

Hydrogenation catalytic activity of substituted cyclopentadienyl titanium complexes anchored on polysiloxanes prepared by a sol–gel procedure

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Abstract

A series of [ω -(tetramethylcyclopentadienyl)alkyl]methylethoxysilanes of general formula $C_5(CH_3)_4H(CH_2)_nSi(CH_3)_k(OCH_2CH_3)_{3-k}$ ($n = 1, k = 0-2$; $n = 2, k = 1$; $n = 3, k = 0, 2$) has been synthesized. Pentamethylcyclopentadiene-containing polysiloxanes have been prepared from these functionalizing agents and tetraethoxysilane by a sol–gel procedure and characterized by ^{13}C CP MAS solid-state NMR spectroscopy. Polysiloxane-anchored cyclopentadienyl- and pentamethylcyclopentadienyl–titanium complexes have been obtained by deprotonation of a polysiloxane ($n = 1, k = 0$) followed by reaction with $CpTiCl_3$ and Cp^*TiCl_3 . The anchored complexes were catalytically active in the hydrogenation of 1-octene. Their structure was examined by solid-state NMR and X-ray photoelectron spectroscopy.

Keywords: Titanium; Hydrogenation; Cyclopentadienyl; Polysiloxane; Photoelectron spectroscopy; Nuclear magnetic resonance

1. Introduction

Considerable work has recently been devoted to the immobilization of reagents and catalysts [1–3]. Transition metal complexes have been immobilized (heterogenized) either on organic or inorganic supports, the most frequently used method being the modification of the surface of an inorganic oxide or of a polymer backbone with suitable ligands capable of anchoring the metal complexes. Organofunctionalized polysiloxanes prepared by a sol–gel procedure [4–6] represent a class of supports intermediate between those of an organic and inorganic nature, and have received renewed and detailed attention quite recently [7,8]. So far attention has focused on phosphines as ligands for anchoring catalysts but many other functional groups have been used as anchorage groups for non-catalytic purposes. It is therefore somewhat surprising that cyclopentadienyls have only in marginally been studied as anchoring ligands [9–12], since about 80% of all known organometallic compounds contain cyclopentadienyl or substituted cyclopentadienyl as a ligand [13].

We found the dimerization of monosubstituted cyclopentadienes to be a serious obstacle in the surface functionalization of oxide supports. We therefore prepared novel functionalization agents based on pentamethylcyclopentadiene [14]. As we were preparing a full paper describing this work, Jutzi et al. [15] reported the synthesis of this highly promising class of compounds and briefly described the preparation of polysiloxanes functionalized with pentamethylcyclopentadiene groups by a sol–gel reaction.

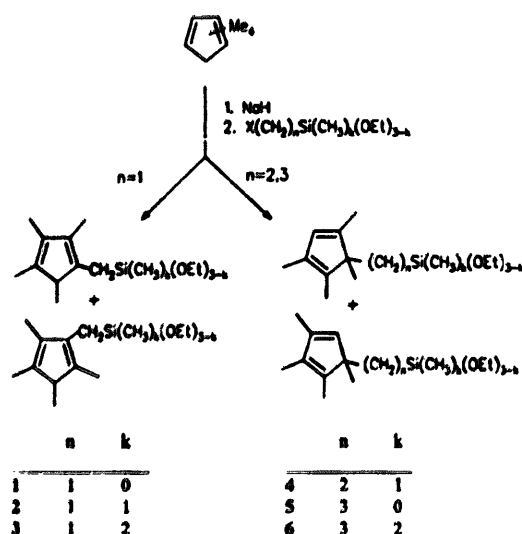
We now wish to report in detail the preparation of such materials via a sol–gel procedure, the use of ^{13}C CP MAS solid-state NMR (see, for example, Ref. [16]) and X-ray photoelectron spectroscopy for their structure elucidation and their use in catalyst heterogenization for the hydrogenation of olefinic double bonds.

2. Results and discussion

2.1. Synthesis of functionalizing agents

The reaction of (ω -chloroalkyl)methylethoxysilanes with sodium tetramethylcyclopentadienide, prepared from tetramethylcyclopentadienes (mixture of isomers,

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Scheme 1. Preparation of $[\omega$ -(tetramethylcyclopentadienyl)alkyl]methylthoxy silanes.

main component 1,2,3,4-tetramethylcyclopentadiene) and sodium hydride in dimethylformamide (Scheme 1), gives various isomers of $[\omega$ -(tetramethylcyclopentadienyl)alkyl]methylthoxysilanes, 1–6, depending on the length of the oligomethylene spacer between the ring and the silicon atom. Two isomers with the spacer bound to the double-bond carbon of the ring are formed exclusively when $n = 1$, while two isomers with the spacer bound to the aliphatic quaternary carbon are the main products when $n = 2, 3$. The third possible isomer was not found in the latter case. All isomers were produced in approximately equimolar ratios as determined by NMR spectroscopy.

