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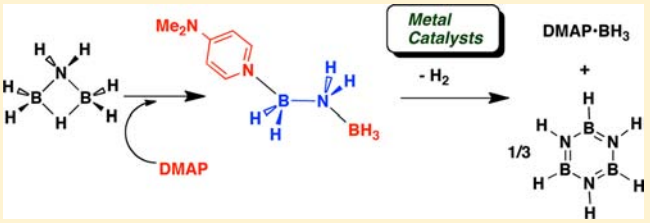
Donor–Acceptor Complexation and Dehydrogenation Chemistry of Aminoboranes

Adam C. Malcolm, Kyle J. Sabourin, Robert McDonald, Michael J. Ferguson, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

ABSTRACT: A series of formal donor–acceptor adducts of aminoborane (H_2BNH_2) and its N-substituted analogues (H_2BNRR') were prepared: LB-$H_2BNRR'_2$-BH_3 (LB = DMAP, IPr, $IPrCH_2$ and PCy_3; R and R′ = H, Me or *t*Bu; IPr = $[(HCNDipp)_2C:]$ and Dipp = 2,6-*i*$Pr_2C_6H_3$). To potentially access complexes of molecular boron nitride, LB-BN-LA (LA = Lewis acid), preliminary dehydrogenation chemistry involving the parent aminoborane adducts LB-H_2BNH_2-BH_3 was investigated using $[Rh(COD)Cl]_2$, CuBr, and $NiBr_2$ as dehydrogenation catalysts. In place of isolating the intended dehydrogenated BN donor–acceptor complexes, the formation of borazine was noted as a major product. Attempts to prepare the fluoroarylborane-capped aminoborane complexes, LB-H_2BNH_2-$B(C_6F_5)_3$, are also described.

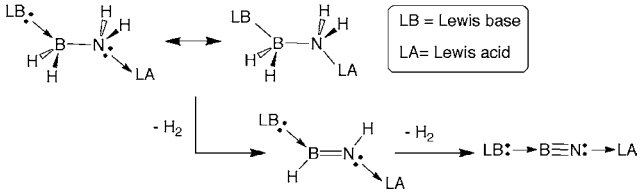


INTRODUCTION

Ammonia borane (AB), $H_3N{\cdot}BH_3$, has been extensively explored as a chemical source of hydrogen[1,2] and as a precursor for the synthesis of boron nitride (BN) ceramics.[3] $H_3N{\cdot}BH_3$ is also of fundamental interest because of its isoelectronic and isolobal relationship with ethane, $H_3C{-}CH_3$. A key difference between inorganic B–N analogues, such as AB, and their hydrocarbon counterparts is the existence of polar B–N bonds in the former species and the presence of protic ($N{-}H^{\delta+}$) and hydridic ($B{-}H^{\delta-}$) residues which enable facile loss of H_2 via nonconventional $H^{\delta-}\cdots{}^{\delta+}H$ interactions. Both the parent species $H_2B{=}NH_2$ and $HB{\equiv}NH$ have been isolated under cryogenic conditions;[4,5] however unlike AB, they are elusive at room temperature because of their propensity to spontaneously polymerize.[6]

Boron nitride (BN) is a synthetic material that is isostructural with diamond in its cubic form[7] with comparable hardness and thermal stability. These properties coupled with its electrically insulating and thermal conducting behavior makes BN a promising material for the microelectronics industry.[8] To date, most methods for preparing BN require high temperatures (>1500 °C) and/or specialized equipment;[9,10] however some milder routes to BN are now emerging.[11] Given our prior experiences in stabilizing reactive molecular fragments (e.g., EH_2 and H_2EEH_2; E = Si, Ge, and/or Sn) via a general donor–acceptor stabilization protocol,[12−14] we were interested in accessing complexes of molecular BN which could later release BN to form bulk boron nitride under mild conditions (Scheme 1). This paper reports a series of complexes of the general form LB-H_2BNH_2-LA (LB = Lewis base; LA = Lewis acid),[15] and our attempts to generate metastable complexes of BN, LB-B≡N-LA, via dehydrogenation chemistry.

Scheme 1. Donor–Acceptor Complexation of H_2BNH_2 and Proposed Dehydrogenation Chemistry



RESULTS AND DISCUSSION

Synthesis of Donor–Acceptor Complexes of the Parent Aminoborane (H_2BNH_2). Free H_2BNH_2 is a challenging substrate to handle as it readily forms oligomeric borazanes $[H_2BNH_2]_x$ (x = 2–5).[16] Thus our goal was to generate stable adducts of H_2BNH_2 from which productive dehydrogenation chemistry could transpire (Scheme 1). Starting from the known μ-aminodiborane, $H_2NB_2H_5$ (**1**),[15b] we were able to induce the nucleophilic scission of a bridging B–H bond in **1** in the presence of the carbon-based donor, $IPrCH_2$ [$IPrCH_2$ = $(HCNDipp)_2C{=}CH_2$; Dipp = 2,6-*i*$Pr_2C_6H_3$)]. $IPrCH_2$ has recently been shown to be an effective Lewis base in an analogous fashion as N-heterocyclic carbenes (NHCs).[17] Upon addition of $IPrCH_2$ to a solution of **1**, the target complex, $IPrCH_2$-H_2BNH_2-BH_3 (**2**), precipitated from solution and was subsequently isolated as a white solid in a 62% yield (Scheme 2). The formation of the **2** was confirmed by NMR (^1H, ^{11}B, $^1H\{^{11}B\}$, GCOSY), and IR spectroscopy; however because of extensive twinning within crystals of **2**, only

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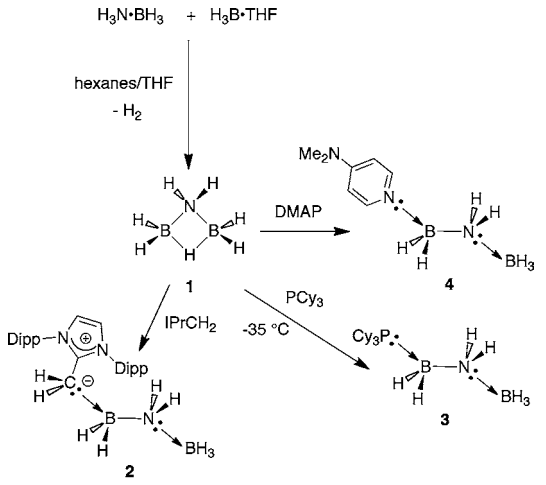
Scheme 2. Synthesis of the H_2BNH_2 Complexes (2–4) Featuring Carbon-, Phosphorus-, and Nitrogen-Donors



atom connectivity could be established by single-crystal X-ray crystallography.

The presence of a coordinating $IPrCH_2$ unit in **2** was verified by ^1H NMR spectroscopy, while the adjacent $BH_2-NH_2-BH_3$ unit was located in the form of triplet (BH_2) and quartet resonances (BH_3) in the proton-coupled ^{11}B NMR spectrum (triplet, $\delta = -14.7$, $^1J_{B-H} = 95$ Hz; quartet, $\delta = -21.9$, $^1J_{B-H} = 87$ Hz). Linkage of the nucleophilic $-CH_2$ group of $IPrCH_2$ to the -BH_2- unit of the inorganic chain was substantiated by a $^1H\{^{11}B\}$ aoGCOSY study; the resonance corresponding to the boron-bound hydrogen atoms of the -BH_2- group at 1.40 ppm showed off-diagonal coupling to a resonance at 1.88 ppm belonging to the proximal terminal $-CH_2$ residue of the $IPrCH_2$ donor. The ^1H NMR resonance corresponding to the central -NH_2- unit in **2** could not be identified; however, an N–H stretching band at 3340 cm^{-1} could be located by IR spectroscopy.

The isolation of $IPrCH_2$-H_2BNH_2-BH_3 (**2**) in pure form was thwarted by its decomposition in solvents in which it is soluble. For example, compound **2** slowly decomposes in chlorinated solvents (CH_2Cl_2, $ClCH_2CH_2Cl$, and $CHCl_3$), while significantly accelerated decomposition occurs when **2** is dissolved in tetrahydrofuran (THF, decomposition half-life = ca. 24 h.). The decomposition product in each case yields a clearly resolved pentet at −40.6 ppm in the ^{11}B NMR spectrum ($^1J_{B-H} = 81$ Hz), consistent with the presence of a BH_4^- anion. In addition, the ^1H NMR spectrum of the decomposition product contains a downfield-positioned singlet at 8.18 ppm (in $CDCl_3$), which matches the backbone alkene C–H resonance in the imidazolium cation [$IPrCH_3^+$] (IPr = [(HCNDipp)$_2$C:); moreover diagnostic resonances due to the [$IPrCH_3$]$^+$ cation can be located by $^{13}C\{^1H\}$ NMR spectroscopy.[18] As a result, compound **2** can only be obtained in about 90% purity with the predominant contaminant being [$IPrCH_3$]BH_4 (see Supporting Information, Figures S1 and S2).[19] No further decomposition occurs when **2** is stored in the solid state under N_2, nor when **2** is mixed with arene solvents, such as toluene, in which **2** is only sparingly soluble; attempts to purify **2** via recrystallization from arene solvents failed because of the low solubility of this compound in these solvent media. We are currently exploring the fate of the extruded B–N product(s) formed during the decomposition of **2** into [$IPrCH_3$]BH_4.

It was found that the overall reaction pathway used to access compound **2** could also be used to prepare H_2BNH_2 adducts with alternate Lewis basic (LB) donors: LB-H_2BNH_2-BH_3 (Scheme 2). When the strong σ-donor, tricyclohexylphosphine (Cy_3P), was added to **1** at room temperature, the known phosphine-borane adduct, $Cy_3P{\cdot}BH_3$,[20] was formed as the major phosphorus-containing product in a ca. 90% yield: ^{31}P NMR spectroscopy afforded a singlet at 22.9 ppm with resolvable coupling to boron (1:1:1:1 quartet, $^1J_{P-B} = 64$ Hz), while a corresponding doublet resonance was detected by $^{11}B\{^1H\}$ NMR spectroscopy (−46.3 ppm, $^1J_{B-P} = 63$ Hz).[20] The minor soluble product formed in the reaction of Cy_3P with **1** was present in about 10% yield and was tentatively assigned as the previously unknown species Cy_3P-H_2BNH_2-BH_3 on the basis of ^{31}P and ^{11}B NMR spectroscopy [^{11}B NMR: $\delta = -21.0$ (br) and −17.5 (br); $^{31}P\{^1H\}$ NMR: $\delta = 10.2$ (br)]. This species could be obtained in a much greater isolated yield if the solution of **1** was first cooled to −35 °C prior to the addition of solid PCy_3. After workup of the reaction mixture, Cy_3P-H_2BNH_2-BH_3 (**3**) was isolated as a colorless solid in a 61% yield and identified by single-crystal X-ray crystallography (Figure 1). The internal and terminal B–N bond lengths in **3** are 1.564(2) and 1.608(2) Å, respectively, and are consistent with the presence of B–N single bonds. The Cy_3P-H_2BNH_2-BH_3 array rests in a slightly canted *anti* conformation with a P–B–N–B torsion angle of 174.29(12)°.

