated Polymerization of Polar Functionalized Carbenes[a]



[a]P = growing polymer chain, E = CO_2R, R = alcohol moiety of the ester.

Interestingly, there seems to be a shift from unsaturated to saturated chains at higher masses indicating that both types of chains are produced by different catalytic species (see for example Figures S3−15 and S3−16 in the Supporting Information). This observation points to the presence of two different active species, differing in their chain-termination behavior. This agrees with our previous computational results about β−H elimination, and the fact that EtO− or HO−end groups are only observed for the (dominating) saturated oligomers, but not for the (minor) unsaturated ones with vinylic end-groups.

The most straightforward explanation for these results is that the Rh(diene) precatalysts get modified under the applied catalytic reaction conditions in the beginning of the reaction with EDA (Scheme 3). Considering the previously described large effect of the employed diene ligand on the M_w, M_n and PDI of the polymer obtained,[13,17] catalyst modification is likely to occur at the diene ligand.

The ability of these modified Rh(diene′) species to undergo β-H elimination seems to be absent or markedly suppressed compared to the starting Rh(diene) species. The formation of oligomers with two hydrogen end-groups further implies that some of the chains must have started growing from a rhodium-hydride complex. These could be formed by prior β-H elimination of an oligomeric chain[32] or ethanol,[43−46] by protonation at the metal, or by activation of the diene ligand.[47,48] Since the oligomers must be formed by different active species than the polymers (see Figure 2), the Rh(diene′) species probably get further modified to form the polymer forming Rh(diene″) species after the incubation time. On the basis of our previous kinetic studies, it seems that the oligomer and polymer forming species can exist as independent active species for about 30 min during the incubation time of the reaction, after which only polymerization activity remains.[17]

These produce only high molecular weight and stereoregular polymers instead of short (and atactic) oligomers. As we will show in the following, the catalyst activation process leads eventually to formation of two (or more) active polymer-forming Rh-species.

Polymerization Activity of a Variety of Well-Defined Rh-Alkyl, Aryl, and Allyl Complexes. Migratory carbene insertion polymerization (Scheme 4) requires the presence of a Rh−C bond,[17] which is not present in the precatalysts **1**−**7**.[17] We therefore wondered if the low initiation efficiencies (∼5%) observed in the polymerization with these (pre)catalysts is simply an effect of slow chain-start (i.e., Rh−C bond formation) or perhaps a more complicated (ligand) modification process to form the active polymer forming species. Slow chain-start can be prevented by the use of well-defined Rh^I(diene)-alkyl complexes, and if this is the only activation process higher initiation efficiencies are expected for such complexes containing a preformed Rh−C bond. Similar strategies were used to increase the initiation efficiencies in, for example, the polymerization of substituted acetylenes and isocyanides.[49−53]

Therefore, we decided to investigate a series of different Rh^I(cod)-alkyl, aryl, hydride, and allyl complexes (**8**−**15**) in the polymerization of EDA (see Figures 3 and 6 and Table 1). A broad variety was used to ensure that our results are not hampered by fast decomposition of the often labile compounds before the actual start of the polymerization experiment. We also included the Rh^{III} compound [Rh(TACN)Me_3] (**16**, TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) in our studies, which is one of the few reported Rh-based olefin insertion polymerization catalysts.[54]

Table 1 summarizes the results of the polymerization experiments in comparison to **1**. Remarkably, and contrary to expectations based on a slow chain-start mechanism, in all cases, the polymer yields for the tested compounds **8**−**16** are lower or comparable to those obtained with **1**. The same is true for the amount of active polymer forming Rh-species.[55] Hence, only inefficient chain-start (i.e., Rh-alkyl bond formation) at the unmodified Rh^I(diene) species does not explain the low initiation efficiencies.

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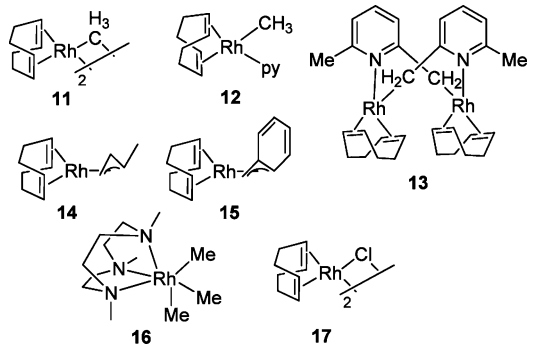

Figure 6. Influence of chain-initiation: different Rh complexes studied in the polymerization of EDA (py = pyridine).

The polymer yield drops when the Rh:EDA ratio is lowered (entries 1 and 2, 9 and 10, 12 and 14), and the different catalysts produce quite comparable molecular weights (130–270 kDa at 1:50 ratios). Noteworthy is further that catalyst **16** shows no catalytic activity in the polymerization of EDA even after activation with an acid.[56]

To investigate the possible influence of air on the activity of these rather sensitive compounds, **9**, **10**, and **15** were also tested under strictly inert conditions using EDA which had been washed, dried, and distilled under Ar.[57] Catalyst precursors **9** and **15** give virtually identical results (see entries 3, 4 and 12, 13), and the polymer yield increases upon exposing allyl complex **10** to air (entries 5 and 6). The effect of air on increasing the actual amount of active Rh species in case of **10** is, however, small.

The above results indicate that the low initiation efficiencies are not likely caused by a slow chain-start, but rather because of a more complicated catalyst activation process. The Rh complexes are rather *precatalysts* that need to be activated, most likely by diene ligand modification under the applied reaction conditions.

Dilution-Kinetic Studies. To obtain more information about the carbene polymerization process, we decided to study the influence of the [EDA] and [catalyst] concentrations on the polymerization kinetics, and the obtained molecular weights and yields. We focused on the behavior of precatalyst **1** (giving the highest polymer yields) in these studies.

Simply increasing the substrate to catalyst ratio leads to a substantial drop of the polymer yield, and therefore we decided to dilute the absolute reaction mixture by increasing the solvent volume (see Table 2). Interestingly, this leads to a strong increase of the reaction rate and higher polymer yields of up to 65%. At the same time the weight averaged molecular weights and the polydispersities increase as well. The SEC-traces of the polymer samples show that the latter effect is caused by a bimodal polymer distribution, which shows only at lower concentrations (Figure 7a).

The SEC traces show the activity of two different active species, **A** and **B**. At higher concentrations species **A** is dominating the reactivity, but upon dilution species **B** becomes dominant. Quite remarkably, species **B** produces polymer of a

Table 2. Polymerization of EDA with 1 at Different Catalyst and Substrate Concentrations[a]

entry	solvent (mL)	polymer yield (%)	M_w (kDa)	M_w/M_n
1	5	45	150	3.6
2	15	52	160	4.0
3	25	65	160	3.7
4	35	58	180	4.4
5	45	57	170	4.3
6	70	58	170	4.7
7	100	44	180	4.9
8	200	40	180	5.1
9[b]	5	34	170	3.4
10[b]	25	39	250	4.5
11[b]	45	45	270	4.9
12[b]	70	31	200	4.9

[a]Conditions: 0.04 mmol catalyst; 2 mmol EDA, chloroform, room temperature, reaction time: 14 h. [b]Under strict inert conditions; chloroform without ethanol, EDA and chloroform distilled and dried.

