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New Stable Titanocene and Zirconocene Catalyst Precursors for Polysilane Synthesis *via* Dehydrocoupling of Hydrosilanes

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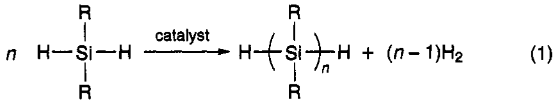
Summary: The titanium and zirconium complexes $(\eta^5\text{-}C_5H_5)_2M(OAr)_2$ *(M = Ti, Zr; Ar =* C_6H_5, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-CNC_6H_4*) are shown to be convenient, stable precursors of dehydrocoupling catalysts. Their reactions with a primary silane, at 50 °C or below, generate active catalysts for* $RSiH_3$ *dehydrocoupling at 20 °C.*

Polysilanes have a number of potential applications owing to their unusual electronic, optical, and chemical properties.[1] These polymers, in most cases, are prepared using the Wurtz coupling of dichlorosilanes by sodium.[1] Alternative polymerization reactions have been developed since they, in principle, could present significant advantages. Among other interesting methods for synthesizing polysilanes, redistribution, electrochemical, disilene polymerization, and cyclosilane ring-opening polymerization reactions have been explored.[2] Another method involves the transition-metal-catalyzed dehydrocoupling of silanes (eq 1).



$$n\ H-\underset{R}{\overset{R}{Si}}-H \xrightarrow{\text{catalyst}} H\left(\underset{R}{\overset{R}{Si}}\right)_nH + (n-1)H_2 \qquad (1)$$

The development of catalysts for the dehydrocoupling reaction began with the discovery of Harrod and coworkers that $(\eta^5\text{-}C_5H_5)_2TiMe_2$ and $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ initiated the polycondensation of primary silanes $RSiH_3$.[3] Since then, other transition-metal catalysts have been found, but the group 4 metallocene complexes provide the most active of the dehydrocoupling catalysts.[4–13] The reaction usually produces linear chains containing ca. 10–30 silicon atoms, together with cyclic oligomers. Despite their sometimes low molecular weight, the $MeSiH_3$-derived polysilanes can be converted in high yield to pure SiC.[14] We also have showed that preceramic polysilanes are easily obtained from the reaction of 1,4-disilapentane, in the presence of a titanium catalyst, and lead to high yields of SiC.[15]

We observed recently that $(\eta^5\text{-}C_5H_5)_2TiMe_2$ and $(\eta^5\text{-}C_5H_5)_2TiCl_2$/*n*-BuLi dehydrocoupling catalysts, in the presence of oxygen, can be deactivated to a latent catalytic species.[15] The latter, upon heating, regenerate an active catalyst for the dehydrocoupling reaction. This observation led us to examine the reactions of metallocene complexes containing titanium–oxygen bonds. We wish to report here that $(\eta^5\text{-}C_5H_5)_2M(OAr)_2$ species (M = Ti, Zr) are stable and tunable precursors of active catalytic species for the dehydrocoupling reaction of silanes.

Results and Discussion

We first examined the readily prepared diphenoxytitanocene $(\eta^5\text{-}C_5H_5)_2Ti(OPh_2)$[16] as a catalyst for the polymerization of phenylsilane. No reaction occurred at room temperature between $PhSiH_3$ and $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ (0.1 mol %). When it was heated to 50 °C for 15 min, the reaction mixture turned dark blue and hydrogen evolution began. The generated catalytic species was then active at room temperature, and a viscous polymer was formed after 24 h (eq 2). The polymerization rates observed and the products obtained were similar to those using $(\eta^5\text{-}C_5H_5)_2TiMe_2$[3] and $(\eta^5\text{-}C_5H_5)_2TiCl_2$/*n*-BuLi)[7] as catalysts. GPC analysis

