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Reversible borohydride formation from aluminium hydrides and {H(9-BBN)}$_2$: structural, thermodynamic and reactivity studies†

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A series of novel β-diketiminate stabilised aluminium borohydrides of the type (Nacnac)Al(R){H$_2$(9-BBN)} has been synthesised offering variation in both the auxiliary R substituent and in the Nacnac backbone itself. A number of these complexes show unusual dissociation of the borane from the aluminium hydride in solution under ambient conditions. The lability of the borane is shown (by variable temperature NMR analyses) to be influenced by the electronic character of *both* the aluminium-bound R substituent and the Nacnac ligand itself, such that electron-withdrawing substituents lead to greater dissociation of the borane. Comparison of these complexes with related systems featuring the tetrahydroborate [BH$_4$]$^-$ ligand illustrates the impact of the boron-bound substituents on the ability of the borane fragment to dissociate from the aluminium hydride. This dissociative behaviour is shown to be highly influential on the ability of the borohydride complexes to reduce carbon dioxide in a stoichiometric manner.

Introduction

The use of elements from the s- and p-blocks of the Periodic Table in the activation of small molecule substrates is an area of significant recent interest, reflecting, at least in part, their ready availability and environmental compatibility.[1] Moreover, by extension, a number of *catalytic* transformations have been developed which draw on these elements in the active species.[2] Within this realm, aluminium hydride catalysts have been developed for a range of hydro-elementation reactions of unsaturated substrates.[3,4] Much of this work has focused on the catalytic reduction of unsaturated C–C and C–O bonds, employing boranes as the stoichiometric reductant. Thus, a number of systems have been shown to be capable of the catalytic hydroboration of alkenes and alkynes,[5–10] and recent reports also describe the use of aluminium hydrides in the hydroboration of aldehydes/ketones and CO$_2$, in both stoichiometric and catalytic fashion (Fig. 1).[8–16] While these systems typically employ mild boranes such as pinacolborane (HBpin) to effect the catalytic hydroboration of aldehydes and ketones, more reactive B–H bonds such as those in catecholborane, 9-borabicyclo[3.3.1]nonane, {H(9-BBN)}$_2$, and H$_3$B·SMe$_2$ are required to reduce CO$_2$.[16]

At a general level, a prevailing feature of organo-group 13 hydrides is their tendency to form M–H–M bridges.[17–24] Among the mixed hydrides of the group 13 elements, aluminium borohydride complexes have attracted the most attention, with a range of examples having been characterised by spectroscopic and crystallographic methods, including Me$_2$Al(BH$_4$), Al(BH$_4$)$_3$ and adducts of the form L·Al(BH$_4$)$_3$ (*e.g.* L = NMe$_3$, NH$_2$Me).[25–31] Complexes which feature bulky, chelating ligands at the aluminium centre have been reported to show significantly enhanced thermal stability. Thus, the

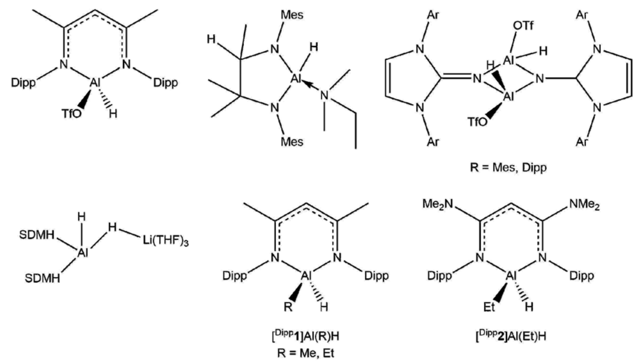

Fig. 1 Examples of aluminium hydrides which effect catalytic hydroboration of aldehydes/ketones and the stoichiometric reduction of CO$_2$

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β-diketiminate-supported systems $\{HC(MeCNDipp)_2\}Al(R)(BH_4)$ (= $[^{Dipp}\mathbf{1}]Al(R)(BH_4)$, where R = BH_4 or Et) are sufficiently thermally stable to be crystallographically characterised in the solid state, and feature $[BH_4]^-$ ligands bound to the aluminium centres *via* two bridging Al–H–B interactions.[16,32,33] Whilst the majority of aluminium borohydride complexes feature the $[BH_4]^-$ ligand, a number of systems have also been reported in which the boron centre bears substituents other than hydrides, including $[B(C_6F_5)_2]$ and [9-BBN] fragments.[34–37]

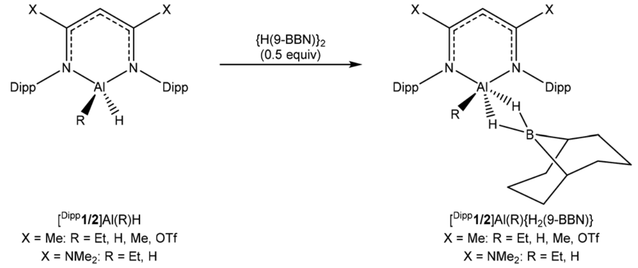
Despite the widely-exhibited tendency of aluminium hydrides to form bridging Al–H–B interactions in the presence of boranes, the formation of such interactions in the context of alane-catalysed hydroboration reactions has not been widely investigated. On the other hand, the formation of borohydride complexes has been shown to be influential in achieving catalytic turnover in the nickel-hydride-catalysed reduction of CO_2 by boranes.[38] The nickel pincer complexes $\{2,6\text{-}(R_2PO)_2C_6H_3\}NiH$ (R = ^{t}Bu, ^{i}Pr) form borohydride complexes in the presence of $H_3B{\cdot}THF$, $\{H(9\text{-}BBN)\}_2$ and HBcat. The latter two complexes exist in equilibrium with the nickel hydride and the borane at room temperature and catalyse the reduction of CO_2 to methanol derivatives with maximum TOFs of 100 h^{-1}. By contrast, the $\{2,6\text{-}(R_2PO)_2C_6H_3\}Ni(BH_4)$ systems (R = ^{t}Bu, ^{i}Pr) show no borane dissociation and no catalytic activity.[38]

In view of these observations, and the known ability of β-diketiminate stabilised aluminium hydrides both to react with CO_2 and to form tetrahydroborate complexes, we set out to investigate the chemistry of these hydride compounds towards a range of boranes, including $\{H(9\text{-}BBN)\}_2$. We report on these studies in this publication, which examines sequentially (i) the synthesis of a range of β-diketiminate stabilised aluminium borohydrides; (ii) the thermodynamics of dissociation of the borane from the aluminium hydride; and (iii) the impact of this dissociation behaviour on the reactivity of the aluminium borohydrides towards CO_2.

