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Isolable zirconium hydride species in the reaction of amido complexes with amine-boranes†

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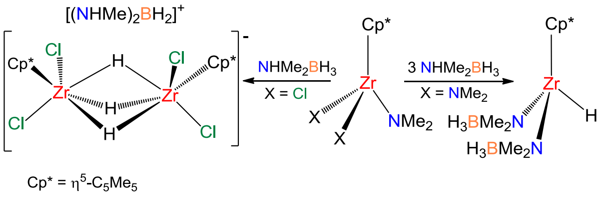
Graphical Abstract:

Mono-, di- and trinuclear zirconium hydride species have been isolated in the reaction of half-sandwich amido complexes with amine–borane adducts.

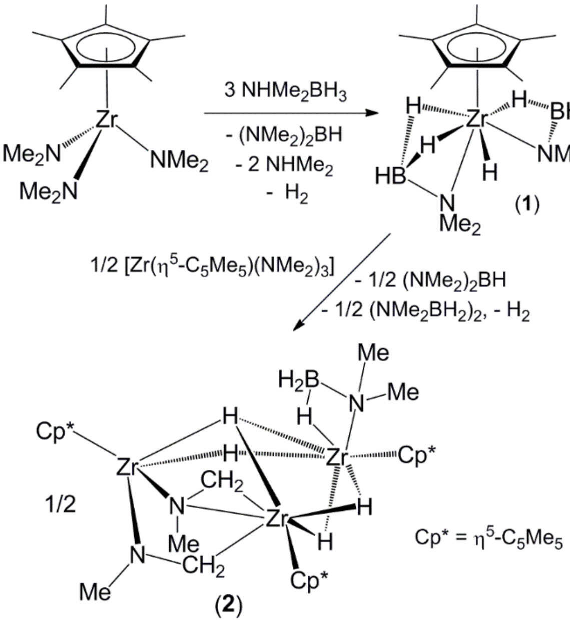


Abstract:

Mono-, di- and trinuclear zirconium hydride species have been isolated in the treatment of amido complexes $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_nCl_{3\text{-}n}]$ (n = 3, 1) with amine–borane adducts NHR_2BH_3 (R_2 = Me_2, H*t*Bu). The reactions involve the formation of amidoborane ligands with Zr···H-B interactions which readily undergo β-hydride elimination to give hydride functions.

The reactivity of amine–boranes in presence of metal complexes has received intense attention in the last decade.[1] Motivations in this area include the isolation of hydrogen storage materials, the preparation of B–N oligomers and polymers, and the generation of reactive hydride species. The extensive chemistry developed in this highly active field of study involves the treatment of NHR_2BH_3 with metal complexes from across the periodic table. Group 4 complexes are among the most studied examples, especially in the field of metal catalyzed amine–borane dehydrogenation because their high reactivity and mechanistic interest. The majority of these investigations have been carried out with Group 4 metallocene $[M(\eta^5\text{-}C_5R_5)_2X_n]$ complexes with metals in different oxidation states (from +2 to +4),[2,3,4] but non-metallocene derivatives have been also explored.[5] Remarkably, Rosenthal and co-workers have also studied homoleptic amido species $[M(NMe_2)_4]$ (M = Ti, Zr) as active catalysts for the dehydrocoupling of N,N-dimethylamine-borane.[4] Attempts to isolate key intermediates in the dehydrogenation of amine–boranes have led to the study of stoichiometric version of those reactions. In s-block and early transition metal systems, the first step appears to be N-H activation and formation of amidoborane complexes.[1,3,5,6,7] Herein we describe the preliminary results obtained in the stoichiometric reactions of the half-sandwich zirconium(IV) amido complexes $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_nCl_{3-n}]$ with amine–borane adducts NHR_2BH_3. The structures and properties of the resultant hydride complexes are discussed as well as their formation via β-hydride elimination of amidoborane intermediates.