Table 1. Polymerization of EDA with Rh-Alkyl/Aryl Complexes[a]

entry	catalyst precursor	Rh:EDA	solvent	polymer yield (%)	M_w (kDa)	M_w/M_n	chains:Rh (%)[b]
0	**1**	1:50	$CHCl_3$	50	150	3.6	5.2
1	**8**	1:50	$CHCl_3$	41	270	6.3[c]	4.1
2[d]	**8**	1:500	$CHCl_3$	3	125	4.1	4.8
3[e]	**9**	1:50	DCM	16	180	3.1	1.1
4	**9**	1:50	DCM	19	200	3.6	1.5
5[e]	**10**	1:50	DCM	10	210	4.2	0.8
6[f]	**10**	1:50	DCM	40	280	3.1	1.9
7[d,g]	**11**	1:200	Et_2O	3	160	8.3[c]	2.6
8[d,g]	**12**	1:100	Et_2O/DCM	6	220	8.3[c]	1.9
9	**13**	1:50	$CHCl_3$	36	130	3.2	3.9
10	**13**	1:90	DCM	10	80	3.3	3.1
11	**14**	1:50	DCM	14	230	3.6	1.0
12	**15**	1:50	DCM	25	160	3.1	2.1
13[e]	**15**	1:50	DCM	26	180	3.1	2.0
14	**15**	1:200	DCM	8	135	3.8	3.9
15[h]	**16**	1:100	DCM	no reaction			

[a]Conditions if not indicated otherwise: 5 mL of $CHCl_3$ or distilled and dried CH_2Cl_2 or Et_2O, 2 mmol EDA, room temperature, reaction time: 14 h. [b]Number of polymer chains per Rh in % (mol/mol × 100%). [c]Bimodal distribution. [d]Conversion not complete. [e]Strict inert conditions using distilled and degassed EDA. [f]Catalyst in solution exposed to air for 1 h before addition of EDA. [g]Prepared in situ without isolation; for details see Experimental Section. [h]Activated by addition of 1.75 equiv of $HBAr^F$.

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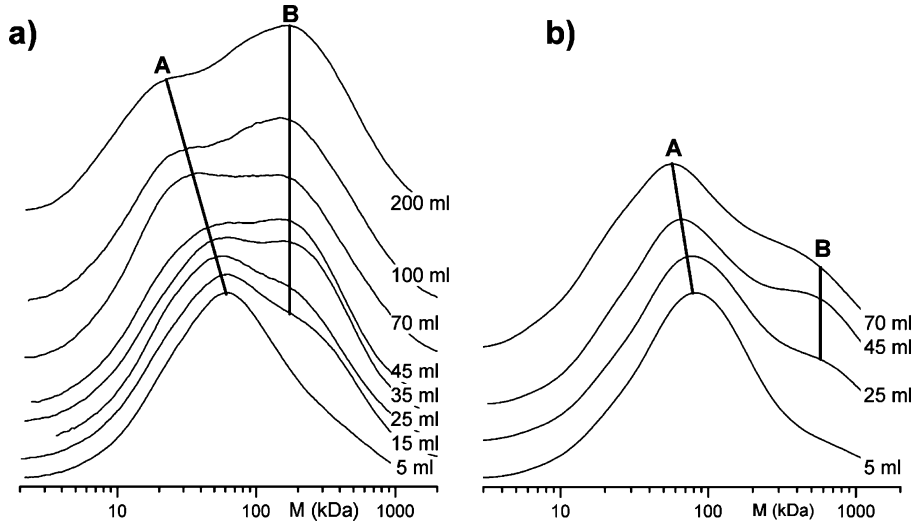

Figure 7. SEC-traces of polymer samples obtained in diluted reaction mixtures of precatalyst **1** and EDA in chloroform (the peak intensities were adjusted to obtain a clear picture). (a) In chloroform containing ethanol as stabilizer and (b) under strict inert conditions with pure chloroform.

constant molecular weight, independent of the applied concentration, while the polymer produced by species **A** shifts to lower molecular weight upon dilution (Figure 7).

On the basis of the above-described MALDI-ToF MS end-group analysis of the oligomers, we suspected that the increased polymer yields upon dilution could be the result of a higher relative amount of ethanol present in the reaction mixture under these conditions (EtOH is present as the solvent stabilizer in chloroform). We therefore repeated some of the dilution experiments in pure chloroform from which we removed the ethanol stabilizer (Table 2, entries 9–12). Indeed, the increase in yield in this case is lower, but dilution under these conditions still has a beneficial influence.[58] There is also a bimodal distribution, although somehow less pronounced (Figure 7b). Remarkably, the obtained molecular weights are higher in the absence of ethanol,[59] especially those produced by species **B**.

These data point to a chain-transfer mechanism involving EtOH (and H_2O) as the chain-transfer agent.[59] The role of EtOH (and H_2O) as a chain-transfer agent was further investigated in detail, and is described below.

To obtain more information about the different reactivity of species **A** and **B** in the carbene polymerization reaction, we performed a kinetic study under diluted conditions. This was done by monitoring the reaction in 45 mL of chloroform in time (Table 3). In marked contrast to more concentrated solutions, the reaction in diluted solutions leads already within 10 min to the formation of high molecular weight polymers in moderate yield. Under these diluted conditions the polymerization reaction is dominated by species **B**, and chain-propagation at **B** becomes apparently much faster than chain-propagation at species **A** (which dominates at higher concentrations).[60] The polymer yield increases with time (Table 3), while the molecular weight of the polymer produced by **B** does not change significantly (Figure 8). In contrast, the polymer produced by **A** still grows in time (Figure 8). Both chain-propagation and (EtOH mediated) chain-transfer at **A**, are relatively slow on the time scale of these experiments, and substantially slower than for **B**. The combined activity of **A** and **B** under diluted conditions (45 mL of solvent) leads to markedly different results than those obtained previously at higher concentrations.[61]

Table 3. Polymerization of EDA with 1 under Diluted Conditions, Monitored in Time[a]

entry	time (min)	polymer yield (%)	M_w (kDa)	M_w/M_n
1	10	17	169	4.0
2	25	22	167	4.0
3	40	25	176	4.0
4	55	27	181	3.7

[a]Conditions: 0.04 mmol of **1**, 2 mmol of EDA, 45 mL of chloroform, room temperature.

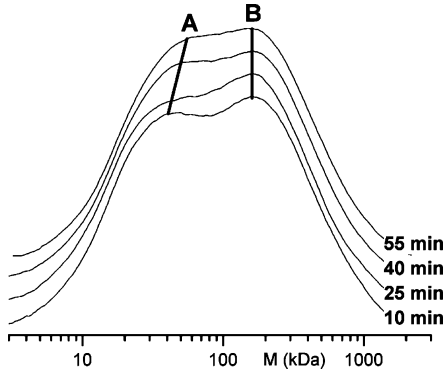

Figure 8. SEC-traces of polymer samples obtained in a diluted reaction mixture (45 mL) of **1** and EDA in chloroform at different reaction times (the peak intensities were adjusted to obtain a clear picture).

The formation of two different active polymerization species depending on the reaction conditions supports our hypothesis that an activation process occurs that changes the activity from atactic oligomerization to stereoregular polymerization (Scheme 3).

The above observations can be summarized in the following way:

– The carbene polymerization reaction involves at least two different active Rh species, **A** and **B**.

