

# Synthesis and structure of $[\text{Cp}_2\text{Zr}(\text{OPr}^i)(\text{HOPr}^i)]^+$ and its activity in the polymerisation of propene oxide

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## Abstract

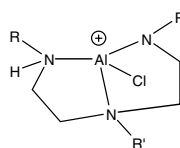
The reaction of  $\text{Cp}_2\text{Zr}(\text{OPr}^i)_2$  with  $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  in dichloromethane at room temperature gives  $[\text{Cp}_2\text{Zr}(\text{OPr}^i)(\text{HOPr}^i)]^+[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^- \cdot \text{Et}_2\text{O}$  in high yield. The crystal structure is reported. The complex contains a short Zr-alkoxide and a longer Zr-alcohol bond; the OH group of the coordinated isopropanol is hydrogen-bonded to a diethyl ether molecule. The complex initiates the polymerisation of propylene oxide, most probably via a cationic mechanism.  
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**Keywords:** Zirconium; Metallocene; Catalysis; Propene oxide; Polymerisation

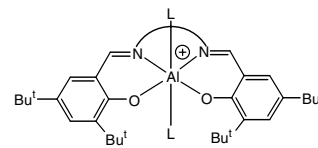
## 1. Introduction

Poly(propylene oxide) (PPO) is produced worldwide at a scale of several million tons p.a. as a key component of many lubricants, detergents, surfactants and polyurethanes [1–3]. It can be polymerised in a variety of ways, anionically using base catalysis, cationically using acids or Lewis acids, or by coordination catalysis. Anionic polymerisation uses in the simplest case KOH, although this can be accompanied by chain transfer to monomer and formation of allyl alcohols. In this case, the strongly basic catalyst must be removed at the end of the polymerisation. Cationic polymerisation can be initiated by  $\text{CPh}_3^+$  salts,  $\text{HBF}_4$  or  $\text{BF}_3$ ; although such polymerisations are fast, they are usually accompanied by low-molecular weight by-products. Mixtures of main group organometallics with water have been widely explored, examples being hydrolysis products of  $\text{AlR}_3$  ( $\text{R} = \text{Et}, \text{Bu}^i$ ) [4],  $\text{ZnR}_2$  [5–7] and  $\text{MgEt}_2$  [8]. A series of well-defined aluminium chelate complexes are also effective,

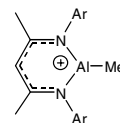
notably Inoue's  $\text{AlCl}(\text{porphyrin})$  compounds for the immortal polymerisation of PO [9], as well as aluminium salen [10] and tridentate nitrogen complexes [11]. More recently, the activity of cationic aluminium complexes such as **1–5** has been explored [11–13], e.g., **4** gave very high molecular weight PPO with low polydispersity. Chen and co-workers [13] also investigated a series of strong Lewis acids  $\text{M}(\text{C}_6\text{F}_5)_3$  ( $\text{M} = \text{B}, \text{Al}$ ) and related compounds in conjunction with protonic co-initiators; in all cases modest molecular weight PPO was obtained.



**1**,  $\text{R} = \text{R}' = \text{SiMe}_3$     **2**,  $\text{R} = \text{SiMe}_3, \text{R}' = \text{Me}$   
**3**,  $\text{R} = \text{Pr}^i, \text{R}' = \text{Me}$



