New titanium and zirconium complexes with M–NH$_2$ bonds formed by facile deprotonation of H$_3$N·B(C$_6$F$_5$)$_3$

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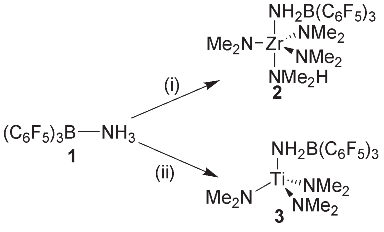
Facile deprotonation of $H_3N{\cdot}B(C_6F_5)_3$ with $[M(NMe_2)_4]$ (M = Zr or Ti) yields the novel amidoborate complexes $[Zr(NMe_2)_3\{NH_2B(C_6F_5)_3\}(HNMe_2)]$ and $[Ti(NMe_2)_3\{NH_2B(C_6F_5)_3\}]$.

Tris(pentafluorophenyl)boron continues to attract considerable attention as an activator in polymerisation catalysis[1] and as a catalyst for organic transformations.[2] Its Lewis acidity has also been utilised in the synthesis of poorly coordinating anions, for example the amidodiborate $[H_2N\{B(C_6F_5)_3\}_2]^-$.[3] Recently there has been increased interest in the structure and reactivity of neutral Brønsted acidic adducts of $B(C_6F_5)_3$.[4] The best studied example, $H_2O{\cdot}B(C_6F_5)_3$,[5] has been shown to protonate M–R bonds, yielding complexes with $[HOB(C_6F_5)_3]^-$ and $[OB(C_6F_5)_3]^{2-}$ ligands.[6,7] However, to date there are no reports describing similar reactivity with $H_3N{\cdot}B(C_6F_5)_3$.[8]

Considerable attention has been focused on determining the course of reactions between $[M(NR_2)_4]$ and NH_3, since they play a key role in the chemical vapour deposition of the technologically important metal nitride materials [MN] (M = Ti, Zr).[9] While intermediates involving NH_2, NH and N ligands have been postulated,[10] isolable models have been restricted to N-bridged polynuclear complexes stabilised by sterically demanding ancillary ligands.[11,12] We report here the reactivity of $H_3N{\cdot}B(C_6F_5)_3$ towards $[M(NMe_2)_4]$ and the isolation of Lewis acid stabilised examples of terminal amido (NH_2) ligation.

Treatment of a toluene solution of $[Zr(NMe_2)_4]$ with $H_3N{\cdot}B(C_6F_5)_3$[13] (**1**) resulted in the immediate precipitation of a colourless microcrystalline solid **2** (Scheme 1). Compound **2** proved to be insoluble in aromatic and chlorocarbon solvents but could be recrystallised from tetrahydrofuran solution, without affecting the elemental composition.[14] The ^1H NMR spectrum (THF-d$_8$) consisted of two singlets at δ 2.88 and 2.70, indicating two NMe_2 environments in a 3 : 1 ratio, while the new ^{11}B NMR signal at δ −2.4 was consistent with conversion of $H_3N{\cdot}B(C_6F_5)_3$ (δ −4.9) into an amidoborate $[NH_2B(C_6F_5)_3]$ ligand. 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 **2** as $[Zr(NMe_2)_3\{NH_2B(C_6F_5)_3\}(HNMe_2)]$.



Scheme 1 Synthesis of compounds **2** and **3**. (i) RT, toluene, $[Zr(NMe_2)_4]$; (ii) 0 °C, light petroleum, $[Ti(NMe_2)_4]$.

Despite the poor solubility of **2** very small crystals were obtained by layering two toluene solutions of $[Zr(NMe_2)_4]$ and **1**. The solid state structure was determined by diffraction methods using synchrotron radiation and confirmed the proposed composition.† Compound **2** forms a distorted trigonal bipyramid in which the amidoborate and amino ligands are coordinated *trans* to one another (N(1)–Zr(1)–N(5) = 173.45(13)°) (Fig. 1). 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.[15] There is no structural precedent for a Zr–NH$_2$–BX$_3$ moiety. However, we have reported the synthesis of the complexes $[Zr(Cp)\{C_5H_4B(C_6F_5)_2\}(RHN)Cl]$ (R = ^{t}Bu or H), which contain a chelating Zr–NHR–B(C$_6$F$_5$)$_2$ arrangement.[16]