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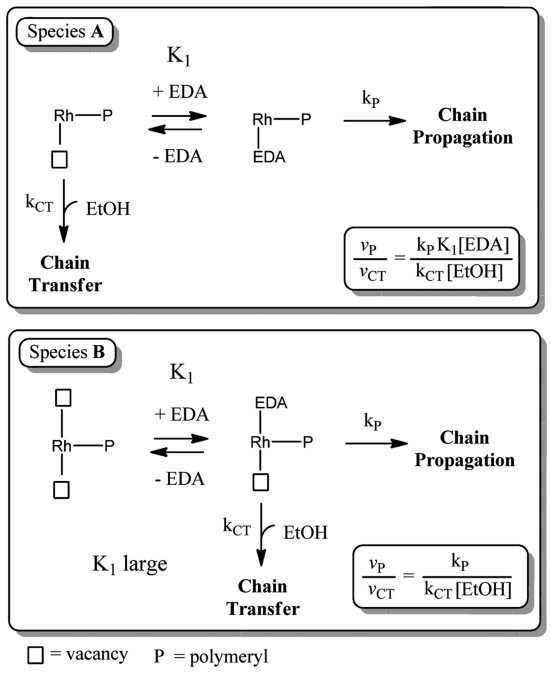
- Species **B** produces polymer with a constant molecular weight, which is independent of dilution but strongly dependent on the absolute [EtOH] concentration. For species **B** this reveals an EtOH mediated chain-transfer mechanism and a chain-propagation mechanism which is effectively zero order in the [EDA] concentration.
- Species **A** produces substantially lower molecular weight polymers upon dilution, revealing kinetics with a positive order in [EDA]. Chain-propagation and (EtOH mediated) chain-transfer at **A** are both relatively slow on the time scale of the experiments, and substantially slower than for **B**.

These observations are most conveniently interpreted by the kinetic models shown in Scheme 5. The main differences

Scheme 5. Mechanistic Model Explaining the Carbene Polymerization Kinetics of A and B



between the kinetic models for **A** and **B** are basically that for species **A** the affinity for EDA is low and chain-propagation and EtOH mediated chain-transfer compete for the same vacancy, while **B** has a higher affinity for EDA (leading to effectively zero order kinetics in [EDA]) and chain-transfer and chain-propagation can proceed from the same intermediate. This readily explains the large influence of the absolute [EtOH] concentration on the obtained molecular weights (determined by v_P/v_{CT}) while at the same time the polymer molecular weights produced by **B** are not influenced by dilution of the reaction mixture.

The models in Scheme 5 also explain why dilution leads to a shift from dominating activity of **A** to dominating activity of **B** at lower concentrations (zero order reaction kinetics in [EDA] for **B**, but not for **A**). In addition to these kinetic differences, we cannot exclude the possibility that **A** and **B** are perhaps formed in different ratios depending on the applied concentrations, which would also contribute to the observed shift in relative activities. Possibly **A** is formed only in the presence of a relatively high concentration of EDA or could be a static dinuclear species formed only at higher concentrations.[62]

Alcohol-Mediated Chain-Transfer. To further investigate the chain-transfer properties of water and alcohols in Rh-mediated carbene polymerization reactions, we decided to investigate in detail the influence of different concentrations of water and alcohols on the obtained polymer yields and molecular weights. For this purpose, we first removed the ethanol stabilizer from the solvent (commercial chloroform contains varying amounts of ethanol). In all experiments in Table 4, we used precatalyst **1**, [Rh(cod)(L-pro)] (Figure 3), that gives moderate to high polymer yields.[13,17]

Table 4. Polymerization of EDA with Precatalyst 1 in Pure Chloroform and Different Amounts of Added Water, Methanol, or Ethanol[a]

entry	remarks[b]	polymer yield (%)	M_w (kDa)	M_n (kDa)	M_w/M_n	chains:Rh (%)[c]
1[d]		34	170	51	3.4	3.8
2		39	140	46	3.1	3.6
3[d]	0.7 eq. H_2O	41	110	40	2.7	4.4
4	1 eq. H_2O	39	140	42	3.2	4.1
5	10 eq. H_2O	28	150	36	4.2	3.5
6	100 eq. H_2O	24	110	29	3.8	3.6
7	1 eq. MeOH	40	120	40	2.9	4.4
8	10 eq. MeOH	43	100	34	2.9	5.7
9	100 eq. MeOH	44	80	24	3.2	8.1
10	1 mL MeOH	22	90	24	3.6	4.0
11	1 eq. EtOH	40	150	43	3.4	4.0
12	10 eq. EtOH	46	120	38	3.2	5.2
13	100 eq. EtOH	50	100	32	3.2	6.7
14	1 mL EtOH	41	90	30	2.9	5.9
15[e]	"normal" $CHCl_3$	45	150	42	3.6	4.6

[a]Conditions: 0.04 mmol **1**, 5 mL distilled and dried $CHCl_3$ without added stabilizer, 2 mmol EDA, room temperature, reaction time: 14 h. [b]Equivalents of water, methanol, and ethanol in relation to catalyst. [c]Number of polymer chains per Rh in % (mol/mol × 100%). [d]Under inert conditions with distilled EDA. [e]$CHCl_3$ as obtained from the supplier containing 0.5−1.5% EtOH as stabilizer.

Performing the reaction under argon with distilled and dried EDA leads to a drop of the polymer yield by ∼10%, while the molecular weight of the polymer increases slightly (entry 1 in Table 4). Interestingly, the yield is significantly *higher* if the experiment is repeated with EDA as obtained from the supplier (i.e., containing traces of water and dichloromethane as stabilizer; Table 4, entry 2), although still not as high as under standard conditions (entry 15). It appears that substoichiometric amounts of water increase the polymer yield significantly. This is confirmed if the experiment is repeated under inert conditions, but with addition of a very small amount of water (entry 3).[63] Higher amounts of water lead to a decrease in the molecular weight (reflected in the number average M_n) and a drop in yield (entries 4−6). Hence, besides its likely role as a chain-transfer agent (and possibly catalyst activator), water is apparently also involved in catalyst deactivation at higher concentrations. In contrast, alcohols act mainly as chain-transfer agents and much higher amounts can

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Table 5. Polymerization of EDA with [{Rh(cod)(μ-Cl)}$_2$] (17) in Dichloromethane/Alcohol Mixtures[a]

entry	alcohol	polymer yield (%)	M_w (kDa)	M_n (kDa)	M_w/M_n	chains:Rh (%)[b]	N[c]	pK_a[d]
1		20	135	60	2.2	1.4		
2	MeOH	15	20	13	1.6	6.9	7.54	29.0
3	EtOH	20	25	13	1.9	5.9	7.44	29.8
4	CF_3CH_2OH	9	100	23	4.3	1.6	1.23	23.5
5	CCl_3CH_2OH	6	110	28	4.1	0.9		
6	*n*-PrOH	18	25	12	2.1	6.6	7.05	
7	*i*-PrOH	24	40	17	2.3	6.1	6.49	30.3
8	*n*-BuOH	25	30	15	2.0	6.3		
9	*sec*-BuOH	25	45	19	2.4	5.6		
10	*t*-BuOH	22	45	23	2.0	5.7		32.2

[a]Conditions: 0.02 mmol **2**, 2 mmol of EDA, 5 mL of CH_2Cl_2, 1 mL of alcohol, reaction time: 14 h. [b]Number of polymer chains per Rh in % (mol/mol ×100%). [c]Nucleophilicity[67] [d]pK_a values in DMSO.[68]

be added without apparent catalyst deactivation. Addition of ethanol leads to higher yields (up to 50%), while the molecular weight of the polymer clearly drops in the presence of higher ethanol concentrations (entries 11−14).[64] Methanol has a similar effect, but the polymer yield increases less while its influence on the molecular weights is larger. The clear influence of water and alcohols on the polymerization reaction is in line with the above conclusions based on MALDI-ToF MS experiments concerning the oligomeric fractions (vide supra).

