In situ generation of highly active olefin metathesis initiators

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Abstract

A ruthenium based benzylidene complex bearing an *O,N*-bidentate Schiff base ligand exhibits poor olefin metathesis activity but generates a highly active catalyst system when treated with acidic cocatalysts. Various Lewis acids were able to boost the ring opening metathesis polymerization (ROMP) of cycloocta-1,5-diene (COD). The best results were obtained with trichlorosilane (HSiCl$_3$), which was also found to improve metathesis activity of the Grubbs second generation catalyst [RuCl$_2$(=CHPh)(H$_2$IMes)(PCy$_3$)] in the ROMP of COD and the ring closing metathesis (RCM) of diethyl diallylmalonate.
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1. Introduction

In the past several years, extensive research made olefin metathesis evolve towards a reaction method with numerous applications in polymer, inorganic and organic chemistry [1]. The search for efficient olefin metathesis initiators has culminated in the discovery of well-defined ruthenium carbene catalysts, such as the Grubbs first generation catalyst **1** and the Grubbs second generation catalyst **2** [2]. To expand the scope of this ruthenium family, a number of different derivatives have been investigated and described in literature. A possible approach is the coordination of so-called *dangling* ligands, which gives access to robust and stable catalysts [3–11]. Catalyst **3**, which bears an *O,N*-chelating Schiff base ligand, is air and moisture stable and shows negligible olefin metathesis activity at room temperature. Its *dangling* ligand stabilizes the resting state of the catalyst while one coordination site becomes available at elevated temperature [6]. Next to heat activation, a suitable activation strategy is the addition of cocatalysts which

stimulate the dissociation of a ligand to generate a coordinatively unsaturated species. Common cocatalysts are Brönsted and Lewis acids [7,12–17].
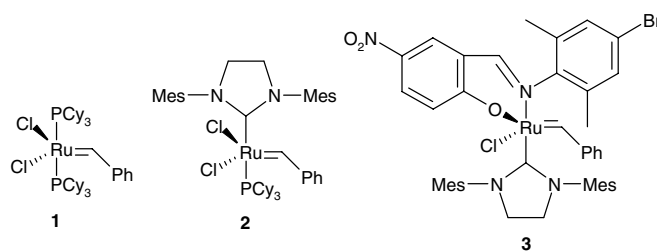
In this contribution, we wish to report on the conditions under which the in situ activation of catalyst **3** was achieved. The observation that trichlorosilane (HSiCl$_3$) addition allowed substrate/catalyst ratios beyond the reach of the Grubbs catalyst **2** prompted us to examine a range of chlorosilanes and Lewis acids as activators. To compare the catalytic activity of the different catalytic systems, we focused on their performance in the ROMP reaction of the low strain cyclic olefin *cis,cis*-cycloocta-1,5-diene (COD) and the RCM of diethyl diallylmalonate.

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2. Results and discussion

As witnessed by Fig. 1, complex **3** shows low activity in the ROMP of COD. This should be attributed to an extremely slow initiation step requiring dissociation of the N-arm of the Schiff base; a process that is unfavorable due to chelate effects. Also Grubbs catalyst **2** displays a significant initiation period, illustrating its low phosphine dissociation rate [18–20]. Catalyst initiation of both complexes was found to be triggered by the addition of trichlorosilane (HSiCl₃). A similar activity enhancement was obtained in the RCM of diethyl diallylmalonate. (Fig. 2) Hitherto, no effective phosphine scavengers were reported in literature for the Grubbs second generation complex **2** [21]. The potential of HSiCl₃ as activating agent was thus found to be quite appealing (Table 1, entries 1–4).

In situ activation of the Schiff base catalyst **3** is of particular interest for reaction injection molding (RIM) applications. In a typical RIM process an inactive procatalyst (feed 1) is combined with a cocatalyst (feed 2) just before injection into the reaction mold. Mixing then allows the formation of an active catalyst which starts the polymerization. When thinking of commercial applications, low catalyst loadings are critical. Entries 6–8 in Table 1 demonstrate that when HSiCl₃ was used as activator, remarkably high turn over numbers were achieved, resulting in nice colorless polymers. The polymers were analyzed by GPC to determine their molecular weight and polydispersity, and by ¹³C NMR to obtain the *cis*-fraction of the double bonds. Secondary chain transfer causes a higher *trans*-olefin content and shorter polymer chains.