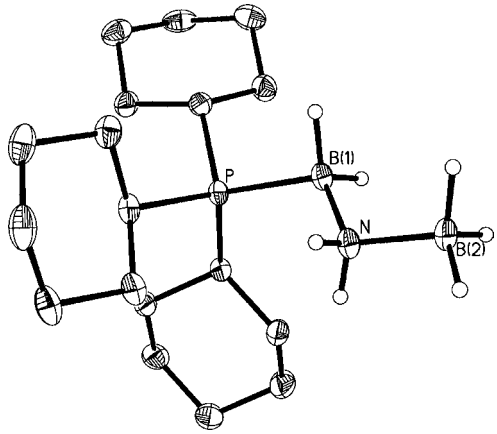


Figure 1. Thermal ellipsoid plot (30% probability) of Cy_3P-H_2BNH_2-BH_3 (**3**), with carbon-bound hydrogen atoms and dichloromethane solvate omitted for clarity. Compound **3** cocrystallized with 4% Cy_3P-H_2BNH_2-BH_2Cl.[19] Selected bond lengths [Å] and angles [deg]: P–B(1) 1.9730(17), B(1)–N 1.564(2), B(1)–H 1.155(18) and 1.086(18), N–H 0.847(19) and 0.93(2), N–B(2) 1.608(2), B(2)–H 1.164(18), 1.157(19), and 1.12(2); P–B(1)–N 115.61(11), B(1)–N–(B2) 114.84(13); P–B(1)–N–B(2) torsion angle = 174.29(12).

In contrast to $IPrCH_2$-H_2BNH_2-BH_3 **2**, the phosphine-capped analogue **3** is indefinitely stable in both ethereal and arene solvents, and can be crystallized from halogenated hydrocarbon solvents without noticeable decomposition. When a sample of **3** was heated to 100 °C in toluene, a reaction mixture containing unreacted **3** (5%) and $Cy_3P{\cdot}BH_3$ (85%) (^{11}B and $^{31}P\{^1H\}$ NMR) with traces of borazine ([$HBNH$]$_3$, 6%) and cyclotriborazane ([H_2BNH_2]$_3$, 4%) as soluble products was obtained. A small amount of a white solid remained that was not soluble in halogenated, arene or etheral solvents, which possibly contained boron–nitrogen oligomers, [H_2BNH_2]$_x$ and/or polymers.

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Dimethylaminopyridine (DMAP) is known to be an effective Lewis base for the stabilization of electron-deficient main group species.[21] Thus we were interested in seeing if this donor could be used to form complexes featuring the parent aminoborane residue, H_2BNH_2. To this end, we treated the μ-aminodiborane (**1**) with DMAP and gratifyingly observed the clean formation of DMAP-H_2BNH_2-BH_3 (**4**) as a white solid in a high isolated yield of 75% (Scheme 2).

The solid state structure of **4** is presented in Figure 2, and notably, the N_{DMAP}-BH_2-NH_2-BH_3 array in **4** adopts a *gauche*

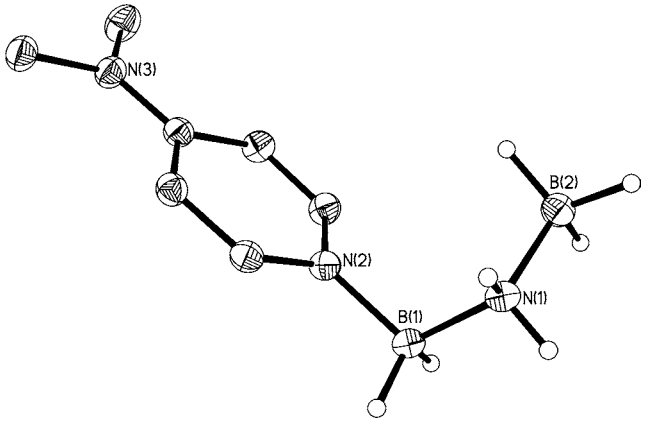
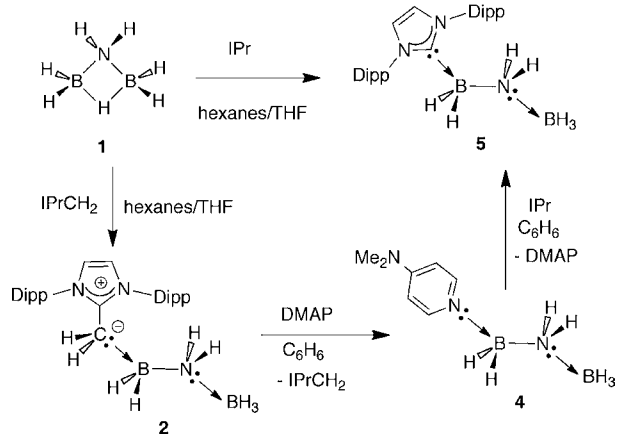


Figure 2. Thermal ellipsoid plot (30% probability) of DMAP-H_2BNH_2-BH_3 (**4**), with carbon-bound hydrogen atoms and hexane solvate molecules omitted for clarity. Selected bond lengths [Å] and angles [deg]: N(2)−B(1) 1.5728(15), B(1)−N(1) 1.5720(17), N(1)−B(2) 1.5939(16), B(1)−H 1.109(13), and 1.125(13), B(2)−H 1.102(15), 1.145(14) and 1.147(17); N(2)−B(1)−N(1) 110.44(9), B(1)−N(1)−B(2) 118.68(9); N(2)−B(1)−N(1)−B(2) torsion angle = 65.71(13).

conformation about the B−N bond vector [torsion angle = 65.71(13)°]. The central H_2B-NH_2 bond distance in **4** is 1.5720(17) Å, which is the same within experimental error as the B−N bond length in $H_3N{\cdot}BH_3$ [1.58(2) Å].[22] The B−N bond length involving the terminally bound BH_3 group in **4** is 1.5939(16) Å, and this value lies within the range of B−N distances found in Shore's inorganic butane analogue, $H_3NBH_2NH_2BH_3$ [1.588−1.600 Å].[15c,23] The ^{11}B NMR spectrum of **4** clearly shows the presence of -BH_2- and -BH_3 groups in the form of triplet [δ = −3.7, $^1J_{B-H}$ = 100 Hz] and quartet resonances [δ = −21.8 ppm, $^1J_{B-H}$ = 92 Hz], respectively. Because of the low number of resonances in the ^{1}H NMR spectrum of **4**, the central -NH_2- unit can be readily located as a broad singlet at 2.19 ppm. Selectively decoupled ^{1}H{^{11}B} NMR experiments enabled the BH_2 and BH_3 groups to be identified, as quadrupolar broadening of these resonances by ^{11}B nuclei (I = 3/2) was suppressed; the same technique was also used to visualize the 3-bond coupling between the terminal -BH_3 unit and the adjacent -NH_2- group in **4** ($^3J_{H-H}$ = 4.4 Hz).

Our initial forays into donor−acceptor chemistry involved the strong σ-donor IPr (IPr = [(HCNDipp)C:].[12] In pursuit of the carbene-capped complex IPr-H_2B-NH_2-BH_3, IPr was combined with the aminodiborane **1**. Each time a new product with a ^{11}B NMR resonance at −18.2 ppm (broad) was detected along with varying quantities (ca. 30−65%) of the known NHC adduct IPr·BH_3[24] (δ = −35 ppm, quartet, $^1J_{B-H}$ = 86 H, in C_6D_6). As part of our efforts to obtain comparative donor strengths within the LB-H_2BNH_2-BH_3 series, an improved route to the target NHC-bound chain IPr-H_2BNH_2-BH_3 (**5**) was found (Scheme 3). Of the three reported complexes **2**−**4**,

Scheme 3. Donor Substitution Chemistry Involving the Aminoborane Complexes 2, 4, and 5



the $IPrCH_2$ derivative **2** has been shown to be the least thermally stable (vide supra); thus we reasoned that the $IPrCH_2$-*B* bond in **2** would be more labile than the related Cy_3P-B and DMAP-B linkages in **3** and **4**. Treatment of $IPrCH_2$-H_2BNH_2-BH_3 (**2**) with 1 equiv of DMAP in benzene yielded the DMAP adduct (**4**) and $IPrCH_2$ as major products by NMR spectroscopy. In an analogous fashion, ligand exchange chemistry transpired between DMAP-H_2BNH_2-BH_3 (**4**) and IPr to afford the new carbene-aminoborane adduct IPr-H_2BNH_2-BH_3 (**5**) in a 42% isolated yield; this species gave a broad ^{11}B{^{1}H} NMR signal at −18.2 ppm due to coincident −BH_2- and −BH_3 groups, with no resolvable coupling noted in the proton-coupled ^{11}B NMR spectrum (see Supporting Information, Figure S6).[19] Crystals of **5** suitable for X-ray crystallography were grown from a saturated solution in CH_2Cl_2/hexanes, and the refined structure is presented in Figure 3.

The reaction sequence outlined in Scheme 3 nicely illustrates the relative donor strength of IPr > DMAP > $IPrCH_2$ among the adducts **2**, **4**, and **5**. The successful syntheses of these complexes and the phosphine-capped aminoborane Cy_3P-H_2BNH_2-BH_3 (**3**) provide a suite of aminoborane donor−acceptor adducts which could be potentially dehydrogenated to afford trapped B−N species of higher bond orders (Scheme 1).

Synthesis of the N-Methylated Aminoborane Complexes, LB-BH_2NMe_2-BH_3. To more directly probe the thermal lability of the terminal donor−acceptor interactions in the aminoborane adducts LB-H_2BNR_2-BH_3, a series of N-methylated adducts were prepared to avoid competing dehydrogenation chemistry that could transpire if N−H and B−H residues were present within the same molecule. The stable adduct DMAP-H_2BNMe_2-BH_3 (**7**) was obtained through a similar ring-opening pathway as used to prepare the H_2BNH_2 adducts (**2**−**4**) (Scheme 4). The required μ-dimethylaminodiborane (**6**)[25a,b] was synthesized by the reaction of the in situ generated dimer $[Me_2NBH_2]_2$ (^{11}B NMR: triplet, δ = 4.75 ppm, $^1J_{B-H}$ = 113 Hz) with 1 equiv of $H_3B{\cdot}THF$ at 60 °C (Scheme 4). To facilitate the formation of $[Me_2NBH_2]_2$, the dehydrocoupling of $Me_2NH{\cdot}BH_3$ to generate $[Me_2NBH_2]_2$, was catalyzed by $[Rh(COD)Cl]_2$.[25c−g,26] Addition of 1 equiv of DMAP to **6** caused ring-opening and precipitation of the

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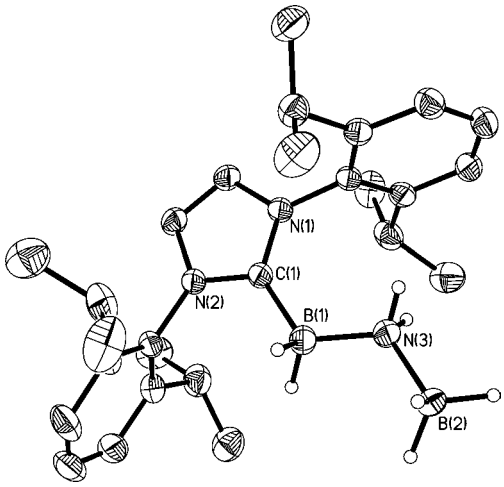
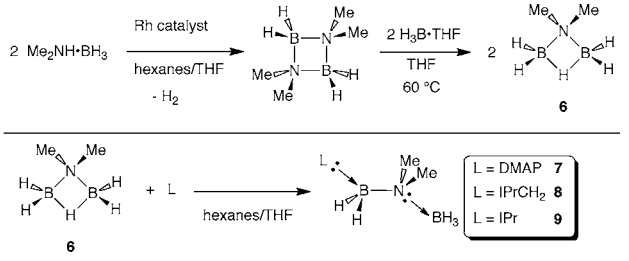


Figure 3. Thermal ellipsoid plot (30% probability) of IPr-H_2BNH_2-BH_3 (**5**), with carbon-bound hydrogen atoms and dichloromethane solvate molecule omitted for clarity. B–H and N–H bond lengths were constrained during refinement. Selected bond lengths [Å] and angles [deg]: C(1)–B(1) 1.618(2), B(1)–N(3) 1.540(3), N(3)–B(2) 1.605(2), B(1)–H 1.13(2) and 1.15(2), B(2)–H 1.176(15), 1.192(15) and 1.179(15), N(3)–H 0.95(2), C(1)–B(1)–N(3) 116.93(15), B(1)–N(3)–B(2) 115.48(15), C(1)–B(1)–N(3)–B(2) torsion angle = 179.90(19).