In all cases lower polymer molecular weights (M_n) are produced in the presence of higher alcohol concentrations. At the same time, we observe an increase of the number of formed polymer chains per Rh at higher alcohol concentrations. These observations reveal a relatively slow alcohol-mediated chain-transfer process that is faster at higher alcohol concentrations. However, even at high alcohol concentrations the chain-transfer process remains relatively slow compared to chain-propagation. This, in combination with a low percentage of active Rh catalyst species, explains why still a low absolute number of polymer chains is being produced, even with the occurrence of chain-transfer.[65] We will discuss the alcohol-mediated chain-transfer aspect in more detail below.

The influence of using different alcohols of varying nucleophilicity and acidity was evaluated. This time we used [{Rh(cod)(μ-Cl)}$_2$] (**17**, Figure 6) as the catalyst. This dimeric complex can break-up easily and should be able to form the active species in the presence of alcohols. Catalyst **17** affords polymers in lower yields compared to **1**, but with comparable molecular weights (Table 5, entry 1). In accordance with our results above, the addition of alcohols leads to shorter polymers. For instance, after addition of 1 mL of ethanol the polymer yield (20%) is the same but the molecular weight and therefore the number of polymer chains per Rh change (entry 3). Assuming that the amount of active polymerization catalyst stays essentially the same, we can conclude that chain-transfer is around five times faster. The same is observed for MeOH, PrOH, and BuOH. Remarkably, trifluoroethanol and trichloroethanol give lower polymer yields than the other alcohols, but distinctly higher molecular weights (Table 5, entries 4 and 5). This means that chain-termination cannot proceed by direct protonation of the Rh−C bond of a growing polymer chain, because in that case one would expect to form the shortest polymers in the presence of the most acidic alcohols (i.e., trifluoroethanol and trichloroethanol). Instead, the rate of chain-transfer in the presence of alcohols appears to be mainly a function of the nucleophilicity of the alcohol (which correlates with its metal binding affinity). Increasing the steric bulk of the alcohol leads to an increase in the polymer molecular weights, and the chain-transfer process is clearly slower (entries 6−10).[66]

The alcohol-mediated chain-transfer process now allows us to prepare much shorter syndiotactic polymers, which are in a range suitable for MALDI-ToF MS measurements, and thus allow a proper chain-end analysis of the syndiotactic material produced in these catalytic reactions. In this respect it is important to note here that the addition of alcohols does not influence the stereochemistry of the polymers. The polymeric fraction still reveals sharp signals in the ^{1}H and ^{13}C NMR spectra characteristic for well-defined syndiotactic polymers.[13,16,17] However, the reaction in the presence of alcohols does influence the product distribution of the oligomeric fraction. In fact, in the presence of higher alcohol concentrations, the formed syndiotactic polymers become so short that part of the obtained syndiotactic polymeric material (still having a relatively broad molecular weight distribution) remains within the oligomeric fraction. Hence, the thus obtained oligomeric material is a mixture of the ill-defined, atactic oligomers (which are always obtained as a brown oily byproduct) and short but well-defined syndiotactic oligomers. This is obvious from ^{1}H NMR spectroscopic analysis of the oligomeric fraction, which shows the presence of short stereoregular polymer reflected in a backbone signal at δ 3.1 ppm (Figure S5−3 in the Supporting Information). The syndiotactic and atactic oligomers can be separated from each other on a short silica column ($CHCl_3$ eluent), on which the brown atactic oil remains absorbed, while the short syndiotactic material runs and can be easily flushed off the column (obtained as a white solid revealing the same sharp signals in the ^{1}H and ^{13}C NMR spectra as reported for the syndiotactic polymers[13,16,17]). This means that the polymer yields in Table 5 are somewhat underestimated.

Remarkably, the short, but well-defined syndiotactic material obtained in the presence of excess MeOH has a completely different behavior in MALDI-ToF mass spectrometry when compared to the ill-defined atactic oligomeric side-products (vide supra, see also ref 17). While the MALDI-ToF mass spectra of the atactic oligomers revealed weak signals at lower masses (and complicated patterns because of the presence of different end-groups), the syndiotactic material (Table 5, entry 2) reveals a very clear repeating pattern with strong signals (Figure 9, top) showing only one set of end-groups: Na^+[H−$(CHCO_2Et)_n$−OMe]. In fact, these signals are so strong that even in the nonseparated mixture of atactic and syndiotactic oligomers the signals of the syndiotactic material completely

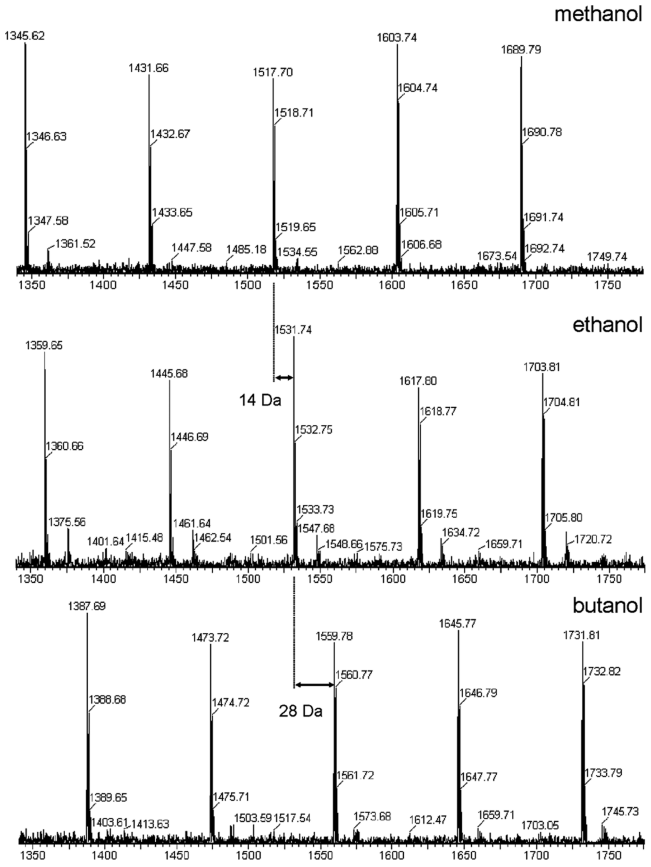


Figure 9. Part of the MALDI-ToF mass spectra (reflectron mode) of oligomers obtained with [{Rh(cod)(μ-Cl)}$_2$] (**17**) in the presence of methanol (top), ethanol (middle) and butanol (bottom).

dominate the MALDI-ToF mass spectrum, resulting in an identical spectrum as obtained for the separated syndiotactic oligomers.[69] The oligomers prepared in the presence of 1 mL of ethanol and butanol (Table 5, entries 3 and 8) were also analyzed with MALDI-ToF MS.[70] In all cases the MALDI-ToF mass spectra show very clear repeating patterns with mass differences of 86 Da (Figure 9), which corresponds to the mass of the carbene formed from EDA, thus proving the carbene insertion chain-growth pathway. All obtained patterns are consistent with a poly carbene chain having one hydrogen and one alkoxy end-group, and sodium as the charge carrier: $Na^+[H-(CHCO_2Et)_n-OR]$. Correspondingly, the series of the oligomers prepared in the presence of ethanol and butanol are shifted by 14 and 42 Da to higher masses compared to methanol.

Because of the short chain-length of the polymer prepared in the presence of methanol (Table 5, entry 2), we were also able to obtain a MALDI-ToF mass spectrum of the longer (MeOH insoluble) polymeric fraction (see Figure 10; linear detection mode). The series correspond again with $Na^+[H-(CHCO_2Et)_n-OMe]$. Hence the data reveal that the added alcohols end-up as chain-ends, and confirm their role as chain-transfer agents.

