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PAPER

# Tris(pyrazolyl)borate amidoborane complexes of the group 4 metals†

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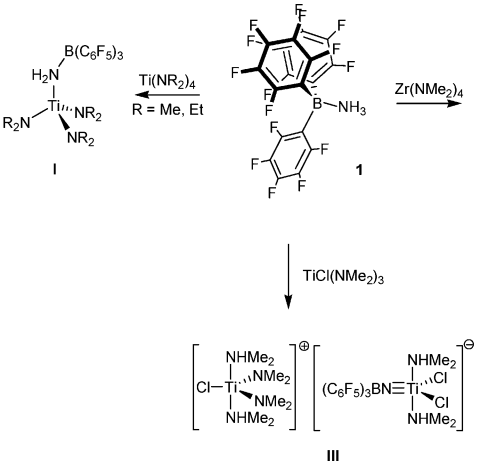
Treatment of the tris(pyrazolyl)borate metal triamides Tp′M(NMe$_2$)$_3$, where Tp′ = (C$_3$H$_3$N$_2$)$_3$BH (Tp) or (3,5-Me$_2$C$_3$HN$_2$)$_3$BH (Tp*) and M = Ti, Zr and Hf, with the Brønsted acidic Lewis adduct (C$_6$F$_5$)$_3$B·NH$_3$ in toluene solution leads to the formation of Tp′M(NMe$_2$)$_2${NH$_2$B(C$_6$F$_5$)$_3$} complexes. The exception to this was the attempted preparation of Tp*Ti(NMe$_2$)$_2${NH$_2$B(C$_6$F$_5$)$_3$} which was unsuccessful. Where Tp′ = Tp and M = Ti and Zr and where Tp′ = Tp* and M = Zr the complexes have been characterized by single crystal X-ray diffraction methods, revealing the first examples of octahedral amidoborane complexes of the group 4 metals. Attempts to drive the reactions to completion resulted in competing preferential hydrolysis of the amidoborane group, regenerating (C$_6$F$_5$)$_3$B·NH$_3$.

## Introduction

Interest in amineboranes as molecular hydrogen storage materials has resulted in intense recent investigation of amidoborane complexes of early transition metals as models for intermediates in catalytic dehydrogenation.[1] Furthermore, the isoelectronic relationship between amidoborane and alkyl ligands has prompted studies of their structure and bonding.[2] Complexes of amidoboranes are also believed to be intermediates in the technologically-important production of metal nitride materials.[3]

We have shown that the elimination of amine in reactions between metal amides and the Brønsted acidic ammonia adduct of tris(pentafluorophenyl)borane, (C$_6$F$_5$)$_3$B·NH$_3$, (**1**) provides a route to complexes of the amidoborane ligand [(C$_6$F$_5$)$_3$BNH$_2$]$^-$.[4–6] For example, treatment of Ti(NR$_2$)$_4$ (R = Me, Et) with **1** results in replacement of one dialkylamide ligand with an amidoborane ligand to give Ti(NR$_2$)$_3${NH$_2$B(C$_6$F$_5$)$_3$} (**I**, Scheme 1), with the subsequent evolution of the corresponding dialkylamine; **I** is a tetrahedral complex containing an NH$_2$B(C$_6$F$_5$)$_3$ ligand. However, Zr(NMe$_2$)$_4$ reacts with **1** to produce the five-coordinate amidoborane complex Zr(NMe$_2$)$_3$(NHMe$_2$){NH$_2$B(C$_6$F$_5$)$_3$} (**II**) with dimethylamine being retained in the metal coordination sphere.[4,5]

Under certain circumstances, the remaining protic hydrogens on nitrogen are lost leading to the formation of anionic trigonal bipyramidal coordination complexes, such as **III**, of the formally trianionic nitridoborane ligand.[7] The tris(pentafluorophenyl)borane serves as a protecting group for the terminal nitride functionality. Current investigations are exploring both the mechanism of the formation of these nitridoborane complexes and their subsequent derivitization.



**Scheme 1**

Substitution of one of the amide ligands in complexes such as **I** and **II** for a monoanionic facially coordinating tridentate ligand is of interest since it should lead to the first examples of octahedral group 4 metal amidoborane complexes. It may also provide a favourable steric environment for a nitridoborane complex, providing complementary shielding for the metal centre. The utilization of a sterically-demanding polydentate ligand has been demonstrated to be effective in restricting, but not eliminating, oligomerization of the metal nitrogen multiply bonded species.[8]

The tris(pyrazolyl)borate ligands (Tp′), are versatile facially binding tridentate donors,[9] in which the substituents on the pyrazolyl rings allow for tuning of the steric and electronic properties.[10,11] The most common of these is the hydridotris(3,5-dimethylpyrazolyl)borate anion (Tp*).[10] Studies of group 4 Tp′ complexes have encompassed chloro,[12,13] alkyl,[14] amido,[15] carbonyl,[16] hydrazido,[17] and imido ligands,[18] while derivatives have been used in catalysis.[19]

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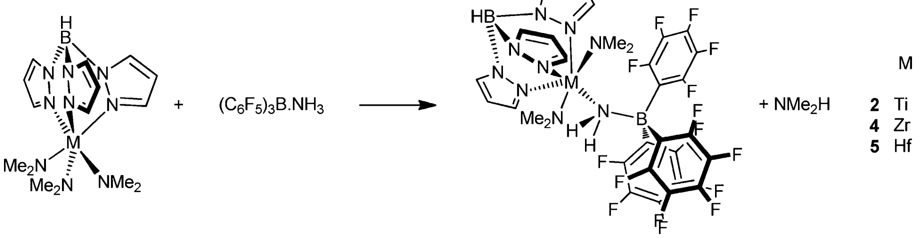


**Scheme 2**

Group 4 monocyclopentadienyl and metallocene amidoborane complexes of the form $Cp_nMR_{3-n}\{NH_2B(C_6F_5)_3\}$, ($n$ = 1, R = $NMe_2$, $NEt_2$, M = Ti, Zr; $n$ = 2, R = Me, M = Zr, Hf) have been previously described.[5] Group 4 Tp amidoborane complexes are unprecedented in the literature.[20] Herein the reactions of $Tp'M(NMe_2)_3$ with $(C_6F_5)_3B{\cdot}NH_3$ are described and the structure and reactivity of the resulting products reported.

