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Synthesis and characterization of new alkoxide and aryloxide derivatives of titanium and zirconium. X-ray molecular structure of $[ZrCp_2(OC_6F_5)_2]$

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Abstract

Lithium or sodium alkoxides MOR (R = $CH_2CH{=}CMe_2$; M = Li **1**; Na **2**; R = C_6F_5; M = Li **3**) were prepared by reaction of the alcohols with *n*-butyl lithium or sodium metal in hexane. Reaction of a hexane suspension of **3** with $SiClMe_3$ afforded $SiMe_3(OC_6F_5)$ **4**, whereas the reaction of 3 equivalents of C_6F_5OH with $AlMe_3$ in hexane led to $Al(OC_6F_5)_3$ **5**. Compounds **1** or **2** react with one equivalent of $[TiCp^*Cl_2Me]$ ($Cp^* = C_5Me_5$) in toluene to give $[TiCp^*ClMe(OCH_2CH{=}CMe_2)]$ **6**. Complex **6** reacts with $AlEtCl_2$ to give quantitatively $[TiCp^*Cl_3]$. In the presence of water, the hydrolysis of **6** takes place giving the μ-oxo compound $[\{(TiCp^*Cl)(\mu-O)\}_3]$. $[TiCp^*Cl_2Me]$ reacted with an excess of the alcohol C_6F_5OH to give $[TiCp^*(OC_6F_5)_3]$ **7**. $[ZrCp_2Cl_2]$ reacted with two equivalents of pentafluorophenol in the presence of aniline to give the dialkoxide $[ZrCp_2(OC_6F_5)_2]$ **8**. When the same reaction was carried out in a 1 : 1 molar ratio, a mixture of **8** and the chloroalkoxide $[ZrCp_2Cl(OC_6F_5)]$ **9** was obtained. A clean reaction takes place when the μ-oxo compound $[(ZrCp_2Me)_2(\mu\text{-}O)]$ is treated with two equivalents of pentafluorophenol, leading to the isolation of the alkoxo complex $[\{ZrCp_2(OC_6F_5)\}_2(\mu\text{-}O)]$ **10**. The methylalkoxo derivative $[ZrCp_2Me(OC_6F_5)]$ **11**, was obtained by reaction of $[ZrCp_2ClMe]$ with one equivalent of **3**. Alternative methods can also be followed to synthesize **8** and **11**. The crystal and molecular structure of **8** has been determined by X-ray diffraction methods. The most interesting feature of this structure is the disposition of the (C_6F_5) ring planes, which are located practically on the reflection plane defined by O(1), Zr(1) and O(1)'.

Keywords: Titanium; Zirconium; Alkoxides; X-ray diffraction; Group 4; Cyclopentadienyl

1. Introduction

Many Group 4 metallocene-type complexes of titanium and zirconium have been studied as stereo- and regio-selective catalysts for Ziegler-Natta polymerization of α-olefins in the presence of Lewis acids. The use of $AlEtCl_2$ to activate titanocene complexes for C–C bond formation through intramolecular insertion of olefins has been recently reported [1]. Similar studies for acetylene insertion with complexes of Group 4d metals are also known [2]. All these studies have been carried out with alkyl derivatives of titanium and zirconium. Alkoxide and related aryloxides, represented as RO^-, constitute a class of hard ligands that complement the traditional use of soft ligands in organotransition metal chemistry. By appropriate selection of R, the control of steric and electronic properties at the metal is possible. These OR^- can, in this way, modify the reactivity of the metal centre in different types of reaction. Some alkoxide or aryloxide derivatives have been used as catalysts in olefin polymerization processes [3]. We are interested in the synthesis and characterization of alkoxide and aryloxide derivatives of the Group 4 metals by using OR^-. We report in this paper the synthesis and characterization of the complexes MOR [R = $CH_2CH{=}CMe_2$; M = Li (**1**) Na (**2**). R = C_6F_5; M = Li (**3**)], $SiMe_3(OC_6F_5)$ (**4**) and $Al(OC_6F_5)_3$ (**5**) and the use of these reagents to prepare the alkoxide complexes $[TiCp^*ClMe(OCH_2CH{=}CMe_2)]$ (**6**), $[TiCp^*(OC_6F_5)_3]$ (**7**), $[ZrCp_2(OC_6F_5)_2]$ (**8**), $[ZrCp_2Cl(OC_6F_5)]$ (**9**), $[\{ZrCp_2(OC_6F_5)\}_2(\mu\text{-}O)]$ (**10**) and $[ZrCp_2Me(OC_6F_5)]$ (**11**) and the characterization of **8** by X-ray diffraction methods.

