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Group IV Metallocene *Bis*(trimethylsilyl)acetylene Complexes as Catalysts in the Dehydrocoupling Polymerization of 1,2-Disubstituted Hydrodisilanes

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Summary. The catalytic activities of five *bis*(trimethylsilyl)acetylene complexes of group IV metallocenes in the dehydrocoupling reaction of various 1,2-disubstituted hydrodisilanes were investigated. The reactions were monitored by GC/MS analysis in the early stages, and the polymers were characterized by NMR spectroscopy and gel permeation chromatography.

Keywords. Alkyne complexes; Dehydropolymerization; Polysilanes; Titanocene; Zirconocene; Catalysis.

Bis(trimethylsilyl)acetylen-Komplexe von Metallocenen der 4 Nebengruppe als Katalysatoren in der dehydrierenden Polymerisation von 1,2-disubstituierten Hydrodisilanen

Zusammenfassung. Die katalytische Aktivität von fünf *Bis*(trimethylsilyl)acetylen-Komplexen von Metallocenen der 4. Nebengruppe bei der dehydrierenden Polymerisation von verschiedenen 1,2-disubstituierten Disilanen wurde untersucht. Zu Beginn (während der Bildung von Oligomeren) wurden die Reaktionen mittels GC/MS verfolgt. Die erhaltenen Polymere wurden mittels NMR-Spektroskopie und Gelpermeationschromatographie charakterisiert.

Introduction

Since the discovery of the dehydropolymerization of hydrosilanes with group IV metallocenes (Eq. (1)) by *Harrod et al.* in 1985 [1], several catalyst precursors have

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been investigated with respect to this reaction. Most of them are dialkyl- or diarylmetallocenes or precursors thereof [1–4].

$$n\,RR'\mathrm{SiH}_2 \xrightarrow[-(n-1)\,H_2]{\text{catalyst}} \mathrm{H}(RR'\mathrm{Si})_n\mathrm{H} \tag{1}$$

Whereas silylmetallocene compounds can directly enter the catalytic cycle of σ-bond metathesis [5, 6], the carbon substituted metallocenes are proposed to enter the catalytic cycle *via* the naked metallocene Cp_2M. [3, 7] As metallocene-alkyne complexes are sources for Cp_2M moieties under mild conditions [8, 9], they are likely to exhibit catalytic activities similar to that of the above mentioned catalyst precursors. In a previous report the potential of these complexes in the dehydrocoupling reaction of methylphenylsilane, diphenylsilane, and phenylsilane has been demonstrated [10]. In the present study we would like to disclose our results on the catalytic behavior of the same type of metal complexes with 1,2-disubstituted hydrodisilanes. The latter are known to exhibit a chemistry different from that of phenylsilane [11–13].

Results and Discussion

The reactivities of $Cp_2\mathrm{Ti}(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})$ (**1**), $Cp_2\mathrm{Zr}(THF)(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})$ (**2**), $Cp_2\mathrm{Zr}(py)(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})$ (**3**), *rac*-$(EBTHI)\mathrm{Ti}(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})$ (**4**, *EBTHI* = ethylene*bis*(tetrahydroindenyl), and *rac*-$(EBTHI)\mathrm{Zr}(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})$ (**5**) with respect to 1,2-dimethyldisilane, 1-methyl-2-phenyldisilane, and 1,2-diphenyldisilane have been investigated. Catalysts were evaluated according to the GPC data of the produced polymers. These are shown in Table 1 for the polymerizations of 1,2-diphenyldisilane and 1-methyl-2-phenyldisilane. The polymerization experiments with 1,2-dimethyldisilane resulted in the formation of a completely insoluble material for which no GPC trace could be obtained. The early stages of the reactions were analyzed by GC/MS to obtain some insight into the structure of the polymers formed and also to learn more about the mechanism of the reactions. Both structural and mechanistic details reflected in the GC/MS data are outlined below.

^{29}Si and ^{1}H NMR spectra of the polymers were not found to be particularly useful with respect to assignments of stereoselectivity. They seem to be essentially

Table 1. GPC[a] data for the dehydropolymerization of 1,2-diphenyldisilane and 1-methyl-2-phenyldisilane catalyzed by titanocene and zirconocene alkyne complexes

	Metallocene				
Monomer	**1**	**2**	**3**	**4**	**5**
$\mathrm{H_2PhSiSiPhH_2}$	M_n = 900	1.400	1.050	–	530
———	M_w = 1.100	1.800	1.400	–	600
$\mathrm{H_2MeSiSiPhH_2}$	M_n = 1.400	2.900	1.500	940	1.050
	M_w = 2.600	16.000	2.700	1.400	1.600

[a] Obtained against polystyrene standards (eluent *THF*) of samples subjected to polymerization conditions for 7 days at 40°C

identical with those obtained from reactions catalyzed by Cp_2ZrMe_2 [11, 12] or Cp_2ZrCl_2/2BuLi. This may be caused by the higher molecular weight of the polymers in comparison to polyphenylsilane. On the other hand, in their recent review *Gauvin*, *Harrod*, and *Woo* [4] point out that what was first assigned to be a stereochemically more homogeneous polymer actually was later found to consist largely of cyclics.

Polymerization of 1,2-dimethyldisilane

The results of the polymerization reactions of 1,2-dimethyldisilane catalyzed by metallocene alkyne complexes are in good accordance with the results of *Weinberger* and *Henge* [11] who used Cp_2TiMe_2 and Cp_2ZrMe_2 as catalysts. In the reaction catalyzed by **1**, GC/MS indicates the formation of linear oligomers up to the hexasilane at the beginning of the reaction. Oligomers with even and odd numbers of Si atoms in the chain are formed to the same extent. This indicates that the disilane is cleaved in the first step of the polymer formation reaction. As the reaction proceeds, the concentrations of branched and cyclic oligomers up to the decasilane increase as indicated by GC/MS [14]. After two days of reaction at room temperature, a completely insoluble crosslinked polymethylsilane is obtained.