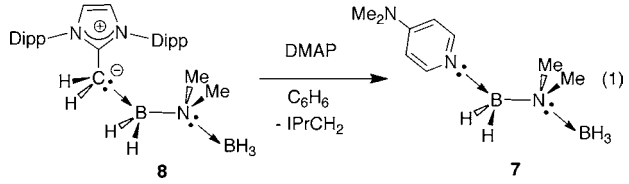
Scheme 4. Synthesis of μ-Dimethylaminodiborane (6) and the Corresponding H_2BNMe_2 Adducts 7–9



desired linear adduct, DMAP-H_2BNMe_2-BH_3 (**7**), from a hexanes/THF mixture as a pale yellow solid in a 63% yield. Using the same methodology, stable adducts involving $IPrCH_2$ and IPr donors (**8** and **9**) were also be prepared (Scheme 4). All of the N-methylated analogues **7**–**9** show indefinite stability in the solid state, as well as in refluxing toluene and THF, respectively.

The crystallographically determined structures of adducts **7**–**9** are shown collectively in Figure 4. The central H_2BNMe_2 units in **7** and **8** (L = DMAP and $IPrCH_2$) bear structurally similar *gauche* LB–B–N–B conformations as the parent H_2BNH_2 adduct **4**; however, an *anti* conformation was found within the IPr adduct, IPr-H_2BNMe_2-BH_3 (**9**) [C_{IPr}–B–N–$B_{terminal}$ torsion angle = 178.38(12)°]. This difference may in part be due to the increased steric bulk of IPr, relative to the $IPrCH_2$ and DMAP donors, which cause the $H_2BNMe_2BH_3$ chain to take on an alternate low energy conformation. Shore and co-workers have recently determined that for the compound H_3N-H_2BNH_2-BH_3 both *anti* and *gauche* conformers could be selectively crystallized depending on the absence or presence of 18-crown-6 in the crystalline lattice.[27] Shore's observations, in conjunction with the presence of both *anti* and *gauche* conformations in our adducts LB-H_2BNR_2-BH_3 (R = H and Me) imply that there is a low rotational energy barrier about the central B–N bonds in these species. Notably, Nutt and McKee reported that the *gauche* isomer of H_3N-H_2BNH_2-BH_3 is more stable than the *anti* form by 11.2 kcal/mol in the gas phase, while a rotational barrier of 13.1 kcal/mol was estimated.[28]

DMAP-H_2BNMe_2-BH_3 (**7**), $IPrCH_2$-H_2BNMe_2-BH_3 (**8**), and IPr-H_2BNMe_2-BH_3 (**9**) exhibit similar H_2B-NMe_2 bond lengths of 1.5801(18), 1.585(8) *avg.*, and 1.588(2) Å, respectively. The terminal Me_2N-BH_3 bond lengths in these chains are slightly elongated with respect to the internal B–N bonds [e.g., B(2)–N(3) distance in **9** is 1.617(2) Å]. For comparison, a related amine-borane chain, Me_2NH-H_2BNMe_2-BH_3 was crystallographically characterized by Nöth and co-workers, and a narrow B–N bond length range of 1.589(2) to 1.600(2) Å was noted for the internal and external B–N linkages.[29] Despite the similarity in the intrachain B–N bond lengths between **7** and **8**, it was experimentally confirmed that DMAP is a stronger Lewis base than $IPrCH_2$ in this system. The reaction of 1 equiv of DMAP with $IPrCH_2$-H_2BNMe_2-BH_3 (**8**) quantitatively yielded DMAP-H_2BNMe_2-BH_3 (**7**) along with free $IPrCH_2$ (eq 1), which parallels the ligand substitution chemistry described already for the parent LB-H_2BNH_2-BH_3 adducts (Scheme 2).



Theoretical studies (B3LYP/cc-pVDZ)[19] were performed on DMAP-H_2BNH_2-BH_3 (**4**), DMAP-H_2BNMe_2-BH_3 (**7**), and the structurally truncated model complexes, $ImMe_2CH_2$-H_2BNH_2-BH_3 (**2′**) and $ImMe_2CH_2$-H_2BNMe_2-BH_3 (**8′**) [$ImMe_2CH_2$ = $(HCNMe)_2CCH_2$]. The density functional theory (DFT) calculations indicate the presence of polar and dative internal and terminal B–N bonds ($B^{\delta+}$-$N^{\delta-}$), while the accompanying LB-BH_2 interactions also show dative character; furthermore, there is reasonable agreement between the X-ray structural data and the calculated bond lengths and angles.[19] The Wiberg bond indices for the central B–N bonds in **2′**, **4**, **7**, and **8′** are nearly identical to each other (0.60 to 0.69) and are only slightly higher in value than the indices found for the terminal $-NR_2$-BH_3 bonds in the same compounds; these results mirror the structural data obtained by X-ray crystallography. Although some variations are present, the B–N bonds in each of the studied chains are derived from orbital hybrids of sp^3character, consistent with the tetrahedral geometries present at B and N. In addition, significant intramolecular B–$H^{\delta-}\cdots{}^{\delta+}$H–N hydrogen bonding interactions within the $-BH_2NH_2BH_3$ arrays in **2′** and **4** are present, as illustrated by the delocalized molecular orbital shown in Figure 5.

Dehydrocoupling Chemistry of the Parent Aminoborane Adducts. As indicated in Scheme 1, we were interested in accessing complexes bearing the unsaturated B–N entities, HB=NH and B≡N as encapsulated units for the future development of low temperature routes to bulk boron nitride. Given the successful synthesis of a family of donor–acceptor complexes LB-H_2BNH_2-BH_3 (compounds **2**–**5**), we then expanded our investigations to include their dehydrogenation chemistry. Because of the thermal instability of the $IPrCH_2$ analogue, **2**, we focused our studies on the more stable

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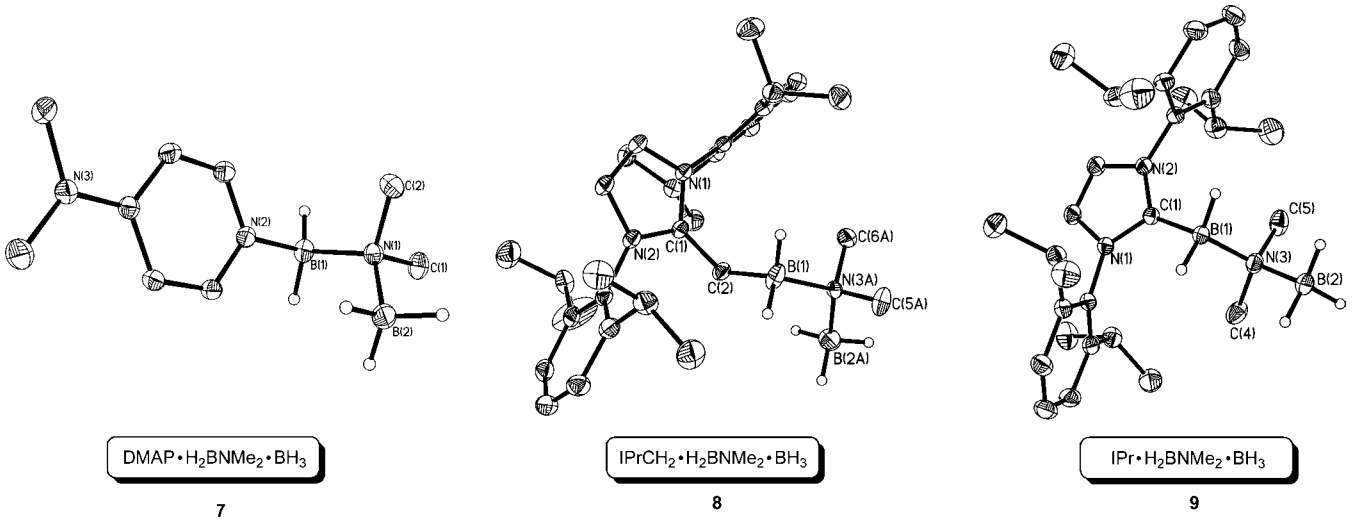


Figure 4. Thermal ellipsoid plots (30% probability) of DMAP-H_2BNMe_2-BH_3 (**7**), $IPrCH_2$-H_2BNMe_2-BH_3 (**8**), and IPr-H_2BNMe_2-BH_3 (**9**) with carbon-bound hydrogen atoms and solvate molecules omitted for clarity; compound **8** contains a disordered NMe_2BH_3 unit. Selected bond lengths [Å] and angles [deg]: *Compound 7:* N(2)−B(1) 1.5722(19), B(1)−N(1) 1.5801(18), N(1)−C(1) 1.4835(16), N(1)−C(2) 1.4800(17), N(1)−B(2) 1.6020(19), B(1)−H 1.115(14) and 1.104(15), B(2)−H 1.130(15), 1.130(16), and 1.126(18); N(2)−B(1)−N(1) 111.32(11), B(1)−N(1)−B(2) 114.53(11); N(2)−B(1)−N(1)−B(2) torsion angle = 60.99(15). *Compound 8*; values involving a disordered NMe_2BH_3 unit in square brackets: C(2)−B(1) 1.659(3), B(1)−N(3A) 1.589(6) [1.581(6)], N(3A)−C(5A) 1.507(13) [1.470(14)], N(3A)−C(6A) 1.496(12) [1.441(13)], N(3A)−B(2A) 1.596(14) [1.585(17)], C(2)−B(1)−N(3A) 106.2(4) [120.4(4)], B(1)−N(3A)−B(2A) 120.5(8) [106.9(9)]; C(2)−B(1)−N(3A)−B(2A) torsion angle = 52.9(7) [59.3(8)]. *Compound 9*: C(1)−B(1) 1.639(2), B(1)−N(3) 1.588(2), N(3)−C(4) 1.477(2), N(3)−C(5) 1.475(2), N(3)−B(2) 1.617(2), B(1)−H 1.146(18) and 1.130(18), B(2)−H 1.12(2), 1.16(2), and 1.16(2); C(1)−B(1)−N(3) 114.39(12), B(1)−N(3)−B(2) 110.63(13); C(1)−B(1)−N(3)−B(2) torsion angle = 178.38(12).