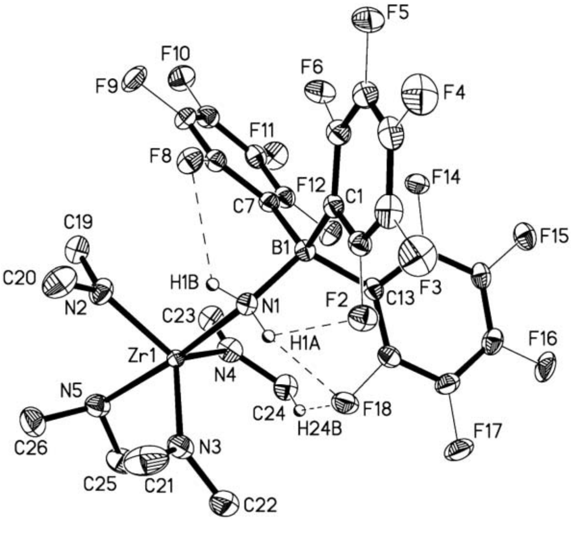


Fig. 1 Structure of **2** (50% displacement ellipsoids; hydrogen atoms not participating in hydrogen bonding omitted for clarity). Selected distances [Å] and angles [°]: Zr(1)–N(3) 2.030(4), Zr(1)–N(2) 2.035(4), Zr(1)–N(4) 2.039(3), Zr(1)–N(1) 2.356(3), Zr(1)–N(5) 2.424(4), B(1)–N(1) 1.587(5), F(2)···H(1A) 2.22(5), F(8)···H(1B) 2.44(7), F(18)···H(1A) 2.22(5); N(4)–Zr(1)–N(1) 101.25(13), N(2)–Zr(1)–N(5) 84.37(14), N(4)–Zr(1)–N(5) 84.18(14), N(1)–Zr(1)–N(5) 173.45(13), B(1)–N(1)–Zr(1) 126.3(2), N(1)–H(1B)···F8 117.3, N(1)–H(1A)···F(2) 128.4, N(1)–H(1A)···F(18) 113.8.

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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 compound **3**. In contrast to **2**, **3** proved to be sufficiently soluble in benzene-d_6 to allow multinuclear NMR characterization. The ^1H NMR spectrum consisted of a single resonance at δ 2.59 for the NMe_2 group and a broad singlet at δ 2.23, which we assign to an $[NH_2B(C_6F_5)_3]$ ligand. The ^{11}B resonance was found at δ −5.8. Compound **3** was therefore formulated as $[Ti(NMe_2)_3\{NH_2B(C_6F_5)_3\}]$. While **3** appeared to be indefinitely stable under nitrogen in the solid state, it decomposed slowly in solution above 0 °C, giving rise to an oil. Decomposition (in toluene-d_8 solution) led to a number of unidentified boron-containing products and was accompanied by the formation of C_6F_5H.

The structure was confirmed by X-ray diffraction.† The titanium is in a distorted tetrahedral environment, coordinated by three amido and one amidoborate ligand (Fig. 2). Bond lengths in the $Ti(NMe_2)_3$ fragment are in the range normally observed for $LTi(NMe_2)_3$ complexes.[15b,17] This is the first example of a monodentate amidoborate ligand bound to titanium. The closest structural precedents are Kol's five-coordinate chelating diaminoborate tris(amido) complex, which shows Ti–N(B) bond lengths of 2.282(4) and 2.302(3) Å,[18] and $[Ti(Cp)\{C_5H_4B(C_6F_5)_2\}\{^tBuHN\}Cl]$ (Ti–N = 2.294(2) Å).[16] The Ti–N(1) bond length in **3** is significantly shorter, 2.152(2) Å.

