Dehydrogenation of amine-boranes with a frustrated Lewis pair[†]

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Bulky tertiary phosphine/borane Lewis pairs $P'Bu_3/B(C_6F_5)_3$ 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 H₂ 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'Bu₃/B(C₆F₅)₃ rapidly and cleanly dehydrogenates amine—boranes at room temperature, with concomitant formation of the phosphonium borohydride salt ['Bu₃PH][HB(C₆F₅)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'Bu₃/B(C₆F₅)₃ was formed according to

 $\begin{array}{c} P'Bu_{3}+B(C_{6}F_{5})_{3}+R_{2}NH'BH_{3} & \overbrace{}^{C_{6}D_{5}Cl} ['Bu_{3}PH][HB(C_{6}F_{5})_{3}]+(R_{2}NBH_{2})_{x}\\ & \overbrace{}^{25 \circ C}\\ R=Me, \ x=2\\ R=H, \ x=n\\ & Scheme \ 1 \end{array}$

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA, USA. E-mail: ajmiller@caltech.edu; Fax: +1 626 585 0147; Tel: +1 626 395 6576 † Electronic supplementary information (ESI) available: Full

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literature procedures in $C_6D_5Cl_2^{22}$ and no discernable reaction was observed by NMR. The pre-formed FLP was added to a C₆D₅Cl solution of Me₂NH·BH₃ at 25 °C, giving a clear colorless solution.^{30 1}H, ³¹P (Fig. 1), ¹⁹F, and ¹¹B (Fig. 2) NMR experiments confirmed that >95% of the FLP-derived product was $[{}^{t}Bu_{3}PH][HB(C_{6}F_{5})_{3}]^{22}$ The major dehydrocoupling product was dimeric (Me₂NBH₂)₂, assigned by a diagnostic ¹¹B 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 Me₂N=BH₂ (¹¹B δ 37.6, t, J_{HB} = 127 Hz) and HB(NMe₂)₂ (¹¹B δ 28.5, d, J_{HB} = 124 Hz), dissipated over time, leaving $\sim 97\%$ dimeric (Me₂NBH₂)₂ along with traces of $(BH_2)_2NMe_2(\mu-H)$ (A) and $H_3B\cdot NMe_2BH_2$. NHMe₂ (**B**).³¹ This product distribution is similar to that observed in metal-catalyzed dehydrocoupling of Me2NH·BH3;32,33 thermolysis of a Me₂NH·BH₃ melt at 150 °C also affords (Me₂NBH₂)₂, along with trace impurities including HB(NMe₂)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 ³¹P NMR spectrum.



Fig. 2 11 B NMR spectrum shortly after FLP-mediated dehydrocoupling of Me₂NH·BH₃. The underlying broad feature arises from borosilicate glass in the probe construction.

in C₆D₅Cl a few minutes prior to addition of P'Bu₃, several products including only ~ 50% (Me₂NBH₂)₂ are produced. On the other hand, combining P'Bu₃ and Me₂NH·BH₃ in C₆D₅Cl, followed by addition of B(C₆F₅)₃ led to near-quantitative formation of ['Bu₃PH][HB(C₆F₅)₃] and (Me₂NBH₂)₂.³⁵

To explore the possibility of H₂ release and amine–borane regeneration, the mixture of ['Bu₃PH][HB(C₆F₅)₃] and (Me₂NBH₂)₂ was heated between 90 and 130 °C. Complete decomposition of the dimer to a variety of species was observed; only BH₃·P'Bu₃ and [HB(C₆F₅)₃]⁻ were readily identified by ¹¹B NMR,³⁶ leaving this experiment inconclusive. In isolation, (Me₂NBH₂)₂ is stable up to 450 °C in the gas phase³³ and 130 °C in a melt.³⁴ Similarly, it has been reported that ['Bu₃PH][HB(C₆F₅)₃] is stable to H₂ loss up to 150 °C.²²

The FLP system can dehydrogenate NH₃·BH₃ as well (Scheme 1). Treatment of $NH_3 \cdot BH_3$ with $P^tBu_3/B(C_6F_5)_3$ afforded once again ['Bu₃PH][HB(C₆F₅)₃] as a principal product (85%, ³¹P NMR; $\sim 80\%$, ¹⁹F NMR). The major dehydrocoupling product is consistent with branched-chain polyaminoborane ((NH₂BH₂)_n, broad ¹¹B NMR, δ -7.7, -14.4, -27.2) as observed upon thermolysis of NH₃·BH₃ in ionic liquids.^{37,38} The other ¹¹B signals correspond to $[HB(C_6F_5)_3]^-$ and two smaller peaks which could be Lewis adducts between P'Bu₃ and boranes; two broad resonances in the ³¹P 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 NH₃·BH₃, consistent with some amount of deactivation of the FLP before quantitative dehydrocoupling could take place. Neither the insoluble cyclic pentamer (NH₂BH₂)₅^{4,10} nor long linear polymers⁴⁰ were detected, in contrast to a number of metal-catalyzed reactions. Treatment of NH₃·BH₃ with excess FLP did not lead to detectable amounts of borazine, suggesting that only 1 equiv. of H2 could be released using this method.

 $B(C_6F_5)_3$ by itself can *catalytically* dehydrogenate $NH_3 \cdot BH_3$,⁴¹ but only at elevated temperatures; no significant amounts of product are observed under the present conditions without P'Bu₃. Importantly, $B(C_6F_5)_3$ by itself is unable to dehydrocouple $Me_2NH \cdot BH_3$,³³ leading us to conclude that the FLP is essential for rapid, ambient-condition dehydrocoupling.

The mechanism of heterolytic cleavage of H₂ 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 H₂ approaches the pair and is cleaved in a concerted fashion. Since the heterolytic dehydrogenation of amine–boranes constitutes a net transfer of H₂ and gives a similar product, one could invoke a similar mechanism. We prefer an alternative, stepwise mechanism in which B(C₆F₅)₃ first abstracts a hydride from Me₂NH·BH₃, followed by fast deprotonation of the resulting [Me₂NHBH₂]⁺, affording the Me₂N=BH₂ unit that dimerizes to the final product (Scheme 2). In the absence of P'Bu₃, oligomerization of the cationic intermediate might take place (as suggested by Baker for the reaction of acid with NH₃·BH₃⁴¹) 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 $B(C_6F_5)_3$ are capable of rapidly dehydrocoupling Me₂NH·BH₃ and NH₃·BH₃. While the current FLP systems could serve as H₂ storage compounds themselves,²¹ their weight % capacity is far from ideal. Using FLPs as a H₂ shuttle with lighter, non-frustrated amine– boranes as the terminal H₂ storage medium is perhaps more attractive. Recent advances in H₂ 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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