The reaction of $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ with three equivalents of N,N-dimethylamine-borane in benzene-d_6 at room temperature was monitored by ^1H and ^{11}B NMR spectroscopy (Scheme 1). After 5 min, the spectra showed complete consumption of the reagents and revealed resonance signals assignable to compound $[Zr(\eta^5\text{-}C_5Me_5)H(NMe_2BH_3)_2]$ (**1**) along with those due to $NHMe_2$, H_2, and $(NMe_2)_2BH$.[‡] A plausible mechanism for the formation of **1** would involve elimination of $NHMe_2$ to give the $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2BH_3)_3]$ intermediate. This sterically encumbered tris(dimethylamidoborane) complex readily undergoes β–hydride elimination in one amidoborano ligand to form complex **1** along with dimethylaminoborane. However, the cyclic dimer $(NMe_2BH_2)_2$ was not detected in the NMR spectra,[‡] and the observed bis(dimethylamino)borane and H_2 by-products are presumably the result of the reaction of dimethylaminoborane with $NHMe_2$.[8]



Scheme 1. Reaction of $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ with $NHMe_2BH_3$

Complex **1** was isolated as a light brown solid in 80% yield through the reaction of $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ with six equiv of $NHMe_2BH_3$ in hexane at room temperature. Noteworthy, the analogous treatment of the tris(amido) reagent with three equiv of N,N-dimethylamine-borano in hexane afforded a red solution from which crystals of the zirconium polyhydride $[\{Zr(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}H)(\mu\text{-}H)_3(\mu\text{-}CH_2NMe)_2(NMe_2BH_3)]$ (**2**) were grown at –35 °C. The conversion of the mononuclear bis(amidoborane) hydride complex **1** to the trinuclear derivative **2** in benzene-d_6 solution was examined by several NMR tube experiments. Complex **1** is thermally stable in benzene-d_6 solutions at temperatures lower than 55 °C and remains unaltered after addition of excess $NHMe_2BH_3$ at room temperature. However, **1** readily reacts with a half equivalent of $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ to give compound **2**. ^1H and ^{11}B NMR spectra indicate that this reaction in benzene-d_6 after 24 h at room temperature appears to be quantitative to give $(NMe_2)_2BH$ and $(NMe_2BH_2)_2$ as detected by-products (Scheme 1).[‡] Thus, we suggest that when only three equiv of $NHMe_2BH_3$ were used in the reaction with $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$, part of the amine–borane reagent decomposed in the solution leading to a mixture of **1** and $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$, which subsequently could react to form complex **2**. Indeed, in a preparative scale experiment, complex **2** was isolated as red crystals in 50% yield by treatment of **1** with $[Zr(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ in hexane for 3 days. The formation of bridging imine(2-) fragments $\mu\text{-}CH_2NMe$ from dimethylamido ligands has been already noted in the literature.[9]

The IR spectrum (KBr) of **1** reveals one strong band at 1560 cm^{-1} for the ν_{MH} stretching vibration.[7a,10] In addition, the spectrum shows several bands in the range 2468–2320 cm^{-1}, characteristics of terminal B–H bonds, and absorptions between 2058 and 1870 cm^{-1} for ν_{BH} vibrations of bridging B–H bonds. These data are consistent with the existence of M···H–B interactions in the solid-state structure as those determined by an X-ray crystallographic determination of crystals grown from a hexane solution at –35 °C (Fig. 1). The molecular structure of **1** shows two dimethylamidoborane ligands acting in a chelating fashion to the zirconium center but those ligands exhibit different coordination modes, namely κ^2*N*,*H*-NMe_2BH_3 and κ^3*N*,*H*,*H*-NMe_2BH_3. The former NMe_2BH_3 ligand binds to the metal through one Zr–N bond and one Zr···H-B interaction with Zr(1)–N(1) and

Zr(1)···B(1) distances of 2.306(3) and 2.680(5) Å, respectively.[7] The second NMe_2BH_3 ligand exhibits two Zr···H–B interactions in addition to the zirconium-nitrogen bond with Zr(1)–N(2) and Zr(1)···B(2) lengths of 2.353(3) and 2.359(5) Å, respectively.[5] The coordination sphere of the zirconium atom is completed by one terminal hydrogen atom (Zr(1)–H(1) 1.83(4) Å) and the pentamethylcyclopentadienyl ligand to give a seven-coordinate geometry about the metal center if the centroid of the η^5-C_5Me_5 is considered.

