Synthesis and Structures of Cyclopentadienyl Fluoro and Chloro Complexes of a Triad (Ti, Zr, Hf) containing Acyclic and Cyclic Siloxane Building Blocks†

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Cyclic and acyclic monocyclopentadienyl fluoro and chloro titanium siloxanes have been synthesised. The fluoro complexes are cyclic, whereas acyclic chloro derivatives are accessible when using bulky cyclopentadienyl ligands. Acyclic bis(cyclopentadienyl) fluoro and chloro siloxanes of titanium, zirconium and hafnium have also been prepared. The crystal structures of two cyclic titanium derivatives $[\{(C_5Me_4Et)FTiOSiBu^t_2O\}_2]$ [triclinic, space group $P\bar{1}$, $a = 9.644(3)$, $b = 11.397(3)$, $c = 11.822(3)$ Å, $\alpha = 116.702(10)$, $\beta = 104.507(12)$, $\gamma = 98.906(8)°$, $Z = 1$] and $[\{(C_5H_4Me)FTiOSiBu^t_2O\}_2]$ [monoclinic, space group $C2/c$, $a = 29.75(2)$, $b = 13.152(8)$, $c = 22.332(11)$ Å, $\beta = 124.88(3)°$, $Z = 8$] have been determined.

Due to catalytic activity, the chemistry of polymetallaorganosiloxanes containing transition-metal oxide fragments has attracted increasing interest over the past few years.[1] Organometallic complexes of the titanium triad are widely used as reagents for the syntheses of organic compounds and as catalysts for the preparation of polymers. The Si–O systems find application as catalytically active surfaces by promoting the activity of the catalytic species, so it can be reasonably expected that the incorporation of titanium in a siloxane skeleton would have a cooperative effect in the activation processes.[2]

To continue our work on the chemistry of Group 4 metalasiloxane complexes,[3] we report herein the synthesis and X-ray crystallographic characterization of cyclopentadienyl derivatives.

Results and Discussion

Treatment of a cyclopentadienyl titanium trichloride with an equimolar amount of $SiBu^t_2(OH)_2$ in toluene in the presence of NEt_3 results in the formation of acyclic or cyclic complexes depending on the substituents on the cyclopentadienyl ligand. With pentamethyl- and ethyltetramethyl-cyclopentadienyl, the acyclic titanium siloxane complexes **1a** and **1b** are formed respectively [equation (1); R_5 = Me_5 **1a** or Me_4Et **1b**].

$$[Ti(C_5R_5)Cl_3] + SiBu^t_2(OH)_2 \xrightarrow[-HCl]{NEt_3} \underset{\mathbf{1}}{[(C_5R_5)Cl_2TiOSiBu^t_2(OH)]} \quad (1)$$

However, the methylcyclopentadienyl precursor yields the eight-membered cyclic titanium siloxane product **2** [equation (2)] (analytical and physical data are given in Table 1). Consequently, compound **2** might be formed *via* the acyclic intermediate $[(C_5H_4Me)Cl_2TiOSiBu^t_2(OH)]$ under elimination of HCl.

$$\begin{tikzcd}
2[Ti(C_5H_4Me)Cl_3] + 2SiBu^t_2(OH)_2 \arrow[r, "NEt_3", "-4HCl"'] \arrow[d] & {} \\
& \underset{\mathbf{2}}{[\{(C_5H_4Me)ClTiOSiBu^t_2O\}_2]} \quad (2) \\
{[(C_5H_4Me)Cl_2TiOSiBu^t_2(OH)]} \arrow[ur] &
\end{tikzcd}$$

The reactivity of $[Ti(C_5R_5)F_3]$ with $SiBu^t_2(OSnMe_3)_2$ differs from that of $[Ti(C_5R_5)Cl_3]$, leading to the titanium siloxane eight-membered ring complexes **3** regardless of the C_5R_5 ligand [equation (3); R_5 = Me_5 **3a**, Me_4Et **3b** or H_4Me **3c**].

$$2[Ti(C_5R_5)F_3] + 2SiBu^t_2(OSnMe_3)_2 \xrightarrow{-4SnMe_3F} \underset{\mathbf{3}}{[\{(C_5R_5)FTiOSiBu^t_2O\}_2]} \quad (3)$$

In contrast $[Ti(C_5R_5)Cl_3]$ reacts with $SiBu^t_2(OSnMe_3)_2$ to yield $[(C_5R_5)Cl_2TiOSiBu^t_2(OSnMe_3)]$ **5** (R_5 = Me_4Et) or the cyclic complex **2** (R_5 = H_4Me).

Treatment of **1a** and **1b** with $SnMe_3F$ results in the formation of the eight-membered cyclic compounds **3a** and **3b**, rather than giving the acyclic fluoro derivatives $[(C_5R_5)F_2TiOSiBu^t_2(OH)]$ (R_5 = Me_5 or Me_4Et). In contrast the corresponding chloro complexes **1a** and **1b** are very stable, both in the solid state and in solution. Complex **3c** has also been obtained by fluorination of **2** with $SnMe_3F$.

The hydrolysis of **1a** results in the formation of the *cis* eight-membered ring isomer $[\{(C_5Me_5)(OH)TiOSiBu^t_2O\}_2]$[4] as the only product. This is presumably due to O–H···O bond formation. The ^1H NMR spectrum of the hydrolysis product shows two Bu^t signals.