Results and discussion

Syntheses of novel β-diketiminato aluminium dialkylborohydride complexes

Treatment of the aluminium hydride complexes $\{HC(MeCNDipp)_2\}Al(R)H$ (= $[^{Dipp}\mathbf{1}]Al(R)H$, where R = Et, H, Me or OTf) with 0.5 equivalents of $\{H(9\text{-}BBN)\}_2$ at room temperature cleanly yields the respective Nacnac-ligated aluminium borohydride complexes $[^{Dipp}\mathbf{1}]Al(R)\{H_2(9\text{-}BBN)\}$ in high yields (R = Et: 71%; R = H: 91%; R = Me: 55%; R = OTf: 89%; Scheme 1). Related complexes featuring the electronically modified (backbone NMe_2-containing) *N*-nacnac ligand can also be accessed readily. Thus, addition of 0.5 equivalents of $\{H(9\text{-}BBN)\}_2$ to $\{HC(Me_2NCNDipp)_2\}Al(R)H$ (= $[^{Dipp}\mathbf{2}]Al(R)H$, where R = Et or H) in toluene yields the corresponding dialkylborohydride complexes in 47% and 66% yield, respectively. Each has been characterised by standard spectroscopic and analytical techniques, and their molecular structures determined by X-ray crystallography (Fig. 2). In the case of dihydride complexes $[^{Dipp}\mathbf{1}]AlH_2$ and $[^{Dipp}\mathbf{2}]AlH_2$, the addition of excess $\{H(9\text{-}BBN)\}_2$ does not lead to coordination of the second Al–H bond, as is observed in the formation of $[^{Dipp}\mathbf{1}]Al(BH_4)_2$ from $H_3B{\cdot}THF$.[32] This presumably relates to the increased steric bulk of $\{H(9\text{-}BBN)\}_2$ (*cf.* $H_3B{\cdot}THF$).



Scheme 1 Synthesis of novel aluminium borohydride complexes $[^{Dipp}\mathbf{1/2}]Al(R)\{H_2(9\text{-}BBN)\}$ (**1**: R = Et, H, Me, OTf; **2**: R = Et, H).

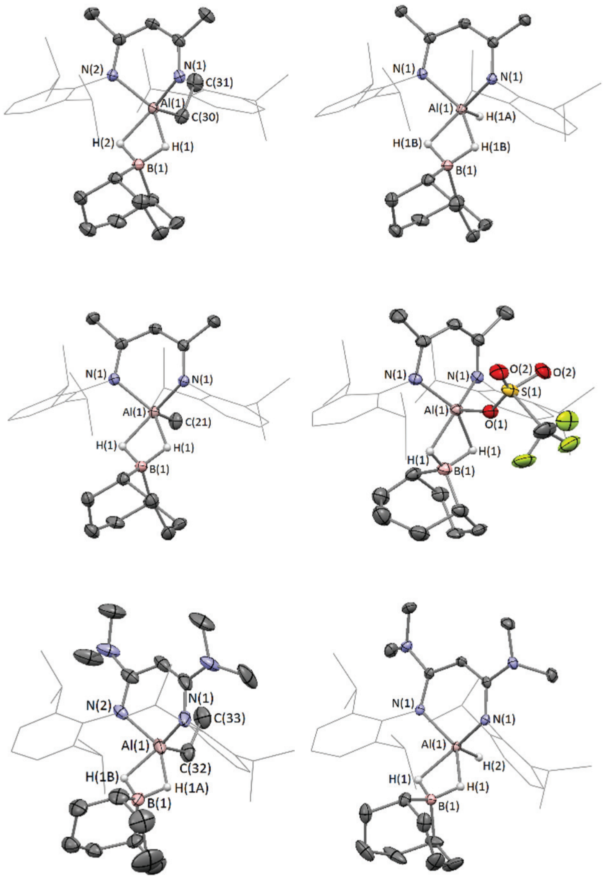


Fig. 2 Molecular structures of $[^{Dipp}\mathbf{1}]Al(Et)\{H_2(9\text{-}BBN)\}$ (top left), $[^{Dipp}\mathbf{1}]Al(H)\{H_2(9\text{-}BBN)\}$ (top right), $[^{Dipp}\mathbf{1}]Al(Me)\{H_2(9\text{-}BBN)\}$ (middle left), $[^{Dipp}\mathbf{1}]Al(OTf)\{H_2(9\text{-}BBN)\}$ (middle right), $[^{Dipp}\mathbf{2}]Al(Et)\{H_2(9\text{-}BBN)\}$ (bottom left) and $[^{Dipp}\mathbf{2}]Al(H)\{H_2(9\text{-}BBN)\}$ (bottom right), as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected H atoms and solvate molecule for $[^{Dipp}\mathbf{1}]Al(OTf)\{H_2(9\text{-}BBN)\}$ and $[^{Dipp}\mathbf{2}]Al(Et)\{H_2(9\text{-}BBN)\}$ omitted, and Dipp groups shown in wireframe for clarity. Al–Hs and Al–H–B located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°) are listed in Table 1.

