DOI: 10.1002/chem.200601751

The Synthesis, Structure and Reactivity of $B(C_6F_5)_3$-Stabilised Amide ($M{-}NH_2$) Complexes of the Group 4 Metals

Andrew J. Mountford,[a] William Clegg,[b] Simon J. Coles,[c] Ross W. Harrington,[b] Peter N. Horton,[c] Simon M. Humphrey,[d] Michael B. Hursthouse,[c] Joseph A. Wright,[a] and Simon J. Lancaster*[a]

Abstract: Treatment of the homoleptic titanium amides $[Ti(NR_2)_4]$ (R = Me or Et) with the Brønsted acidic reagent $H_3N{\cdot}B(C_6F_5)_3$ results in the elimination of one molecule of amine and the formation of the four-coordinate amidoborate complexes $[Ti(NR_2)_3\{NH_2B(C_6F_5)_3\}]$, the identity of which was confirmed by X-ray crystallography. The reaction with $[Zr(NMe_2)_4]$ proceeds similarly but with retention of the amine ligand to give the trigonal-bipyramidal complex $[Zr(NMe_2)_3\{NH_2B(C_6F_5)_3\}(NMe_2H)]$. Cyclopentadienyl (Cp) amidoborate complexes, $[MCp(NR_2)_2\{NH_2B(C_6F_5)_3\}]$ (M = Ti, R = Me or Et; M = Zr, R = Me) can be prepared from $[MCp(NR_2)_3]$ and $H_3N{\cdot}B(C_6F_5)_3$, and exhibit greater thermal stability than the cyclopentadienyl-free compounds. $H_3N{\cdot}B(C_6F_5)_3$ reacts with *n*BuLi or $LiN(SiMe_3)_2$ to give $LiNH_2B(C_6F_5)_3$, which complexes with strong Lewis acids to form ion pairs that contain weakly coordinating anions. The attempted synthesis of metallocene amidoborate complexes from dialkyl or diamide precursors and $H_3N{\cdot}B(C_6F_5)_3$ was unsuccessful. However, $LiNH_2B(C_6F_5)_3$ does react with the highly electrophilic reagents $[MCp_2Me(\mu\text{-}Me)B(C_6F_5)_3]$ to give $[MCp_2Me(\mu\text{-}NH_2)B(C_6F_5)_3]$ (M = Zr or Hf). Comparison of the molecular structures of the Group 4 amidoborate complexes reveals very similar B−N, Ti−N and Zr−N bond lengths, which are consistent with a description of the bonding as a dative interaction between an $\{M(L)_n(NH_2)\}$ fragment and the Lewis acid $B(C_6F_5)_3$. Each of the structures has an intramolecular hydrogen-bonding arrangement in which one of the nitrogen-bonded hydrogen atoms participates in a bifurcated F···H···F interaction to *ortho*-F atoms.

Keywords: boranes • hydrogen bonds • Lewis acids • noncovalent interactions • titanium

Introduction

Homoleptic dialkylamide complexes of the Group 4 metals were first reported over forty years ago.[1] Initial studies focussed upon their reactivity towards protic reagents and they quickly became established as versatile precursors in a variety of synthetic procedures.[2,3] This propensity of the metal amides to undergo protolysis means that complexes of monoalkyamide ligands often exhibit low thermal stability with respect to intra- or intermolecular amine elimination to yield imido complexes.[4] It is therefore unsurprising that the only structurally authenticated examples of Group 4 metal complexes with the parent terminal amide (NH_2) ligand are the sterically protected titanium(III) metallocenes $[TiCp'_2(NH_2)]$ (in which $Cp' = \eta^5\text{-}C_5Me_5$ (**I**) or $\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3$), prepared by the reaction between the respective methyl complex and ammonia.[5–7]

Reaction with ammonia is employed to promote the controlled chemical deposition of the technologically important metal nitride materials [TiN] and $[Zr_3N_4]$ from tetrakis(dimethylamido)titanium or -zirconium. The initially formed species is assumed to be $[M(NMe_2)_3(NH_2)]$ and intermediates involving NH_2, NH and N ligands have been postulated.[8,9] Interest in this process has driven a number of investigations into the course of reactions between Brønsted

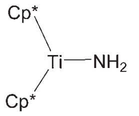
---

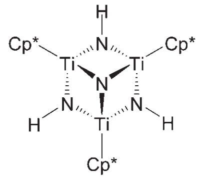
[a] Dr. A. J. Mountford, Dr. J. A. Wright, Dr. S. J. Lancaster
Wolfson Materials and Catalysis Centre
School of Chemical Sciences and Pharmacy
University of East Anglia, Norwich, NR4 7TJ (UK)
Fax: (+44) 1603-592-009
E-mail: S.Lancaster@uea.ac.uk

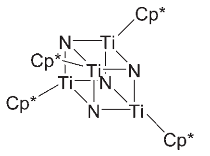
[b] Prof. W. Clegg, Dr. R. W. Harrington
School of Natural Sciences (Chemistry)
University of Newcastle, Newcastle upon Tyne NE1 7RU (UK)

[c] Dr. S. J. Coles, Dr. P. N. Horton, Prof. M. B. Hursthouse
School of Chemistry, University of Southampton
Highfield, Southampton, SO17 1BJ (UK)

[d] Dr. S. M. Humphrey
University Chemical Laboratory, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)

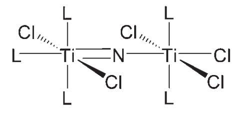




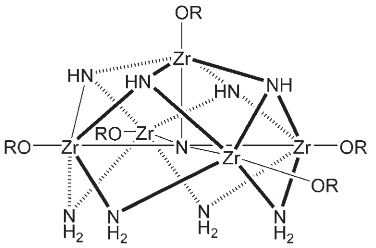


Cp* = η5-pentamethylcyclopentadienyl

I **II** **III**



L = 3,5-lutidine **IV**



RO = (*t*Bu)$_3$CO **V**

basic Group 4 metal compounds and ammonia. Typically, they react with one or more of the weakly acidic N−H groups to give polynuclear products with bridging amido, imido and nitrido ligands (**II**–**V**) even where sterically demanding ancillary ligands are employed.[10–14]

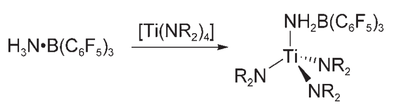
Complexation of ammonia with a strongly Lewis acidic reagent profoundly modulates its reactivity, evidently by preventing it from functioning as a Lewis base and providing steric protection, but also through polarisation of the N−H bonds rendering it more Brønsted acidic.[15] Tris(pentafluorophenyl)borane has, after initial demonstration as a Lewis acidic activator for polymerisation catalysts, found applications in fields as diverse as organic synthesis and materials.[16] This is due both to practical considerations, such as its resistance to hydrolysis and convenient crystalline form, as well as to the chemical properties of electrophilicity and stability, and the steric encumbrance imparted by the pentafluorophenyl groups. Experimental studies suggest that the Lewis acid strength of $B(C_6F_5)_3$ lies between those of BF_3 and BCl_3.[17] The ammonia adduct of tris(pentafluorophenyl)borane was amongst the first derivatives reported, but prior to our investigations its chemistry has remained largely unexplored.[18] This is in sharp contrast to $H_2O{\cdot}B(C_6F_5)_3$, which has been utilised in protonolysis reactions to yield complexes containing $[HOB(C_6F_5)_3]^-$ and $[OB(C_6F_5)_3]^{2-}$ ligands[19] or to derive weakly coordinating anions.[20,21]

We recently reported preliminary results demonstrating that the ammonia adduct $H_3N{\cdot}B(C_6F_5)_3$ reacts as a Brønsted acid with tetrakis(dimethylamido)metal complexes, $[M(NMe_2)_4]$ (M = Ti, Zr), to give $B(C_6F_5)_3$-stabilised M−NH_2 species.[22] Herein, we describe the scope of this experimental method, the reactivity of the resulting complexes, and present an alternative synthetic strategy to amidoborate complexes utilising less basic transition metal precursors.

Results and Discussion

Synthesis and characterisation: During the course of investigations into the reactivity of $H_3N{\cdot}B(C_6F_5)_3$ (**1**) it became evident that scrupulous attention must be paid to the purity of the reagent; in particular it is essential to ensure that the sample is not contaminated with $H_3N{\cdot}B(C_6F_5)_3{\cdot}NH_3$. Exposing a solution of $B(C_6F_5)_3$ in hexane to anhydrous ammonia gas yields a material with a C:N ratio of 18:2, due to a second associated NH_3 equivalent. Analytically pure **1** can be prepared by dissolving the crude material in toluene, removing the volatiles, and recrystallising from a dichloromethane/light petroleum mixture.[23,24]

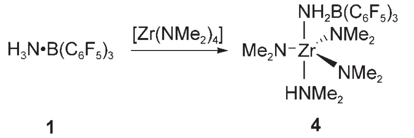
Treatment of a light petroleum solution of $[Ti(NMe_2)_4]$ with **1** at 0 °C (Scheme 1), followed by concentration and cooling to −25 °C overnight, yielded nearly colourless crystals of **2**. The ^1H ([D$_6$]benzene) NMR spectrum consisted of a resonance at $\delta = 2.59$ ppm (2H) and a broad singlet at $\delta = 2.23$ ppm (18H), which we assign to the $[N\mathit{H}_2B(C_6F_5)_3]$ ligand and NMe_2 groups, respectively. The ^{11}B resonance was found at $\delta = -5.8$ ppm. Compound **2** was therefore formulated as $[Ti(NMe_2)_3\{NH_2B(C_6F_5)_3\}]$. The reaction between $[Ti(NEt_2)_4]$ and **1** in toluene at 0 °C proceeded similarly, affording $[Ti(NEt_2)_3\{NH_2B(C_6F_5)_3\}]$ (**3**) after removal of the volatiles as a yellow oily material in moderate (41 %) yield. The spectroscopic characteristics of the $NH_2B(C_6F_5)_3$ ligand were very similar to those in **2**, with ^1H and ^{11}B NMR resonances at $\delta = 2.46$ and −5.4 ppm, while the diethylamido groups afforded characteristic and well-resolved quartet and triplet signals at $\delta = 3.20$ and 0.70 ppm, respectively. For both **2** and **3** the elemental analyses were consistent with the proposed compositions.



1 **2**: R = Me **3**: R = Et

Scheme 1.

