DALTON
FULL PAPER

Synthesis and crystal structure of the tris(amide) cations $[M\{N(SiMe_3)_2\}_3]^+$ (M = Zr or Hf): evidence for M–Si–C interactions

Jane R. Galsworthy,[a] **Malcolm L. H. Green,***[a] **Neil Maxted**[a] **and Matthias Müller**[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford, UK OX1 3PD*

Reaction of the strong Lewis acid $B(C_6F_5)_3$ with $[M\{N(SiMe_3)_2\}_3Me]$ (M = Zr or Hf) gave the compounds $[M\{N(SiMe_3)_2\}_3][MeB(C_6F_5)_3]$. Crystallographic analyses of these compounds revealed the formation of multicentre bonds between the $SiCH_3$ units of the amide ligands and the otherwise electron-deficient metal centre. The new tris(amide) complexes $[M\{N(Ph)SiMe_3\}_3Cl]$ and $[M\{N(Ph)SiMe_3\}_3Me]$ (M = Zr or Hf) have also been synthesized.

Interaction of the Lewis-acid molecule, $B(C_6F_5)_3$, with the metallocene complexes $[M(C_5H_5)_2R_2]$ (M = Group IV metal, R = alkyl) results in addition to the alkyl moiety and formation of $[R(C_5H_5)_2M(\mu\text{-}R)B(C_6F_5)_3]$.[1] The electrophilic metal centre thus formed frequently exhibits unusual bonding features as a means of alleviating its charge deficiency. These compounds often exist as a solvent-dependent, tight ion pair, exhibiting a degree of α-agostic interaction between the metal centre and methyl hydrogen atoms of the anion.[2] Alternatively the metal centre may relieve its electronic deficiency by the addition of a solvent molecule, as observed for $[Zr(C_5H_5)Me_2(\eta^6\text{-}C_6H_5Me)][MeB(C_6F_5)_3]$ which is formed by the reaction of $[Zr(C_5H_5)Me_3]$ with $B(C_6F_5)_3$ in toluene.[3]

Recently we reported the reaction of $[U\{N(SiMe_3)_2\}_3H]$ with $B(C_6F_5)_3$ which gives the zwitterion $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)SiMe_2CH_2B(C_6F_5)_3\}]$ with concomitant elimination of dihydrogen. This compound has been structurally characterised by single-crystal X-ray and neutron diffraction studies (Fig. 1).[4] Several reports of M–Si–CH_3 multicentre bonds exist in the chemistry of lanthanide and actinide complexes although typically the Si–C bond forms part of a metal-bound alkyl ligand, *e.g.* $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2]^+$.[5]

Here we report the synthesis of the new Group IV tris(amide) compounds $[M\{N(Ph)SiMe_3\}_3Me]$ (M = Zr or Hf) and the reactions of these compounds and the previously reported complexes $[M\{N(SiMe_3)_2\}_3Me]$ with $B(C_6F_5)_3$. Our aim was to explore the generality of the methyl-abstraction reaction using this Lewis-acid molecule.

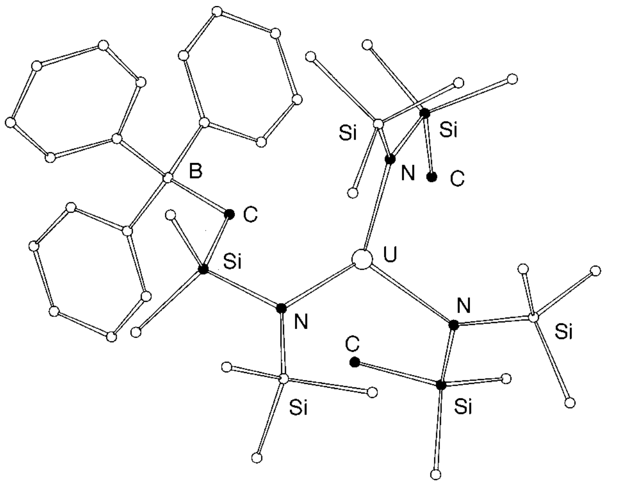

Fig. 1 Structure of $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)SiMe_2CH_2B(C_6F_5)_3\}]$ in the crystal. All black atoms co-ordinate the uranium atom by strong covalent (N) or weaker multicentre bonds (Si, C). All hydrogen and fluorine atoms are omitted for clarity

Results and Discussion

Treatment of $[M\{N(SiMe_3)_2\}_3Me]$ (M = Zr or Hf) with 1 equivalent of $B(C_6F_5)_3$ in pentane yields $[M\{N(SiMe_3)_2\}_3][MeB(C_6F_5)_3]$ (M = Zr **1** or Hf **2**) as white solids which can be recrystallised from toluene. Complexes **1** and **2** have been characterised by crystal structure determination and by ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopies (Table 1). An upfield shift of the ^{11}B NMR spectroscopic resonance of $B(C_6F_5)_3$ (δ 58) to δ −14.7 is observed for both species upon reaction. The signal is characteristic of the $[MeB(C_6F_5)_3]^-$ anion and indicates that, in solution (C_6D_6 and CD_2Cl_2), the Me^- group has been transferred from the metal centre to the boron atom and that the cation and anion are completely dissociated.

