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# Unprecedented reactivity of an aluminium hydride complex with $\text{ArNH}_2\text{BH}_3$ : nucleophilic substitution *versus* deprotonation†

Sjoerd Harder\*<sup>a</sup> and Jan Spielmann<sup>b</sup>

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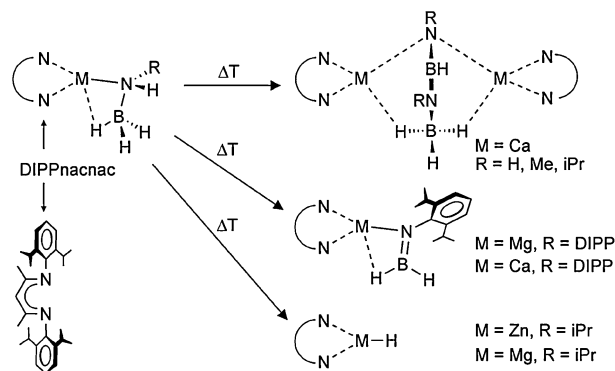
DOI: 10.1039/c1cc14689k

Reaction of  $\text{DIPPnacnacAlH}_2$  with  $\text{DIPPNH}_2\text{BH}_3$  did not give the anticipated deprotonation but nucleophilic substitution at B was observed instead. The product  $\text{DIPPnacnacAl}(\text{BH}_4)_2$  was isolated and structurally characterized. Nucleophilic displacement at B might play a role in mechanistic pathways related to metal amidoborane complexes.

Early main group metal amidoboranes have been identified as advantageous hydrogen storage materials that, in contrast to ammonia-borane, release hydrogen at significantly lower temperatures without foaming and borazine contamination.<sup>1–3</sup> In addition, the near thermoneutrality of hydrogen release is promising in the search for possible reversibility.

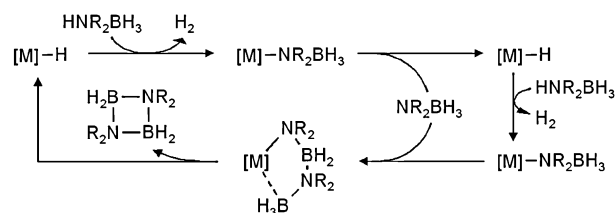
Although this work is very much the domain of solid-state chemists we recently demonstrated that molecular chemists can contribute to this field by using molecular model systems that allow for isolation of intermediates.<sup>4–9</sup> The latter are based on complexes that contain the bulky, strongly bidentate coordinating,  $\beta$ -diketiminato ligand DIPPnacnac; DIPPnacnac =  $\text{CH}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2$ . These complexes are soluble in most organic solvents and form a platform for solution NMR studies and single crystal structure investigations. Thus, we revealed the identity of new species that are useful in mechanistic considerations for the hydrogen release process in solid metal amidoborane materials<sup>10,11</sup> (Scheme 1).

Part of our investigation deals with the influence and role of the metal. Hitherto we have not been able to isolate a  $\beta$ -diketiminato zinc amidoborane complex: all attempts led to formation of a zinc hydride complex (Scheme 1) which is presumably formed by the rapid decomposition of a zinc amidoborane intermediate through  $\beta$ -H elimination.<sup>7</sup> In the follow-up work we now address the possibility to prepare a  $\beta$ -diketiminato aluminium amidoborane complex. Such a complex could provide information on the stability and reactivity of amidoborane complexes with a highly Lewis-acidic metal center.