In compounds 1–3 the hydrogen atom remaining on the ring is in an allylic position and can be abstracted in a subsequent deprotonation step, whereas anchorage of a transition metal complex to the 1,3-diene moiety of the ring can be achieved with compounds 4–6.

The key information for distinguishing between compounds 1–3 and 4–6 comes from ^{13}C NMR spectra. The former compounds exhibit in their spectra a pair of signals of ring aliphatic methylene carbons at about δ 51 ppm and four pairs of double-bond quaternary carbons between δ 132 and 137 ppm (signals sometimes overlap). The latter compounds exhibit in their spectra a pair of signals of aliphatic quaternary carbons between δ 55 and 57 ppm and a pair of signals of double-bond methine carbons together with three pairs of double-bond quaternary carbons between δ 120 and 149 ppm. Since the signals of both groups lie in the same regions of the spectrum, a standard attached proton test (APT) experiment was employed to determine the multiplicity of the signals.

The results are in accord with data on similar functionalizing agents reported by Jutzi et al. [15]. While deprotonation of tetramethylcyclopentadienes by sodium

hydride in DMF followed by reaction with a chloroalkylsilane [14] gives somewhat lower yields than the reaction of potassium tetramethylcyclopentadienide with an iodoalkylsilane in THF [15], the former reaction is more straightforward and allows an extra step of the Finkelstein transhalogenation and careful purification from acetone which caused problems in subsequent reaction to be bypassed. In our hands, the yield of 1 increased by 24% on employing $(\text{C}_5\text{Me}_2\text{H})^-\text{K}^+$ and iodomethyltriethoxysilane.

2.2. Preparation of functionalized supports via the sol-gel procedure

Three catalysts produced by the sol-gel process were tested with the aim of finding those conditions which allow maximum incorporation of pentamethylcyclopentadiene groups into the polysiloxane. Acid catalysis (HCl) has recently been used in a study [17] aimed at determining the uniformity of the methyl group distribution within the polysiloxane. Alkaline catalysis (e.g. using ammonia) of hydrolysis and condensation is another standard method [4] for polysiloxane preparation. In our experiments, however, both methods gave materials which were inferior as far as their cyclopentadienyl group content was concerned to polysiloxanes prepared by the sol-gel procedure using dibutyltin diacetate as a catalyst [18], as confirmed by ^{13}C CP MAS NMR spectroscopy. For this reason, dibutyltin diacetate was used as a catalyst throughout this work.

However, there is a disadvantage using this catalyst in that extra signals attributed to dibutyltin fragments appear in the solid-state ^{13}C NMR spectra. Because of the broadness of the signals in the solid-state NMR spectra, these appear as two signals of unequal intensity at δ ca. 26 and 13 ppm and thus almost coincide with the signal of the ring methyl carbons at δ 11 ppm.

Two methods for preparing functionalized polysiloxanes have been compared differing only in the purity of the tetraethoxysilane used. In method A freshly distilled tetraethoxysilane was employed in the sol-gel process, while in method B commercial tetraethoxysilane was used as received. The product prepared via method A formed a polymeric gel which was crushed mechanically and sieved after drying. The product prepared according route B separated from the reaction mixture as a particulate gel and formed an ultrafine powder after drying in which the diameter of the particles was of the order of μm . The ^{13}C CP MAS NMR spectra of both materials were essentially identical.

Generally, the assignment of the signals in the ^{13}C CP MAS solid-state NMR spectra could be achieved with the help of the solution NMR spectra of the functionalizing agents. Apart from the signals of the dibutyltin fragments mentioned above, there are usually

Table 1

Chemical shifts (δ , ppm) in the ^{13}C CP MAS NMR spectra of pentamethylcyclopentadiene-containing polysiloxanes

Functionalizing agent	SiCH ₃ -	ring CH ₃ + CH ₂ Si	OCH ₂ CH ₃	OCH ₃	OCH ₂ CH ₃	ring =C=	CH ₂ CH ₂ Si	CH ₂ CH ₂ CH ₂ Si
1	–	11	18	51	59	134	–	–
2	–5	10	17	51	59	138	–	–
3	0	10	17	51	59	132	–	–
4	–2	11	17	51	59	130,140,148	–	–
5	–	11	18	51	59	131,140	38	–
6	0	11	18	51	59	132	36	47

strong signals around δ 17 ppm and 59 ppm which have been assigned to residual unhydrolyzed ethoxy groups, and a signal at δ 51 ppm corresponding to the methoxy groups formed by transesterification during the sol–gel process [4]. Ring methyls, together with the carbon of the methylene spacer directly bound to the silicon atom, resonate at δ 11 ppm and the quarternary carbon atoms of the double bonds on the ring appear at δ 130–148 ppm. The signal of aliphatic methine carbon of the ring should appear at ca. δ 50 ppm but is obscured by the methoxy resonance. When the functionalization agent used for polysiloxane preparation contained a spacer longer than one methylene, resonances of the spacer atoms appear in the corresponding positions shifted successively to lower field from the resonance of the silicon-bound methylene. Methyl groups on the silicon atom resonate at high field. The values of the ^{13}C chemical shifts are summarized in Table 1.