## Results and Discussion

The substituent-free tris(pyrazolyl)borate triamide $TpTi(NMe_2)_3$ was treated with one equivalent of **1** in toluene solution (Scheme 2). Monitoring the reaction by $^1H$ and $^{19}F$ NMR suggested incomplete conversion of the reactants to a new compound **2**. Sparging the reaction mixture with nitrogen did not improve conversion and lead to suspected partial hydrolysis to $\{TpTi(NMe_2)_2\}_2\{\mu\text{-}O\}$ (**3**) and this observation is discussed further in the supplementary information.† If an excess of $TpTi(NMe_2)_3$ was used a simple $^{19}F$ NMR spectrum was obtained, with one set of signals indicating equivalence of all three $C_6F_5$ rings; the *o*-F signal was found at higher frequency ($\delta$ −132.7 ppm) from that observed for **1**, while the *p*-F and *m*-F signals appeared at lower frequencies than the starting material ($\delta$ −159.3 ppm and −164.3 ppm, respectively). The $^{11}B$ NMR displayed a broad resonance at −3.36 ppm corresponding to the Tp boron atom and a singlet at −7.7 ppm for the $(C_6F_5)_3B$ group. Whilst the Tp boron chemical shift displays minimal change, the $(C_6F_5)_3B$ boron signal is indicative of a reaction and appears at significantly lower frequency to that of **1**. As one would expect, the $^1H$ NMR displayed a mixture of signals corresponding to both the starting material and **2**.

Simplification of the $^1H$ NMR spectrum with respect to the Tp and $NMe_2$ signals was achieved through the addition of an excess of **1** (the $NH_3$ signal from **1** was still visible in the $^1H$ NMR spectrum). The three pyrazolyl rings are no longer equivalent in the $C_s$ symmetric product and the ring *trans* to the amidoborane has distinctly different spectroscopic characteristics. A pair of doublets, in the ratio 2 : 1, corresponding to the protons in the C5 positions are observed and a pair of triplet signals at significantly lower frequency are assigned to the protons attached to the C4 positions. There is also a doublet signal integrating to 2H at $\delta$ 7.52 ppm belonging to the proton on C3 for two of the pyrazolyl rings; the third C3 hydrogen atom signal was coincident with the solvent peak, (Fig. S1†). The $NH_2$ group gave a characteristic broad signal at $\delta$ 3.18 ppm similar to those previously observed.[4,5] The resonance for the dimethylamide ligands was found at $\delta$ 3.07 ppm, shifted to very slightly lower frequency relative to the starting material at $\delta$ 3.13 ppm. In this case the $^{19}F$ NMR spectrum displayed signals for both **1** and **2**. On the basis of these spectroscopic data, compound **2** was formulated as $TpTi(NMe_2)_2\{NH_2B(C_6F_5)_3\}$.

Attempts to isolate an analytically pure sample of **2** through fractional crystallization were frustrated by the similarity in solubility, across a range of solvents, between both starting materials and the products and as a result elemental analysis data were not obtained. A mixture of red and yellow crystals, which were not readily separated, was obtained from a solution containing an excess of $TpTi(NMe_2)_3$ in light petroleum. X-ray analysis revealed the red crystals to be the starting material $TpTi(NMe_2)_3$ which has previously been structurally characterized[15] and the yellow crystals to be **2** (Fig. 1).

Compound **2** exhibits a distorted octahedral geometry. The bond to the pyrazolyl ring of the Tp ligand *trans* to the amidoborane ligand (Ti(1)–N(1)) is significantly shorter than the other two Ti–N(Tp) bonds lengths (Table 1). This may be due to a greater *trans* influence of the amide ligands *versus* the amidoborane ligand. In the solid state $TpTi(NMe_2)_3$ is distorted such that one of the Ti–N(Tp) bonds is longer than the other two.[15] The two longer Ti–N(Tp) bonds in **2** are comparable to the shorter of the bond lengths observed in $TpTi(NMe_2)_3$. The amidoborane Ti–N bond (2.254(2) Å) is slightly longer than that observed for similar titanium amidoborane complexes (2.125(2)–2.170(2) Å) with the Ti–N(dimethylamido) bond lengths lying within the expected range.[4,5] Whilst the B–N bond length is unremarkable the Ti–N–B bond angle, at 139.44(12)°, is significantly larger than previously observed, even for the analogous $CpTi(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ complex (133.76(10)°).[5] The opening of the bond angle and the extension of the Ti–N bond are presumably due to steric interactions with the other ligands. Compound **2** is the first structurally characterized titanium amidoborane to exhibit a definitively octahedral geometry.[21] The hydrogen atoms of the amidoborane ligand participate in intramolecular hydrogen bonds

**Table 1** Selected bond lengths (Å) and angles (°); estimated standard deviations are in parentheses

| | **2** | **$4{\cdot}CH_2Cl_2$** | **6·pentane** |
|---|---|---|---|
| M(1)–N(1) | 2.163(2) | 2.299(2) | 2.308(7) |
| M(1)–N(11) | 2.254(2) | 2.396(2) | 2.356(6) |
| M(1)–N(21) | 2.276(2) | 2.421(2) | 2.362(7) |
| M(1)–N(31) | 1.903(2) | 2.037(2) | 2.052(6) |
| M(1)–N(41) | 1.900(2) | 2.017(2) | 2.004(7) |
| M(1)–N(51) | 2.215(2) | 2.347(2) | 2.386(7) |
| N(51)–B(52) | 1.596(3) | 1.596(3) | 1.596(12) |
| Mean B(52)–C | 1.659 | 1.656 | 1.661 |
| M(1)–N(51)–B(52) | 139.44(12) | 135.41(14) | 145.1(5) |

