Dehydrogenation of amine–boranes with a frustrated Lewis pair†

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Bulky tertiary phosphine/borane Lewis pairs $P^tBu_3/B(C_6F_5)_3$ react with amine–boranes to afford dehydrocoupling products and phosphonium borohydride salts.

Amine–boranes are the subject of intense interest due to their potential application in hydrogen storage schemes.^{1,2} A number of fast and efficient transition metal dehydrocoupling catalysts have been discovered,^{3–7} and various coordination compounds relevant to the catalytic pathways have been isolated.^{8–10} Progress has also been made in the challenging area of regeneration of spent ammonia–borane fuel.^{11–13} Theoretical studies^{14,15} of one amine–borane dehydrocoupling system employing *N*-heterocyclic carbenes (NHCs) as ligands³ suggested that the free NHC could heterolytically dehydrogenate $NH_3 \cdot BH_3$, yielding $(NH_2BH_2)_n$ and $NHC-H_2$, similar to the H_2 cleavage reactivity of Bertrand's carbenes.¹⁶ Because the reactivity of these NHC species has been compared to that of bulky phosphine/borane “frustrated Lewis pairs” (FLPs), it occurred to us that FLPs might also be able to dehydrogenate amine–boranes.

FLPs—combinations of particularly bulky Lewis acids and bases that are unable to form traditional Lewis acid/base pairs¹⁷—exhibit a number of unusual reactions,^{18–20} in particular the heterolytic cleavage of H_2 ,^{21–23} which has been utilized for metal-free catalytic hydrogenation of bulky imines.^{24,25} Amine activation reactions have also been reported.^{26,27} To our knowledge, however, no dehydrogenation reactions have been reported using these systems,²⁸ although calculations suggest such reactions should be possible.²⁹ Herein we report that the simple frustrated Lewis pair $P^tBu_3/B(C_6F_5)_3$ rapidly and cleanly dehydrogenates amine–boranes at room temperature, with concomitant formation of the phosphonium borohydride salt $[P^tBu_3PH][HB(C_6F_5)_3]$ (Scheme 1).

Initial experiments were carried out with $Me_2NH \cdot BH_3$, a common model for $NH_3 \cdot BH_3$ which has desirable solubility properties and generally releases only 1 equivalent of H_2 . The frustrated Lewis pair $P^tBu_3/B(C_6F_5)_3$ was formed according to

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literature procedures in C_6D_5Cl ,²² and no discernable reaction was observed by NMR. The pre-formed FLP was added to a C_6D_5Cl solution of $Me_2NH \cdot BH_3$ at 25 °C, giving a clear colorless solution.³⁰ ^1H , ^{31}P (Fig. 1), ^{19}F , and ^{11}B (Fig. 2) NMR experiments confirmed that >95% of the FLP-derived product was $[P^tBu_3PH][HB(C_6F_5)_3]$.²² The major dehydrocoupling product was dimeric $(Me_2NBH_2)_2$, assigned by a diagnostic ^{11}B NMR resonance at δ 5.2 (t, $J_{BH} = 112$ Hz), and by signals in the ^1H NMR spectrum at δ 2.28 (s, Me_2N) and δ 2.83 (1 : 1 : 1 : 1 q, $J_{BH} = 112$ Hz, BH_2). Minor side products, including monomeric $Me_2N=BH_2$ (^{11}B δ 37.6, t, $J_{HB} = 127$ Hz) and $HB(NMe_2)_2$ (^{11}B δ 28.5, d, $J_{HB} = 124$ Hz), dissipated over time, leaving ~97% dimeric $(Me_2NBH_2)_2$ along with traces of $(BH_2)_2NMe_2(\mu-H)$ (A) and $H_3B \cdot NMe_2BH_2 \cdot NHMe_2$ (B).³¹ This product distribution is similar to that observed in metal-catalyzed dehydrocoupling of $Me_2NH \cdot BH_3$,^{32,33} thermolysis of a $Me_2NH \cdot BH_3$ melt at 150 °C also affords $(Me_2NBH_2)_2$, along with trace impurities including $HB(NMe_2)_2$.^{33,34}

The order of reagent addition is important in the dehydrocoupling reaction. If $B(C_6F_5)_3$ and $Me_2NH \cdot BH_3$ are dissolved

Fig. 1 ^1H NMR spectrum after FLP-mediated dehydrocoupling of $Me_2NH \cdot BH_3$. Left inset is a blow-up of the borohydride ^1H NMR resonances; right inset is the ^{31}P NMR spectrum.