To determine whether zirconium amides reacted similarly, we treated a solution of $[Zr(NMe_2)_4]$ in toluene with **1**, resulting in the immediate precipitation of a colourless microcrystalline solid **4** (Scheme 2). Compound **4** proved to be insoluble in aromatic and chlorocarbon solvents, but could be recrystallised without ligand exchange from a tetrahydrofuran solution. The ^1H NMR spectrum ([D$_8$]tetrahydrofuran) consisted of two singlets at $\delta = 2.88$ and 2.70 ppm, which we

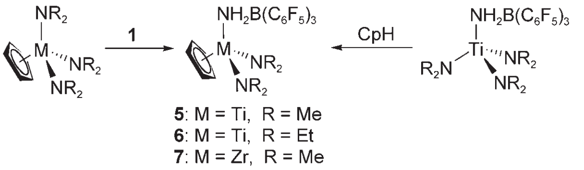


1 **4**

Scheme 2.

interpreted as two NMe_2 environments in a 3:1 ratio, with the $NH_2B(C_6F_5)_3$ resonance observed at $\delta = 2.79$ ppm. The ^{11}B NMR signal at $\delta = -2.4$ ppm was consistent with conversion of $H_3N{\cdot}B(C_6F_5)_3$ ($\delta = -6.9$ ppm) into an amidoborate $[NH_2B(C_6F_5)_3]^-$ ion.[23,25] Further evidence for the presence of an NH_2 group was provided by the observation of bands at 3364 and 3293 cm^{-1} in the FT-IR spectrum. On the basis of the elemental analysis and spectroscopic data we formulated complex **4** as the five-coordinate amine adduct $[Zr(NMe_2)_3\{NH_2B(C_6F_5)_3\}(HNMe_2)]$, which we were subsequently able to confirm crystallographically. Presumably, the greater size of zirconium favours the retention of the amino ($HNMe_2$) ligand in **4**, whereas it is released from the coordination sphere during the course of the reaction to form the four-coordinate titanium complex **2**. Compounds **2**–**4** can be regarded as $B(C_6F_5)_3$-stabilised $[M(NMe_2)_3(NH_2)]$ complexes, the first intermediates in the ammonia-promoted deposition of metal nitrides from $[M(NMe_2)_4]$.

To ascertain the scope of the amine elimination approach, toluene solutions of $[TiCp(NMe_2)_3]$, $[TiCp(NEt_2)_3]$ and $[ZrCp(NMe_2)_3]$ were treated with one equivalent of **1** at room temperature (Scheme 3). The reactions all proceeded with evolution of one equivalent of amine, giving the cyclopentadienyl complexes, $[TiCp(NMe_2)_2\{NH_2B(C_6F_5)_3\}]$ (**5**), $[TiCp(NEt_2)_2\{NH_2B(C_6F_5)_3\}]$ (**6**) and $[ZrCp(NMe_2)_2\{NH_2B(C_6F_5)_3\}]$ (**7**), respectively ($Cp = \eta^5\text{-}C_5H_5$). Compounds **5** and **7** were isolated as yellow crystalline solids after removal of the volatiles under reduced pressure, while the diethylamido complex **6** was precipitated by addition of light petroleum to the reaction mixture. Compounds **5** and **6** could be more conveniently prepared by treating **2** and **3** with one equivalent of cyclopentadiene in toluene at 0 °C, obviating the use of titanium–Cp precursors, $[TiCp(NR_2)_3]$ (Scheme 3). Unlike **4**, cyclopentadienyl complex **7** dissolved readily in $[D_6]$benzene, revealing rather minor differences between the multinuclear NMR spectra of the titanium (**5**) and zirconium complexes (**7**). In the ^1H NMR spectra of **5**, **6** and **7**, the $NH_2B(C_6F_5)_3$ signals were located at $\delta = 2.62$, 2.63 and 2.41 ppm, respectively. Singlet resonances at $\delta = 5.50$ (**5**), 5.96 (**6**) and 5.62 ppm (**7**) integrating to 5 H could be assigned as the cyclopentadienyl ligands, and there was no suggestion of dimethylamine coordination to the zirconium centre in **7**, in contrast to **4**. The methyl resonances in **5** and **7** appeared at $\delta = 2.49$ and 2.33 ppm, respectively. The diastereotopic methylene hydrogen atoms in **6** give rise to two multiplets centred at $\delta = 3.77$ and 3.60 ppm. The ^{11}B chemical shifts differ only slightly in compounds **5** ($\delta = -4.8$ ppm), **6** ($\delta = -4.9$ ppm) and **7** ($\delta = -5.5$ ppm), and the ^{19}F spectra of all three complexes are also very similar (Table 1). The corresponding elemental analyses were in good agreement with the proposed structures. Complexes **5** and **7** were structurally characterised by X-ray diffraction methods.



Scheme 3. Synthesis of compounds **5**–**7**.

Table 1. Selected multinuclear NMR data (δ in ppm) for compounds **1**–**11**. (NMR spectra recorded in $[D_6]$benzene at room temperature unless otherwise stated.)

	^1H		^{11}B	^{19}F		
	NH_2	Cp		*ortho*	*para*	*meta*
1	2.67	–	−6.9	−135.3	−155.5	−162.9
2	2.23	–	−5.8	−134.2	−158.6	−163.9
3	2.46	–	−5.4	−133.6	−158.3	−163.9
4[a]	2.79	–	−2.4	−131.1	−160.0	−163.5
5	2.62	5.50	−4.8	−133.7	−157.9	−163.8
6	2.63	5.96	−4.9	−133.5	−159.6	−165.0
7	2.41	5.62	−5.5	−134.8	−157.5	−164.1
8a	0.85	–	−6.1	−137.1	−160.4	−164.8
8b	1.03	–	−5.8	−135.0	−162.0	−166.1
9[b]	4.16	–	−6.3	[c]	[c]	[c]
10	2.31	5.71	−5.4	−135.5	−158.3	−164.2
11	2.34	5.65	−4.9	−134.9	−158.1	−164.2

[a] $[D_8]$THF at room temperature. [b] $[D_1]$Chloroform. [c] Many signals.

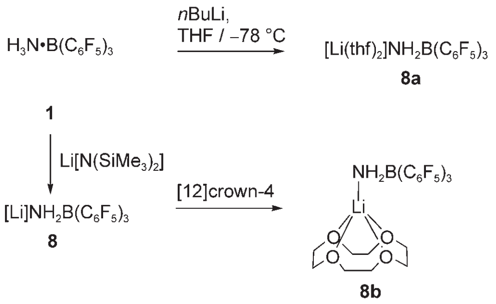
The amidoborate complexes **2**–**4** exhibited marked differences in their thermal sensitivity. Compound **2**, whilst stable in the solid state, decomposes slowly in hydrocarbon solution above 0 °C precipitating an oil. Monitoring the decomposition of **2** (in $[D_8]$toluene solution) by ^1H, ^{11}B and ^{19}F NMR spectroscopy revealed a complex product mixture including a number of unidentified boron-containing compounds accompanied by the formation of C_6F_5H. Complex **3** is significantly more stable and decomposes only very slowly in toluene at room temperature, again giving rise to a mixture of products including C_6F_5H. Complex **4** proved indefinitely stable at room temperature in solution, but decomposition was observed when heating in toluene for extended periods. The cyclopentadienyl complexes **5**–**7** exhibited significantly better thermal stability with no evidence for decomposition at room temperature, even after standing for several days under nitrogen.

Attempts to prepare bis(cyclopentadienyl) compounds, $[MCp_2(NR_2)\{NH_2B(C_6F_5)_3\}]$, through addition of two equivalents of cyclopentadiene to **2** and **3** were unsuccessful, affording only the mono-Cp complexes, whilst analogous treatment of **4** led to a mixture of products.[26] Gently heating these reaction mixtures under a nitrogen flow, designed to remove $HNMe_2$, merely accelerated the competing decomposition of **2**–**4** to give, among other species, C_6F_5H.

Attempts to prepare bis(amidoborate) complexes were unsuccessful; under conditions mild enough to prevent decomposition amidoborates complexes **2**–**4** fail to react with further equivalents of **1**. The restricted scope of methods depending upon the Brønsted acidity of **1** was further illustrated by a failure to react with either $[MCp_2(NMe_2)_2]$ or $[MCp_2Me_2]$.

The apparent limitations of the amine and alkane elimination pathways prompted us to explore whether an alternative metathesis approach employing $[M\{H_2NB(C_6F_5)_3\}]$ reagents might provide access to metallocene amidoborate complexes. We recently reported the synthesis of the amidodiborate ion $[H_2N\{B(C_6F_5)_3\}_2]^-$ through treatment of $NaNH_2$ with two equivalents of $B(C_6F_5)_3$.[27] However, while lithium amidoborohydrides, $Li[R_2NBX_3]$, are well known in which X is hydrogen,[28] the pentafluorophenyl analogues ($X{=}C_6F_5$) are unprecedented. In keeping with the more highly developed chemistry of $H_2O{\cdot}B(C_6F_5)_3$, the hydroxyborate ion, $[HOB(C_6F_5)_3]^-$, has been reported as the [K(dibenzo[18]crown-6)]$^+$ and $[Et_3NH]^+$ salts.[21]

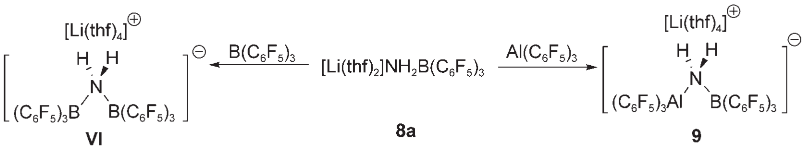
Treatment of **1** with *n*BuLi in tetrahydrofuran followed by solvent removal led to the isolation of a colourless glass (**8a**; Scheme 4). The ^{1}H spectrum ([D$_6$]benzene) consisted of two peaks of equal integration at $\delta = 3.08$ and 1.18 ppm corresponding to coordinated tetrahdrofuran, and a singlet resonance at $\delta = 0.85$ ppm that was assigned to nitrogen-bonded hydrogen atoms. Evidently the NH_2 group in **8a** is in a significantly more shielded environment than those in compounds **2**–**7** ($\delta = 2.23$–2.79 ppm). The ^{11}B signal was essentially unchanged from that of the neutral adduct at $\delta = -6.1$ ppm. A better indication for the formation of an anionic species was provided by the reduction in the chemical shift difference between the *para*-F and *meta*-F resonances in the ^{19}F spectrum ($\Delta\delta(p,m) = 4.4$ ppm for **8a** versus 7.4 ppm for **1**).[25] In light of the NMR assignment, and a consistent elemental analysis result, the product was formulated as $[Li(thf)_2][H_2NB(C_6F_5)_3]$ (**8a**; Scheme 4).[29]



Scheme 4.

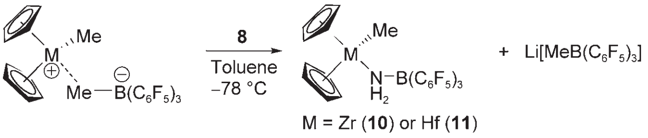
Unfortunately, **8a** proved to be very poorly crystalline and attempts to grow single crystals from a number of solvent mixtures were unsuccessful. Treatment of a solution of **1** in toluene with the non-nucleophilic base $Li[N(SiMe_3)_2]$ led to isolation of the base-free analogue $Li[H_2NB(C_6F_5)_3]$ (**8**) as a colourless solid. The only noteworthy spectroscopic difference between these two compounds, besides the absence of THF resonances, was the slightly higher field shift of the NH_2 signal in base-free **8** ($\delta = 0.51$ ppm). Attempts to crystallise **8** were again unsuccessful and invariably led to recovery of oily material. Crystals suitable for X-ray crystallography were eventually obtained only after the addition of one equivalent of [12]crown-4 giving **8b** (Scheme 4). Incorporation of the crown ether was confirmed by elemental analysis and the ^{1}H NMR spectrum, which contained corresponding peaks at $\delta = 2.71$ and 2.27 ppm, whilst the NH_2 singlet of **8b** is found at $\delta = 1.03$ ppm.