Intrigued by these results more experiments were carried out applying different cocatalysts. All tested silane compounds HSiMeCl₂, HSiMe₂Cl, SiMe₂Cl₂ and SiCl₄ were found to activate complex **3** (Table 2, entries 1–4). Furthermore, polymerization was accelerated by the strong Lewis
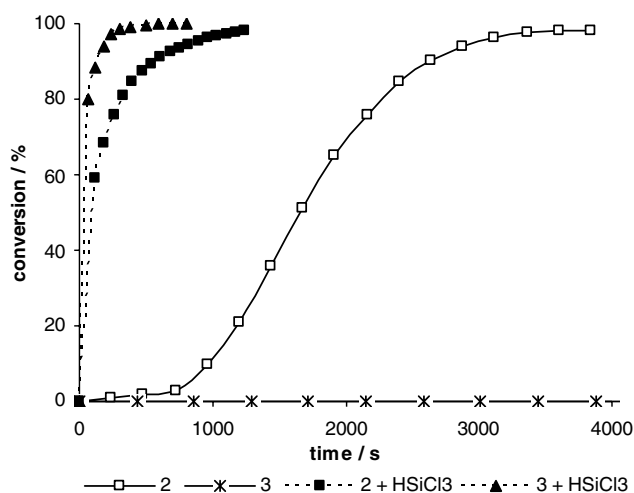

Fig. 2. Monitoring RCM of diethyl diallylmalonate via ¹H NMR spectroscopy (CD₂Cl₂, 25 °C) cat. conc. = 4.52 mM. cat./substrate/HSiCl₃ = 1/200/25. HSiCl₃ was diluted in substrate prior to addition.

acids BF₃ and AlCl₃ (Table 2, entries 5–7). Entry 6 shows that 1 equiv of a strong Lewis acid was sufficient for a fast reactivity enhancement of the Schiff base catalyst. Also CuCl, a known phosphine scavenger, was used as activating species (Table 2, entries 8–9). The activation was little effective, which we assign to slow reaction between the undissolved CuCl and the ruthenium complex. CuCl is known to activate Grubbs complexes by the formation of insoluble phosphine–copper adducts, but was not reported before to activate a phosphine free olefin metathesis initiator [22–24].

NMR-scale experiments were carried out to gain some understanding on the activation mechanism. Fig. 3 shows parts of the ¹H spectra of complex **3** in reaction with diverse acids. The spectrum resulting from reaction with ethereal HCl was included for comparison. ¹H signals at δ 10.03 (s, Ar–C(=O)H), δ 8.58 (singlet, O₂NC–CH of nitrosalicyl aldehyde moiety) and δ 8.42 (d, O₂NC–CH–CH of nitrosalicyl aldehyde moiety) indicate decondensation of the imine bond into the corresponding aldehyde and amine (Fig. 3 (ii)). Reaction of **3** with a large excess (70 equiv) of dry HSiCl₃ afforded a ¹H spectrum showing only signals of the starting complex and of HSiCl₃; no shifts of catalyst protons were observed (Fig. 3 (iii)) This took us by surprise since this mixture polymerized COD without any initiation period, indicating a fast reaction between catalyst and silane. Moreover, the residue upon evaporation of a toluene solution of **3** and HSiCl₃ was analyzed as pure complex **3** displaying no metathesis activity at room temperature. Addition of a new small portion of HSiCl₃ resulted again in quick activation allowing immediate ROMP reaction. We therefore assume that the trichlorosilane forms an adduct with the two electrons on the nitrogen of the Schiff base and this in a reversible way. Such a hypothesis finds support in recent research from Nakash et al. describing the fast, reversible reaction between silanes and pyridine