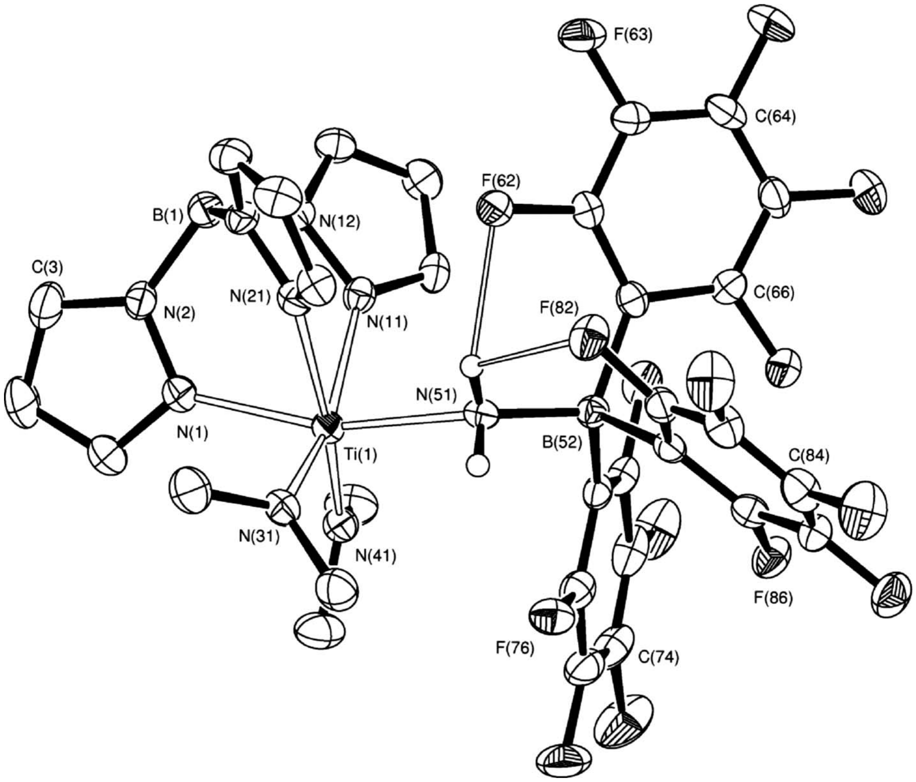


**Fig. 1** ORTEP of **2** with displacement ellipsoids drawn at the 50% probability level. Tp and methyl hydrogen atoms have been omitted for clarity.

to *o*-F atoms, one of which is a bifurcated intramolecular hydrogen bond to two *o*-F atoms, while the second hydrogen displays a somewhat longer intermolecular contact (2.41(2) Å) to an *o*-F atom of the third $C_6F_5$ ring. Similar interactions have been described for the solid state structure of **1** and other amine adducts[22,23] and intramolecular hydrogen bonding interactions are invariably present in related amidoborane complexes.[24]

The zirconium analogue of **2**, $TpZr(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (**4**) was prepared through the reaction of $TpZr(NMe_2)_3$ and **1** in toluene solution, following a similar procedure to that employed for **2**. Here too following the reaction by $^1H$ and $^{19}F$ NMR spectroscopy indicated incomplete conversion. Reaction of **1** with a slight excess of $TpZr(NMe_2)_3$ was sufficient for the reaction to reach completion with respect to **1**, yielding a clean $^{19}F$ NMR spectrum. For zirconium the solubility differences were such that pure **4** could be obtained as a yellow solid simply by washing with light petroleum.

The $^{19}F$ NMR spectrum of **4** gave one set of resonances indicating that the $C_6F_5$ groups are equivalent, which is consistent with unhindered rotation about the B–N bond. The chemical shift difference between the *para* and *meta* signals ($\Delta(\delta_{p\text{-}F} - \delta_{m\text{-}F})$) for the product was observed to be smaller and the peaks at lower frequency than in **1**; this is consistent with **2** and related amidoborane complexes and reflects greater anionic character.[4,5] The $^1H$ NMR spectrum includes pairs of doublets at $\delta$ 7.75 and 7.74 (C5) and 7.70 and 7.39 (C3), and a pair of triplet signals at $\delta$ 6.28 and 6.25 ppm (C4). For all three pairs the signals were in a 2 : 1 ratio, consistent with $C_s$ symmetry in solution. The dimethylamide methyl signal was observed at $\delta$ 2.70 ppm, with the $NH_2$ of the amidoborane at $\delta$ 3.06 ppm. Integration of these peaks against the Tp signals confirmed the substitution of only one dimethylamide ligand. Treatment with a further equivalent of **1** at room temperature did not result in the substitution of a second dimethylamide ligand. The $^{11}B$ NMR spectrum consisted of a broad signal assigned to the Tp boron atom, and a sharp singlet at lower frequency corresponding to the amidoborane boron atom.

Compound **4** was successfully crystallized from both light petroleum and dichloromethane/light petroleum solutions. X-ray diffraction studies revealed that both structures were in the space group $P2_1/n$ and the complexes are essentially isostructural. The minor differences in the unit cell parameters were a consequence of the solvent of crystallization and small variations in the solid state structure of **4**, Fig. 2. The results described here are those for the dichloromethane solvate the refinement of which was marginally better than that for the hexane solvate. The Tp ligand coordinates to one face of a distorted octahedral zirconium centre. The pyrazolyl ring *trans* to the amidoborane ligand displays a significantly shorter Zr–N bond length than the other two pyrazolyl rings, as observed for **2**. The Zr–N bond lengths to the dimethylamide ligands are slightly shorter than observed in the starting material[15] but are consistent with those observed for $Zr(NMe_2)_3(HNMe_2)\{NH_2B(C_6F_5)_3\}$.[4] The bond lengths found for **4·CH₂Cl₂** are very similar to those observed for the analogous complex $CpZr(NMe_2)_2\{NH_2B(C_6F_5)_3\}$; the Zr(1)–N(51) (amidoborate) bond length, at 2.347(2) Å in **4·CH₂Cl₂**, is only slightly longer than in the Cp analogue (2.3053(13) Å). The M–N–B bond angle is smaller in **4·CH₂Cl₂** than that observed for **2** which reflects the reduction in steric crowding at the larger metal centre. However, the Zr–N–B bond angle remains larger than the corresponding angle in the Cp complex.[4,5]