The ^1H NMR spectra of the eight-membered cyclic fluoro titanium siloxane complexes **3a**–**3c** show the presence of two isomers, presumably *cis* and *trans*. The abundance of the *trans* isomer is always higher than that of the other one and in the cases of **3b** and **3c** the *trans* isomer has been characterized by single-crystal X-ray diffraction. In the other isomer the lack

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and physical data for the complexes

Complex	M.p./°C	Colour	Yield (%)	Mass spectrum,[a] *m/z*	Analysis (%)[b]		
					C	H	F
1a $[(C_5Me_5)Cl_2TiOSiBu^t_2(OH)]$	149–151	Orange	93	371	50.1 (50.35)	7.85 (7.95)	
1b $[(C_5Me_4Et)Cl_2TiOSiBu^t_2(OH)]$	83–85	Orange	92	385	51.2 (51.50)	8.10 (8.15)	
2 $[\{(C_5H_4Me)ClTiOSiBu^t_2O\}_2]$	222–223	Pale-yellow	85	615	49.8 (49.95)	7.40 (7.45)	
3a $[\{(C_5Me_5)FTiOSiBu^t_2O\}_2]$	257–258	Yellow	86	695	57.2 (57.45)	8.70 (8.80)	5.05 (5.05)
3b $[\{(C_5Me_4Et)FTiOSiBu^t_2O\}_2]$	196–197	Yellow	90	723	58.3 (58.45)	8.95 (8.95)	4.70 (4.85)
3c $[\{(C_5H_4Me)FTiOSiBu^t_2O\}_2]$	185–186	White	85	583	52.5 (52.50)	7.75 (7.80)	5.90 (5.95)
4a $[(C_5H_4Me)_2ClTiOSiBu^t_2(OH)]$	120–121	Red	84	359	57.5 (57.60)	7.85 (7.90)	
4b $[(C_5H_4Me)_2ClZrOSiBu^t_2(OH)]$	113–114	White	85	401	52.2 (52.25)	7.10 (7.20)	
4c $[(C_5H_4Me)_2FZrOSiBu^t_2(OSnMe_3)]$	72–74	White	88	549	45.3 (45.55)	6.80 (6.75)	3.20 (3.15)
4d $[(C_5H_5)_2ClHfOSiBu^t_2(OH)]$	152–153	White	85	463	41.5 (41.60)	5.35 (5.60)	
4e $[(C_5H_4Me)_2ClZrOSiBu^t_2(OSiMe_3)]$	90–92	White	88	473	51.7 (51.90)	7.70 (7.70)	
5 $[(C_5Me_4Et)Cl_2TiOSiBu^t_2(OSnMe_3)]$	75–77	Orange	85	549	43.3 (43.55)	7.15 (7.25)	

[a] Corresponding to $[M - \mathrm{Bu}]^+$ (100%). [b] Calculated values in parentheses.

of a centre of symmetry in the molecule causes two pairs of magnetically inequivalent $\mathrm{Bu^t}$ groups. This would be the case for a *cis* isomer which consequently would show two signals for the protons of the $\mathrm{Bu^t}$ groups on the same silicon, or for a *trans* isomer with a non-centrosymmetric conformation of the eight-membered ring. In **3c** the corresponding probe signals for the acentric and *trans* isomers are observed at δ 1.07, 0.95 and 1.01, respectively. The ^{19}F NMR spectra of **3a**–**3c** show two signals for the acentric and *trans* isomers; that for the latter always appearing at higher field. In the series of complexes **3a**–**3c** as the size of the C_5R_5 ligand increases there is a decrease in the acentric–*trans* ratio of the isomers (acentric–*trans* ratio: **3c** 1 : 4, **3a** 1 : 7, **3b** 1 : 8).

Titanocene, zirconocene and hafnocene dichloride react with $SiBu^t_2(OH)_2$ in the presence of NEt_3 resulting in the monosubstituted silanol complexes **4a**, **4b** and **4d**. Zirconocene difluoride reacts with $SiBu^t_2(OSnMe_3)_2$ to give **4c** while titanocene difluoride and dichloride do not react at all with $SiBu^t_2(OSnMe_3)_2$ [equation (4)].

$$[M(C_5R_5)_2X_2] + SiBu^t_2(OR')_2 \xrightarrow[-R'X]{} [(C_5R_5)_2XMOSiBu^t_2(OR')] \quad (4)$$

4

	M	R′	R_5	X
4a	Ti	H	H_4Me	Cl
4b	Zr	H	H_4Me	Cl
4c	Zr	$SnMe_3$	H_4Me	F
4d	Hf	H	H_5	Cl

The greater inertness of the Ti derivatives in the analogous reactions of $[Ti(C_5H_4Me)X_2]$ and $[Zr(C_5H_4Me)X_2]$ (X = F or Cl) with $SiBu^t_2(OSnMe_3)_2$ might be due to steric factors. For example, complex **4b** reacts with $SiMe_3Cl$ in the presence of NEt_3, resulting in the siloxane derivative $[(C_5H_4Me)_2ClZrOSiBu^t_2(OSiMe_3)]$ **4e**, however **4a** does not react with $SiMe_3Cl$ under the same conditions. Although $[Ti(C_5H_4Me)_2Cl_2]$ reacts with $SiBu^t_2(OH)_2$ to form **4a**, it does not show any reaction with $SiBu^t_2(OH)(OSiMe_3)$, whereas $[Zr(C_5H_4Me)_2Cl_2]$ reacts with the latter to yield **4e**.

The IR spectra of these complexes show strong absorptions due to the Ti–O–Si vibrations (≈920 cm^{-1}).[5a] Complexes **1a**, **1b**, **4a**, **4b** and **4d** also reveal two characteristic ν(SiO–H) absorptions at 3660 and 3490 cm^{-1} and their mass spectra (electron impact, EI) show relatively low intensities for the molecular ions; however, $[M - \mathrm{Bu}]^+$ is observed with 100% intensity.

