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A novel route to advanced model systems for silica-immobilized olefin polymerization catalysts

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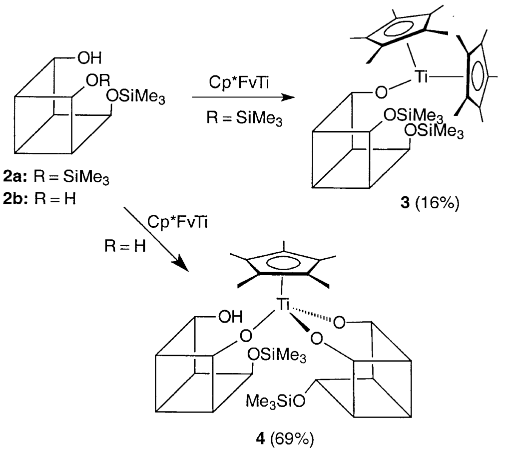
Constituting a novel synthetic route to model compounds for titanium catalysts immobilized on silica, the disilylated silsesquioxane derivative $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ 2a, has been reacted with the 'tucked-in' fulvene complex Cp*Ti($C_5Me_4CH_2$) to give the titanium(III) silsesquioxane $Cp^*{}_2Ti[Cy_7Si_7O_{10}(OSiMe_3)_2]$ 3, while treatment of Cp*Ti($C_5Me_4CH_2$) with $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ 2b affords the mono(pentamethylcyclopentadienyl) complex $Cp^*Ti[Cy_7Si_7O_{11}(OSiMe_3)][Cy_7Si_7O_{10}(OH)(OSiMe_3)]$ 4 which is an advanced model compound for a catalytically active titanium center on a silica surface.



Scheme 1 Synthesis of complexes **3** and **4**.† *Reaction conditions*: toluene, 2 h reflux, crystallization from hexane.

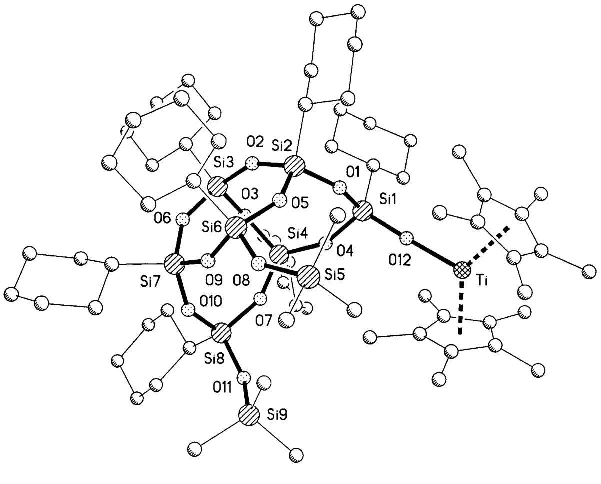


Fig. 1 Structure of **3** in the crystal. Selected interatomic distances (Å) and bond angles (°): Ti–O(12) 1.927(2), Si(1)–O(12) 1.595(2), Ti–C 2.411(3) (av.), Ti–O(12)–Si(1) 177.8(1), Si(6)–O(8)–Si(5) 146.1(1), Si(8)–O(11)–Si(9) 147.7(1).

Silsesquioxanes of the general formula $(RSiO_{1.5})_n$ are an unusual class of organosilicon compounds offering numerous exciting applications in catalysis[1] and materials science[2,3] alike. According to Feher *et al.*, incompletely condensed silsesquioxanes such as $Cy_7Si_7O_9(OH)_3$ **1** (Cy = cyclohexyl) share structural similarities with β-cristobalite and β-tridymite and are thus quite realistic models for the silanol sites on silica surfaces.[4–10] These include the first trivalent titanasilsesquioxane, blue dimeric $[Cy_7Si_7O_{12}Ti]_2$, which was prepared by treatment of **1** with $Ti[N(SiMe_3)_2]_3$.[7] It is now generally accepted that metallasilsesquioxanes derived from **1** are suitable model systems for heterogeneous silica-supported transition metal catalysts. Moreover, it has turned out that certain metallasilsesquioxanes, especially those of Ti and V, are veritable catalysts themselves *e.g.* in the metathesis, polymerization and epoxidation of olefins.[1] We report here a novel preparative route leading to model compounds for titanium olefin polymerization catalysts immobilized on silica surfaces which involves addition of functionalized silsesquioxane precursors across the Ti–C bond of the 'tucked in' fulvene titanium complex (η^5-C_5Me_5)(η^5,η^1-$C_5Me_4CH_2$)Ti (= Cp*FvTi).[11–13]

Treatment of Cp*FvTi with 1 equivalent of the disilylated silsesquioxane precursor **2a** resulted in clean formation of the titanium(III) silsesquioxane complex **3** which was isolated in the form of air-sensitive, dark green crystals (Scheme 1). The low isolated yield (16%) can be traced back to the very high solubility of **3** even in non-polar organic solvents.