2.3. Anchorage of titanium complexes and their catalytic activity

The polysiloxane prepared from 1 was treated with a large excess of *n*-butyl-lithium at 60°C to convert the polysiloxane-bound pentamethylcyclopentadiene to an anion capable of further reaction with a transition metal compound.

After reaction with *n*-butyl-lithium and careful washing, the polysiloxane was treated with an excess (calculated in relation to the maximum possible content of substituted cyclopentadienyl groups on the polysiloxane, i.e. 1.13 mmol g⁻¹) of (η^5 -cyclopentadienyl)titanium trichloride or (η^5 -pentamethylcyclopentadienyl)titanium trichloride in toluene solution.

In the presence of an excess of both trichlorides, the polysiloxane-anchored complexes prepared via both routes A and B exhibit the same brownish red (Cp^{*}) or violet (Cp) colour. The colour is retained in materials prepared via method A after washing and drying. However, ultrafine powders prepared by method B gradually change colour in the absence of an excess of trichloride, first to green and then to blue after a few days.

The titanium contents of the anchored complexes varied from 1.25% to 4.53% (Table 2) corresponding to metal loadings of 0.26–0.95 mmol g⁻¹ a larger quantity

than is typical for metal complexes anchored on to an inorganic support. Comparison of these values with the maximum possible content of substituted cyclopentadienyl groups shows that not all the bound Cp^{*} groups react, especially in reactions involving Cp^{*}TiCl₃.

The catalytic activity of anchored titanium complex/*n*-butyl-lithium systems towards hydrogenation is also summarized in Table 2. A 12-fold excess of butyl-lithium was employed by analogy with known homogeneous systems, this being adjudged capable of securing the reduction of titanium to the low-valent state necessary for the reaction provided that the titanium atom is accessible. Only complexes supported on polysiloxanes prepared via route B exhibited catalytic activity. Complexes supported on polysiloxanes prepared via route A were not catalytically active even after prolonged treatment with concentrated *n*-butyl-lithium solution or with an excess of LiAlH₄ in boiling THF.

The hydrogenation activity of the polysiloxane-supported CpTi moiety was 6.5-times lower than that of a

Table 2

Hydrogenation of 1-octene catalyzed by titanium complex supported on a polysiloxane prepared from 1^a

Ti complex anchored/method of polysiloxane preparation	Ti content (%)	Run No.	Turnover frequency (mol mol ⁻¹ min ⁻¹)
CpTiCl ₃ /A	3.25	1	0
CpTiCl ₃ /B	4.44	1	14.5
CpTiCl ₃ /B	4.27 ^b	1	5.1
CpTiCl ₃ /B	4.53 ^c	1	3.0
CpTiCl ₃ /B	4.53 ^c	2	2.1
CpTiCl ₃ /B	4.53 ^c	3	1.4
CpTiCl ₃ /B	4.53 ^c	4	1.0
Cp [*] TiCl ₃ /A	2.03	1	0
Cp [*] TiCl ₃ /B	1.25 ^d	1	28.8
Cp [*] TiCl ₃ /B	1.25 ^d	2	19.2
CpTiCl ₃	^e	1	94.3
Cp [*] TiCl ₃	^e	1	21.7

^a Conditions: constant hydrogen pressure of 1 atm, 60°C, solvent toluene, 2 mol% of Ti, butyl-lithium/Ti ratio-1:12.

^b The catalyst was not dried after Ti anchorage but introduced as a toluene suspension.

^c The same as ^b but after standing for 2 months.

^d Catalytic system without butyl-lithium.

^e Homogeneous catalytic system.

homogeneous system containing $\text{Cp}^*\text{CpTiCl}_2$. Although the catalyst may be introduced directly as a suspension, its activity is lower but maintained even after a prolonged period of standing. The catalyst could be recycled four times with gradual loss of activity although the titanium content remained constant within experimental error during the recycling.

The hydrogenation activity of the polysiloxane-supported Cp^*Ti moiety was slightly greater than that of a homogeneous system containing $\text{Cp}_2^*\text{TiCl}_2$. The catalyst is active even in the absence of butyl-lithium and can be reused although the catalytic activity drops.