The implications of the gathered data are illustrated in Scheme 6, and can be summarized as follows: The decrease of the molecular weight with increasing amounts of alcohol (Table 5) and the detection of mainly saturated chains in the MALDI-ToF MS experiments (vide supra) prove that chain-termination occurs

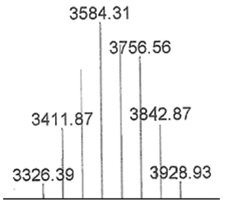
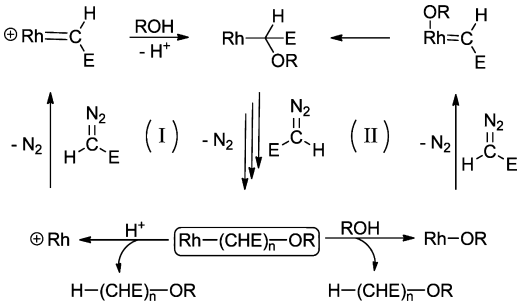


Figure 10. Part of the MALDI-ToF mass spectrum (obtained in linear mode) of polymer obtained with **17** in the presence of methanol.

Scheme 6. Proposed Chain-Initiation and Chain-Transfer Mechanisms for Carbene Polymerization in the Presence of Alcohols



most probably via alcohol-mediated protonolysis of the rhodium-bound growing chains (framed species in Scheme 6).

The occurrence of alkoxy end-groups, the somewhat increased yields, and the higher number of chains per Rh produced upon addition of alcohols further demonstrate their importance in chain-initiation and chain-transfer. Chain-initiation could well occur by nucleophilic attack at a nonchain bearing Rh-carbene unit (pathway I, left upper side) or via carbene insertion into a Rh-alkoxide bond (pathway II, right side).

Protonation at the metal (with concomitant coordination of the alkoxide, that is, formal oxidative addition of the alcohol H−OR bond), followed by reductive elimination of the thus formed alkyl-hydride species, or direct protonation of the Rh−C bond (again with concomitant coordination of the alkoxide) would both be likely chain-transfer pathways in case of low-valent Rh^I species, and would also explain the formation of saturated $H-(CHCOOR)_n-OR$ polymer chains (pathway I, Scheme 6). However, the rate of these pathways should correlate with the acidity of the alcohol. Hence, if chain-transfer would occur by direct protonation of low-valent Rh^I−polymeryl species (Scheme 6; pathway I), the chain-length should be dependent on the pK_a of the alcohol. This is clearly not the case (see Table 5), and therefore pathway I (Scheme 6) can be excluded as the chain-transfer mechanism. Hence, an alternative chain-transfer pathway in which the nucleophilicity of the alcohol is more important must be operative (pathway II, Scheme 6).

The most likely nucleophilic pathway for alcohol-mediated chain transfer is depicted in Scheme 7 (pathway A), and involves coordination of the alcohol to an active rhodium-polymer chain species (a_1), followed by intramolecular (σ-bond metathesis type) proton transfer from the alcohol ligand to the Rh-bound polymer chain (a_2). However, as correctly pointed-out by a referee, the data do not fully exclude an alternative mechanism (Scheme 7, pathway B) involving direct S_N2-type nucleophilic attack of the alcohol at the Rh−C bond (b_1) followed by protonation of Rh^I to form a Rh−H species (b_2).

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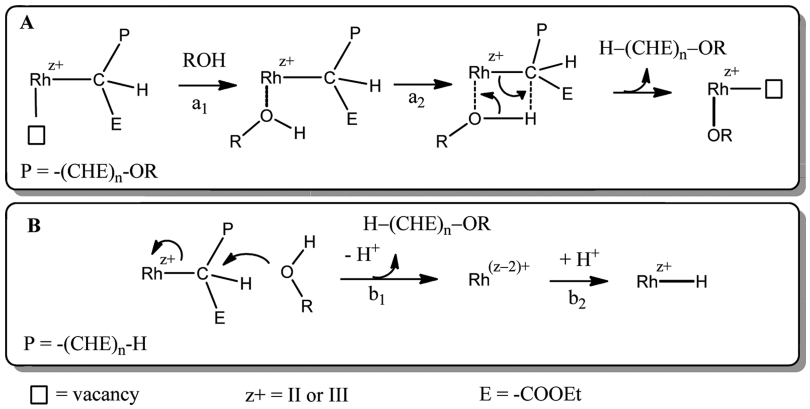
Scheme 7. Possible Nucleophilic Pathways for Alcohol-Mediated Chain-Transfer[a]



[a]Mechanism **A** involves alcohol coordination (a_1) followed by (σ-bond metathesis type) intramolecular proton transfer (a_2). Mechanism **B** involves direct S_N2-type nucleophilic attack of the alcohol at the Rh–C bond (b1) followed by protonation of Rh^I to form a Rh–H species (b_2). Note that a new chain starts growing at a Rh–OR moiety in case of pathway A, but at a Rh–H moiety in case of pathway B.

For higher-valent (e.g., Rh^{III} or Rh^{II}), hence more electrophilic active rhodium species, both pathways (A and B in Scheme 7) become preferred over pathway I in Scheme 6. The rate of these processes should correlate with the nucleophilicity of the alcohol rather than its acidity, and this is exactly what is observed: The obtained chain-lengths are clearly correlated with the nucleophilicity of the applied alcohol (Table 5). This is an important mechanistic observation, because the involvement of higher-valent electrophilic Rh^{II} or Rh^{III} species is not directly expected when starting from the applied Rh^I oxidation state precatalysts. These observations further underline the importance of the initial catalyst activation process.

We consider pathway B in Scheme 7 less likely than pathway A. It is doubtful if the sp^3 carbon atom is sterically suitably accessible and if the Rh–C(sp^3) bond is sufficiently polarized toward the (less electronegative) Rh atom to allow S_N2-type nucleophilic attack at this carbon atom from outside by an alcohol (b_1, pathway B). In fact there are only a few rare precedents for related reactions at transition metals.[71] In contrast, pathway A involves a more common intramolecular (σ-bond metathesis type) protonolysis of the Rh–C bond with a normal Rh–C polarization. Furthermore, the observation of proton-terminated H–$(CHCO_2Et)_n$–H oligomers (vide supra) advocate the viability of a (nucleophilic) protonolysis mechanism (such as pathway A, Scheme 7). Hence, combined with the nucleophilic nature of the alcohol-mediated chain-transfer process, we consider pathway A in Scheme 7 as the most likely chain-transfer pathway.[72]

CONCLUSIONS

Detailed end-group analysis, dilution-kinetic studies, and a comparison of the activity of well-defined catalysts containing a preformed Rh–C bond has provided valuable new mechanistic information about Rh-mediated carbene polymerization reactions. The obtained data unveil the mechanisms of chain-initiation and chain-termination during the polymerization process, and shed new light on the processes leading to catalyst activation. The use of well-defined Rh^I(cod)-alkyl, aryl, and allyl complexes does *not* lead to better initiation efficiencies or higher polymer yields, thus pointing to a more complex catalyst activation processes under the applied reaction conditions. Indeed, dilution-kinetic studies reveal a complex, multistep catalyst activation process. Catalyst modification first leads to oligomerization activity with a suppressed tendency toward β-hydrogen elimination, and accordingly a shift to saturated oligomeric chains that are generated by protonolysis. Further catalyst modifications lead to a shift from atactic oligomerization to stereoregular high molecular weight polymerization activity. Remarkably, under diluted conditions the activity of two different polymer forming species is apparent, and these species differ largely in their chain-propagation and chain-transfer behavior. This surprising result adds another remarkable aspect to this new polymerization reaction.

