Synthesis and structure of a magnesium–amidoborane complex and its role in catalytic formation of a new bis-aminoborane ligand†

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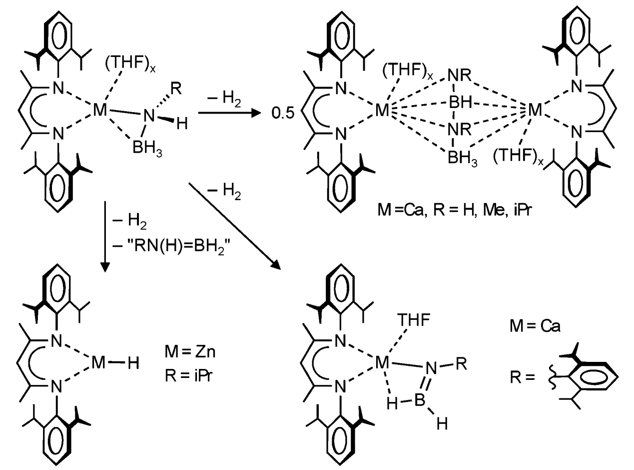
A synthetic route to a magnesium–amidoborane complex and its role in the catalytic conversion of a substituted ammonia–borane RNH_2BH_3 into $HB(NHR)_2$ is discussed.

The recently introduced early main group metal amidoborane compounds $LiNH_2BH_3$, $NaNH_2BH_3$ and $Ca(NH_2BH_3)_2$ show high potential as future hydrogen storage materials.[1,2] The elimination of molecular hydrogen in these compounds displays several advantages over that in NH_3BH_3. Among these are a significantly lower hydrogen release temperature and near thermoneutrality which might facilitate development of a reversible hydrogen up-take process.

We recently initiated studies on heteroleptic calcium amidoborane complexes containing a large DIPP-nacnac ligand (Scheme 1, DIPP-nacnac = $CH\{(CMe)(2,6\text{-}i\mathrm{Pr}_2C_6H_3N)\}_2$).[3] Solubilization of the calcium amidoborane complex allowed investigation of the hydrogen release process under homogeneous conditions and crystallization of the decomposition products. In addition, we investigated the effect of substituents on nitrogen.[4] A large substituent inhibits dimerization during hydrogen release and we could isolate a complex containing a borylamide anion $RN{=}BH_2^-$ (Scheme 1).



Scheme 1

Attempted isolation of a zinc amidoborane complex, however, gave quantitative conversion into a zinc hydride species (Scheme 1).[5] In order to understand the effect of the metal on the stability and decomposition of metal amidoborane complexes in general, we here report our preliminary investigations on the synthesis of a magnesium amidoborane complex with a large substituent on nitrogen.

Addition of one equivalent of $(DIPP)NH_2BH_3$ to a solution of $(DIPP\text{-}nacnac)MgN(SiMe_3)_2$ in benzene at 20 °C immediately gave vigorous evolution of H_2 gas. As all $(DIPP)NH_2BH_3$ had reacted but the starting material $(DIPP\text{-}nacnac)MgN(SiMe_3)_2$ was hardly consumed, the formation of H_2 gas was not due to the instability of the expected magnesium amidoborane complex but rather to a catalytic decomposition of $(DIPP)NH_2BH_3$. This decomposition reaction is clean and the only product was fully characterized as $HB[NH(DIPP)]_2$ by NMR and X-ray diffraction (Fig. 1).‡ The N and B atoms display close to planar conformations and could be regarded as *sp*^{2}-hybridized. Their coplanar arrangement allows for delocalization of the *p*-lone pairs on both N atoms into the empty p-orbital on B and explains the short B–N bond distances. This species represents a hitherto unknown bis(amino)borane, a class of compounds which has received considerable attention: double deprotonation gives access to dianionic bora-amidinate (bam) ligands $HB(NR)_2^{2-}$ which are isolobal to the mono-anionic amidinate $HC(NR)_2^-$.[6]

Scheme 2 shows the proposed mechanism of formation. In the first step the expected magnesium amidoborane complex is formed. This product could react with the acidic ammonia–borane $(DIPP)NH_2BH_3$ and eliminate H_2. A 1,3-H shift from one B to the other affords $HB[NH(DIPP)]_2$ and $(DIPP\text{-}nacnac)MgBH_4$. The latter borate complex could react with $(DIPP)NH_2BH_3$ to give $(DIPP\text{-}nacnac)MgNH(DIPP)BH_3$ and BH_3. Alternatively, *β*-hydride elimination could afford $(DIPP\text{-}nacnac)MgH$, $HB[NH(DIPP)]_2$ and BH_3. The highly reactive magnesium hydride complex could either deprotonate $(DIPP)NH_2BH_3$ or react with BH_3 to give $(DIPP\text{-}nacnac)MgBH_4$.