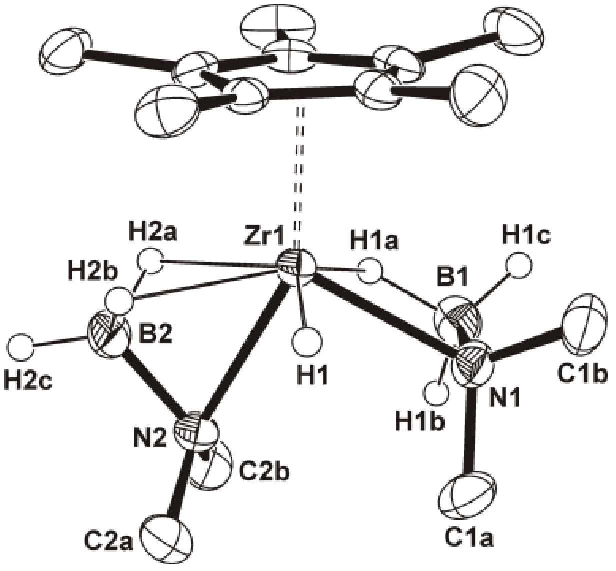


Fig. 1 Crystal structure of complex **1** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the methyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Zr(1)–N(1) 2.306(3), Zr(1)–N(2) 2.353(3), Zr(1)–H(1) 1.83(4), Zr(1)···B(1) 2.680(5), Zr(1)···B(2) 2.359(5), N(1)–Zr(1)–N(2) 90.5(1), Zr(1)–N(1)–B(1) 85.6(2), Zr(1)–N(2)–B(2) 71.3(2).

In contrast to the solid-state structure, ^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR spectra of **1** in benzene-d_6 at room temperature are consistent with C_s symmetry in solution. The ^{1}H NMR spectrum shows one broad 1:1:1:1 quartet resonance at $\delta = 0.76$ ($^{1}J(H,B) = 88.5$ Hz) for the

BH_3 groups, while one well-defined quartet resonance at $\delta = -7.3$ ($^1J(B,H) = 89.7$ Hz) was observed in the ^{11}B NMR spectrum confirming that all the hydrogen atoms of the BH_3 groups are equivalent on the NMR time scale. The methyl groups of each NMe_2BH_3 ligand are magnetically inequivalent in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The low-field resonance for the hydride ligand at $\delta = 6.76$ in the ^1H NMR spectrum is similar to those found for terminal zirconium hydrides.[7a,11]

Compound **2** was also characterized by an X-ray crystal structure determination (Fig. 2). The central core consists of three zirconium atoms forming a scalene triangle (Zr(1)···Zr(2) 3.417(1) Å, Zr(1)···Zr(3) 3.222(1) Å, Zr(2)···Zr(3) 3.066(1) Å), wherein one face is capped by a hydrogen atom. A κ^2*N*,*H*-NMe_2BH_3 ligand binds to Zr(1) through one Zr–N bond and one Zr···H-B interaction (Zr(1)–N(1) and Zr(1)···B(1) distances of 2.317(6) and 2.657(10) Å, respectively) in a fashion similar to that of **1**. In addition, the Zr(1) atom is connected to Zr(2) and Zr(3) atoms through one μ-H and two μ-H bridging hydride ligands, respectively. The Zr(2) and Zr(3) atoms are ligated by two μ-CH_2NMe imine ligands which exhibit different coordination modes. The nitrogen atom, N(2), of one of them exhibits a trigonal-planar geometry (sum of angles 359.7°) and it is bound to Zr(2) with a short distance of 1.984(6) Å, which is indicative of π-donation of the nitrogen electron pair to the zirconium center. In contrast, the nitrogen atom, N(3), of the other μ-CH_2NMe ligand is bound to both zirconium atoms by Zr–N bonds of essentially equal distance (Zr(2)–N(3) and Zr(3)–N(3) are 2.191(6) and 2.232(6) Å, respectively). Thus, the N(3) atom adopts the rare basal-trigonal-pyramidal geometry (the nitrogen atom centered in the triangular basal face of a pyramidal coordination polyhedron) in contrast to the tetrahedral environment found in the imine ligand of complex $[W_2Cl_3(NMe_2)_2L_2(\mu\text{-}CHCH_2)(\mu\text{-}CH_2NMe)]$.[9a] This rare bridging mode of one μ-CH_2NMe imine ligand in **2** is most likely due to the steric repulsion of the bulky η^5-C_5Me_5 ligand bonded to the Zr(2) atom.