**Scheme 1** Thermal decomposition of  $\beta$ -diketiminato metal amidoborane model compounds.

From previous work on the use of  $\text{AlH}_3/\text{NH}_3\text{BH}_3$  mixtures for the synthesis of ceramic Al/B/N materials, it is suspected that aluminium amidoboranes could be quite unstable towards  $\text{H}_2$  loss.<sup>12</sup> Likewise, Hill's recent investigations on catalytic dehydrocoupling of  $\text{HNMe}_2\text{BH}_3$  by group 3 metal compounds like  $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$  and  $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_3$  underscore the high instability of amidoborane complexes with significantly Lewis-acidic metals like  $\text{Y}^{3+}$  and  $\text{Sc}^{3+}$ .<sup>13</sup> Rapid  $\beta$ -H elimination and formation of highly reactive  $\text{Me}_2\text{N}=\text{BH}_2$  led to formation of the anion:  $\text{Me}_2\text{N}-\text{BH}_2-\text{NMe}_2-\text{BH}_3^-$  (Scheme 2). A similar species was also found in Mg-catalyzed reactions.<sup>14,15</sup> This is proposedly an intermediate on the way to our earlier reported  $\text{RN}-\text{BH}-\text{NH}-\text{BH}_3^{2-}$  anion (Scheme 1).<sup>4</sup> As the anion  $\text{Me}_2\text{N}-\text{BH}_2-\text{NMe}_2-\text{BH}_3^-$  lacks protic N–H units for further dehydrogenation it could be trapped as a product. Recent publications by Wright *et al.* corroborate the high instability of Al amidoborane complexes: reaction of  $\text{Al}(\text{NMe}_2)_3$  with two equivalents of  $\text{HNMe}_2\text{BH}_3$  gave the complex  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ .<sup>16</sup> Further evidence for instability



**Scheme 2** Tentative mechanism for the catalytic dehydrocoupling of  $\text{HNR}_2\text{BH}_3$ .

<sup>a</sup> Stratingh Institute, University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands. E-mail: s.harder@rug.nl; Fax: +31 50 3634296; Tel: +31 50 3634322

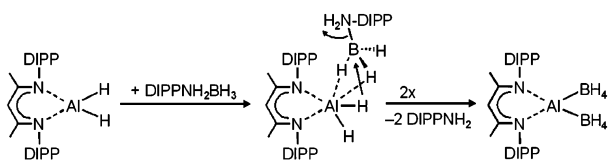
<sup>b</sup> Fachbereich Chemie, Universitätsstraße 5, 45117 Essen, Germany

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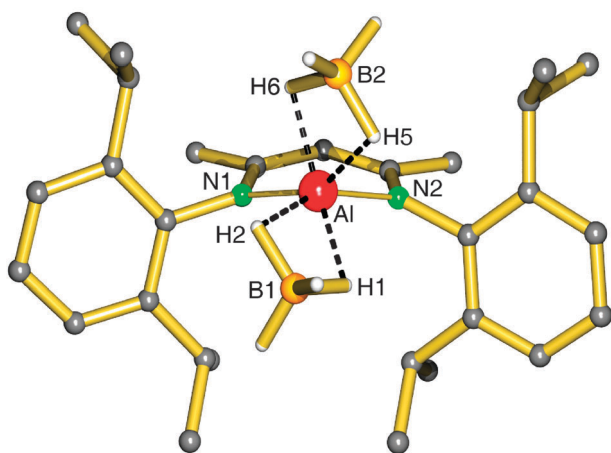
of amidoboranes with Lewis-acidic metals like  $Y^{3+}$  is reported by Grochala *et al.*: under ambient conditions  $Y(NH_2BH_3)_3/(LiCl)_3$  spontaneously decomposes within days.<sup>17</sup>

Despite indications for the high instability of Al amidoborane complexes,  $LiAl(NH_2BH_3)_4$  is exemplarily described in a recent patent.<sup>18</sup> We investigated the possibility to obtain a  $\beta$ -diketiminato aluminium amidoborane complex. Steric bulky ligands could prevent B–H agostic interactions and block the  $\beta$ -H elimination pathway. As  $[DIPPNacnacMgH]_2$ <sup>19</sup> was found to be an excellent precursor for the syntheses of a series of Mg amidoborane complexes in near quantitative yields,<sup>8,20</sup> we pursued this deprotonation route with the highly potent reagent  $DIPPNacnacAlH_2$ .<sup>21</sup> Stoichiometric reaction with several ammonia-boranes like  $NH_3BH_3$ ,  $MeNH_2BH_3$  and  $iPrNH_2BH_3$  proceeded with gas evolution but led to complicated reaction mixtures from which no defined products could be isolated. In contrast, the reaction with  $DIPPNH_2BH_3$  proceeded smoothly already at room temperature but no gas evolution was visible (Scheme 3). Monitoring the reaction with <sup>11</sup>B NMR showed that the consumption of  $DIPPNH_2BH_3$  (broad signal at  $-15.1$  ppm) is complete within one hour. The clean formation of a product with a characteristic quintet at  $-36.6$  ppm ( $^1J_{BH} = 85.3$  Hz) is indicative of formation of the  $BH_4^-$  ion. Crystallization from cold hexane and subsequent analysis by X-ray diffraction revealed the complex  $DIPPNacnacAl(BH_4)_2$  (Fig. 1).