The utility of $Li[H_2NB(C_6F_5)_3]$ was initially established by treating a solution of **8a** in toluene with a further equivalent of $B(C_6F_5)_3$, generating the known amidodiborate anion (**VI**; Scheme 5), the identity of which was verified by comparison to the literature data.[27] Reaction of **8a** with $Al(C_6F_5)_3$, in place of $B(C_6F_5)_3$, in tetrahydrofuran gives the novel ion pair $[Li(thf)_4][\{(C_6F_5)_3B\}NH_2\{Al(C_6F_5)_3\}]$ (**9**) as a crude colourless glass. Salt **9** can be purified by recrystallisation from a tetrahydrofuran/light petroleum solvent mixture. ^{1}H NMR spectroscopy ([D$_1$]chloroform) revealed a resonance at $\delta = 4.16$ ppm, assigned as NH_2, which is somewhat higher field than $\delta = 5.42$ ppm found for the amidodiborate anion.[27] The relative integrations of the NH_2 and THF peaks were consistent with the formulated stoichiometry, as was the elemental analysis. The ^{11}B spectrum had a single resonance at $\delta = -6.3$ ppm, whilst the ^{19}F NMR spectrum contained two sets of *ortho*-, *para*- and *meta*-signals corresponding to two distinct C_6F_5 environments as expected. We note that one of the two *ortho*-F resonances was found at appreciably higher field ($\delta = -134.3$ ppm) than the other ($\delta = -122.9$ ppm). By comparison to data for the *ortho*-F chemical shift values of the base-free Lewis acids $[M(C_6F_5)_3]$ (M = B, Al) and those observed for $[M(C_6F_5)_3(L)]$ compounds,[23] the higher field resonance was confidently attributed to the $B(C_6F_5)_3$ fragment. Perfluorinated anions formed by the complexation of dibasic anions, such as $[NH_2]^-$, with Lewis acids, such as $B(C_6F_5)_3$, have found applications as weakly coordinating counteranions.[30] The anion in **9** is a novel addition to this class and the sequential synthesis suggests the facile synthesis of further examples of asymmetric amido-centred weakly coordinating anions.



Scheme 5.

Following these initial successes with the strongly electrophilic $B(C_6F_5)_3$ and $Al(C_6F_5)_3$, we attempted the preparation of metallocene amidoborate complexes. Treatment of the metallocene dichlorides $[MCl_2Cp_2]$ (M = Ti, Zr) with one equivalent of **8** did not lead to $[MClCp_2\{NH_2B(C_6F_5)_3\}]$, but resulted only in recovery of unreacted starting materials even after extended reaction times. Evidently, $[MCl_2Cp_2]$ is insufficiently electrophilic to undergo reaction with **8**. The zwitterionic reagents [$MCp_2(Me)\{MeB(C_6F_5)_3\}$] (M = Zr and Hf) are known as precursors to highly electrophilic polymerisation catalysts.[16,31] The reactions between these zwitterions and one equivalent of compound **8** in toluene afforded the pale yellow amidoborate complexes [M = Zr (**10**) and Hf (**11**)] accompanied by Li[$MeB(C_6F_5)_3$] precipitation (Scheme 6). As expected, the ^{1}H NMR spectra of **10** and **11** are very similar, consisting of three resonances with relative integrations of 10:3:2 corresponding to the cyclopentadienyl, methyl and amidoborate substituents, respectively. The ^{11}B and ^{19}F data closely resemble those of compounds **2**–**7** (Table 1). Compounds **10** and **11** were therefore formulated as [$MCp_2(Me)\{NH_2B(C_6F_5)_3\}$], which proved consistent with the elemental analysis results and was subsequently confirmed by the structural determination of **11** (see below).



Scheme 6.

Crystallography: Crystals of **2** and **3** suitable for X-ray diffraction were grown from solutions of he compounds in light petroleum and toluene, respectively. In both **2** (Figure 1) and **3** (Figure 2) the titanium is in a distorted tetrahedral environment, coordinated by three amido and one amidoborate ligand. The principal bond lengths and angles (Table 2) show remarkably little difference between the methyl (**2**) and ethyl (**3**) amido complexes, suggesting a system essentially free of steric congestion. Two resonance forms can be drawn for the bonding of an amidoborate ligand: a donor interaction between a formal amidoborate anion and a positively charged metal centre (Scheme 7a), and interaction of the Lewis acid $B(C_6F_5)_3$ with a Lewis basic $L_nM(NH_2)$ moiety (Scheme 7b). The Ti–N1 bond lengths in **2** (2.152(2) Å) and **3** (2.170(2) Å) are significantly shorter than those found in Kol's five-coordinate chelating diaminoborate tris(amido)complex (**VII**, Ti–N(B) = 2.282(4) and 2.302(3) Å),[32] and [$Ti(Cp)\{C_5H_4B(C_6F_5)_2\}\{t\text{BuHN}\}Cl$]

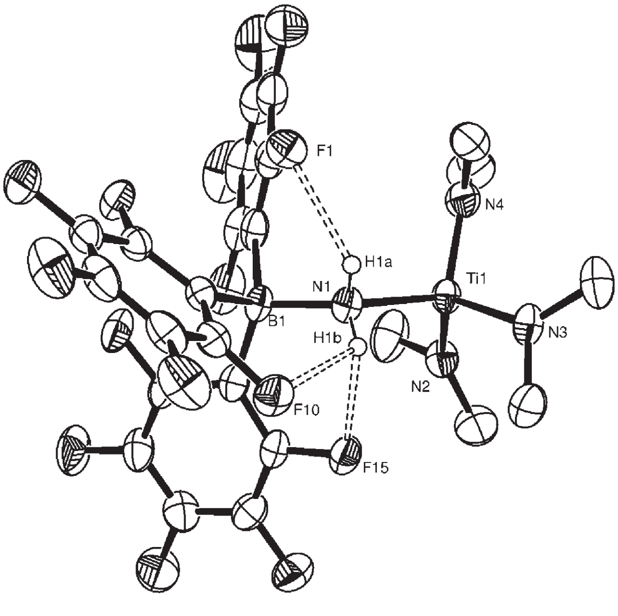


Figure 1. ORTEP representation of the structure of **2** showing 50 % probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

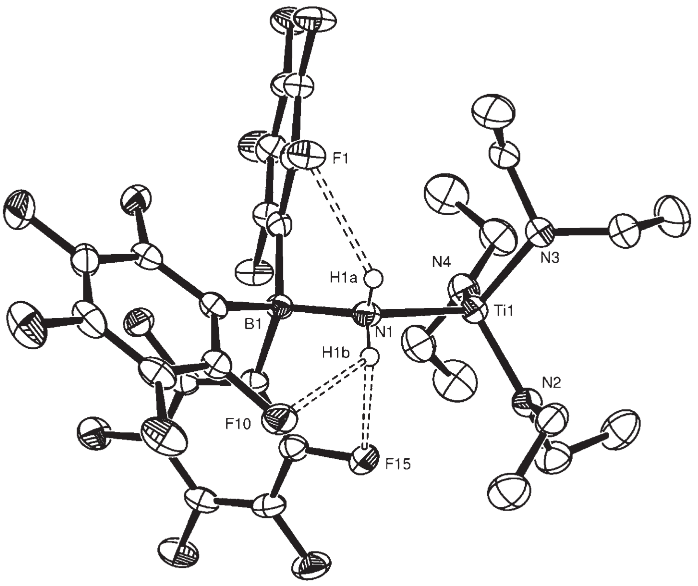
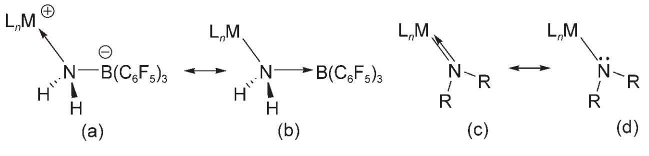


Figure 2. ORTEP representation of the structure of **3** showing 50 % probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

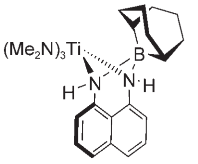
Table 2. Selected bond lengths and angles with estimated standard deviations.

	B–N [Å]	M–NH$_2$ [Å]	M–NR$_2$[a] [Å]	M-N(H)$_2$-B [°]
1	1.623(2)	–	–	–
2	1.606(4)	2.152(2)	1.866	129.43(17)
3	1.595(3)	2.170(2)	1.866	130.30(16)
4	1.587(5)	2.356(3)	2.035	126.3(2)
5	1.598(2)	2.1629(14)	1.891	133.76(10)
7	1.596(2)	2.3053(13)	2.024	130.24(9)
8b	1.551[a]	2.048[a]	–	121.35[a]
9	1.618(3)	1.945(2)	–	128.25(15)
VI	1.628(3)	1.636(2)	–	134.3(2)
11	1.601(4)	2.270(2)	–	135.14(17)

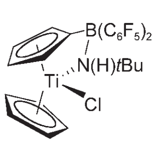
[a] average values



Scheme 7.



VII



VIII

(**VIII**) (Ti–N = 2.294(2) Å), suggesting a significant contribution of resonance form shown in Scheme 7b.[33] The similarity between the B–N bond lengths in **1** (1.623(2) Å), **2** (1.606(4) Å) and **3** (1.595(3) Å) also suggests an essentially dative interaction consistent with resonance form shown in Scheme 7b. The presence of the π-bonding contribution in conventional amide ligands (Scheme 7c) explains why the average Ti–N bond lengths to the dialkylamide ligands are much shorter, at 1.866 Å. These in turn are similar to those found in other structurally characterised dialkylamido complexes including **VII**.[32–35]

Despite the poor solubility of **4**, very small crystals were obtained at the interface between solutions of $[Zr(NMe_2)_4]$ and **1** in toluene and the solid state structure was determined by diffraction methods using synchrotron radiation.[22] Compound **4** adopts a distorted trigonal-bipyramidal geometry in which the amidoborate and amino ligands are coordinated *trans* to one another (N1-Zr1-N5 = 173.45(13)°; Figure 3). Of the five Zr–N bond lengths, those to the $HNMe_2$ (2.424(4) Å) and the three equatorial NMe_2 ligands (average 2.03 Å) are typical of trigonal-bipyramidal zirconium complexes containing these groups.[34] We are not aware of a structural precedent for a Zr-NH_2-BX_3 unit.