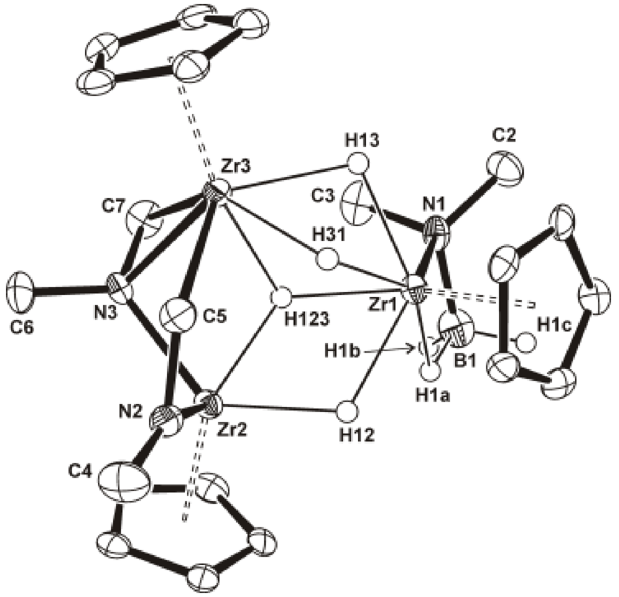
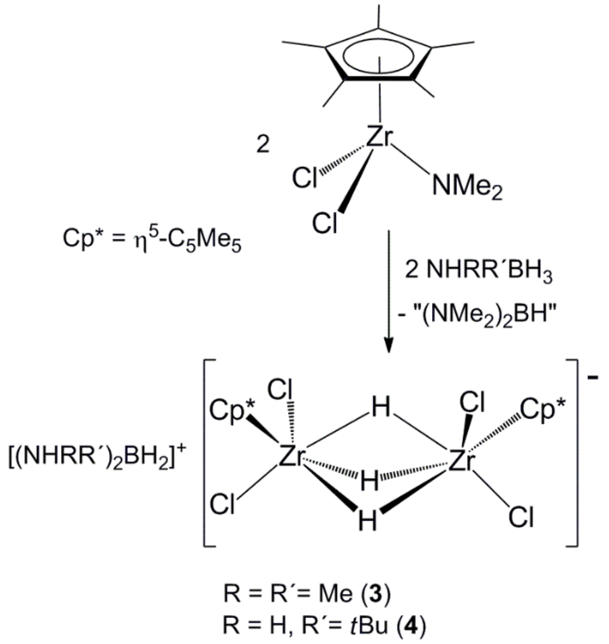


