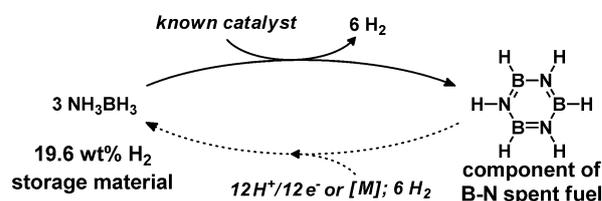


Reduction of Borazines Mediated by Low-Valent Chromium Species**

Tyler J. Carter, Jeff W. Kampf, and Nathaniel K. Szymczak*

The past decade has seen significant effort focused on developing high-capacity H₂ storage materials.^[1] Low-molecular-weight B-N materials, such as ammonia-borane (NH₃BH₃; AB) have received particular attention because of their exceptionally high gravimetric density (19.6 wt %) for chemical H₂ storage.^[2] While the dehydrogenation of B-N materials to afford H₂ has been highly studied,^[3] the low-energy regeneration of spent B-N fuels has received less attention^[4] and remains a coveted goal that needs to be addressed before B-N compounds can be utilized as hydrogen storage materials. However, the direct hydrogenation of spent B-N fuels with H₂ suffers from significant thermodynamic constraints, as revealed by experimental and computational studies,^[5,6] thus limiting rehydrogenation efforts.

Although significant advances were recently reported for the regeneration of spent AB fuels by alternative pathways,^[4c,d] these procedures utilize highly toxic and high-energy reductants (hydrazine and alkyl tin hydrides), which negatively impact the net energy balance for the hydrogen storage system. Accordingly, methods that permit regeneration with minimal energy cost above their associated thermodynamic barrier are of particular interest. Specifically, the hydrogenation of spent AB fuels with a reductant derived from H₂, or discrete H⁺/e⁻ equivalents, is highly desirable. However, experimental studies to address reductive pathways in these systems are lacking, and thus the mechanism for such regeneration strategies is unknown or ill-defined. Therefore, a detailed picture of how reducing equivalents are transferred to B-N-rich molecules is required prior to designing/optimizing catalysts for the regeneration of spent AB fuels. Herein, we report a stepwise metal-mediated borazine reduction strategy that uses hydrides and hydride mimics in conjunction with proton donors to model key reactions that these species could promote on spent AB fuels, using hexamethylborazine as an archetypal substrate.^[7] We demonstrate that stepwise metal-mediated reduction of B=N bonds is achievable, illustrating a key step of spent B-N fuel regeneration (Scheme 1). Because hydride equivalents can be generated using H₂ and/or protonation of reduced metal fragments, these reactions demonstrate the feasibility of a reduction



Scheme 1. Dehydrogenation of B-N materials for hydrogen storage, and the subsequent rehydrogenation strategy under investigation.

strategy that could in principle proceed through low-energy pathways, which remains a challenge for the regeneration of B-N hydrogen storage materials.

The low-valent chromium fragment {Cr(CO)₃} was targeted as a platform capable of binding borazine and subsequently mediating the stepwise reduction of the ring. Prior studies on analogous arene-[Cr(CO)₃] adducts showed that the sequential addition of hydride and proton equivalents afforded cyclohexadiene adducts;^[8] we hypothesized that similar reactivity would be possible when arenes were replaced with borazines. Alkyl-substituted borazines were selected as suitable model substrates for spent AB fuels because the thermodynamic requirements for protio and alkyl B=N bond reduction are similar.^[9] Furthermore, alkyl borazines are less susceptible to B-N cross-linking, and also exhibit low volatility, which allow for greater ease of handling.

The complex $\eta^6\text{-}[(\text{Me}_6\text{B}_3\text{N}_3)\text{Cr}(\text{CO})_3]$ (**1**) was selected for initial studies because it is a stable, synthetically tractable complex that is closely related to $\eta^6\text{-}[(\text{H}_6\text{B}_3\text{N}_3)\text{Cr}(\text{CO})_3]$, which has not been previously isolated as a pure material. Although **1** was previously described,^[10] no structural characterization was reported. Accordingly, following a modification of the previously reported procedure,^[10b] $\eta^6\text{-}[(\text{Me}_6\text{B}_3\text{N}_3)\text{Cr}(\text{CO})_3]$ was prepared in 69% yield and crystallized as orange needles, which were subsequently analyzed by X-ray diffraction. The structure of **1** is similar to that of $\eta^6\text{-}[(\text{Et}_6\text{B}_3\text{N}_3)\text{Cr}(\text{CO})_3]$, the only reported structure of a transition-metal η^6 -borazine complex.^[11] The ring nitrogen atoms are *trans*-disposed to the carbonyl ligands, and the boron atoms are slightly puckered away from the metal center (Figure 1 a; see the Supporting Information for the complete structure). As a result of this distortion from planarity, the N-B-N angles are slightly smaller (ca. 115°) than the B-N-B bond angles (ca. 125°), and the B-N bond distances vary slightly (B1-N1 1.462(5), B2-N2 1.458(5), B3-N3 1.447(5) Å).