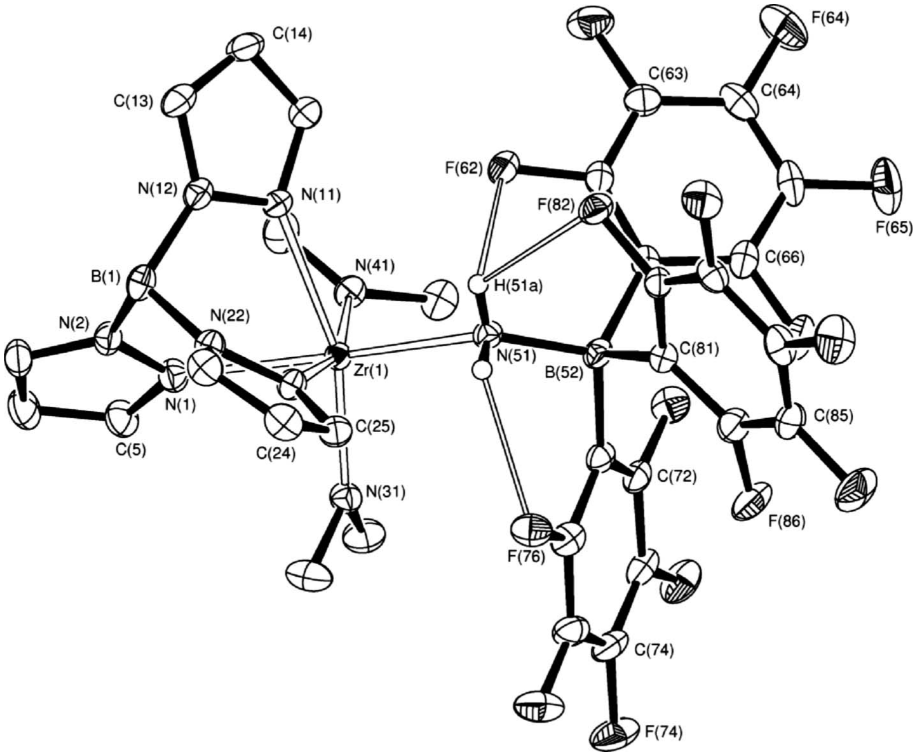


**Fig. 2** ORTEP of **$4\cdot CH_2Cl_2$**: the displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms not engaged in hydrogen bonding and the dichloromethane molecule have been omitted for clarity.

One of the $NH_2$ hydrogen atoms is involved in a single intramolecular hydrogen bond to an *o*-F atom whilst the other hydrogen atom forms a bifurcated hydrogen bond to two *o*-F atoms, one on each of the other two $C_6F_5$ rings (Table S1†).

The most obvious difference between the solid state structures of **2** and **4** is the orientation of the $(C_6F_5)_3B$ moiety with respect to the Tp ligand, as illustrated by the N(dimethylamide)–M–N(51)–B(52) torsion angles (Table 2). This is more easily demonstrated by representing the structures as Newman style projections, viewed along the N(51)–M bond, (Fig. 3). It should be noted that while the nitrogen is four-coordinate, the metal centre is six-coordinate, with approximately 90° angles, thus there are seven groups in the Newman projection of the metal complex that need to be considered. The conformation in **4** appears to minimize the steric interactions between the two bulky ligands but it does leave one of the $NH_2$ hydrogen atoms, H(51a), in an eclipsed configuration with N(11). In **2**, the Ti–$NH_2$ bond has been rotated by approximately 90° with respect to the dimethylamide ligands *versus* **4** and as a result H(51a) now eclipses N(21). This would suggest that the orientation of the $(C_6F_5)_3B$ group with respect to the Tp ligand is a result of the subtle influence of lattice packing forces rather than solely intramolecular steric interactions between groups bound to the metal and amido nitrogen.

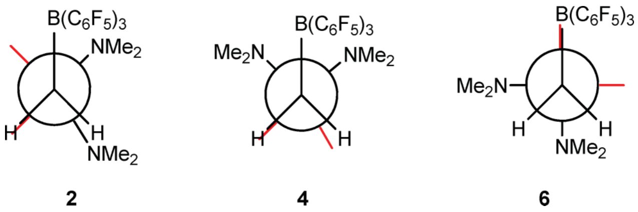


**Fig. 3** Newman style projections looking down the N(51)–M(1) bond. The Tp and Tp* nitrogen atoms *cis* to the $NH_2$ group are indicated in red but have not been labelled for clarity.

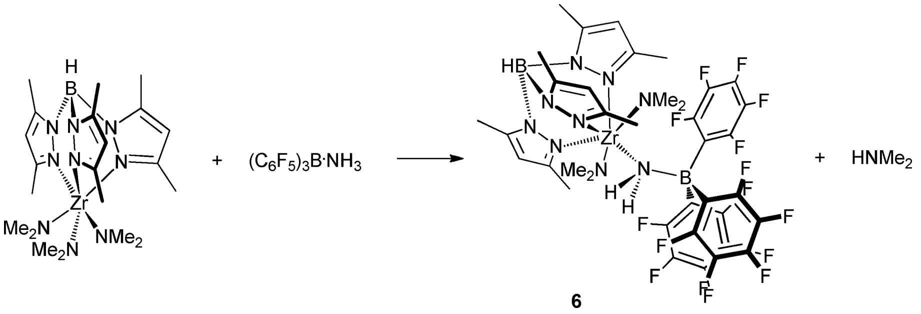
**Table 2** Selected torsion angles (°), estimated standard deviations are in parentheses

| | **2** | **$4\cdot CH_2Cl_2$** | **6·pentane** |
|---|---|---|---|
| N(31)–M(1)–N(51)–B(52) | 141.6(2) | 54.0(2) | −89.2(9) |
| N(41)–M(1)–N(51)–B(52) | 40.3(2) | −51.1(2) | 179.5(9) |