**4**,  $\text{L} = \text{MeOH}$  or  $\text{THF}$



**5**,  $\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^i_2$

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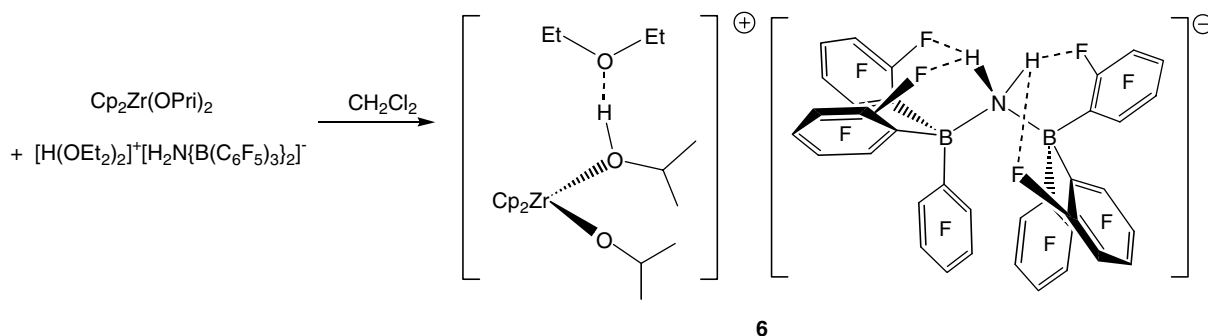
E-mail address: m.bochmann@uea.ac.uk (M. Bochmann).

As part of ongoing investigations in the structural and catalytic chemistry of electrophilic organometallic complexes [14], we report here the synthesis of a rare example of a cationic zirconium alkoxide complex and its use in PO polymerisation.

## 2. Results and discussion

Treatment of  $\text{Cp}_2\text{Zr}(\text{OPr}^i)_2$  with  $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  in dichloromethane at room temperature followed by removal of volatiles afforded a brown oily

foam which was converted into a cream coloured powder on repeated washing with light petroleum. Re-crystallisation from a dichloromethane/light petroleum mixture gave colourless block-like crystals of  $[\text{Cp}_2\text{Zr}(\text{OPr}^i)(\text{HOPr}^i)]^+[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^- \cdot \text{Et}_2\text{O}$  (**6**) (Scheme 1). In spite of solvent removal under vacuum and washings, elemental analysis and the  $^1\text{H}$  NMR spectrum suggested that the compound had retained one molecule of diethyl ether. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra in dichloromethane- $d_2$  at 25 °C showed, however, only one set of signals for two identical isopropoxide ligands.



Scheme 1.

Table 1  
Selected bond length (Å) and angles (°) of **1**

In the cation			
Zr–O(3)	2.1906(18)	Zr–O(4)	1.9033(15)
Zr–C(1x)	2.230	Zr–C(2x)	2.222
Zr–C(11)	2.533(2)	Zr–C(12)	2.545(2)
Zr–C(13)	2.527(2)	Zr–C(14)	2.514(2)
Zr–C(15)	2.500(3)	O(3)–C(31A)	1.516(5)
O(4)–C(41)	1.434(3)	O(3)–C(31B)	1.502(13)
O(3)–H(31)	0.80(3)	H(31)⋯O(11')	1.79(3)
C(1x)–Zr–C(2x)	127.96	O(4)–Zr–O(3)	94.21(8)
C(1x)–Zr–O(4)	109.79	C(2x)–Zr–O(4)	109.01
C(1x)–Zr–O(3)	104.96	C(2x)–Zr–O(3)	105.34
C(31A)–O(3)–Zr	121.0(2)	C(41)–O(4)–Zr	163.76(17)
C(32A)–C(31A)–O(3)	112.0(4)	C(33A)–C(31A)–O(3)	109.3(5)
O(4)–C(41)–C(42)	110.5(3)	O(4)–C(41)–C(43)	109.7(3)
O(3)–H(31)⋯O(11')	178(4)		
In the anion			
N(5)–B(5)	1.624(3)	N(5)–B(8)	1.634(3)
B(5)–C(51)	1.671(3)	B(5)–C(61)	1.646(3)
B(5)–C(71)	1.647(3)		
B(5)–N(5)–B(8)	132.06(16)	N(5)–B(5)–C(51)	106.80(16)
N(5)–B(5)–C(61)	107.85(16)	N(5)–B(5)–C(71)	114.04(17)
C(61)–B(5)–C(51)	111.37(17)	C(71)–B(5)–C(51)	100.76(15)
C(61)–B(5)–C(71)	115.59(16)		
N(5)–H(5a)	0.82(3)	N(5)–H(5b)	0.88(3)
H(5a)⋯F(56)	2.22(3)	H(5a)⋯F(72)	2.31(2)
H(5a)⋯F(86)	2.19(2)	H(5b)⋯F(62)	2.40(3)
H(5b)⋯F(102)	1.97(3)		
N(5)–H(5a)⋯F(56)	133(2)	N(5)–H(5a)⋯F(72)	120(2)
N(5)–H(5a)⋯F(86)	131(2)	N(5)–H(5b)⋯F(62)	121(2)
N(5)–H(5b)⋯F(102)	148(3)		