Although the synthesis of metal-borazine adducts was reported more than forty years ago, to the best of our knowledge, subsequent reactivity studies of these complexes have not been disclosed, with the exception of ligand-displacement studies.^[12] Accordingly, we sought to explore

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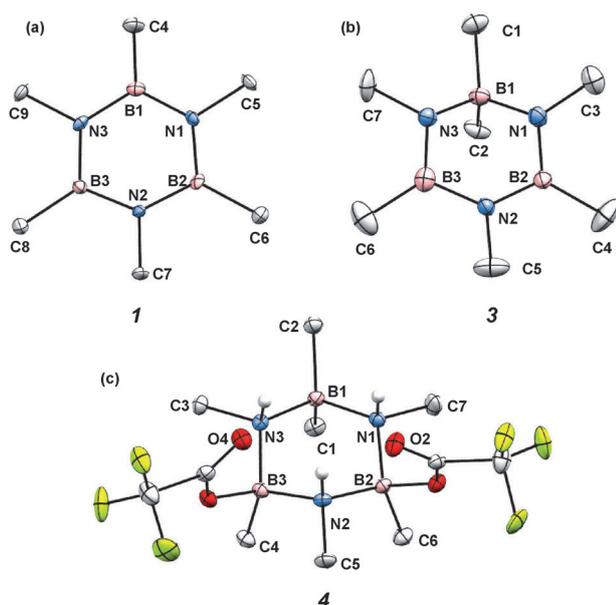


Figure 1. ORTEP of the B_3N_3 units of **1** (a), **3** (b), and **4** (c). $\{Cr(CO)_3\}$, counterions, solvents of crystallization, and hydrogen atoms removed for clarity; ellipsoids are set at 35% probability. Selected B–N bond lengths [Å]: **1**: N1–B2 1.450(5), N1–B1 1.462(5), N2–B1 1.458(5), N2–B3 1.460(5), N3–B3 1.447(5), N3–B1 1.455(6). **4**: N1–B2 1.573(4), N1–B1 1.634(4), N2–C5 1.498(4), N2–B3 1.584(4), N2–B2 1.584(4), N3–B3 1.580(4), N3–B1 1.637(4).

the reactivity of the chromium–borazine adducts to assess whether these fragments can mediate reductive transformations of coordinated borazines. Direct reduction of borazine with hydride reagents has not been reported,^[13,14] and in line with the lack of literature precedent, when $Me_6B_3N_3$ was treated with $LiEt_3BH$ or LiH in ethereal solvents, no reaction occurred (<1% conversion) over the course of 12 days, as monitored by ^{11}B NMR spectroscopy. In contrast, when **1** was treated with 3 equiv $LiEt_3BH$ in diethyl ether at $-35^\circ C$ (Figure 2), a reaction occurred, as assessed by ^{11}B NMR spectroscopic analysis at $-20^\circ C$. 1H NMR spectra obtained at $-20^\circ C$ confirmed that a new compound (**2**) formed, with loss of threefold symmetry as indicated by the inequivalence of the N–CH₃ and B–CH₃ groups. Additionally, a new high-field resonance at $\delta = -2.92$ was observed, consistent with a Cr–H unit.