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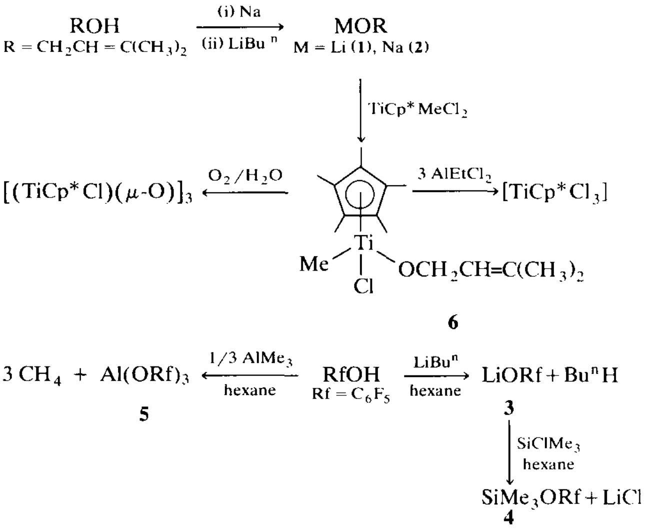
2. Results and discussion

Solid lithium or sodium alkoxides, MOR ($R = CH_2CH{=}CMe_2$; M = Li **1**; Na **2**; $R = C_6F_5$; M = Li **3**) were prepared by reaction of the alcohols with *n*-butyl lithium or sodium metal in hexane. Reaction of a hexane suspension of **3** with $SiClMe_3$ afforded $SiMe_3(OC_6F_5)$ **4**, as an oily yellow liquid, whereas the reaction of 3 equivalents of C_6F_5OH with $AlMe_3$ in hexane led to $Al(OC_6F_5)_3$ 5, as a powdery colourless solid. All these compounds were used as reagents to transfer the alkoxo group to different organo metal complexes of Group 4.



2.1. Titanium complexes

Reaction of **1** or **2** with one equivalent of $[TiCp^*Cl_2Me]$ ($Cp^* = C_5Me_5$) in toluene gave $[TiCp^*ClMe(OCH_2CH{=}CMe_2)]$ **6** as a yellow liquid after filtration of the alkalin metal chloride and evaporation of the solvent. Compound **6** was treated with $AlEtCl_2$ in an attempt to insert the terminal olefin into the titanium–methyl bond to give the oxotitanacycle. However, this led to a different product, which results from a metathetical reaction, the methyl and alkoxo being preferentially transferred to aluminium to give $[TiCp^*Cl_3]$ together with an alkylalkoxoaluminium derivative. The reaction was almost quantitative when 3 equivalents of $AlEtCl_2$ were used. Simultaneous hydrolysis takes place when the reaction is carried out in the presence of water, to give the previously reported [4] trimer $[\{(TiCp^*Cl)(\mu\text{-}O)\}_3]$.

Unresolvable mixtures of chloro-alkoxo compounds were obtained when $[TiCp^*Cl_2Me]$ was treated with different molar ratios of C_6F_5OH, as confirmed by ^1H and ^{19}F NMR spectroscopy. Only when an excess of the alcohol was used, was $[TiCp^*(OC_6F_5)_3]$ **7**, the sole final product, and it was obtained as an orange crystalline solid by cooling its toluene solution.

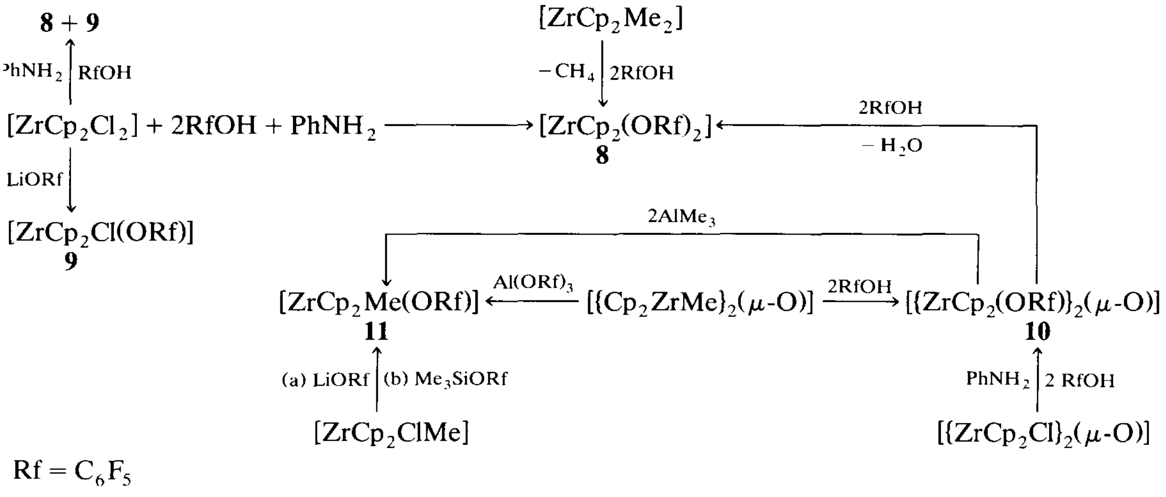
$$[TiCp^*Cl_2Me] + C_6F_5OH(\text{excess}) \longrightarrow \underset{\mathbf{7}}{[TiCp^*(OC_6F_5)_3]} \qquad (1)$$