Crystal Structures of Complexes **3b** *and* **3c**.—The molecular structures of the *trans* isomers of **3b** and **3c** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles for **3b** and **3c** are presented in Tables 2 and 3.

The core in both structures is an eight-membered $(Ti_2Si_2O_4)$ ring, in which the oxo ligands bridge the titanium and silicon atoms. Both rings have a chair conformation. Complex **3b** is centrosymmetric, with the four oxo ligands and two silicon atoms almost in a plane (deviation 0.02 Å)[6] and the titanium atoms 0.54 Å above and below this plane. The fluoro and ethyltetramethylcyclopentadienyl ligands bonded to titanium are in a *trans* position, with the fluorine occupying the *exo* and the substituted cyclopentadienyl group the *endo* positions.

The geometry in **3c** is very close to that in **3b**, but slightly distorted since it lacks the centre of symmetry. The mean deviation from the analogous geometrical least-squares plane described by the six oxygen and silicon atoms is 0.06 Å, with titanium lying 0.53 and 0.17 Å on either side of the plane.

The metal atoms in both structures possess slightly distorted tetrahedral environments. In **3c** two distinctly different pairs of Ti–O–Si angles are found (166.9 and 146.9°), a feature also evident in $[(Br_2TiOSiBu^t_2O)_2]$ (155 and 169°).[3]

The bond distances between the metals and ligands are comparable in both structures (see Tables 2 and 3), but slightly longer to the titanium atom in **3b**, which might be due to the bulkier substituents on the cyclopentadienyl ligand. The bond lengths (Å) to titanium are in line with those determined in related $[\{Ti(C_5R_5)X(\mu\text{-}O)\}_n]$ compounds [X = Cl, n = 3,[7a] C_5Me_5(centroid)–Ti 2.045, Ti–O 1.823(5); X = Cl, n = 4,[7b] C_5H_4Me(centroid)–Ti 2.038, Ti–O 1.800(1); X = F, n = 4,[8] C_5Me_5(centroid)–Ti 2.047, Ti–O 1.8161(9), Ti–F 1.845(5) Å]. The values for the Si–O bond lengths [1.6438(14) **3b**, 1.643(3) Å **3c**] are close to those determined in $[(Cl_2TiOSiBu^t_2O)_2]$ [1.661(2) Å].[3]

Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Toluene, hexane and tetrahydrofuran (thf) were distilled prior to use from benzophenone under nitrogen. The compounds $SiBu^t_2(OH)_2$,[9] $[Ti(C_5Me_5)Cl_3]$,[10a] $[Ti(C_5Me_4Et)Cl_3]$,[10b] $[Ti(C_5H_4Me)Cl_3]$,[10c] $[Ti(C_5H_4Me)_2Cl_2]$,[11] $[Zr(C_5H_4Me)_2Cl_2]$,[11] $[Ti(C_5R_5)F_3]$ (R_5 = Me_5, H_4Me or Me_4Et),[12] $[Ti(C_5H_4Me)_2F_2]$[12] and $[(C_5Me_5)Cl_2TiOSiBu^t_2(OH)]$ **1a**[4] were prepared as described in the literature, and $[Hf(C_5H_5)_2Cl_2]$ was purchased from Aldrich. The NMR spectra were recorded on a Bruker AM 250 spectrometer, IR spectra on a Perkin-Elmer Bio-Rad Digilab FTS-7 and mass spectra on Finnigan MAT 8230 and Varian MAT CH5 (EI) systems. The ^1H, ^{13}C

