Mononuclear Ti≡N complexes formed by the facile multiple deprotonation of $H_3N{\cdot}B(C_6F_5)_3$: the importance of chloride ligands†

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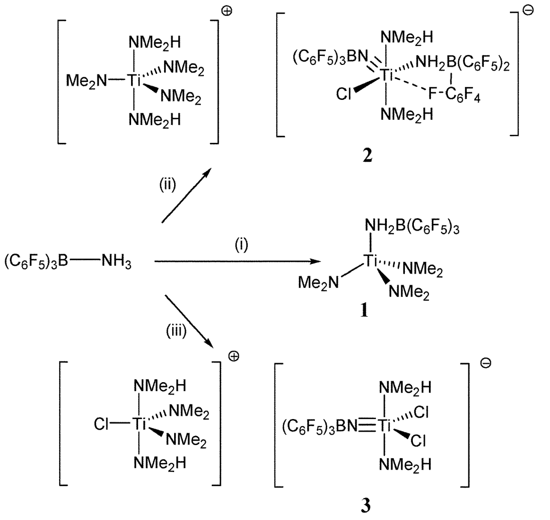
The crystalline ion-pair $[TiCl(NMe_2)_2(NMe_2H)_2]^+[TiCl_2\{NB(C_6F_5)_3\}(NMe_2H)_2]^-$, in which the anion has a triply bonded nitridoborate ligand, is formed through the multiple activation of $H_3N{\cdot}B(C_6F_5)_3$ when treated with $[Ti(NMe_2)_3Cl]$.

Chemical vapour deposition of the technologically important material TiN from titanium amide precursors is promoted by ammonia and the process has been the subject of intense investigation. Theoretical and experimental studies point to the intermediacy of amide, imide and nitride complexes of titanium.[1] The isolation of chemical models for these intermediates has tended to require bulky stabilising ligands and isolated nitrido complexes invariably feature the ligand adopting a bridging mode between two or more titanium centres.[2]

Tris(pentafluorophenyl)boron forms adducts with a great variety of sterically unencumbered bases and has a Lewis acidity comparable to that of boron trifluoride.[3,4] The relative inertness of the B–C bonds and steric shielding provided by the pentafluorophenyl substituents render the $B(C_6F_5)_3$ group compatible with highly reactive reagents.[3a,5] This combination of Lewis acidity and stability has been exploited in weakly coordinating anion synthesis, in cation generation and in catalysing organic transformations.[3a,6–8] $B(C_6F_5)_3$ has been shown to enhance the Brønsted acidity of coordinated protic donors and to be very effective at the stabilisation of otherwise highly reactive basic intermediates.[9,10]

We recently reported that ammonia forms a robust adduct with tris(pentafluorophenyl)boron in which the N–H functionalities are activated towards both supramolecular second coordination sphere interactions and reaction with Brønsted bases.[11,12] Treatment of $H_3N{\cdot}B(C_6F_5)_3$ with $Ti(NMe_2)_4$ leads to the facile elimination of one equivalent of NMe_2H and the generation of the amidoborate complex, $Ti(NMe_2)_3\{H_2NB(C_6F_5)_3\}$ (**1**) (Scheme 1).[12]



Scheme 1 Synthesis of compounds **1–3**: (i) $Ti(NMe_2)_4$, light petroleum, 0 °C; (ii) not known; (iii) $TiCl(NMe_2)_3$, toluene, RT.

The successful isolation of compound **1**, the five-coordinate zirconium analogue $Zr(NMe_2)_3\{H_2NB(C_6F_5)_3\}(NMe_2H)$ and related cyclopentadienyl complexes demonstrated that $B(C_6F_5)_3$ is effective in stabilising $[L_nM(NH_2)]$ fragments. Compound **1** retains protic hydrogens and therefore the potential for further amine elimination forming well-defined imido or nitrido ligand complexes. However, in practice **1** decomposes slowly above 0 °C in toluene solution giving an intractable mixture of products, including pentafluorobenzene.[12]