Fig. 1. Monitoring ROMP of COD via ¹H NMR spectroscopy (CDCl₃, 20 °C)—conditions: cat./COD/acid = 1/3000/70, cat. conc. = 0.452 mM. HSiCl₃ was diluted in COD monomer prior to addition.
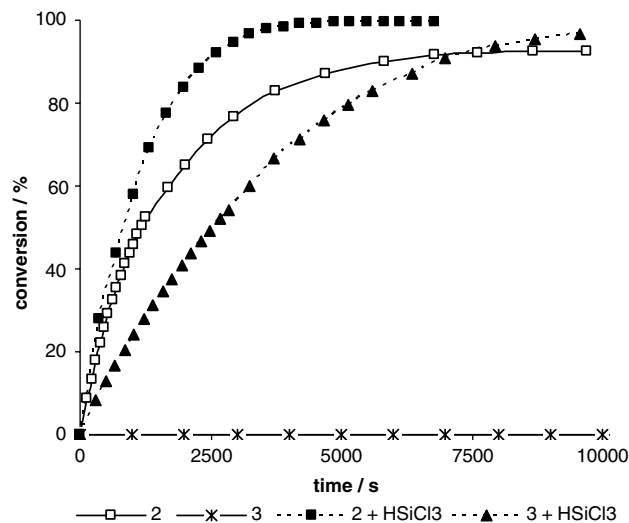
Table 1
ROMP of COD

Entry	Catalyst	Acid	Catalyst/COD/acid	Time (min)	Conversion[a] (%)	cis-(%)[b]	M_n[c]	PDI[c]
1	**2**	–	1/3000/0	30	100	13	55800	1.7
2	**2**	–	1/30000/0	[d]	31	51	80400	1.7
3	**2**	HSiCl₃	1/30000/70	30	46			
				60	100	25	134000	1.8
4	**2**	HSiCl₃	1/300000/300	60	12			
				[d]	[e]	70	161700	1.7
5	**3**	–	1/300/0	60	0	–	–	–
6	**3**	HSiCl₃	1/30000/70	30	93			
				60	100	14	114700	1.9
7	**3**	HSiCl₃	1/300000/300	30	78			
				60	85			
				[d]	100	46	269000	1.7
8	**3**	HSiCl₃	1/3000000/1000	30	21	–	–	–
				[d]	[e]	64	363000	1.7

[a] Determined by ^{1}H NMR spectroscopy.
[b] Percent olefin with *cis*-configuration in the polymer backbone—ratio based on ^{13}C NMR spectra (δ 32.9: allylic carbon *trans*—27.6: allylic carbon *cis*).
[c] Determined by GPC (CHCl₃) analysis. Results are relative to polystyrene standards.
[d] Overnight.
[e] Decomposition of catalyst, conversion not further increased.

Table 2
Conversions obtained from the ROMP of COD using catalyst **3**

Entry	Acid	Catalyst/COD/acid	Time (min)	Conversion[a] (%)	cis-(%)[b]	M_n[c]	PDI[c]
1	HSiMeCl₂	1/30000/70	30	91			
			60	100	36	169400	1.7
2	HSiMe₂Cl	1/30000/70	30	50			
			60	55			
			[d]	[e]	61	118200	1.7
3	SiMe₂Cl₂	1/30000/70	120	6			
			[d]	7	79	74700	1.7
4	SiCl₄	1/30000/70	30	77			
			60	89			
			[d]	93	64	181800	1.7
5	BF₃[f]	1/30000/70	30	13			
			120	[e]	72	78100	1.7
6	AlCl₃[g]	1/3000/1	30	100	17	54100	1.8
7	AlCl₃[g]	1/30000/70	60	7			
			[d]	15	74	82900	1.7
8	CuCl	1/3000/100[h]	60	41			
			120	63			
			[d]	100	38	72900	1.8
9	CuCl	1/30000/70[h]	120	2	–	–	–

[a] Determined by ^{1}H NMR spectroscopy.
[b] Percent olefin with *cis*-configuration in the polymer backbone—ratio based on ^{13}C NMR spectra (δ 32.9: allylic carbon *trans*—27.6: allylic carbon *cis*).
[c] Determined by GPC (CHCl₃) analysis. Results are relative to polystyrene standards.
[d] Overnight.
[e] Decomposition of catalyst, conversion not further increased.
[f] BF₃ solution in Et₂O.
[g] AlCl₃ solution in THF.
[h] CuCl = undissolved.