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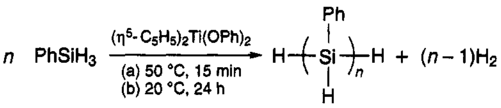
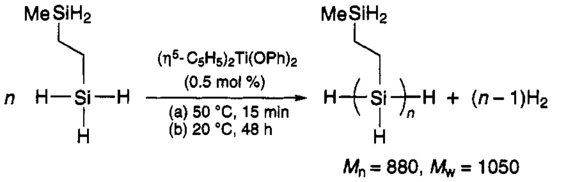


$$n\ PhSiH_3 \xrightarrow[\text{(a) 50 °C, 15 min; (b) 20 °C, 24 h}]{(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2} H\text{-}(SiPhH)_n\text{-}H + (n-1)H_2 \quad (2)$$

revealed a bimodal molecular weight distribution:[17] cyclic oligomers (25%) and linear chains (M_n = 2050, M_w = 2700) (cf. Table 1).

The phenoxytitanium complex was also found to be active for the condensation and cross-linking of 1,4-disilapentane (eq 3). Although the rate was slower than



$$n\ H\text{-}Si(H)(CH_2CH_2SiH_2Me)\text{-}H \xrightarrow[\text{(a) 50 °C, 15 min; (b) 20 °C, 48 h}]{(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2\ (0.5\ \text{mol}\ \%)} H\text{-}(Si(H)(CH_2CH_2SiH_2Me))_n\text{-}H + (n-1)H_2 \quad (3)$$

M_n = 880, M_w = 1050

for $PhSiH_3$, it was similar to that observed with $(\eta^5\text{-}C_5H_5)_2TiMe_2$ or $(\eta^5\text{-}C_5H_5)TiCl_2/2$ n-BuLi.[15] Slow rates have been reported for the condensation of alkylsilanes.[3,7] After activation of the catalyst, only the SiH_3 groups reacted at room temperature to give a linear oligomer with dangling $SiMeH_2$ groups. The latter then condensed further to a cross-linked insoluble material upon heating.

The reaction of secondary silanes occurred only at high temperature. Thus at 100 °C, Ph_2SiH_2 reacted in the presence of 0.2 mol % of $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ to give a 10% yield of the dimer $Ph_2SiHSiHPh_2$. $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ catalyst precursor does not appear to be very effective for the condensation of secondary silanes.

In all cases, an induction period and an initial heating of the titanium complex in the presence of the silane was necessary to generate an active catalytic species. This is consistent with the initial in situ reduction of the Ti−OPh complex to form a Ti−H complex.[15,18] Although we did not isolate the titanium species, this is supported by the results of the reaction of di-*n*-butylsilane. At 110 °C, $n\text{-}Bu_2SiH_2$ reacted with 5 mol % of $(\eta^5\text{-}C_5H_5)Ti(OPh)_2$ to give mono- and diphenoxysilanes in the initial stage of the reaction (eq 4). These, together with 90.6% of unreacted $n\text{-}Bu_2SiH_2$, were identified by GC/mass spectrometric analysis of the crude mixture after 30 min of reaction.

$$n\text{-}Bu_2SiH_2 \xrightarrow[(5\ \text{mol}\ \%)]{(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2} \underset{2.2\%}{n\text{-}Bu_2Si(H)(OPh)} + \underset{2.8\%}{n\text{-}Bu_2Si(OPh)_2} + \underset{4.4\%}{n\text{-}Bu_2Si(H)Si(H)\text{-}n\text{-}Bu_2} \quad (4)$$

Interestingly, the reactivity of the titanium complex can be increased. We observed that substituted diphenoxytitanocenes ($(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4R\text{-}p)_2$, R = Cl, Me, CN, OMe) react with phenylsilane at room temperature to give, after an induction period varying between 10 min and 2 h, an active catalyst leading to phenylsilane polymer with characteristics similar to those in the previous case (cf. Table 1). The use of substituted phenoxides mainly influences the induction period. It allows the generation of an active species at 20 or 25 °C. The parent phenoxide required 15 min at 50 °C. Whereas the same proportion of cyclic oligomers was obtained, a slightly higher value of average molecular weight was found for the linear chain fraction by use of the more reactive titanium catalyst precursor $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4OMe\text{-}p)_2$ (Table 1, entry 2). The results obtained with $(\eta^5\text{-}C_5H_5)_2TiMe_2$ as catalyst under the same reaction conditions are also given for comparison (cf. entry 6). Regardless of the titanium complex used, the obtained polymer exhibited similar characteristics, indicating that the actual catalyst probably consists of the same titanium species.