Complex **2** (Figure 2) crystallizes as a lithium etherate bridged dimer, and contains a dearomatized borazine unit coordinated to a $\{Cr(CO)_3\}$ fragment. The hydride ligand was located from the difference map and was found to exist as a B–H–Cr bridging unit. Notably, the B–N bond distances are asymmetric around the ring, with the B1–N1 and B1–N3 distances significantly elongated compared to **1**, increasing from 1.462(5) and 1.455(6) to 1.532(3) and 1.533(3) Å, respectively, whereas the B3–N2 distance is shorter, decreasing from 1.460(5) to 1.444(4) Å (Figure 2); the former B–N bond distances are consistent with reduction of the B–N bond order. Additionally, the N1–B1–N3 angle is reduced from $114.5(3)^\circ$ to $105.9(2)^\circ$, confirming tetrahedral geometry about B1. These distortions imply that the partial aromatic character of hexamethylborazine^[15] is effectively disrupted, and

represents successful delivery of a hydride unit to a borazine fragment. Attempts to establish further reactivity from **2** were hampered by significant thermal instability.^[16]

In contrast to the thermal instability of products obtained from the reaction of **1** with hydride nucleophiles, similar reactions with anionic alkyl sources afforded thermally robust products that were amenable to subsequent reactivity studies. For example, when solutions containing **1** were treated with one equiv $MeMgBr$, a new, thermally stable, compound (**3**) was generated in quantitative yield. Similar to **2**, 1H NMR spectroscopic analysis confirmed the loss of threefold symmetry, and the introduction of new N–CH₃ resonances at $\delta = 2.85$ and 2.42 , (integrating 2:1), as well as three new B–CH₃ resonances at $\delta = -0.83$, -0.07 , and 0.55 (integrating to 1:1:2). The ^{11}B NMR spectrum revealed two new resonances at $\delta = 3.90$ and 31.0 , concomitant with loss of the resonance at $\delta = 27.2$ for **1**. IR spectroscopy further aided the analysis, with new ν_{CO} bands observable at 1925 , 1763 , and 1694 cm^{-1} (shifted from 1947 and 1845 cm^{-1} in **1**), which are consistent with enhanced nucleophilic character at chromium. In contrast to the hydride addition product (**2**), **3** is readily isolable and stable at room temperatures if stored under inert atmosphere for periods exceeding two months.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a THF solution of **3**. The solid-state structure is geometrically similar to **2** about the borazine unit, however the metal binding mode is distinct. In contrast to the $\kappa^2-N,N'-(\mu-H)$ mode observed in **2**, the borazine unit of **3** engages in an η^5 binding mode with no bridging CH₃ unit and a significant out-of-plane distortion of B1. The B–N bond distances and angles are similar to the isolated hydride addition product (Figure 2, Figure 1b), which confirms that this species is a suitable surrogate for further reactivity studies.

Following isolation of a stable, anionic, dearomatized borazine unit, we sought to complete a single B–N bond reduction cycle by the addition of a suitable proton donor. The reaction of **3** with a single equivalent of HCl or 2-methoxy-6-methylpyridinium chloride yielded mixtures of products, the distribution of which was dependent on the acid strength, reaction temperature, and solvent used.^[17] Note that diene-type products obtained by single H^+ addition are predicted to have limited thermodynamic stability relative to the corresponding borazine or monoene species.^[5,18] Thus, we targeted a quench/trap method to capture unstable and reactive diene intermediates by derivatization. Because HX additions to borazine (X = Cl, Br) were previously reported,^[19] we examined acids that feature coordinating anions as trapping reagents, and initiated our studies with H^+ donors featuring attenuated acidity relative to HCl.

To confirm the efficacy of this approach with non-hydrohalic acids, $Me_6B_3N_3$ was treated with excess $DOAc^F$ ($[D_1]$ trifluoroacetic acid)^[20] in frozen dimethoxyethane solvent, which was then allowed to thaw to room temperature. Consistent with prior reports on triple HX addition to borazine, a new B–N product formed that was identified as the 3:1 $DOAc^F$ –borazine adduct, $OAc^F_3Me_3B_3N_3Me_3D_3$. Confirmation of the empirical formula was provided by elemental analyses, and the solution structure was interro-