The ^1H NMR spectrum of complex **6** shows one singlet at δ 0.79 due to the methyl group bound to titanium, along with a singlet at δ 1.80 corresponding to the methyl protons of the cyclopentadienyl ring. The alkoxo ligand gives rise to a doublet at δ 4.74 for both protons of the methylene group, a triplet at δ 5.40 for the internal olefinic carbon-bonded proton and two singlets at δ 1.46 and δ 1.52 for methyl protons of both inequivalent methyl groups bound to the terminal olefinic carbon. A similar behaviour is also observed in the ^{13}C NMR spectrum, which shows one singlet (δ 134.9) and one doublet (δ 123.9; $J(C\text{–}H) = 157.7$ Hz) for the two olefinic carbons, one triplet at δ 72.9 ($J(C\text{–}H) = 142.5$ Hz) for the oxygen-bonded methylene carbon and two quadruplets at δ 17.9 ($J(C\text{–}H) = 125.9$ Hz) and δ 25.6 ($J(C\text{–}H) = 125.4$ Hz) owing to the inequivalent methyl carbons. The mass spectrum shows the presence of the parent ion at 318 (M^+). The ^1H and ^{19}F NMR spectra of complex **7** show the expected singlet for the methyl protons of the cyclopentadienyl ring and the three signals for the pentafluorophenyl group (see Experimental section).

2.2. Zirconium complexes

$[ZrCp_2Cl_2]$ reacted with two equivalents of pentaflurophenol in the presence of aniline to give the dialkoxide $[ZrCp_2(OC_6F_5)_2]$ **8**. When the same reaction was carried out in a 1 : 1 molar ratio, a mixture of **8** and the chloroalkoxide $[ZrCp_2Cl(OC_6F_5)]$ **9** was obtained. The separation of **8** and **9** is difficult as they possess similar solubility in most solvents. Therefore this method is not ideal for obtaining pure **9**, which can be easily isolated in high yield by the reaction of the dichloride with one equivalent of the lithium salt, **3**.

Alternative methods can also be followed to synthesize **8**. The most convenient method consists of the reaction of the dimethylzirconium complex with toluene solutions of the alcohol, with the resultant evolution of methane. An equally clean reaction takes place when the μ-oxo dimer $[(ZrCp_2Me)_2(\mu\text{-}O)]$ is treated with two equivalents of pentafluorophenol, leading to the alkoxo dimer $[\{ZrCp_2(OC_6F_5)\}_2(\mu\text{-}O)]$ **10**. Further alcoholysis of **10** by an excess of alcohol is an alternative way to obtain **8** in high yield. The best method to obtain the methylalkoxo derivative $[ZrCp_2Me(OC_6F_5)]$ **11** is based on the reaction of $[ZrCp_2ClMe]$ with one equivalent of **3**. Complex **11** can also be obtained in lower yields: (a) by reaction of **10** with $AlMe_3$; (b) by



reaction of the μ-oxo methyl dimer with **5**; and (c) by reaction of [ZrCp$_2$ClMe] with **4**. All the new complexes were characterized by analysis, IR and ^{1}H and ^{19}F NMR spectroscopy and the molecular structure of complex **8** was studied by X-ray diffraction methods. All the compounds show one singlet in the ^{1}H spectra and three signals are observed in the ^{19}F NMR spectra (see experimental section).

2.3. Crystal structure of [ZrCp$_2$(OC$_6$F$_5$)$_2$] (8)

The molecular structure of **8** is shown in Fig. 1 with the atomic labelling scheme. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are displayed in Table 1. Selected bond distances and bond angles are given in Table 2. Only a half of the molecule exists in the asymmetrical unit of the unit cell, the other half is generated by a C_2 crystallographic axis passing through the Zr atom.

The molecular structure consists of a typical bent-sandwich geometry, with two ligands in the equatorial plane. Coordination around the Zr atom is pseudo-tetrahedral if the centroids of the Cp rings are assumed to occupy single coordination sites. The angles of this pseudotetrahedron, ranging from 130° in Cp–Zr–Cp′ to 96° in O(1)–Zr–O(1)′, are normal for this type of structures [5].