N.B. C(1x) and C(2x) are the centroids of the two Cp rings.

The structure of **6** was elucidated by X-ray crystallography. Selected bond lengths and angles are collected in Table 1. The cation in **6** (**6**<sup>+</sup>, Fig. 1) shows the expected pseudo-tetrahedral geometry, with one  $\sigma$ -bonded isopropoxide and one isopropanol donor ligand. The hydroxyl hydrogen atom of the isopropanol ligand was located and refined freely, and found to link the cation and the ether solvent molecule through an O(3)–H(31)···O(11') hydrogen bond. There is disorder in both the isopropanol ligand and the ether molecule; alternative sites for the CHMe<sub>2</sub> group and the  $\alpha$ -carbon atoms of the ethyl groups were identified and have been refined satisfactorily.

The Zr–O bond distances in **6**<sup>+</sup> differ significantly, with a short Zr–O(4) bond of 1.9033(15) Å to the isopropoxide and a longer n-donor bond of 2.1906(18) Å to the alcohol ligand. The  $\pi$ -contribution to the Zr–O(4) bond is confirmed by the wide Zr–O(4)–C(41) angle of 163.76(17)°, while Zr–O(3)–C(31A) is much more acute, 121.0(2)°.

The anion in **6** (Fig. 2) shows the same features as those reported earlier for [Na(OEt<sub>2</sub>)<sub>4</sub>][H<sub>2</sub>N{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>] [15], i.e., the bent BNB core (angle 132.06(16)°) with a distorted tetrahedral geometry about N(5). The amino hydrogen atoms were identified in difference maps and were refined freely and satisfactorily. H(5a) forms three intramolecular hydrogen bonds with *o*-F atoms of both

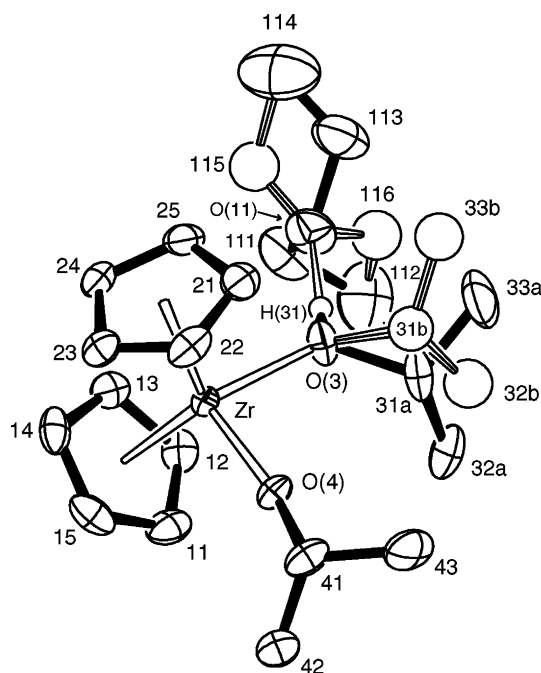


Fig. 1. View of the cation and hydrogen-bonded solvent molecule in [Cp<sub>2</sub>Zr(O'Pr)(HO'Pr)][H<sub>2</sub>N{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>]·Et<sub>2</sub>O, indicating the atom numbering scheme; atoms labelled 'n' represent the carbon atoms C(n). The minor components of disordered groups are shown with 3-line bonds and circular atoms (representing isotropic refinement). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