Although speculative, the proposed mechanism is underscored by several observations.

(i) Cooling of the reaction mixture gave a small crop of colourless crystals which could be identified as $(DIPP\text{-}nacnac)MgBH_4$ by NMR and X-ray diffraction (*vide infra*).

(ii) Addition of catalytic amounts of $(DIPP\text{-}nacnac)MgBH_4$ to a solution of $(DIPP)NH_2BH_3$ likewise resulted in quantitative formation of $HB[NH(DIPP)]_2$. This makes it a likely intermediate in the catalytic cycle.

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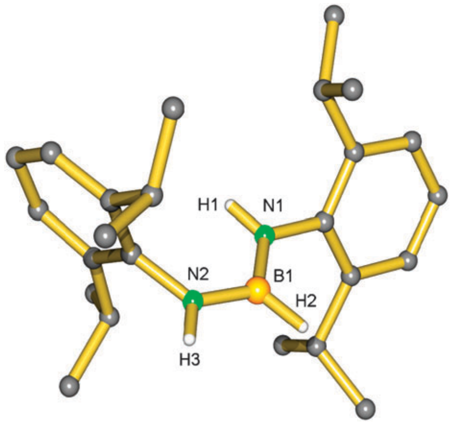
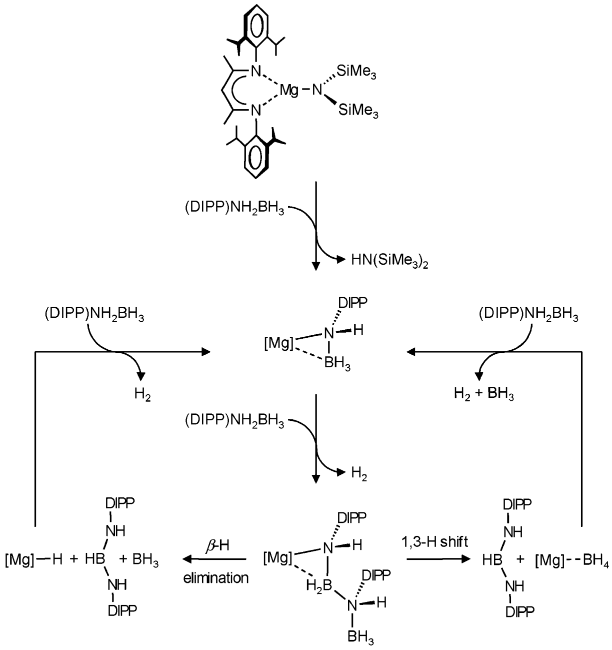


Fig. 1 The molecular structure of $HB[NH(DIPP)]_2$; most hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): B1–N1 1.415(2), B1–N2 1.414(2), N1–B1–N2 121.9(1).



Scheme 2

(iii) The by-product "BH_3" could be identified in the ^1H NMR spectrum as B_2H_6 (the product $HB[NH(DIPP)]_2$ does not react with diborane).

Although the Mg-mediated conversion of $(DIPP)NH_2BH_3$ into $HB[NH(DIPP)]_2$, BH_3 and H_2 (eqn (1)) is a quantitative and clean reaction, we developed a more atom-efficient route. It was found that $(DIPP)NH_2$ and $H_3B{\cdot}SMe_2$ in a 2/1 ratio can be converted quantitatively to $HB[NH(DIPP)]_2$ and H_2 (eqn (2)). Commercially available n-Bu_2Mg works equally well as a catalyst, however, a higher temperature (60 °C) is essential to prevent precipitation of the salt $Mg(BH_4)_2$. This simple route allows an economically large scale preparation of this bis(amino)borane. Its twofold deprotonated form, the bora-amidinate $HB[N(DIPP)]_2^{2-}$, would be the first bam ligand with a H-substituent in the backbone and is isolobal to a versatile sterically congested amidinate: $HC[N(DIPP)]_2^-$. The scope of this dianionic bam ligand in organometallic chemistry is currently under investigation.