The solid-state molecular structures of complexes **1** and **2** are presented in Fig. 2(*a*) and 2(*b*), respectively and display similar features. The structures contain discrete ionic species in which the methyl group bonded to boron is fully dissociated from the metal centre. The M–CH_3 distance is 5.527(2) (**1**) and 5.499(2) Å (**2**) and precludes any interaction between the metal atom and the boron-bound methyl moiety. Close inspection of the co-ordination sphere around the Group IV atom reveals that each metal centre is pyramidally co-ordinated by three amide ligands and the zirconium atom lies 0.688(2) Å above the plane of N(1), N(2) and N(3) whilst the hafnium atom is 0.707(2) Å above the analogous N(1)N(2)N(3) plane [Fig. 3(*a*), 3(*b*)]. Each amide ligand has one of its six $SiCH_3$ units located in close proximity to the metal atom with Zr–Si distances of about 3.00 Å, Hf–Si distances of *ca.* 2.98 Å, Zr–C distances of *ca.* 2.75 Å, Hf–C distances *ca.* 2.73 Å, Zr–H distances of 2.66 Å and Hf–H distances of 2.61 Å (see Tables 2 and 3). These co-ordinated $NSiCH_3$ moieties, the atoms of which are indicated by black circles in Figs. 3(*a*), 3(*b*) and 4(*a*), 4(*b*), are related by local C_3 pseudo-symmetry [Fig. 4(*a*), 4(*b*)]. The metal atom lies on the three-fold axis and three $SiCH_3$ units point towards the metal centre. The three Si–C bonds close to the metal centre are significantly longer [1.902(1), 1.903(1) and 1.895(1) Å in compound **1**, 1.902(1), 1.905(2) and 1.894(2) Å in **2**] than the remaining 15, non-co-ordinating Si–C bonds which are in the ranges 1.854–1.868 (**1**), 1.853–1.869 Å (**2**). This bonding contrasts with that observed for $[M\{N(SiMe_3)_2\}_3Me]$, M = Zr or Hf, where no metal–silyl type interactions were observed.[6]

However similar features have been observed in [U{N(Si-

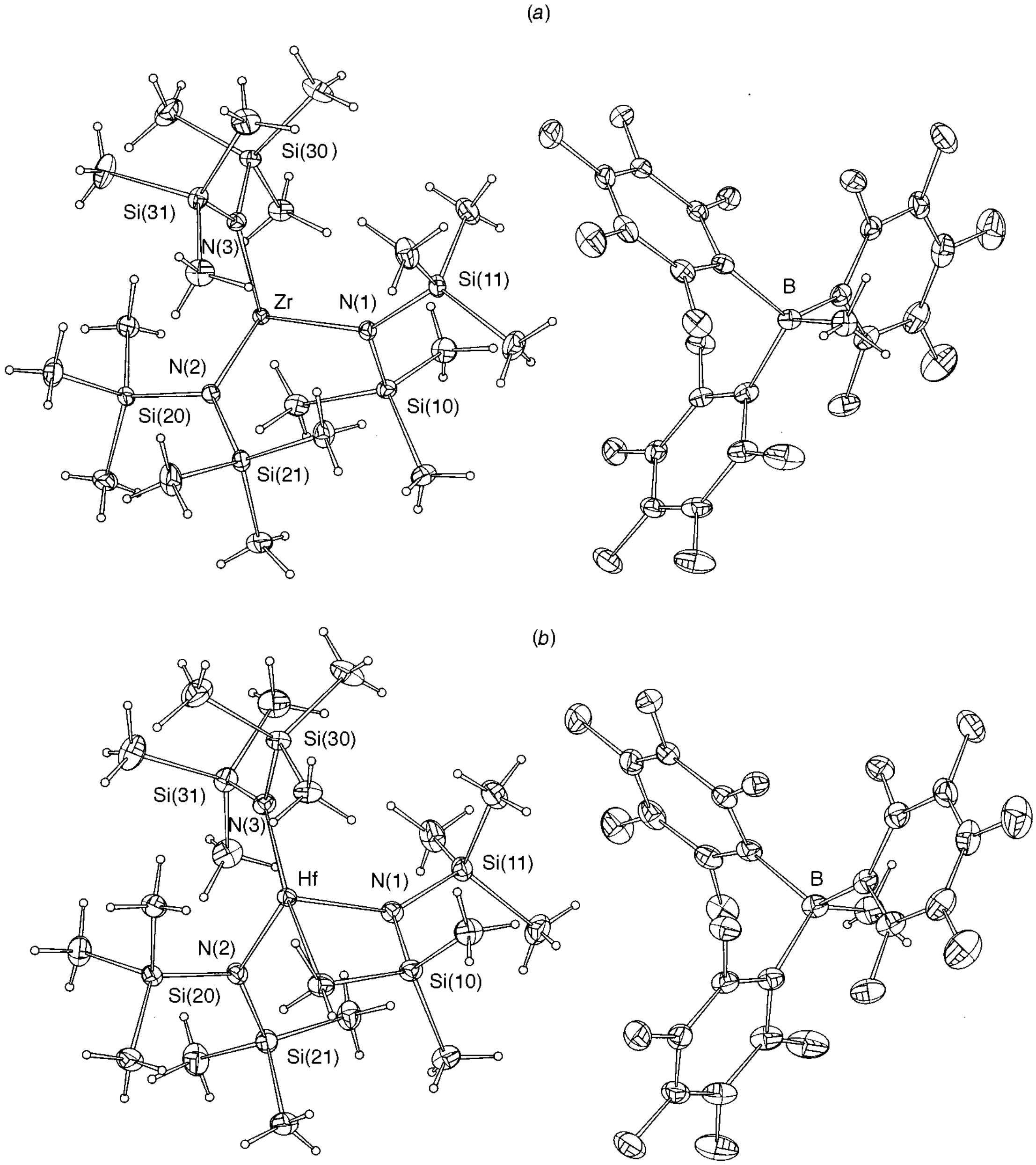

Fig. 2 Structures of compounds **1** (*a*) and **2** (*b*) in the crystal. Ellipsoids are drawn at 50% probability. The hydrogen, carbon and fluorine atoms are not labelled for clarity

$Me_3)_2\}_2\{N(SiMe_3)SiMe_2CH_2B(C_6F_5)_3\}]$ where the electron deficiency of the metal centre is compensated by the formation of multicentre bonds between the U atom and $SiCH_2$ units of the amide ligands.[4] The uranium atom is pyramidally co-ordinated by three amide ligands and lies 0.7 Å above the plane that these nitrogen atoms form. Each amide ligand has one of its six $SiCH_2$ entities located in close proximity to the uranium atom and short U–Si and U–C distances suggest the formation of multicentre bonds between the Si–C bonds and uranium.