[25]. The formation of a similar silane–amine complex between HSiCl₃ and the Schiff base imine moiety in **3** would imply that electron donation from the basic nitrogen towards the ruthenium center is prevented. A 14-electron active species is formed which enables olefin coordination and fast metathesis reaction. On the other hand, lack of an observable reaction between HSiCl₃ and **3** might be due to the fact that only an undetectable small amount of catalyst initiates and hence catalyzes the reaction. However, it is plausible that the use of over 70 equiv of acid would be sufficient to activate the Schiff base catalyst to an ^{1}H NMR detectable extent. The addition of a small excess of the strong Lewis acid BF₃ to complex **3**, led to quick loss of alkylidene moiety. Reaction of 1 equiv AlCl₃ with the Schiff base complex proceeded somewhat slower and allowed the observation of a small ^{1}H signal at 16.75 ppm. After 15 min
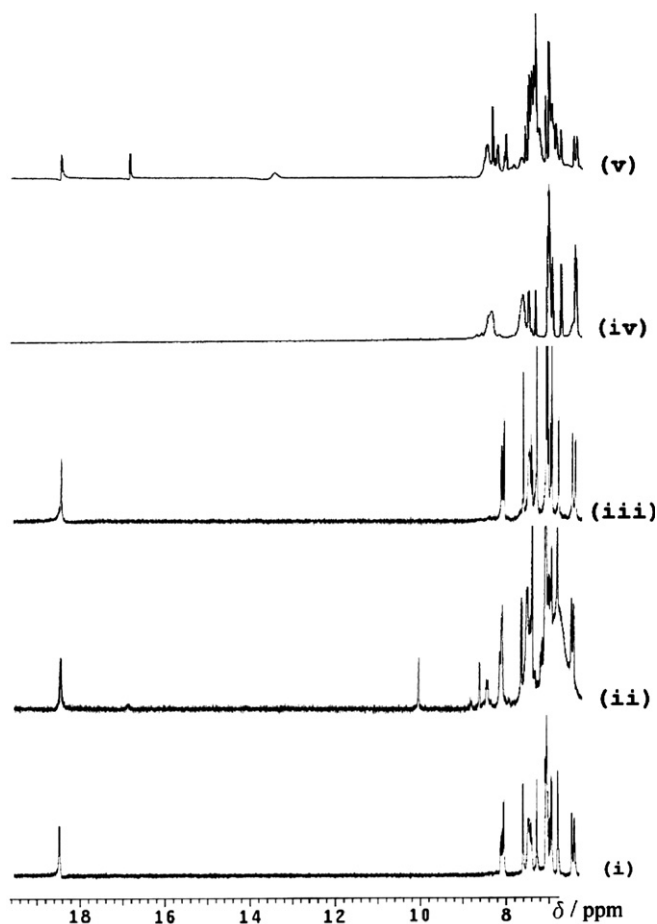
Fig. 3. ^{1}H NMR spectra in CDCl$_3$. For clarity, only part of the spectra are shown: (i) **3**, (ii) **3** + 5 equiv HCl soln in Et$_2$O (15 min), (iii) **3** + 70 equiv HSiCl$_3$ (after 5 min, unchanged after 2 h, 4 h), (iv) **3** + 1 equiv AlCl$_3$ soln in THF (15 min), (v) **3** + 1 equiv AlCl$_3$ soln in THF (3 h).

of reaction time this broad signal had almost faded away, and virtually no resonance of an α-benzylidene proton was left (Fig. 3 (iv)). Nevertheless, this solution still exhibited very good ROMP activity when added to COD. Therefore monitoring of the reaction was continued and after more than 2 h, ^{1}H resonances appeared at δ 18.51 and δ 16.91 (Fig. 3 (v)). While the most downfield signal likely corresponds to the starting complex, the δ 16.91 signal should be assigned to the α-benzylidene proton of a new in situ generated catalyst. A resonance with approximately the same chemical shift was found for the HCl activation. A broad signal at δ 8.49 was ascribed to protonation of the Schiff base N-atom, while the one at δ 13.52 results from a protonated phenoxide moiety of the Schiff base. These are convincing arguments for the in situ generation of HCl caused by reaction of the initially added AlCl$_3$. However, since the catalyst was found to be initiated immediately upon acid addition and the HCl generation was retarded as much as possible by using moisture free conditions, simple protonation of the Schiff base N is expected to be of minor importance in the actual polymerization process.