Fig. 2 ^{11}B NMR spectrum shortly after FLP-mediated dehydrocoupling of $Me_2NH \cdot BH_3$. The underlying broad feature arises from borosilicate glass in the probe construction.

in $\text{C}_6\text{D}_5\text{Cl}$ a few minutes prior to addition of P^tBu_3 , several products including only $\sim 50\%$ $(\text{Me}_2\text{NBH}_2)_2$ are produced. On the other hand, combining P^tBu_3 and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ in $\text{C}_6\text{D}_5\text{Cl}$, followed by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ led to near-quantitative formation of $[\text{P}^t\text{Bu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ and $(\text{Me}_2\text{NBH}_2)_2$.³⁵

To explore the possibility of H_2 release and amine–borane regeneration, the mixture of $[\text{P}^t\text{Bu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ and $(\text{Me}_2\text{NBH}_2)_2$ was heated between 90 and 130 °C. Complete decomposition of the dimer to a variety of species was observed; only $\text{BH}_3\cdot\text{P}^t\text{Bu}_3$ and $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ were readily identified by ^{11}B NMR,³⁶ leaving this experiment inconclusive. In isolation, $(\text{Me}_2\text{NBH}_2)_2$ is stable up to 450 °C in the gas phase³³ and 130 °C in a melt.³⁴ Similarly, it has been reported that $[\text{P}^t\text{Bu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ is stable to H_2 loss up to 150 °C.²²

The FLP system can dehydrogenate $\text{NH}_3\cdot\text{BH}_3$ as well (Scheme 1). Treatment of $\text{NH}_3\cdot\text{BH}_3$ with $\text{P}^t\text{Bu}_3/\text{B}(\text{C}_6\text{F}_5)_3$ afforded once again $[\text{P}^t\text{Bu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ as a principal product (85%, ^{31}P NMR; $\sim 80\%$, ^{19}F NMR). The major dehydrocoupling product is consistent with branched-chain polyaminoborane $(\text{NH}_2\text{BH}_2)_n$, broad ^{11}B NMR, δ -7.7 , -14.4 , -27.2 as observed upon thermolysis of $\text{NH}_3\cdot\text{BH}_3$ in ionic liquids.^{37,38} The other ^{11}B signals correspond to $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and two smaller peaks which could be Lewis adducts between P^tBu_3 and boranes; two broad resonances in the ^{31}P NMR spectrum are consistent with this formulation. Apparently dehydrocoupling is more favorable than forming stable Lewis pairs, although in this case some of that competing pathway is observed.³⁹ Some insoluble colorless material was extracted with pyridine and shown to be unreacted $\text{NH}_3\cdot\text{BH}_3$, consistent with some amount of deactivation of the FLP before quantitative dehydrocoupling could take place. Neither the insoluble cyclic pentamer $(\text{NH}_2\text{BH}_2)_5$ ^{4,10} nor long linear polymers⁴⁰ were detected, in contrast to a number of metal-catalyzed reactions. Treatment of $\text{NH}_3\cdot\text{BH}_3$ with excess FLP did not lead to detectable amounts of borazine, suggesting that only 1 equiv. of H_2 could be released using this method.

$\text{B}(\text{C}_6\text{F}_5)_3$ by itself can *catalytically* dehydrogenate $\text{NH}_3\cdot\text{BH}_3$,⁴¹ but only at elevated temperatures; no significant amounts of product are observed under the present conditions without P^tBu_3 . Importantly, $\text{B}(\text{C}_6\text{F}_5)_3$ by itself is unable to dehydrocouple $\text{Me}_2\text{NH}\cdot\text{BH}_3$,³³ leading us to conclude that the FLP is essential for rapid, ambient-condition dehydrocoupling.

The mechanism of heterolytic cleavage of H_2 by FLPs has not been fully elucidated, although a number of theoretical studies have been performed.^{18,42–44} DFT calculations suggest that a weak interaction holds the borane and phosphine in proximity; a molecule of H_2 approaches the pair and is cleaved in a concerted fashion. Since the heterolytic dehydrogenation of amine–boranes constitutes a net transfer of H_2 and gives a similar product, one could invoke a similar mechanism. We prefer an alternative, stepwise mechanism in which $\text{B}(\text{C}_6\text{F}_5)_3$ first abstracts a hydride from $\text{Me}_2\text{NH}\cdot\text{BH}_3$, followed by fast deprotonation of the resulting $[\text{Me}_2\text{NHBH}_2]^+$, affording the $\text{Me}_2\text{N}=\text{BH}_2$ unit that dimerizes to the final product (Scheme 2). In the absence of P^tBu_3 , oligomerization of the cationic intermediate might take place (as suggested by Baker for the reaction of acid with $\text{NH}_3\cdot\text{BH}_3$ ⁴¹) accounting for the multiple side products observed.

Scheme 2 Proposed mechanism for FLP-mediated dehydrocoupling.

We have shown that frustrated Lewis pairs consisting of bulky tertiary phosphines and $\text{B}(\text{C}_6\text{F}_5)_3$ are capable of rapidly dehydrocoupling $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and $\text{NH}_3\cdot\text{BH}_3$. While the current FLP systems could serve as H_2 storage compounds themselves,²¹ their weight % capacity is far from ideal. Using FLPs as a H_2 shuttle with lighter, non-frustrated amine–boranes as the terminal H_2 storage medium is perhaps more attractive. Recent advances in H_2 release from FLPs^{23,45} may open the door to catalytic dehydrocoupling, and indeed perhaps dehydrogenation of a wider variety of substrates.

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