In contrast, work by Horton and co-workers,[7,8] describing the reactions of $B(C_6F_5)_3$ with zirconium diamide dialkyl complexes, has uncovered no evidence for the formation of M–Si–C multicentre interactions. The complex $[Zr\{N(SiMe_3)_2\}_2(CH_2Ph)_2]$ reacts with this Lewis acid, eliminating C_6H_5Me and forming $[Zr(CH_2SiMe_2NSiMe_3)\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}\{N(SiMe_3)_2\}]$, which has been characterised by NMR spectroscopy.[7] A similar reaction is observed between $[Zr\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}R_2]$ and $B(C_6F_5)_3$ when $R = CH_2Ph$. However when R = Me alkyl abstraction ocurs and NMR spectroscopic data suggest the presence of a covalent interaction between the cation, $[N_3ZrMe]^+$, and the $[MeB(C_6F_5)_3]^-$ anion.[8]

The multicentre M–Si–C interactions observed in the solid-state structures of compounds **1** and **2** cannot be detected in their room-temperature ^1H and ^{13}C NMR spectra which are consistent with the presence of only one type of $SiMe_3$ group. On cooling a sample of **1** in CD_2Cl_2 solution to 213 K a broadening and partial splitting of the signal assigned to the $SiMe_3$ groups is observed although slow-exchange conditions of these molecules could not be achieved. These findings suggest that $M\text{–}Si\text{–}CH_3$ multicentre interactions are present in solution but that there is a low rotational energy barrier. The compound $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2]^+$ possesses two types of $SiMe_3$ moieties in the solid state, by virtue of $La\text{–}Si\text{–}CH_3$ interactions, and has been studied by variable-temperature ^{13}C NMR spectroscopy. The two different $SiMe_3$ environments cannot be discerned at room temperature but on cooling to 183 K two signals can be resolved.[5] For both compounds **1** and **2** a ^1H NMR spectroscopic resonance due to the methyl group of the $[MeB(C_6F_5)_3]^-$ anion was not detected, presumably due to line broadening caused by coupling to the quadrupolar ^{11}B nucleus.

In compounds **1** and **2** the formation of multicentre $M\text{–}Si\text{–}CH_3$ interactions appears to be driven by the need to relieve the electron deficiency of the metal cation. We wondered whether these interactions could be displaced by co-ordination

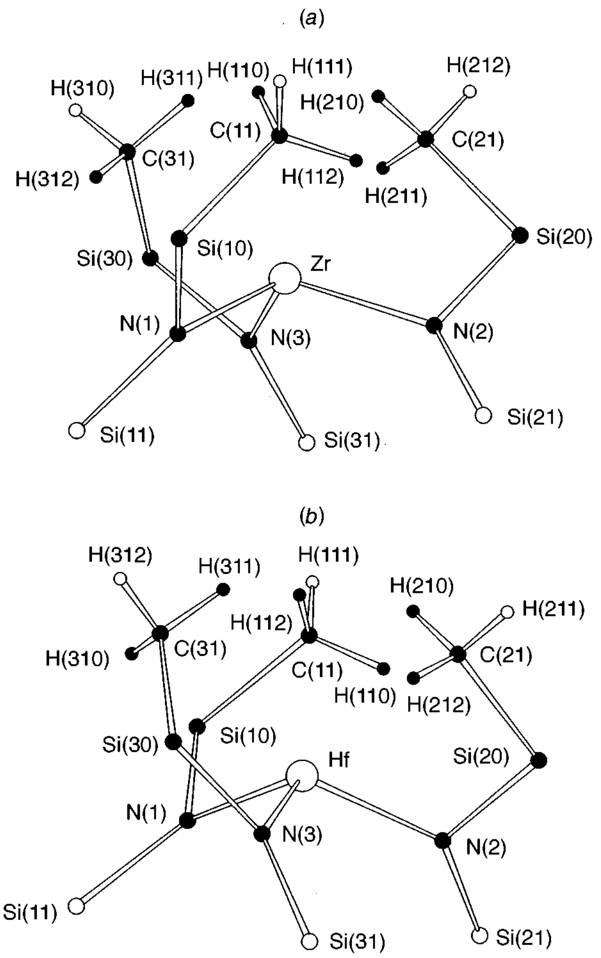

Fig. 3 The co-ordination sphere around the zirconium atom of compounds **1** (*a*) and the hafnium atom of **2** (*b*). All black atoms co-ordinate the metal atoms by strong covalent (N) or weaker multicentre (Si, C) bonds