The most interesting feature of this structure is the

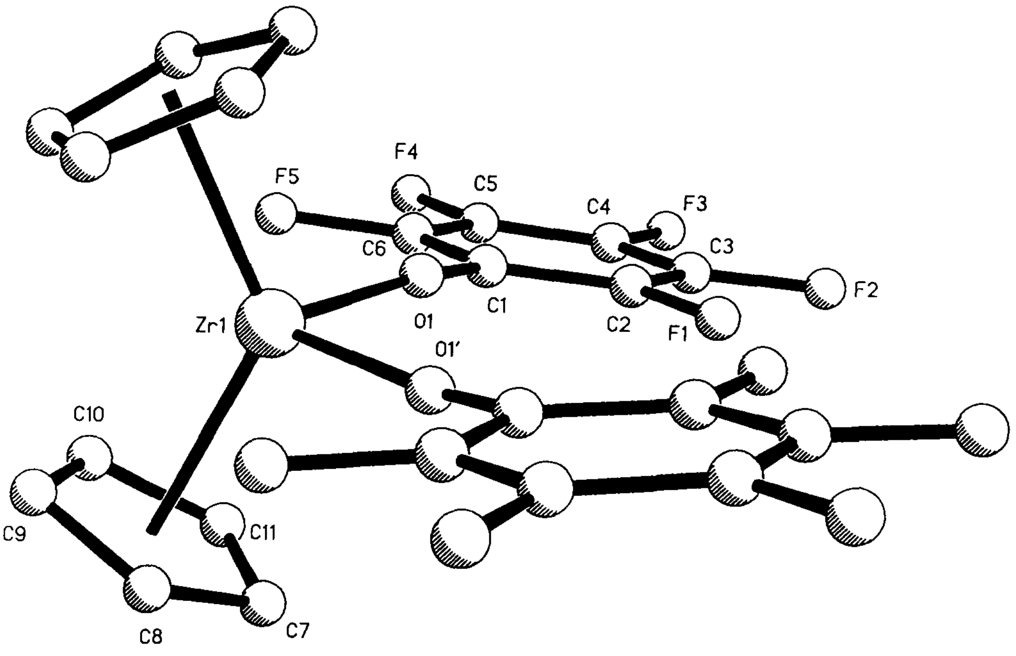


Fig. 1. ORTEP view of molecular structure of compound **8** with the atomic labelling scheme.

Table 1
Table of positional parameters and their estimated standard deviations for compound **8**

Atom	*x*	*y*	*z*	B (A2)
ZR1	0.000	0.14110(4)	0.250	3.639(6)
F1	−0.0479(2)	0.5897(3)	0.3233(1)	7.40(5)
F2	−0.1215(2)	0.7396(3)	0.4375(2)	9.24(7)
F3	−0.1824(2)	0.5915(3)	0.5594(1)	10.11(6)
F4	−0.1640(2)	0.2935(4)	0.5660(1)	9.69(7)
F5	−0.0895(2)	0.1407(2)	0.4523(2)	8.56(7)
O1	−0.0274(2)	0.2889(3)	0.3288(1)	6.66(5)
C1	−0.0671(2)	0.3606(3)	0.3841(2)	4.59(5)
C2	−0.0772(2)	0.5136(3)	0.3827(2)	4.81(6)
C3	−0.1156(2)	0.5911(4)	0.4407(2)	5.81(7)
C4	−0.1459(2)	0.5159(5)	0.5023(2)	6.25(8)
C5	−0.1362(2)	0.3662(4)	0.5057(2)	6.01(8)
C6	−0.0975(2)	0.2896(4)	0.4473(2)	5.47(7)
C7	−0.1811(3)	0.1483(4)	0.1967(3)	6.95(9)
C8	−0.1289(3)	0.0399(6)	0.1583(2)	8.7(1)
C9	−0.1063(3)	−0.0747(4)	0.2088(3)	8.6(1)
C10	−0.1436(3)	−0.0313(5)	0.2745(3)	9.2(1)
C11	−0.1896(3)	0.1037(5)	0.2668(3)	8.0(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a2*B(1,1)+b2*B(2,2)+c2*B(3,3)+ab(\cos\ \mathrm{gamma})*B(1,2)+ac(\cos\ \mathrm{beta})*B(1,3)+bc(\cos\ \mathrm{alpha})*B(2,3)]$.

Table 2
Selected bond distances (Å) and bond angles (°) for compound **8**

ZR1–O1	1.991(2)	ZR1–C7	2.526(4)
ZR1–C8	2.503(4)	ZR1–C9	2.486(4)
ZR1–C10	2.478(4)	ZR1–C11	2.518(4)
ZR1–CP1	2.215	C7–C8	1.386(6)
C7–C11	1.342(7)	C8–C9	1.403(7)
C9–C10	1.357(7)	C10–C11	1.358(6)
O–C1	1.311(4)		
O1–ZR1–O1′	96.3(1)	ZR1–O1–C1	163.7(2)
O1–C1–C2	120.9(3)	O1–C1–C6	122.6(2)

Numbers in parentheses are estimated standard deviations in the least significant digits. CP1 is the centroid of C7, C8, C9, C10, C11.

disposition of the (C_6F_5) ring planes, which are located practically on the reflection plane defined by O(1), Zr(1) and O(1)′, making an angle of 9.7(3)° with this plane. Due to steric reasons, this probably forces the angle Zr(1)–O(1)–C(1) to be bent away from the centre of the system with a value of 163.7°, but this is nevertheless smaller than that found in other phenoxoderivatives. For the same reason the O(1)–Zr(1)–O(1)′ angle is larger (96°) that in other similar systems.