The chain-initiation and chain-termination processes were further investigated by detailed analysis of the oligomeric fractions by MALDI-ToF MS. Chain-initiation can occur by insertion of a preformed carbene into a Rh-ligand or Rh-hydride bond or by attack of water and/or alcohol on a Rh-carbene moiety. Chain-termination takes place mainly by (nucleophilic) protonolysis of the Rh–C bond of the growing chain. In the absence of alcohols, chain-initiation can occur by insertion of a preformed carbene into a Rh-ligand or Rh-hydride bond, but in the presence of alcohols (or water) the dominant chain-initiation process takes place by (internal or external) nucleophilic attack of the alcohol (or water) at a Rh-carbene moiety. Chain-termination mainly involves nucleophilic (σ-bond metathesis type) protonolysis, and leads to chain-transfer. A remarkable feature of the chain-transfer process is a clear correlation between the chain-length of the polymer and the nucleophilic character of the alcohol. This points to an electrophilic polymer producing Rh-species, and thereby suggests that the active species has a higher oxidation state (i.e., Rh^{II} or Rh^{III}) than the starting Rh^I precatalysts.

The results obtained in the presence of alcohols are very different than those under alcohol free conditions. In the absence of alcohols, chain-transfer is very slow compared to chain-propagation so that chain-growth can be observed in time and block-type copolymers can be prepared.[13,16,17] Addition of alcohols accelerates chain-transfer. This is a significant finding that not only features a new control-factor to steer the polymer molecular weights, but also allows true catalytic turnover.

EXPERIMENTAL SECTION

General Procedures. All manipulations, except the polymerization reactions, were performed under an argon atmosphere using standard Schlenk techniques. All solvents

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used for metal complex synthesis were dried over and distilled from sodium (diethyl ether, pentane, THF, toluene) or CaH_2 (dichloromethane, methanol). The syntheses and catalytic activity of [Rh(cod)(L-pro)] (**1**),[13,17] [Rh(dcp)(L-pro)] (**2**),[17] [Rh(nbd)(L-pro)] (**3**),[17] [Rh(dmcod)(L-pro)] (**5**),[15] [{Rh(cod)(μ-OAc)}]$_2$ (**6**),[17,34] and [Rh(cod)(gly)] (**7**)[17] have been described previously. [{Rh(cod)H}$_4$] (**9**),[35] [Rh(cod)(η^3-C_6H_9)] (**10**),[36] [{Rh(cod)(μ-CH_3)}$_2$] (**11**),[73] [{Rh(cod)(py)-(CH_3)}] (**12**),[74] [{Rh(cod)(μ-CH_2-py-6Me-*C*,*N*)}$_2$] (**13**),[75] [Rh(cod)(η^3-C_4H_7)] (**14**),[76] [Rh(cod)(η^3-Bz)] (**15**),[77] [Rh-(TACN)(Me)$_3$] (**16**),[54] [{Rh(hxd)(μ-Cl)}$_2$],[78] [{Rh(cod)(μ-Cl)}]$_2$ (**17**),[79] and $HBAr^{F80}$ were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and used without further purification.

For the polymerization reactions, chloroform (stabilized by ethanol; 0.5−1.5%w/v) and dichloromethane were purchased from Biosolve and used as such if not otherwise mentioned. Ethyl diazoacetate (EDA) was used as purchased from Aldrich (up to 15% dichloromethane, actual content determined by NMR). For inert conditions, the experiments were undertaken under an argon atmosphere in flame-dried glassware. For some of the experiments, chloroform was shaken with concentrated H_2SO_4 to remove ethanol, washed extensively with water, dried and distilled over $CaCl_2$, degassed and stored over molecular sieves at −20 °C. EDA was washed as a diethyl ether solution with aq. Na_2CO_3, dried over $MgSO_4$, distilled, degassed, and stored at 4 °C over molecular sieves in the dark.

NMR spectroscopy experiments were carried out on a Varian Inova 500 spectrometer (500 and 125 MHz for ^{1}H and ^{13}C, respectively) or a Varian Mercury 300 spectrometer (300 and 75 MHz for ^{1}H and ^{13}C, respectively). Assignment of the signals was aided by COSY, ^{13}C HSQC and APT experiments. Solvent shift reference for ^{1}H NMR spectroscopy: $CDCl_3$: 7.26 ppm; for ^{13}C NMR spectroscopy: $CDCl_3$: 77.0 ppm. Abbreviations used are s = singlet, d = doublet, dd = doublet of doublets, m = multiplet). Elemental analyses (CHN) were performed by the Kolbe analytical laboratory in Mülheim a/d Ruhr (Germany). Molecular-weight distributions were measured using size-exclusion chromatography (SEC) on a Shimadzu LC-20AD system with two PLgel 5 μm MIXED-C columns 300 mm × 7.5 mm (Polymer Laboratories) in series (1 mL/min and T = 35 °C) or with Waters Styragel HR1, HR2, and HR4 (300 mm × 7.8 mm) columns in series (1 mL/min and T = 40 °C) and a Shimadzu RID-10A refractive-index detector, using dichloromethane as mobile phase. Polystyrene standards in the range of 760−1,880,000 g/mol (Aldrich) were used for calibration. Further abbreviations used in the text: AcO = acetate, cod = 1,5-cyclooctadiene, dcp = *endo*-dicyclopentadiene, dmcod = 1,5-dimethylcyclooctadiene, gly = glycinate, hxd = 1,5-hexadiene, Mes = mesityl, nbd = norbornadiene, pro = prolinate, py = pyridine, Bz = benzyl, EDA = ethyl diazoacetate, and PEA = poly(ethyl 2-ylidene-acetate).