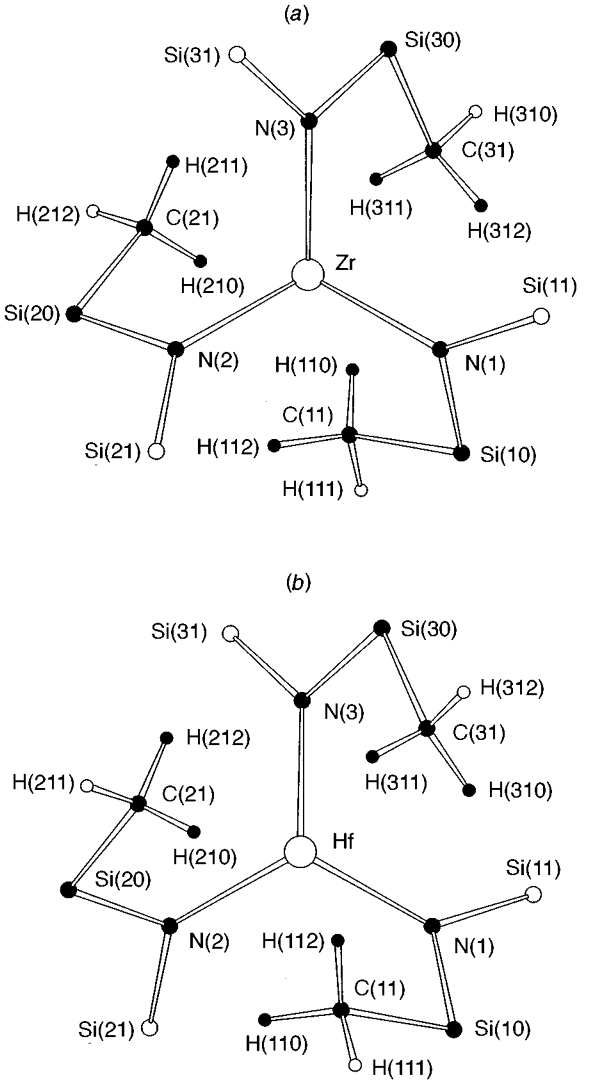

Fig. 4 The co-ordination sphere around the metal centres of compounds **1** (*a*) and **2** (*b*) demonstrating the local C_3 pseudo-symmetry

$$H_2NPh \xrightarrow{(i)} Li(NHPh) \xrightarrow{(ii)} HN(SiMe_3)Ph \xrightarrow{(i)} [\{LiN(Ph)SiMe_3\}_2]\cdot Et_2O$$

Scheme 1 (i) LiBu^n, pentane, −78 °C; (ii) SiMe$_3$Cl, Et$_2$O, −45 °C

of a two-electron donor ligand to the metal and accordingly attempted to prepare $[M\{N(SiMe_3)_2\}_3L][MeB(C_6F_5)_3]$ (L = PMe$_3$, PPh$_3$, pyridine or ethene) by reaction of the relevant ligand with compound **1**. Both phosphines failed to react indicating that the metal centre is well shielded by the amide ligands. In light of this finding it is unsurprising that compound **1** also failed to react with ethene, with or without addition of $(MeAlO)_n$ to the reaction. However, reaction of compound **1** with 1 equivalent of pyridine resulted in the formation of $[Zr\{N(SiMe_3)_2\}_3Me]$ and $C_5H_5N{\cdot}B(C_6F_5)_3$.[9] One feasible reaction mechanism proceeds *via* attack at the boron atom by pyridine to generate transient Me$^-$ which then reacts with the metal cation to yield $[Zr\{N(SiMe_3)_2\}_3Me]$. The strength of the B–N bond may supply the thermodynamic incentive for this reaction pathway. These findings imply that the $N(SiMe_3)_2$ ligands play a dual role in effectively satisfying the electronic requirements of the metal centre and providing sufficient steric congestion around the metal atom to render it inert to addition of nucleophiles.

In order to explore the reaction of less sterically demanding (tris)amide complexes with $B(C_6F_5)_3$ the new compounds $[M\{N(Ph)SiMe_3\}_3Cl]$ (M = Zr **3** or Hf **4**) and their methyl derivatives $[M\{N(Ph)SiMe_3\}_3Me]$ (M = Zr **5** or Hf **6**) were prepared. The amide, LiN(Ph)SiMe$_3$, has not been reported but is readily synthesized according to Scheme 1 and can be isolated as a 2 : 1 complex with diethyl ether. Characterising data for the lithium salt are given in Table 1. Compounds **3** and **4** are readily prepared using the same procedure as colourless, pentane-soluble, microcrystals. Formation of the methyl derivatives **5** and **6** is easily effected by reaction of **3** and **4** with LiMe. Characterising data for compounds **3**–**6** are given in Table 1. The compounds are quite sensitive and rapidly become yellow at room temperature, even in the solid state, and satisfactory elemental analyses could not be obtained for **6**. The methyl derivatives react with chlorinated solvents to reform the chloro complexes. It has been previously reported that $[Zr\{N(SiMe_3)_2\}_3Me]$ reacts in solution on exposure to UV radiation to eliminate methane and form the metallocyclic species $[Zr\{N(SiMe_3)_2\}_2\{N(SiMe_3)[SiMe_2(\mu\text{-}CH_2)]\}]$.[10]

The methyl derivatives, **5** and **6**, were treated with 1 equivalent of $B(C_6F_5)_3$ in pentane and yielded green oils. A ^{11}B NMR spectrum (CDCl$_3$) of the crude mixture from both reactions exhibited a resonance at δ −15.4 suggesting that the desired $[M\{N(Ph)SiMe_3\}_3][MeB(C_6F_5)_3]$ species had formed in *ca.* 50% yield. Unfortunately attempts to purify the reaction mixture failed to isolate any products. It was hoped that the reaction of complexes **5** and **6** with $B(C_6F_5)_3$ would generate reactive tris(amide) cations due to the smaller size and decreased electron-donating power of the N(Ph)SiMe$_3$ ligand. However, although *in situ* spectroscopic evidence suggests that the desired species are formed, it appears that the electronic and steric properties of the smaller ligand do not stabilise the $[M\{N(Ph)SiMe_3\}_3]^+$ cation sufficiently.