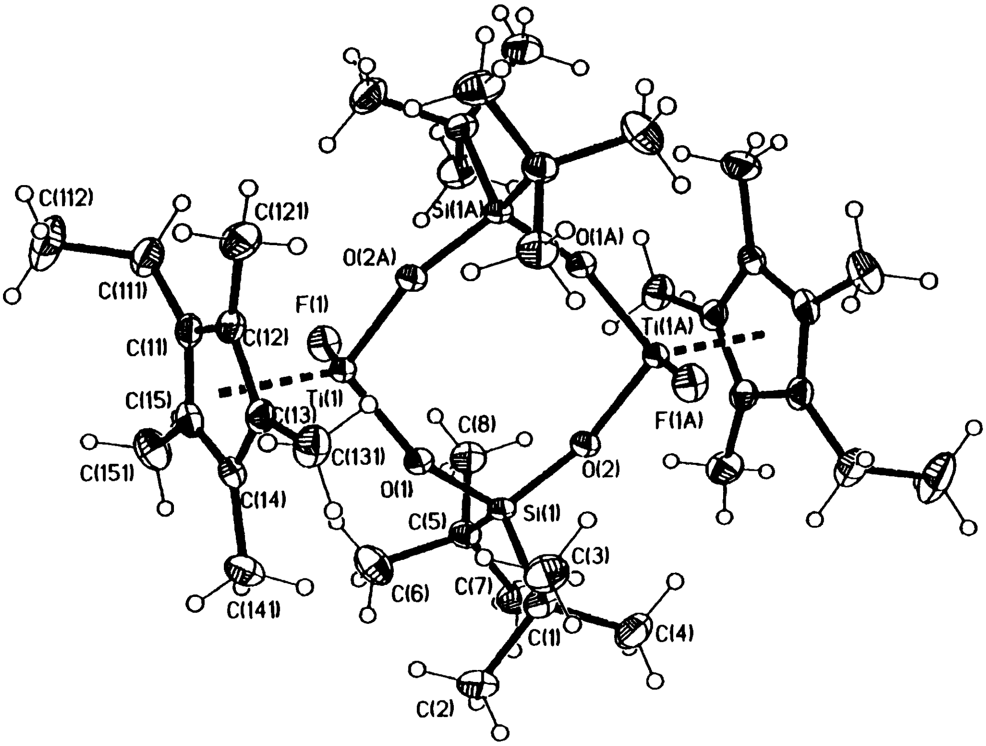

Fig. 1 Molecular structure of complex **3b**

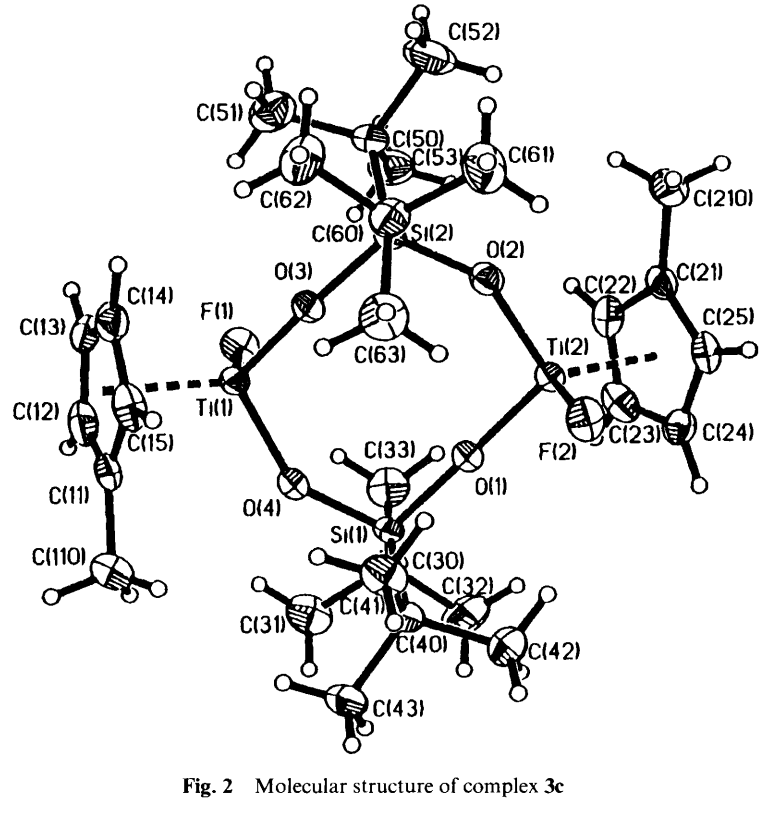

Fig. 2 Molecular structure of complex **3c**

and ^{19}F NMR data are listed in ppm downfield from $SiMe_4$ and $CFCl_3$, respectively. Microanalyses were performed by microanalytisches Laboratorium Beller, Göttingen, and in this institute.

Preparations.—$SiBu^t_2(OH)(OSiMe_3)$. A solution of $SiMe_3Cl$ (1.40 g, 13 mmol) in toluene (10 cm^3) was added to a suspension of $SiBu^t_2(OH)_2$ (1.76 g, 10 mmol) in toluene (50 cm^3) and NEt_3 (2 cm^3). The mixture was stirred overnight and the solvent removed under vacuum. The residue was extracted with hexane and the product obtained after removal of the solvent. ^1H NMR ($CDCl_3$): δ 2.12 (1 H, br, OH), 0.99 [18 H, s, 2 $C(CH_3)_3$], 0.14 [9 H, s, $Si(CH_3)_3$]. Correct elemental analysis was obtained.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3b**

Ti(1)–O(2A)	1.8225(14)	Ti(1)–F(1)	1.8229(12)
Ti(1)–O(1)	1.8317(13)	Si(1)–O(1)	1.6438(14)
Si(1)–C(1)	1.908(2)	Ti(1)–Cp*	2.058
O(2A)–Ti(1)–F(1)	103.31(6)	O(1)–Ti(1)–O(2A)	104.66(6)
F(1)–Ti(1)–O(1)	103.70(6)	O(1)–Si(1)–O(2)	110.22(7)
O(1)–Si(1)–C(5)	106.19(8)	O(2)–Si(1)–C(5)	108.58(8)
O(1)–Si(1)–C(1)	109.08(8)	O(2)–Si(1)–C(1)	105.81(8)
C(5)–Si(1)–C(1)	116.92(9)	Si(1)–O(1)–Ti(1)	153.09(9)
Si(1)–O(2)–Ti(1A)	152.62(9)		

* Corresponds to the ring centroid.

Table 3 Selected bond lengths (Å) and angles (°) for complex **3c**

Ti(1)–O(3)	1.794(3)	Ti(1)–O(4)	1.810(3)
Ti(1)–F(1)	1.815(2)	Ti(2)–O(1)	1.801(3)
Ti(2)–F(2)	1.819(2)	Ti(2)–O(2)	1.820(3)
Si(1)–O(4)	1.645(3)	Si(1)–O(1)	1.646(3)
Si(1)–C(30)	1.893(4)	Si(1)–C(40)	1.894(4)
Si(2)–O(2)	1.636(3)	Si(2)–O(3)	1.646(3)
Si(2)–C(50)	1.890(4)	Si(2)–C(60)	1.897(4)
Ti(1)–Cp(1)*	2.061	Ti(2)–Cp(2)*	2.047
O(3)–Ti(1)–O(4)	104.62(12)	O(3)–Ti(1)–F(1)	103.26(11)
O(4)–Ti(1)–F(1)	104.06(11)	O(1)–Ti(2)–F(2)	102.32(11)
O(1)–Ti(2)–O(2)	104.90(12)	F(2)–Ti(2)–O(2)	102.41(11)
O(1)–Si(1)–O(4)	108.94(13)	O(4)–Si(1)–C(30)	106.1(2)
O(1)–Si(1)–C(30)	108.7(2)	O(4)–Si(1)–C(40)	108.5(2)
O(1)–Si(1)–C(40)	106.1(2)	C(30)–Si(1)–C(40)	118.3(2)
O(2)–Si(2)–O(3)	109.18(14)	O(2)–Si(2)–C(50)	109.1(2)
O(3)–Si(2)–C(50)	105.7(2)	O(2)–Si(2)–C(60)	107.2(2)
O(3)–Si(2)–C(60)	107.3(2)	C(50)–Si(2)–C(60)	118.2(2)
Si(1)–O(1)–Ti(2)	166.1(2)	Si(2)–O(2)–Ti(2)	147.7(2)
Si(1)–O(3)–Ti(1)	167.6(2)	Si(1)–O(4)–Ti(1)	146.1(2)