In the Zr catalyzed reactions (compounds **2** and **3**), more branched silanes than linear ones are formed from the beginning. The isomer patterns of the GC/MS traces obtained from the reaction catalyzed by **2** and **3** are almost identical. Insoluble polymethylsilane was obtained after two days of reaction at room temperature.

In the *Ziegler-Natta* polymerization of propene, ethylene bridged metallocenes such as ethylene*bis*(indenyl) (*EBI*) ziroconocene or ethylene*bis*(tetrahydroindenyl) (*EBTHI*) zirconocene have been found to be of particular use to control tacticity in the polymer. Reports by *Harrod* [15], *Waymouth* [16], and *Corey* [17] seem to indicate a similar effect in the dehydrocoupling polymerization of silanes.

Our experiments with *EBTHI* bridged compounds **4** and **5** gave results different from those with **1**–**3** in a sense that almost no oligomers with an odd number of Si atoms in the chain were formed. Direct coupling of the disilane predominates over the previously observed cleavage and chain growth by monosilyl observed in the polymerization of disilanes catalyzed by non-bridged catalysts. These findings suggest that the *EBTHI* ligand preferentially effects Si–H activation, whereas the *Cp* catalysts preferentially activate Si–Si bonds.

GC/MS analysis of the reaction mixtures also revealed the presence of 1,2-*bis*(trimethylsilyl)ethene and 1,2-*bis*(trimethylsilyl)ethane, which is quite unusual since 1,2-*bis*(trimethylsilyl)acetylene was observed as the only product deriving from the catalyst precursor in all other reactions studied so far.

Polymerization of 1-methyl-2-phenyldisilane

In the reactions catalyzed by **1**, **2**, and **3**, again the disilane is cleaved in the polymer formation reaction as the GC/MS analysis indicates growth of the oligomers by monosilyl units. From the MS data [14] we find that isomers in which the new silyl group is added to the phenyl substituted end of the disilane are formed to a bigger extent. Therefore, in the isomeric ratios of the trisilanes Me/Ph/Me is favoured over Ph/Me/Me and more Ph/Ph/Me is formed than Ph/Me/Ph. The same is true for the isomeric ratios of the higher oligomers. We attribute this behavior to the preferential activation of the Si–H bond in SiPhH units over those in SiMeH units. Unlike 1,2-dimethyldisilane, 1-methyl-2-phenyldisilane is also cleaved by the *EBTHI* bridged catalysts **4** and **5**. Diphenyldisilane, triphenyltrisilane, and other trisilanes are formed to a bigger extent than the direct coupling products of the starting disilane. **4** and **5** also produce a significant amount of Ph_2SiH_2. The molecular weight data of the polymers are given in Table 1.

Polymerization of 1,2-Diphenyldisilane

In the reactions with all five catalysts, triphenyltrisilane is formed besides the disproportionation products Ph_2SiH_2 and $Ph_2HSiSiPhH_2$. This again indicates polysilane formation by monosilyl units. Due to their molecular weight, higher oligomers than tetrasilane could not be detected by GC/MS.

Conclusion

The common feature of all five alkyne complexes tested as dehydropolymerization catalysts is a lowered reactivity compared to the $Cp_2M\mathrm{Me}_2$ and $Cp_2M\mathrm{Cl}_2$/2BuLi systems ($M = \mathrm{Ti, Zr}$). Whereas the achievable molecular weight of the polymers and the isomer patterns of the low molecular weight oligomers are essentially the same as in the reactions catalyzed by the analogous non-alkyne complexes, the reactions proceed much more slowly and often only at elevated temperatures (40°C). This may indicate that the alkyne ligand is not completely removed from the coordination sphere of the active metal center or still competes with the SiH substrates for the free coordination site. The addition of silane to the complexes induces a color change from black (**3**) or light red (**4**) to yellow for the Zr complexes and from yellow to dark green for Ti compounds. The colors of the reaction solutions are not as intense and appear slightly different from those usually observed in metallocene catalyzed dehydropolymerization reactions. This suggests that either the predominant metal species are different from those in non-alkyne systems or that the catalyst concentration is much lower than expected (*vide infra*).

In an attempt to obtain some information about the active catalytic species present in the system, we tried to react complexes **1** and **3** with 1,2-dimethyldisilane in stoichiometric ratios. Much to our surprise, the expected 1:1 adduct was not formed. The only products detected by NMR spectroscopy were silane oligomers and the metallocene starting materials. Since it has been recently outlined that Si–H activation can occur even in the presence of η^2-alkynyl substituents [18, 19], it appears possible that the actual catalytic species still contains the 1,2-*bis*(trimethylsilyl)acetylene ligand. A different explanation may be that only a very small amount of the complex is converted into the active species.

Experimental

Compounds **1–5** were synthesized according to Refs. [8] and [9]. For 1,2-diphenyldisilane and 1,2-dimethyldisilane, see Refs. [20] and [21]. 1-Methyl-2-phenyldisilane was obtained from *LAH* reduction of the respective triflate compound.

The polymerizations were carried out under an inert atmosphere of argon using *Schlenk* techniques. Solvents were freshly distilled from sodium/potassium alloy. In each case 0.5 ml toluene and 1 g of the monomer were added to the respective metallocene complex (1 mol%). The polymerizations of 1,2-dimethyldisilane were carried out at room temperature, all others at 40°C.

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