The amidoborate ligands in both **2** and **3** exhibit intramolecular N–H···F–C hydrogen-bonding interactions between the amido NH_2 and *ortho*-fluorines. Similar interactions have been reported in a number of neutral and anionic protic adducts of $B(C_6F_5)_3$.[3–5] In compounds **2** and **3** the specific pattern in which one NH is engaged in a bifurcated H-bond with two *o*-F acceptors and the second has a single longer contact to a third *o*-F is strikingly similar to that seen in primary amine adducts of $B(C_6F_5)_3$.[19]

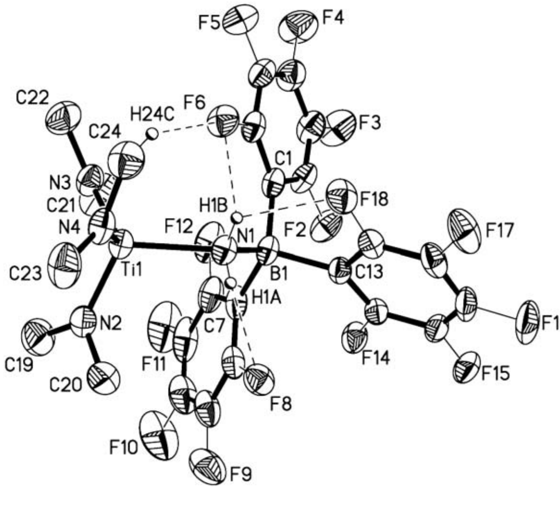

Fig. 2 Structure of **3** (50% displacement ellipsoids; hydrogen atoms not participating in hydrogen bonding omitted for clarity). Selected distances [Å] and angles [°]: Ti(1)–N(3) 1.860(2), Ti(1)–N(2) 1.868(3), Ti(1)–N(4) 1.871(2), Ti(1)–N(1) 2.152(2), B(1)–N(1) 1.605(4), F(6)···H(1B) 2.23(3), F(8)···H(1A) 2.35(3), F(18)···H(1B) 2.22(3); N(3)–Ti(1)–N(1) 113.23(11), N(2)–Ti(1)–N(1) 111.88(11), N(4)–Ti(1)–N(1) 102.60(10), B(1)–N(1)–Ti(1) 129.52(17), N(1)–H(1A)···F(8) 130.9, N(1)–H(1B)···F(6) 114.5, N(1)–H(1B)···F(18) 122.4.

In summary, $H_3N\cdot B(C_6F_5)_3$ reacts as a Brønsted acid with $[M(NMe_2)_4]$ yielding the first examples of group 4 monodentate amidoborate complexes, **2** and **3**. Complexes **2** and **3** can be regarded as $B(C_6F_5)_3$-stabilised $[M(NMe_2)_3(NH_2)]$, the first intermediates in the ammonia-promoted deposition of MN from $[M(NMe_2)_4]$.