Table 1 Analytical and spectroscopic data for compounds **1–6** and [{LiN(Ph)SiMe$_3$}$_2$·Et$_2$O]

Compound [a]	Spectroscopic data [b]
1 [Zr{N(SiMe$_3$)$_2$}$_3$][MeB(C$_6$F$_5$)$_3$] C, 39.8 (40.4); H, 5.2 (5.2); B, 0.9 (1.0); N, 3.8 (3.8)	^{1}H:[c] 0.12 (s, 27 H, CH$_3$) ^{13}C:[d] 148.5 (d, *J* 226, C$_6$F$_5$), 137.0 (d, *J* 280, C$_6$F$_5$), 136.7 (d, *J* 230, C$_6$F$_5$), 11.2 [s (br), BCH$_3$], 3.4 (s, SiCH$_3$) ^{11}B: −14.7 (s) ^{19}F:[d] −13.60 (d, *J* 20), −169.30 (t, *J* 21), −172.04 (t, *J* 24)
2 [Hf{N(SiMe$_3$)$_2$}$_3$][MeB(C$_6$F$_5$)$_3$] C, 37.3 (37.5); H, 4.6 (4.81); B, 1.0 (0.93); N, 3.2 (3.54)	^{1}H: 0.13 (s, CH$_3$) ^{13}C:[d] 148.8 (d, *J* 240, C$_6$F$_5$), 138.2 (d, *J* 240, C$_6$F$_5$), 137.1 (d, *J* 250, C$_6$F$_5$), 10.2 [s (br), BCH$_3$], 2.0 (s, SiCH$_3$) ^{11}B: −14.6 (s) ^{19}F: −137.67 (d, *J* 24), −165.67 (t, *J* 21), −165.89 (t, *J* 21)
3 [Zr{N(Ph)SiMe$_3$}$_3$Cl] C, 51.0 (52.4); H, 7.0 (6.8); Cl, 4.9 (5.7); N, 6.5 (6.8)	^{1}H: 7.07 (t, *J* 8.0, 6 H, *m*-H of C$_6$H$_5$), 6.91 (t, *J* 7.9, 3 H, *p*-H of C$_6$H$_5$), 6.12 (d, *J* 7.5, 6 H, *o*-H of C$_6$H$_5$), 0.20 (s, 27 H, SiCH$_3$) ^{13}C: δ 147.8 (s, *ipso*-C of C$_6$H$_5$), 129.2 (s, *m*-C of C$_6$H$_5$), 128.3 (s, *p*-C of C$_6$H$_5$), 124.5 (s, *o*-C of C$_6$H$_5$), 1.0 (s, SiCH$_3$)
4 [Hf{N(Ph)SiMe$_3$}$_3$Cl] C, 45.2 (45.9); H, 6.1 (6.0); Cl, 4.7 (5.0); N, 5.9 (6.0)	^{1}H: 7.07 (t, *J* 7.5, 6 H, *m*-H of C$_6$H$_5$), 6.90 (t, *J* 6.5, 3 H, *p*-H of C$_6$H$_5$), 6.55 (d, *J* 7.0, 6 H, *o*-H of C$_6$H$_5$), 0.19 (s, 27 H, SiCH$_3$) ^{13}C: 147.9 (s, *ipso*-C of C$_6$H$_5$), 129.0 (s, *m*-C of C$_6$H$_5$), 128.4 (s, *p*-C of C$_6$H$_5$), 124.2 (s, *o*-C of C$_6$H$_5$), 1.0 (s, SiCH$_3$)
5 [Zr{N(Ph)SiMe$_3$}$_3$Me] C, 55.8 (56.2); H, 7.9 (7.5); N, 6.6 (7.0)	^{1}H: 7.13 (t, *J* 8.5, 6 H, *m*-H of C$_6$H$_5$), 6.96 (t, *J* 7.5, 3 H, *p*-H of C$_6$H$_5$), 6.88 (d, *J* 8.5, 6 H, *o*-H of C$_6$H$_5$), 0.39 (s, 3 H, ZrCH$_3$), 0.18 (s, 27 H, SiCH$_3$) ^{13}C: 145.9 (s, *ipso*-C of C$_6$H$_5$), 129.4 (s, *m*-C of C$_6$H$_5$), 129.2 (s, *p*-C of C$_6$H$_5$), 124.2 (s, *o*-C of C$_6$H$_5$), 41.2 (s, ZrCH$_3$), 1.0 (s, SiCH$_3$).
6 [Hf{N(Ph)SiMe$_3$}$_3$Me]	^{1}H: 7.15 (t, *J* 7.9, 6 H, *m*-H of C$_6$H$_5$), 6.95 (t, *J* 8.5, 3 H, *p*-H of C$_6$H$_5$), 6.82 (d, *J* 6.3, 6 H, *o*-C of C$_6$H$_5$), 0.39 (s, 3 H, ZrCH$_3$), 0.17 (s, 27 H, SiCH$_3$) ^{13}C: 146.1 (s, *ipso*-C of C$_6$H$_5$), 129.3 (s, *m*-C of C$_6$H$_5$), 129.2 (s, *p*-C of C$_6$H$_5$), 124.1 (s, *o*-C of C$_6$H$_5$), 45.6 (s, HfCH$_3$), 1.0 (s, SiCH$_3$)
[{LiN(Ph)SiMe$_3$}$_2$·Et$_2$O]	^{1}H: 7.17 (t, *J* 7.6, 12 H, *m*-H of C$_6$H$_5$), 6.76 (d, *J* 8.1, 12 H, *o*-H of C$_6$H$_5$), 6.65 (t, *J* 6.3, 6 H, *p*-H of C$_6$H$_5$), 3.03 (q, *J* 7.8, 4 H, CH$_2$O), 0.74 (t, *J* 7.2, 6 H, C*H*$_3$CH$_2$O), 0.27 (s, 36 H, SiCH$_3$)

[a] Analytical data given as found (calculated) in %. [b] NMR data (C$_6$D$_6$, 298 K), unless otherwise stated, given as: chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment]. [c] Methyl resonance too broad to be located. [d] In CD$_2$Cl$_2$.