Fig. 2 Crystal structure of complex **2** (thermal ellipsoids at the 50% probability level). Methyl groups of the η^5-C_5Me_5 ligands and hydrogen atoms of the methyl and methylene moieties are not shown for clarity. Selected lengths (Å) and angles (deg): Zr(1)–N(1) 2.317(6), Zr(1)···B(1) 2.657(10), Zr(2)–N(2) 1.984(6), Zr(2)–N(3) 2.191(6), Zr(3)–N(3) 2.232(6), Zr(3)–C(5) 2.446(7), Zr(3)–C(7) 2.307(7), Zr–H 1.92(7)–2.13(9), Zr(1)···Zr(2) 3.417(1), Zr(1)···Zr(3) 3.222(1), Zr(2)···Zr(3) 3.066(1), Zr(1)–N(1)–B(1) 84.6(5), Zr(2)–N(2)–C(5) 92.6(4), Zr(2)–N(3)–C(7) 125.6(5), Zr(2)–N(3)–Zr(3) 87.8(2), Zr(3)–N(3)–C(7) 74.1(4), Zr(3)–C(5)–N(2) 128.2(5), Zr(3)–C(7)–N(3) 68.5(4).

In accord with the C_1 symmetry determined in the solid-state structure, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** in benzene-d_6 at ambient temperature reveals resonance signals for three different η^5-C_5Me_5 ligands. The methyl groups of the NMe_2BH_3 are inequivalent in the ^{1}H and ^{13}C{^{1}H} NMR spectra and a broad resonance at $\delta = -15.7$ was observed in the ^{11}B NMR spectrum indicating that the Zr···H–B interaction is maintained in solution. In addition, the ^{1}H NMR spectrum shows two AB spin systems for the CH_2 groups of the μ-CH_2NMe imine ligands. Broad resonances at δ = 0.94, 0.41 and –2.01 in the ^{1}H NMR spectrum were assigned to three bridging hydride ligands of **2** by integration, but the expected resonance for the fourth μ_n-H ligand was not located in the spectrum due to its broad nature or to the coincidence with other signals.

Treatment of the mono(dimethylamido) zirconium derivative $[Zr(\eta^5\text{-}C_5Me_5)Cl_2(NMe_2)]$ with one equivalent of $NHMe_2BH_3$ in hexane at room temperature afforded the precipitation of the ionic compound $[(NHMe_2)_2BH_2][\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]$ (**3**) (Scheme 2). Compound **3** was isolated in 68% yield as a white powder, which is very soluble in chlorinated and aromatic hydrocarbon solvents, although it slowly decomposes in solution according to ^{1}H NMR spectroscopy (*vide infra*). The IR spectrum (KBr) of **3** shows one strong absorption at 3188 cm^{-1} for the ν_{NH} vibrations and one medium intensity band at 2456 cm^{-1} for the ν_{BH} vibrations of the terminal B–H bonds of the boronium cation $[(NHMe_2)_2BH_2]^+$.[12] In addition, the IR spectrum of **3** reveals a very strong absorption at 1457 cm^{-1}, which is tentatively assigned to the Zr–H stretching of the Zr–H–Zr fragments.[10,13] The ^{1}H NMR spectrum of **3** in chloroform-d_1 exhibits one sharp singlet for the η^5-C_5Me_5 groups and one broad resonance (δ = 3.96) for the three bridging hydride ligands of the $[\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]^-$ anion. In addition, the spectrum shows one broad resonance at δ = 5.46 and a doublet at δ = 2.61 (^3J(H,H) = 6.0 Hz) for the NH and CH_3 protons of the boronium cation $[(NHMe_2)_2BH_2]^+$.[12b,14] The ^{11}B NMR spectrum in chloroform-d_1 reveals one broad resonance signal at δ = –0.7, which compares well with those reported for other salts containing the same boronium cation.[14]



Scheme 2 Synthesis of complexes $[(NHRR')_2BH_2][\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]$

Compound **3** in benzene-d_6 solution decomposes completely within 24 h at room temperature. The ^{1}H NMR spectrum of the resultant colorless solution showed resonance signals for H_2, $(NMe_2)_2BH$, and several unidentified species. Noteworthy, compound **3** is more stable in chloroform-d_1 solution, and the ^{1}H NMR spectrum taken after 1 day at room temperature showed the formation of the deuterated cation $[(NDMe_2)_2BH_2]^+$ without any change in the resonance signals of the dinuclear anion $[\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]^-$. However, evidence for the partial decomposition of **3** in chloroform-d_1 was observed in the ^{1}H NMR spectrum after 4 days at room temperature.