The X-ray structure of **3**‡ (Fig. 1) shows that upon protonation of the coordinated tetramethylfulvene ligand a $Cp^*{}_2Ti$ unit has been generated which is now coordinated to a 'model silanized silica surface'. The Ti–O bond length in **3** is 1.927(2) Å. In accordance with the presence of a decamethyltitanocene(III) derivative a very broad ^1H NMR signal ($\nu_{1/2} \cong$ 1000 Hz) at δ 14.6 could be unambiguously assigned to the C_5Me_5 protons which is in good agreement with values reported by Pattiasina *et al.* for a series of $Cp^*{}_2TiX$ complexes (X = Cl, Br, I, BH_4, NMe_2, OBu^t, O_2CH; δ 14.1–18.4, $\nu_{1/2}$ = 620–5000 Hz).[12,13]

The new synthetic route using the fulvene precursor Cp*FvTi was also successfully employed in the preparation of a compound which can be regarded as one of the most advanced molecular models for a catalytically active titanium center on a silica surface. Reaction of Cp*FvTi with the monosilylated silsesquioxane precursor **2b** in refluxing toluene afforded a yellow crystalline material which was shown to be the novel mono-Cp* titanium(IV) silsesquioxane complex $Cp^*Ti[Cy_7Si_7O_{11}(OSiMe_3)][Cy_7Si_7O_{10}(OH)(OSiMe_3)]$ **4** (69% yield). The surprising outcome of this reaction is the exclusive formation of a Cp^*Ti^{IV} complex in which two silsesquioxanes are bonded in different ways to a single titanium center. In the course of the reaction 1 equivalent of pentamethylcyclopentadiene is eliminated (GC control).

An X-ray diffraction analysis‡ (Fig. 2) clearly shows that **4** is an advanced and highly 'realistic' molecular model for a Ti olefin polymerization catalyst immobilized on a silica surface. A mono(pentamethylcyclopentadienyl) titanium unit resides on

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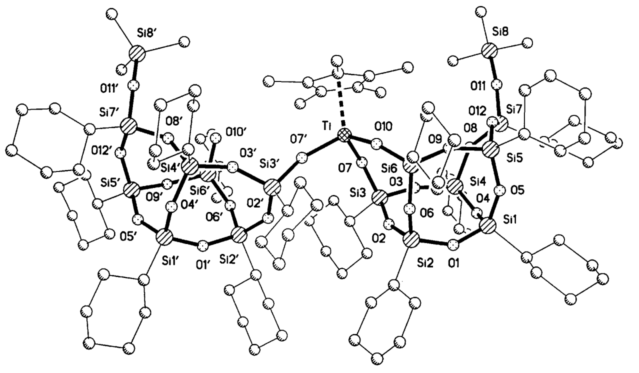

Fig. 2 Structure of **4** in the crystal. Selected interatomic distances (Å) and bond angles (°): Ti–O7 1.789(3), Ti–O7′ 1.794(3), Ti–O10 1.805(3), Ti–C 2.317(5), Si3–O7 1.575(3), Si3′–O7′ 1.571(3), Si6–O10 1.580(3); O7–Ti–O7′ 104.3(2), O7–Ti–O10 103.9(2), O7′–Ti–O10 105.3(2), Ti–O7–Si3 148.9(2), Ti–O7′–Si3′ 162.9(2), Ti–O10–Si6 154.8(2).

a 'model silica surface' formed by one chelating and one monodentate silsesquioxane ligand. With an average of 1.796(3) Å the three Ti–O bond lengths are virtually identical. A highly unusual feature of **4** making this compound a particular 'realistic' model system is a silanol function in close proximity to the Ti center. Very weak hydrogen bonding interaction of this silanol group with a cage oxygen atom (C8′) apparently prevents the molecule from intermolecular protonation of the remaining Cp* ligand, thereby 'taming' the reactivity of the Si–OH function.

We conclude that reactions of the fulvene precursor Cp*FvTi with functionalized silsesquioxanes represent a novel salt-free route to advanced molecular model systems for Ti olefin polymerization catalysts immobilized on a silica surface. The new method should have the potential of being more generally applicable to other silsesquioxane reagents as well as the zirconium analogues.