We have measured the ^{13}C NMR spectra of some of the catalysts (Figs. 1 and 2, see discussion below) in an attempt to elucidate the differences in catalytic activity between complexes anchored on to polysiloxanes prepared by method A or method B. In order to support the validity of quantitative conclusions, several measurements of the dependence of the signal intensity on the contact time were also carried out. For the aliphatic carbon part of the spectra, cross-polarization constants T_{CH} are lower than 1 ms and spin-lattice relaxation times in the rotating frame $T_{1\rho\text{H}}$ are between 20–30 ms, leading to signal attenuation of about 80%. For the quarternary carbon part of the spectra, the cross-polarization

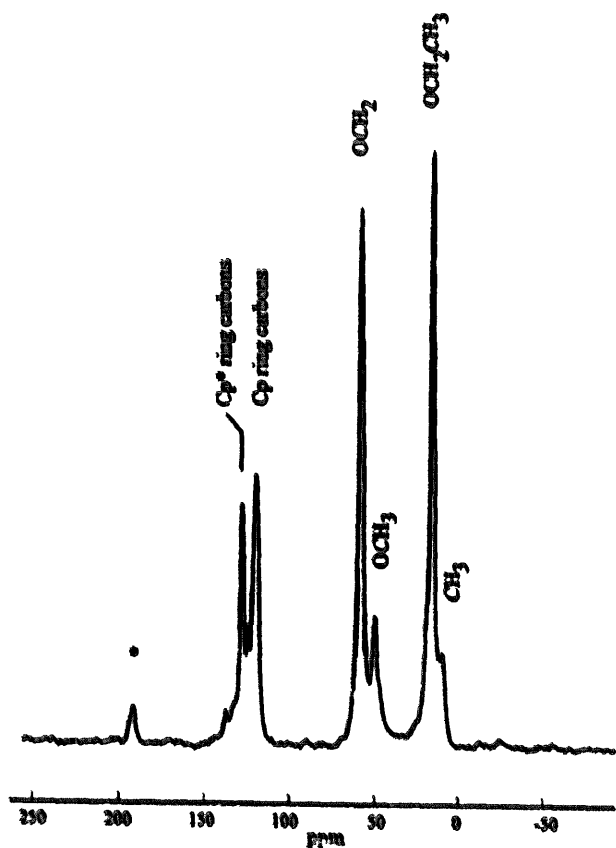


Fig. 1. ^{13}C CP MAS NMR spectrum of CpTi anchored on a polysiloxane prepared according to method A. \cdot Denotes a rotational side band.

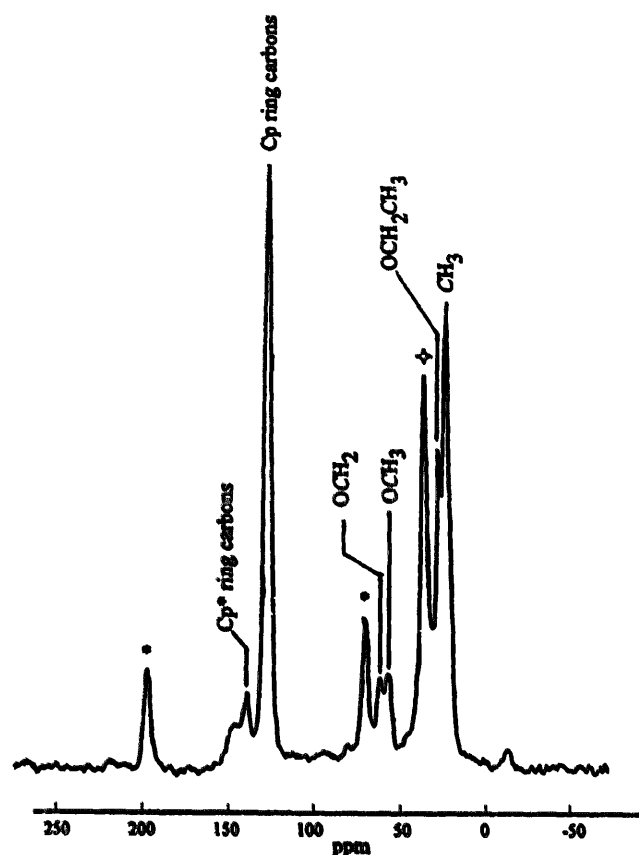


Fig. 2. ^{13}C CP MAS NMR spectrum of CpTi anchored on a polysiloxane prepared according to method B. \cdot Denotes a rotational side band; \times denotes the signal from dibutyltin diacetate.

constants are 5 ± 2 ms, relaxation times $T_{1\rho\text{H}}$ about 10 ms and signal attenuation $40\% \pm 10\%$. Even with these values, possible differences in the signal attenuation for different samples cannot explain the differences observed in the intensity of the signals.