$$2\,(\mathrm{DIPP})\mathrm{NH_2BH_3} \xrightarrow[\text{toluene, 20 °C}]{\substack{\text{5 mol\%}\\ \text{(DIPP-nacnac)MgN(SiMe}_3)_2}} \mathrm{HB[NH(DIPP)]_2 + BH_3 + 2\,H_2} \tag{1}$$

$$2\,(\mathrm{DIPP})\mathrm{NH_2} + \mathrm{H_3B{\bullet}SMe_2} \xrightarrow[\text{toluene, 60 °C}]{\substack{\text{2.5 mol\%}\\ (n\mathrm{Bu})_2\mathrm{Mg}}} \mathrm{HB[NH(DIPP)]_2 + 2\,H_2} \tag{2}$$

Crystals of $(DIPP\text{-}nacnac)MgBH_4$, isolated from Mg-mediated catalytic formation of $HB[NH(DIPP)]_2$, were analyzed by X-ray diffraction.‡ A solvent-free dinuclear complex with terminal chelating DIPP-nacnac ligands and bridging BH_4^- ions is observed (Fig. 2; hydrogen atoms in BH_4^- have been located and refined). The BH_4^- ions coordinate to both Mg^{2+} centers in a bidentate fashion in which one of the hydride atoms bridges both metals. This bridging bonding mode has never been observed in magnesium tetrahydridoborate complexes but is known in lithium chemistry (*e.g.* in $[(TMEDA)LiBH_4]_2$).[7] It differs from $Mg{\cdots}D_2BD_2{\cdots}Mg$ bridging in $[Mg(BD_4)_2]_\infty$.[8] Heavier alkaline–earth metal borate complexes typically show $(\eta^3)HBH_3{\cdots}M^{2+}$ contacts (M = Ca, Sr, Ba).[9,10] The bridging nature of the BH_4^- ions in the current structure results in $Mg{\cdots}B$ distances (average 2.538(2) Å) that are much longer than that of 2.241(2) Å in $(DIPP\text{-}nacnac)MgBH_4{\cdot}OEt_2$.[11] In the latter structure BH_4^- is bound to Mg^{2+} in η^3-fashion.

The attempted synthesis of the amidoborane complex $(DIPP\text{-}nacnac)MgNH(DIPP)BH_3$ resulted in catalytic conversion of $(DIPP)NH_2BH_3$ into $HB[NH(DIPP)]_2$. This is likely due to the low reactivity of the $Mg–N(SiMe_3)_2$ functionality: slow formation of the magnesium amidoborane complex allows for its subsequent reaction with the substrate $(DIPP)NH_2BH_3$. The recently published magnesium hydride complex $[(DIPP\text{-}nacnac)MgH]_2$,[12] however, is much more reactive and deprotonates $(DIPP)NH_2BH_3$ in toluene immediately already at 0 °C. Under these conditions no side reactions are observed and $(DIPP\text{-}nacnac)MgNH(DIPP)BH_3$ could be isolated in 59% crystalline yield. Although it crystallizes in the form of small cubes, a structure could be determined (Fig. 3).‡ The monomeric solvent-free complex shows side-on coordination of the amidoborane anion to Mg^{2+}. This magnesium amidoborane complex is quite stable towards elimination of hydrogen. Decomposition in either benzene or THF solution starts at temperatures well over 100 °C. The stability of this magnesium amidoborane complex underscores the mechanism proposed for catalytic formation of $HB[NH(DIPP)]_2$ in Scheme 2 and excludes a mechanism with an intermediate containing the boryl amide $(DIPP)N = BH_2^-$. Further details on the decomposition of $(DIPP\text{-}nacnac)MgN(DIPP)HBH_3$ as well as that of other magnesium amidoborane complexes will be described in a forthcoming paper.[13]

In summary, reaction of the heteroleptic magnesium complex $(DIPP\text{-}nacnac)MgN(SiMe_3)_2$ with $(DIPP)NH_2BH_3$

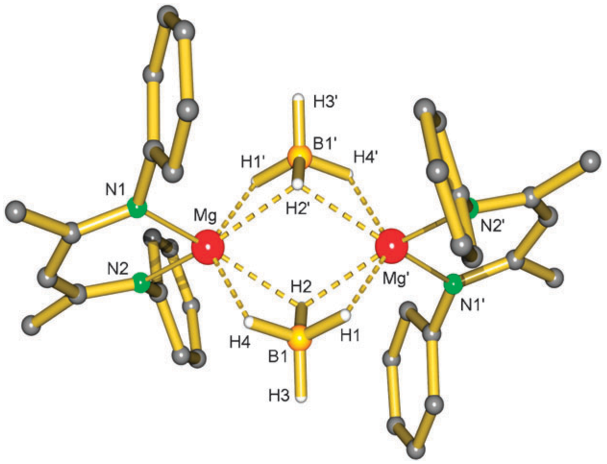


Fig. 2 The molecular structure of $[(\text{DIPP-nacnac})\text{MgBH}_4]_2$ (the *i*Pr substituents and most hydrogen atoms have been omitted for clarity). Selected bond distances (Å): Mg–N1 2.035(1), Mg–N2 2.041(1), Mg–H1′ 1.95(2), Mg–H2′ 2.20(2), Mg–H2 2.34(2), Mg–H4 1.96(2), Mg···B1 2.541(2), Mg···B1′ 2.535(2).