* Corresponds to the ring centroid.

$SiBu^t{}_2(OSnMe_3)_2$. To a solution of $SiBu^t{}_2(OH)_2$ (3.52 g, 20 mmol) in thf (50 cm^3), LiBu (16 cm^3, 2.5 mol dm^{-3} in hexane, 40 mmol) was added slowly at 0 °C. After the addition was complete, the mixture was allowed to warm to room temperature and refluxed for 30 min. A solution of $SnMe_3Cl$ (7.96 g, 40 mmol) in thf (30 cm^3) was added to the above solution and refluxed for 30 min. The solvents were removed under vacuum and the residue extracted with hexane. A waxy solid was obtained after distillation *in vacuo* at 90 °C/10^{-2} Torr. ^1H NMR (C_6D_6): δ 1.20 [18 H, s, $C(CH_3)_3$], 0.25 [18 H, s, $Sn(CH_3)_3$]. Correct elemental analysis was obtained

$[Zr(C_5H_4Me)_2F_2]$. A mixture of $[Zr(C_5H_4Me)_2Cl_2]$ (1.28 g, 4 mmol) and $SnMe_3F$ (1.46 g, 8 mmol) in toluene (70 cm^3) was stirred for 6 h at room temperature and refluxed for 4 h. The solvent was removed *in vacuo* and the residue sublimed at 120 °C/10^{-2} Torr. A white solid was obtained (1.05 g, 91%), m.p. 134–136 °C. NMR ($CDCl_3$): ^1H, δ 6.27 (4 H, m, 2 C_5H_2), 6.02 (4 H, m, 2 C_5H_2), 2.13 (6 H, s, 2 CH_3); ^{19}F, δ 17.04 (s). Correct elemental analysis was obtained

$[(C_5Me_4Et)Cl_2TiOSiBu^t{}_2(OH)]$ **1b**. A solution of $[Ti(C_5Me_4Et)Cl_3]$ (1.21 g, 4.0 mmol) in toluene (40 cm^3) was added dropwise to a mixture of $SiBu^t{}_2(OH)_2$ (0.70 g, 4.0 mmol) and NEt_3 (0.51 g, 5.0 mmol) in toluene (30 cm^3) at 0 °C. The solution was stirred at room temperature for 10 h and filtered. The solvent was removed *in vacuo* and the residue recrystallized from hexane (60 cm^3). An orange solid was obtained (1.63 g, 92%). NMR: ^1H (C_6D_6), δ 2.67 [2 H, q, *J*(HH) 7.7, CH_2], 2.06 [6 H, s, $C_5(CH_3)_4$], 2.05 [6 H, s, $C_5(CH_3)_4$], 1.34 (1 H, br, OH), 1.17 [18 H, s, 2 $C(CH_3)_3$], 0.82 [3 H, t, *J*(HH) 7.7, CH_3]; ^1H ($CDCl_3$), δ 2.73 [2 H, q, *J*(HH) 7.7, CH_2], 2.25 [6 H, s, $C_5(CH_3)_4$], 2.24 [6 H, s, $C_5(CH_3)_4$], 2.11 (1 H, br, OH), 1.03 [18 H, s, 2 $C(CH_3)_3$], 1.02 [3 H, t, *J*(HH) 7.7 Hz, CH_3]; ^{13}C (C_6D_6), δ 137.9, 132.9, 131.9 [$\mathit{C}_5(CH_3)_4$], 27.9 [$C(\mathit{C}H_3)_3$], 22.2 [$\mathit{C}(CH_3)_3$], 21.7 (CH_2), 14.3, 13.1, 12.9 (CH_3); ^{13}C ($CDCl_3$), δ 138.2, 133.2, 132.2 [$\mathit{C}_5(CH_3)_4$], 27.6 [$C(\mathit{C}H_3)_3$], 21.9 [$\mathit{C}(CH_3)_3$], 21.4 (CH_2), 14.2, 13.2, 13.0 (CH_3). IR (Nujol): 3619s, 1051w, 923s, 829m, 646m, 486m, 442s, 396s cm^{-1}.