Synthesis of [Rh(hxd)(L-pro)] (4). A solution of L-proline (166 mg, 1.4 mmol) and sodium hydroxide (58 mg, 1.4 mmol) in methanol (8 mL) was added to an orange suspension of [{Rh(hxd)(μ-Cl)}$_2$] (318 mg, 0.7 mmol) in methanol (5 mL). The obtained clear orange solution was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the yellow solid was extracted with dichloromethane (20 + 10 + 10 mL). The product was recrystallized from hot methanol, yielding orange crystals suitable for X-ray diffraction (148 mg, 0.5 mmol, 35%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) (mixture of two isomers): δ 4.81 (br m, 1H, C*H*═CH_2), 4.68 (br m, 1H, C*H*═CH_2), 4.10 (br m, 1H, C*H*═CH_2), 3.90 (d, J = 7 Hz, 1H, CH═CH_2), 4.0−3.8 (br m, 4H, 2× COO−CH, NH, C*H*═CH_2), 3.65 (br m, 1H, NH), 3.59 (d, J = 7 Hz, 1H, CH═CH_2), 2.99 (br m, 2H, 2× NH−CH_2), 2.92 (d, J = 7 Hz, 1H, CH═CH_2), 2.87 (d, J = 13 Hz, 1H, CH═CH_2), 2.65 (br m, 1H, CH_2═CH−CH_2), 2.47 (br m, 3H, 2× CH═CH_2, CH_2═CH−CH_2), 2.33 (br m, 1H, CH_2═CH−CH_2), 2.3−2.0 (br m, 6H, CH═CH_2, CH_2═CH−CH_2, 4× COO−CH−CH_2), 2.0−1.9 (br m, 3H, CH_2═CH−CH_2, 2× NH−CH_2−CH_2), 1.85 (d, 1H, J = 13 Hz, CH═CH_2), 1.7−1.5 (br m, 3H, 2× NH−CH_2−CH_2, CH_2═CH−CH_2), 1.50 (br m, 1H, CH_2═CH−CH_2), 1.20 (br m, 1H, CH_2═CH−CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 89.8, 89.4 (br, 2× *C*H═CH_2), 78.3, 77.5 (br, 2× *C*H═CH_2), 67.1, (br, CH═CH_2), 64.1 (COO−CH), 62.5 (br, CH═*C*H_2), 53.0 (br, CH═*C*H_2), 49.5, 49.4 (br, 2× NH−CH_2), 48.5 (br, CH═*C*H_2), 29.8 (br, 2× COO−CH−CH_2), 25.3 (br, 2× NH−CH_2−*C*H_2) ppm (the C═O and CH_2═CH−*C*H_2 signals were not observed). Elemental analysis for $C_{11}H_{18}NO_2Rh$: calcd. C 44.16, H 6.06, N 4.68; found C 43.93, H 6.01, N 4.62%. Summary of the crystal data for: **4**, $C_{11}H_{18}NO_2Rh$, M_r = 299.17, crystal size = 0.20 × 0.06 × 0.05 mm, orthorhombic, space group: $P2_12_12_1$, a = 10.3322(4) Å, b = 10.5059(5) Å, c = 10.5751(5) Å, V = 1147.53(9) Å^3, Z = 4, ρ_{calcd} = 1.732 g cm^{-3}, F(000) = 608, μ(MoKα) = 14.68 cm^{-1}, T = 208(2) K, λ(MoKα) = 0.71073 Å, θ range = 2.73 to 27.49°, reflections collected = 12655, unique =2624 (R_{int} = 0.0326), final R indices [$I > 2\sigma(I)$] = R_1 = 0.0254, wR_2 = 0.0422, R indices (all data) = R_1 = 0.0300, wR_2 = 0.0454. See Supporting Information for more details.

Synthesis of [Rh(cod)(PPh_3)(Mes)] (8).[81] Mesityllithium was prepared by addition of *n*-butyllithium (0.4 mL; 1 mmol of a 2.5 M solution in hexanes) to a cooled (−50 °C) solution of 2-bromomesitylene (0.15 mL; 200 mg; 1 mmol) in tetrahydrofuran (5 mL). The solution was stirred for 10 min and subsequently warmed to room temperature. A yellow solution of [{Rh(cod)(μ-Cl)}]$_2$ (123 mg; 0.25 mmol) and triphenylphosphine (295 mg; 1.13 mmol) in tetrahydrofuran (10 mL) was added to the solution at room temperature. After stirring the obtained orange solution for 30 min, methanol (2 mL) was added. The solvent was removed in vacuo, and the product was purified by column chromatography (aluminum oxide 90 active neutral (Merck), toluene). The yellow fraction was collected, and the solvent was evaporated. Washing with pentane (3× ∼1 mL) and drying in vacuo afforded an orange solid (110 mg; 37%). Cooling (−20 °C) a solution of **7** in *n*-hexane yielded crystals suitable for X-ray diffraction.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.34−7.28 and 7.24−7.18 (m, 15H, PPh_3), 6.38 (s, 2H, CH_{Mes}), 4.66 (m, 2H, CH═CH), 3.67 (m, 2H, CH═CH), 2.5−2.3 (m, 4H, CH_2−cod), 2.37 (s, 6H, *o*-Me), 2.2−2.1 (m, 2H, CH_2−cod), 2.1−2.0 (m, 2H, CH_2−cod), 2.12 (s, 3H, *p*−Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 142.54 (d, J = 2 Hz, C_q), 134.10 (d, J_{C-P} = 11 Hz, PPh_3−CH), 133.96 (s, C_q), 133.68 (s, C_q), 131.10 (s, C_q), 129.02 (d, J_{C-P} = 2 Hz, PPh_3−*p*−CH), 127.50 (d, J_{C-P} = 9 Hz, PPh_3−CH), 126.22 (s, Mes−CH), 93.67 (dd, $^1J_{C-Rh}$ = 10 Hz, $^2J_{C-P}$ = 10 Hz, CH═CH *trans* to PPh_3), 86.12 (d, $^1J_{C-Rh}$ = 7 Hz, CH═CH *trans* to Mes), 31.01 (s, cod−CH_2), 30.51 (d, $^3J_{C-P}$ = 2 Hz, cod−CH_2), 26.04 (s, CH_3), 20.58 (s, CH_3) ppm. ^{13}P NMR (121 MHz, $CDCl_3$, 298 K): δ 25.70 (d, $^1J_{P-Rh}$ = 181 Hz) ppm. Elemental analysis for $C_{35}H_{38}PRh$: calcd. C 70.94, H 6.46; found C 71.27, H 6.29%.

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Summary of the crystal data for: **8**, $C_{35}H_{38}PRh$, M_r = 592.53, crystal size =0.27 × 0.15 × 0.08 mm, monoclinic, space group: *C2/c*, *a* = 32.151(4) Å, *b* = 9.3724(10) Å, *c* = 19.869(3) Å, β = 107.394(9)°, *V* = 5713.5(13) Å^3, *Z* = 8, ρ_{calcd} = 1.378 g cm^{-3}, *F*(000) = 2464, μ(MoKα) = 6.76 cm^{-1}, *T* = 208(2) K, λ(MoKα) = 0.71073 Å, θ range = 2.15 to 27.50°, reflections collected = 84976, unique = 6567 (R_{int} = 0.0551), final *R* indices [$I > 2\sigma(I)$] = R_1 = 0.0403, wR_2 = 0.0905, *R* indices (all data) = R_1 = 0.0502, wR_2 = 0.0940. See Supporting Information for more details.

Standard Experiment for Polymerization of Carbenes. EDA (2 mmol) was added to a yellow solution of catalyst precursor (0.04 mmol or less according to chosen ratio or complex composition) in chloroform (5 mL) or dichloromethane (5 mL). Upon addition, N_2 gas evolution was visible, and the color of the reaction mixture became slightly darker. The mixture was stirred for 14 h at room temperature. Subsequently the solvent was removed in vacuo, and methanol was added to the oily residue. The precipitate was centrifuged and washed with methanol until the washings were colorless. The resulting white powder was dried in vacuo and identified as poly(ethyl 2-ylidene-acetate) (PEA) using ^{1}H NMR spectroscopy. For the dilution experiments larger amounts of chloroform were used.

Polymerization of Carbenes with Catalyst Precursor 1. Alcohol or water and subsequently EDA (2 mmol) were added to a yellow solution of **1** (0.04 mmol) in chloroform (5 mL). Upon addition, gas evolution was visible and the color of the reaction mixture became slightly darker. The mixture was stirred for 14 h at room temperature, then the solvent was removed in vacuo and methanol added to the oily residue. The precipitate was centrifuged and washed with methanol until the washings were colorless. The resulting white powder was dried in vacuo and identified as PEA using ^{1}H NMR spectroscopy.

Polymerization of Carbenes with Catalyst Precursors 10, 14, and 15. The more sensitive compounds **10**, **14**, and **15** were handled under inert conditions, solved in 5 mL of degassed dichloromethane and only exposed to air when EDA was added. Subsequent procedure as above.