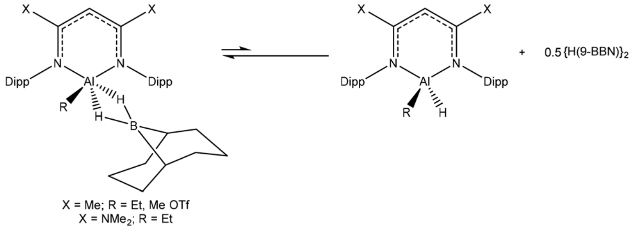
Common features observed in the respective ^{1}H NMR spectra of these new dialkylborohydride complexes include four doublets for the Dipp methyls and two septets for the Dipp methine groups, consistent with effective C_s symmetry at aluminium. In the cases of the hydride complexes $[^{\text{Dipp}}\mathbf{1/2}]$Al(H){$H_2$(9-BBN)}$_2$, the terminal aluminium-bound hydrogen gives rise to a quadrupolar-broadened ^{1}H NMR resonance at a chemical shift typical of an aluminium hydride (δ_H = 4.58 and 4.48 ppm, respectively). A resonance associated with the bridging Al–H–B protons has been reported at δ_H = 1.61 ppm for a related complex by Uhl and Erker;[37] in the cases of our new systems, this is presumably obscured by the resonances associated with the 9-BBN and Dipp ^{i}Pr substituents, and broadened due to the quadrupolar ^{27}Al nucleus (I = 5/2). In the case of $[^{\text{Dipp}}\mathbf{1}]$Al(R){$H_2$(9-BBN)} (R = Me or Et) and $[^{\text{Dipp}}\mathbf{2}]$Al(Et){$H_2$(9-BBN)}$_2$, the aluminium alkyl resonances are shifted considerably downfield relative to those of their hydride precursors (*e.g.* $[^{\text{Dipp}}\mathbf{1}]$Al(Me){$H_2$(9-BBN)}$_2$: $\delta_H = -0.10$ ppm; $[^{\text{Dipp}}\mathbf{1}]$Al(Me)H: $\delta_H = -0.74$ ppm).[16] This presumably reflects decreased shielding, arising from a reduction of the σ-donating character of the aluminium-bound hydride on coordination to the borane. The ^{11}B NMR resonances, which narrow upon ^{1}H decoupling, are characteristic of four-coordinate boron environments of the type $[R_2BH_2]^-$ (where R = alkyl), *e.g.* $\delta_B = -15.6$ ppm for $[^{\text{Dipp}}\mathbf{1}]$Al(Et){$H_2$(9-BBN)}.[39–41]

The infrared spectra of these complexes each feature two broad absorptions which are characteristic of the symmetric and antisymmetric stretches associated with Al(H)$_2$B bridge (*e.g.* $[^{\text{Dipp}}\mathbf{1}]$Al(Et){$H_2$(9-BBN)}$_2$, $\nu_{\text{Al–H–B}}$ = 2066, 2026 cm^{-1}).[36,42]

The molecular structure of each of the novel borohydride complexes features coordination at aluminium of the $[H_2(BBN)]^-$ ligand *via* two 3c–2e Al–H–B bonds. Geometrically, ligation is based around a 4-membered AlH$_2$B ring, with the [H_2(9-BBN)] fragment featuring the expected tetrahedral boron centre. The aluminium centre in each case features a coordination number of five, with the geometry being close to square pyramidal (see Table 1 for τ values); the two β-diketiminate nitrogen donors and the bridging hydrogens constitute the basal plane, with the R substituent occupying the apical position. In each case, both of the bridging hydrogens (together with the terminal Al–Hs in the cases of $[^{\text{Dipp}}\mathbf{1/2}]$Al(H){$H_2$(9-BBN)}) could be located in the difference Fourier map and refined isotropically; the terminal hydrides are found at distances consistent with those reported for terminal Al–H bonds.[43] The Al–B separation in each case is only marginally longer than the sum of the covalent radii (1.21 + 0.84 = 2.05 Å), in accordance with previous reports of Al(H)$_2$B units featuring 3-centre-2-electron bonding interactions.[37,44] A comparison between the Nacnac aluminium borohydrides and their *N*-nacnac analogues reveals a marginal lengthening of the Al–B distances in the latter. This may indicate that binding of the borohydride ligand is weaker in the case of $[^{\text{Dipp}}\mathbf{2}]$Al(R){$H_2$(9-BBN)} (R = Et, H). In addition, the Al–B distances in the Nacnac complexes are somewhat longer than those reported for related complexes bearing the 'parent' $[BH_4]^-$ ligand (*e.g.* $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) 2.2333(19) Å).[16,32,36] This comparison of the Al–B distances of analogous complexes bearing the $[BH_4]^-$ and $[H_2(9\text{-BBN})]^-$ ligands implies that binding of the borohydride moiety is – if anything – weaker in the case of the $[H_2(9\text{-BBN})]^-$ fragment.

Exploring dissociation of the borane fragment

In solution, borohydride complexes of both types $[^{\text{Dipp}}\mathbf{1}]$Al(R){$H_2$(9-BBN)} (where R = Et, Me or OTf) and $[^{\text{Dipp}}\mathbf{2}]$Al(R){$H_2$(9-BBN)} (where R = Et) exist in equilibrium with the corresponding hydride ($[^{\text{Dipp}}\mathbf{1/2}]$Al(R)H) and the dimeric free borane, {H(9-BBN)}$_2$ – the latter signalled by a resonance in the ^{11}B NMR spectrum at δ_B = 27.9 ppm (Scheme 2). The availability of isolated samples of these complexes allowed the thermodynamic parameters associated with the borane/borohydride equilibrium to be investigated. In particular, the effects of temperature on this equilibrium allow for the calculation of $\Delta H°$ and $\Delta S°$ for borane dissociation through a van't Hoff analysis (see Table 2 and ESI†). In the cases of $[^{\text{Dipp}}\mathbf{1/2}]$Al(H){$H_2$(9-BBN)}, the respective ^{11}B NMR spectra reveal the liberation of only a trace amount of borane even at elevated temperatures. At higher temperatures still, the ^{1}H NMR spectra are very broad and preclude reliable determination of $\Delta H°$ and $\Delta S°$. Qualitatively, however, these observations suggest relatively tight



Scheme 2 Aluminium borohydride complexes $[^{\text{Dipp}}\mathbf{1/2}]$Al(R){$H_2$(9-BBN)} (**1**: R = Et, Me, OTf; **2**: R = Et) exist in equilibrium with the corresponding hydrides and the (dimeric) free borane in solution.