Compound **5** was crystallised from a concentrated solution of **5** in toluene at −25° C. The geometry about titanium is distorted tetrahedral (Figure 4) and the B–N and Ti–N bond lengths are very similar to those found for **2** and **3**. The average Ti–$C_{(Cp)}$ distance at 2.370 Å is within the expected range for titanium complexes with a combination of cyclopentadienyl and amido ligands.

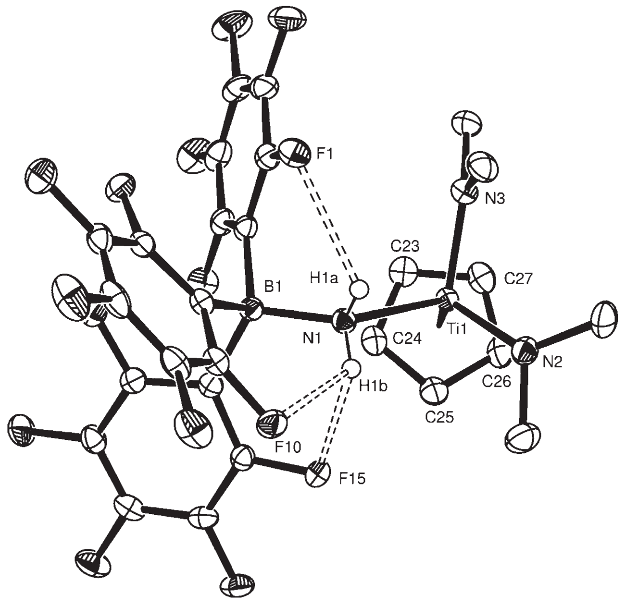


Figure 4. ORTEP representation of the structure of **5** showing 50% probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

Crystals of **7** suitable for X-ray crystallography were isolated from a concentrated solution of **7** in toluene as the toluene solvate. The solid-state structure of **7** (Figure 5) confirms a four-coordinate zirconium complex, resembling the

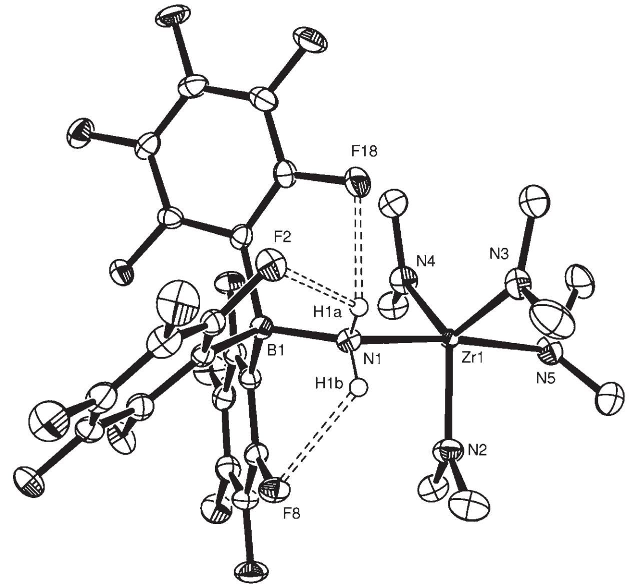


Figure 3. ORTEP representation of the structure of **4** showing 50% probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

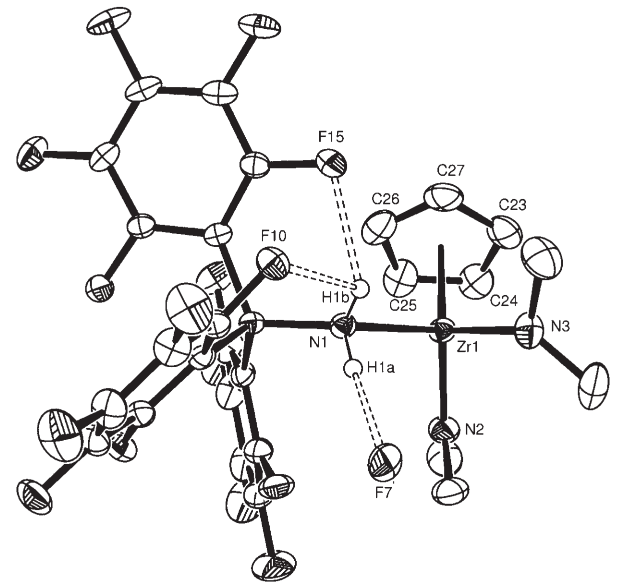


Figure 5. ORTEP representation of the structure of **7** showing 50% probability ellipsoids; a toluene molecule and hydrogen atoms other than those bound to N1 have been omitted for clarity.

titanium analogue **5**. The Zr–NH_2 distance (2.3053(13) Å) is shorter than was observed in five-coordinate **4** (2.356(3) Å). As a result, the B-N-Zr bond angle in **7** (130.24(9)°) is slightly greater than that in **4** (126.3(2)°) due to an increased steric interaction between the borate group and Zr-bound ligands. The Zr–NMe_2 bond lengths in **4** and **7** are comparable and the Zr–C_{Cp} average distance in the latter is typical for half-sandwich amide complexes at 2.514 Å.[36,37] The B–N distances in **4** and **7** are similar to those in **2** and **3**, suggesting that the bonding is again best described as a dative interaction between the $\{Zr(L)_n(NH_2)\}$ moiety and $B(C_6F_5)_3$.

Crystals of $[Li([12]crown\text{-}4)][H_2NB(C_6F_5)_3]$ (**8b**) suitable for crystal structure determination were grown by cooling a solution of the compound in a mixture of light petroleum and dichloromethane (Figure 6). Salt **8b** crystallises with two very similar ion pairs in the asymmetric unit, with the crown ether on one of the cations disordered over two positions. The average B–N bond length in the two molecules of **8b** (1.551 Å) is distinctly shorter than that in **1** (1.623(2) Å) in accordance with a stronger B–N interaction, implying a greater contribution of resonance form shown in Scheme 7a than that seen for **2**–**7**. The geometry at lithium is that of a distorted tetragonal pyramid, and closely resembles that of $([12]crown\text{-}4)Li(Me)_2NBH_3$ (**IX**; structure not shown),[38] with four Li···O contacts varying in length between 1.960(12) and 2.361(12) Å. The average Li···N distance (2.048 Å) is slightly longer than in **IX** (2.002 Å).

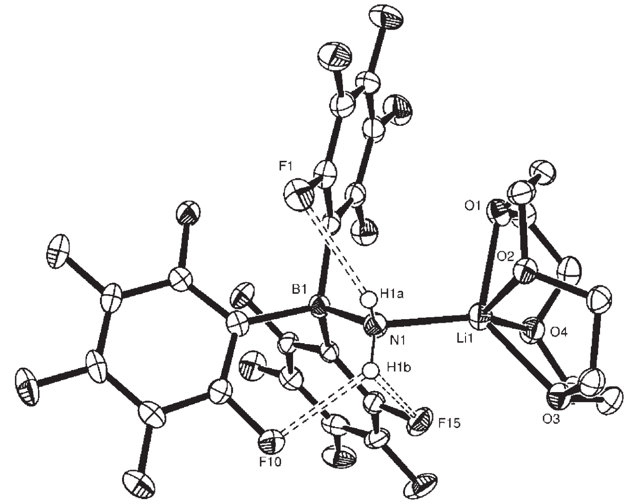


Figure 6. ORTEP representation of the structure of one of two crystallographically independent ion pairs in **8b** showing 50% probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

Crystals of **9** suitable for X-ray diffraction were obtained by cooling a solution of **9** in dichloromethane layered with light petroleum. In agreement with the relative integrations of the proton spectrum, the countercation in **9** contains four THF molecules, one of which is disordered over two positions. Figure 7 depicts the solid-state structure of the anion. The geometry at nitrogen, with an Al-N-B angle of 128.25(15)°, is somewhat less distorted from tetrahedral because of the longer Al–N versus B–N bond than that in the amidodiborate anion **VI** (in which B-N-B is 134.3(2)°).[27] The B–N distance (1.618(3) Å) is slightly greater than those observed in the amidoborate complexes **2**–**5** and **7**, but very close to those in **1** and **VI**. At 1.945(2) Å, the Al–N bond length is slightly shorter than in the alane adducts $(Me_3C)(H)_2N{\cdot}Al(C_6F_5)_3$ and $Me_2(H)N{\cdot}Al(C_6F_5)_3$ (1.9965(18) and 1.983(3) Å, respectively), which is in keeping with bonding to a smaller, more basic group.[23]

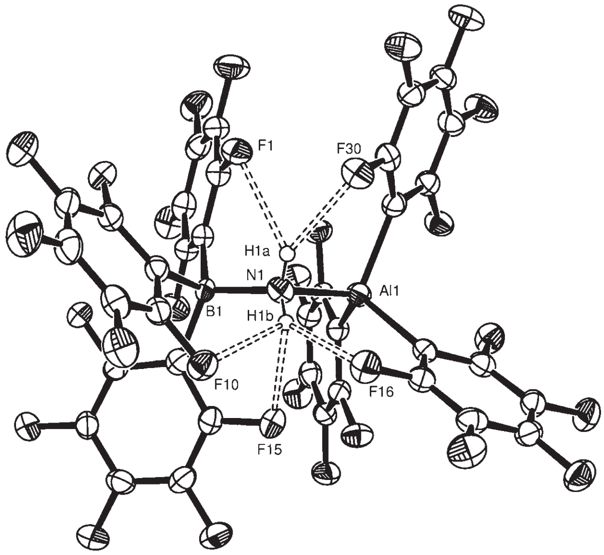


Figure 7. ORTEP representation of the structure of the anionic component of **9** showing 50% probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

X-ray quality crystals of **11** were obtained by cooling a toluene solution layered with light petroleum. The approximately tetrahedral molecular geometry of **11** (Figure 8) was elucidated by a diffraction study. The B–N distance at 1.601(4) Å is comparable to the corresponding bond lengths observed in the solid-state structures of the amidoborate complexes **2**–**5** and **7**, suggesting similar bonding to that present in these complexes. As one would expect for hafnium, the Hf–NH_2 bond length (2.270(2) Å) is very slightly shorter than the Zr–NH_2 distance in **7**. The Hf–C_{Me} distance shows no significant variation from those found in the parent dimethyl $[Cp_2HfMe_2]$ (**X**).[39] It appears that the considerable steric clash between the pentafluorophenyl and cyclopentadienyl rings accounts for the more acute N-Hf-C angle of 92.11(10)° versus C-Hf-C 95.8(5)° in **X**[40] and the B-N-Hf angle (135.14(17)°), which is the most obtuse of any of the amidoborate complexes.