Polymerization of Carbenes with Catalyst Precursor 11.[73] A suspension of [{Rh(cod)(μ-Cl)}$_2$] (39 mg; 0.08 mmol) in diethyl ether was cooled to −70 °C. Methyllithium (0.1 mL; 0.16 mmol; 1.6 M in Et_2O) was added, and the obtained orange solution was stirred for 1 h at −70 °C. The clear orange solution was warmed to −40 °C and EDA (3.9 g; 32 mmol) was added. The color of the reaction mixture became darker and then yellow. No N_2 gas evolution was observed at this point. The reaction vessel was placed in an ice bath and stirred for 2 h, during which gas evolved, and the color of the reaction mixture turned orange. After 45 min at 0 °C the mixture became turbid. The reaction mixture was stored overnight at 4 °C. After warming to room temperature, a white precipitate was visible in the orange solution. The solid product was filtered and washed with diethyl ether and dried in vacuo. Yield: 80 mg; 3%.

Polymerization of Carbenes with Catalyst Precursor 12.[74] Complex **12** was prepared from [{Rh(cod)(μ-Cl)}$_2$] (20 mg; 0.04 mmol), methyllithium (0.05 mL; 0.08 mmol; 1.6 M in diethyl ether), and pyridine (0.01 mL; 0.1 mmol) in diethyl ether (20 mL). Without isolation, EDA (0.9 g; 8 mmol) in dichloromethane (10 mL) was added to the reaction mixture. The color of the solution changed from yellow to orange. After this as described for the standard experiment. Yield: 40 mg; 6%.

Polymerization of Carbenes with Complex 16. EDA (0.5 mL) was added to a solution of **16** (0.02 g; 0.04 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 2 h during which no N_2 gas evolution was observed. Subsequently, $HBAr^F$ (64 mg; 0.07 mmol) was added. Analysis by ^{1}H NMR spectroscopy showed that no reaction occurred.

Polymerization of Carbenes with Catalyst Precursor 17. EDA (2 mmol) was added to a yellow solution of **17** (0.02 mmol) in dichloromethane (5 mL) with or without an alcohol (1 mL). The mixture was stirred for 14 h at room temperature and then worked up as described above.

MALDI-ToF Mass Spectrometry. The mass spectra were recorded using a Kratos Axima-CFR MALDI-ToF mass spectrometer (Kratos Analytical Ltd., Manchester, England), equipped with a nitrogen laser (λ = 337 nm), operating with a pulse repetition rate of 10 Hz. Positive ion spectra were recorded in reflectron mode, accumulating at least 100 acquisitions. Ions were accelerated at 20 kV, applying a pulsed extraction delay time optimized for *m*/*z* 1000. The instrument was externally calibrated, using five peptide solutions in the mass range of 700 to 5700 Da. For these solutions a maximum deviation of 50 mDa of the true mass was found. The matrix, 2-(4-hydroxyphenylazo)benzoic acid (HABA, 20 mg/mL) and the oligomers (7 mg/mL) were dissolved in THF, the polymers (7 mg/mL) were dissolved in chloroform. The measurements were performed with and without the addition of salts (sodium and lithium trifluoroacetate).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected structural data of complexes **4** and **8** obtained by X-ray analysis, the CIF-files, additional characterization of the oligomer fraction by IR spectroscopy and elemental analysis, a complete list of all recorded MALDI-ToF mass spectra of the oligomers and a conclusive discussion of the assignments of series, selected NMR spectra of the oligomers, and an overlay of the SEC-traces of the polymers as obtained in the experiments described in Table 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Despite the fact that the oligomers and the polymers[17] are formed from different active species, they are both formed by a (migratory) carbene insertion mechanism (see Scheme 1) as revealed by the clear carbene-monomer repetitive patterns in the mass spectra. The ill-defined structure of the oligomers is best explained by rapid β-H elimination and reinsertion, which is somehow suppressed for the active species that forms the polymers.[32] We show in the following section that the findings from the oligomer end-group analysis can be used to accelerate chain-transfer in the polymerization reaction, thus showing that chain-initiation and chain-termination processes for the polymer and oligomer forming species are similar.
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(37) See the Supporting Information for the complete mass spectra of the oligomeric fractions obtained with precatalysts 1−10 and additional information.
(38) Hydroxyl groups were already detected as end-groups in polymer samples produced by Ir catalysts.[13]
(39) This leaves the possibility that the unsaturated oligomeric chains still have Rh attached to the vinylic chain-end. Addition of Li^+ or Na^+ salts leads then to doubly charged ions which are not detected.
(40) In dichloromethane in the absence of ethanol, mainly unsaturated chains are detected in the MALDI-ToF mass spectra. However, these conditions do not lead to higher polymer yields, longer polymers or higher initiation efficiencies.
(41) The formation of saturated chains might also occur by protonation in the workup with methanol. However, since the oligomers are mainly formed in the beginning of the reaction,[17] this would mean that chain-growth would stop with the metal atom still attached to the chain. This seems unlikely, also in view of the observed ethoxy and hydroxyl end-groups.
(42) Chain-transfer initiated by protonation also explains why labeling experiments and addition of competing olefins does not lead to a change of the molecular weight of the oligomers.[32] It might well be that β-H elimination occurs only once and/or for only one active species. Indeed, we do not find unsaturated chains with the ethoxy end-group, indicating that both mechanisms do not occur simultaneously.
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(55) We calculate the initiation efficiency as the number of formed polymer chains per Rh center. Of course this number only reflects the true initiation efficiency if no chain-transfer takes place (as was demonstrated under normal conditions).[17]
(56) We used 1.75 equiv of $HBAr^F$ to generate a mixture of the mono- and dication. It was shown by Flood and co-workers that the dicationic complex is more active in ethylene polymerization.[51]
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(58) The increased yields observed upon using higher amounts of solvent (from which EtOH was removed) could in part be caused by a higher absolute amount of water remaining as trace amounts in the solvent.
(59) This was confirmed by repeating the reactions under diluted conditions (70 mL solvent) in chloroform containing different amounts of EtOH (in the range of 0−5%). These data clearly show that for both species **A** and species **B** the molecular weight of the polymer they produce drops substantially in the presence of higher EtOH concentrations. See Figure S4−1 in the Supporting Information.
(60) At high concentrations, the molecular weight is much lower after this short period.[17]

(61) Monitoring the reaction with EDA at *higher concentrations* (5 mL of solvent volume) clearly allowed us to observe the chain-growth process in time, which is completely dominated by the activity of species **A** under these more concentrated conditions (the conditions of most of our previous experiments), and proceeds quite slowly (over a course of ~14 h).[17] This enabled us to prepare block copolymers using two different diazoesters in our previous studies.[16] Under *diluted conditions* this behavior can still be observed for the polymer produced by species **A**, which grows in time (see Figure 8), but not for **B**.
(62) We can exclude that **A** and **B** are in rapid equilibrium with each other, because that would lead to an averaged activity producing polymer with a monomodal molecular weight distribution.
(63) The observation that traces of water have a strong influence on the yield was confirmed in several repeated experiments.
(64) In "normal" chloroform the amount of ethanol varies according to the supplier between 0.5 and 1.5%, which corresponds to ~20−60 equivalents. A comparison between entries 1, 2, 12, 13, and 15 in Table 4 shows that the resulting yields are most probably a combination of the influence of the stabilizer and traces of water.
(65) Chain-transfer also explains the higher polymer yields obtained using lower alcohol concentrations, but under these conditions we cannot exclude an additional beneficial effect of the added alcohols on the formation of the active Rh-species.
(66) The lower nucleophilicity of water compared to methanol and ethanol also explains why the addition of water has a smaller influence on the activation efficiency in the experiments presented in Table 5 (N = 5.20 and pK_a = 31.4). However, the low solubility of water in chloroform may also contribute to these observations.
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