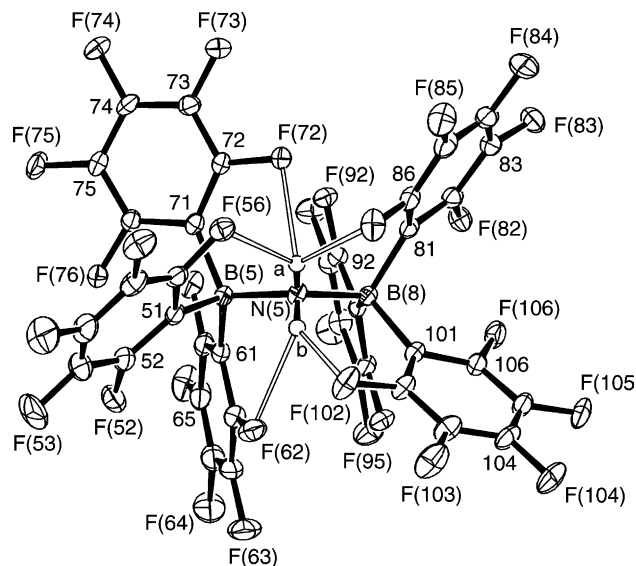


Fig. 2. View of the anion in [Cp<sub>2</sub>Zr(O'Pr)(HO'Pr)][H<sub>2</sub>N{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>]·Et<sub>2</sub>O. The amino hydrogen atoms H(5a) and H(5b) are labelled a and b.

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> groups; H(5b) is involved in a bifurcated hydrogen-bonded system which also bridges the two halves of the ion.

There are only few examples of structurally characterised cationic zirconocene alkoxides. Some time ago Collins reported the structure of [Cp<sub>2</sub>ZrOBu'(THF)]<sup>+</sup>, which shows a similar difference in Zr–O bond length to the alkoxide (1.899(3) Å) and n-donor ligand (2.200(4) Å) [16]. Jordan and co-workers [17] found a similarly short Zr–O bond and wide Zr–O–C angle in the chelating pentenoxo complex [Cp<sub>2</sub>ZrOCMe<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>CH=CH<sub>2</sub>]<sup>+</sup>.

Polymerisations of propylene oxide catalysed by **6** were carried out in neat monomer at room temperature, at a monomer:Zr ratio of 3400:1. Moderate evolution of heat was observed during the first few minutes of the reactions. Aliquots were collected at the times indicated in Table 2. The reaction is initially fast but is well controlled after the first few minutes. However, there is no increase in molecular weight with time. The polymer was obtained as a clear viscous oil.

The ring opening polymerisation (ROP) of PO by catalysts such as **6** can in principle occur either by nucleophilic attack on coordinated monomer (Scheme 2, path A), or via a cationic “activated chain end” process (path B).

Gel permeation chromatograms of PPO samples obtained from **6** showed the presence of low-molecular weight oligomers. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra indicated that the polymer had a regiorregular microstructure [18], as illustrated in Fig. 3, e.g., note the multiplicity of methine resonances at  $\delta$  74.5–76.0. These findings are consistent with a cationic polymerisation mechanism (path B).

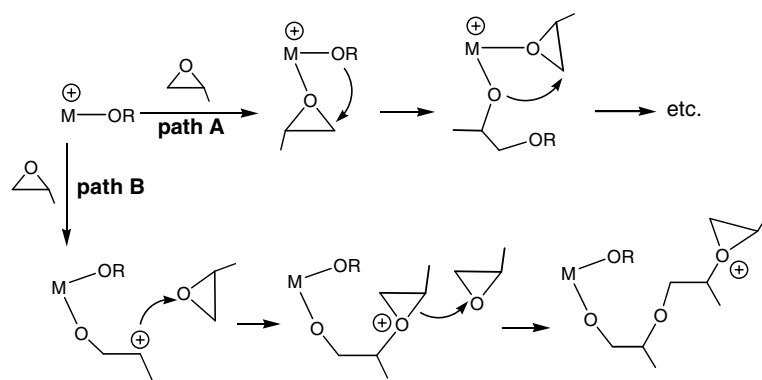
Table 2  
Propene oxide polymerisation with **6** at 20 °C<sup>a</sup>