The use of a metal phenoxide catalyst precursor was also extended to the zirconocene complex (entries 7 and 8). Phenylsilane seemed to react at room temperature with the readily available $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$[20] with a slight hydrogen evolution, but the generation of an active catalyst required heating at 50 °C for 15 min. In this case, the polycondensation gave a lower amount of cyclic oligomers. The molecular weights generally tend to be higher with zirconium catalysts.[6,21,22] A moderate increase of M_n and M_w was found with diphenoxyzirconocene catalyst.

The complexes $(\eta^5\text{-}C_5H_5)_2M(OPh)_2$ (M = Ti, Zr) were stable for more than 24 h in the presence of the monomers at 20 °C. Upon gentle heating, they give rise to active dehydrocoupling catalysts which then induce polycondensation at 20 °C. We have previously shown the interest of using a latent catalyst in the processing of related preceramic polysilanes.[15] Diphenoxytitanocene and -zirconocene, which did not generate active catalytic species at 20 °C, represent stable latent precursors of dehydrocoupling catalysts. When substituted phenoxide complexes are used, with either electron-donating or electron-withdrawing substituents, the active catalyst formed more easily at 20 or 25 °C.

Two approaches have been previously used to obtain active catalysts: presynthesized complexes $(\eta^5\text{-}C_5H_5)_2MR_2$ and in situ generation from metallocene dichloride $(\eta^5\text{-}C_5H_5)_2MCl_2$. Disadvantages in the use of $(\eta^5\text{-}C_5H_5)_2MR_2$ catalysts include their required synthesis from a metallocene dichloride and their generally low stability. The "in situ generation" by alkylation of dichlorometallocene with butyllithium, which requires a combination of commercially available reagents, is convenient. However, we think that the metallocene diphenoxides, which are readily accessible air-stable complexes, constitute an interesting alternative catalyst source. Whereas $(\eta^5\text{-}C_5H_5)_2TiMe_2$ and $(\eta^5\text{-}C_5H_5)_2TiCl_2/BuLi$ even at 20 °C generate active catalytic species, diphenoxytitanocene and -zirconocene are stable at this temperature and only require a gentle heating in order to generate the catalytic species which, once formed, are active at 20 °C. The monomer itself serves as a reagent to generate the active species. The latter can be formed at 50 °C from phenoxide complexes or at 20 °C from para-substituted phenoxide complexes.

Experimental Section

General Conditions. All reactions (catalyst synthesis and polymerization) were carried out under an atmosphere of dry

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[17] Molecular weight determined by GPC analysis in THF with polystyrene standards (UV detection).

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Table 1. Dehydrocoupling of $PhSiH_3$ (Eq 2)

entry no.	catalyst[a]	induction period	reaction conditions[b]	% of polymer as nonvolatile cyclics[c]	linear polysilane M_w (M_w/M_n)[d]
1	$(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$	15 min/50 °C	neat/24 h (20 °C)	25	2400 (1.25)
2	$(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4OMe\text{-}p)_2$	2 h/20 °C	neat/48 h (20 °C)	25	3100 (1.55)
3	$(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4Cl\text{-}p)_2$	10 min/25 °C	neat/72 h (25 °C)	30	2200 (1.35)
4	$(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4CN\text{-}p)_2$	30 min/25 °C	neat/72 h (25 °C)	30	2200 (1.38)
5	$(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4Me\text{-}p)_2$	20 min/25 °C	neat/72 h (25 °C)	30	2300 (1.35)
6	$(\eta^5\text{-}C_5H_5)_2TiMe_2$	15 min/20 °C	neat/15 h (20 °C)	25	2700 (1.35)
7	$(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$	15 min/50 °C	neat/72 h (20 °C)	10	3200 (1.45)
8[e]	$(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$	15 min/50 °C	neat/72 h (20 °C)	10	3750 (1.5)

[a] Catalyst concentration: 0.1 mol% throughout. [b] Conversion >95%. [c] Cf. Experimental Section. [d] Determined by GPC, the molecular weight values are relative to polystyrene standards; UV detector. [e] The polymerization was carried out by slow addition of the monomer over a 48 h period.

argon. Solvents were dried using standard techniques. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were obtained with a Bruker AC 250 (^1H, ^{13}C) or a Bruker WP 200 SY (^{29}Si) (solvent $CDCl_3$, TMS as an internal standard).