During the course of our initial studies, in what was intended as a repeat preparation of compound **1**, we isolated a small quantity of yellow plate-like crystals within a viscous oil. Crystallographic characterisation revealed the solid fraction to be the ion-pair $[Ti(NMe_2)_3(NMe_2H)_2]^+[TiCl\{NB(C_6F_5)_3\}\{H_2NB(C_6F_5)_3\}(NMe_2H)_2]^-$ (**2**).[13] To the best of our knowledge, compound **2** was the first structurally characterised example of a mononuclear titanium nitride. The nature of the sample meant that we were unable to collect supporting spectroscopic or elemental analysis data. The formation of **2** was consistent with the starting materials being contaminated with chloride but, despite repeated attempts, including combining one equivalent of $Ti(NMe_2)_4$ with one equivalent of $TiCl(NMe_2)_3$ and two equivalents of $H_3N{\cdot}B(C_6F_5)_3$, exactly matching the product composition, we were unable to reproduce the synthesis of compound **2**.[14] The irreproducibility and failure to yield a rational synthesis has until now rendered the discovery of the first Ti≡N complex as frustrating as it was initially exciting. However, a second serendipitous result has provided a reproducible route to such species and offers some insight into the chemical requirements for multiple N–H activation.

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† Electronic supplementary information (ESI) available: ORTEP view of **3**. CCDC 696254. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812785a

By analogy to the synthesis of complex **1**, $TiCl(NMe_2)_3$ and $H_3N{\cdot}B(C_6F_5)_3$ would be expected to react giving $TiCl(NMe_2)_2\{H_2NB(C_6F_5)_3\}$. Monitoring the reaction by ^1H and ^{19}F NMR in C_6D_6 was hampered by the formation of an insoluble oil. Employing C_6D_6–$C_6H_4F_2$ (80 : 20) as the reaction medium revealed a complex mixture. When the reaction was conducted in toluene on a preparative scale, vacuum distillation of the resulting orange solution yielded an amorphous foam. Crystalline samples of **3** were obtained by dissolving the crude mixture of products in dichloromethane adding light petroleum and cooling in the freezer overnight.‡ The synthesis is reproducible in 25% yield. The crystal quality proved to be highly sensitive to amine loss and X-ray quality crystals could be reliably obtained only if dimethylamine was added during recrystallisation.

The structure of **3** was elucidated by diffraction methods (the anion is shown in Fig. 1) and the asymmetric unit consists of the ion-pair $[TiCl(NMe_2)_2(NMe_2H)_2]^+[TiCl_2\{NB(C_6F_5)_3\}(NMe_2H)_2]^-$ and half a disordered dichloromethane molecule. Both the cation and the anion have trigonal bipyramidal geometries. In each case the axial positions are occupied by a pair of dimethylamine ligands. The neutral amine donor character was evident from the angles at nitrogen and the hydrogen atoms bound to nitrogen were located in a difference map. In contrast, the amide ligands in the equatorial positions of the cation are essentially planar. The most significant structural feature is the presence of the $Ti{\equiv}N$ fragment coordinated to $B(C_6F_5)_3$ in the anion. Confirmation of the triple bond character was provided by the short Ti–N bond length, 1.671(3) Å, and near-linear Ti–N–B angle, 166.01(17)°. The respective coordination polyhedra are completed by chloride ligands.

The cation geometry in **3** closely resembles that in compound **2**, with one of the three equatorial amide ligands replaced by a chloride. If one neglects the weak coordination of a (sixth) fluorine donor in compound **2** then the two anions are structurally rather similar. In both instances there are chloride and nitridoborate ligands in the plane between the axial dimethylamine ligands; in **3** the amidoborate ligand of **2** is replaced by a second chloride. At 1.665(2) Å the Ti–N bond length in **2** is very similar to that of **3** and both are comparable to those found in imido complexes such as Ti(salophen)(=$NCPh_3$) (1.686(4) Å).[15] While **2** and **3** are the only examples of nitridoborate complexes of titanium, later transition metal examples such as $[Re\{NB(C_6F_5)_3\}(PMePh_2)(S_2CNEt_2)_2]$ are known.[16] The B–N bond lengths found in the nitridoborate ligands of **2**, **3** and later transition metal examples are consistently shorter than those found for amidoborate ligands such as that in **1**.[10]