Despite many attempts, we were not able to grow suitable crystals of compound **3** for an X-ray crystal structure determination. Thus, we explore the reactivity of the mono(dimethylamido) zirconium derivative with N-*tert*-butylamine-borane. The reaction of $[Zr(\eta^5\text{-}C_5Me_5)Cl_2(NMe_2)]$ with one equiv of NH_2tBuBH_3 in hexane at room temperature afforded the precipitation of the ionic compound $[(NH_2tBu)_2BH_2][\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}$

$H)_3]$ (**4**) in 52% yield. Compound **4** is inevitably contaminated by the analogous salt **3** with the $[(NHMe_2)_2BH_2]^+$ cation (≤ 5% by ^{1}H NMR spectroscopy), which shows a similar solubility in common solvents. Fortunately, suitable crystals of **4**·CH_2Cl_2 for an X-ray crystallographic study were obtained from a dichloromethane solution at –15 °C (Fig. 3). The solid-state structure of compound **4** contains dinuclear anionic fragments $[\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]^-$ associated with the boronium cations through N–H···Cl hydrogen bonding interactions. These interactions lead to right and left-helical chains along the crystals (see Fig. S1 and Table S5 in the ESI). The cation $[(NH_2\textit{t}Bu)_2BH_2]^+$ shows B and N atoms in a distorted tetrahedral coordination with B–N bond lengths of 1.595(5) Å, which are similar to those determined in the $[(NH_3)_2BH_2]^+$ ion.[15] The anionic fragment shows two $\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}$ units connected by three bridging hydrogen atoms. Thus, each zirconium atom adopts a distorted octahedral geometry if the centroid of the η^5-C_5Me_5 is considered. The Zr···Zr separation of 3.106(3) Å in **4** is similar to those reported for other dinuclear zirconium complexes with three bridging hydride ligands (3.102(1)–3.163(1) Å).[16]

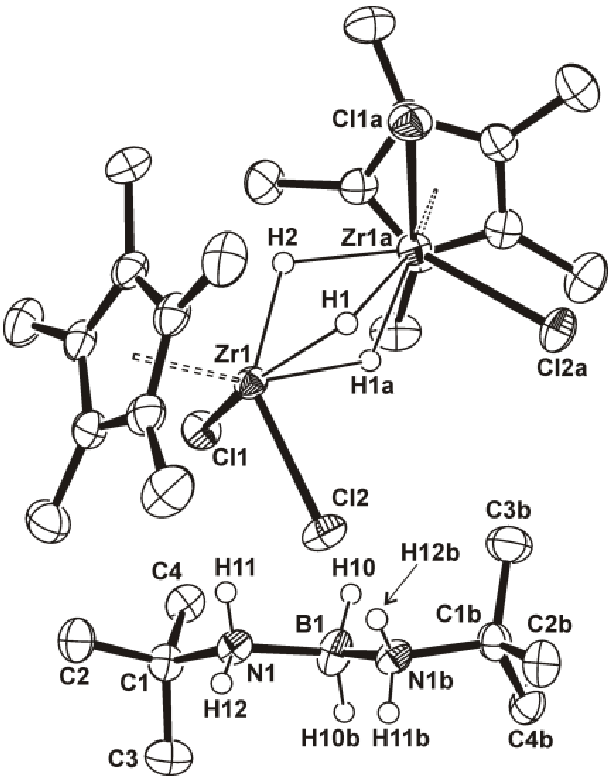


Fig. 3 Crystal structure of complex **4**·CH_2Cl_2 (thermal ellipsoids at the 50% probability level). Dichloromethane solvent molecule and hydrogen atoms of the methyl groups are not shown for clarity. Selected lengths (Å) and angles (deg): B(1)–N(1) 1.595(5), Zr(1)–H(1) 1.80(4), Zr(1)–H(2) 1.91(3), Zr(1)–Cl(1) 2.470(1), Zr(1)–Cl(2) 2.458(2), Zr(1)···Zr(1)a 3.106(3), N(1)–B(1)–N(1)b 105.6(4), Cl(1)–Zr(1)–Cl(2) 98.8(1), H(1)–Zr(1)–H(2) 63(2), H(1)–Zr(1)–H(1)a 63(2). Symmetry code: (a) – x + 3/4, – y + 3/4, z; (b) – x + 5/4, y, – z + 1/4.