Gel permeation chromatography of polysilanes was carried out on THF solutions with a Waters Millipore 510. A UV detector, Waters Model 441, and a differential refractometer, Waters Model 410, were used. All molecular weights are reported with respect to polystyrene standards.

The following compounds were prepared according to literature procedures: $PhSiH_3$,[23] Ph_2SiH_2,[23] $(\eta^5\text{-}C_5H_5)_2TiMe_2$,[18] $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$,[16] $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4Cl\text{-}p)_2$,[16] $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4Me\text{-}p)_2$,[16] $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$.[20]

$(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4OMe\text{-}p)_2$.[19] This known complex[19] was obtained according to a slight modification of the reported procedure. To a suspension of $NaNH_2$ (7.5 mL, 1.6 M in toluene) diluted with toluene (50 mL) was added dichlorotitanocene (1.25 g, 10 mmol). *p*-Methoxyphenol (1.24 g, 10 mmol) in 25 mL of toluene then was added dropwise; the mixture was refluxed for 10 min and then cooled to room temperature. The reaction mixture was filtered and the solvent removed in vacuo. The residue was crystallized from a toluene/pentane mixture to give 1.75 g (70%) of product, mp 87–89 °C. ^1H NMR ($CDCl_3$; δ, ppm): 6.69 (8H, q); 6.23 (10H, s); 3.77 (6H, s). ^{13}C NMR ($CDCl_3$; δ ppm): 165.2; 152.5; 118.1; 115.8; 114.4; 55.9. Anal. Calcd for $C_{24}H_{24}O_4Ti$: C, 67.92; H, 5.70. Found: C, 67.55; H, 5.99.

$(\eta\text{-}C_5H_5)_2Ti(OC_6H_4CN\text{-}p)_2$. This was prepared by using the above procedure. The residue was crystallized from a toluene/hexane mixture to give 1.15 g (60%) of product, mp 175–176 °C. ^1H NMR ($CDCl_3$; δ, ppm): 7.53 (4H, d); 6.62 (4H, d); 6.32 (10H, s). ^{13}C NMR ($CDCl_3$; δ ppm): 173.7; 134.4; 120.5; 119.1; 117.3; 101.8. Anal. Calcd for $C_{24}H_{18}O_2N_2Ti$: C, 69.56; H, 4.35; N, 6.76. Found: C, 69.34; H, 4.66; N, 6.38.

Reactions of Dihydrosilanes. Diphenylsilanes. $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ (7.3 mg, 0.02 mmol) was dissolved in Ph_2SiH_2 (1.84 g, 10 mmol). The mixture, upon heating at 80 °C, turned dark blue and hydrogen was evolved. After 5 h, the mixture was cooled to room temperature. Crystallization from pentane gave $Ph_2Si(H)Si(H)Ph_2$ (0.35 g, 10%), mp 80 °C (lit.[24] mp 78–80 °C).

Di-*n*-butylsilane. $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ (50 mg, 0.14 mmol) and di-*n*-butylsilane (375 mg, 2.6 mmol) were mixed under argon and heated to 110 °C. The solution color change from yellow to dark brown was accompanied by some gas evolution. The mixture was then heated to 130 °C for 30 min and subsequently was allowed to cool to room temperature. The crude reaction mixture was analyzed by GC/MS (temperature range 100–200 °C, 10 °C/min) and revealed $n\text{-}Bu_2SiH_2$ (retention time, 154 s; M_r, 144; yield, 91%), $n\text{-}Bu_2Si(OPh)H$ (retention time, 728 s; M_r, 236; yield, 2.2%), $n\text{-}Bu_4Si_2H_4$ (retention time, 834 s; M_r 286; yield, 4.4%), and $n\text{-}Bu_2Si(OPh)_2$ (retention time, 1424 s; M_r 328; yield, 2.8%).