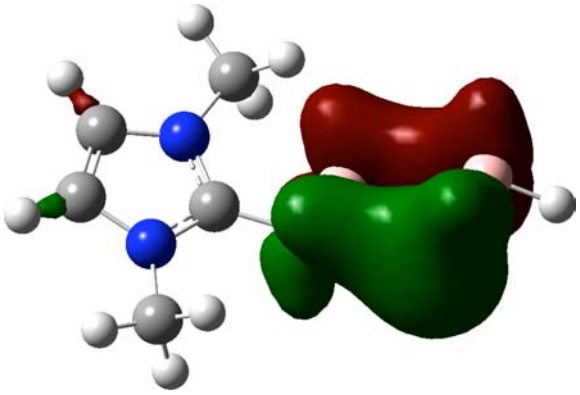
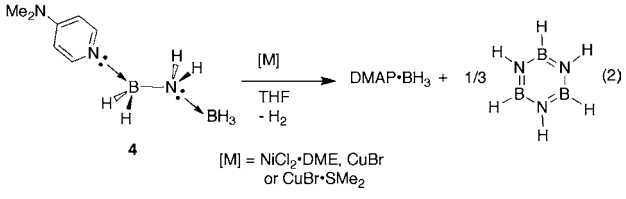


Figure 5. HOMO-18 for $ImMe_2CH_2$-H_2BNH_2-BH_3 (**2′**) as derived from a DFT study showing orbital overlap between B−H and N−H bonding orbitals.

DMAP adduct, **4**. It has been well established in the literature that Rh(I) complexes are very effective at inducing the rapid catalytic dehydrocoupling of amine-borane adducts ($R_2NH{\cdot}BH_3$; R = alkyl, aryl or H).[25,26] To our surprise, when DMAP-H_2BNH_2-BH_3 (**4**) was combined with substoichiometric quantities of $[Rh(COD)Cl]_2$ in THF, no reaction was evident at both room temperature or in refluxing THF by in situ ^{11}B NMR spectroscopy. A small quantity of a black powder was generated, presumably precipitated Rh metal or clusters; however in each case unreacted DMAP-H_2BNH_2-BH_3 was recovered and identified by NMR spectroscopy.

The DMAP adduct (**4**) is completely stable at room temperature in THF and in chlorinated solvents, which is in contrast to $IPrCH_2$-BH_2NH_2-BH_3 (**2**) which decomposes in these solvents over time. However, heating of a solution of **4** in refluxing benzene affords the known adduct, DMAP·BH_3 (^{11}B NMR: quartet, δ = −13.9 ppm, $^1J_{B-H}$ = 93 Hz) and borazine $[HBNH]_3$ (^{11}B NMR: d, δ = 30.6 ppm, $^1J_{B-H}$ = 141 Hz),[30] implying that thermal dehydrogenation of **4** had transpired. Interestingly the observed 3:1 ratio of the ^{11}B NMR signals for DMAP·BH_3 and borazine is lower than the 1:1 ratio expected if decomposition according to eq 2 was the sole process. The nature of this dehydrogenation reaction will be discussed in detail later on in this paper.



Recently Liu and co-workers reported that transition metal halides (MX and MX_2, M = Fe, Ni, Co, Cu; X = F, Cl, Br, and I) are effective precatalysts for the dehydrogenation of substituted amine-boranes, $RH_2B{\cdot}NH_2R$ (R = alkyl).[31] To induce H_2 elimination from DMAP-H_2BNH_2-BH_3 (**4**) we conducted a series of additional dehydrogenation trials using the protocol developed by the Liu group.[31] When **4** was reacted with substoichiometric quantities of DME·$NiBr_2$ (16 mol %) at room temperature in THF for two days, ^{11}B NMR spectroscopy of the reaction mixture showed about a 50% conversion of **4** into DMAP·BH_3 and borazine. When either CuBr or Me_2S·CuBr were investigated as catalysts, compound **4** was consumed entirely after two days in both cases, yielding DMAP·BH_3 and borazine as major soluble products (eq 2) along with the formation of an unidentified broad singlet at 5.5 ppm (ca. 5% by integration). This result, when taken with the thermolysis of **4**, imply that the DMAP adduct (**4**) can undergo one formal dehydrogenation event, which results in the formal

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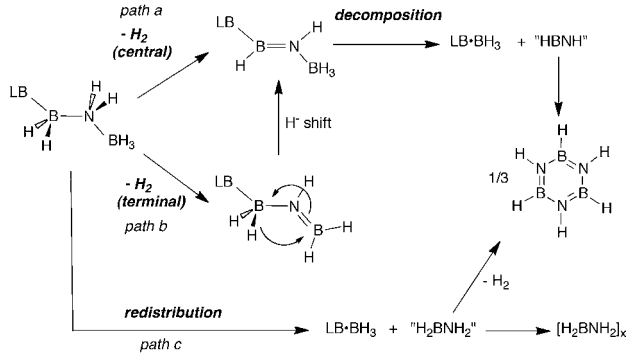
extrusion of HBNH in the form of its trimer, borazine $[HBNH]_3$.

The generation of borazine in the dehydrogenation of **4** represents a potentially useful synthetic route to this heterocycle. Borazine has been utilized as a precursor for the low-pressure synthesis of boron nitride;[32] however, most routes to this B−N species yield only moderate amounts of this volatile compound and require extensive purification steps.[33] It should be mentioned that replacement of THF in the above dehydrogenation chemistry with a less volatile solvent (such as triglyme) will be needed to effectively isolate borazine in pure form because of its similar boiling point as THF; such experiments are ongoing in our laboratories.

At this time, we do not know the mechanism by which H_2 elimination from DMAP-H_2BNH_2-BH_3 occurs; however, there exists three possible pathways (Scheme 5): (a) direct H_2 loss

Scheme 5. Possible Dehydrogenation Reaction Pathways for H_2BNH_2 Adducts

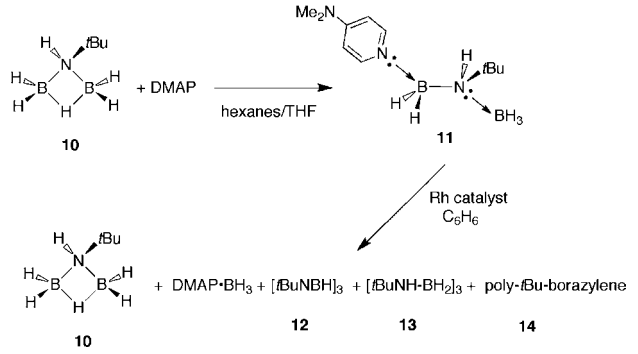


from a central -H_2BNH_2- unit to give an encapsulated HB═NH moiety; (b) loss of H_2 from a terminal $-NH_2-BH_3$ unit followed by a hydride shift to give a similar LB-HB═NH-BH_3 adduct, which later decomposes to give borazine and LB·BH_3 (LB = Lewis base); (c) redistribution of DMAP-H_2BNH_2-BH_3 to give DMAP·BH_3 and transient H_2BNH_2 that either undergoes self-oligomerization (to give insoluble $[H_2BNH_2]_x$) or further dehydrogenation to yield borazine. Recent theoretical studies have indicated a possible preference for *pathway b* over *pathway a* given a calculated lower activation energy for H_2 loss via a terminal BH_3 group.[34] Support for *pathway c* is found in recent studies from the Manners group wherein both thermal and Ir^I catalyzed redistribution of Me_3N-$BH_2NMe_2BH_3$ to give Me_3N-BH_3 and $[Me_2NBH_2]_2$ (presumably via transient Me_2N═BH_2) was reported.[15e] We are currently exploring the synthesis of selectively deuterated analogues of **4** to further probe which dehydrogenation pathway is operating.

Synthesis of DMAP-$H_2BN(t$Bu)-BH_3 and Dehydrogenation Chemistry. We then decided to add steric bulk to the H_2BNR_2 unit via the synthesis of the *tert*-butylated adduct, DMAP-$H_2BNH(t$Bu)-BH_3 (**11**). It was hypothesized that the *t*Bu group would also increase the electron density on nitrogen via inductive effects resulting in a stronger bonding interaction with the terminal BH_3 unit, and in turn, provide access to the novel the dehydrogenated adduct DMAP-HB═N(*t*Bu)-BH_3.

DMAP-$H_2BNH(t$Bu)-BH_3 (**11**) was synthesized by ring-opening of the μ-aminodiborane $(t$Bu)NHB_2H_5 (**10**)[35a] with DMAP (Scheme 6). The *tert*-butylated aminoborane complex **11** precipitated as a pure white solid (73% yield) from the hexanes/THF reaction mixture and was characterized by a

Scheme 6. Synthesis and Catalytic Dehydrogenation of DMAP-$H_2BNH(t$Bu)-BH_3 (11)



combination of NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography (Figure 6). Comparable

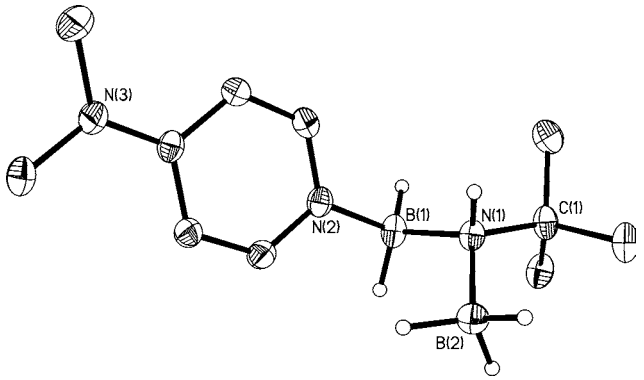


Figure 6. Thermal ellipsoid plot (30% probability) of DMAP-$H_2BNH(t$Bu)-BH_3 (**11**), with carbon-bound hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: N(2)−B(1) 1.583(2), B(1)−N(1) 1.593(2), N(1)−B(2) 1.623(2), N(1)−C(1) 1.519(2), B(1)−H 1.11(2) and 1.11(2), B(2)−H 1.14(2), 1.17(2) and 1.16(2); N(2)−B(1)−N(2) 108.95(13), B(1)−N(1)−C(1) 112.87(12), B(1)−N(1)−B(2) 110.57(14); N(2)−B(1)−N(1)−B(2) torsion angle = 76.66(18).

spectral features were observed in **11** as found in the related DMAP adducts **4** and **7**; however, the existence of magnetically inequivalent hydrides within the internal BH_2 group in **11** was noted in the ^1H NMR spectrum; the assignment of these distinct B−H hydrides (at 2.64 and 2.95 ppm) was made using selective $^1H\{^{11}B\}$ decoupling experiments at the resonant ^{11}B frequency for the BH_2 group. Weller and co-workers also noted similar inequivalence of the internal B−H groups in $MeNH_2$-BH_2-NMe(H)-BH_3.[36]

As shown in Figure 6, compound **11** crystallizes in a *gauche* conformation [$N_{DMAP}-B-N-B_{terminal}$ torsion angle = 76.66(18)°], and has a coordinative N_{DMAP}-BH_2 bond length [1.583(2) Å] that is similar in value, within experimental error (3σ), as the respective N_{DMAP}-B bonds present in the parent adduct DMAP-H_2BNH_2-BH_3 (**4**) [1.5728(15) Å], and the methylated analogue DMAP-H_2BNMe_2-BH_3 (**7**) [1.5722(19) Å].