The Zr(1)–O(1) distance is very short (1.991(2) Å) when compared with the single Zr–O bond distance (2.2 Å), showing significant multiple-bond character by pπ-dπ interaction with the vacant d orbitals of the metal. Large Zr–O–C angles and short Zr–O distances are consistent either with π donation from the alkoxide oxygen lone pairs to the metal or with highly ionic alkoxide oxygen character [10]. Nevertheless, the Zr–O–C angle found for complex **8** is smaller and the Zr–O distance is longer than those found in compounds where strong pπ-dπ donation has been claimed: [ZrCp$_2$(O–^{t}Bu)Ru(CO)$_2$Cp](Zr–O–C 169.6 (4)°, *d*(Zr–O) 1.910 (4) Å) [6], [Zr{HB-3,5-Me$_3$pz}$_2$(O-^{t}Bu)(η^2-CMeNCMe$_3$)] (Zr–O–C 174.4 (6)°, *d*(Zr–O) 1.924 (6) Å) [7], [ZrCp$_2$(OSiPh$_3$)$_2$(DME)](Zr–O–Si 171 (1)°, *d*(Zr–O) 1.91 (1) Å) [8], [Zr$_2$(O^{i}Pr)$_8$(HO-^{i}Pr)$_2$- (*d*(Zr–O) 1.943 Å average) [9], and Zr(OCCH$_3$-(CF$_3$)$_2$)$_4$](Zr–O–C 163.9° average, *d*(Zr–O) 1.916 Å average) [10]. The angle found for the fluoroalkoxide [Zr(OCCH$_3$(CF$_3$)$_2$)$_4$] is very similar to that found in compound **8**. The Zr–C (Cp ring) distances are fairly uniform, ranging from 2.526 (3) to 2.478 (4) Å. The Cp (centroid) is at 2.215 Å from the Zr atom. The C–C distances and angles in the Cp and phenyl systems are normal, and the C–F distances have a mean value of 1.338 Å.

3. Experimental section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and vacuum-line techniques or a glove box model HE-63-P. Solvents were purified by distillation from an appropriate drying/deoxygenated agent (sodium/benzophenone for THF and diethyl ether, sodium for toluene and sodium/potassium alloy for hexane). [TiCp*Cl$_2$Me], [1] [ZrCp$_2$(CH$_3$)$_2$], [12] [ZrCp$_2$Cl(CH$_3$)], [13] [{ZrCp$_2$Cl}$_2$(μ-O)] [14] and [{ZrCp$_2$(CH$_3$)}$_2$(μ-O)] [15] were prepared according to literature procedures. [ZrCp$_2$Cl$_2$] (Aldrich), (CH$_3$)$_2$C=CHCH$_2$OH (Fluka), C$_6$F$_5$OH (Aldrich), LiBu^n (Ventron), AlMe$_3$ (Aldrich), AlEtCl$_2$ (Aldrich), SiClMe$_3$ (Ventron), pyridine (Aldrich), aniline (Aldrich) and sodium metal (Aldrich) were obtained commercially. NMR spectra were recorded on Varian FT-80 and Varian Unity FT-300 instruments (^{1}H shifts were referenced to SiMe$_4$ and CCl$_3$F was used as an internal reference for ^{19}F chemical shifts). Mass spectra were obtained with a Hewlett-Packard 5890 spectrometer. Elemental analyses for C and H were carried out on a Perkin-Elmer 240B microanalyzer.

3.1. Preparation of SiMe$_3$O(C$_6$F$_5$) (4)

SiClMe$_3$ (2.81 g, 3.27 ml, 25.90 mmol) was added at −40°C to a suspension of LiOC$_6$F$_5$ (5 g, 25.90 mmol) in hexane (200 ml). The reaction mixture was warmed to room temperature and then stirred for 24 h. After filtration the solution was evaporated to yield a yellow liquid which was characterized as **4**. ^{1}H NMR (C$_6$D$_6$, 25°C, 300 MHz.): δ 0.06 (s). ^{19}F NMR (C$_6$D$_6$, 25°C, 282 MHz.): δ − 160.7 (d, *o*-C$_6$F$_5$), − 166.22 (t, *m*-C$_6$F$_5$), − 168.4 (t, *p*-C$_6$F$_5$).

*3.2. Preparation of [TiCp*ClMe(OCH$_2$CH=CMe$_2$)] (**6**)*

Method 1

45 ml of a 1.6 M solution of ^{n}BuLi (4.46 g, 69.7 mmol) in hexane were added to a solution of dry $(CH_3)_2C{=}CHCH_2OH$ (7 ml, 6 g, 69.7 mmol) in hexane (50 ml). A white precipitate was formed immediately. The suspension was allowed to warm to room temperature. After 2 h, the solution was filtered and the solid washed with cold hexane (2 × 20 ml) an dried under vacuum to give 6.22 g (97% yield) of compound **1**.

[TiCp*Cl$_2$Me] (1.76 g, 6.54 mmol) and LiOCH$_2$-CH=CMe$_2$ (0.60 g, 6.54 mmol) were transferred to a 100 ml Schlenk flask. Cold toluene (30 ml) was added slowly to the flask which was cooled in an acetone bath at −78°C. After stirring for 24 h the orange of the solution had changed to pale yellow. The solution was filtered and the toluene removed in vacuo to afford a yellow oil and a small quantity of white precipitate. Hexane (5 ml) was added and the oil frozen at −78°C. The solvent was decanted. The orange solid was washed once at −78°C with cold pentane, to yield the chiral titanium complex **6** as a viscous oil.