In addition to the above studies, the surface stoichiometry of the two samples of anchored titanium complexes was determined by X-ray photoelectron spectroscopy (Fig. 3). The polysiloxane-supported CpTi prepared according to the method A (sample A, Fig. 3, spectrum 2) has the surface composition $\text{Si}_{1.00}\text{C}_{0.93}^{\alpha}\text{C}_{0.40}^{\beta}\text{O}_{2.26}\text{Cl}_{0.44}\text{Ti}_{\sim 0.03}$ and the same catalyst prepared according to method B (sample B, Fig. 3, spectrum 1) has the composition $\text{Si}_{1.00}\text{C}_{1.23}\text{O}_{2.26}\text{Cl}_{1.62}\text{Ti}_{0.18}$. There is obviously a striking difference in the titanium content of both surface layers with sample B having about six-times more titanium atoms in the surface layer than sample A, whereas in the bulk the ratio is only 1.4. This result suggests a non-uniform distribution of titanium in sample B, i.e. the sample generating an active hydrogenation catalyst, the increased concentration of titanium in the surface layer probably contributing to its availability for the catalytic process.

Sample B also has a carbon content which is 2.5-times

higher than that of sample A, the value of the C 1s core level binding energy obtained (285.2 ± 0.2 eV) being consistent with the presence of carbon atoms involved in $-C-C-$ and/or $-C-H$ bonds [19]. In the C 1s spectra of sample A, two chemically inequivalent types of carbon atoms were identified (see Fig. 4), i.e. α -carbons with a C 1s binding energy identical to that of the carbon atoms of sample B within experimental error and β -carbon atoms with a C 1s binding energy of 286.4 ± 0.2 eV corresponding to atoms bonded to more electronegative neighbours such as oxygen [19].

The solid-state ^{13}C NMR spectra support these results. In sample B (Fig. 2), significant carbon signals from the cyclopentadienyl ring carbons at δ 121 ppm and ring methyl carbons at δ 14 ppm are present while in sample A (Fig. 1) signals from ethoxy groups at δ 17 ppm and 59 ppm are apparent. The lower proportion of residual ethoxy groups in sample B could be due to the use of commercial tetraethoxysilane which is already partially hydrolysed and condensed, although no differences in the 1H , ^{13}C and ^{29}Si spectra of commercial and freshly distilled $Si(OEt)_4$ were observed.

A notable difference between the ^{13}C CP MAS NMR spectra of both samples is the different ratio of signals at δ 121 ppm and 129 ppm, which have been assigned to ring carbons of the unsubstituted and substituted rings, respectively. The ratio is much higher in sample B and may be explained by a higher proportion of cyclopentadienyl rings not bound (via titanium) to the substituted cyclopentadienyl rings of the polysiloxane in this sample. We were unable to determine the binding atom precisely but the value of the Ti 2p binding energy (458.7 eV) is close to known values for cyclopentadienyltitanium complexes containing electronegative substituents [19]. We suggest oxygen as the binding atom for the cyclopentadienyltitanium moiety since OLi groups may be formed on the polysiloxane after treat-

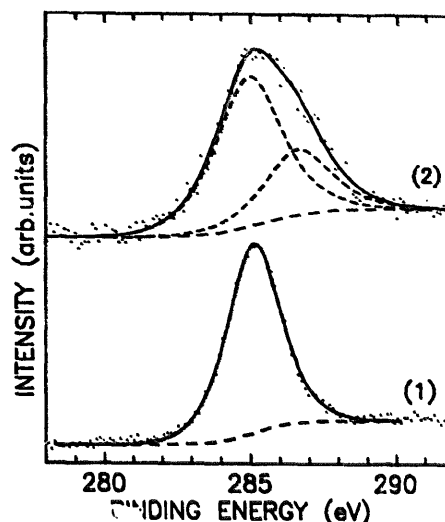


Fig. 4. Fitted C 1s core level spectra of (1) sample B and (2) sample A.

ment with butyl-lithium and can react with Cp^*TiCl_3 . It should be mentioned at this point that polysiloxanes prepared from tetraethoxysilane alone and subject to further treatment in the same manner as those containing the functionalizing agent also retained titanium but were not catalytically active.

In conclusion, it is suggested that the differences in catalytic activity may be attributed to the different morphologies of the starting polysiloxanes which lead to different methods of anchoring of the titanium complexes and hence different availabilities for catalytic centres formed on the substrates.