Short intramolecular C–H···F contacts are present in both **2** and **4** and must play a major role in the orientation of the $(C_6F_5)_3B$ group with respect to the Tp ligand. In **$4\cdot CH_2Cl_2$** there is one intramolecular short H···F contact (2.22(3) Å) from a pyrazolyl C3 hydrogen atom H(15) to an *o*-F atom F(62). In **2** a similar short H···F interaction, C(15)–H(15)···F(72) at 2.36(2) Å, is observed.[25]

The adduct **1** reacts with $TpHf(NMe_2)_3$ and, as observed for **4**, complete conversion to $TpHf(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (**5**) required the addition of a slight excess of $TpHf(NMe_2)_3$. The reaction was monitored by $^1H$ and $^{19}F$ NMR and, once complete, the volatiles were removed under reduced pressure and the resulting solid was washed with light petroleum to afford the pure product as a colourless solid. The $^1H$, $^{19}F$ and $^{11}B$ NMR data of **5** are in close agreement with those of **4** suggesting the solution state structure of **5** is essentially the same as that of **4**.

Following the method employed for the preparation of **2**, **1** was treated with one equivalent of $Tp^*Ti(NMe_2)_3$. In this case the $^1H$, $^{11}B$ and $^{19}F$ NMR spectra of the crude reaction



Scheme 3

mixture indicated a complex mixture of different products, which proved intractable. In light of the selective, if incomplete, reaction to form **2** and successful preparation of the Tp* zirconium complex described below it seems probable that the generation of Tp*Ti(NMe$_2$)$_2${NH$_2$B(C$_6$F$_5$)$_3$} is disfavoured on steric grounds leading to a number of possible competing reaction pathways.[26]

Tp*Zr(NMe$_2$)$_3$ and **1** react to form Tp*Zr(NMe$_2$)$_2$-{NH$_2$B(C$_6$F$_5$)$_3$} (**6**) (Scheme 3) and, as found with the substituent-free tris(pyrazolyl)borate systems **4** and **5**, the use of a small excess of Tp*Zr(NMe$_2$)$_3$ facilitates the isolation of analytically pure **6** as yellow crystals. The $^1$H NMR spectra of the product showed two singlets in the ratio 2 : 1 at $\delta$ 5.68 and 5.75 ppm, which corresponded to the CH group at C4 of the pyrazolyl ring. Two pairs of singlets in the 2 : 1 ratio were observed at $\delta$ 2.39 and 2.33 ppm and $\delta$ 2.11 and 1.93 ppm corresponding to the methyl signals from the pyrazolyl rings of the $C_s$ symmetric Tp* complex, the signal at higher frequency presumably being due to the methyl group on C3. The signal for the methyl groups of the dimethylamide ligand in **6** was observed as a sharp singlet at slightly higher frequency ($\delta$ 2.88 ppm) than observed for **4** ($\delta$ 2.70 ppm). The $^{19}$F NMR spectrum of **6** displays one set of three signals: the *o*-F signal is in close agreement with **4**, while the *p*-F and *m*-F signals are found at slightly lower frequencies. The $^{11}$B NMR displays a singlet peak belonging to the (C$_6$F$_5$)$_3$B boron atom at $\delta$ −7.9 while the BH peak is very broad, almost disappearing into the baseline at $\delta$ −9.2 ppm; the BH coupling could not be resolved.

The solid state structure of **6** was elucidated by X-ray diffraction methods (Fig. 4) and contains a disordered solvent molecule (believed to be *n*-pentane) in the crystal lattice. As observed for the Tp analogues, the zirconium centre in **6** exhibits a distorted octahedral geometry with the expected facial Tp* coordination geometry. The Zr–N bond lengths to the Tp* ligand are all shorter than observed in the starting material[15] and display the now familiar pattern with the Zr–N bond length to the pyrazolyl ring *trans* to the amidoborate ligand (2.308(7) Å) being significantly shorter than the other two bonds to the Tp* ligand. The bonding parameters for the dimethylamide ligands are consistent with those

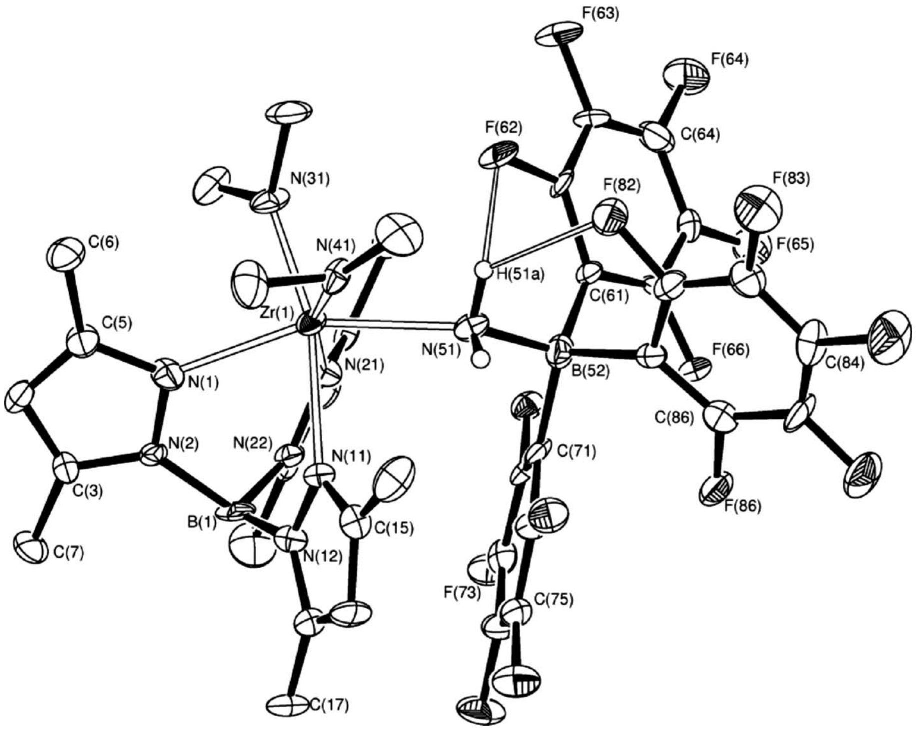


**Fig. 4** ORTEP of **6** drawn at the 40% probability level. The disordered solvent molecule and hydrogen atoms not bonded to nitrogen have been omitted for clarity.