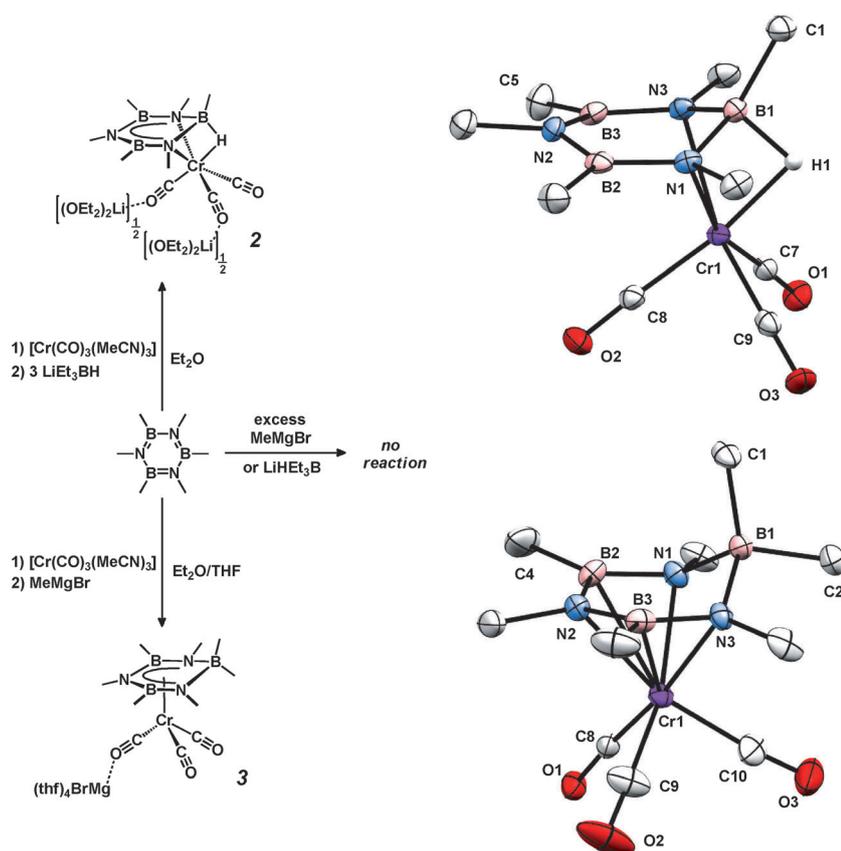


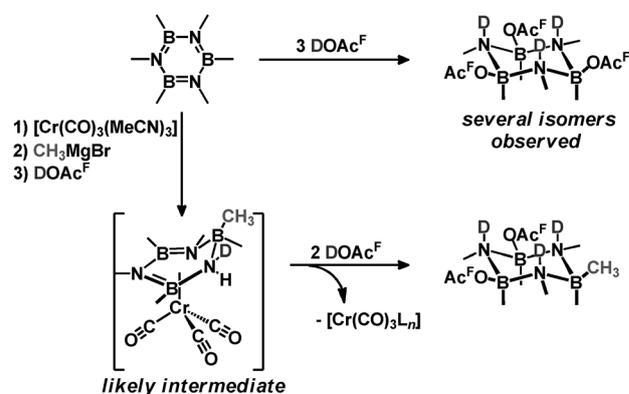
Figure 2. Reactivity of $\text{Me}_6\text{B}_3\text{N}_3$ with hydride and alkyl nucleophiles in the presence (top and bottom path) and absence (middle path) of $[\text{Cr}(\text{CO})_3(\text{MeCN})_3]$, along with solid-state structures of **2** and **3**. Ellipsoids are set at 35% probability. Selected bond lengths [Å] and angles [°]: **2**: N1–B2 1.446(4), N1–B1 1.532(3), N2–B2 1.439(4), N2–B3 1.444(4), N3–B3 1.445(4), N3–B1 1.533(3); N1–B1–N3 105.9(2), N1–B1–C1 120.1(2), N3–B1–C1 119.5(2). **3**: N1–B1 1.594(8), N2–B3 1.477(9), N3–B1 1.617(9); N1–B1–N3 97.5(5), N1–B1–C2 112.3(5), N3–B1–C2 107.3(5), N3–B1–C1 116.0(5), C2–B1–C1 110.7(6).

gated by a suite of multinuclear NMR spectroscopic (^1H , ^{11}B , ^2H , ^{19}F , ^{13}C) experiments. The NMR spectra revealed a mixture of isomers, noted by ^1H and ^{19}F resonances that appeared at similar chemical shifts, all of which exhibited an identical ^{11}B resonance (δ 5.87). Furthermore, the IR spectrum illustrated new ν_{ND} bands at 2407 and 2380 cm^{-1} .^[21] The collection of spectroscopic data provided evidence consistent with the proposed structure. Unfortunately, the presence of multiple isomeric species hindered crystallization, and thus precluded analysis by X-ray crystallography.