In sample A, prepared from the polymeric gel-type polysiloxane, the Cp^*Ti moiety is probably bound to Cp^* groups in an approximately equimolar ratio, the violet (or red in the case of Cp^*Ti) colour suggesting the formation of a polysiloxane-supported analogue of $Cp^*CpTiCl_2$ (or $Cp_2^*TiCl_2$). The concentration of this anchored complex in the surface layer, however, is low. This leads to low access of the substrate and hence a low catalytic activity.

Sample B, prepared from microparticulate gel-type polysiloxane, contains a Cp^*Ti moiety bound to the polysiloxane via some element other than carbon, probably oxygen. The colour changes occurring during the preparation of the anchored complex suggest the formation of a low-valent titanium species even at this stage in the process. With the bulkier Cp^*Ti this low-valent titanium species is stable for a sufficiently long period of time that the anchored complex can be used without additional reducing agent. The availability of the titanium catalytic centres in the surface layer of the solid catalyst to substrates is likely to be the decisive factor as far as the subsequent catalytic activity is concerned.

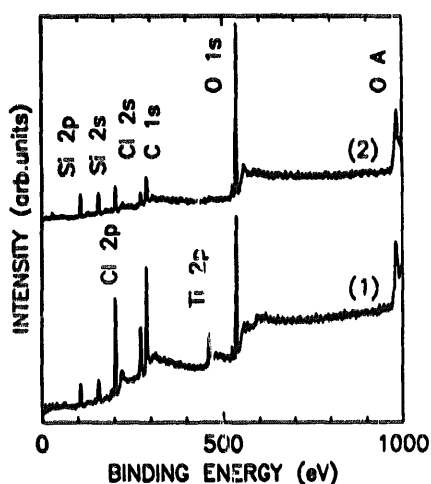


Fig. 3. XPS survey spectra of (1) sample B and (2) sample A.

3. Experimental details

The sol-gel preparations of the functionalized polysiloxanes were carried out in air, all other manipulations were undertaken under an argon atmosphere. Solvents and 1-octene were dried by standard procedures and stored under argon. CpTiCl_3 [20] and *n*-butyl-lithium solution in *n*-heptane were prepared according to published procedures. Cp^*TiCl_3 was prepared from $\text{Cp}^*\text{MgCl} \cdot \text{THF}$ [21] and TiCl_4 . (ω -Chloroalkyl)methylethoxysilanes were from the laboratory stock and were freshly distilled before use in the reaction. Their purity was checked by ^1H , ^{13}C and ^{29}Si NMR spectroscopy.

Solution NMR spectra were measured on a Varian UNITY 200 spectrometer at 200.1 MHz, 50.3 MHz and 39.7 MHz for ^1H , ^{13}C and ^{29}Si , respectively. Infrared spectra were measured on a NICOLET IMPACT 400 FT-IR instrument with a resolution of 2 cm^{-1} . Mass spectra were measured by a GC/MS method on a capillary gas chromatograph (Varian, model 3500) equipped with a mass detector (Finnigan MAT, model ITD 800).

The CP MAS ^{13}C solid-state NMR spectra were recorded on a Bruker MSL 200 spectrometer using double-bearing ZrO_2 rotors with a Teflon cap. The spinning speed in all experiments was varied in the range 3400–3600 Hz. A contact time of 2 ms was chosen for approaching the maximum of polarization transfer for both protonated and non-protonated carbons and the recycle delay was 6 s. All ^{13}C NMR spectra were externally referenced to glycine (δ 176.03 ppm).

X-Ray photoelectron spectra (XPS) were measured on a VG ESCA 3 Mk II electron spectrometer using Al $K\alpha$ radiation ($h\nu = 1486.6\text{ eV}$). The spectrometer was operated in the fixed analyzer transmission mode. The background pressure during spectra accumulation was typically 10^{-6} Pa . Detailed scans were taken over the Si 2p, Si 2s, C 1s, Cl 2p, Ti 2p and O 1s spectral regions. Core-level binding energies were determined with an accuracy of $\pm 0.2\text{ eV}$. The peak positions and areas were determined by fitting the unsmoothed experimental data after subtracting the non-linear [22] background. Theoretical photo-ionization cross-sections [23] and mean free electron paths calculated from the equations suggested by Seah and Dench [24] were used to convert peak areas into elemental concentrations. The samples were stored under dry dinitrogen during transport into the electron spectrometer to avoid any reaction with the ambient atmosphere.

3.1. [ω -(Tetramethylcyclopentadienyl)alkyl]methylethoxysilanes

These were prepared by analogy with the preparation of (tetramethylcyclopentadienylmethyl)triethoxysilane

(1) [14]. A typical procedure was as follows. Sodium hydride (4.6 g, 0.19 mol) was suspended in DMF (100 ml) and tetramethylcyclopentadiene isomers (24.8 g, 0.20 mol) added with stirring. The mixture was stirred for 3 h at laboratory temperature and then cooled to -20°C when chloromethyltriethoxysilane (60.6 g, 0.29 mol) in DMF (35 ml) was added slowly. After standing overnight at room temperature, the solids were filtered off and the product obtained by distillation in vacuo, b.p. $104\text{--}106^\circ\text{C}/1\text{ Torr}$. Yield 30.0 g (53%).