Method 2

Dry $(CH_3)_2C{=}CHCH_2OH$ (7 ml, 6 g, 69.7 mmol) was solved in hexane (100 ml) and sodium metal (1.6 g, 69.7 mmol) was added. The mixture was then heated under reflux for 1 week. The fine white solid formed was separated from any unreacted sodium metal with a wide bore, teflon transfer tube. The volatiles were then removed in vacuo and the white solid washed with hexane to give 6.25 g (83% yield) of compound **2**.

[TiCp*Cl$_2$Me] (1.76 g, 6.54 mmol) and NaO-CH$_2$CH=CMe$_2$ (0.71 g, 6.54 mmol) were transferred to a 100 ml Schlenk flask. Cold toluene (30 ml) was added slowly to the Schlenk flask cooled in an acetone bath at −78°C. Compound **6** was obtained as described above.

Anal. Found: C, 60.33; H, 8.27. Calc. for $C_{16}H_{27}$-ClOTi: C, 60.29; H, 8.54% ^{1}H NMR (C_6D_6, 25°C, 300 MHz.) δ 0.79 (s, 3H, Ti–CH$_3$), 1.46 (s, 3H, CH$_3$–C=), 1.52 (s, 3H, CH$_3$–C=), 1.80 (s, 15H, C$_5$Me$_5$), 4.74 (d, 2H, CH$_2$), 5.40 (t, 1H, CH). 13C NMR (C_6D_6, 25°C, 75 MHz.): δ 11.8 [q, J(CH) = 126.9 Hz., C$_5$(*C*H$_3$)$_5$], 17.9 [q, J(CH) = 125.9 Hz., =C(*C*H$_3$)$_2$], 25.6 [q, J(CH) = 125.4 Hz., =C(*C*H$_3$)$_2$], 55.6 (q, J(CH) = 124.9 Hz., Ti–CH$_3$), 72.9 (t, J(CH) = 142.5 Hz, CH$_2$), 123.9 (d, J(CH) = 157.7 Hz., -CH=), 124.5 [s, *C*$_5$(CH$_3$)$_5$], 134.9 [s, =C(CH$_3$)$_2$]. $m/z = 318$ {[M]$^+$}

*3.3. Reaction of [TiCp*ClMe(OCH$_2$CH=CMe$_2$)] and AlEtCl$_2$*

[TiCp*ClMe(OCH$_2$CH=CMe$_2$)] (1.86 g, mmol) was dissolved in toluene (30 ml) at −78°C. A 3-fold excess of a 1.8 M solution of AlEtCl$_2$ (2.23 g, 9.74 ml) in toluene was slowly added to the orange solution. The solution changed immediately to a bright red. The reaction mixture was stirred for 2 h at low temperature and then quenched with an excess of pyridine. After warming to room temperature, the volatiles were removed in vacuo to leave a bright red gum. After washing with hexane the gum was mixed with toluene to give a red solution and yellow insoluble residue. Both hexane and toluene solutions yielded [TiCp*Cl$_3$].

3.4. Preparation of [TiCp(OC$_6$F$_5$)$_3$] (7)*

A solution of freshly distilled C$_6$F$_5$OH (1.86 ml, 3.5 g, 19.0 mmol) in hexane (10 ml) was added dropwise at room temperature to a stirred solution of [TiCp*-Cl$_2$Me] (1.35 g, 5.02 mmol) in toluene (50 ml). The orange solution darkened and after 15 min it became dark orange and a gas was evolved. The solution was filtered, and the volume reduced in vacuo to 15–20 ml. On addition of hexane and subsequent cooling to −30°C a dark orange microcrystalline solid was obtained, which was identified as **7**.

Anal. Found: C, 46.24; H, 2.07. Calc. for $C_{28}H_{15}$-$F_{15}O_3Ti$: C, 45.92; H, 2.06% ^{1}H NMR (C_6D_6, 25°C, 300 MHz.) δ 1.78 (s, 15H, C$_5$Me$_5$). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.) δ − 162.2 (d, *o*-C$_6$F$_5$), −166.6 (t, *m*-C$_6$F$_5$), −169.3 (t, *p*-C$_6$F$_5$).

3.5. Preparation of [ZrCp$_2$(OC$_6$F$_5$)$_2$] (8)

Method 1

A suspension of [ZrCp$_2$Cl$_2$] (0.5 g, 1.7 mmol) in diethyl ether (40 ml) was treated with a solution of freshly distilled C$_6$F$_5$OH (0.33 ml, 0.62 g, 3.4 mmol) in diethyl ether (25 ml) in the presence of aniline (3.4 mmol). After 30 min the precipitation of (PhNH$_3$)Cl was observed. This solid was filtered off and the filtrate was evaporated to dryness under vacuum to give a white solid, which was washed with hexane (3 × 20 ml), recrystallized from toluene/hexane, and characterized as **8** (0.94 g, 95% yield).