Polycondensation of Phenylsilane. The polymerizations of $PhSiH_3$ were performed under argon using 0.1 mol % of the titanium or zirconium catalyst without any solvent. The results are given in Table 1. The catalysis by $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ is described as an example.

Catalysis by $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$. $PhSiH_3$ (2.16 g, 20 mmol) and $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ (7.3 mg, 0.2 mmol) were mixed under argon. After dissolution, the solution was slowly heated to 50 °C. After 15 min at 50 °C, the mixture turned dark blue. It was cooled to room temperature and stirred for 24 h. Volatile materials were then removed under vacuum, and the residue was solubilized in toluene and filtered through a Florisil column. The polysilane obtained after removal of the solvent (yield >95%) exhibited characteristics similar to those previously reported.[3] ^1H NMR ($CDCl_3$; δ, ppm): 4.1–5.2 (m), 6.5–7.5 (m). ^{29}Si NMR ($CDCl_3$; δ, ppm): −50 to −65 (m). IR (neat): ν(Si–H) 2110 cm^{-1}. GPC (on crude polymer, UV detector): 25% cyclics; 75% linear polymer with $M_w = 2400$, $M_w/M_n = 1.25$. The proportion of cyclics was determined by GPC and by ^1H NMR by comparing the ratio of resonances above 5 ppm and those below 4.8 ppm.[21] The activation of the catalyst can also be performed at 30 °C. A 4 h induction period was then necessary before the polymerization occurred, leading to the same polysilane.

Catalysis by $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4OMe\text{-}p)_2$. The reaction of $PhSiH_3$ in the presence of $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4OMe\text{-}p)_2$ was performed as above. When this titanium complex was used, there was a 1–2 h induction period at 20 °C before polycondensation with hydrogen evolution commenced.

Catalysis by $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4Cl\text{-}p)_2$, $(\eta^5\text{-}C_5H_5)_2Ti(OC_6H_4CN\text{-}p)_2$, and $(\eta^5\text{-}C_5H_5)_2Ti(O\text{-}C_6H_4Me\text{-}p)_2$. The reaction of $PhSiH_3$ in the presence of these titanium catalysts was performed as above. The induction periods at 25 °C were respectively 10, 30, and 20 min, and the polycondensation proceeded as above.

Catalysis by $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$. The reaction was performed as described in the case of the catalysis by $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$. An induction period of 15 min at 50 °C, after which time the solution turned yellow, was necessary to obtain polycondensation at room temperature.

Polycondensation of 1,4-Disilapentane. The reaction was conducted as above using 1,4-disilapentane (10.4 g, 100 mmol) and $(\eta^5\text{-}C_5H_5)_2Ti(OPh)_2$ (180 mg, 0.5 mmol) as catalyst. After 48 h the reaction was stopped by bubbling air through the liquid until the intense color disappeared. The mixture was diluted with toluene and filtered through a Florisil column. The polysilane was collected after removal of the solvent. GPC (detector: refractive index): $M_w = 1041$, $M_n/M_w = 1.16$. ^1H NMR (80 MHz; δ, $CDCl_3$): 0.0 (t, ^3J(H,H) = 3.5 Hz, 3H); 0.9 (m, 4H), 3.8 (m, 3H). ^{13}C NMR (62.9 MHz; δ, $CDCl_3$): 8.3 (CH_3); 1.4–5.5 (CH_2); 8.1–9.9 (CH_2). ^{29}Si NMR (49.7 MHz; δ, $CDCl_3$): −65 to −49 (SiH, SiH_2); −30.2 (t, ^2J(Si–H) = 189 Hz). IR (hexane): ν 2134 cm^{-1} (SiH). Anal. Found: C, 35.11; H, 10.15.

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