With the *tert*-butyl substituted adduct **11** in hand, we decided to explore dehydrogenative chemistry to access the iminoborane adduct DMAP-HB═N(*t*Bu)-BH_3. Combining **11** with a catalytic amount of Me_2S·CuBr in benzene (for 12 h at room temperature) resulted in the formation of DMAP·BH_3 and the

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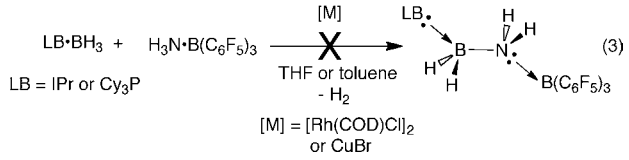
μ-aminodiborane (tBu)NHB_2H_5 (**10**) in 15 and 21% yields, respectively, with 64% unreacted **11**, as determined by ^{11}B NMR spectroscopic analysis of the reaction mixture. We then reacted **11** with a catalytic amount of $[Rh(COD)Cl]_2$ in benzene at room temperature, and noted the formation of a series of products by in situ ^{11}B NMR spectroscopy (Scheme 6): specifically, the presence of $[t$BuNBH$]_3$ (**12**, 5%, d, −25.2 ppm, $^1J_{B-H}$ = 143 Hz), $[t$BuNH-$BH_2]_3$ (**13**, 31%, t, −4.7 ppm, $^1J_{B-H}$ = 95 Hz), poly-*tert*-butylborazylene (**14**, 11%, br s, −30.1),[35] DMAP·BH_3 (31%), and **10** (21%) was observed. The formation of large quantities of the known cycloborazane trimer, $[t$BuNH-$BH_2]_3$ is interesting as this product is not generated when **11** is kept in benzene in the absence of Rh catalyst. One possible pathway to this species could involve transfer hydrogenation chemistry between N-*tert*-butyl borazine $[t$BuNBH$]_3$ and **11** to yield the hydrogenated trimer $[t$BuNH-$BH_2]_3$ and products stemming from the dehydrogenation of **11**.[37] Interestingly, our findings also corroborate studies conducted by Wright and co-workers, who showed that the dehydrocoupling of tBuH_2N·BH_3 with $Al(NMe_2)_3$ as a catalyst resulted in mixtures of the trimers **12** and **13**, and related B−N oligomers (such as **14**).[35b]

Attempted Syntheses of $B(C_6F_5)_3$-Terminated Aminoborane Adducts, LB-H_2BNH_2-$B(C_6F_5)_3$. Given the lack of success in isolating dehydrogenated adducts of the general form LB-H_2BNH_2-BH_3, we decided to target complexes in which the terminal BH_3 group was replaced by the arylfluoroborane Lewis acid, $B(C_6F_5)_3$, LB-H_2BNH_2-$B(C_6F_5)_3$. Not only would this confine any dehydrogenation chemistry to the central H_2BNH_2 unit but also the high Lewis acidity of $B(C_6F_5)_3$[38] might encourage the eventual formation of a metastable complex of boron nitride LB-B≡N-$B(C_6F_5)_3$ following the dehydrogenation chemistry outlined in Scheme 1.

To investigate if the terminal BH_3 unit in the aminoborane adducts LB-H_2BNH_2-BH_3 could be displaced by $B(C_6F_5)_3$, Cy_3P-H_2BNH_2-BH_3 (**3**) was combined with 1 equiv of $B(C_6F_5)_3$ in a 10:1 toluene/THF solvent mixture. The reaction was monitored in situ by NMR, and after 3 h, numerous products were observed by ^{31}P and ^{11}B NMR spectroscopy, with no sign of the potential products $[Cy_3P(C_6F_4)BF(C_6F_5)_2]$, the $[HB(C_6F_5)_3]^-$ anion, $[HBNH]_3$, $[H_2BNH_2]_3$ or $Cy_3P·BH_3$ noted;[20,38c] commensurate with the above data, the resulting $^{19}F\{^1H\}$ NMR spectrum contained many resonances from −130 to −170 ppm (>30 signals). Unfortunately, equally complicated spectra were obtained when the related LB-H_2BNH_2-BH_3 adducts were reacted with $B(C_6F_5)_3$, thus clean $BH_3/B(C_6F_5)_3$ exchange involving these species does not appear to be feasible.

Positing that $BH_3/B(C_6F_5)_3$ Lewis acid exchange might transpire in a system where competing dehydrogenation chemistry cannot occur, we reacted the methylated aminoborane adduct DMAP-H_2BNMe_2-BH_3 (**7**) with $B(C_6F_5)_3$. Reaction of **7** with $B(C_6F_5)_3$ in toluene yielded a mixture of products by ^{11}B NMR. The mixture contained unreacted **7** (ca. 53%), small quantities of $[Me_2N-BH_2]_2$ (8%), two minor unknown products [20 ppm (br s, 7%) and 11.5 ppm (d, $^1J_{B-H}$ = 101 Hz, 7%)], and a doublet at −25 ppm ($^1J_{B-H}$ = 95 Hz, ca. 25%) corresponding to the $[HB(C_6F_5)_3]^-$ anion.[39] It is evident that hydride transfer from a BH_2 or BH_3 group in **7** to $B(C_6F_5)_3$ occurred; however, the nature of the corresponding cation (partnered with $[HB(C_6F_5)_3]^-$) is unknown at this time.

Because of the lack of clean $BH_3/B(C_6F_5)_3$ exchange chemistry involving the adducts **3** and **4** and $B(C_6F_5)_3$ we attempted to independently synthesize the adducts Cy_3P-H_2BNH_2-$B(C_6F_5)_3$ and IPr-H_2BNH_2-$B(C_6F_5)_3$ via a different synthetic route. Scheer and co-workers reported the dehydrogenative coupling of the phosphine complex, $H_3P·W(CO)_5$ with trimethylamine-alane or -gallane adducts [$Me_3N·EH_3$; E = Al and Ga] to give the novel donor−acceptor complexes, Me_3N-H_2E-PH_2-$W(CO)_5$.[14a] Therefore we explored analogous chemistry involving the known borane adducts IPr·BH_3 and $Cy_3P·BH_3$, and the ammonia adduct $H_3N·B(C_6F_5)_3$ to potentially afford the aminoborane complexes, LB-H_2BNH_2-$B(C_6F_5)_3$ (eq 3). However when these reactions were



(3)

conducted at room temperature or in refluxing solvent (toluene or THF), no reaction occurred. Furthermore, attempts to induce dehydrogenation chemistry in the presence of the dehydrogenation catalysts $[Rh(COD)Cl]_2$ and CuBr failed to yield any observable chemistry. At the moment we are exploring salt metathesis routes to the desired arylfluoroborane-terminated adducts.

CONCLUSION

In summary we have prepared formal donor−acceptor adducts of the parent aminoborane H_2BNH_2, LB-H_2BNH_2-BH_3 (LB = $IPrCH_2$, Cy_3P, DMAP and IPr). Initial studies have demonstrated that the DMAP adduct DMAP-H_2BNH_2-BH_3 can undergo a single dehydrogenation event upon heating, or in the presence of metal catalysts, to yield borazine and the involatile adduct DMAP·BH_3. In addition, the preparation of N-substituted adducts LB-H_2BNR_2-BH_3 was reported along with comparative thermolysis chemistry and theoretical bonding analyses. Attempts to replace terminal BH_3 Lewis acid groups with the stronger Lewis acid $B(C_6F_5)_3$ to yield complexes of the general form LB-H_2BNH_2-$B(C_6F_5)_3$ were unsuccessful. Future work will involve exploring alternate pathways toward intercepting molecular BN as metastable adducts, LB-B≡N-LA, and the use of these species as molecular sources of bulk boron nitride.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using Grubbs-type solvent purification system manufactured by Innovative Technology, Inc.,[40] degassed (freeze−pump−thaw method) and stored under an atmosphere of nitrogen prior to use. $H_3N·BH_3$, tBu$NH_2·BH_3$, $B(C_6F_5)_3$, and Cy_3P were purchased from Aldrich and used as received. $Me_2NH·BH_3$, $H_3B·THF$, and dimethylaminopyridine (DMAP) were purchased from Alfa Aesar and used as received. 1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr),[41] 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-methylidene ($IPrCH_2$),[17b] $H_3N·B(C_6F_5)_3$,[38c] IPr·BH_3,[24] and $Cy_3P·BH_3$[42] were prepared following literature procedures. ^{11}B and $^{19}F\{^1H\}$ NMR spectra were collected on a Varian iNova-400 spectrometer, while ^1H and $^{13}C\{^1H\}$ NMR spectra were either collected on Varian iNova 400 or Varian VNMRS-500 spectrometers. Samples were referenced externally to $SiMe_4$ (^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$), $F_3B·OEt_2$ (^{11}B, $^{11}B\{^1H\}$) and $CFCl_3$ ($^{19}F\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR

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Table 1. Crystallographic Data for Compounds 3−5, 7−9, and 11

	3	4	5	7[b]	8	9	11
formula	$C_{19.50}H_{43}B_2Cl_3NP$	$C_7H_{17}B_2N_3$	$C_{28}H_{45}B_2Cl_2N_3$	$C_9H_{21}B_2N_3$	$C_{31}H_{51}B_2ClN_3$	$C_{32}H_{54}B_2N_3$	$C_{11}H_{25}B_2N_3$
fw	450.49	164.86	516.19	192.91	522.82	502.40	220.96
cryst. dimens. (mm)	0.34 × 0.29 × 0.26	0.23 × 0.13 × 0.06	0.36 × 0.33 × 0.19	0.38 × 0.36 × 0.31	0.61 × 0.36 × 0.27	0.23 × 0.23 × 0.15	0.33 × 0.15 × 0.04
cryst. syst.	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
unit cell							
a (Å)	10.9130 (6)	11.2392 (2)	9.3058 (3)	8.4065 (6)	10.2412 (5)	12.7575 (2)	8.0183 (2)
b (Å)	18.3557 (10)	7.4511 (1)	9.4670 (3)	10.0395 (8)	12.9371 (7)	19.0656 (3)	18.0715 (4)
c (Å)	13.6997 (8)	12.1976 (2)	20.3326 (7)	14.3963 (11)	24.8848 (13)	13.1625 (2)	9.9072 (2)
α (deg)			77.8380 (13)				
β (deg)	110.9230 (10)	101.0881 (9)	85.7537 (13)		99.8480 (10)	93.3871 (9)	91.7241 (13)
γ (deg)			61.4232 (15)				
V (Å^3)	2563.3 (2)	1002.41 (3)	1536.99 (9)	1215.01 (16)	3248.4 (3)	3195.91 (9)	1434.93 (6)
Z	4	4	2	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.171	1.092	1.115	1.055	1.069	1.044	1.023
μ (mm^{-1})	0.430	0.496	2.034	0.062	0.140	0.440	0.448
T (K)	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	55.32	140.02	137.20	55.04	50.50	141.44	141.86
total data	22370	1822	10182	10623	22840	20925	9552
unique data (R_{int})	5933 (0.0424)	1822 (0.0000)	5335 (0.0117)	2782 (0.0354)	5886 (0.0286)	5834 (0.0184)	2706 (0.0393)
observed data [$I > 2\sigma(I)$]	4489	1637	4978	2418	4738	5320	2149
params.	232	140	393	150	376	346	171
R_1 [$I > 2\sigma(I)$][a]	0.0422	0.0336	0.0621	0.0359	0.0570	0.0555	0.0533
wR_2 [all data][a]	0.1252	0.0956	0.1675	0.0886	0.1725	0.1623	0.1564
difference map $\Delta\rho$ (e Å^{-3})	0.300/−0.204	0.156/−0.146	0.313/−0.319	0.165/−0.120	0.386/−0.627	0.424/−0.436	0.397/−0.216

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [b] Flack parameter = −1.6(19).

spectrometer as Nujol mulls between NaCl plates. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray Crystallography. Crystals suitable for X-ray diffraction studies were removed from a vial (in a glovebox) and immediately coated with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.[43] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to −100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces.[44] Crystal structures were solved using direct methods (**3**, **4**, **5**, **7**, **8**, **9**, and **11**: SHELXD[45,46]), and refined using SHELXS-97 (Table 1). The assignment of hydrogen atoms positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Special Refinement Conditions. *Compound* ***3.*** Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent dichloromethane chlorine or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure[47] as implemented in PLATON.[48] A total solvent-accessible void volume of 734 Å^3 with a total electron count of 248 (consistent with 6 molecules of solvent dichloromethane, or 1.5 molecules per formula unit of the Cy_3P-BH_2NH_2-BH_3 molecules) was found in the cell.