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Zr–N(1)	2.027(1)	Si(10)–C(11)	1.902(1)
Zr–N(2)	2.022(1)	Si(20)–C(21)	1.903(1)
Zr–N(3)	2.047(1)	Si(30)–C(31)	1.895(1)
Zr–Si(10)	2.9843(3)	Zr–H(110)	2.65(2)
Zr–Si(20)	2.9907(3)	Zr–H(112)	2.58(2)
Zr–Si(30)	3.0336(3)	Zr–H(210)	2.63(2)
Zr–C(11)	2.697(1)	Zr–H(211))	2.62(2)
Zr–C(21)	2.736(1)	Zr–H(311)	2.75(2)
Zr–C(31)	2.806(1)	Zr–H(312)	2.72(2)
Zr–N(1)–Si(10)	104.06(5)	Zr–N(1)–Si(11)	134.25(5)
Zr–N(2)–Si(20)	104.61(5)	Zr–N(2)–Si(21)	133.07(6)
Zr–N(3)–Si(30)	105.96(5)	Zr–N(3)–Si(31)	133.04(6)

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

Hf–N(1)	2.014(2)	Si(10)–C(11)	1.902(1)
Hf–N(2)	2.015(1)	Si(20)–C(21)	1.905(2)
Hf–N(3)	2.034(1)	Si(30)–C(31)	1.894(2)
Hf–Si(10)	2.9631(5)	Hf–H(110)	2.55(3)
Hf–Si(20)	2.9709(5)	Hf–H(112)	2.54(3)
Hf–Si(30)	3.0200(4)	Hf–H(210)	2.57(3)
Hf–C(11)	2.668(2)	Hf–H(212)	2.60(3)
Hf–C(21)	2.716(2)	Hf–H(310)	2.64(3)
Hf–C(31)	2.794(2)	Hf–H(311)	2.75(3)
Hf–N(1)–Si(11)	135.15(8)	Hf–N(1)–Si(10)	103.51(7)
Hf–N(2)–Si(21)	133.72(8)	Hf–N(2)–Si(20)	104.04(7)
Hf–N(3)–Si(31)	133.61(8)	Hf–N(3)–Si(30)	105.85(7)

Experimental

Fourier-transform ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 and 96 MHz respectively, ^{13}C NMR spectra on a Bruker AM 300 spectrometer at 75.5 MHz or Varian Unity plus 500 spectrometer at 125 MHz, ^{19}F NMR spectra on a Varian Unity plus 500 spectrometer at 470 MHz: ^{1}H and ^{13}C shifts are reported with respect to δ 0 for SiMe$_4$, ^{11}B with respect to δ 0 for BF$_3$·OEt$_2$, ^{19}F with respect to δ 0 for CFCl$_3$; all downfield shifts are positive. Microanalyses were obtained from the microanalytical laboratory of this department.

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N$_2$ before use. The compounds NaN(SiMe$_3$)$_2$, ZrCl$_4$, HfCl$_4$, LiMe (1.4 M solution in hexane), LiBu^n (1.4 M solution in pentane), H$_2$NPh and SiMe$_3$Cl were used as received (Aldrich). The compounds [Zr{N(SiMe$_3$)$_2$}$_3$Cl],[6] [Hf{N(SiMe$_3$)$_2$}$_3$Cl],[6] [Zr{N(SiMe$_3$)$_2$}$_3$Me],[6] [Hf{N(SiMe$_3$)$_2$}$_3$Me][6] and B(C$_6$F$_5$)$_3$[11] were prepared as previously described.

Preparations

[Zr{N(SiMe$_3$)$_2$}$_3$][MeB(C$_6$F$_5$)$_3$] 1. The compound [Zr{N(SiMe$_3$)$_2$}$_3$Me] (265 mg, 0.45 mmol) in pentane (40 cm^3) was treated with B(C$_6$F$_5$)$_3$ (231 mg, 0.45 mmol) in pentane (25 cm^3) by slow addition. There was immediate formation of a white precipitate and after stirring for 1 h the volatiles were removed *in vacuo*. The solid (300 mg, 60% crude yield) was washed with pentane and extracted with toluene. Concentration of this solution and cooling to −20 °C gave colourless block shaped crystals.

[Hf{N(SiMe$_3$)$_2$}$_3$][MeB(C$_6$F$_5$)$_3$] 2. The compound [Hf{N(SiMe$_3$)$_2$}$_3$Me] (550 mg, 0.816 mmol) in pentane (80 cm^3) was treated dropwise with B(C$_6$F$_5$)$_3$ (418 mg, 0.816 mmol) in pentane (40 cm^3). There was immediate formation of a white precipitate. Treatment as above gave colourless block shaped crystals. Yield 370 mg, 38%.

LiN(Ph)SiMe$_3$. Aniline (15 g, 0.16 mol) was dissolved in pentane (100 cm^3) and cooled to −78 °C. A 2.5 M pentane solution of $LiBu^n$ (64.4 cm^3, 0.16 mol) was added dropwise and then stirred for 3 h to give a white precipitate. The reaction mixture was allowed to warm to room temperature and the supernatant liquid filtered off to leave an air-sensitive solid. Without further purification the solid was dissolved in diethyl ether (100 cm^3), cooled to −45 °C, and $SiMe_3Cl$ (20.5 cm^3, 0.16 mol) added dropwise. After stirring for 2 h a white precipitate had formed. All volatiles were removed *in vacuo* and the resulting solid was extracted with pentane (3 × 70 cm^3). The pentane filtrate was cooled to −78 °C and $LiBu^n$ (64.4 cm^3, 0.082 mol) added dropwise; immediately a cream precipitate formed. The reaction was allowed to warm to room temperature, stirred for a further hour and then the solvent removed *in vacuo*. The product was washed with pentane and the creamy white solid dried *in vacuo* before being extracted with diethyl ether (3 × 40 cm^3). The filtrate was concentrated and recrystallised to yield a white solid. Proton NMR spectroscopic data of the compound were consistent with the molecular formula $[\{LiN(Ph)SiMe_3\}_2]\cdot Et_2O$. Yield 29.03 g, 79%.