The crystal structure shows a monomeric complex in which the Al center is chelated by the bulky  $DIPPNacnac$  ligand (with Al–N distances similar to those in  $DIPPNacnacAlH_2$ )<sup>21,22</sup> and binds to two  $\kappa^2$ - $BH_4^-$  ions, one nearly in the plane of the  $DIPPNacnac$  ligand and the other outside this plane.



**Scheme 3** Reaction of  $DIPPNacnacAlH_2$  with  $DIPPNH_2BH_3$ .



**Fig. 1** Crystal structure of  $DIPPNacnacAl(BH_4)_2$ . Selected bond distances (Å): Al–N1 1.898(3), Al–N2 1.898(3), Al···B1 2.207(4), Al···B2 2.231(6), Al–H1 1.78(4), Al–H2 1.74(5), Al–H5 1.76(4), Al–H6 1.81(5).

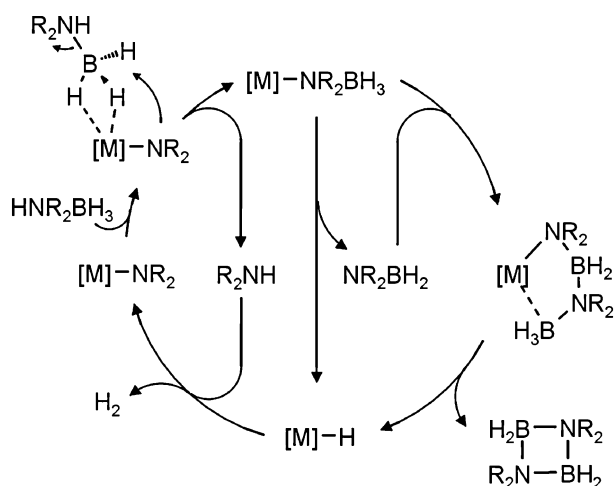
The bidentate chelation of these borate ligands is typical for Al and also found in simple aluminium borates like  $Al(BH_4)_3$  and  $Me_2Al(BH_4)$ .<sup>23</sup> The average Al···B distance in  $DIPPNacnacAl(BH_4)_2$  of 2.219(5) Å is in between those of the latter two aluminium borate complexes (2.12(2) Å and 2.411(6) Å, respectively).

From the catalytic conversion,  $2DIPPNH_2BH_3 \rightarrow HB[N(H)DIPP]_2 + BH_3 + 2H_2$ , with the Mg catalyst  $DIPPNacnacMgN(SiMe_3)_2$  we isolated the borate complex  $[DIPPNacnacMg(BH_4)]_2$  as the residual metal species.<sup>5</sup> However, a similar reaction scheme cannot be applied to the here reported formation of  $DIPPNacnacAl(BH_4)_2$ . <sup>11</sup>B NMR spectra only show signals for the  $BH_4^-$  ion. Monitoring the reaction by <sup>1</sup>H NMR shows no sign of  $H_2$  evolution but rapid formation of  $DIPPNH_2$ . We therefore propose a mechanism in which  $DIPPNH_2BH_3$  precoordinates to the Lewis-acidic  $Al^{3+}$  center, thus activating the  $sp^3$ -hybridized B for nucleophilic substitution (Scheme 3).

Although there are only few reports on systematic studies of nucleophilic displacement reactions at tetracoordinated B, its isolobal relationship with C atoms in methane-type compounds suggests that similar principles could apply. Indeed, experimental as well as theoretical evidence confirm the existence of  $S_N1$ -B and  $S_N2$ -B reactions.<sup>24–26</sup> The identity reaction,  $NH_3 + BH_3NH_3 \rightarrow NH_3BH_3 + NH_3$ , preferably proceeds *via* a second-order  $S_N2$  mechanism.<sup>25</sup> Although activation energies for  $S_N2$ -B are substantially higher than for similar  $S_N2$  reactions on C,<sup>26</sup> the calculated value of  $13.8$  kcal mol<sup>-1</sup> (MP3/6-31G\*)<sup>25</sup> is low enough to consider this reaction in mechanistic investigations. As the activation energy for  $S_N1$ -B type reactions equals the B–N bond dissociation energy (exp. 31.1 kcal mol<sup>-1</sup>,<sup>27</sup> calc. 33.1 kcal mol<sup>-1</sup>,<sup>25</sup> MP3/6-31G\*) the  $S_N2$ -B mechanism is likely favoured. It should be noted, however, that temperature and substituents on N and/or B influence the energy difference between  $S_N2$ -B and  $S_N1$ -B to such an extent that both can be operative simultaneously.<sup>24,26</sup>