of the zirconium amidoboranes previously reported.[4,5] The Zr(1)–N(51) bond (2.386(7) Å) in **6** is slightly longer than observed for **4**, presumably as a result of increased steric hindrance at the metal centre. This also accounts for the Zr–N–B bond angle at 145.1(5)° being far larger than those observed previously. The N–B bond length is consistent with those other complexes reported herein.

The solid state structure of **6** displays a similar hydrogen bonding pattern to that observed for **2**, Table S1.† One of the $NH_2$ hydrogen atoms participates in a bifurcated intramolecular hydrogen bond to two *o*-F atoms while the other makes a rather longer contact to an *o*-F atom of the third $C_6F_5$ ring.[27] The $(C_6F_5)_3B$ group eclipses one of the 3,5-dimethylpyrazolyl rings (Fig. 3), which is surprising considering the increased steric bulk of the Tp* ligand and the apparent absence of any notable intramolecular interactions.[28]

## Conclusion

The triamides $TpM(NMe_2)_3$ (M = Ti, Zr and Hf) react with $(C_6F_5)_3B{\cdot}NH_3$ in toluene to form tris(pyrazolyl)borate amidoborane complexes of the form $TpM(NMe_2)_2\{NH_2B(C_6F_5)_3\}$. Structural analysis of the titanium and zirconium complexes revealed the expected distorted octahedral geometries.

The chemistry proceeds similarly for the Tp* complex of zirconium and the solid state structure of **6** is similar to the Tp complex, **4**, with the differences being attributable to the greater steric demands of the Tp* *vs.* Tp ligands. In contrast, the analogous Tp*Ti complex proved inaccessible and attempted synthesis led only to a complex product mixture.

In summary, steric limitations notwithstanding, $Tp'M(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ complexes are both accessible and relatively stable. We have seen no evidence for further amine elimination and the formation of imido or nitridoborane complexes.

## Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques in pre-dried glassware. Solvents were dried using an appropriate drying agent and distilled under nitrogen prior to use: dichloromethane ($CaH_2$), light petroleum (Na/K alloy or sodium/dyglyme/benzophenone) and toluene (sodium). Samples for NMR analysis were prepared using degassed deuterated solvents dried over activated 4 Å molecular sieves. NMR spectra were obtained using a Bruker Avance DPX300 spectrometer at 22 °C, *J* values are given in Hz. Chemical shifts are reported in ppm and referenced to residual solvent resonances ($^1H$, $^{13}C\{^1H\}$); $^{19}F$ is relative to $CFCl_3$; $^{11}B$ is relative to $Et_2O{\cdot}BF_3$. Elemental analyses were carried out at Medac Ltd and at the Department of Health and Human Sciences, London Metropolitan University. The syntheses of $(C_6F_5)_3B$, $(C_6F_5)_3B{\cdot}NH_3$, $TpTi(NMe_2)_3$, $TpZr(NMe_2)_3$, $TpHf(NMe_2)_3$, $Tp^*Ti(NMe_2)_3$ and $Tp^*Zr(NMe_2)$ were conducted according to the literature procedures.[10,15,22,29–31]

### $HB(C_3H_3N_2)_3Ti(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (2)

$TpTi(NMe_2)_3$ (0.39 g, 1 mmol) and $(C_6F_5)_3B{\cdot}NH_3$ (0.53 g, 1 mmol) were dissolved in toluene (80 $cm^3$) and nitrogen was bubbled through the solution for a period of 4 h. The volatiles were removed under vacuum and the product extracted with light petroleum. Cooling the solution to –25 °C yielded a mixed crop of red crystals of the titanium starting material and yellow crystals of the product $TpTi(NMe_2)_2\{NH_2B(C_6F_5)_3\}$, **2**. Due to the separation problems discussed above satisfactory elemental analysis results could not be obtained. $\delta_H$/ppm (300.1 MHz, $CDCl_3$) 7.74 (1H, d, $J_{HH}$ 1.8, CH, C5), 7.70 (2H, d, $J_{HH}$ 2.1, CH, C5), 7.52 (2H, d, $J_{HH}$ 2.0, CH, C3), 6.24 (1H, t, $J_{HH}$ 2.2, CH, C4), 6.19 (2H, t, $J_{HH}$ 2.2, CH, C4), 3.18 (2H, br, $NH_2$), 3.07 (12H, s, $NCH_3$). $\delta_C$/ppm (75.5 MHz, $CDCl_3$) 141.4 (CH), 139.8 (CH), 135.4 (CH), 135.1(CH), 105.8 (CH), 105.5 (CH), 49.4 ($CH_3$). $\delta_B$/ppm (96.3 MHz, $CDCl_3$) –3.36 (1B, br, BH), –7.69 (s, $(C_6F_5)_3B$). $\delta_F$/ppm (282.4 MHz, $CDCl_3$) –132.7 (6F, d, $^3J_{FF}$ 21, *o*-F), –159.3 (3F, t, $J_{FF}$ 21, *p*-F), –164.3 (6F, m, *m*-F).