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Notes and references

† All manipulations were performed under dry and oxygen-free nitrogen using Schlenk-line or glovebox techniques. Toluene, tetrahydrofuran, and light petroleum were dried over appropriate drying agents [Na (toluene), Na/K alloy (light petroleum), Na/benzophenone (THF)] and distilled under nitrogen prior to use. ^1H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker DPX 300. Chemical shifts are reported in δ units downfield from TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F), $Et_2O\cdot BF_3$ (^{11}B), with the solvent as the reference signal. Elemental analyses were carried out by Medac. **2**: A solution of $Zr(NMe_2)_4$ (0.50 g, 1.9 mmol) in toluene (10 mL) was layered over a cooled (−20 °C) solution of **1** (0.99 g, 1.9 mmol) in toluene (10 mL). The mixture was allowed to warm to room temperature, during which time a crystalline precipitate formed at the layer interface. After 30 minutes the solid was isolated by filtration (1.2 g, 81%). ^1H NMR (300.13 MHz, THF-d_8, 24 °C) δ 2.88 (s, 18H, CH_3), 2.79 (br, 2H, NH_2), 2.70 (s, 6H, CH_2). ^{13}C NMR (75.47 MHz, THF-d_8, 24 °C) δ 44.9 (CH_3), 42.4 (CH_3). ^{11}B NMR (96.29 MHz, THF-d_8, 24 °C) δ −2.4. ^{19}F NMR (282.40 MHz, THF-d_8, 24 °C) δ −131.05 (d, 6F, ^3J (F,F) = 19.8 Hz, *o*-F), −160.01 (t, 3F, ^3J (F,F) = 19.8 Hz, *p*-F), −163.49 (m, 6F, *m*-F). IR (nujol cm^{-1}): 3364, 3292 (NH). Elemental analysis calcd (%) for $C_{26}H_{21}BF_{15}N_5Zr$: C 39.21, H 3.42, N 8.79; found: C 39.15, H 3.33, N 8.67. **3**: $Ti(NMe_2)_4$ (0.439 g, 2.0 mmol) was added to a suspension of **1** (1.036 g, 2.0 mmol) in light petroleum (15 mL) at −20 °C. The mixture was warmed to 0 °C and the reactants dissolved, affording a homogeneous yellow solution. Yellow plates suitable for X-ray crystallography were obtained by cooling the solution to −25 °C overnight (0.92 g, 65%). ^1H NMR (300.13 MHz, benzene-d_6, 24 °C) δ 2.59 (s, 18H, CH_3), 2.23 (br, 2H, NH_2). ^{13}C NMR (75.47 MHz, benzene-d_6, 24 °C) δ 43.1 (CH_3). ^{11}B NMR (96.29 MHz, benzene-d_6, 24 °C) δ −5.8. ^{19}F NMR (282.40 MHz, benzene-d_6, 24 °C) δ −134.17 (d, 6F, ^3J (F,F) = 16.9 Hz, *o*-F), −158.61 (t, 3F, ^3J (F,F) = 22.6 Hz, *p*-F), −163.93 (m, 6F, *m*-F). IR (nujol cm^{-1}): 3348, 3281 (NH). Elemental analysis calcd (%) for $C_{24}H_{20}BF_{15}N_4Ti$: C 40.71, H 2.85, N 7.91; found: C 40.85, H 2.94, N 7.39. Suitable crystals were immersed in perfluoropolyether oil, mounted on glass fibres and fixed in a low-temperature N_2 stream. Intensity data for complex **2** were measured at the Synchrotron Radiation Source at Daresbury on a Bruker SMART 1 K CCD diffractometer (λ = 0.6892 Å) at 120 K using thin slice ω-scans. Complex **3** was analysed at Cambridge on a Nonius KappaCCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). Data for **3** were collected at 180 K using ϕ- and ω-scans of 1.0°. Absorption corrections for **3** were made using the SORTAV[20] utilities and data were processed using the DENZO/SCALEPACK programs.[21] The structures were determined by direct methods using the software packages SHELXTL[22] (**2**) and SIR-92[23] (**3**) and refined by full-matrix least-squares methods for all unique F^2, with all non-hydrogen atoms anisotropic. Crystal data for **2**: $C_{26}H_{27}BF_{15}N_5Zr$, M_r = 796.56, orthorhombic, space group $Pca2_1$, a = 10.7826(18), b = 16.140(3), c = 17.502(3) Å, V = 3045.9(9) Å^3, Z = 4, ρ_{calcd} = 1.737 Mg m^{-3}, silicon-monochromated synchrotron radiation, λ = 0.6892 Å, T = 120(2) K, μ = 0.481 mm^{-1}. Of the 20458 measured reflections, 6128 were independent (R_{int} = 0.0602). The final refinement converged at R_1 = 0.0439 ($I > 2\sigma(I)$), wR_2 = 0.1066 for all

data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.69/0.69$ e$\AA^{-3}$. All H atoms were located in difference syntheses and those attached to N atoms were freely refined to avoid presuppositions about their geometry. The polar axis direction for this space group was confirmed by refinement of the enantiopole parameter to a value insignificantly different from zero. CCDC 258171. Crystal data for **3**: $C_{24}H_{20}BF_{15}N_4Ti$, M_r = 708.15, monoclinic, space group $P2_1/c$, a = 13.5564(2), b = 13.1607(2), c =15.8983(3) Å, β = 98.2522(7)°, V = 2807.07(8) Å^3, Z = 4, ρ_{calcd} = 1.676 Mg m^{-3}, λ = 0.71073 Å, T = 180(2) K, μ(Mo-Kα) = 0.428 mm^{-1}. Of the 16178 measured reflections, 6417 were independent (R_{int} = 0.0528). The final refinement converged at R_1 = 0.0547 ($I > 2\sigma(I)$), wR_2 = 0.1467 for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.66/0.47$ e$\AA^{-3}$. All hydrogen atoms were located in a difference map and allowed to refine freely, with fixed values for U_{iso}, set at 1.2 times U_{eq} of the parent atom. CCDC 258172. See http://www.rsc.org/suppdata/cc/b5/b500407a/ for crystallographic data in .cif or other electronic format.

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