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## COMMUNICATION

## The hafnium-mediated NH activation of an amido-borane<sup>†</sup>

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Treatment of Cp<sub>2</sub>HfCl<sub>2</sub> with two equivalents of LiNH<sub>2</sub>BH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> in toluene solution yields Cp<sub>2</sub>Hf{NHBH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}, which has been crystallographically characterised. The otherwise base-free [NHBH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] complex is stabilised by an agostic interaction.

Group 4 metallocene complexes have recently been demonstrated to be effective for the catalytic dehydrogenation of amine–borane adducts. Manners and co-workers have proposed a titanium amidoborane hydride, stabilised by agostic B–H····Ti interactions, as an intermediate in the catalytic cycle.<sup>1</sup> Roesler *et al.* have isolated the zirconium amidoborane hydride, Cp<sub>2</sub>Zr(H)NH<sub>2</sub>BH<sub>3</sub> which also has an agostic β–H interaction.<sup>2</sup>

We have shown that amidoborane complexes of all the group 4 metals are accessible through the reaction of the Brønsted acidic adduct  $H_3N \cdot B(C_6F_5)_3$  with metal bases.<sup>3</sup> In particular circumstances, further NH activation resulted in the formation of nitridoborane complexes.<sup>4</sup>

We have recently developed a convenient synthesis of the dimethylsulfide adduct of bis(pentafluorophenyl)borane.<sup>5</sup> This adduct undergoes facile donor exchange with ammonia to yield  $H_3N \cdot BH(C_6F_5)_2$  (1) (Scheme 1).† Herein we communicate the first complexes of the  $[NH_2BH(C_6F_5)_2]$  ligand and the subsequent NH activation to form a remarkable imidoborane hafnium complex.

Treatment of a toluene solution of 1 with *n*-BuLi results in deprotonation and formation of the lithium salt [Li]



Scheme 1 The synthesis of complexes 1–4.

 $[NH_2BH(C_6F_5)_2]$  (2). The identity of 2 was confirmed through crystallisation of the 12-crown-4 chelate.†

Following similar reaction conditions to those described for the synthesis of Cp<sub>2</sub>Zr(Cl)NH<sub>2</sub>BH<sub>3</sub>,<sup>2</sup> the treatment of Cp<sub>2</sub>ZrCl<sub>2</sub> with one equivalent of the thf solvate of **2** in toluene solution between -78 °C and room temperature resulted in a product mixture giving an extremely complex <sup>1</sup>H NMR spectrum with at least seven resonances in the cyclopentadienyl region alone. Under these conditions, similarly complex spectra were obtained in the analogous reaction with Cp<sub>2</sub>HfCl<sub>2</sub>. However, on one occasion we were able to isolate a very small quantity of a crystalline material from a thf/light petroleum solvent mixture. Single crystal X-ray diffraction revealed the hafnocene bis(amidoborane), Cp<sub>2</sub>Hf{NH<sub>2</sub>BH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}<sub>2</sub> (**3**) as a tetrahydrofuran (thf) solvate, the structure of which is described below. All attempts to reproduce the synthesis and isolation of **3** have proven unsuccessful.<sup>6</sup>

The elusive nature of compound 3 was addressed by the screening of a series of alternative reaction conditions. In one such experiment the treatment of Cp2HfCl2 with two equivalents of the ether-free salt 2 in toluene between -78 °C and room temperature resulted in a crude reaction mixture giving only three resonances in the cyclopentadienyl region of the <sup>1</sup>H NMR spectrum, indicating three components in the crude reaction mixture (Fig. S3, ESI<sup> $\dagger$ </sup>). At  $\delta$  5.29, 5.28 and 5.16 all three signals were found at lower frequency than Cp<sub>2</sub>HfCl<sub>2</sub>, which was not evident in the spectrum. Fractional crystallisation from mixtures of toluene and light petroleum yielded colourless blocks. Characterisation by multinuclear NMR spectroscopy indicated the formation of a new hafnocene complex, with the signal at  $\delta$  5.16 proving to belong to the isolated crystals. Broad <sup>1</sup>H NMR resonances at  $\delta$  7.59 and -0.83 were consistent with NH and BH groups, respectively, but did not give the expected integration for thf-free 3. The <sup>11</sup>B and <sup>19</sup>F NMR spectra were consistent with a single BH( $C_6F_5$ )<sub>2</sub> environment. The structure was ultimately determined by X-ray diffraction methods revealing 4 as the hafnocene complex  $Cp_2Hf{NHBH(C_6F_5)_2}$ . In contrast to 3, the synthesis of 4 has proven to be fully reproducible.<sup>‡</sup>