### $\{HB(C_3H_3N_2)_3Ti(NMe_2)_2\}_2\{\mu\text{-}O\}$ (3)

During an attempt to repeat the preparation of **2**, following the general procedure outline above but using dichloromethane as the solvent, adventitious water was introduced to yield the μ-O species and regenerate $(C_6F_5)_3B{\cdot}NH_3$. Elemental analysis found: C 43.6, H 6.1, N 31.3. Calculated for $C_{26}H_{44}B_2N_{16}OTi_2$: C 43.7, H 6.2, N 31.4. $\delta_H$/ppm (300.1 MHz, $CDCl_3$) 7.74 (4H, m, CH), 7.57 (2H, d, $J_{HH}$ 2.2, CH), 6.27 (1H, t, $J_{HH}$ 2.2, CH), 6.11 (2H, t, $J_{HH}$ 2.1, CH), 3.42 (12H, s, $NCH_3$). $\delta_C$/ppm (75.5 MHz, $CDCl_3$) 142.3 (CH), 140.9 (CH), 134.6 (CH), 134.0 (CH), 105.0 (CH), 104.5 (CH), 50.33 ($CH_3$). $\delta_B$/ppm (96.3 MHz, $CDCl_3$) –3.88 (d, $J_{BH}$ 112).

### $HB(C_3H_3N_2)_3Zr(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (4)

A combination of $TpZr(NMe_2)_3$ (5.10 g, 11.7 mmol) and $(C_6F_5)_3B{\cdot}NH_3$ (5.69 g, 10.8 mmol) was dissolved in toluene (180 $cm^3$) and nitrogen was bubbled through the solution for four hours. The volatiles were removed under reduced pressure and the crude product obtained as a foam which was washed with light petroleum to yield a yellow solid (6.87 g, 6.9 mmol, 64%). X-ray quality crystals were grown by cooling the light petroleum washings to –25 °C (**4·hexane**), or by recrystallization of the product from a dichloromethane/light petroleum solution at –25 °C (**4·$CH_2Cl_2$**). Elemental analysis found: C 40.3, H 2.7, N 13.6. Calculated for $C_{31}H_{24}B_2F_{15}N_9Zr$: C 40.5, H 2.6, N 13.7. $\delta_H$/ppm (300.1 MHz, $CDCl_3$) 7.75 (2H, d, $J_{HH}$ 2.2 CH), 7.74 (1H, d, $J_{HH}$ 2.1, CH), 7.70 (2H, d, $J_{HH}$ 2.0, CH), 7.39 (1H, d, $J_{HH}$ 1.8, CH), 6.28 (2H, t, $J_{HH}$ 2.1, CH), 6.25 (1H, t, $J_{HH}$ 2.1, CH) 3.06 (2H, br, $NH_2$) 2.70 (12H, s, $CH_3$). $\delta_C$/ppm (75.5 MHz, $CDCl_3$) 142.9 (CH), 141.2 (CH), 136.5 (CH), 136.2 CH), 106.0 (CH), 105.9 (CH), 43.00($CH_3$). $\delta_B$/ppm (96.3 MHz, $CDCl_3$) –3.13 (br, BH), –8.24 ($(C_6F_5)_3B$). $\delta_F$/ppm (282.4 MHz, $CDCl_3$) –133.3 (6F, m, *o*-F), –159.0 (3F, t, $J_{FF}$ 20, *p*-F), –164.1 (6F, m, *m*-F).

### $HB(C_3H_3N_2)_3Hf(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (5)

Samples of $(C_6F_5)_3B{\cdot}NH_3$ (0.53 g, 1 mmol) and $TpHf(NMe_2)_3$ (0.52 g, 1 mmol) were combined and dissolved in toluene (20 $cm^3$), the solution was stirred at room temperature and the reaction monitored by $^1H$ and $^{19}F$ NMR spectroscopy. The volatiles were removed by vacuum distillation to yield the crude product as a colourless foam. This was then washed with light petroleum to yield the pure product as a colourless solid (0.61 g, 0.6 mmol, 61%). Elemental analysis found: C 36.9, H 2.3, N 12.5. Calculated

**Table 3** Crystallographic data

| | **2** | **4·hexane** | **$4\cdot CH_2Cl_2$** | **6·pentane** |
|---|---|---|---|---|
| Chemical formula | $C_{31}H_{24}B_2F_{15}N_9Ti$ | $C_{31}H_{24}B_2F_{15}N_9Zr$, $C_6H_{14}$ | $C_{31}H_{24}B_2F_{15}N_9Zr$, $CH_2Cl_2$ | $C_{37}H_{36}B_2F_{15}N_9Zr$, $C_5H_{12}$ |
| M | 877.1 | 1006.6 | 1005.4 | 1076.7 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $I2/a$<br>(equiv. to no. 15) | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 27.3497(5) | 12.6960(4) | 12.9240(2) | 11.2726(5) |
| $b$/Å | 12.7238(2) | 24.1645(8) | 23.2383(3) | 11.8733(6) |
| $c$/Å | 21.1149(4) | 14.1775(5) | 13.4537(3) | 17.9169(8) |
| $\alpha$ (°) | 90 | 90 | 90 | 80.540(4) |
| $\beta$ (°) | 95.083(2) | 105.824(3) | 103.201(2) | 89.161(4) |
| $\gamma$ (°) | 90 | 90 | 90 | 81.252(4) |
| $V$/Å$^3$ | 7318.9(2) | 4184.7(2) | 3933.80(12) | 2337.8(2) |
| $T$/K | 140(1) | 140(1) | 140(1) | 140(1) |
| $Z$ | 8 | 4 | 4 | 2 |
| $\theta$ max/° | 27.5 | 25 | 27.5 | 22.5 |
| Reflections measured | 52275 | 44382 | 53224 | 18358 |
| Unique reflections, $R_{int}$ | 8377, 0.054 | 7352, 0.073 | 9024, 0.049 | 6062, 0.159 |
| Observed data | 4887 | 5407 | 6101 | 3533 |
| w$R_2$, $R_1$ (observed data) | 0.072, 0.033 | 0.088, 0.052 | 0.070, 0.032 | 0.118, 0.086 |
| w$R_2$, $R_1$ (all data) | 0.083, 0.068 | 0.099, 0.082 | 0.078, 0.059 | 0.146, 0.171 |
| Largest difference peak | 0.31 | 0.57 | 0.75 | 0.47 |