Compound ***4.*** The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program CELL_NOW.[49] The second twin component can be related to the first component by 180° rotation about the [1 0 1] axis in real space and about the [5/6 0 1] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELX-97 HKLF 5 reflection file with the data integration program SAINT (version 7.68A),[50] using all reflection data (exactly overlapped, partially overlapped, and non-overlapped). The refined value of the twin fraction (SHELXL-97 BASF parameter) was 0.292(2).

Compound ***5.*** Distance restraints (by use of the SHELXL SADI instruction) were applied to the disordered isopropyl group for the following bonds: C32−C37A and C32−C37B; C37A−C38A, C37A−C39A, C37B−C38B, and C37B−C39B. Distance restrains (SADI) were also applied to the N−H and B−H bonds: B1−H1B1 and B1−H1BB; B2−H2BA, B2−H2BB, B2−H2BC; N3−H3NA, N3−H3NB. The disordered solvent dichloromethane molecule was subjected to both C−Cl distance restraints (SADI) and "rigid bond" restraints by use of the SHELXL DELU instruction. Finally, an "anti-bumping" restraint was applied to the H1BB···H2SB distance between one of the hydrogen atoms of the minor orientation of the disordered solvent dichloromethane and one of the hydrogen atoms attached to B1.

Compound ***8.*** The B1−N3A and B1−N3B distances were restrained to be approximately equal by use of SHELXL SADI instruction during refinement. The C1S−C1S′ distance was restrained to be a target value of 1.50(2) Å during refinement.

Compound ***9:*** Distances within the disordered solvent *n*-hexane molecule were restrained during refinement: d(C1SA-C1SA′) = d(C1SA-C2SA) = d(C2SA-C3SA) = d(C1SB-C1SB′) = d(C1SB-C2SB) = d(C2SB-C3SB) = 1.52(2) Å; d(C1SA···C2SA′) = d(C1SA···C2SA′) = d(C1SA···C3SA) = 2.46(2) Å (primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 1/2)).

Synthetic Procedures. Synthesis of Aminodiborane, $NH_2B_2H_5$ (1). Ammonia-borane (61.7 mg, 2.00 mmol) was taken up as a slurry in 15 mL of hexanes, and H_3B·THF (2.00 mL, 1.0 M solution in THF, 2.00 mmol) was added. The resulting cloudy solution was stirred for 3 days at room temperature to yield a colorless solution. The solution volume was concentrated by half under vacuum and filtered. The presence of **1** can be determined by diluting a small

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aliquot of the reaction mixture with C_6D_6 for ^{11}B NMR analysis. ^{11}B NMR (128 MHz, C_6D_6): δ = −26.6 ppm [d of t, $^1J_{BH}$ = 27 Hz (B−H bridging) and 138 Hz (B−H terminal)]. In all subsequent reactions, the formation of **1** was assumed to be quantitative for the purpose of calculating reactant quantities and product yields.

Synthesis of IPrCH$_2$-H$_2$BNH$_2$-BH$_3$ (2). A solution of IPrCH$_2$ (0.859 g, 2.13 mmol) in 3 mL of hexanes was added to a purified solution of $NH_2B_2H_5$ (**1**) (made from 66.0 mg of $H_3N{\cdot}BH_3$, 2.14 mmol) in 5:1 hexanes/THF to give a white slurry which was stirred at room temperature for 2 h. The mother liquor was decanted, and the white precipitate was washed with 2 × 6 mL portions of hexanes and toluene. The product was dried under vacuum, to give **2** as a white powder (0.587 g, 62%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, 4H, $^3J_{HH}$ = 7.5 Hz, Ar*H*), 7.34 (d, 2H, $^3J_{HH}$ = 7.5 Hz, Ar*H*), 7.00 (s, 2H, −N-C*H*), 2.56 (septet, 4H, $^3J_{HH}$ = 6.5 Hz, −C*H*(CH$_3$)$_2$), 1.88 (br t, 2H, $^3J_{HH}$ = 4.0 Hz, IPrC*H*$_2$), 1.41 (s, 2H, -B*H*$_2$NH$_2$BH$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling), 1.35 (d, 12H $^3J_{HH}$ = 6.5 Hz, −CH(C*H*$_3$)$_2$), 1.16 (d, 12H, $^3J_{HH}$ = 6.5 Hz, −CH(C*H*$_3$)$_2$), 1.06 (s, 3H, -BH$_2$NH$_2$B*H*$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling); the −N*H*$_2$- group was not located. $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ = 162.3 (Ar*C*), 145.7 (Ar*C*), 131.4 (Ar*C*), 130.8 (Ar*C*), 124.7 (-N-CH), 121.3 (-N-*C*(CH$_2$)-N-), 28.9 (−CH(CH$_3$)$_2$), 25.7 (−CH(CH$_3$)$_2$), 22.6 (IPrCH$_2$). ^{11}B (128 MHz, $CDCl_3$): δ = −14.7 (br t, $^1J_{BH}$ = 95 Hz, -*B*H$_2$NH$_2$BH$_3$), −21.9 (br q, $^1J_{BH}$ = 87 Hz, -BH$_2$NH$_2$*B*H$_3$). IR (Nujol/cm^{-1}): 3340 (s, νNH), 2351 (s, νBH), 2304 (s, νBH), 2219 (s, νBH). Anal. Calcd. for $C_{28}H_{45}B_2N_3$: C, 75.52; H, 10.19; N, 9.44. Found: C, 74.02; H, 11.24; N, 8.49. Mp (°C) 148−149. Compound **2** was always obtained with about 10% of [IPrCH$_3$]BH$_4$ as a contaminant (vide infra); thus satisfactory elemental analyses could not be obtained (see the Supporting Information, Figures S1 and S2).[19]

Decomposition of IPrCH$_2$-H$_2$BNH$_2$-BH$_3$ (2) in Solution. To investigate its decomposition, compound **2** (75.3 mg, 0.168 mmol) was dissolved in 8 mL of THF and stirred at room temperature. An aliquot of solution was removed and analyzed by ^{11}B NMR spectroscopy every hour. Initial measurements (<15 min.) showed no signs of decomposition. After 24 h about 50% had decomposed into [IPrCH$_3$][BH$_4$] by integration of the ^{11}B NMR spectrum. After 48 h about 90% had decomposed into the same product. Volatiles were removed in vacuo, and white residue was analyzed by ^1H and ^{11}B NMR to yield a crude sample of [IPrCH$_3$][BH$_4$], containing about 10% of **2**.

NMR Data for [IPrCH$_3$][BH$_4$]. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 2H, −N-C*H*), 7.65 (t, 4H, $^3J_{HH}$ = 8.0 Hz, Ar*H*), 7.44 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar*H*), 2.34 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, −C*H*(CH$_3$)$_2$), 2.14 (s, 3H, IPrC*H*$_3$), 1.32 (d, 12H, $^3J_{HH}$ = 6.8 Hz, −CH(C*H*$_3$)$_2$), 1.23 (d, 12H, $^3J_{HH}$ = 6.8 Hz, −CH(C*H*$_3$)$_2$), 0.33 (q, 4H, $^1J_{BH}$ = 81.5 Hz, B*H*$_4^-$). ^{11}B (128 MHz, $CDCl_3$): δ = −40.6 (pentet, $^1J_{BH}$ = 81 Hz, *B*H$_4^-$). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ = 145.7 (−N−*C*-N), 144.9 (Ar*C*), 132.6 (Ar*C*), 129.0 (Ar*C*), 126.2 (Ar*C*), 125.4 (-N-CH), 29.2 (−CH(CH$_3$)$_2$), 24.6 (−CH(CH$_3$)$_2$), 23.4 (−CH(CH$_3$)$_2$), 10.9 (IPrCH$_3$).

Synthesis of Cy$_3$P-H$_2$BNH$_2$-BH$_3$ (3). To a cold (−35 °C) solution of **1** (made from 0.0696 g of $H_3N{\cdot}BH_3$, 2.25 mmol) in 15 mL of 5:1 hexanes/THF was added PCy$_3$ (630 mg, 2.25 mmol). The resulting mixture was stirred at reduced temperature for 1 h, which clouded to give a white slurry after 16 h at room temperature. The mother liquor was then decanted, and the white solid was washed with two 6 mL portions of 5:1 hexanes/THF. The product was dried under vacuum, giving **3** as a white powder (0.440 g, 61%). Crystals of **3** suitable for X-ray crystallography (colorless prisms) were obtained by cooling a saturated dichloromethane/hexanes solution to −35 °C.

^1H NMR (400 MHz, C_6D_6): δ = 2.51 (br s, 3H, -BH$_2$NH$_2$B*H*$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling), 2.42 (br s, 2H, -B*H*$_2$NH$_2$BH$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling), 2.20 (br s, 2H, -N*H*$_2$), 1.96 (q, 3H, $^3J_{HH}$ = 12.0 Hz, P(C$_6$*H*$_{11}$)$_3$), 1.84 (d, 6H, $^3J_{HH}$ = 13.0 Hz, P(C$_6$*H*$_{11}$)$_3$), 1.59 (d, 6H, $^3J_{HH}$ = 9.2 Hz, P(C$_6$*H*$_{11}$)$_3$), 1.51 (d, 3H, $^3J_{HH}$ = 9.6 Hz, P(C$_6$*H*$_{11}$)$_3$), 1.25 (q, 6H, $^3J_{HH}$ = 12.0 Hz, P(C$_6$*H*$_{11}$)$_3$), 1.02 (m, 9H, P(C$_6$*H*$_{11}$)$_3$). $^{13}C\{^1H\}$ (125 MHz, C_6D_6): δ = 31.2 (d, $^1J_{PC}$ = 29 Hz, P*C*y$_3$), 28.5 (P*C*y$_3$), 27.4 (d, $^2J_{PC}$ = 10 Hz, P*C*y$_3$), 26.2 (P*C*y$_3$). ^{11}B (128 MHz, C_6D_6): δ = −17.5 (br, -BH$_2$NH$_2$*B*H$_3$), −21.0 (br, -*B*H$_2$NH$_2$BH$_3$). $^{31}P\{^1H\}$ (161 MHz, C_6D_6): δ = 10.2 (br). IR (Nujol/cm^{-1}): 3233 (w, νNH), 2299 (w, νBH), 2204 (w, νBH), 2190 (w, νBH). Anal. Calcd. for $C_{18}H_{40}B_2NP$: C, 66.91; H, 12.48; N, 4.33. Found: C, 66.93; H, 12.40; N, 4.14. Mp (°C) 117−119.