Nucleophilic displacement is a common reaction for masked boranes, like  $BH_3(THF)$  or  $BH_3(Me_2S)$ :  $AlH_3$  reacts with  $BH_3(THF)$  to a range of  $AlH_{3-n}(BH_4)_n$  species.<sup>28</sup> However, ammonia-boranes with protic N–H units generally react with Al hydrides by proton abstraction.<sup>12,16</sup> Deprotonation of the amine is highly favoured on account of the acidifying effect of  $BH_3$  coordination. Whereas the more ionic Mg and Ca hydride complexes rapidly deprotonate any ammonia-borane,<sup>4,8</sup> the basicity of  $DIPPNacnacAlH_2$  is likely tempered by the high Lewis-acidity of  $Al^{3+}$ . The same Lewis-acidity determines the course of the reaction by activation of  $DIPPNH_2BH_3$  for nucleophilic substitution (Scheme 3).

It is not clear whether the observed hydride-amine replacement is a special case for aryl-substituted ammonia-boranes. On account of the high  $pK_b$  values for aryl amines ( $pK_b$  aniline 9.40) the B–N bond should be weaker than that in  $NH_3BH_3$  ( $pK_b$   $NH_3$  4.77). The low calculated activation energy for  $NH_3$  substitution in ammonia-boranes,<sup>25</sup> however, suggests that nucleophilic displacement could play a role in reactions of metal species with any ammonia-borane (it is suspected that Lewis-acid activation, as sketched in Scheme 3, even lowers this transition state). It should be noticed that thermal decomposition of  $NH_3BH_3$  proceeds through a key intermediate



**Scheme 4** Alternative catalytic scheme for dehydrocoupling of  $\text{HNR}_2\text{BH}_3$  (based on nucleophilic substitution).

$[\text{H}_2\text{B}(\text{NH}_3)_2]^+[\text{BH}_4]^-$  (DADB) which is proposed to be formed by substitution reactions on B centers.<sup>29</sup>

In the light of these results, alternative mechanisms could be operative in catalytic ammonia-borane dehydrogenation. *E.g.* the recently reported dehydrogenation,  $2\text{HNMe}_2\text{BH}_3 \rightarrow (\text{H}_2\text{BNMe}_2)_2 + 2\text{H}_2$ , by  $\text{Al}(\text{NMe}_2)_3$  alternatively could proceed through the coupled cycles shown in the general Scheme 4. The difference with the earlier proposed mechanism (Scheme 2)<sup>14–16</sup> is that the  $[\text{M}]\text{-NR}_2\text{BH}_3$  is not formed by deprotonation but by substitution. Reaction of the leaving group  $\text{HNR}_2$  with  $[\text{M}]\text{-H}$  would regenerate the metal amide catalyst  $[\text{M}]\text{-NR}_2$ . Such species could be formed in the reaction from any nucleophilic metal complex with ammonia-borane. The importance of nucleophilic substitution is naturally dependent on the nature of the substituents R and the Lewis-acidity of the metal but could be an alternative to be taken into account in a discussion of reaction mechanisms.

As aluminium amidoborane complexes are apparently not formed by attempted deprotonation of  $\text{DIPPNH}_2\text{BH}_3$ , we also investigated the salt metathesis route. Reaction of  $\text{DIPPnacnacAlCl}_2$  with two equivalents of  $\text{KNR}(\text{H})\text{BH}_3$  ( $\text{R} = i\text{Pr}$  or  $\text{DIPP}$ ) in THF gave in good yields  $\text{DIPPnacnacAlH}_2$ . This is likely formed by double  $\beta$ -hydrogen elimination in the expected product. This not only demonstrates the instability of aluminium amidoborane complexes but especially underscores the usefulness of amidoboranes in the preparation of metal hydride complexes (see ESI† for this alternative synthetic route to  $\text{DIPPnacnacAlH}_2$ ).