Fig. 1 shows the structure of the bis(amidoborane) complex 3.<sup>7</sup> There are two thf molecules within the crystal lattice. There are a further two thf molecules (one of which is disordered over two positions), engaged in hydrogen bonding to the  $NH_2$  groups (Table S1, ESI†). The second hydrogen atom on each  $NH_2$  group is involved in an intramolecular hydrogen bond to an *o*-F atom.<sup>8</sup>

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Compounds 1–4, ORTEP figures for 1 and 2, a table of hydrogen bonds for 3, a <sup>1</sup>H NMR spectrum of the crude reaction mixture for 4, synthetic details for compounds 1, 2 and 3. CCDC 814619–814622. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11320h



Fig. 1 ORTEP representation of the structure of 3·4(thf) showing 50% probability ellipsoids; two molecules of thf, and hydrogen atoms on the Cp ring and thf molecules have been omitted for clarity. Selected distances [Å] and angles [°]: Hf(1)–N(11) 2.283(2), Hf(1)–N(41) 2.249(2), Hf(1)–centroid[C(1)–C(5)] 2.501(3), Hf(1)–centroid[C(6)–C(10)] 2.498(3), Hf(1)···H(42) 2.09(3), N(11)–B(12) 1.592(4), N(41)–B(42) 1.538(4); N(11)–Hf(1)–N(41) 77.30(8), centroid[C(1)–C(5)]–Hf(1)–centroid[C(6)–C(10)] 131.11, B(12)–N(11)–Hf(1) 122.05(17), B(42)–N(41)–Hf(1) 90.98(15).

The bonding of the Cp<sub>2</sub>Hf fragment is unremarkable. The amidoborane ligands exhibit distorted tetrahedral geometries about the nitrogen centres. For Hf(1)–N(11)–B(12) the angle is 122.05(17)°, which is more obtuse than the tetrahedral ideal but smaller than the 135.14(17)° found for Cp<sub>2</sub>Hf(CH<sub>3</sub>){NH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>},<sup>3b</sup> reflecting the intermediate steric demands of the borane. While the two Hf–N bond lengths are similar, the second Hf(1)–N(41)–B(42) angle is only 90.98(15)°. This dramatic distortion is the result of a  $\beta$ -agostic Hf–H interaction.

Fig. 2 depicts the solid state structure of complex, 4 PhMe. There is a single  $[NHBH(C_6F_5)_2]$  ligand coordinated in the



Fig. 2 ORTEP representation of the structure of 4-PhMe showing 50% probability ellipsoids; hydrogen atoms except for H(1b) and H(1n) and a toluene molecule have been omitted for clarity. Selected distances [Å] and angles [°]: Hf(1)–N(1) 2.282(6), Hf(1)–centroid[C(1)–C(5)] 2.486(8), Hf(1)–centroid[C(1)–C(5)] 2.449(10), Hf(1)-···H(1b) 2.10(6), N(1)–B(1) 1.509(10), centroid[C(1)–C(5)]–Hf(1)–centroid[C(6)–C(10)] 133.65, B(1)–N(1)–Hf(1) 86.7(4).



Chart 1 Resonance forms of compound 4.

wedge between the two cyclopentadienyl groups. While a hydrogen atom was located on the boron atom, the data did not suffice to crystallographically locate hydrogen bound to nitrogen. The presence of a single hydrogen atom on nitrogen was inferred by the requirement for charge balance with the  $[Cp_2Hf]^{2+}$  fragment and the structure modelled accordingly. This treatment is supported by the single proton integration of the resonance at  $\delta$  7.59 ppm in the <sup>1</sup>H NMR spectrum. The coordination environment of the hafnium atom is completed by the agostic interaction described below. Formulation of the  $[NHBH(C_6F_5)_2]$  ligand as an imidoborane is at odds with the observation that at 2.282(6) Å the Hf-N distance is similar to that found for **3** and  $Cp_2Hf(CH_3)\{NH_2B(C_6F_5)_3\}$  and substantially longer than those previously reported for hafnium imides.<sup>9</sup> A number of resonance forms can be drawn for complex 4 (A–C, Chart 1).<sup>10</sup> The pattern of relatively long Hf–N, short B-N and long Hf-H distances suggest that, rather than A, the greatest contribution is from resonance structure **B**.