Run	Time (min)	Yield (g)	Conv. (%)	TOF <sup>b</sup>	$M_w^c$	$M_w/M_n$
1	15	2.5	30.1	69	3300	2.1
2	30	2.8	33.7	38	3900	2.0
3	45	3.3	39.7	30	4000	2.4
4	60	3.5	42.2	24	2200	2.1
5	75	4.7	56.6	26	3700	2.1
6	90	5.6	67.5	25	2200	2.1

<sup>a</sup> Conditions: 0.042 mmol **6**, 10 mL neat PO, no co-solvent; PO/Zr ratio = 3400:1, 20 °C.

<sup>b</sup> Turnover frequency in mol PO (mol Zr min)<sup>-1</sup>.

<sup>c</sup> Molecular weights determined by GPC relative to polystyrene standards.



Scheme 2.

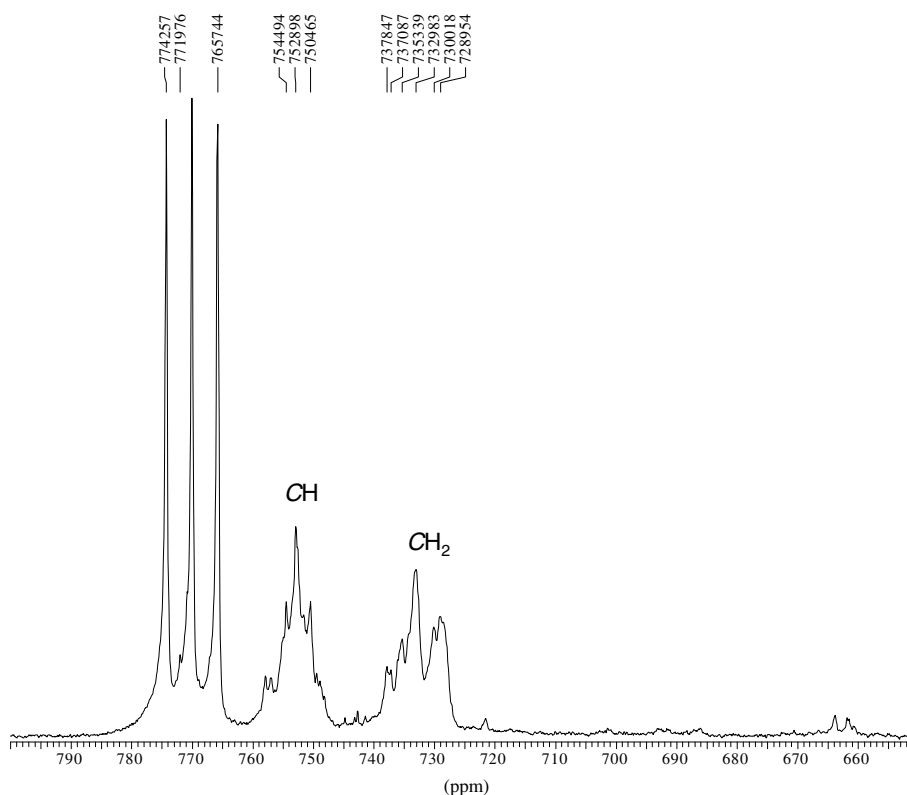


Fig. 3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (75.5 MHz) of PPO generated with **6**.