$[Zr\{N(Ph)SiMe_3\}_3Cl]$ 3. A solution of $[\{LiN(Ph)SiMe_3\}_2]\cdot Et_2O$ (4.02 g, 9.65 mmol) in diethyl ether (60 cm^3) was added to a suspension of $ZrCl_4$ (1.5 g, 6.4 mmol) in diethyl ether (30 cm^3). The reaction was stirred for 18 h before removal of the solvent under reduced pressure. The solid was extracted with pentane (3 × 40 cm^3) and the filtrate concentrated to 10 cm^3; colourless crystals formed on cooling to −20 °C. Yield 2.93 g, 74%.

$[Hf\{N(Ph)SiMe_3\}_3Cl]$ 4. A solution of $[\{LiN(Ph)SiMe_3\}_2]\cdot Et_2O$ (1.95 g, 4.68 mmol) in diethyl ether (60 cm^3) was added to a suspension of $HfCl_4$ (1.0 g, 3.1 mmol) in diethyl ether (30 cm^3). The reaction was stirred for 6 h before removal of the solvent under reduced pressure. The solid was extracted with pentane (3 × 30 cm^3) and the filtrate concentrated to 20 cm^3; colourless crystals formed on cooling to −20 °C. Yield 1.07 g, 49%.

$[Zr\{N(Ph)SiMe_3\}_3Me]$ 5. The compound $[Zr\{N(Ph)SiMe_3\}_3Cl]$ (1.0 g, 1.6 mmol) in diethyl ether (40 cm^3) was cooled to −50 °C. Methyllithium (1.6 mmol as 1.15 cm^3 of a 1.4 M solution in hexane) was added carefully and the reaction stirred for 2 h before removal of the solvent under reduced pressure. The solid was extracted with pentane (3 × 40 cm^3) and the solvent removed to yield a light brown powder. Yield 0.82 g, 85%.

$[Hf\{N(Ph)SiMe_3\}_3Me]$ 6. The compound $[Hf\{N(Ph)SiMe_3\}_3Cl]$ (1.0 g, 1.6 mmol) in diethyl ether (30 cm^3) was cooled to −50 °C. Methyllithium (0.56 mmol as 0.4 cm^3 of a 1.4 M solution in hexane) was added carefully and the reaction stirred for 2 h before removal of the solvent under reduced pressure. The solid was extracted with pentane (3 × 40 cm^3) and the solvent removed to yield a light brown powder. Yield 0.28 g, 72%.

Reactions of $[Zr\{N(SiMe_3)_2\}_3][MeB(C_6F_5)_3]$ 1 with nucleophiles

With PMe_3. The compound $[Zr\{N(SiMe_3)_2\}_3][MeB(C_6F_5)_3]$ **1** (27 mg, 0.025 mmol) in C_6D_6 (0.5 cm^3) was treated with a small excess of PMe_3 (0.509 M toluene solution). The resulting ^1H, ^{11}B and ^{31}P NMR spectra of the reaction mixture corresponded to those of the starting reagents.

With PPh_3. Compound **1** (20 mg, 0.018 mmol) and PPh_3 (7 mg, 0.027 mmol) were dissolved together in C_6D_6 (0.5 cm^3). The ^1H, ^{11}B and ^{31}P NMR spectra of the reaction mixture corresponded to those of the starting reagents.

With pyridine. Compound **1** (320 mg, 0.291 mmol) was dissolved in toluene (60 cm^3). A 0.1 M pyridine solution in toluene (2.92 cm^3, 0.292 mmol) was added and stirred for 2 h. The solvent was removed *in vacuo* to give a pale yellow solid. Extraction with hexane (120 cm^3) yielded a white solid which was identified by ^1H and ^{11}B NMR spectroscopy as a mixture of $C_5H_5N\cdot B(C_6F_5)_3$ and $[Zr\{N(SiMe_3)_2\}_3Me]$.

With ethene. Compound **1** (320 mg, 0.291 mmol) was dissolved in toluene (10 cm^3) and ethene was bubbled through the solution. After 1 h no reaction was observed so $(MeAlO)_n$ (320 mg, 0.291 mmol) was added. After a further 1 h no formation of polyethylene was observed.

Reaction of $[Zr\{N(Ph)SiMe_3\}_3Me]$ with $B(C_6F_5)_3$

The compound $[Zr\{N(Ph)SiMe_3\}_3Me]$ (300 mg, 0.50 mmol) in pentane (60 cm^3) was treated dropwise with $B(C_6F_5)_3$ (256 mg, 0.50 mmol) in pentane (60 cm^3). After stirring for 18 h the solvent was filtered off from a grey powder. Addition of either toluene or CH_2Cl_2 to the solid produced the immediate formation of a green solution which was concentrated *in vacuo* to yield a green oil. Examination of the crude product by ^{11}B NMR spectroscopy revealed two major signals at δ −5.7 and −15.4 but unfortunately no single product could be isolated from the mixture .

NMR tube reaction of $[Hf\{N(Ph)SiMe_3\}_3Me]$ with $B(C_6F_5)_3$

The compounds $[Hf\{N(Ph)SiMe_3\}_3Me]$ and $B(C_6F_5)_3$ were mixed in a 1 : 1 ratio and then dissolved in C_6D_6 (0.5 cm^3). After 18 h a ^{11}B NMR spectrum of the mixture exhibited peaks at δ −5.9 and −15.4.