Despite this distinction the  $[NHBH(C_6F_5)_2]$  group can be formally regarded as a Lewis acid stabilised terminal (NH) imido ligand. We have now been able to demonstrate the successful stabilisation of substituent-free terminal amido, imido and nitrido groups through this strategy.<sup>3,4</sup> Perhaps even more remarkable is that in addition to the bulky nitrogen substituent those previously structurally characterised examples of terminal imido zirconocene and hafnocene complexes also required basic donor ligands. In **4** this role is taken by the agostic BH group.

Compounds **3** and **4** are rare examples of structurally characterised hafnium complexes with agostic interactions. At 2.09(3) Å and 2.10(6) Å the H–Hf distances are very close to the sum of the covalent radii.<sup>11,12</sup> In **3** particularly there are similarities to the bonding patterns seen in  $Cp_2ZrX\{NH_2BH_3\}$  (where X = H, Cl).<sup>2</sup> A titanium complex in which there is an agostic interaction with a BH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> fragment has been reported.<sup>13</sup> While the B–H distance for the agostic hydride in **4** is not significantly different from that in **1**, the reduction in the BH coupling constant from 112 Hz in **1** to 63 Hz in **4** is consistent with a weakening of the B–H bond.<sup>14</sup>

The isolation of **4** in respectable yield requires the treatment of  $Cp_2HfCl_2$  with two equivalents of **2**. The first step is presumably a metathesis reaction to yield  $Cp_2Hf(Cl)\{NH_2BH(C_6F_5)_2\}$  (I) (Scheme 2). From I, three mechanisms can be envisaged for the generation of **4** (i–iii). In (i) the second equivalent of **2** functions as a base, deprotonating I and eliminating LiCl to generate **4**. If instead the second equivalent also reacts through a metathesis pathway with I the result will be the hafnocene bis(amidoborane) (**3**). Roesler *et al.* proposed essentially the same mechanism to form  $Cp_2Zr(NH_2BH_3)_2$ ; however, these complexes were believed to be unstable with respect to  $\beta$ -hydride elimination and the formation of amidoborane hydrides  $Cp_2Zr(H)(NH_2BH_3)$ .<sup>2</sup> If the current system follows



Scheme 2 Three proposed mechanisms (i-iii) for formation of 4.

an analogous pathway (ii) the formation of 4 follows from the resulting hafnocene amidoborane hydride (II) undergoing an intramolecular  $\alpha$ -NH activation eliminating H<sub>2</sub>. However, we recognise that 3 may also be an intermediate for direct  $\alpha$ -NH activation and formation of 4 through elimination of  $H_3N \cdot BH(C_6F_5)_2$  (mechanism (iii)). Distinguishing between the mechanisms is not straightforward. The yield of 4 is not quantitative and the crude reaction mixture invariably contains  $H_3N \cdot BH(C_6F_5)_2$  because this is the ultimate product of hydrolysis of all the hafnium complexes in Scheme 2 and therefore its presence does not immediately discount mechanism (ii).  $[H_2NB(C_6F_5)_2]_n$  the putative  $\beta$ -hydride elimination product from mechanism (ii) has not been unequivocally identified but the <sup>19</sup>F NMR spectrum of the crude reaction mixture includes additional resonances which may be consistent with this material. This point requires further investigation.

In summary, two equivalents of  $[Li][NH_2BH(C_6F_5)_2]$ react with Cp<sub>2</sub>HfCl<sub>2</sub> to yield the remarkable imidoborane complex Cp<sub>2</sub>Hf{NHBH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>} (4). Compound 4 and the crystallographically characterised bis(amidoborane) 3 are stabilised by agostic interactions. Confirmation of the mechanism of formation of 4 and determination of its reactivity are the subjects of current investigation. We aim to establish whether the reaction proceeds through a bis(amidoborane) intermediate, and if so to determine the conditions under which it can be stabilised by thf solvation or whether Cp<sub>2</sub>Hf{NH<sub>2</sub>BH(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}-4thf (3) is simply a by-product obtained when the reaction is conducted in the presence of tetrahydrofuran.