Hydrogen bonding: We and others have previously shown that despite the poor hydrogen-bond acceptor character of organofluorine[41] intramolecular hydrogen-bonding is prevalent in neutral and anionic adducts of $B(C_6F_5)_3$.[21–23,27,41] Although solution-phase hydrogen bonding was evident from

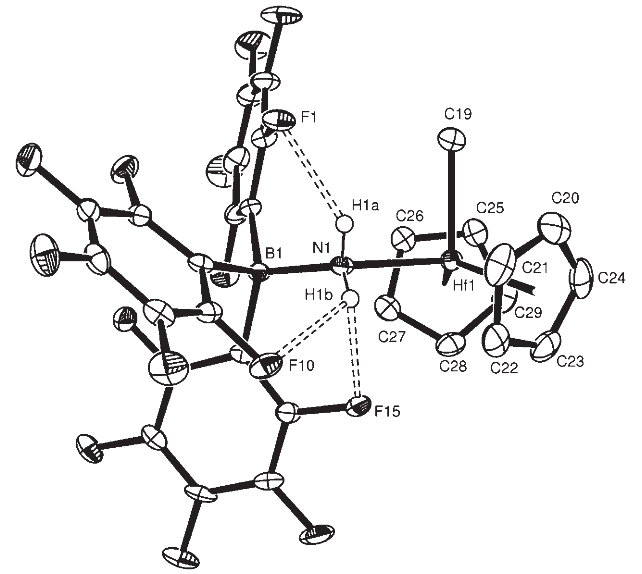


Figure 8. ORTEP representation of the structure of **11** showing 50% probability ellipsoids; hydrogen atoms other than those bound to N1 have been omitted for clarity.

spectroscopic characterisation of secondary amine adducts such as $(H)Me_2N{\cdot}B(C_6F_5)_3$,[23] NMR spectroscopy provided no conclusive indication for the presence of intramolecular N−H···F interactions in the amidoborate complexes **2**–**11**. However, determination of the solid-state structures of **2**–**5**, **7**, **8b**, **9** and **11** all revealed one or more short hydrogen–fluorine contacts.

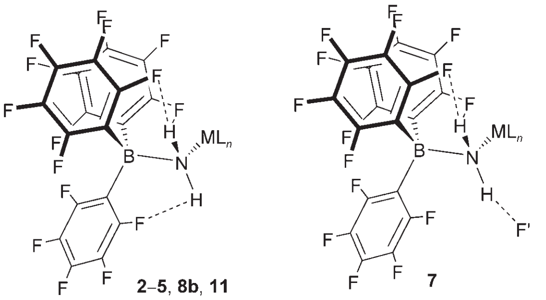
The pattern of intramolecular hydrogen bonding (Table 3) is remarkably similar in amidoborate complexes **2**–**5**, **8b** and **11**, whereby one hydrogen atom is engaged in a three-centred F···H···F (bifurcated) arrangement, whilst the other associates with a single fluorine atom in a discernibly longer interaction (Scheme 8). In this respect, these complexes closely resemble the structurally characterised examples of primary amine adducts of $B(C_6F_5)_3$.[21] It may be that the bifurcated hydrogen-bonding interaction makes a small but significant contribution to the stability of these complexes. The intramolecular hydrogen-bonding arrangement in **7** differs slightly from that observed in the other amidoborate complexes, in that the second hydrogen atom does not participate in a longer intramolecular interaction to an *ortho*-F, but instead engages in a near-linear intermolecular interaction with a *meta*-fluorine atom on a neighbouring molecule, affording a supramolecular architecture composed of infinite one-dimensional chains as shown in Figure 9.

The composition of the anion **9** is exceptional in this study in that here the NH_2 moiety is bound to not one but two $M(C_6F_5)_3$ groups. As one would expect, the intramolecular hydrogen-bonding arrangement in **9** is similar to that in the amidodiborate ion $[H_2N\{B(C_6F_5)_3\}_2]^-$ (**VI**), in which one of the amino hydrogen atoms engages in a trifurcated (H···F_3) and the other a bifurcated interaction to *ortho*-fluorine atoms (Table 3 and Scheme 8).

Table 3. Selected parameters for hydrogen···fluorine contacts.

	N−H [Å]	H···F [Å]	N···F [Å]	N−H···F [°]
2				
N1−H1a···F1	0.855(18)	2.29(3)	2.911(3)	130(3)
N1−H1b···F10	0.884(18)	2.24(3)	2.811(3)	122(3)
N1−H1b···F15	0.884(18)	2.25(3)	2.739(3)	115(3)
3				
N1−H1a···F1	0.85(3)	2.35(3)	2.929(3)	126(3)
N1−H1b···F10	0.85(3)	2.19(3)	2.822(3)	131(3)
N1−H1b···F15	0.85(3)	2.37(3)	2.742(3)	107(2)
4				
N1−H1a···F2	0.96(6)	2.22(6)	2.916(4)	128(4)
N1−H1b···F8	0.89(7)	2.47(7)	2.975(4)	117(5)
N1−H1a···F18	0.96(6)	2.21(5)	2.747(5)	114(4)
5				
N1−H1a···F1	0.85(2)	2.49(2)	2.9807(18)	117.6(17)
N1−H1b···F10	0.88(2)	2.21(2)	2.7931(18)	124.2(18)
N1−H1b···F15	0.88(2)	2.26(2)	2.7895(18)	118.4(17)
7				
N1−H1a···F7′[a]	0.873(16)	2.210(16)	3.0676(16)	167(2)
N1−H1b···F10	0.908(16)	2.35(2)	2.8601(16)	115.8(18)
N1−H1b···F15	0.908(16)	2.22(2)	2.7793(16)	119.2(18)
8b				
N1−H1 A···F1	0.899(15)	2.328(19)	2.9541(18)	126.7(16)
N1−H1B···F10	0.887(15)	2.339(19)	2.9627(18)	127.4(17)
N1−H1B···F15	0.887(15)	2.34(2)	2.6582(19)	101.4(15)
N101−H2 A···F101	0.884(15)	2.349(18)	2.9548(18)	125.8(16)
N101−H2B···F110	0.869(15)	2.298(18)	2.9058(17)	127.0(16)
N101−H2B···F115	0.869(15)	2.40(2)	2.6765(18)	98.8(14)
9				
N1−H1a···F1	0.887(17)	2.44(3)	2.966(3)	119(2)
N1−H1b···F10	0.860(17)	2.31(2)	2.889(3)	125(2)
N1−H1b···F15	0.860(17)	2.23(3)	2.721(3)	116(2)
N1−H1b···F16	0.860(17)	2.21(2)	2.917(3)	140(2)
N1−H1a···F30	0.887(17)	2.17(2)	2.953(3)	146(2)
11				
N1−H1a···F1	0.868(18)	2.24(3)	2.865(3)	129(3)
N1−H1b···F10	0.871(18)	2.24(3)	2.870(3)	129(3)
N1−H1b···F15	0.871(18)	2.34(3)	2.663(3)	102(2)

[a] This is an intermolecular interaction.



Scheme 8. Schematic representation of the hydrogen-bonding patterns found in the structurally characterised amidoborate complexes.

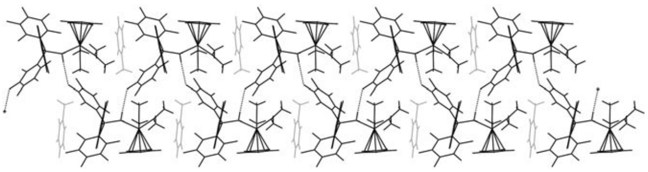


Figure 9. The intermolecular hydrogen-bonding interactions and incorporation of toluene in **7**.

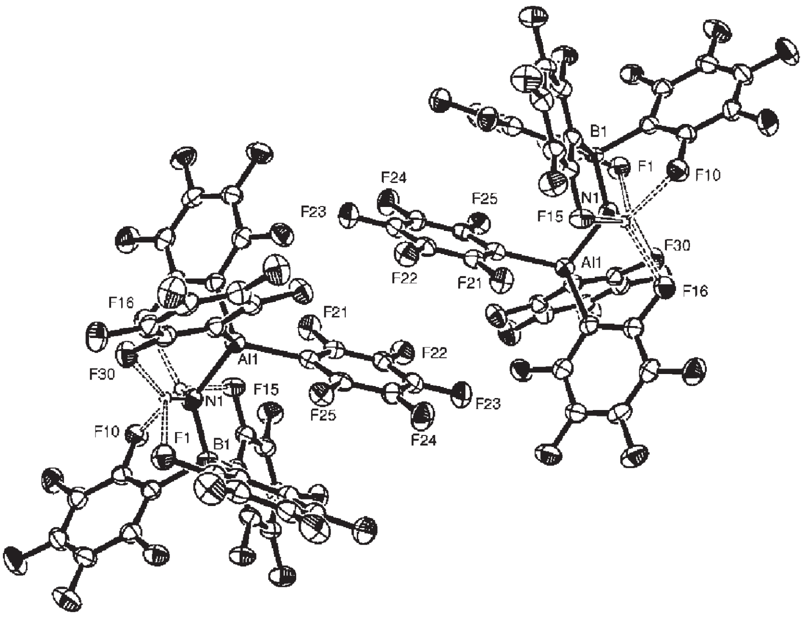


Figure 10. The intramolecular hydrogen-bonding and the offset face-to-face $C_6F_5\cdots C_6F_5$ interactions for anions of **9**.

The one C_6F_5 group in **9** that does not participate in intramolecular hydrogen bonding engages in an offset face-to-face interaction with a symmetry-related C_6F_5 substituent on a neighbouring anion. In this way, the anions are paired throughout the crystal structure as shown in Figure 10.

Conclusion

$H_3N\cdot B(C_6F_5)_3$ reacts as a Brønsted acid with strongly basic reagents such as the titanium or zirconium metal amides $[M(L)(NR_2)_3]$ ($L = Cp$, NR_2; $R = Me$, Et) yielding amidoborate complexes, or *n*BuLi giving lithium amidoborates. It does not react with less basic metallocene complexes such as $[MCp_2Me_2]$ and $[MCp_2(NR_2)_2]$; however, metallocene amidoborate complexes can be prepared through the alternative salt metathesis route between $LiNH_2B(C_6F_5)_3$ and $[MCp_2Me(\mu\text{-}Me)B(C_6F_5)_3]$.

Structural analysis revealed distorted tetrahedral geometries in all but $[Zr(NMe_2)_3\{NH_2B(C_6F_5)_3\}(HNMe_2)]$, which retains Me_2NH and has a five-coordinate distorted trigonal-bipyramidal geometry. Analysis of the M–N and N–B distances in these complexes suggests that the bonding is best described as the dative interaction between an $\{M(L)_n(NH_2)\}$ fragment and the Lewis acid $B(C_6F_5)_3$. Each of the structures has an intramolecular hydrogen-bonding arrangement in which one of the nitrogen-bonded hydrogen atoms participates in a bifurcated $F\cdots H\cdots F$ interaction to *ortho*-F atoms. In all but $[ZrCp(NMe_2)_2\{NH_2B(C_6F_5)_3\}]$, in which the second hydrogen bond is intermolecular, the second NH group is engaged in a longer intramolecular interaction to a single *ortho*-F atom.