$[\{(C_5H_4Me)ClTiOSiBu^t{}_2O\}_2]$ **2**. This compound was prepared following the same method as described for **1b** using $[Ti(C_5H_4Me)Cl_3]$ (0.93 g, 4.0 mmol) in toluene (30 cm^3) and $SiBu^t{}_2(OH)_2$ (0.70 g, 4.0 mmol). Pale-yellow crystals were separated (1.14 g, 85%). NMR: ^1H (C_6D_6), δ 6.23–6.21 (4 H, m, 2 C_5H_2), 6.16–6.12 (4 H, m, 2 C_5H_2), 2.17 [6 H, t, *J*(HH) 0.54, 2 CH_3], 1.22 [36 H, s, 4 $C(CH_3)_3$]; ^1H ($CDCl_3$), δ 6.40–6.35 (8 H, m, 2 C_5H_4), 2.35 (6 H, s, 2 CH_3), 1.06 [36 H, s, 4 $C(CH_3)_3$]; ^{13}C ($CDCl_3$), δ 131.3, 119.4, 116.1 (C_5H_4), 27.8 [$C(\mathit{C}H_3)_3$], 22.5 [$\mathit{C}(CH_3)_3$], 15.8 (CH_3). IR (Nujol): 3119w, 3098w, 1501m, 1361m, 926s, 815s, 650s, 456s, 394m, 357m cm^{-1}.

$[\{(C_5Me_5)FTiOSiBu^t{}_2O\}_2]$ **3a**. *Method 1*. A mixture of compound **1a** (0.86 g, 2.0 mmol) and $SnMe_3F$ (0.73 g, 4.0 mmol) in toluene (50 cm^3) was stirred for 4 h. The solvent was removed *in vacuo* after all the $SnMe_3F$ had dissolved and hexane (70 cm^3) added to the residue. The solution was filtered and cooled to 2 °C. Yellow crystals and an orange solid appeared. The solution was warmed to room temperature whereupon the orange solid was filtered off and the filtrate cooled again. Yellow crystals were formed (0.27 g, 37%). NMR (mixture of isomers): ^1H ($CDCl_3$), δ 2.12 [s, $C_5(CH_3)_5$], 2.06 [s, $C_5(CH_3)_5$], 1.02 and 0.96 [s, $C(CH_3)_3$], 0.95 [s, $C(CH_3)_3$], ratio 1 : 7; ^{19}F ($CDCl_3$), δ 97.7 (s), 77.9 (s). IR (Nujol): 963s, 919s, 876s, 826s, 694m, 650s cm^{-1}.

Method 2. A solution of $SiBu^t{}_2(OSnMe_3)_2$ (1.00 g, 2.0 mmol) in thf (20 cm^3) was added dropwise to a solution of $[Ti(C_5Me_5)F_3]$ (0.48 g, 2.0 mmol) in thf (25 cm^3). The solution was stirred for 8 h and filtered The solvent was removed *in vacuo* and the residue extracted with hexane (60 cm^3). A yellow solid was obtained (0.65 g, 86%).

$[\{(C_5Me_4Et)FTiOSiBu^t{}_2O\}_2]$ **3b**. This compound was prepared using the same methods as for **3a**. Crystals suitable for X-ray diffraction were obtained from hexane solution at 0 °C. NMR (mixture of isomers): ^1H (C_6D_6), δ 2.68 [4 H, q, *J*(HH) 7.6, 2 CH_2], 2.09 and 2.02 [s, $C_5(CH_3)_4$], 2.08 and 2.01 [s, $C_5(CH_3)_4$], 1.28 [s, $C(CH_3)_3$], 1.27 and 1.23 [s, $C(CH_3)_3$], 0.90 [6 H, t, *J*(HH) 7.6 Hz, 2 CH_3], ratio 1 : 8; ^{19}F (C_6D_6), δ 134.0 (s), 110.3 (s). IR (Nujol): 946s, 919s, 827s, 648s, 614s, 457m, 427s, 358s cm^{-1}.

$[\{(C_5H_4Me)FTiOSiBu^t{}_2O\}_2]$ **3c**. This compound was prepared according to method 1 for **3a** using compound **2** (0.73 g, 1.0 mmol) and $SnMe_3F$ (0.37 g, 2.0 mmol). A white solid was obtained (0.54 g, 85%). With method 2 using $[Ti(C_5H_4Me)F_3]$ (0.37 g, 2.0 mmol) and $SiBu^t{}_2(OSnMe_3)_2$ (1.00 g, 2.0 mmol), a yield of 0.51 g (81%) was obtained. Crystals suitable for X-ray diffraction were obtained from $CDCl_3$ solution at room temperature. NMR (mixture of isomers): ^1H ($CDCl_3$), δ 6.41–6.40 (4 H, m, 2 C_5H_2), 6.20 (4 H, br, 2 C_5H_2), 2.28 (6 H, s, 2 CH_3), 1.01 [s, $C(CH_3)_3$], 1.07 and 0.95 [s, $C(CH_3)_3$], ratio 1 : 4; ^{19}F ($CDCl_3$), δ 105.6 (s), 97.7 (s); ^{13}C ($CDCl_3$), δ 131.3, 131.2, 117.2, 115.9, 115.4 (C_5H_4), 27.8, 27.6, 27.5, 22.9, 21.7, 20.7, 14.6. IR (Nujol): 966s, 932s, 808s, 652s, 635m, 452m, 407s, 360s cm^{-1}.

$[(C_5H_4Me)_2ClTiOSiBu^t{}_2(OH)]$ **4a**. A solution of $[Ti(C_5H_4Me)_2Cl_2]$ (0.55 g, 2.0 mmol) in toluene (30 cm^3) was added dropwise to a solution of $SiBu^t{}_2(OH)_2$ (0.35 g, 2.0 mmol) and NEt_3 (1 cm^3) in toluene (30 cm^3). After 16 h the solution was filtered. The solvent was removed *in vacuo* and the residue washed with hexane to give a red solid (0.70 g, 84%). ^1H NMR ($CDCl_3$): δ 6.32–6.18 (6 H, m, 2 C_5H_3), 5.83–5.79 (2 H, m, 2 C_5H), 2.22 (6 H, s, 2 CH_3), 1.85 (1 H, s, OH), 0.98 [18 H, s, 2 $C(CH_3)_3$]. IR (Nujol): 3660s, 3490s, 3107m, 1708w, 1501m, 1041m, 942s, 926s, 827s, 644s, 448s, 396s cm^{-1}.