Complex **6** also polymerises cyclohexene oxide (CHO), although in that case the reaction needs to be moderated with an inert solvent. Thus 2 mL CHO in 50 mL toluene in the presence of **6** (42  $\mu$ mol, monomer/initiator ratio = 470:1) at room temperature gave complete conversion within <5 min. The resulting polymer possessed relatively high molecular weight ( $M_w = 31,000$ ,  $M_w/M_n = 3.2$ ), although this is somewhat lower than PCHO molecular weights obtained with cationic zinc and magnesium complexes under similar conditions [19].

### 3. Conclusion

The reaction of zirconocene bis(isopropoxide) with the strong Brønsted acid  $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  readily affords salts of the corresponding cation  $[\text{Cp}_2\text{Zr}(\text{OR})(\text{ROH})]^+$ . The alcohol ligand is stabilised by hydrogen bonding to a diethyl ether molecule. The zirconocene complex polymerises propylene oxide and cyclohexene oxide, apparently via a cationic mechanism.

## 4. Experimental

### 4.1. General procedures

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were dried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane) and distilled under nitrogen from sodium (toluene), sodium–potassium alloy (light petroleum, bp 40–60 °C), sodium–benzophenone (THF, diethyl ether) or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. Compounds  $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  [15] and  $\text{Cp}_2\text{Zr}(\text{OPr}^i)_2$  [20] were prepared according to literature methods. Propene oxide and cyclohexene oxide were dried for a minimum of 24 h over fresh calcium hydride, then distilled under vacuum and stored over activated 4 Å molecular sieves. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer.  $^1\text{H}$  NMR spectra (300.1 MHz) were referenced to the residual solvent proton of the deuterated solvent used.  $^{13}\text{C}$  NMR spectra (75.5 MHz) were referenced internally to the D-coupled  $^{13}\text{C}$  resonances of the NMR solvent. Gel permeation chromatography (GPC) measurements were carried out in THF solution at 30 °C with antioxidant, using a Polymer Laboratories PL-GPC-220 instrument equipped with PL 2  $\times$  mixed-bed D 30 cm, 5 mm columns at a nominal elution rate of 1.0 mL/min with refractive index detection. The instrument was calibrated with monodisperse polystyrene standards.

Preparation of  $[\text{Cp}_2\text{Zr}(\text{OPr}^i)(\text{HOPr}^i)][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2] \cdot \text{Et}_2\text{O}$  (**6**).  $\text{Cp}_2\text{Zr}(\text{OPr}^i)_2$  (0.278 g, 0.82 mmol) and  $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  (0.943 g, 0.79 mmol) were dissolved in 10 mL  $\text{CH}_2\text{Cl}_2$  at room temperature. Removing the solvent from the beige solution left a light brown oily foam which was washed repeatedly with light petroleum to give a powdery solid. Recrystallisation from  $\text{CH}_2\text{Cl}_2$  layered with light petroleum at 26 °C afforded clear, colourless block-like crystals of **6** (0.55 g, 0.38 mmol, 48%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C, 300.13 MHz):  $\delta$  6.99 (m, br, 1H, OH), 6.46 (s, 10H, Cp), 5.72 (m, br, 2H,  $\text{NH}_2$ ), 4.37 (m, 2H,  $J_{\text{HH}} = 6$  Hz,  $\text{OCHMe}_2$ ), 3.73 (m, 4H,  $J_{\text{HH}} = 7$  Hz,  $\text{OCH}_2\text{Me}$ ), 1.33 (m, 18H,  $\text{OCHMe}_2$  and  $\text{OCH}_2\text{Me}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C, 75.5 MHz):  $\delta$  148.3 (dt,  $^1J_{\text{CF}} = 959$  Hz, *m*-C of  $\text{C}_6\text{F}_5$ ), 139.5 (dt,  $^1J_{\text{CF}} = 994$  Hz, *p*-C of  $\text{C}_6\text{F}_5$ ), 137.1 (dt,  $^1J_{\text{CF}} = 955$  Hz, *o*-C of  $\text{C}_6\text{F}_5$ ), 121.3 (m, br, *ipso*-C of  $\text{C}_6\text{F}_5$ ), 115.3 (Cp), 78.9 ( $\text{OCHMe}_2$ ), 66.2 ( $\text{OCH}_2\text{Me}$ ), 24.7 (m,  $\text{OCHMe}_2$ ), 15.0 ( $\text{OCH}_2\text{Me}$ ).  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C, 96.29 MHz):  $\delta$  5.20.  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C, 282.4 MHz):  $\delta$  133.5 (d,  $J_{\text{FF}} = 20$  Hz, *o*-F), 160.6 (tr,  $J_{\text{FF}} = 20$  Hz, *p*-F), 166.1 (tr,  $J_{\text{FF}} = 20$  Hz, *m*-F). Anal. Calc. for  $\text{C}_{56}\text{H}_{37}\text{B}_2\text{F}_{30}\text{NO}_3\text{Zr}$ : C, 46.23; H, 2.56; N, 0.96. Found: C, 45.79; H, 2.56; N, 0.96.