All of these observations clearly do not allow us to propose one unambiguous mechanism for the acid activation. Moreover, it should be noted that for the Grubbs second generation catalyst **2**, the activation process will proceed in a different way since no Schiff base is present. However, it can be assumed that the electron pair of the phosphine and the electron pair on the nitrogen of the Schiff base react with HSiCl$_3$ in a rather analogous way.

3. Conclusion

The main achievement of this study was the development of catalyst systems allowing the generation of large amounts of polymer using small catalyst loadings. Studies aimed at applying these in situ activated catalysts to industrially relevant applications are currently ongoing.

4. Experimental

4.1. General remarks

Synthetic manipulations were performed under an oxygen free argon atmosphere using standard Schlenk techniques. Reactions were carried out in dried, distilled and degassed solvents. COD and chlorosilanes were dried over calcium hydride, distilled and degassed by standard freeze–pump–thaw cycles. HCl was purchased from Acros as a 1 N solution in Et$_2$O. Other chemicals were purchased from Aldrich, –BF$_3$ as a 1 N solution in Et$_2$O and AlCl$_3$ as a 0.5 M solution in THF– and used as received. NMR spectra were recorded with a Varian Unity-300 spectrometer. Complex **3** was prepared according to the literature procedure [6].

4.2. Catalytic reactions

Monitoring ROMP of COD (Fig. 1): After charging an NMR-tube with the appropriate amount of catalyst dissolved in CDCl$_3$, COD or a COD/acid mixture was added. The polymerization was monitored as a function of time at 20 °C by integrating olefinic ^{1}H signals of the formed polymer (5.38–4.44 ppm) and the consumed monomer (5.58 ppm).

Monitoring RCM of diethyl diallylmalonate (Fig. 2): An NMR-tube was charged with 0.6 mL of a catalyst solution in CD$_2$Cl$_2$ (4.52 mM or 2.712 μmol catalyst per experiment). Next, 200 equiv or 0.13 mL of diethyl diallylmalonate was added and the NMR tube was closed. HSiCl$_3$ was diluted in diethyl diallylmalonate prior to addition in such a way that the catalyst/substrate/HSiCl$_3$ ratio was 1/200/25. The progress of the ring closing reaction was monitored at 25 °C by integration of ^{1}H signals of allylic protons of the ring closed product (2.25 ppm) and of the substrate (2.64 ppm).

Representative procedure for ROMP tests (Tables 1 and 2): Prior to the polymerization experiments, various COD/acid mixtures were prepared in Schlenk tubes, which made it possible to add monomer and acid to the reaction

vials in the mentioned ratios. Small oven-dried glass vials with septum were charged with a stir bar and the appropriate amounts of catalyst taken from a CH_2Cl_2 stock solution. The dichloromethane was subsequently evaporated, and the glass vials with solid catalyst were kept under argon atmosphere. To start the ROMP test, 200 μL of toluene was added in order to dissolve the catalyst. The appropriate amount of COD/acid mixture was then transferred to the vial containing the catalyst via syringe, under vigorous stirring at room temperature. After a certain time span, a small quantity of the reaction mixture, which had become viscous, was taken out of the vial and solved in $CDCl_3$. The conversion was then easily determined by ^1H NMR spectroscopy.

4.3. Remarks

  (i) The acid/catalyst ratios varies from 1 up to 1000 which can be considered rather high. This is due to the low catalyst loadings and to the fact that acids like trichlorosilane are difficult to add in small excess when doing reproducible small scale reactions even though the acid is diluted in the monomer before addition. As a consequence of the big acid excesses, the required reaction times are often very low and the reaction mixture becomes viscous in only seconds of time. We presume that smaller excesses of acid would be sufficient to activate the catalyst in a satisfying manner, which would be possible when using bigger batches of monomer.

  (ii) All solvents were thoroughly dried in order to avoid reaction of the chlorosilanes with water leading to in situ formation of HCl.

Acknowledgements

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