Complementary to the addition of DOAc^{F} to $\text{Me}_6\text{B}_3\text{N}_3$ noted above, the addition of excess (5 equiv) DOAc^{F} to **3** afforded $\text{OAc}^{\text{F}}_2\text{Me}_4\text{B}_3\text{N}_3\text{Me}_3\text{D}_3$ (**4**) in 40% yield (Scheme 2). Following crystallization from a saturated pentane solution, a dominant isomer was obtained (75%) in which all three deuterium atoms are axial and the installed OAc^{F} groups are equatorial. The solution structure was deduced by multinuclear NMR spectroscopy, and visualized by three distinct B–CH₃ resonances in the ^1H NMR spectrum appearing at $\delta = -0.10$ (s, 6H), -0.28 (s, 3H), and -0.31 (s, 3H) and two resonances present in the ^{11}B NMR spectrum at $\delta = 0.94$ and 6.31. The spectral data was further supported by the solid-state structure (Figure 1c), featuring a chair conformation in

which all ring atoms exhibit tetrahedral geometry and the installed deuteride atoms and OAc^{F} groups are all axial. The B–N bonds neighboring the methylated boron atom are slightly longer (1.634(4), and 1.637(4) Å) than those neighboring OAc^{F} substituted atoms (between 1.573–1.584 Å) and consistent with the enhanced donor ability of the methyl group compared to OAc^{F} . Close-contact interactions exist between the oxygen atoms of OAc^{F} (O2 and O4) and the ND unit of N2 (ca. 2.9 Å), consistent with a bifurcated hydrogen bond. This intramolecular interaction most likely provides sufficient stabilization to favor the isomer that exhibits several unfavorable $\text{CH}_3\cdots\text{CH}_3$ 1,3-diaxial interactions. Unfortunately, attempts to repeat the quench/trap strategy using **2** did not proceed cleanly and were complicated by the competitive protolytic release of H_2 .

Crystallographic characterization of the series of partial B_3N_3 reduction products provides a snapshot of how B–N materials can be sequentially reduced, lending insight toward the design of B–N spent-fuel-regeneration systems. As noted by Werner and others,^[10d,11,22] coordination of borazine to $[\text{Cr}(\text{CO})_3]$ induces subtle structural changes, most clearly illustrated by the slight out-of-plane distortions of the B–N atoms (deviation from planarity in **1** = 8.2–9.1°).^[23] However, the consistent B–N bond lengths (ca. 1.45 Å) suggest that the partial electron delocalization observed for free borazines is maintained upon coordination. Addition of a hydride or methyl anion disrupts the ring conjugation by the introduction of an sp^3 -hybridized boron atom (N3–B1–N1 angles of 105.9 and 97.5° for **2** and **3**, respectively), and asymmetry is introduced into the B_3N_3 bonding manifold. Bond distances similar to cyclotriborazane ($\text{H}_2\text{B}_3\text{N}_3$; CTB) (1.53 in **2** and 1.59/1.62 Å in **3**) and free



Scheme 2. Reaction of $\text{Me}_6\text{B}_3\text{N}_3$ with DOAc^{F} (top path) and reduction of $\text{Me}_6\text{B}_3\text{N}_3$ mediated by $\{\text{Cr}(\text{CO})_3\}$ using a quench/trap process.

borazines (1.43–1.48 Å for both **2** and **3**) are both present, which suggests that the independent reduction of each B=N bond may be possible. Quenching/trapping the proposed diene product with DOAc^F affords a substituted CTB (**5**) with irregular bond lengths that retains the installed methyl group. The structural changes associated with the reduction of the B-N unit clearly illustrate a successful initial reduction cycle of borazine and the feasibility of a metal-mediated reduction strategy.

In summary, this communication demonstrates the successful reduction of a model for spent AB fuels, Me₆B₃N₃, mediated by a low-valent chromium source. Of particular note, an alkyl borazine was activated by coordination to a {Cr(CO)₃} fragment, which facilitated methyl and hydride transfer to the borazine ring, thus establishing a metal-mediated reduction pathway. Protonation released a proposed diene fragment that was subsequently trapped by two DOAc^F addition reactions across the remaining B=N bonds.

The disclosed reactions represent the first well-defined examples of metal-mediated reduction of an alkyl borazine, which, because of its similarity to the products of AB dehydrogenation, provides support to a potentially new B-N regeneration strategy. These reactions are of interest for further studies that target metal-mediated hydrogenation pathways of B=N fragments because metal hydrides are readily generated by hydrogenation and/or protonation of reduced metal complexes. Accordingly, investigations into reductive reactivity with alternative reductants and proton donors are underway, as well as efforts that employ a similar approach to reduce H₆B₃N₃ and polyborazylene.

Experimental Section

General experimental details and characterization data for all of the reported compounds are included in the Supporting Information. CCDC 895042, 895043, 895044, and 895045 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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