### 4.2. X-ray diffraction crystal data of **6**

$\text{C}_{16}\text{H}_{25}\text{O}_2\text{Zr}$ ,  $\text{C}_{36}\text{H}_2\text{B}_2\text{F}_{30}\text{N}$ ,  $\text{C}_4\text{H}_{10}\text{O}$ ,  $M = 1454.7$ . Monoclinic, space group  $P2_1/n$  (equiv. to no. 14),  $a = 18.8361(2)$ ,  $b = 15.7194(2)$ ,  $c = 20.5952(2)$  Å,  $\beta = 109.580(1)^\circ$ ,  $V = 5745.45(11)$  Å<sup>3</sup>.  $Z = 4$ ,  $D_c = 1.682$  g cm<sup>-3</sup>,  $F(000) = 2896$ ,  $T = 180(1)$  K,  $\mu(\text{Mo K}\alpha) = 3.4$  cm<sup>-1</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å.

Crystals are clear, colourless blocks. Data were collected on an oil-coated crystal (0.32  $\times$  0.23  $\times$  0.21 mm) mounted on a glass fibre and fixed in the cold nitrogen stream on a Nonius KappaCCD diffractometer equipped with Mo K $\alpha$  radiation and graphite monochromator. Total no. of reflections recorded, to  $\theta_{\text{max}} = 27.5^\circ$ , was 48,505 of which 13,088 were unique ( $R_{\text{int}} = 0.035$ ); 10,116 were 'observed' with  $I > 2\sigma_I$ .

Data were processed using the DENZO and SCALEPACK programs [21]. Absorption corrections were applied in the SORTAV [22] routine. The structure was determined by the PATT and TEXP routines in the SHELXS program and refined by full-matrix least-squares methods, on  $F^2$ s, in SHELXL [23]. The isopropanol ligand in the cation, and the  $\alpha$ -carbon atoms of the solvent ethyl groups were found to be disordered with alternative sites. The non-hydrogen atoms (except the minor components of the disordered groups) were refined with anisotropic thermal parameters. Hydrogen atoms in the cation ligands and solvent molecules were included in idealised positions and their  $U_{\text{iso}}$  values were set to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms; the amine

hydrogen atoms in the anion, and the hydroxyl hydrogen in the cation, were identified from difference maps and were refined freely. At the conclusion of the refinement,  $wR_2 = 0.101$  and  $R_1 = 0.060$  for all 13,088 reflections weighted  $w = [\sigma^2(F_o^2) + (0.0422P)^2 + 3.12P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ ; for the ‘observed’ data only,  $R_1 = 0.040$ . In the final difference map, the highest peaks (to ca.  $0.48 \text{ e } \text{Å}^{-3}$ ) were in the solvent molecule. Scattering factors for neutral atoms were taken from reference [24]. Computer programs used in this analysis have been noted above or in Table 4 of reference [25], and were run on a Silicon Graphics Indy at the University of East Anglia, or a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

### Acknowledgements

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2004.07.012](https://doi.org/10.1016/j.jorganchem.2004.07.012).

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