Table 1 Comparison of key structural parameters of β-diketiminate aluminium borohydrides

	Distance of Al from C_3N_2 plane/Å	τ	d(Al–B)/Å	d(Al–N)/Å
$[^{\text{Dipp}}\mathbf{1}]$Al(Et){$H_2$(9-BBN)}	0.790	0.036	2.2513(12)	1.9179(9), 1.9191(9)
$[^{\text{Dipp}}\mathbf{1}]$Al(H){$H_2$(9-BBN)}	0.732	0	2.228(2)	1.8994(10)
$[^{\text{Dipp}}\mathbf{1}]$Al(Me){$H_2$(9-BBN)}	0.760	0	2.235(3)	1.9118(13)
$[^{\text{Dipp}}\mathbf{1}]$Al(OTf){$H_2$(9-BBN)}	0.766	0	2.166(3)	1.8711(16)
$[^{\text{Dipp}}\mathbf{2}]$Al(Et){$H_2$(9-BBN)}	0.738	0.15	2.268(3)	1.922(2), 1.926(2)
$[^{\text{Dipp}}\mathbf{2}]$Al(H){$H_2$(9-BBN)}	0.546	0	2.2676(18)	1.9069(9)

Table 2 $\Delta H°$, $\Delta S°$ and ΔG°_{298} values for dissociation of the borane from aluminium borohydride complexes, as determined by van't Hoff analyses

	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	ΔG°_{298} (kJ mol^{-1})
$[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)}	54.7 (±2.29)	115.4 (±7.25)	20.3
$[^{\text{Dipp}}\mathbf{1}]$Al(OTf){H$_2$(9-BBN)}	27.9 (±0.78)	64.9 (±2.42)	−19.3
$[^{\text{Dipp}}\mathbf{2}]$Al(Et){H$_2$(9-BBN)}	43.5 (±1.10)	98.9 (±3.49)	−29.7

binding of the borane to the aluminium hydride in these complexes – they display no hint of dissociation at room temperature.

With the exception of the systems for which R = H, the thermodynamic parameters associated with borane dissociation could readily be determined (*i.e.* for complexes featuring R = Et or OTf substituents). The thermodynamic data obtained from van't Hoff analyses are consistent with the idea that cleavage of the bridging Al–H–B bonds can be accomplished with relatively minor energetic changes to the system. This facile borane dissociation is a feature that is, to the best of our knowledge, unreported for aluminium complexes, even those which feature the $[H_2(\text{9-BBN})]^-$ fragment.[36,37] The coordinatively saturated and sterically crowded nature of the aluminium centres in these systems presumably contributes to the weak binding of the borane fragment. Moreover, comparison of the $\Delta H^{\circ}_{\text{diss}}$ values (Table 2) reveals weaker binding of the borane for aluminium hydrides that bear σ-withdrawing groups either at the metal centre or the ligand backbone. In light of this, and the fact that the presence of such groups is known to *reduce* the polarity of Al–H bonds $[\text{Al}(\delta^+)\text{–H}(\delta^-)]$, we propose that the strength of binding of the borane fragment in the borohydride complexes is dominated by the donor capabilities of the aluminium hydride towards the boron centre. The interaction of the boron hydride with the aluminium centre (*i.e.* donation of electron density in the opposite sense) might be expected to play less of a role within the overall binding interaction due to the coordinatively saturated nature of the aluminium centre.

Finally, we sought to investigate whether borane lability might also be a factor for the related tetrahydroborate complex $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$). However, neither the ^{1}H or ^{11}B NMR spectrum shows any evidence for dissociation of the borane in solution at room temperature or even at temperatures up to 375 K. This difference in the lability of the borane is also reflected in the reactivity of $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)} and $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) towards the Lewis base 4-(dimethylamino)pyridine (DMAP). Thus, the addition of one equivalent of DMAP to a solution of $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)} in benzene-d$_6$ at room temperature brings about immediate dissociation of the complex, generating the free aluminium hydride and (DMAP)·{H(9-BBN)}.[45] By contrast, no displacement of the borane by DMAP occurs for $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) under comparable conditions. Sequestration of the borane from this system could only be brought about by heating the solution to 80 °C for 5 h, after which $[^{\text{Dipp}}\mathbf{1}]$Al(Et)H and (DMAP)·BH$_3$ were obtained as the sole products.[46] This difference in behaviour represents further evidence for weaker binding of the $[H_2(\text{9BBN})]^-$ fragment at the aluminium centre (compared to $[BH_4]^-$), in line with the longer Al–B distance observed for $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)}.

Reactivity towards CO$_2$

Metal borohydride complexes have been utilised in the catalytic hydroboration of CO$_2$. However, such complexes are typically considered to be resting states for the catalyst and dissociation of the borane is required in order to liberate the 'active' metal hydride for reaction with CO$_2$.[38,47] With this in mind we wondered whether the contrasting lability of the borane in the borohydride complexes $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)} and $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) would lead to differing reactivity towards CO$_2$. Accordingly, $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) does not appear to react with CO$_2$ (1 bar) in benzene-d$_6$ over the course of 24 h at room temperature and requires heating to 80 °C for 10 d to show consumption of the borohydride (>90%). Moreover, this reaction does not proceed in a selective manner and the ^{1}H NMR spectrum of the resulting product mixture reveals the formation of *ca.* six Nacnac-ligated species, including $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(OBHOMe), a product previously shown to be formed in the reaction of $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(OCOH) with H$_3$B·SMe$_2$.[16] By contrast $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)} reacts readily with CO$_2$ at room temperature, with complete consumption of the aluminium starting material occurring over the course of 3 h. Over this period a mixture of $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(OCOH) (which can be independently synthesized *via* the reaction of $[^{\text{Dipp}}\mathbf{1}]$Al(Et)H with CO$_2$), {H(9-BBN)}$_2$ and $[^{\text{Dipp}}\mathbf{1}]$Al(Et){OCH$_2$O(9-BBN)} is formed.[16] Further reaction occurs over the course of an additional 6 h to selectively yield $[^{\text{Dipp}}\mathbf{1}]$Al(Et){OCH$_2$O(9-BBN)}; this compound has previously been reported to be formed *via* the hydroboration of the formate C═O bond in $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(OCOH) by {H(9-BBN)}$_2$. The reactivities of the related dialkylborohydride complexes $[^{\text{Dipp}}\mathbf{1}]$Al(Me){H$_2$(9-BBN)} and $[^{\text{Dipp}}\mathbf{2}]$Al(Et){H$_2$(9-BBN)} towards CO$_2$ are similar to that observed for $[^{\text{Dipp}}\mathbf{1}]$Al(Et){H$_2$(9-BBN)}. As such, we postulate that CO$_2$ does not directly react with the dialkylborohydride complexes, but rather with the corresponding hydride complex, present in low concentration in solution *via* dissociation of the borane. This phenomenon is consistent with the observed lack of reactivity for $[^{\text{Dipp}}\mathbf{1}]$Al(Et)(BH$_4$) towards CO$_2$ at room temperature (under which conditions no dissociation of the borane occurs) and also the reported reactivity of nickel borohydride complexes with CO$_2$.[38]