Crystallography

Crystals of compounds **1** and **2** were grown from toluene at 253 K and then dried *in vacuo*. In each case a crystal was immersed in highly viscous perfluoropolyether to exclude oxygen. It was then mounted on a glass fibre and plunged in a cold (100 K) nitrogen stream.

Crystal data. Compound **1**, $C_{37}H_{57}BF_{15}N_3Si_6Zr$, $M = 1099.40$, triclinic, space group $P\bar{1}$, $a = 11.360(1)$, $b = 12.860(1)$, $c = 17.640(1)$ Å, $\alpha = 81.395(2)$, $\beta = 88.717(2)$, $\gamma = 78.529(2)°$, $U = 2479.04$ Å^3, $Z = 2$, $D_c = 1.462$ Mg m^{-3}, $\mu = 4.41$ cm^{-1}, colourless crystals, crystal dimensions 0.2 × 0.2 × 0.3 mm. Compound **2**, $C_{37}H_{57}BF_{15}HfN_3Si_6$, $M = 1186.67$, triclinic, space group $P\bar{1}$, $a = 11.354(1)$, $b = 12.863(1)$, $c = 17.616(1)$ Å, $\alpha = 81.367(1)$, $\beta = 88.676(1)$, $\gamma = 78.520(1)°$, $U = 2493.0$ Å^3, $Z = 2$, $D_c = 1.58$ Mg m^{-3}, $\mu = 23.00$ cm^{-1}, colourless crystals, crystal dimensions 0.3 × 0.4 × 0.5 mm.

Data collection and processing. The data for compounds **1** and **2** were collected at 100 K on an Enraf-Nonius DIP2020 image-plate diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). An Oxford Cryosystems CRYOSTREAM cooling system was used. For compound **1** 28 322 reflections were measured ($1 < \theta < 26°$, $\pm h$, $\pm k$, $\pm l$), 9741 unique of which 8858 had $I > 3\sigma(I)$. The images were processed with the DENZO and SCALEPAK programs.[12] For compound **2** 27 942 reflections were measured ($1 < \theta < 26°$, $\pm h$, $\pm k$, $\pm l$), 9728 unique of which 9320 had $I > 3\sigma(I)$. Corrections for Lorentz-polarisation effects and for absorption (multiscan) were performed.

Structure solution and refinement. The crystal structures were solved by direct methods and refined by the full-matrix least-squares method. For compound **1** all non-hydrogen atoms were refined with anisotropic and all hydrogen atoms with isotropic displacement parameters. 797 Refined parameters and 8858 observations resulted in a ratio observations : refined parameters of 11.1 : 1. A correction for secondary extinction was applied and refinement completed using a Chebyshev weighting scheme[13] with parameters 0.65, 0.204 and 1.30. Refinement on F converged at $R = 0.024$, $R' = 0.028$ and goodness of fit = 1.08. A final Fourier-difference synthesis showed minimum and maximum residual electron densities of -0.29 and 0.36 e Å^{-3}.

For compound **2** all non-hydrogen atoms were refined in anisotropic approximation. The positions of the hydrogen atoms were refined with fixed isotropic displacement parameters ($U_{iso} = 0.05$ Å^2). 740 Refined parameters and 9320 observations resulted in a ratio observations : refined parameters of 12.6 : 1. A correction for secondary extinction was applied and refinement completed using a Chebyshev weighting scheme[14] with parameters 2.97, -1.29 and 2.34 was applied. Refinement on F converged at $R = 0.022$, $R' = 0.025$ and goodness of fit = 1.09. A Fourier-difference synthesis showed minimum and maximum residual electron densities of -0.89 and 0.89 e Å^{-3}.

All crystallographic calculations were carried out using the CRYSTALS program package.[15]

CCDC reference number 186/786.

Acknowledgements

We thank the University of Oxford for a Violette and Samuel Glasstone Fellowship (to J. R. G.), the Deutsche Forschung Gemeinschaft (M. M.) and the EPSRC for support of this work.

References

1 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 3623.
2 M. Bochmann and S. J. Lancaster, *Organometallics*, 1994, **13**, 2235.
3 D. J. Gillis, M.-J. Tuboret and M. C. Baird, *J. Am. Chem. Soc.*, 1993, **115**, 2543.
4 M. Müller, V. C. Williams, L. H. Doerrer, M. A. Leech, S. A. Mason, M. L. H. Green and K. Prout, *Inorg. Chem.*, in the press.
5 H. van der Hejden, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1989, **8**, 255.
6 R. Anderson, *Inorg. Chem.*, 1979, **18**, 1724.
7 A. D. Horton and J. de With, *Chem Commun.*, 1996, 1375.
8 A. D. Horton, J. de With, A. J. van der Linden and H. van de Weg, *Organometallics*, 1996, **15**, 2672.
9 J. R. Galsworthy, M. L. H. Green, M. Müller and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1997, 1309.
10 D. C. Bradley, H. Chudzynska, J. D. J. Backer-Dirks, M. B. Hursthouse, A. A. Ibrahim, M. Motevalli and A. C. Sullivan, *Polyhedron*, 1990, **9**, 1423.
11 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245.
12 D. Gewirth, *The HKL Manual*, written with the co-operation of the program authors, Z. Otwinowski and W. Minor, Yale University, 1995.
13 E. Prince, *Mathematical Techniques in Crystallography and Material Sciences*, Springer, New York, 1982.
14 *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C.
15 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS Issue 10*, Chemical Crystallography Laboratory, University of Oxford, 1996.

Received 16*th September* 1997; *Paper* 7/06720H