for $C_{31}H_{24}B_2F_{15}HfN_9$: C 36.95, H 2.4, N 12.5. $\delta_H$/ppm (300.1 MHz, $CDCl_3$) 7.77 (2H, d, $J_{HH}$ 2.1, CH), 7.75 (1H, d, $J_{HH}$ 2.2, CH), 7.68 (2H, d, $J_{HH}$ 2.1, CH), 7.46 (1H, d, $J_{HH}$ 2.0, CH), 6.28 (1H, t, $J_{HH}$ 2.3, CH), 6.27 (2H, t, $J_{HH}$ 2.2, CH), 3.17 (2H, br, $NH_2$), 2.77 (12H, s, $CH_3$). $\delta_C$/ppm (75.5 MHz, $CDCl_3$) 143.3 (CH), 141.5 (CH), 136.6 (CH), 106.1 (CH), 43.00 ($CH_3$). $\delta_B$/ppm (96.3 MHz, $CDCl_3$) −3.12 (br, BH), −8.09 (s, $(C_6F_5)_3B$). $\delta_F$/ppm (282.4 MHz, $CDCl_3$) −133.3 (6F, d, $J_{FF}$ 23, *o*-F), −158.9 (3F, t, $J_{FF}$ 21, *p*-F), −164.1 (6F, m, *m*-F).

### $HB(C_5H_7N_2)_3Zr(NMe_2)_2\{NH_2B(C_6F_5)_3\}$ (6)

Samples of $(C_6F_5)_3B\cdot NH_3$ (0.79 g, 1.5 mmol) and $Tp^*Zr(NMe_2)_3$ (0.77 g, 1.5 mmol) were combined and dissolved in toluene (180 cm$^3$). The reaction was stirred at room temperature until the $^{19}$F NMR indicated that the major component in solution was the desired product (*ca.* 13 h). The volatiles were removed under reduced pressure and the product extracted with light petroleum and cooled to −25 °C whereupon an impure yellow precipitate separated. The pure product was obtained in very low yield by recrystallization from dichloromethane/light petroleum (0.03 g, 0.03 mmol, 2%). Elemental analysis found: C 44.1, H 3.5, N 12.6. Calculated for $C_{37}H_{36}B_2F_{15}N_9Zr$: C 44.2, H 3.6, N 12.6. $\delta_H$/ppm (300.1 MHz, $CDCl_3$): 5.75 (1H, s, CH), 5.68 (2H, s, CH), 3.05 (2H, br, $NH_2$), 2.88 (12H, $NCH_3$), 2.39 (6H, s, $CH_3$), 2.33 (3H, s, $CH_3$), 2.11 (3H, s, $CH_3$), 1.93 (6H, s, $CH_3$). $\delta_B$/ppm (96.3 MHz, $CDCl_3$): −7.90 (s, $(C_6F_5)_3B$), −9.20 (br, BH). $\delta_F$/ppm (282.4 MHz, $CDCl_3$): −133.2 (6F, d, $J_{FF}$ 23, *o*-F), −159.6 (3F, t, $J_{FF}$ 21, *p*-F), −164.9 (6F, m, *m*-F). Collection of $^{13}$C NMR data was precluded by the extremely low yield and priority was given to providing sufficient material for crystallography and elemental analysis.

## Crystal Structure Analyses

Diffraction data were collected at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer, and processed using the CrysAlis-CCD and RED programs.[32] In each case, the structure was determined by direct method routines in the SHELXS program and refined by full-matrix least-squares methods on $F^2$ in SHELXL[33] within the WinGX program suite.[34] The results are collated in Table 3. Scattering factors for neutral atoms were taken from literature values.[35]

Full resolution of the structure of **4·hexane** was hindered by a poorly defined solvent molecule, presumed to be hexane, within the crystal lattice. A full solution for the solvent molecule could not be obtained as four carbon atoms were identified but disordered over two positions and kept isotropic while two further carbon atoms were located and refined anisotropically but displayed very large displacement parameters. The six identified carbon atoms did not link together in any sensible fashion to form a recognizable molecule; furthermore location of these additional part atoms was restricted due to low quality data. Hydrogen atoms for the solvent molecule were therefore not included in the model but have been included in the molecular formula.

Recrystallization of **4** from a dichloromethane/light petroleum solution at −25 °C provided a crop of colourless crystals (**$4\cdot CH_2Cl_2$**). Analysis by X-ray diffraction techniques illustrated both **4·hexane** and **$4\cdot CH_2Cl_2$** crystallizing in the same space group, the unit cell dimensions being slightly different due to the presence of a well resolved dichloromethane molecule in the crystal lattice of **$4\cdot CH_2Cl_2$**. The structures of the zirconium complexes in both **4·hexane** and **$4\cdot CH_2Cl_2$** are very similar but are not perfectly isostructural. The most noteworthy differences occur in the angles about zirconium, with the N(41)–Zr(1)–N(1) angle differing by over 2°. The bond lengths about the zirconium atom and the Zr–N–B bond angle in **$4\cdot CH_2Cl_2$** agree with those in **4·hexane** within experimental error and in **$4\cdot CH_2Cl_2$** there are no interactions with the dichloromethane solvent molecule.

All the hydrogen atoms within the zirconium complex in both structures **4·hexane** and **$4\cdot CH_2Cl_2$** were located in difference maps and refined freely. Both structures exhibit the same hydrogen bonding arrangement, with the hydrogen bond lengths and angles in good agreement.

Full structure resolution of the solvent molecule in **6·pentane**, presumed to be a pentane fraction from light petroleum, proved impossible due to its highly disordered nature. Five carbon atoms were located in difference maps, two of which have been modelled over two positions, to form a straight alkyl chain. All carbon atoms were modelled anisotropically. The hydrogen atoms have not been modelled but have been included in the formula. A low cut-off value for theta was used due to there being no reliable/significant intensity data beyond this value.

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