Experimental Section

All manipulations were performed under dry and oxygen-free nitrogen using Schlenk-line or glove-box techniques. Solvents were dried over Na (toluene), Na/K alloy (light petroleum), Na/benzophenone (THF) and CaH_2 (dichloromethane) and distilled under nitrogen prior to use. ^1H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer. Chemical shifts (δ) are reported relative to TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F) and $Et_2O\cdot BF_3$ (^{11}B). Elemental analyses were carried out by the in-house service, School of Chemical Sciences and Pharmacy, UEA. The titanium amide complexes $[Ti(NR_2)_4]$ ($R = Me$, Et) were provided by Epichem Ltd. $[Zr(NMe_2)_4]$ was prepared according to the literature procedure.[3] The cyclopentadienyl compounds $[MCp(NR_2)_3]$ ($M = Ti$, Zr; $R = Me$, Et) were produced by treating the corresponding tetra(amide) complexes with one equivalent of cyclopentadiene.[2] The remaining reagents were acquired from Aldrich, Fischer, Fluorochem or Lancaster and used as supplied. The syntheses of compounds **1**,[23] **2** and **4**[22] and $Al(C_6F_5)_3\cdot$toluene[43] have been reported elsewhere.

$[Ti(NEt_2)_3\{NH_2B(C_6F_5)_3\}]$ (3): $[Ti(NEt_2)_4]$ (0.24 mL, 0.7 mmol) was added to a suspension of **1** (0.35 g, 0.7 mmol) in light petroleum (15 mL) at −20 °C. The mixture was warmed to 0 °C and the reactants dissolved, affording a homogeneous orange solution. Block-shaped crystals suitable for X-ray crystallography were obtained by concentrating the solution and cooling to −25 °C overnight (0.23 g, 41 %). ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 3.20$ (q, $^3J(H,H) = 4.1$ Hz, 12H; CH_2), 2.46 (s, 2H; NH_2), 0.70 ppm (t, $^3J(H,H) = 4.1$ Hz, 18H; CH_3); $^{13}C\{^1H\}$ NMR (75.4 MHz, [D$_6$]benzene, 20 °C): $\delta = 44.4$ (CH_2), 14.7 ppm (CH_3); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C) $\delta = -5.4$ ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): $\delta = -133.6$ (d, $^3J(F,F) = 25$ Hz, 6F; *o*-F), −158.3 (t, $^3J(F,F) = 20$ Hz, 3F; *p*-F), −163.9 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for $C_{30}H_{32}BF_{15}N_4Ti$: C 45.48, H 4.07, N 7.07; found: C 45.72 H 3.94, N 7.03.

$[TiCp(NMe_2)_2\{NH_2B(C_6F_5)_3\}]$ (5)

Method 1: A solution of **1** (0.79 g, 1.5 mmol) in toluene (10 mL) was treated with $[TiCp(NMe_2)_3]$ (1.4 mL of a 1.06 M solution in light petroleum, 1.5 mmol) at room temperature. The reaction mixture was stirred for 30 mins before the volatiles were removed under reduced pressure. The product, a yellow powder, was obtained in high purity according to multinuclear NMR spectroscopy and elemental analysis (0.74 g, 68 %). Crystals suitable for X-ray diffraction were obtained by recrystallisation from a concentrated solution of the complex in toluene at −25 °C. ^1H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 5.50$ (s, 5H; C_5H_5), 2.62 (s, 2H; NH_2), 2.49 ppm (s, 12H; CH_3); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C): $\delta = -4.8$ ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): $\delta = -133.7$ (d, $^3J(F,F) = 23$ Hz, 6F; *o*-F), −157.9 (t, $^3J(F,F) = 20$ Hz, 3F; *p*-F), −163.8 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for $C_{27}H_{19}BF_{15}N_3Ti$: C 44.48, H 2.63, N 5.76; found: C 44.22, H 2.67, N 5.48.

Method 2: Compound **2** (0.47 g, 0.7 mmol) was treated with one equivalent of cyclopentadiene (0.05 g, 0.8 mmol) in toluene (10 mL) at −78 °C. The solution was stirred whilst warming to room temperature before the solvent and dimethylamine were removed under vacuum giving a yellow powder (1.2 g, 73 %). The spectroscopic data confirmed that this product was identical to that afforded by Method 1.

[TiCp(NEt$_2$)$_2${NH$_2$B(C$_6$F$_5$)$_3$}] (6): In an analogous fashion to **5**, compound **6** was prepared following two different procedures.

Method 1: A solution of compound **1** (1.45 g, 2.7 mmol) in toluene (10 mL) was treated with [TiCp(NEt$_2$)$_3$] (0.90 g, 2.7 mmol) at room temperature. This solution was layered with an equal volume of light petroleum, which slowly diffused to give a fine orange precipitate that could be isolated by filtration. The product was crystallised from a light petroleum/dichloromethane mixture cooled to −25 °C overnight to give yellow plates suitable for X-ray crystallography (1.17 g, 55 %). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 5.96$ (s, 5H; C$_5$*H*$_5$), 3.77 (m, 4H; C*H*$_2$), 3.60 (m, 4H; C*H*$_2$), 2.63 (s, 2H; N*H*$_2$), 1.02 ppm (t, ^3J(H,H) = 4.1 Hz, 12H; C*H*$_3$); ^{13}C{^{1}H} NMR (75. 4 MHz, [D$_6$]benzene, 20 °C): $\delta = 114.3$ (*C*$_5$H$_5$), 47.5 (*C*H$_2$), 13.6 ppm (*C*H$_3$); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C): $\delta = -4.9$ ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): $\delta = -133.5$ (d, ^3J(F,F) = 23 Hz, 6F; *o*-F), −159.6 (t, ^3J(F,F) = 20 Hz, 3F; *p*-F), −165.0 ppm(m, 6F; *m*-F); elemental analysis calcd (%) for $C_{31}H_{27}BF_{15}N_3Ti$: C 47.42, H 3.47, N 5.35; found: C 46.95, H 3.50, N 5.52.

Method 2: One equivalent of cyclopentadiene (0.05 g, 0.8 mmol) was added to a solution of compound **3** (0.5 g, 0.6 mmol) in toluene (10 mL), affording a homogeneous solution that produced yellow plates when concentrated and cooled to −25 °C for several hours (0.28 g, 0.4 mmol, 60 %). Multinuclear NMR and elemental analysis confirmed that these crystals were identical in composition to those obtained by Method 1.

[ZrCp(NMe$_2$)$_2${NH$_2$B(C$_6$F$_5$)$_3$}] (7): A solution of [ZrCp(NMe$_2$)$_3$] (5 mL of a 0.77 M solution in toluene, 3.9 mmol) in toluene was treated with **1** (2.04 g, 3.9 mmol) at room temperature. After stirring for 1 h the volatiles were distilled off. The resultant yellow solid was recrystallised from a toluene/light petroleum mixture, which was cooled in the freezer overnight affording X-ray quality crystals of the product (2.17 g, 72 %). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 5.62$ (s, 5H; C$_5$*H*$_5$), 2.41 (s, 2H; N*H*$_2$), 2.33 ppm (s, 12H; C*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]benzene, 20 °C): $\delta = 113.0$ (*C*$_5$H$_5$), 42.8 ppm (*C*H$_3$); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C): $\delta = -5.5$ ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): $\delta = -134.8$ (d, ^3J(F,F) = 20 Hz, 6F; *o*-F), −157.5 (t, ^3J(F,F) = 20 Hz, 3F; *p*-F), −164.1 ppm (t, ^3J(F,F) = 20 Hz, 6F; *m*-F); elemental analysis calcd (%) for $C_{27}H_{19}BF_{15}N_3Zr\cdot(C_7H_8)$: C 47.23, H 3.15, N 4.86; found: C 46.68, H 3.19, N 4.70.

[Li(thf)$_2$][NH$_2$B(C$_6$F$_5$)$_3$] (8a): A solution of **1** (1.79 g, 3.4 mmol) in tetrahydrofuran (20 mL) was treated with *n*BuLi (2.02 mL of a 1.7 M solution in *n*-hexane, 3.4 mmol) at −78 °C. The reaction mixture was allowed to

Table 4. Summary of X-ray collection data.

	2	3	5
formula	$C_{24}H_{20}BF_{15}N_4Ti$	$C_{30}H_{32}BF_{15}N_4Ti$	$C_{27}H_{19}BF_{15}N_3Ti$
M_r	708.15	792.31	729.16
crystal description	yellow block	yellow block	orange prism
crystal dimensions [mm]	0.23 × 0.10 × 0.05	0.22 × 0.16 × 0.12	0.30 × 0.30 × 0.20
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	*Pbca*
a [Å]	13.5564(2)	18.6201(10)	15.5101(18)
b [Å]	13.1607(2)	10.8987(8)	18.853(3)
c [Å]	15.8983(3)	18.048(2)	19.271(4)
α [°]	90	90	90
β [°]	98.2520(10)	113.675(7)	90
γ [°]	90	90	90
V [Å^3]	2807.08(8)	3354.4(5)	5635.1(17)
Z	4	4	8
T [K]	180(2)	120(2)	120(2)
μ [mm^{-1}]	0.428	0.368	0.429
data collected	16209	37949	43759
unique data	6432	7716	6457
R_{int}	0.0575	0.0572	0.0437
R_1 [$I > 2\sigma(I)$]	0.0555	0.0507	0.0353
wR_2 (all data)	0.1559	0.1195	0.0864

	7	8b	9	11
formula	$C_{34}H_{27}BF_{15}N_3Zr$	$C_{26}H_{18}BF_{15}LiNO_4$	$C_{52}H_{34}AlBF_{30}LiNO_4$	$C_{29}H_{15}BF_{15}HfN$
M_r	864.62	711.16	1351.53	851.72
crystal description	colourless slab	colourless slab	colourless slab	colourless block
crystal dimensions [mm]	0.20 × 0.20 × 0.10	0.38 × 0.36 × 0.12	0.34 × 0.24 × 0.10	0.34 × 0.20 × 0.20
crystal system	orthorhombic	triclinic	triclinic	triclinic
space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.3905(7)	9.9010(8)	10.435(2)	10.6160(7)
b [Å]	15.2875(15)	17.1591(15)	16.6081(18)	11.3990(7)
c [Å]	19.7267(14)	17.3007(10)	16.961(2)	12.3130(9)
α [°]	90	105.836(4)	101.095(10)	77.169(6)
β [°]	90	95.186(6)	97.485(13)	85.911(6)
γ [°]	90	94.076(6)	108.234(11)	68.576(5)
V [Å^3]	3435.1(5)	2802.0(4)	2682.0(7)	1352.35(16)
Z	4	2	2	2
T [K]	120(2)	120(2)	120(2)	120(2)
μ [mm^{-1}]	0.433	0.177	0.190	3.984
data collected	87136	55749	52490	25960
unique data	7866	12834	12315	6017
R_{int}	0.0292	0.0402	0.0527	0. 0334
R_1 [$I > 2\sigma(I)$]	0.0230	0.0404	0.0545	0.0233
wR_2 (all data)	0.0613	0.0989	0.1208	0.0573

warm to room temperature and then stirred for a further hour. The volatiles were subsequently removed under reduced pressure affording the product as a colourless oil (1.85 g, 2.7 mmol, 80%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): δ=3.08 (m, 8H; OC$_4$*H*$_8$), 1.18 (m, 8H; OC$_4$*H*$_8$), 0.85 ppm (s, 2H; N*H*$_2$); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C): δ=−6.1 ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): δ=−137.1 (d, ^3J(F,F)=23 Hz, 6F; *o*-F), −160.4 (t, ^3J(F,F)=20 Hz, 3F; *p*-F), −164.8 ppm (m, 6F; *m*-F).