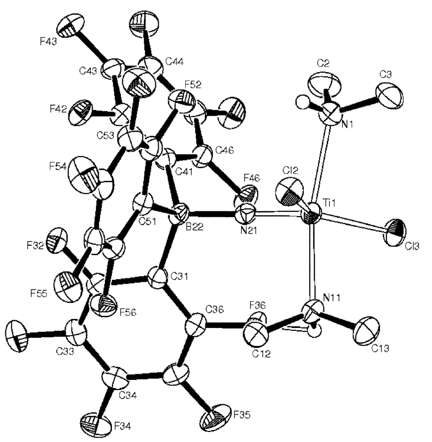

Fig. 1 Structure of the anion of **3** (50% displacement ellipsoids; methyl group H atoms omitted for clarity). Selected distances [Å] and angles [°]: N(21)–B(22) 1.526(4), Ti(1)–N(1) 2.223(3), Ti(1)–N(11) 2.211(3), Ti(1)–N(21) 1.671(3), Ti(1)–Cl(2) 2.398(3), Ti(1)–Cl(3) 2.381(2); B(22)–N(21)–Ti(1) 166.01(17), N(11)–Ti(1)–N(1) 163.06(9), N(21)–Ti(1)–N(1) 98.57(12), N(21)–Ti(1)–N(11) 97.67(13), N(21)–Ti(1)–Cl(2) 108.21(7), N(21)–Ti(1)–Cl(3) 110.48(9).

In sharp contrast to **2**, the synthesis of ion-pair **3** has been successfully repeated on a number of occasions and the material can be isolated and purified by recrystallisation, giving elemental analysis in good agreement with the theoretical values. Compound **3** is ionic and poorly soluble in aromatic and chlorocarbon solvents and was therefore spectroscopically characterised in an 80 : 20 deuterated benzene–1,2-difluorobenzene solvent. The NMR spectra of compound **3** are entirely consistent with the solid-state formulation. The ^1H NMR spectrum has doublet resonances for two electronically very different dimethylamine methyl environments at δ 2.46 and 1.87 ppm, the lowest frequency being presumably due to the anion, and a singlet at δ 3.03 ppm of equal intensity for the two amide ligands of the cation.[17] The ^{11}B and ^{19}F NMR spectra each show one set of signals, somewhat removed from those found for amidoborate groups. Solutions of compound **3** are extremely sensitive to hydrolysis, giving a titanium-containing precipitate and $H_3N{\cdot}B(C_6F_5)_3$.

It is tempting to speculate on the existence of a whole series of related complexes of the general formula $[Ti(Cl)_x(NMe_2)_{3-x}(NMe_2H)_2]^+[Ti(Cl)_y(NMe_2)_z\{NB(C_6F_5)_3\}\{H_2NB(C_6F_5)_3\}_{2-y-z}(NMe_2H)_2]^-$. However, it is salutary to note that, while the reagent ratio employed in the preparation of **3** would be expected to give a product with one chloride ligand and one $B(C_6F_5)_3$ group per titanium centre, **3** actually contains three chloride ligands and only one $B(C_6F_5)_3$ group to two titanium centres. Ligand exchange between coordinatively unsaturated titanium species is likely to be an extremely facile process and it therefore seems probable that the formation of **3** from the complex mixture observed by NMR is driven either by greater thermodynamic stability or by poorer solubility in comparison to $[Ti(NMe_2)_3(NMe_2H)_2]^+[Ti(Cl)_2\{NB(C_6F_5)_3\}(NMe_2H)_2]^-$ and its isomers.

In conclusion, the reaction between $H_3N{\cdot}B(C_6F_5)_3$ and $Ti(NMe_2)_4$ leads to the isolation of $Ti(NMe_2)_3\{H_2NB(C_6F_5)_3\}$, which decomposes slowly giving a plethora of products. The replacement of one amide ligand for a chloride ligand destabilises the amidoborate complex and leads to the formation of nitridoborate complexes, one of which crystallises selectively from dichloromethane solution. Formally, the generation of a nitridoborate ligand represents multiple deprotonation of $H_3N{\cdot}B(C_6F_5)_3$, but determining the mechanism of this reaction will require further investigation. Compound **3** promises a facile and convenient entry into the chemistry of $Ti{\equiv}N$ complexes.