Synthesis of DMAP-H$_2$BNH$_2$-BH$_3$ (4). A solution of p-dimethylaminopyridine (0.0918 g, 0.75 mmol) in 5 mL of 5:1 hexanes/THF was added to a solution of $NH_2B_2H_5$ (made from 23.2 mg of $H_3N{\cdot}BH_3$, 0.75 mmol) in 10 mL of 5:1 hexanes/THF solvent mixture. The resulting mixture clouded to give a white slurry after 8 h. The mother liquor was then decanted, and the white solid was washed with 6 mL portions of hexanes, diethyl ether and toluene. The product was dried under vacuum, giving **4** as a white powder (0.0920 g, 74%). Crystals of **4** suitable for X-ray crystallography (colorless needles) were obtained by cooling a saturated dichloroethane/Et$_2$O solution to −35 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, 2H, $^3J_{HH}$ = 7.3 Hz, Ar*H*), 6.57 (d, 2H, $^3J_{HH}$ = 7.3 Hz, Ar*H*), 3.13 (s, 6H, -N(C*H*$_3$)$_2$), 2.79 (s, 2H, -B*H*$_2$NH$_2$BH$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling), 2.19 (br s, 2H, -BH$_2$N*H*$_2$BH$_3$), 1.26 (t, 3H, $^3J_{HH}$ = 4.4 Hz, -BH$_2$NH$_2$B*H*$_3$, assignment made by selective $^1H\{^{11}B\}$ decoupling). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ = 155.8 (Ar*C*), 147.4 (Ar*C*), 106.2 (Ar*C*), 39.6 (Ar−N(*C*H$_3$)$_2$). ^{11}B (128 MHz, $CDCl_3$): δ = −3.7 (t, $^1J_{BH}$ = 100 Hz, -*B*H$_2$NH$_2$BH$_3$), −21.8 (q, $^1J_{BH}$ = 92 Hz, -BH$_2$NH$_2$*B*H$_3$). IR (Nujol/cm^{-1}): 3301 (w, νNH), 2364 (w, νBH), 2297 (w, νBH), 2243 (w, νBH). Mp (°C) 138−139. Despite repeated attempts, combustion analyses gave consistently low values for nitrogen content (lower by ca. 2%). See the Supporting Information, Figures S3 and S4 for copies of the NMR spectra of **4**.[19]

Thermolysis of DMAP-H$_2$BNH$_2$-BH$_3$ (4). Ten milligrams of **4** was dissolved in 0.5 mL of benzene and sealed in a J. Young NMR tube under an atmosphere of nitrogen. The sample was heated at 100 °C for 24 h. The in situ ^{11}B NMR analysis showed the presence of DMAP·BH$_3$ and borazine (doublet at 30.6 ppm, $^1J_{BH}$ = 141 Hz) in a 3:1 ratio by integration of peaks, with trace (<5%) starting material. The volatiles were removed in vacuo and the white residue (ca. 5 mg) was identified as DMAP·BH$_3$ by NMR.

NMR Data for DMAP·BH$_3$:[51] ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 6.49 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 3.08 (s, 6H, -N(C*H*$_3$)$_2$). ^{11}B (128 MHz, $CDCl_3$): δ = −13.9 (q, $^1J_{BH}$ = 93 Hz, -*B*H$_3$).

Dehydrogenation of DMAP-H$_2$BNH$_2$-BH$_3$ (4). (i) To a solution of **4** (34.2 mg, 0.207 mmol) in 5 mL of THF was added about 1.0 mg of [Rh(COD)Cl]$_2$ (1 mol %). The solution was initially clear yellow, and turned black-green after 2 h. An aliquot of the solution was then analyzed by ^{11}B NMR at the initiation of reaction and after 60 h, showing only the presence of **4** and no other soluble products. The mother liquor was decanted and dried in vacuo to recover 71% of starting material.

(ii) 20.7 mg (0.126 mmol) of **4** and 6.2 mg of NiBr$_2$·DME (0.02 mmol, 16 mol % cat., DME = dimethoxyethane) were dissolved in 6 mL of THF to yield a golden brown solution that quickly turned black. The mixture was stirred for 48 h to yield a clear colorless solution with black precipitate. ^{11}B NMR analysis of this clear solution showed that 50% of the starting material remained, with the new products DMAP·BH$_3$ (40%) and borazine (10%) formed.

(iii) 19.8 mg (0.120 mmol) of **4** and 8.1 mg of CuBr·SMe$_2$ (32 mol %) were dissolved in 6 mL of THF to yield a light yellow solution that quickly turned black after 10 min. The mixture was stirred for 48 h to give a clear colorless solution with a black metallic precipitate. ^{11}B NMR analysis of this clear solution showed no signs of starting material, with the presence of DMAP·BH$_3$ (65%) and borazine (30%), and one unidentified product (5%, br s, 5.5 ppm) detected.

(iv) 21.5 mg (0.130 mmol) of **4** and 6.0 mg of CuBr (32 mol %) were dissolved in 6 mL of THF to yield a pale yellow solution that turned black after 2 h. The mixture was stirred for 48 h to give a clear colorless solution with a black metallic precipitate. ^{11}B NMR of this clear solution showed no signs of starting material, with the presence

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of DMAP·BH_3 (65%) and borazine (30%), and one unidentified product (5%, br s, 5.5 ppm) detected.

Synthesis of IPr-H_2BNH_2-BH_3 (5) from the Reaction of 4 and IPr. IPr (110.0 mg, 0.284 mmol) and **4** (18.9 mg, 0.115 mmol) were taken up in 5 mL of benzene, and stirred at room temperature to yield a clear golden solution after 8 h. The volatiles were removed in vacuo to yield a pale yellow solid, and the solid was washed with 10 mL of hexanes, and then 5 mL of a 1:1 hexanes/benzene solvent mixture. The remaining solid was dried under vacuum to yield **5** as a white solid (20.9 mg, 42%). X-ray quality crystals were obtained by cooling a hexanes/dichloromethane solution of **5** to −35 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (t, 4H, $^3J_{H-H}$ = 7 Hz, Ar*H*), 7.08 (d, 2H, $^3J_{HH}$ = 7 Hz, Ar*H*), 6.42 (s, 2H, -N-C*H*), 2.90 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, −C*H*(CH_3)$_2$), 2.25 (s, 2H, -B*H*$_2$NH$_2$BH$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 2.11 (s, 3H, -BH$_2$NH$_2$B*H*$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 1.85 (s, 2H, -BH$_2$N*H*$_2$BH$_3$), 1.43 (d, 12H, $^3J_{HH}$ = 6.8 Hz, −CH(C*H*$_3$)$_2$), 0.98 (d, 12H, $^3J_{HH}$ = 6.7 Hz, −CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ = 146.1 (Ar*C*), 133.7 (Ar*C*), 130.8 (Ar*C*), 128.3 (Ar*C*), 124.5 (-N-CH), 122.7 (Ar*C*), 28.8 (−*C*H(CH$_3$)$_2$), 25.8 (−CH(*C*H$_3$)$_2$), 22.9 (−CH-(*C*H$_3$)$_2$). ^{11}B{^{1}H} (128 MHz, $CDCl_3$): δ = −18.2 (br). IR (Nujol/cm^{-1}): 3211 (w, νNH), 2444, 2170, 2201, 2197 (w, νBH). Mp (°C): 144−145. Despite repeated attempts, combustion analyses gave consistently low values for nitrogen content (lower by ca. 2%). See the Supporting Information, Figures S5 and S6 for copies of the NMR spectra of **5**.[19]

Synthesis of Dimethylaminodiborane, $(CH_3)_2NB_2H_5$ (6). $Me_2NH·BH_3$ (0.162 g, 2.75 mmol) was dissolved in 6 mL of 5:1 hexanes/THF and combined with 1.0 mg of [Rh(COD)Cl]$_2$. Immediately the solution turned clear yellow, and within 2 h the solution was dark black-green. The mixture was stirred for 16 h at room temperature and filtered through a plug of silica; the presence of [Me_2NBH_2]$_2$ was confirmed by ^{11}B NMR spectroscopy which showed a triplet at 4.75 ppm ($^1J_{BH}$ = 113 Hz).[52] One equivalent of H_3B·THF (2.7 mL, 1.0 M solution in THF, 2.7 mmol) was added, and the clear colorless mixture was heated at 60 °C for 8 h to yield **6** by ^{11}B NMR (128 MHz, THF): δ = −17.5 (br t, $^1J_{BH}$ = 147 Hz). The observed ^{11}B NMR resonance for **6** was in agreement with data reported previously for this compound.[2Sd,g] In all subsequent reactions, the formation of **6** was assumed to be quantitative for the purpose of calculating reactant quantities and product yields.

Synthesis of DMAP-$H_2BN(CH_3)_2$-BH_3 (7). A solution of *p*-dimethylaminopyridine (0.336 g, 2.75 mmol) in 5 mL of 5:1 hexanes:THF was combined with a 15 mL solution of $N(CH_3)_2B_2H_5$ prepared in situ (from 2.74 mmol of $Me_2NH·BH_3$). The initially clear colorless solution turned to a pale yellow slurry, and the reaction mixture was stirred for 8 h at room temperature. The volatiles were removed under vacuum, and the solid material was washed with 4 mL portions of hexanes, diethyl ether, and benzene. The volatiles were then removed under vacuum to give **7** as a pale yellow solid (0.332 g, 63%). Crystals of **7** suitable for X-ray crystallography (colorless prisms) were grown by cooling a concentrated hexanes/THF solution to −35 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, 2H, $^3J_{HH}$ = 6.0 Hz, Ar*H*), 6.52 (d, 2H, $^3J_{HH}$ = 6.0 Hz, Ar*H*), 3.10 (s, 6H, -BH$_2$N-(C*H*$_3$)$_2$BH$_3$), 2.55 (s, 2H, -B*H*$_2$N(CH$_3$)$_2$BH$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 2.23 (s, 6H, -N(C*H*$_3$)$_2$), 1.32 (t, 3H, $^3J_{HH}$ = 4.4 Hz, -BH$_2$N(CH$_3$)$_2$B*H*$_3$, assignment made by selective ^{1}H{^{11}B} decoupling). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ = 155.8 (Ar*C*), 148.6 (Ar*C*), 105.5 (Ar*C*), 50.0 (-BH$_2$N(CH$_3$)$_2$BH$_3$), 39.6 (-N-(CH$_3$)$_2$). ^{11}B (128 MHz, $CDCl_3$): δ = 1.8 (br t, -*B*H$_2$N(CH$_3$)$_2$BH$_3$), −12.5 (q, $^1J_{BH}$ = 91 Hz, -BH$_2$N(CH$_3$)$_2$*B*H$_3$). IR (Nujol/cm^{-1}): 2394 (w, νBH), 2354 (w, νBH), 2330 (w, νBH), 2281 (w, νBH). Anal. Calcd. for $C_9H_{21}B_2N_3$: C, 56.04; H, 10.97; N, 21.78. Found: C, 55.98; H, 10.94; N, 21.43. Mp (°C): 131−131.5.