[LiNH$_2$B(C$_6$F$_5$)$_3$] (8): Treatment of **1** (0.85 g, 1.6 mmol) with Li[N(SiMe$_3$)$_2$] (0.27 g, 1.6 mmol) in toluene (10 mL) at −78 °C afforded a homogeneous, colourless solution once the reaction mixture had equilibrated at room temperature. Removal of the solvent and HN(SiMe$_3$)$_2$ under reduced pressure afforded **8** as a colourless solid.

Caution: Although we have encountered no problems handling **8**, a referee has pointed out that the related salt [Li][MeB(C$_6$F$_5$)$_3$] has been found to be explosively unstable in the solid state.[44]

[Li([12]crown-4)][NH$_2$B(C$_6$F$_5$)$_3$] (8b): Crystallisation of **8** from a light petroleum/dichloromethane solution treated with one equivalent of [12]crown-4 resulted in blocks suitable for X-ray crystallography (0.30 g, 26%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): δ=2.71 (br, 8H; [12]crown-4), 2.27 (br, 8H; [12]crown-4), 1.03 ppm (s, 2H; N*H*$_2$); ^{11}B NMR (96.3 MHz, [D$_6$]benzene, 20 °C): δ=−5.8 ppm; ^{19}F NMR (282.4 MHz, [D$_6$]benzene, 20 °C): δ=−135.0 (d, ^3J(F,F)=23 Hz, 6F; *o*-F), −162.0 (t, ^3J(F,F)=20 Hz, 3F; *p*-F), −166.1 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for C$_{26}$H$_{18}$BF$_{15}$LiNO$_4$: C 43.91, H 2.55, N 1.97; found: C 44.08, H 2.58, N 1.99.

[Li(thf)$_4$][{(C$_6$F$_5$)$_3$B}NH$_2${Al(C$_6$F$_5$)$_3$}] (9): A solution of **8a** (1.1 g, 1.6 mmol) in tetrahydrofuran (10 mL) was treated with Al(C$_6$F$_5$)$_3$·toluene (1.0 g, 1.6 mmol) at −78 °C. Warming the reaction mixture to room temperature resulted in the precipitation of a colourless oil. All volatiles were removed under reduced pressure affording a sticky residue, which was re-dissolved in tetrahydrofuran and then layered with light petroleum. Reducing the temperature of this system to −25 °C overnight was sufficient to give good quality colourless crystals suitable for X-ray crystallography (1.0 g, 47%). ^{1}H NMR (300 MHz, [D$_1$]chloroform, 20 °C): δ=4.16 (br, 2H; N*H*$_2$), 3.76 (m, 4H; OC$_4$*H*$_8$), 1.94 ppm (m, 4H; OC$_4$*H*$_8$); ^{11}B NMR (96.3 MHz, [D$_1$]chloroform, 20 °C): δ=−6.3 ppm; ^{19}F NMR (282.4 MHz, [D$_1$]chloroform, 20 °C): δ=−122.9 (d, ^3J(F,F)=20 Hz, 6F; *o*-F), −134.3 (d, ^3J(F,F)=23 Hz, 6F; *o*-F), −156.0 (t, ^3J(F,F)=20 Hz, 3F; *p*-F), −159.9 (t, ^3J(F,F)=20 Hz, 3F; *p*-F), −163.3 (t, ^3J(F,F)=20 Hz, 6F; *m*-F), −165.4 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for C$_{52}$H$_{34}$AlBF$_{30}$NO$_4$: C 46.21, H 2.54, N 1.04; found: C 46.21, H 2.33, N 1.12.

[ZrCp$_2$(Me){NH$_2$B(C$_6$F$_5$)$_3$}] (10): [ZrCp$_2$Me$_2$] (0.69 g, 2.7 mmol) was treated with B(C$_6$F$_5$)$_3$ (1.40 g, 2.7 mmol) in toluene (10 mL) at −78 °C affording a suspension which dissolved approaching room temperature. After stirring for a further 30 mins, the reaction mixture was re-cooled to −78 °C and Li[NH$_2$B(C$_6$F$_5$)$_3$] (1.46 g, 2.7 mmol, prepared in the manner outlined in **8b**) was added. After stirring overnight at room temperature, Li[MeB(C$_6$F$_5$)$_3$] was removed by filtration to give a homogeneous solution. Removal of the solvent under reduced pressure gave the product as a yellow solid (0.99 g, 49%). ^{1}H NMR (300 MHz, 50:50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=5.71 (s, 10H; C$_5$*H*$_5$), 2.31 (s, 2H; N*H*$_2$), 0.12 ppm (s, 3H; C*H*$_3$); ^{11}B NMR (96.3 MHz, 50: 50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=−5.4 ppm; ^{19}F NMR (282.4 MHz, 50: 50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=−135.5 (d, ^3J(F,F)=18 Hz, 6F; *o*-F), −158.3 (t, ^3J(F,F)=20 Hz, 3F; *p*-F), −164.2 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for C$_{29}$H$_{15}$BF$_{15}$NZr: C 45.56, H 1.98, N 1.83; found: C 45.36, H 1.57, N 1.97.

[HfCp$_2$(Me){NH$_2$B(C$_6$F$_5$)$_3$}] (11): Compound **11** was prepared by a similar method to that described for **10**, for which the zwitterionic species [HfCp$_2$(Me){MeB(C$_6$F$_5$)$_3$}] (1.8 mmol) was prepared in situ and subsequently treated with one equivalent of Li[NH$_2$B(C$_6$F$_5$)$_3$] (1.8 mmol, 0.94 g). After stirring for 12 h, the solvent was removed under reduced pressure and the product extracted in toluene (10 mL). Yellow block-shaped crystals suitable for X-ray crystallography were obtained by layering this solution with light petroleum and cooling overnight (0.46 g, 30%). ^{1}H NMR (300 MHz, 50: 50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=5.65 (s, 10H; C$_5$*H*$_5$), 2.34 (s, 2H; N*H*$_2$), −0.08 ppm (s, 3H; C*H*$_3$); ^{11}B NMR (96.3 MHz, 50: 50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=−4.9 ppm; ^{19}F NMR (282.4 MHz, 50: 50 [D$_6$]benzene/1,2-C$_6$H$_4$F$_2$, 20 °C): δ=−134.9 (d, ^3J(F,F)=17 Hz, 6F; *o*-F), −158.1 (t, ^3J(F,F)=23 Hz, 3F; *p*-F), −164.2 ppm (m, 6F; *m*-F); elemental analysis calcd (%) for C$_{29}$H$_{15}$BF$_{15}$HfN: C 40.90, H 1.78, N 1.64; found: C 41.05, H 2.04, N 1.63.

X-ray crystallography: A summary of the crystallographic data for compounds **2**, **3**, **5**, **7**, **8b**, **9** and **10** are given in Table 4. All data sets were collected on an Enraf–Nonius Kappa CCD area detector diffractometer (Mo$_{K\alpha}$ radiation, λ=0.71073 Å) and an Oxford Cryosystems low-temperature device, operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. Crystals were suspended in perfluoronated polyether oil, mounted on a glass fibre and transferred directly to the cold N$_2$ stream of the diffractometer. Data collection and reduction were carried out using the software packages COLLECT, SCALEPACK, and DENZO.[45] Structure solutions were carried out by direct methods using SHELXS[46] (**3**, **5**, **7**, **11**) or SIR-92[47] (**2**). In all cases refinement was carried out by full-matrix least-squares methods against F^2 using SHELXL-97[46] within the WINGX program suite.[48] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to N1 were in all cases located experimentally in the Fourier difference map. All other hydrogen atoms were included using a riding model.

CCDC-629870 (**2**), CCDC-629871 (**3**), CCDC-629872 (**5**), CCDC-629873 (**7**), CCDC-629874 (**8b**), CCDC-629875 (**9**) and CCDC-629876 (**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structural data for compound **4** have previously been reported,[22] and has deposit number CCDC-258171.

Acknowledgements

We gratefully acknowledge the contribution of the Engineering and Physical Sciences Research Council (EPSRC) in providing funding for the National Crystallographic Service and a project studentship for A.J.M., the Council for the Central Laboratories of the Research Councils (CCLRC) for access to the Synchrotron Radiation Source at Daresbury and Epichem Ltd. for provision of titanium amide reagents.

---

[1] D. C. Bradley, I. M. Thomas, *Proc. Chem. Soc.* **1959**, 225–226; D. C. Bradley, I. M. Thomas, *J. Chem. Soc.* **1960**, 3857–3861.

[2] I. M. Thomas, *Can. J. Chem.* **1961**, *39*, 1386–1388; G. Chandra, M. F. Lappert, *J. Chem. Soc. A* **1968**, 1940–1945; M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides: Syntheses, Structures and Physical and Chemical Properties*, Ellis Horwood, Chichester (UK), **1980**.

[3] For more recent examples of the application of homoleptic amides see: G. M. Diamond, R. F. Jordan, J. L. Petersen, *Organometallics* **1996**, *15*, 4030–4037; J. N. Christopher, G. M. Diamond, R. F. Jordan, J. L. Petersen, *Organometallics* **1996**, *15*, 4038–4044; G. M. Diamond, R. F. Jordan, J. L. Petersen, *Organometallics* **1996**, *15*, 4045–4053.

[4] See for example: C. T. Vroegop, J. H. Teuben, F. van Bolhuis, J. G. M. van der Linden, *J. Chem. Soc. Chem. Commun.* **1983**, 550–552; S. J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, *Organometallics* **2000**, *19*, 1599–1608.

[5] E. Brady, J. R. Telford, G. Mitchell, W. Lukens, *Acta Crystallogr. Sect. C* **1995**, *51*, 558–560.

[6] C. D. Sofield, M .D. Walter, R. A. Andersen, *Acta Crystallogr. Sect. C* **2004**, *60*, m465–m466.