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Notes and references

† *Selected spectroscopic and analytical data*: **3**: green crystals, mp 294 °C. δ_H(CDCl$_3$, 25 °C): 14.6 (br, $\nu_{1/2} \cong$ 1000 Hz, C$_5$Me$_5$), 2.2–0.4 (m br, 95H, Cy-CH$_2$, Cy-CH, OSiMe$_3$). Anal. Calc. for $C_{68}H_{125}O_{12}Si_9Ti$ (1435.38): C, 56.9; H, 8.8. Found: C, 56.0; H, 8.7%. **4**: Yellow crystals, mp 248–252 °C. IR (KBr): 3430w br, 2922vs, 2852vs, 1461vs, 1448vs, 1269s, 1196vs, 1129vs, br, 1016vs br, 939s, 891vs (Si–OH), 849s (Si–OH), 825m, 742m, 508vs br, 471vs cm^{-1}. δ_H(CDCl$_3$, 25 °C): 2.97 (s, 1H, Si–OH), 2.43 (s, 15H, C$_5$Me$_5$), 2.17 (m, br, 32H, Cy-CH$_2$), 1.77 (m, br, 69H, Cy-CH$_2$), 1.36 (m, br, 39H, Cy-CH$_2$), 1.07 (m, br, 14H, Cy-CH), 0.36 (s, 9H, OSiMe$_3$), 0.33 (s, 9H, OSiMe$_3$). δ_C(C$_6$D$_6$, 25 °C): 127.4 (*C*$_5$Me$_5$), 28.8–27.3 (m, Cy-CH$_2$), 26.5–23.9 (m, Cy-CH), 12.9 (C$_5$*Me*$_5$), 2.5 (OSiMe$_3$), 2.3 (OSiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 25 °C): δ 9.6, 7.9 (OSiMe$_3$); −66.3 to −69.1 (m). Anal. Calc. for $C_{100}H_{187}O_{24}Si_{16}Ti$ (2270.82): C, 52.9; H, 8.3. Found: C, 53.4; H, 8.3%.

‡ *Crystal data*: the measurements on **3** and **4** were performed at −100 °C using a Siemens SMART CCD system with Mo-Kα X-radiation (λ = 0.71073 Å) and graphite monochromator. Selected crystals of **3** and **4** were coated with mineral oil, mounted on a glass fibre and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. As an absorption correction the SADABS routine was applied.

3: $C_{68}H_{125}O_{12}Si_9Ti \cdot 0.5\ C_7H_8$, M = 1481.46, monoclinic, space group $P2_1/n$, a = 13.087(1), b = 26.163(1), c = 24.449(2) Å, β = 97.616(3)°, U = 8297.5 Å^3, Z = 4, D_c = 1.186 Mg m^{-3}, $F(000)$ = 3208, μ(Mo-Kα) = 0.29 mm^{-1}, max./min. transmission 1.00/0.57, green prism 0.88 × 0.41 × 0.36 mm. A total of 54689 reflections were collected, over a range $1.7 < \theta < 28.3°$, of which 20363 were independent (R_{int} = 0.053). The structure was solved by direct methods. Refinement was by full-matrix least squares on F^2 and converged to $R1$ = 0.054 (conventional) and $wR2$ = 0.136 (all data), with goodness of fit = 1.02, 844 refined parameters, weighting scheme $[\sigma^2(F_o{}^2) + 0.0822P)^2 + 1.1511P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

4: $C_{100}H_{188}O_{24}Si_{16}Ti \cdot 1.5C_7H_8$, M = 2410.04, triclinic, space group $P\bar{1}$, a = 12.0428(3), b = 22.461(2), c = 25.540(2) Å, α = 106.667(3), β = 99.602(3), γ = 100.045 (3)°, U = 6342 Å^3, Z = 2, D_c = 1.262 Mg m^{-3}, $F(000)$ = 2602, μ(Mo-Kα) = 0.28 mm^{-1}, max./min. transmission 1.00/0.79, pale yellow prism 0.45 × 0.35 × 0.30 mm. A total of 31546 reflections were collected, over a range of $0.9 < \theta < 26.7°$, of which 24118 were independent (R_{int} = 0.034). The structure was solved by direct methods.[14] Refinement was by full-matrix least squares on F^2 and converged to $R1$ = 0.080 (conventional) and $wR2$ = 0.194 (all data), with goodness of fit = 1.040, 1382 refined parameters, weighting scheme $[\sigma(F_o{}^2) + 0.0487P)^2 + 17.2592P]$, where $P = (F_o{}^2 + 2F_o{}^2)/3$.[15]

CCDC 182/1793. See http://www.rsc.org/suppdata/cc/b0/b007854i/ for crystallographic files in .cif format.

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