$[(C_5H_4Me)_2ClZrOSiBu^t{}_2(OH)]$ **4b**. This compound was prepared by the same method as **4a** using $[Zr(C_5H_4Me)_2Cl_2]$ (0.64 g, 2.0 mmol) and in a yield of 0.78 g (85%). NMR: ^1H

Table 4 Crystallographic data for complexes **3b** and **3c**

Compound	**3b**	**3c**
Empirical formula	$C_{38}H_{70}F_2O_4Si_2Ti_2$	$C_{28}H_{50}F_2O_4Si_2Ti_2 \cdot 0.5\ C_6H_6$
M	780.9	640.6 + 39.1
T/°C	−123(2)	−123(2)
Crystal dimensions/mm	0.6 × 0.5 × 0.2	0.6 × 0.4 × 0.15
Crystal system, habit	Triclinic, yellow plates	Monoclinic, colourless plates
Space group	$P\bar{1}$	$C2/c$
a/Å	9.644(3)	29.75(2)
b/Å	11.397(3)	13.152(8)
c/Å	11.822(3)	22.332(11)
α/°	116.702(10)	90
β/°	104.507(12)	124.88(3)
γ/°	98.906(8)	90
U/Å^3	1068.9(4)	7167(7)
Z	1	8
D_c/Mg m^{-3}	1.213	1.260
μ/mm^{-1}	0.473	0.554
F(000)	420	2888
Measured 2θ range/°	7–50	7–45
Data measured, unique,	7480, 3761	5926, 4644
R,^{a} $wR2^b$ ($I > 2\sigma I$)	0.032, 0.086	0.046, 0.111
R, $wR2$ (all data)	0.036, 0.091	0.058, 0.133
Goodness of fit S^c	1.042	1.049
Weighting factors a, b^d	0.0379, 0.7728	0.0550, 26.0830
Refined parameters	228	399
Largest difference peak, hole/e Å^{-3}	0.364, −0.254	0.416, −0.412

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{\frac{1}{2}}$. ^{c} $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(n-p)\}^{\frac{1}{2}}$. ^{d} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = (F_o^2 + 2F_c^2)/3$.

Table 5 Atomic coordinates (× 10^4) for compound **3b**

Atom	x	y	z
Ti(1)	6 374(1)	7 101(1)	274(1)
Si(1)	5 979(1)	5 960(1)	2 401(1)
F(1)	4 918(1)	7 943(1)	461(1)
O(1)	6 616(2)	6 588(1)	1 556(1)
O(2)	4 586(2)	4 513(1)	1 344(1)
C(1)	7 528(2)	5 477(2)	3 296(2)
C(2)	8 763(3)	6 724(2)	4 572(2)
C(3)	8 263(3)	4 710(2)	2 287(2)
C(4)	6 849(3)	4 493(2)	3 719(2)
C(5)	5 221(2)	7 295(2)	3 519(2)
C(6)	6 289(3)	8 760(2)	4 128(2)
C(7)	5 005(3)	7 106(3)	4 679(2)
C(8)	3 677(2)	7 177(2)	2 621(2)
C(11)	7 466(2)	8 756(2)	−235(2)
C(12)	8 038(2)	7 628(2)	−739(2)
C(13)	8 878(2)	7 549(2)	381(2)
C(14)	8 873(2)	8 658(2)	1 582(2)
C(15)	7 996(2)	9 401(2)	1 207(2)
C(111)	6 544(2)	9 245(2)	−1 058(2)
C(121)	7 831(3)	6 708(2)	−2 202(2)
C(131)	9 696(2)	6 508(2)	304(2)
C(141)	9 718(3)	9 007(2)	3 007(2)
C(151)	7 678(3)	10 662(2)	2 148(2)
C(112)	7 551(3)	10 234(3)	−1 282(3)

($CDCl_3$), δ 6.24–6.15 (6 H, m, 2 C_5H_3), 5.91–5.87 (2 H, m, 2 C_5H), 2.22 (6 H, s, 2 CH_3), 1.79 (1 H, s, OH), 0.98 [18 H, s, 2 $C(CH_3)_3$]; ^{13}C ($CDCl_3$), δ 127.2, 118.3, 113.3, 112.9, 109.7 (C_5H_4), 27.7 [$C(CH_3)_3$], 20.7 [$C(CH_3)_3$], 15.3 (CH_3); ^{29}Si ($CDCl_3$), δ −13.1. IR (Nujol): 3660m, 3490 (br), m, 3099m, 1497w, 1051m, 1037m, 954s, 826s, 804s, 644m, 447m, 365m cm^{-1}.

[$(C_5H_4Me)_2FZrOSiBu^t_2(OSnMe_3)$] **4c**. A solution of $SiBu^t_2(OSnMe_3)_2$ (1.00 g, 2.0 mmol) in toluene (20 cm^3) was added dropwise to a solution of [$Zr(C_5H_4Me)_2F_2$] (0.57 g, 2.0 mmol) in toluene (30 cm^3). The solution was filtered after 8 h and solvent removed from the filtrate. The residue was recrystallized from pentane (40 cm^3). Colourless crystals were separated out (1.07 g, 88%). NMR: ^1H (C_6D_6), δ 6.18–6.14 (2 H, m, C_5H_2), 6.12–6.08 (2 H, m, C_5H_2), 5.95–5.91 (2 H, m, C_5H_2), 5.59–5.55 (2 H, m, C_5H_2), 2.14 [3 H, t, J(HH) 0.53, CH_3], 2.13 [3 H, t, J(HH) 0.53 Hz, CH_3], 1.18 [18 H, s, 2 $C(CH_3)_3$], 0.28 [9 H, s, $Sn(CH_3)_3$]; ^{19}F (C_6D_6), δ 15.6 (s). IR (Nujol): 3097w, 995s, 939s, 823s, 806s, 643m, 539s, 450m cm^{-1}.