Conclusions

We have shown that β-diketiminate stabilised aluminium hydrides of the form $[^{\text{Dipp}}\mathbf{1/2}]$Al(R)H form dialkylborohydride complexes in the presence of borane $\{H(9\text{-}BBN)\}_2$. These borohydride systems exhibit unusual borane lability under ambient conditions. The extent of dissociation in solution is shown by van't Hoff analyses to be dependent on the polarity of the Al–H bond of the precursor hydride, which is itself influenced by the electronic character of both the aluminium-bound substituent and β-diketiminate backbone. The related system, $[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)(BH_4)$, does not show borane dissociation even under more forcing conditions, presumably reflecting the greater Lewis acidity (and smaller steric demands) of the BH_3 fragment over R_2BH. Consistently, the borohydride complexes $[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)(BH_4)$ and $[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)\{H_2(9\text{-}BBN)\}$ are shown to have distinctly different labilities towards CO_2, arising from the availability (or not) of the 'free' aluminium hydride in solution.

Experimental section

General details

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS and stored over potassium. NMR spectra were measured in benzene-d_6 or toluene-d_8 (both dried over potassium), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were measured on Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometers; ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B and ^{27}Al NMR spectra were referenced with respect to $BF_3{\cdot}OEt_2$ and $[Al(H_2O)_6]^{3+}$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. The syntheses of $[^{\mathrm{Dipp}}\mathbf{1}]AlH_2$,[48] $[^{\mathrm{Dipp}}\mathbf{1}]Al(OTf)H$,[11] $[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)H$, $[^{\mathrm{Dipp}}\mathbf{1}]Al(Me)H$, $[^{\mathrm{Dipp}}\mathbf{2}]AlH_2$ and $[^{\mathrm{Dipp}}\mathbf{2}]Al(Et)H$ [16] were carried out as per literature precedent. All other reagents were used as received.

Crystallographic details

Single-crystal X-ray diffraction data were collected using either an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector or an Enraf-Nonius Kappa CCD diffractometer. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[49] Data were collected at 150 K (unless otherwise stated) using mirror monochromated Cu Kα or Mo Kα radiation (Cu Kα – λ = 1.5418 Å; Mo Kα – λ = 0.71073). Structures were subsequently solved using SHELXT-2014 and refined on F2 using the SHELXL 2014 package and the graphical interface Olex2 or X-Seed.[50–53] Structures have been deposited with the CCDC 1895241–1895245 and 1895263.†

Syntheses of novel compounds

$[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)\{H_2(9\text{-}BBN)\}$. To a solution of $[^{\mathrm{Dipp}}\mathbf{1}]Al(Et)H$ (0.300 g, 0.632 mmol) in toluene (5 mL) was added a solution of $\{H(9\text{-}BBN)\}_2$ (0.077 g, 0.316 mmol of the dimer), also in toluene (3 mL) at room temperature. The reaction mixture was stirred rapidly for 3 h, filtered and concentrated to the point of incipient crystallisation. Storage at −30 °C for several days yielded single crystals suitable for X-ray diffraction. Yield: 0.27 g, 71%. ^1H NMR (400 MHz, benzene-d_6, 298 K): δ_H 0.52 (2H, q, $^3J_{HH}$ = 8.0 Hz, $CH_3C\underline{H}_2Al$), 1.02 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.23 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.39 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.43 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.52 (6H, s, CH_3 of β-diketiminato backbone), 1.14–1.91 (14H, br m, 9-borabicyclo(3.3.1)nonane-CH) 3.22 (2H, sept, $^3J_{HH}$ = 6.7 Hz, CH of Dipp ^{i}Pr), 3.40 (2H, sept, $^3J_{HH}$ = 6.7 Hz, CH of Dipp ^{i}Pr), 4.83 (1H, s, γ-CH), 7.10–7.17 (6H, m, aromatic CH). Signal for CH_3 of Al–Et obscured by Dipp ^{i}Pr, AlH_2B resonance not observed in either ^1H NMR spectra or $^1H\{^{11}B\}$ NMR spectra. $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 298 K): δ_C 4.2 (br, $CH_3\underline{C}H_2Al$), 10.7 ($\underline{C}H_3CH_2Al$), 17.9 (br, B–$\underline{C}$H), 24.3 (CH_3 of β-diketiminato backbone), 24.3 (CH_3 of Dipp ^{i}Pr), 24.7 (B–$CHCH_2\underline{C}H_2$–), 25.0, 25.1, 26.1 (CH_3 of Dipp ^{i}Pr), 27.5, 29.4 (CH of Dipp ^{i}Pr), 34.2 (B–$CH\underline{C}H_2CH_2$–), 99.5 (γ-CH), 124.4, 125.0, 127.5, 141.3, 143.1, 145.5 (ArC of Dipp), 172.2 (NC). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6, 298 K): δ_B −16 (s, $\Delta\omega_{1/2}$ = 212 Hz ^1H decoupled; $\Delta\omega_{1/2}$ = 285 Hz ^1H coupled). ^{27}Al NMR (104 MHz, benzene-d_6, 298 K): δ_{Al} 105. EI-MS: m/z calc. for $C_{329}H_{42}N_2Al$ ([M − (EtH{9-BBN})]$^+$) 445.3163, meas. 445.3184 (100%). IR (nujol/cm^{-1}) $\nu_{Al\text{–}H\text{–}B}$: 2066 (w), 2026 (w). Elemental microanalysis: calc. for $C_{39}H_{62}N_2AlB$: C 78.50% H 10.47% N 4.69% meas. C 78.36% H 10.32% N 4.67%. Crystallographic data: $C_{39}H_{62}N_2AlB$ (M_r = 596.73): monoclinic, $P2_1/c$, a = 10.75290(10), b = 12.94880(10), c = 26.8741(2) Å, β = 94.3816(7)°, V = 3730.94(5) Å^3, Z = 4, ρ_c = 1.062 g cm^{-3}, T = 150 K, λ = 1.54180 Å, μ(Cu Kα) = 0.660 mm^{-1}, 41 741 reflections collected, 7747 independent [R(int) = 0.022] used in all calculations. R_1 = 0.0409, wR_2 = 0.1049 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0438, wR_2 = 0.1074 for all unique reflections. Max. and min. residual electron densities 0.32, −0.22 e Å^{-3}.