In conclusion, despite high N–H acidity in  $\text{DIPPNH}_2\text{BH}_3$ , reaction with  $\text{DIPPnacnacAlH}_2$  proceeds not through a deprotonation protocol but nucleophilic substitution at B is observed instead. This reaction pathway is likely favoured on account of a combination of Lewis-acid activation of

$\text{DIPPNH}_2\text{BH}_3$  and lower basicity of the Al–H compared to early main group metal hydride compounds. Substitution at B is a pathway that should be considered in mechanistic evaluations.

## Notes and references

- H. V. K. Diyablanage, R. P. Shrestha, T. A. Semelsberger, B. L. Scott, M. E. Bowden, B. L. Davis and A. K. Burrell, *Angew. Chem., Int. Ed.*, 2007, **46**, 8995.
- Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nat. Mater.*, 2008, **7**(2), 138.
- Reviews: (a) Y. S. Chua, P. Chen, G. Wu and Z. Xiong, *Chem. Commun.*, 2011, **47**, 5116; (b) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079.
- J. Spielman, G. Jansen, H. Bandmann and S. Harder, *Angew. Chem., Int. Ed.*, 2008, **47**, 6290.
- J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.*, 2009, 6934.
- J. Spielman and S. Harder, *J. Am. Chem. Soc.*, 2009, **131**, 5064.
- J. Spielman, D. Piesik, B. Wittkamp, G. Jansen and S. Harder, *Chem. Commun.*, 2009, 3455.
- J. Spielmann, D. F.-J. Piesik and S. Harder, *Chem.–Eur. J.*, 2010, **16**, 8307.
- J. Spielmann and S. Harder, *Dalton Trans.*, 2011, **40**, 8314.
- D. Y. Kim, N. J. Singh, H. M. Lee and K. S. Kim, *Chem.–Eur. J.*, 2009, **15**, 5598.
- A. T. Luedtke and T. Autrey, *Inorg. Chem.*, 2010, **49**, 3905.
- D. Dou, D. R. Ketchum, E. J. M. Hamilton, P. A. Florian, K. E. Vermillion, P. J. Grandinetti and S. G. Shore, *Chem. Mater.*, 1996, **8**, 2839.
- M. S. Hill, G. Kociok-Köhn and T. P. Robinson, *Chem. Commun.*, 2010, **46**, 7587.
- M. S. Hill, G. Kociok-Köhn and T. P. Robinson, *Chem. Commun.*, 2010, **46**, 7587.
- D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem.–Eur. J.*, 2010, **16**, 8508.
- (a) H. J. Cowley, M. S. Holt, R. L. Melen, J. M. Rawson and D. S. Wright, *Chem. Commun.*, 2010, **46**, 7587; (b) M. H. Hansmann, R. L. Melen and D. S. Wright, *Chem. Sci.*, 2011, **2**, 1554.
- R. V. Genova, K. J. Fijalkowski, A. Budzianowski and W. Grochala, *J. Alloys Compd.*, 2010, **499**, 144.
- A. K. Burrell, B. J. Davis, D. L. Thorn, J. C. Gordon, R. T. Baker, T. A. Semelsberger, W. Tumas, H. Vichalya, K. Diyabalanage and R. P. Shrestha, US pat. 2008/031101.
- S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079.
- J. Spielmann and S. Harder, *unpublished results*.
- C. Cui, H. W. Roesky, H. Hao, H. G. Schmidt and M. Noltemeyer, *Angew. Chem., Int. Ed.*, 2000, **39**, 1815.
- B. Twamley, N. J. Hardman and P. P. Power, *Acta Crystallogr.*, 2001, **E57**, m227.
- S. Aldridge, A. J. Blake, A. J. Downs, R. O. Gould, S. Parsons and C. R. Pulham, *J. Chem. Soc., Dalton Trans.*, 1997, 1007.
- D. E. Walmsley, W. L. Budde and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1971, **93**, 3150.
- S. Toyota, T. Futawaka, M. Asakura, H. Ikeda and M. Oki, *Organometallics*, 1998, **17**, 4155.
- S.-Y. Yang, P. Fleurat-Lessard, I. Hristov and T. Ziegler, *J. Phys. Chem. A*, 2004, **108**, 9461.
- A. Haaland, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 992.
- H. Nöth and R. Rurländer, *Inorg. Chem.*, 1981, **20**, 1062.
- V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen and D. A. Dixon, *J. Phys. Chem. A*, 2007, **111**, 8844.