(Tetramethylcyclopentadienylmethyl)methyldiethoxysilane, mixture of two isomers (2): ^1H NMR (CDCl_3) δ : 0.06 (s, 3H); 0.07 (s, 3H); 0.98 (s, 2H); 1.02 (s, 2H); 1.20 (t, $J = 7.0\text{ Hz}$, 6H); 1.21 (t, $J = 7.0\text{ Hz}$, 6H); 1.74–1.82 (m, 24 H); 2.48 (m, 1H); 2.60 (m, 1H); 3.74 (q, $J = 7.0\text{ Hz}$, 4H); 3.76 (q, $J = 7.0\text{ Hz}$, 4H) ppm. ^{13}C NMR (CDCl_3) δ : -5.01 , -4.81 (CH_3Si); 11.11, 11.25, 11.37, 11.63, 12.07 (ring CH_3); 13.87, 14.24 (CH_2Si); 18.30 ($\text{CH}_3\text{CH}_2\text{O}$); 50.82, 51.34 (ring CH); 58.13 (CH_2O); 132.69, 133.80, 133.98, 134.04, 135.72, 137.14, 137.29, 137.88 (C=) ppm. ^{29}Si NMR (CDCl_3) δ : -8.97 ; -8.56 ppm. MS (m/z): 268 (M^+); 253; 237; 133. IR (cm^{-1} , neat): 2972; 2926; 2874; 1443; 1391; 1256; 1165; 1105; 1082; 951; 851; 812; 775.

(Tetramethylcyclopentadienylmethyl)dimethylethoxysilane, mixture of two isomers (3): ^1H NMR (CDCl_3) δ : 0.07 (s, 6H); 0.09 (s, 6H); 0.97 (s, 2H); 1.01 (s, 2H); 1.18 (t, $J = 7\text{ Hz}$, 3H); 1.19 (t, $J = 7.0\text{ Hz}$, 3H); 1.73–1.81 (m, 24H); 3.65 (q, $J = 7.0\text{ Hz}$, 2H); 3.67 (q, $J = 7.0\text{ Hz}$, 2H) ppm. ^{13}C NMR (CDCl_3) δ : -1.63 , -1.56 (CH_3Si); 10.95, 11.02, 11.14, 11.38, 11.50, 11.63, 11.75, 12.30 (ring CH_3); 15.96, 16.70 (CH_2Si); 18.50 ($\text{CH}_3\text{CH}_2\text{O}$); 50.87, 51.35 (ring CH); 58.33 (CH_2O); 132.24, 133.78, 134.18, 134.58, 135.24, 136.86 (C=) ppm. ^{29}Si NMR (CDCl_3) δ : 14.48; 15.07 ppm. MS (m/z): 238 (M^+); 192; 177; 103. IR (cm^{-1} , neat): 2961; 2910; 2870; 1690; 1443; 1389; 1250; 1165; 1107; 1084; 947; 839; 789; 745.

[2-(Tetramethylcyclopentadienyl)ethyl]methyldiethoxysilane, mixture of two isomers (4): ^1H NMR (CDCl_3) δ : 0.08 (s, 6H); 0.91 (s, 2H); 0.97 (s, 2H); 1.20 (t, $J = 7.0\text{ Hz}$, 12H); 1.60–1.85 (m, 28H); 3.71 (q, $J = 7.0\text{ Hz}$, 8H); 5.65 (s, 1H); 5.80 (s, 1H) ppm. ^{13}C NMR (CDCl_3) δ : -5.05 , -5.02 (CH_3Si); 6.89, 7.90 (CH_2Si); 9.49, 10.72, 12.23, 12.46, 13.95, 18.18, 21.01, 21.61 (ring CH_3); 18.38 ($\text{CH}_3\text{CH}_2\text{O}$); 27.81, 28.93 (CH_3); 55.37, 57.70 (CH_3C); 57.98 (CH_2O); 129.60, 133.49, 139.97, 140.78, 143.46, 148.18 (C=); 132.33, 135.29 (CH=) ppm. ^{29}Si NMR (CDCl_3) δ : -3.11 ; -3.31 ppm. MS (m/z): 282 (M^+); 267; 238; 133. IR (cm^{-1} , neat): 2972; 2922; 2880; 1443; 1389; 1258; 1167; 1105; 1080; 953; 820