$[^{\mathrm{Dipp}}\mathbf{1}]Al(H)\{H_2(9\text{-}BBN)\}$. A solution of $\{H(9\text{-}BBN)\}_2$ (0.181 g, 0.740 mmol of the dimer) in toluene (5 mL) was added to a solution of $[^{\mathrm{Dipp}}\mathbf{1}]AlH_2$ (0.60 g, 1.35 mmol), also in toluene (5 mL). The reaction mixture was stirred at room temperature overnight, leading to the formation of a colourless precipitate. Toluene was added until the precipitate redissolved, and the solution was filtered and concentrated to the point of incipient crystallisation. The solution was gently warmed to redissolve any solid and allowed to cool slowly to room temperature and then to −30 °C. Storage of this solution at −30 °C yielded colourless crystals suitable for X-ray diffraction. Yield: 0.70 g, 91%. ^1H NMR (400 MHz, benzene-d_6, 298 K): δ_H 1.05 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.15 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3

of Dipp ^{i}Pr), 1.39 (12H, 2 × overlapping d, $^{3}J_{HH}$ = 6.8 Hz, 2 × CH_3 of Dipp ^{i}Pr), 1.53 (6H, s, CH_3 of β-diketiminato backbone), 1.22–1.92 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.18 (2H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 3.33 (2H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 4.58 (1H, br s, Al–H), 4.90 (1H, s, γ-CH), 7.11–7.16 (6H, m, aromatic CH). AlH_2B not observed by ^{1}H NMR spectroscopy or ^{1}H{^{11}B} spectroscopy. ^{13}C{^{1}H} NMR (101 MHz, benzene-d$_6$, 298 K): δ_C 17.9 (br, B–$\underline{C}$HCH$_2$CH$_2$–), 23.8 (CH_3 of β-diketiminato backbone), 23.9, 24.5 (2 overlapping signals) (CH_3 of Dipp ^{i}Pr), 24.7 (B–CHCH$_2\underline{C}$H$_2$–), 25.8 (CH_3 of Dipp ^{i}Pr), 28.3, 29.5 (CH of Dipp ^{i}Pr), 34.0 (B–CH$\underline{C}$H$_2$CH$_2$), 97.8 (γ-CH), 124.1, 125.1, 127.6, 140.7, 142.6, 145.5 (ArC of Dipp), 171.4 (NC). ^{11}B{^{1}H} NMR (128 MHz, benzene-d$_6$, 298 K): δ_B −15.7 (s, $\Delta\omega_{1/2}$ = 391 Hz ^{1}H decoupled; $\Delta\omega_{1/2}$ = 585 Hz ^{1}H coupled). ^{27}Al NMR (104 MHz, benzene-d$_6$, 298 K): δ_{Al} not observed. EI-MS: *m*/*z* calc for $C_{29}H_{42}N_2Al$ ([M − (H$_2${9-BBN})]$^+$) 445.3163, meas. 445.2885 (6%). IR (nujol/cm^{-1}) $\nu_{Al–H–B}$: 2065 (w), 2034 (w); $\nu_{Al–H}$: 1846 (s). Elemental microanalysis: calc. for $C_{37}H_{58}N_2AlB$: C 78.15% H 10.28% N 4.93% meas. C 77.87% H 10.15% N 4.87%. Crystallographic data: $C_{37}H_{58}N_2AlB$ (M_r = 568.67): monoclinic, $P2_1/m$, a = 8.9708(3), b = 19.9599(6), c = 10.2247(3) Å, β = 108.937(3) °, V = 1731.71(10) Å^3, Z = 2, ρ_c = 1.091 g cm^{-3}, T = 150 K, λ = 1.54184 Å, μ(Cu Kα) = 0.690 mm^{-1}, 9092 reflections collected, 3663 independent [R(int) = 0.021] used in all calculations. R_1 = 0.0387, wR_2 = 0.0995 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0435, wR_2 = 0.1039 for all unique reflections. Max. and min. residual electron densities 0.28, −0.26 e Å^{-3}.

[^{Dipp}1]Al(Me){H$_2$(9-BBN)}. A Schlenk was charged with [^{Dipp}**1**]Al(Me)H (0.110 g, 0.239 mmol) and {H(9-BBN)}$_2$ (0.029 g, 0.120 mmol of the dimer) and toluene was added (5 mL). The resulting solution was stirred for 3 h at room temperature, filtered and concentrated to the point of incipient crystallisation. Storage at −30 °C for 48 h produced colourless block-like crystals which were isolated and dried *in vacuo*. Yield: 0.08 g, 55%. ^{1}H NMR (400 MHz, benzene-d$_6$, 298 K): δ_H −0.10 (3H, s, AlMe), 1.01 (6H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.15 (6H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.38 (6H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.41 (6H, d, $^{3}J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.53 (6H, s, CH_3 of β-diketiminato backbone), 1.32–1.92 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.27 (4H, 2 × overlapping sept, $^{3}J_{HH}$ = 6.8 Hz, 2 × CH of Dipp ^{i}Pr), 4.91 (1H, s, γ-CH), 7.10–7.16 (6H, m, aromatic CH). AlH_2B not observed by ^{1}H NMR spectroscopy or ^{1}H{^{11}B} spectroscopy. ^{13}C{^{1}H} NMR (101 MHz, benzene-d$_6$, 298 K): δ_C −10.1 (br, CH_3 of AlMe), 17.9 (br, B–$\underline{C}$HCH$_2$CH$_2$–), 24.0 (CH_3 of β-diketiminato backbone), 24.3, 24.6 (CH_3 of Dipp ^{i}Pr), 24.7 (B–CHCH$_2\underline{C}$H$_2$–), 25.1, 26.4 (CH_3 of Dipp ^{i}Pr), 27.9, 29.6 (CH of Dipp ^{i}Pr), 34.2 (B–CH$\underline{C}$H$_2$CH$_2$), 98.4 (γ-CH), 124.2, 125.0, 127.5, 141.2, 143.0, 145.5 (ArC of Dipp), 171.5 (NC). ^{11}B{^{1}H} NMR (128 MHz, benzene-d$_6$, 298 K): δ_B − 15.2 (s, $\Delta\omega_{1/2}$ = 420 Hz ^{1}H decoupled; $\Delta\omega_{1/2}$ = 604 Hz, ^{1}H coupled). ^{27}Al NMR (104 MHz, benzene-d$_6$, 298 K): δ_{Al} not observed. EI-MS: *m*/*z* calc for $C_{29}H_{42}N_2Al$ ([M − Me-(H{9-BBN})]$^+$) 445.3163, meas. 445.3169 (100%). IR (nujol/cm^{-1}) $\nu_{Al–H–B}$: 2065 (w), 2030 (w). Elemental microanalysis: calc. for $C_{38}H_{60}N_2AlB$: C 78.33% H 10.38% N 4.81% meas. C 78.27% H 10.36% N 4.92%. Crystallographic data: $C_{38}H_{58}N_2AlB$ (M_r = 580.65): monoclinic, $P2_1/m$, a = 9.1574(18), b = 20.084(4), c = 10.311(2) Å, β = 109.98(3) °, V = 1782.2(7) Å^3, Z = 2, ρ_c = 1.082 g cm^{-3}, T = 150 K, λ = 0.71073 Å, μ(Mo Kα) = 0.084 mm^{-1}, 13 582 reflections collected, 4180 independent [R(int) = 0.0355] used in all calculations. R_1 = 0.0538, wR_2 = 0.1459 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0743, wR_2 = 0.1608 for all unique reflections. Max. and min. residual electron densities 0.690, −0.291 e Å^{-3}.