[$(C_5H_5)_2ClHfOSiBu^t_2(OH)$] **4d**. This compound was prepared according to the method described for **4a** using [$Hf(C_5H_5)_2Cl_2$] (0.76 g, 2.0 mmol) in a yield of 0.84 g (82%). ^1H NMR ($CDCl_3$): δ 6.28 (10 H, s, 2 C_5H_5), 1.92 (1 H, s, OH), 0.99 [18 H, s, 2 $C(CH_3)_3$]. IR (Nujol): 3648s, 3480m, 1071w, 1016s, 943s, 845s, 646m, 447m cm^{-1}.

[$(C_5Me_4Et)Cl_2TiOSiBu^t_2(OSnMe_3)$] **5**. This compound was prepared similarly to **4c** using [$Ti(C_5Me_4Et)Cl_3$] (0.91 g, 3.0 mmol) and $SiBu^t_2(OSnMe_3)_2$ (1.51 g, 3.0 mmol) and in a yield of 1.54 g (85%). ^1H NMR (C_6D_6): δ 2.71 [2 H, q, J(HH) 7.6, CH_2], 2.11 [6 H, s, $C_5(CH_3)_2$], 2.05 (6 H, s, $C_5(CH_3)_2$], 1.23 [18 H, s, 2 $C(CH_3)_3$], 0.82 [3 H, t, J(HH) 7.6 Hz, CH_3], 0.30 [9 H, s, $Sn(CH_3)_3$]. IR (Nujol): 1192m, 1012s, 909s, 820s, 773s, 646s, 613m, 545m, 446s, 392s cm^{-1}.

Crystal-structure Determinations of Compounds **3b** *and* **3c**.—Crystallographic data are summarized in Table 4. Data were collected on a Siemens-Stoe AED2 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); 2θ–ω scans were used following the learnt profile method.[13]

The stability of three intensity controls was maintained during the data collection to within 3% in both cases. An absorption correction based on psi-scans was applied in both cases, with maximum and minimum transmission factors 0.945, 0.827 for **3b** and 0.978, 0.783 for **3c**. Both structures were solved by direct methods.[14] They were refined by full-matrix least-squares techniques against all data.[15]

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions.

In **3c** a molecule of benzene was found disordered about a two-fold axis. The six atoms were refined on two alternative sites, a definite one, and one generated by symmetry with partial occupation of 0.5. The geometry was constrained to be that of a

Table 6 Atomic coordinates (× 10^4) for compound **3c**

Atom	*x*	*y*	*z*
Ti(1)	562(1)	3122(1)	1006(1)
Ti(2)	2401(1)	1893(1)	2415(1)
Si(1)	1419(1)	2354(1)	606(1)
Si(2)	1463(1)	2276(1)	2754(1)
F(1)	749(1)	4457(2)	1160(1)
F(2)	2372(1)	513(2)	2351(1)
O(1)	1926(1)	2270(2)	1477(1)
O(2)	2047(1)	2155(2)	2846(1)
O(3)	982(1)	2581(2)	1903(1)
O(4)	854(1)	2653(2)	536(1)
C(11)	−299(1)	2547(3)	−69(2)
C(110)	−346(2)	2081(4)	−715(2)
C(12)	−358(2)	3571(3)	41(2)
C(13)	−301(2)	3663(4)	714(2)
C(14)	−208(2)	2704(4)	1015(2)
C(15)	−190(2)	2016(3)	549(2)
C(21)	3228(2)	2401(3)	3544(2)
C(210)	3269(2)	2409(4)	4248(2)
C(22)	3034(2)	3224(3)	3042(2)
C(23)	3064(2)	2937(3)	2459(2)
C(24)	3258(2)	1936(3)	2583(2)
C(25)	3360(2)	1613(3)	3248(2)
C(30)	1562(2)	3449(3)	188(2)
C(31)	1048(2)	3709(3)	−574(2)
C(32)	2046(2)	3234(4)	133(3)
C(33)	1704(2)	4374(3)	684(2)
C(40)	1334(2)	1037(3)	211(2)
C(41)	1101(2)	349(3)	524(2)
C(42)	1891(2)	600(3)	436(2)
C(43)	941(2)	1023(4)	−631(2)
C(50)	1511(2)	3387(3)	3324(2)
C(51)	939(2)	3725(4)	3097(3)
C(52)	1869(2)	3161(4)	4152(2)
C(53)	1768(2)	4281(3)	3175(2)
C(60)	1282(2)	981(3)	2933(2)
C(61)	1771(2)	512(4)	3641(2)
C(62)	788(2)	1033(4)	2986(3)
C(63)	1134(2)	286(3)	2296(2)
C(1)	−73(9)	8019(3)	2529(14)
C(2)	302(8)	7552(13)	2435(11)
C(3)	350(11)	6499(14)	2469(12)
C(4)	24(14)	5913(4)	2596(16)
C(5)	−351(11)	6381(11)	2690(12)
C(6)	−399(8)	7434(12)	2657(11)

regular hexagon with C–C distances of 1.39 Å; similarity and rigid bond restraints were applied on the thermal parameters of the benzene carbons. Atomic coordinates are listed in Tables 5 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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