[3-(Tetramethylcyclopentadienyl)propyl]triethoxysilane, mixture of two isomers (5): ^1H NMR (CDCl_3) δ : 0.49 (m, 2H); 0.75 (m, 2H); 0.85 (s, 3H); 1.18 (t, $J = 7.0\text{ Hz}$, 9H); 1.42 (m, 2H); 1.61 (s, 3H); 1.72 (s,

6H); 3.73 (q, $J = 7.0$ Hz, 6H); 5.73 (s, 1H) ppm. ^{13}C NMR (CDCl_3) δ : 9.56, 12.26, 22.30 (ring CH_3); 10.54, 16.77, 38.60 (CH_2); 18.17 ($\text{CH}_3\text{CH}_2\text{O}$); 58.14 (CH_2O); 58.19, 58.37 (CH_3C); 128.87, 136.00 ($\text{CH}=\text{}$); 131.54, 132.63, 140.00, 140.64, 144.21, 148.83 ($\text{C}=\text{}$) ppm. ^{29}Si NMR (CDCl_3) δ : -44.54 ppm. MS (m/z): 327 (M^+); 281; 235; 122. IR (cm^{-1} , neat): 2972; 2926; 2885; 1443; 1391; 1105; 1082; 955; 793.

[3-(Tetramethylcyclopentadienyl)propyl]dimethylethoxysilane, mixture of two isomers (6): ^1H NMR (CDCl_3) δ : 0.09 (s, 6H); 0.50 (m, 2H); 0.68 (m, 2H); 0.88 (s, 3H); 1.18 (t, $J = 7.0$ Hz, 3H); 1.43 (m, 2H); 1.63 (s, 3H); 1.76 (s, 6H); 3.62 (q, $J = 7.0$ Hz, 2H); 5.78 (s, 1H) ppm. ^{13}C NMR (CDCl_3) δ : -2.16, -2.50 (CH_3Si); 9.59, 10.31, 10.65, 14.03, 14.56, 15.88, 21.40, 22.31 (ring CH_3); 16.84, 17.15, 27.00, 28.85, 39.10, 40.31 (CH_2); 18.49 ($\text{CH}_3\text{CH}_2\text{O}$); 54.56, 56.96 (CH_3C); 58.08 (CH_2O); 120.01, 131.55, 137.82, 140.67, 148.87 ($\text{C}=\text{}$); 128.88, 135.85 ($\text{CH}=\text{}$) ppm. ^{29}Si NMR (CDCl_3) δ : 17.13 ppm. MS (m/z): 267 (M^+); 251; 221; 122. IR (cm^{-1} , neat): 2959; 2924; 2866; 1443; 1389; 1252; 1109; 1080; 945; 837; 783.

3.2. Preparation of functionalized polysiloxanes via the sol-gel procedure

To the stirred mixture of methanol (7.5 ml) and water (2.4 g, 130 mmol), 10.0 g (48 mmol) of tetraethoxysilane (Aldrich, freshly distilled for method A; Aldrich, used as received for method B) were added followed by dibutyltin diacetate (0.38 ml, 1.5 mmol). After 0.5 h, the [ω -(tetramethylcyclopentadienyl)alkyl]methylethoxysilane (6 mmol) was added and the mixture stirred until it started to form a gel (method A) or started to precipitate (method B). The product was left to stand overnight then dried in vacuo over P_4O_{10} . The resulting material was either crushed and sieved (0.09–0.25 mm fraction being used) or stored as a powder.

3.3. Anchoring of titanium complexes

Functionalized polysiloxane (1.0 g) was suspended in a heptane solution of n-butyl-lithium (25 ml, 0.83 mmol per ml) and the mixture stirred at 60–65°C for 4 h. Polysiloxane was decanted and washed twice with 25 ml of toluene, the final separation being filtered with a steel cannula. Then 25 ml of toluene were added followed by 1.8 mmol of solid cyclopentadienyl- or pentamethylcyclopentadienyl-titanium trichloride. The mixture was stirred for 2 h and then left to stand overnight. The product was decanted, washed twice with 25 ml of toluene and dried in vacuo. The titanium content was determined spectrophotometrically after decomposition of the polysiloxane and oxidation to Ti^{IV} with hydrogen peroxide.

3.4. Hydrogenation experiments

The polysiloxane-supported titanium catalyst (0.14 mmol of Ti) was suspended in 12 ml of toluene in the flask of the hydrogenation apparatus [25], 0.31 ml of freshly distilled 1-octene added and the mixture stirred vigorously. After addition of 2 ml of n-butyl-lithium in heptane (0.83 mmol per ml) the consumption of hydrogen gas commenced. Turnover frequency data were calculated from the values of the hydrogen consumption at 90% conversion.

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