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Notes and references

‡ Synthesis and characterisation of **3**. All manipulations were performed under dry and oxygen-free nitrogen using Schlenk-line techniques. Toluene, dichloromethane, and light petroleum were dried over appropriate drying agents [Na, CaH_2, Na/dyglyme, respectively], 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. Elemental analyses were carried out at the London Metropolitan University.

To a solution of $Ti(NMe_2)_4$ (2.20 cm^3, 9.3 mmol) in toluene (120 cm^3) at −65 °C was added neat $TiCl_4$ (0.34 cm^3, 3.1 mmol). The solution was allowed to warm to room temperature and stirred for a further hour. Solid $H_3N{\cdot}B(C_6F_5)_3$ (6.56 g, 12.4 mmol) was added at room temperature and the reaction mixture stirred for 1 h before the solvent was removed under reduced pressure. The resultant orange foamy solid was dissolved in CH_2Cl_2–light petroleum before being cooled to −25 °C to yield an orange precipitate. The pure product was obtained as an orange crystalline solid by dissolving in CH_2Cl_2 and adding a cold solution of excess dimethylamine in light petroleum. A second crop of crystals was obtained by cooling this solution to 0 °C, giving a total yield of 1.074 g, 1.033 mmol, 25%. Elemental analysis found: C, 35.17; H, 4.05; N, 9.38. Calculated for $C_{30.5}H_{41}BCl_4F_{15}N_7Ti_2$: C, 35.25; H, 3.98; N, 9.44%. δ_H (300.1 MHz, C_6D_6–$C_6H_2F_4$) 4.44 (1H, s, CH_2Cl_2), 3.55 (2H, br, NH), 3.03 (12H, s, CH_3), 2.46 (12H, d, $^3J_{H,H}$ 6.1, CH_3), 2.31 (2H, br, NH), 1.87 (12H, d, $^3J_{H,H}$ 6.1, CH_3). δ_C (75.5 MHz, C_6D_6–$C_6H_4F_2$) 43.73, 40.09, 39.66. δ_B (96.3 MHz; C_6D_6–$C_6H_2F_4$) −9.93. δ_F (282.4 MHz, C_6D_6–$C_6H_2F_4$), −132.7 (6F, d, $^3J_{F,F}$ 24, *o*-F), −163.9 (3F, t, $^3J_{F,F}$ 21, *p*-F), −166.7 (6F, t, $^3J_{F,F}$ 20, *m*-F). Suitable crystals were immersed in perfluoropolyether oil, mounted on glass fibres and fixed in a low-temperature N_2 stream. Intensity data for complex **3** were measured at the Synchrotron Radiation Source at Daresbury on a Bruker APEX2 diffractometer using thin slice ω-scans. Absorption corrections were made using the SADABS program[18] and data were processed using the Bruker SAINT program.[19] The structure was determined by direct methods using the software package SHELXS and refined by full-matrix least-squares methods for all unique F^2 in SHELXL,[20] with all non-hydrogen atoms anisotropic. Crystal data for **3**: $C_{22}H_{14}BCl_2F_{15}N_3Ti^-{\cdot}C_8H_{26}ClN_4Ti^+{\cdot}0.5CH_2Cl_2$, M_r = 1039.1, triclinic, space group $P\bar{1}$, a = 10.756(13), b = 13.228(16), c = 16.627(19) Å, α = 77.136(13), β = 72.104(13), γ = 82.074(13)°, V = 2189(5) Å^3, Z = 2, ρ_{calcd} = 1.577 Mg m^{-3}, silicon-monochromated synchrotron radiation, λ = 0.6393 Å, T = 120 K, μ = 0.706 mm^{-1}. Of the 22 679 measured reflections, 12 204 were independent (R_{int} = 0.061). The final refinement converged at R_1 = 0.078 ($I > 2\sigma(I)$), wR_2 = 0.149 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.60/0.47 e Å^{-3}. Hydrogen atoms attached to N atoms were located in difference syntheses and freely refined, methyl group hydrogen atoms were constrained geometrically and CH_2Cl_2 hydrogen atoms were not modelled. CCDC 696254.†

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