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## Notes and references

‡ Synthesis and characterisation of **4**. All manipulations were performed under dry and oxygen-free nitrogen using Schlenk-line techniques. Toluene and light petroleum were dried over appropriate drying agents (Na, Na/dyglyme respectively), and distilled under nitrogen prior to use. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR spectra were recorded on a Bruker DPX 300, *J* values are given in Hz. Chemical shifts are reported in  $\delta$  units downfield from TMS (<sup>1</sup>H, <sup>13</sup>C), CFCl<sub>3</sub> (<sup>19</sup>F), Et<sub>2</sub>O-BF<sub>3</sub> (<sup>11</sup>B), with the solvent as the reference. Elemental analyses were carried out at the London Metropolitan University.

A thf-free solution of  $[Li][NH_2BH(C_6F_5)_2]$  (0.71 g, 1.92 mmol) in toluene (10 cm<sup>3</sup>) was cooled to -78 °C and treated with a solution of Cp<sub>2</sub>HfCl<sub>2</sub> (0.36 g, 0.96 mmol) in toluene (10 cm<sup>3</sup>). The reaction was left to stir at -78 °C for two hours before warming to room temperature. The solvent was removed under reduced pressure and the crude product extracted with toluene (20 cm<sup>3</sup>). Colourless crystals were obtained by concentrating the toluene solution, layering with light petroleum and cooling to -25 °C for 3 days (0.07 g, 0.10 mmol, 11%). Elemental analysis (%): Found: C, 39.37; H, 1.69; N, 1.97. Calculated for C<sub>22</sub>H<sub>12</sub>BF<sub>10</sub>NHf: C, 39.46; H, 1.81; N, 2.09.  $\delta_{\rm H}/{\rm ppm}$  (300.1 MHz, 293 K, C<sub>7</sub>D<sub>8</sub>): 7.59 (1H, s NH), 5.17 (10H, s, C<sub>5</sub>H<sub>5</sub>), -0.83 (1H, q,  $J_{\rm B,H}$  60, BH).  $\delta_{\rm C}/{\rm ppm}$  (75.5 MHz, C<sub>7</sub>D<sub>8</sub>):  $\delta$  103.6 (C<sub>5</sub>H<sub>5</sub>).  $\delta_{\rm B}/{\rm ppm}$  (96.3 MHz, 293 K, C<sub>7</sub>D<sub>8</sub>): -27.5 (d,  $J_{\rm B,H}$  63).  $\delta_{\rm F}/{\rm ppm}$  (282.4 MHz, 293 K, C<sub>7</sub>D<sub>8</sub>): -133.7 (4F, br, *o*-F), -156.3 (2F, t,  ${}^{3}J_{\rm E,\rm F}$  21, *p*-F), -162.4 (4F, br, *m*-F).

Crystals were suspended in oil, mounted on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo-K $\alpha$  radiation and graphite monochromator. Intensity data were measured by  $\omega$ -scans.

Crystal data for 3·4thf:  $C_{34}H_{16}$  B<sub>2</sub>F<sub>20</sub>HfN<sub>2</sub>, 4(C<sub>4</sub>H<sub>8</sub>O), M = 1321.01, Monoclinic, space group  $P_{21/n}$ , a = 13.4352(3) Å, b = 16.4726(3) Å, c = 23.8938(4) Å,  $\beta = 100.440(2)^{\circ}$ , V = 5200.46(17) Å<sup>3</sup>, Z = 4, T = 140(2) K,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $R_1$  [ $I > 2\sigma(I$ ]] = 0.034,  $wR_2$  (all data) = 0.078.

Crystal data for 4-PhMe: C<sub>22</sub>H<sub>12</sub>BF<sub>10</sub>HfN, C<sub>7</sub>H<sub>8</sub>, M = 761.76, Orthorhombic space group  $P2_12_12_1$ , a = 6.707(5) Å, b = 15.957(5) Å, c = 25.116(5) Å, V = 2688(2) Å<sup>3</sup>, Z = 4, T = 140(2) K,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $R_1$  [ $I > 2\sigma(I)$ ] = 0.035,  $wR_2$  (all data) = 0.062.

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