The IR spectrum (KBr) of **4** shows two strong absorptions at 3191 and 3114 cm^{-1} for the ν_{NH} vibrations and one band at 1589 cm^{-1} assignable to the NH_2tBu bending mode. In addition, the absorption at 2484 cm^{-1} for the ν_{BH} vibrations of the terminal B-H bonds of the boronium cation $[(NH_2tBu)_2BH_2]^+$ is similar to that found in complex **3** (2456 cm^{-1}) containing the $[(NHMe_2)_2BH_2]^+$ ion. The IR spectrum of **4** also reveals a very strong absorption at 1463 cm^{-1} for the Zr-H stretching of the Zr-H-Zr fragments, which is close to that (1457 cm^{-1}) observed in compound **3** with the same dinuclear zirconium anion. The ^{1}H NMR spectra of **4** in chloroform-d_1 or benzene-d_6 show sharp singlets for the η^5-C_5Me_5 groups and broad resonances (δ = 3.84 and 4.17, respectively) for the three bridging hydride ligands of the $[\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}H)_3]^-$ anion, which are also comparable to those found in the spectra of **3**. In addition, the ^{1}H NMR spectra show one broad resonance and a sharp singlet for the NH and CH_3 protons of the boronium cation $[(NH_2\textit{t}Bu)_2BH_2]^+$. The ^{11}B NMR spectrum in chloroform-d_1 displays one broad resonance signal at $\delta = -13.1$, which compares well with that ($\delta = -13.0$) reported for the salt $[(NH_2\textit{t}Bu)_2BH_2](BH_4)$.[17]

Studies are underway to elucidate the mechanism of formation of compounds **3** and **4**, but those efforts are hampered by their instability in solution. Nevertheless, plausible mechanisms involve monoamidoborane $[Zr(\eta^5\text{-}C_5Me_5)Cl_2(NR_2BH_3)]$ intermediates, which undergo β–hydride elimination in the amidoborano ligand to generate hydride complexes $[Zr(\eta^5\text{-}C_5Me_5)Cl_2H]$ in the way of formation of compounds **3** and **4**.

In summary, we have shown that the treatment of zirconium(IV) amido complexes with amine–borane adducts NHR_2BH_3 allows the isolation of hydride complexes. The hydride functions are generated by β-hydride elimination in amidoborane ligands which contain Zr···H–B interactions. We are currently investigating the reaction mechanisms of half-sandwich Group 4 complexes with amine–borane adducts, as well as the synthesis of reactive polynuclear hydride species by this route.

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Notes and references

† Electronic Supplementary Information (ESI) available: Experimental details and full characterization data for complexes **1-4**. CCDC 1526639-1526641. For ESI and crystallographic data in CIF and other electronic format see DOI: 10.1039/x0xx00000x.

‡ NMR data for $(NMe_2)_2BH$: ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 2.62 (s, 12H; NMe_2), 4.09 (q, ^1J(H,B) = 130.2 Hz, 1H; BH); ^{11}B NMR (128 MHz, C_6D_6, 20 °C): δ 29.1 (d, ^1J(B,H) = 131.0 Hz; BH). NMR data for $(NMe_2BH_2)_2$: ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 2.23 (s br, 12H; NMe_2), 3.03 (q, ^1J(H,B) = 111.9 Hz, 4H; BH_2); ^{11}B NMR (128 MHz, C_6D_6, 20 °C): δ 5.6 (t, ^1J(B,H) = 111.7 Hz; BH_2).

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