Method 2

A solution of freshly sublimed [ZrCp$_2$(CH$_3$)$_2$] (0.5 g, 1.9 mmol) in toluene (50 ml) was treated with a solution of freshly distilled C$_6$F$_5$OH (0.37 ml, 0.72 g, 3.9 mmol) in diethyl ether (25 ml). The reaction mixture was stirred for 2 h until the evolution of methane was ceased. The resulting solution was evaporated to dryness and the solid obtained washed with hexane (2 × 20 ml). Recrystallization from toluene/hexane gave a white product characterized as **8** (1.11 g, 100% yield).

Method 3

A solution of [{ZrCp$_2$(CH$_3$)}$_2$(μ-O)] (0.5 g, 1.02 mmol) in toluene (50 ml) was treated with a solution of freshly distilled C_6F_5OH (0.38 ml, 0.75 g, 4.1 mmol) in diethyl ether (30 ml). The reaction mixture was stirred for 4 h until the evolution of methane ceased. The resulting solution was evaporated to dryness and the solid obtained washed with hexane (2 × 20 ml) to give a white solid which, after recrystallization from toluene/hexane, was characterized as **8** (0.60 g, 100% yield)

Anal. Found: C, 44.81; H, 1.69. Calc. for $C_{22}H_{10}F_{10}O_2Zr$: C, 44.86, H, 1.69% ^1H NMR (C_6D_6, 25°C, 300 MHz.): δ 5.82 (s, C_5H_5). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.): $\delta - 165.42$ (d, o-C_6F_5), -167.40 (t, m-C_6F_5), -173.52 (td, p-C_6F_5).

3.6. Preparation of $[ZrCp_2Cl(OC_6F_5)]$ (9)

10 ml of a 1.6 M solution of ^{n}BuLi (1.0 g, 15.49 mmol) in hexane were added dropwise (1 h) to a solution of freshly distilled C_6F_5OH (0.9 ml, 1.72 g, 9.29 mmol) in hexane (50 ml) at -20°C. The mixture was slowly warmed at room temperature and then stirred for 2 h. A white solid was formed as the temperature was raised. After filtration, the solid was washed with hexane (3 × 20 ml) to give compound **3** (1.41 g, 80% yield).

A solution containing $LiOC_6F_5$ (0.83 g, 43 mmol) in THF (50 ml) was added dropwise to a solution of $[ZrCp_2Cl_2]$ (1.27 g, m 4.3 mmol) in toluene (20 ml). The reaction mixture was stirred at room temperature for 2 h, to give a clear solution. The solution was evaporated to dryness. The white solid obtained was recrystallized from toluene/hexane to give compound **9** as a white microcrystalline solid (1,3 g, 70% yield).

Anal. Found: C, 43.81; H, 2.36. Calc. for $C_{16}H_{10}ClF_5OZr$: C, 43.71; H, 2.29% ^1H NMR (C_6D_6, 25°C, 300 MHz.): δ 5.85 (s, C_5H_5). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.): $\delta - 164.73$ (d, o-C_6F_5), -167.38 (t, m-C_6F_5), -173.50 (td, p-C_6F_5).

3.7. Preparation of $[\{ZrCp_2(OC_6F_5)\}_2$-$(\mu$-$O)]$ (10)

Method 1

A solution of $[\{ZrCp_2(CH_3)\}_2(\mu$-$O)]$ (0.66 g, 1.34 mmol) in toluene (50 ml) was treated with a solution of freshly distilled C_6F_5OH (0.26 ml, 0.49 g, 2.68 mmol) in diethyl ether (30 ml) at 0°C. The reaction mixture was warmed to room temperature and then stirred for 2 h, until the evolution of methane ceased. The resulting solution was evaporated to dryness and the solid obtained washed with hexane (3 × 20 ml) to give a white solid, which was recrystallized from toluene/hexane and characterized as **10** (1.07 g, 98% yield).

Method 2

A solution of $[\{ZrCp_2Cl\}_2(\mu$-$O)]$ (1 g, 1.88 mmol) in toluene (50 ml) was treated with a solution of freshly distilled C_6F_5OH (0.36 ml, 0.69 g, 3.77 mmol) in the presence of aniline (3.77 mmol). The reaction mixture was stirred for 3 h. $(PhNH_3)Cl$ was observed as a white precipitate. After filtration, the resulting solution was evaporated to dryness and the solid obtained washed with hexane (3 × 20 ml) to give a white solid, which was recrystallized from toluene/hexane and characterized as **10** (1.53 g, 95% yield).

Anal. Found: C, 46.34; H, 2.39. Calc. for $C_{32}H_{20}F_{10}O_3Zr_2$: C, 46.59; H, 2.44% ^1H NMR (C_6D_6, 25°C, 300 MHz.): δ 5.98 (s, C_5H_5). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.): $\delta - 165.28$ (d, o-C_6F_5), -167.6 (t, m-C_6F_5), -174.84 (td, p-C_6F_5).