[7] For other examples of first-row transition-metal amido (M-NH$_2$) complexes see: [Cr] C. Redshaw, G. Wilkinson, B. Hussain-Bates, *J. Chem. Soc. Dalton Trans.* **1992**, 1803–1811; [Fe] D. J. Fox, R. G. Bergman, *J. Am. Chem. Soc.* **2003**, *125*, 8984–8985.

[8] L. E. Toth in *Transition Metal Carbides and Nitrides*, Academic Press, New York, **1971**; D. M. Hoffman, *Polyhedron* **1994**, *13*, 1169–1179, and references therein.

[9] a) L. H. Dubois, *Polyhedron* **1994**, *13*, 1329–1336; b) B. H. Weiller, *J. Am. Chem. Soc.* **1996**, *118*, 4975–4983.

[10] For pentamethylcyclopentadienyl titanium complexes see: (**II**) H. W. Roesky, Y. Bai, M. Noltemeyer, *Angew. Chem.* **1989**, *101*, 788–789; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 754–755; (**III**) P. Gómez-Sal, A. Martin, M. Mena, C. Yélamos, *J. Chem. Soc. Chem. Commun.* **1995**, 2185–2186; A. Abarca, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet, C. Yélamos, *Inorg. Chem.* **2000**, *39*, 642–651; M. García-Castro, A. Martín, M. Mena, J.-M. Poblet, C. Yélamos, *Eur. J. Inorg. Chem.* **2006**, 1155–1160.

[11] Polynuclear titanium complexes stabilised by ligands other than pentamethylcyclopentadienyl have been reported: Z. Duan, J. G. Verkade, *Inorg. Chem.* **1996**, *35*, 5325–5327; (**IV**) C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams, *New J. Chem.* **2000**, *24*, 929–930.

[12] Although titanium examples predominate, related structures have been isolated from the ammonolysis of basic zirconium complexes: (**V**) M. M. Banaszak Holl, P. T. Wolczanski, *J. Am. Chem. Soc.* **1992**, *114*, 3854–3858; G. Bai, P. Müller, H. W. Roesky, I. Usón, *Organometallics* **2000**, *19*, 4675–4677; G. Bai, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Organometallics* **2001**, *20*, 2962–2965; G. Bai, D. Vidovic, H. W. Roesky, J. Magull, *Polyhedron* **2004**, *23*, 1125–1129.

[13] For heterometallic derivatives see: A. Abarca, M. V. Galakhov, J. Gracia, A. Martín, M. Mena, J.-M. Poblet, J. P. Sarasa, C. Yélamos, *Chem. Eur. J.* **2003**, *9*, 2337–2346; M. García-Castro, A. Martín, M. Mena, C. Yélamos, *Organometallics* **2004**, *23*, 1496–1500; A. Martín, M. Mena, A. Perez-Redondo, C. Yélamos, *Inorg. Chem.* **2004**, *43*, 2491–2498; M. García-Castro, J. Gracia, A. Martín, M. Mena, J.-M. Poblet, J. P. Sarasa, C. Yélamos, *Chem. Eur. J.* **2005**, *11*, 1030–1041; A. Martín, M. Mena, A. Pérez-Redondo, C. Yélamos, *Dalton Trans.* **2005**, 2116–2119; A. Martín, N. Martínez-Espada, M. Mena, C. Yélamos, *Inorg. Chem.* **2006**, *45*, 6901–6911.

[14] For reviews of metal nitride chemistry see: K. Dehnicke, J. Strähle, *Angew. Chem.* **1981**, *93*, 451–464; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 413–426; K. Dehnicke, J. Strähle, *Angew. Chem.* **1992**, *104*, 1216–1218; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 955–978.

[15] R. J. Ronan, J. W. Gilje, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 359–363.

[16] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434; W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354; G. Erker, *Dalton Trans.* **2005**, 1883–1890; W. E. Piers, *Adv. Organomet. Chem.* **2005**, *52*, 1–76.

[17] S. Döring, G. Erker, R. Fröhlich, O. Meyer, K. Bergander, *Organometallics* **1998**, *17*, 2183–2187; L. Luo, T. J. Marks, *Top. Catal.* **1999**, *7*, 97–106.

[18] A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212; A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245–250; A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1966**, *5*, 218–225.

[19] G. S. Hill, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, *Organometallics* **1997**, *16*, 525–530; D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, B. Walfort, D. Stalke, *Angew. Chem.* **2002**, *114*, 4470–4472; *Angew. Chem. Int. Ed.* **2002**, *41*, 4294–4296; R. Choukroun, C. Lorber, L. Vendier, *Eur. J. Inorg. Chem.* **2004**, *2004*, 317–321; J. Sánchez-Nieves, L. M. Frutos, P. Royo, O. Castaño, E. Herdtweck, *Organometallics* **2005**, *24*, 2004–2007; J. Sánchez-Nieves, P. Royo, M. E. G. Mosquera, *Eur. J. Inorg. Chem.* **2006**, *2006*, 127–132. See also: C. Bergquist, G. Parkin, *J. Am. Chem. Soc.* **1999**, *121*, 6322–6323; C. Bergquist, T. Fillebeen, M. M. Morlok, G. Parkin, *J. Am. Chem. Soc.* **2003**, *125*, 6189–6199.

[20] The solution phase behaviour of tris(pentafluorophenyl)borane hydrates has also been investigated, including an estimate of the pK_a in acetonitrile solution: C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581–10590; T. Beringhelli, D. Maggioni, G. D'Alfonso, *Organometallics* **2001**, *20*, 4927–4938.

[21] A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer, M. B. Hursthouse, *Chem. Commun.* **1998**, 2529–2530; L. H. Doerrer, M. L. H. Green, *J. Chem. Soc. Dalton Trans.* **1999**, 4325–4329; J. L. Priego, L. H. Doerrer, L. H. Rees, M. L. H. Green, *Chem. Commun.* **2000**, 779–780; M. J. Drewitt, M. Niedermann, M. C. Baird, *Inorg. Chim. Acta* **2002**, *340*, 207–210; I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116–2142; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090; A. Di Saverio, F. Focante, I. Camurati, L. Resconi, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli, A. Sironi, *Inorg. Chem.* **2005**, *44*, 5030–5041.

[22] A. J. Mountford, W. Clegg, R. W. Harrington, S. M. Humphrey, S. J. Lancaster, *Chem. Commun.* **2005**, 2044–2046.

[23] A. J. Mountford, S. J. Lancaster, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse, M. E. Light, *Inorg. Chem.* **2005**, *44*, 5921–5933.

[24] Pure **1** can be obtained directly from $Et_2O{\cdot}B(C_6F_5)_3$ without the need for sublimation following the same procedure: A. M. Fuller, S. J. Lancaster, unpublished results.

[25] A. D. Horton, J. de With, *Organometallics* **1997**, *16*, 5424–5436; J. M. Blackwell, W. E. Piers, M. Parvez, *Org. Lett.* **2000**, *2*, 695–698.

[26] For titanium, this result was not unexpected since Lappert has reported the failure of a similar method to yield $[TiCp_2(NMe_2)_2]$: see reference [2].

[27] S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. L. Hughes, M. Bochmann, *Organometallics* **2002**, *21*, 451–453.

[28] For examples see: a) A. G. Myers, B. H. Yang, D. J. Kopecky, *Tetrahedron Lett.* **1996**, *37*, 3623–3626; b) G. B. Fisher, A. Reem, C. T. Goralski, B. Singaram, *Tetrahedron Lett.* **1997**, *38*, 529–532, and references therein.

[29] The clean conversion of the ammonia adduct **1** to the lithium salt **8a** and its inherent stability was in contrast to the behaviour we had previously observed during attempts to deprotonate a number of primary- and secondary-amine adducts of $B(C_6F_5)_3$ including $t\text{BuN(H)}_2{\cdot}B(C_6F_5)_3$, $(PhCH_2)N(H)_2{\cdot}B(C_6F_5)_3$ and $Me_2N(H){\cdot}B(C_6F_5)_3$, which appeared to undergo immediate decomposition to give a mixture of products: A. J. Mountford and S. J. Lancaster, unpublished results.

[30] M. H. Hannant, J. A. Wright, S. J. Lancaster, D. L. Hughes, P. N. Horton, M. Bochmann, *Dalton Trans.* **2006**, 2415–2426.

[31] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625; M. Bochmann, S. J. Lancaster, M. B. Hursthouse, K. M. A. Malik, *Organometallics* **1994**, *13*, 2235–2243.

[32] G. Bar-Haim, R. Shach, M. Kol, *Chem. Commun.* **1997**, 229–230.

[33] S. J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, *Organometallics* **2000**, *19*, 1599–1608.

[34] P. N. Riley, P. E. Fanwick, I. P. Rothwell, *J. Chem. Soc. Dalton Trans.* **2001**, 181–186; J. M. Tanski, G. Parkin, *Organometallics* **2002**, *21*, 587–589.

[35] L. Kakaliou, W. J. Scanlon, IV, B. Qian, S. W. Back, M. R. Smith, III, D. H. Motry, *Inorg. Chem.* **1999**, *38*, 5964–5977.

[36] D. W. Carpenetti, L. Kloppenburg, J. T. Kupec, J. L. Petersen, *Organometallics* **1996**, *15*, 1572–1581.

[37] T. H. Kim, Y. C. Won, B. Y. Lee, D. M. Shin, Y. K. Chung, *Eur. J. Inorg. Chem.* **2004**, 1522–1529.

[38] H. Nöth, S. Thomas, M. Schmidt, *Chem. Ber.* **1996**, *129*, 451–458.

[39] W. E. Hunter, D. C. Hrncir, R. V. Bynum, R. A. Penttila, J. L. Atwood, *Organometallics* **1983**, *2*, 750–755.

[40] For comparison, the angle between the alkyl and methylborate ligands in *rac*-$Me_2Si(1\text{-indenyl})_2Hf(CH_2SiMe_3)(\mu\text{-}Me)B(C_6F_5)_3$ is 94.3(2)°: F. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, S. M. Humphrey, C. Zuccaccia, A. Macchioni, M. Bochmann, *Organometallics* **2005**, *24*, 1315–1328.

[41] J. D. Dunitz, *ChemBioChem* **2004**, *5*, 614–621; J. D. Dunitz, W. B. Schweizer, *Chem. Eur. J.* **2006**, *12*, 6804–6815, and references therein.

[42] A. J. Mountford, D. L. Hughes, S. J. Lancaster, *Chem. Commun.* **2003**, 2148–2149.

[43] D. Chakraborty, E. Y.-X. Chen, *Inorg. Chem. Commun.* **2002**, *5*, 698–701.

[44] S. Beck, S. Lieber, F. Schaper, A. Geyer, H. H. Brintzinger, *J. Am. Chem. Soc.* **2001**, *123*, 1483–1489.

[45] R. Hooft, COLLECT Data Collection Software, Nonius, B. V., **1998**; Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.

[46] G. M. Sheldrick, SHELX-97 Programs for Crystal Structure Analysis, University of Göttingen (Germany), **1997**.

[47] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[48] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: December 6, 2006