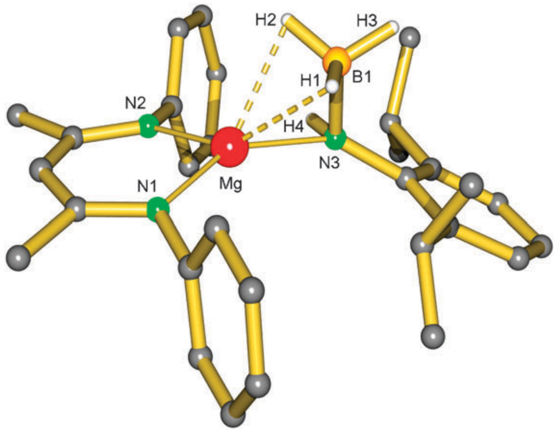


Fig. 3 The molecular structure of $(\text{DIPP-nacnac})\text{MgNH(DIPP)BH}_3$ (the *i*Pr substituents on the DIPP-nacnac ligand and most hydrogen atoms have been omitted for clarity). Selected bond distances (Å): Mg–N1 2.004(5), Mg–N2 2.024(5), Mg–N3 2.083(4), Mg···B1 2.291(7).

resulted in a catalytic decomposition to the bis(amino)borane HB[NH(DIPP)]_2. As this compound can be doubly deprotonated to a potentially useful bam ligand, a convenient atom-efficient route was developed. Magnesium amidoborane complexes are accessible by use of a much more reactive magnesium hydride reagent.

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Notes and references

‡ Crystallographic data for HB[NH(DIPP)]_2: $C_{24}H_{37}BN_2$, M = 364.37, monoclinic, space group $P2_1$, a = 10.2052(9), b = 10.3128(9), c = 11.5048(11) Å, β = 108.727(5)°, U = 1146.71(18) Å^3, Z = 2, D_c = 1.055 g cm^{-3}, $F(000)$ = 400, μ(Mo-Kα) = 0.060 mm^{-1}, 1.9 ≤ θ ≤ 30.1°, 14 398 reflections measured, 6317 unique (R_{int} = 0.054) were used in all calculations, R_1 = 0.0474 [$I > 2\sigma(I)$, 5329 reflections] and wR_2 = 0.1133 (all data); max/min. residual electron density: 0.17/−0.21.

Crystallographic data for $[(\text{DIPP})\text{nacnacMgBH}_4]_2$: $C_{58}H_{90}B_2Mg_2N_4$, M = 913.58, monoclinic, space group $P2_1/n$, a = 14.3266(11), b = 13.9025(8), c = 15.1584(13) Å, β = 106.287(6)°, U = 2898.0(4) Å^3, Z = 2, D_c = 1.047 g cm^{-3}, $F(000)$ = 1000, μ(Mo-Kα) = 0.079 mm^{-1}, 3.5 ≤ θ ≤ 25.6°, 18 615 reflections measured, 5409 unique (R_{int} = 0.049) were used in all calculations, R_1 = 0.0460 [$I > 2\sigma(I)$, 4369 reflections] and wR_2 = 0.1298 (all data); max/min. residual electron density: 0.46/−0.20.

Crystallographic data for $(\text{DIPP-nacnac})\text{MgNH(DIPP)BH}_3$: $C_{41}H_{62}BMgN_3$, M = 632.06, monoclinic, space group $P2_1/c$, a = 18.295(4), b = 11.8119(14), c = 18.846(3) Å, β = 103.004(15)°, U = 3968.2(12) Å^3, Z = 4, D_c = 1.058 g cm^{-3}, $F(000)$ = 1384, μ(Mo-Kα) = 0.075 mm^{-1}, 3.5 ≤ θ ≤ 25.0°, 17 455 reflections measured, 6903 unique (R_{int} = 0.109) were used in all calculations, R_1 = 0.0924 [$I > 2\sigma(I)$, 2340 reflections] and wR_2 = 0.2375 (all data); max/min. residual electron density: 0.34/−0.30.

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