[^{Dipp}1]Al(OTf){H$_2$(9-BBN)}$_2$. To a solution of [^{Dipp}**1**]Al(OTf)H (0.80 g, 1.35 mmol) in toluene (6 mL) was added a solution of {H(9-BBN)}$_2$ (0.18 g, 0.74 mmol of the dimer), also in toluene (5 mL), at room temperature. The solution was stirred overnight, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at −30 °C for 48 h produced colourless crystals of the toluene bis-solvate, suitable for X-ray diffraction. Yield: 0.86 g, 89%. ^{1}H NMR (400 MHz, benzene-d$_6$, 298 K): δ_H 0.93 (6H, d, $^{3}J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.25 (6H, d, $^{3}J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.32 (6H, d, $^{3}J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.47 (6H, d, $^{3}J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.59 (6H, s, CH_3 of β-diketiminato backbone), 1.01–1.93 (14H, m, CH/CH$_2$ of 9-BBN), 2.95 (2H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 3.65 (2H, sept, $^{3}J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 5.20 (1H, s, γ-CH), 7.03–7.19 (6H, m, aromatic CH of Dipp and OCH$_2$Ph). ^{13}C{^{1}H} NMR (101 MHz, benzene-d$_6$, 298 K): δ_C 15.9 (br, B–$\underline{C}$H), 24.1 (CH_3 of β-diketiminato backbone), 24.3, 24.6 (CH_3 of Dipp ^{i}Pr), 24.8 (B–CHCH$_2\underline{C}$H$_2$–), 24.9, 25.4 (CH_3 of Dipp ^{i}Pr), 27.7, 29.3 (CH of Dipp ^{i}Pr), 33.2 (B–CH$\underline{C}$H$_2$CH$_2$–), 101.0 (γ-CH), 124.4, 125.7, 139.1, 143.2, 146.6 (ArC of Dipp), 174.5 (NC). Resonance for CF_3 of OSO_2CF_3 not observed. ^{19}F NMR (376 MHz, benzene-d$_6$, 298 K): δ_F −76.9. ^{11}B{^{1}H} NMR (128 MHz, benzene-d$_6$, 298 K): δ_B −17.5 (s, $\Delta\omega_{1/2}$ 222 Hz (^{1}H decoupled), $\Delta\omega_{1/2}$ 300 Hz (^{1}H coupled). ^{27}Al NMR (104 MHz, benzene-d$_6$, 298 K): δ_{Al} not observed. IR (nujol/cm^{-1}): $\nu_{Al–H–B}$ 2021 (br). EI-MS: *m*/*z* calc for $C_{30}H_{41}N_2AlF_3O_3S$ ([M − (H$_2${9-BBN})]$^+$) 593.2605, meas. 593.2637 (12%). Elemental microanalysis: calc. for $C_{38}H_{57}AlBF_3N_2O_3S$: C 63.68% H 8.02% N 3.91%, meas. C 63.60% H 7.84% N 3.95%. Crystallographic data: $C_{38}H_{57}AlBF_3N_2O_3S{\cdot}2(C_7H_8)$ (M_r = 900.97): orthorhombic, *Pnma*, a = 10.193(2), b = 25.619(5), c = 19.416(4) Å, $\alpha = \beta = \gamma$ = 90°, V = 5070.2(17) Å^3, Z = 4, ρ_c = 1.180 g cm^{-3}, T = 150(2) K, λ = 0.71073 Å, μ(Mo Kα) = 0.134 mm^{-1}, 5897 reflections collected, 4088 independent [R(int) = 0.0333] used in all calculations. R_1 0.0638, wR_2 = 0.1664 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0950, wR_2 = 0.1868 for all unique reflections. Max. and min. residual electron densities 0.379, −0.345 e Å^{-3}.