Attempted Thermolysis of DMAP-$H_2BN(CH_3)_2$-BH_3 (7). Ten milligrams of **6** dissolved in 1 mL of THF was sealed in a J. Young NMR tube under an atmosphere of nitrogen and heated to 100 °C for 24 h. ^{11}B NMR analysis of the reaction mixture showed only the presence of starting material with no decomposition.

Synthesis of IPrCH_2-$H_2BN(CH_3)_2$-BH_3 (8). A solution of IPrCH_2 (0.988 g, 2.45 mmol) in 3 mL of hexanes was added to a solution of $N(CH_3)_2B_2H_5$ (prepared from 0.145 g of $Me_2NH·BH_3$ as described previously, 2.47 mmol). The initially clear and colorless solution turned to a pale yellow slurry, and the reaction mixture was stirred at room temperature for 4 h. The mother liquor was decanted, and the precipitate was washed with hexanes (2 × 4 mL). The product was dried under vacuum to give **8** as a pale yellow powder (0.988 g, 85%). Crystals of **8** suitable for X-ray crystallography (yellow prisms) were grown by cooling a saturated hexanes/dichloroethane solution to −35 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (t, 4H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 7.33 (d, 2H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 6.98 (s, 2H, −N-C*H*), 2.58 (septet, 4H, $^3J_{HH}$ = 7.0 Hz, −C*H*(CH$_3$)$_2$), 1.96 (br t, 2H, $^3J_{HH}$ = 6.0 Hz, IPrC*H*$_2$), 1.97 (s, 2H, -B*H*$_2$N(CH$_3$)$_2$BH$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 1.82 (s, 6H, -BH$_2$N(C*H*$_3$)$_2$BH$_3$), 1.39 (d, 12H, $^3J_{HH}$ = 7.0 Hz, −CH(C*H*$_3$)$_2$), 1.16 (d, 12H, $^3J_{HH}$ = 7.0 Hz, −CH(C*H*$_3$)$_2$), 1.05 (s, 3H, -BH$_2$N(CH$_3$)$_2$B*H*$_3$, assignment made by selective ^{1}H{^{11}B} decoupling). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ = 162.3 (Ar*C*), 145.7 (Ar*C*), 131.2 (Ar*C*), 131.0 (Ar*C*), 124.6 (-N-CH), 121.2 (-N-C*C*H$_2$), 51.6 (-N(*C*H$_3$)$_2$), 29.0 (−*C*H(CH$_3$)$_2$), 25.8 (−CH-(*C*H$_3$)$_2$), 22.6 (IPr*C*H$_2$). ^{11}B (128 MHz, $CDCl_3$): −7.7 (br t, $^1J_{BH}$ = 90 Hz, -*B*H$_2$N(CH$_3$)$_2$BH$_3$), −13.1 (br q, $^1J_{BH}$ = 80 Hz, -BH$_2$N-(CH$_3$)$_2$*B*H$_3$). IR (Nujol/cm^{-1}): 2335 (w, νBH), 2295 (w, νBH). Anal. Calcd. for $C_{30}H_{49}B_2N_3$·(0.5 $ClCH_2CH_2Cl$): C, 71.21; H, 9.83; N, 8.04. Found: C, 72.27; H, 10.17; N, 7.90. Mp (°C) 158−159.

Thermolysis of IPrCH_2-$H_2BN(CH_3)_2$-BH_3 (8). A solution of **8** (ca. 10 mg) in 0.5 mL of C_6D_6 was sealed in a J. Young NMR tube under an atmosphere of nitrogen, and heated to 65 °C for 24 h. ^{11}B and ^{1}H NMR spectroscopy showed no signs of decomposition. The sample was then heated at 100 °C for 24 h. The reaction mixture was analyzed by ^{11}B and ^{1}H NMR spectroscopy. The only identifiable soluble product by in situ ^{11}B NMR spectroscopy was the dimer [Me_2NBH_2]$_2$ (triplet at 4.75, $^1J_{BH}$ = 113 Hz), with trace starting material (9% by integration).

Synthesis of IPr-$H_2BN(CH_3)_2$-BH_3 (9). A solution of N-$(CH_3)_2B_2H_5$ was prepared as described above (from 0.82 mmol of $Me_2NH·BH_3$ and 0.81 mmol of H_3B·THF). To this clear and colorless solution (approximately 10 mL), was added 6 mL of a hexanes solution of IPr (308 mg, 0.79 mmol). The golden brown mixture was initially opaque, but became clear after 12 h. The volatiles were removed in vacuo, yielding crude **9** as a light brown powder (321 mg, 88%). The product was further purified by recrystallization from a saturated solution of 1:1 THF/hexanes at −35 °C (96.0 mg, 26%). Crystals obtained by this method (light yellow prisms) were suitable for X-ray crystallography.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.19 (t, 4H, $^3J_{HH}$ = 8.0 Hz, Ar*H*), 7.10 (d, 2H, $^3J_{HH}$ = 7.9 Hz, Ar*H*), 6.54 (s, 2H, −N-C*H*), 2.98 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, −C*H*(CH$_3$)$_2$), 2.20 (s, 2H, -B*H*$_2$N(CH$_3$)$_2$BH$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 2.09 (s, 6H, -BH$_2$N(C*H*$_3$)$_2$BH$_3$), 2.00 (s, 3H, -BH$_2$N(CH$_3$)$_2$B*H*$_3$, assignment made by selective ^{1}H{^{11}B} decoupling), 1.44 (d, 12H, $^3J_{HH}$ = 6.7 Hz, −CH(C*H*$_3$)$_2$), 0.99 (d, 12H, $^3J_{HH}$ = 6.7 Hz, −CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} (125 MHz, C_6D_6): δ = 161.9 (N-C-N), 146.2 (Ar*C*), 135.4 (Ar*C*), 130.6 (Ar*C*), 124.3 (-N-CH), 123.2 (Ar*C*), 54.6 (-BH$_2$N(CH$_3$)$_2$BH$_3$), 29.1 (−*C*H(CH$_3$)$_2$), 26.2 (−CH(*C*H$_3$)$_2$), 22.4 (−CH(*C*H$_3$)$_2$). ^{11}B (128 MHz, C_6D_6): δ = −10.0 (br s, -BH$_2$N(CH$_3$)$_2$BH$_3$), −11.3 (br s, -*B*H$_2$N(CH$_3$)$_2$BH$_3$). IR (Nujol/cm^{-1}): 2438 (w, νBH), 2334 (w, νBH), 2269 (w, νBH), 2237 (w, νBH). Anal. Calcd. for $C_{29}H_{47}B_2N_3$: C, 75.83; H, 10.31; N, 9.15. Found: C, 75.97; H, 10.77; N, 8.28. Mp (°C): 179−180.

Synthesis of *tert*-Butylaminodiborane, (*t*Bu)HNB_2H_5 (10). *t*BuNH_2·BH_3 (174 mg, 2.00 mmol) was taken up as a slurry in 10 mL of hexanes, and H_3B·THF (2.00 mL, 1.0 M solution in THF, 2.00 mmol) was added to the stirring mixture. The resulting cloudy solution was stirred for 3 days at room temperature to yield a colorless solution. The solution volume was concentrated by half under vacuum and filtered. The presence of (*t*Bu)NHB_2H_5 can be determined by diluting a small aliquot with C_6D_6 for ^{11}B NMR analysis. (^{11}B NMR 128 MHz, C_6D_6): δ = −26.4 ppm [t of d, $^1J_{BH}$ = 30 Hz (B−H

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bridging) and 127 Hz (B−H terminal)]. This ^{11}B resonance matched the value found in the literature,[35a] in which **10** was synthesized in a different manner as reported here. In all subsequent reactions, the formation of **10** was assumed to be quantitative for the purpose of calculating reactant quantities and product yields.

Synthesis of DMAP-H_2BN(*t*Bu)H-BH_3 (11). A solution of p-dimethylaminopyridine (0.329 g, 2.70 mmol) was added to a solution of **10** (made from 2.00 mmol *t*BuH_2N·BH_3) in 10 mL of 5:1 hexanes/THF. The resulting mixture clouded to give a white slurry after 8 h. The mother liquor was then decanted, and the white solid was washed with 4 mL portions of 5:1 hexanes/THF. The product was dried under vacuum, giving **11** as a white powder (0.321 g, 73%). Crystals of **11** suitable for X-ray crystallography (colorless prisms) were obtained by cooling a saturated THF/hexanes solution to −35 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 6.53 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 3.10 (s, 6H, -N(CH_3)$_2$), 2.95 (br s, 1H, -B*H*$_2$N*t*BuHBH_3, assignment made by selective ^{1}H{^{11}B} decoupling), 2.64 (br s, 1H, -B*H*$_2$N(*t*Bu)HBH_3, assignment made by selective ^{1}H{^{11}B} decoupling), 1.80 (br s, 1H, -N*H*(*t*Bu)), 1.31 (s, 9H, -NC(C*H*$_3$)$_3$), 1.08 (d, 3H, $^3J_{HH}$ = 3.6 Hz, -BH_2N(tBu)HB*H*$_3$, assignment made by selective ^{1}H{^{11}B} decoupling). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ = 155.6 (Ar*C*), 147.8 (Ar*C*), 106.3 (Ar*C*), 54.6 (-NC(CH$_3$)$_3$), 39.4 (-N(CH_3)$_2$), 28.3 (-NC(CH_3)$_3$). ^{11}B (128 MHz, $CDCl_3$): δ = −3.4 (br t, -*B*H_2NH*t*BuBH_3), −21.7 (q, $^1J_{BH}$ = 91 Hz, -*B*H_2NH*t*BuBH_3). IR (Nujol/cm^{-1}): 3211 (w, νNH), 2388 (w, νBH), 2357 (w, νBH), 2281 (w, νBH), 2255 (w, νBH). Anal. Calcd. for $C_{11}H_{25}B_2N_3$: C, 59.79; H, 11.40; N, 19.02. Found: C, 59.41; H, 11.09; N, 18.63. Mp (°C): 132−133.

Dehydrogenation of 11 with [Rh(COD)Cl]$_2$. To a solution of **11** (56.9 mg, 0.26 mmol) in 5 mL of toluene was added about 1.0 mg of [Rh(COD)Cl]$_2$ (1 mol %). The solution was initially clear yellow, and turned black after 3 h. After 4 h the reaction was analyzed by in situ ^{11}B NMR spectroscopy; the observed products were [HBN*t*Bu]$_3$ (**12**, 5%, d, −25.2 ppm, $^1J_{B-H}$ = 143 Hz), [H_2BNH*t*Bu]$_3$ (**13**, 31%, t, −4.7 ppm, $^1J_{B-H}$ = 95 Hz), poly-*tert*-butylborazylene (**14**, 11%, br s, −30.1),[35] DMAP·BH_3 (31%), and **10** (21%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. Further details are given in Figures S1−S10 and Tables S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: erivard@ualberta.ca.

Notes

The authors declare no competing financial interest.

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