3.8. Preparation of $[ZrCp_2(CH_3)(OC_6F_5)]$ (11)

Method 1

A 2 M solution of $AlMe_3$ (0.9 ml, 0.13 g, 1.81 mmol) in hexane was solved in toluene (20 ml) and this was added to a toluene solution (50 ml) containing $[\{ZrCp_2(OC_6F_5)\}_2(\mu$-$O)]$ (0.75 g, 0.9 mmol). The reaction mixture was heated at 65–70°C for 2 h. After cooling to room temperature, the solution was evaporated to dryness and the solid obtained was washed with hexane (3 × 20 ml) to give a white solid which was recrystallized from toluene/hexane and characterized as **11** (0.45 g, 60% yield).

Method 2

A solution of $LiOC_6F_5$ (0.24 g, 1.28 mmol) in THF (25 ml) was added dropwise at -40°C, to a solution of $[ZrCp_2Cl(CH_3)]$ (0.35 g, 1.28 mmol) in toluene (50 ml). The reaction mixture was warmed to room temperature and then stirred for 2 h. The solution was filtered and evaporated to dryness to give a white solid which was washed with hexane (3 × 20 ml) and recrystallized from toluene/hexane to give a white solid characterized as **11** (0.32 g, 60% yield).

Method 3

A solution containing freshly distilled C_6F_5OH (2 ml, 3.83 g, 20.7 mmol) in hexane (10 ml) was added dropwise at -30°C, to a solution of $AlMe_3$ (2.9 ml, 0.49 g, 6.9 mmol) in hexane (50 ml). The reaction mixture was slowly warmed to room temperature. After stirring for 2 h a yellow powder was observed. The solution was evaporated to dryness and the solid obtained was washed with hexane (3 × 50 ml) to yield a fine colourless solid, which was characterized as **5** (3.98 g, 100% yield). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.): $\delta - 165.25$ (d, o-C_6F_5), -166.28 (t, m-C_6F_5), -170.8 (td, p-C_6F_5).

A solution of $Al(OC_6F_5)_3$ (0.58, 1.02 mmol) in toluene (30 ml) was added at -40°C, to a solution of $[\{ZrCp_2(CH_3)\}_2(\mu$-$O)]$ (0.5 g, 1.02 mmol) in toluene (50 ml). The reaction mixture was warmed to room temperature. After 3 h of stirring the solution was filtered

Table 3
Crystal data, experimental data and structure refinement procedures for compound **8**

Formula	$C_{22}H_{10}O_2F_{10}Zr_1$
Crystal habit	Prismatic
Color	Colorless
Crystal size (mm^3)	0.30×0.15×0.15
Symmetry	Monoclinic $C2/c$
Unit cell determination	Least squares fit from 25 reflns
Unit cell dimensions:	
a, b, c (Å)	13.023(5), 8.986(2), 18.158(6)
β (°)	91.54(2)
V (Å)	2124(2)
Z	4
$D_{cal.}$, g cm^{-3}	1.61
Mw	798.9
$F(000)$	1026
μ cm^{-1}	7.90
scan mode	$\omega/2\Theta$ scans; $\Theta max = 27°$
$n°$ reflections:	
Measured	6725
Independent observed	2276 $I > 2\sigma(I)$ criterium
Range of hkl	h-18 to 18; k 0 to 12; l 0 to 25
Standard reflections	2 reflections every 120 minutes, no variation
R	0.040
R_W	0.048
Goodness of fit indicator	1.465
Largest parameter shift/error	0.08
Max. peak in final diff. map, e^{-3} Å	0.45

and evaporated to dryness to give a pale yellow solid which was washed with hexane (2 × 20 ml). Recrystallization from toluene/hexane gave a pale-yellow compound, characterized as **11** (0.25 g, 65% yield).

Anal. Found: C, 48.58; H, 3.14. Calc. for $C_{17}H_{13}F_5OZr$: C, 46.68; H, 3.12% ^1H NMR (C_6D_6, 25°C, 300MHz.): δ 0.52 (s, 3H, Me–Zr), 5.70 (s, 10H, C_5H_5). ^{19}F NMR (C_6D_6, 25°C, 282 MHz.): δ – 165.80 (d, o-C_6F_5), – 167.98 (t, m-C_6F_5), – 174.35 (td, p-C_6F_5).

3.9. Structural data for $ZrCp_2(OC_6F_5)_2$ (8)

Crystallographic and experimental details of X-ray crystal structure determination are given in Table 3. Data were collected at room temperature. Intensities were corrected for Lorenz and polarisation effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found in the difference synthesis map, refined one cycle isotropically and then fixed.

Final values of $R = 0.040$ and $R_w = 0.048$ with $R_w = [\Sigma w \| F_o | - | F_c \|^2 w | F_o |^2]$ and $w = 4F_o/[\sigma | F_o |]^2$ were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from International Tables [16]. Calculations were performed with the SDP package [17], and Multan [18] and Dirdif [19] programs on a Microvax II computer.

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Supplementary material available from the Cambridge Crystallographic Data Centre

Tables of anisotropic temperature factors, positional parameters for hydrogen atoms, bond lengths and bond angles for compound **8**. Tables of calculated and observed structure factors are available from the authors.

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