[^{Dipp}2]Al(Et){H$_2$(9-BBN)}. To a solution of [^{Dipp}**2**](Et)H (0.25 g, 0.47 mmol) in toluene (7 mL) was added at room temperature a solution of {H(9-BBN)}$_2$ (0.058 g, 0.235 mmol of the dimer) also in toluene (5 mL). The reaction mixture was stirred at room temperature for 5 h, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at −30 °C overnight yielded colourless, block-like crystals (of the toluene solvate) suitable for X-ray diffraction. Yield: 0.14 g, 47%. ^{1}H NMR (400 MHz, benzene-d$_6$, 298 K): δ_H 0.78 (2H, q, $^{3}J_{HH}$ = 8.0 Hz, CH$_3$C$\underline{H}_2$Al), 0.97 (3H, br t, C$\underline{H}_3$CH$_2$Al), 1.07 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.23 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.40 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.67 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dipp ^{i}Pr), 1.09–1.94 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.22 (6H, s, CH_3 of Me_2N), 2.95 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 3.67 (1H, s, γ-CH), 3.77 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ^{i}Pr), 7.00–7.14 (6H, m, aromatic CH). AlH_2B not observed by ^1H NMR spectroscopy or $^1H\{^{11}B\}$ spectroscopy. $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 298 K): δ_C 0.97 (br, $CH_3\underline{C}H_2Al$), 11.0 ($\underline{C}H_3CH_2Al$), 17.0 (br, B–$\underline{C}HCH_2CH_2$–), 24.3, 24.4 (CH_3 of Dipp ^{i}Pr), 25.1 (B–$CHCH_2\underline{C}H_2$–), 26.5, 26.6 (CH_3 of Dipp ^{i}Pr), 28.5 (2 overlapping signals, 2 × CH of Dipp ^{i}Pr), 33.6 (B–$CH\underline{C}H_2CH_2$), 41.0 (CH_3 of Me_2N), 76.4 (γ-CH), 125.0, 125.4, 126.2, 142.5, 144.1, 145.7 (ArC of Dipp), 167.8 (NC). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6, 298 K): δ_B −17.4 (s, $\Delta\omega_{1/2}$ 253.4 Hz ^1H decoupled; $\Delta\omega_{1/2}$ = 332.9 Hz ^1H coupled). ^{27}Al NMR (104 MHz, benzene-d_6, 298 K): δ_{Al} 109. IR (nujol/cm^{-1}) ν_{Al-H-B}: 2104 (m). Elemental microanalysis: calc. for $C_{41}H_{68}N_4AlB$: C 75.20% H 10.47% N 8.56% meas. C 75.05% H 10.35% N 8.42%. Crystallographic data: $C_{41}H_{68}N_4AlB\cdot C_7H_8$ (M_r = 700.85): monoclinic, 12/*a*, a = 19.0779(5), b = 11.5597(3), c = 39.5676(9) Å, β = 100.891(3) °, V = 8568.9(4) Å^3, Z = 8, ρ_c = 1.087 g cm^{-3}, T = 150 K, λ = 1.54184 Å, μ(Cu Kα) = 0.654 mm^{-1}, 25 090 reflections collected, 8889 independent [R(int) = 0.0257] used in all calculations. R_1 = 0.0677, wR_2 = 0.1917 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0837, wR_2 = 0.2100 for all unique reflections. Max. and min. residual electron densities 0.627, −0.588 e Å^{-3}.

[^{Dipp}2]Al(H){H_2(9-BBN)}. To a solution of [^{Dipp}2]AlH_2 (0.080 g, 0.159 mmol) in toluene (2 mL) at room temperature was added a solution of $\{H(9\text{-}BBN)\}_2$ (0.021 g, 0.0871 mmol of the dimer), also in toluene (1 mL). The reaction mixture was stirred for 1 h at room temperature, during which time a colourless precipitate was evolved. Toluene was subsequently added until this precipitate redissolved. The resulting solution was filtered and stored at −30 °C for 48 h, yielding single colourless crystals which were isolated and dried *in vacuo*. Yield: 0.07 g, 66%. ^1H NMR (400 MHz, benzene-d_6, 298 K): δ_H 1.07 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.17 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.40 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.65 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH_3 of Dipp ^{i}Pr), 1.13–1.99 (14H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.18 (12H, s, CH_3 of Me_2N), 2.91 (2H, sept, $^3J_{HH}$ = 6.7 Hz, CH of Dipp ^{i}Pr), 3.61 (1H, s, γ-CH), 3.79 (2H, sept, $^3J_{HH}$ = 6.7 Hz, CH of Dipp ^{i}Pr), 4.48 (1H, br s, Al–H), 6.94–7.12 (6H, m, aromatic CH). AlH_2B not observed by ^1H NMR spectroscopy or $^1H\{^{11}B\}$ spectroscopy. $^{13}C\{^1H\}$ NMR (126 MHz, benzene-d_6, 298 K): δ_C 17.1 (br, B–$\underline{C}HCH_2CH_2$–), 24.3, 24.8, 25.0 (CH_3 of Dipp ^{i}Pr), 25.6 (B–$CHCH_2\underline{C}H_2$–), 25.7 (CH_3 of Dipp ^{i}Pr), 28.5, 29.0 (CH of Dipp ^{i}Pr), 33.6 (B–$CH\underline{C}H_2CH_2$), 41.3 (CH_3 of Me_2N), 75.1 (γ-CH), 124.8, 125.3, 126.4, 142.1, 143.7, 145.9 (ArC of Dipp), 166.8 (NC). $^{11}B\{^1H\}$ NMR (128 MHz, benzene-d_6, 298 K): δ_B −17.4 (s, $\Delta\omega_{1/2}$ = 200 Hz ^1H decoupled; $\Delta\omega_{1/2}$ = 320 Hz ^1H coupled). ^{27}Al NMR (104 MHz, benzene-d_6, 298 K): δ_{Al} not observed. EI-MS: m/z calc for $C_{31}H_{48}AlN_4$ ($[M - \{H_2(9\text{-}BBN)\}]^+$) 503.3694, meas. 503.3707 (100%). IR (nujol/cm^{-1}) ν_{Al-H-B}: 2103 (m), ν_{Al-H}: 1850 (s). Elemental microanalysis: calc. for $C_{39}H_{64}N_4AlB$: C 74.74% H 10.29% N 8.94% meas. C 74.84% H 10.16% N 8.79%. Crystallographic data: $C_{39}H_{64}N_4AlB$ (M_r = 626.73): monoclinic, $P2_1/m$, a = 9.01940(10), b = 21.1266(3), c = 10.7665(2) Å, β = 113.865(2) °, V = 1876.14(6) Å^3, Z = 2, ρ_c = 1.109 g cm^{-3}, T = 150 K, λ = 1.54184 Å, μ(Cu Kα) = 0.693 mm^{-1}, 13 033 reflections collected, 3997 independent [R(int) = 0.0185] used in all calculations. R_1 = 0.0371, wR_2 = 0.0934 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0400, wR_2 = 0.0963 for all unique reflections. Max. and min. residual electron densities 0.248, −0.231 e Å^{-3}.

Conflicts of interest

There are no conflicts to declare.

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