ORGANOMETALLICS

Manganese-Mediated Hydride Delivery to a Borazine by Stepwise Reduction and Protonation

Tyler J. Carter, Justin Y. Wang, and Nathaniel K. Szymczak*

Department of Chemistry, University of Michigan, 930 North University, Ann Arbor, Michigan 48109, United States

Supporting Information

ABSTRACT: A Mn(CO)₃⁺ fragment coordinates a borazine unit as a π complex, $[(\eta^6-Me_6B_3N_3)Mn(CO)_3]BAr'$. Coordination facilitates the delivery of alkyl and hydride nucleophiles, the latter of which can also be installed by successive reduction/protonation reactions. This system represents an alternative strategy to consider for the reduction of hydrogen depleted B–N molecules, which are relevant to the regeneration of spent B–N hydrogen storage systems.

he need for reversible, high-capacity, hydrogen storage systems remains a significant hurdle to the widespread implementation of hydrogen fuel cells for alternative fuel vehicles.¹ Materials based on boron-nitrogen (B-N) adducts, which include ammonia-borane $(NH_3 \cdot BH_3, AB, 19.6 \text{ wt } \% H_2)$ and its derivatives, such as 3-methyl-1,2-BN-cyclopentane, are promising candidates due to their high gravimetric hydrogen capacity and favorable thermodynamics/kinetics of H₂ release.² However, few examples of the regeneration of spent B-N fuels exist,^{3,4} and furthermore, strategies that can be adapted to lowenergy regeneration pathways are not well-developed. One avenue that has received little attention is the delivery of hydride equivalents by stepwise reduction/protonation of B-N spent fuels. This strategy parallels (electro)catalytic reduction efforts of other small molecules,⁵ and when the applied energy approaches the thermodynamically limiting value for the reduction, energy input can be minimized. Metal coordination may enhance the reactivity of borazine and other B-N species, similar to prior studies on Lewis acidity changes to boron groups in the vicinity of transition metals.⁶ Because metalmediated B=N bond reductions have not been previously explored, we are working to develop an understanding of how transition metals may be used to promote the reductive reactivity of B-N heterocycles in order to uncover strategies that can be adapted to low-energy reduction sequences.

Previous work in our laboratory demonstrated that hexamethylborazine ($Me_6B_3N_3$), a convenient model for spent B–N fuels, due to its low volatility and inability to participate in B–N cross-linking, was activated for subsequent reduction by coordination to a $Cr(CO)_3$ center.⁴ Reduction was achieved by addition of a methyl nucleophile to afford a reduced species that was trapped with 3 equiv of CF₃COOH (HOAc^F), which demonstrated that metal-mediated pathways may indeed be a viable strategy to achieve B==N bond hydrogenation. However, hydride addition afforded a complex with low thermal stability (decomposition above -20 °C), which was too unstable for extensive characterization/reactivity studies. Boron hydrides are crucial intermediates in AB



regeneration strategies and are often introduced using highenergy hydride sources. Of particular note, the first hydride addition to borazines is predicted to be the thermodynamically most demanding step of the reduction sequence.⁷

As such, the generation of boron hydrides without using chemical hydride reagents (Scheme 1) is an attractive

Scheme 1. Metal-Mediated Routes for Hydride Delivery to Borazine



application of metal-mediated reduction pathways. Thus, we targeted a system capable of promoting hydride addition from exogenous sources of electrons and protons as the key proof of principle reaction to establish the viability of a metal-mediated reduction pathway for heterocyclic B==N bonds, which has relevance to spent hydrogen storage materials.

The reduction potentials for $(\eta^6-Me_6B_3N_3)Cr(CO)_3$ were highly negative (<-2.5 V; vs Fc^{0/+}) and irreversible, suggesting that the corresponding reduced adducts were not tractable.⁴ To attain a less cathodic reduction potential for a metal–borazine unit whose protonation would afford an active hydride, we targeted the cationic, and isoelectronic, manganese(I) tricarbonyl fragment. Mn(I)–arene adducts are reduced at ca. –1.5 V (vs Fc^{0/+}),⁸ and we hypothesized that a similar shift would be observed with analogous borazine adducts, allowing reductive reactivity to be effected at less cathodic redox potentials.

In contrast to the multitude of η^6 metal-arene adducts that are structurally characterized for most (26) transition metals,⁹

Received: February 13, 2014 Published: March 24, 2014

the only structurally characterized transition-metal π complexes of borazine share the formula $[(\eta^6-R_6B_3N_3)Cr(CO)_3]$.¹⁰ This likely stems from reaction incompatibilities, as the known synthetic methods to promote η^6 coordination are not readily translated from established metal-arene syntheses. For example, the direct syntheses of Mn-arene complexes typically proceed in neat arene at reflux with Mn(CO)₅Br in the presence of Ag(I) or $AlCl_3$ or, alternatively, using acidic conditions from $Mn_2(CO)_{10}$ in the presence of $HOAc^F$ and $(CF_3CO)_2O$.¹¹ Borazines react with most acids, including HOAc^F and AlCl₃,^{4,12} and in our hands, reactions of Mn(CO)_sBr with assorted Ag(I) salts in the presence of Me₆B₃N₃ did not afford the desired product. The poor reactivity is likely due to borazine's weaker binding affinity in comparison to that of arenes, which decreases the associated driving force for the necessary ligand exchange reaction,¹³ due to competitive binding with many solvents and counteranions. These limitations were overcome by careful selection of reaction conditions; when Me₆B₃N₃ and Mn(CO)₅Br were heated to 90 °C in di-n-butyl ether in the presence of the halide abstracting agent TlBAr', (BAr' = tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate) featuring a weakly coordinating anion, the target compound $[(\eta^6-Me_6B_3N_3)Mn(CO)_3]BAr'$ (1) was obtained in 65% yield.

Coordination of $Me_6B_3N_3$ was confirmed by ¹¹B NMR spectroscopy, which revealed a new resonance at 32.0 ppm, shifted 6 ppm upfield from the signal for free $Me_6B_3N_3$. Further structural data were obtained from the IR spectrum, which displayed new ν_{CO} bands at 2072 and 1999 cm⁻¹, consistent with the predicted $C_{3\nu}$ symmetry. Single crystals were obtained by cooling a solution of 1 in CH₂Cl₂, Et₂O, and pentane to -35°C and analyzed by X-ray diffraction. The solid-state structure (Figure 1b) confirmed the η^6 coordination of $Me_6B_3N_3$ to the $Mn(CO)_3^+$ fragment.



Figure 1. (a) Synthesis of **1**. (b) X-ray crystal structure of **1**. Thermal ellipsoids are shown at 35% probability. Hydrogen atoms and the BAr' counteranion are omitted for clarity. (c) Cyclic voltammogram of **1** in 0.1 M $["Bu₄N]PF_6$ in CH₂Cl₂ (scan rate 100 mV s⁻¹).

Given that the only structurally characterized π complexes of borazine contain Cr(0), the salient structural features of 1 were examined and compared to those of (η^6 -Me₆B₃N₃)Cr(CO)₃. Both complexes display similar structural metrics. The slight deviation from planarity observed in (η^6 -Me₆B₃N₃)Cr(CO)₃ (9.11°, measured as the angle between the B1, N1, N3 and N1, N2, N3 planes) is more pronounced in the structure of 1 (12.08°). The average B–N bond distance of 1.459 Å for 1 and 1.455 Å for (η^6 -Me₆B₃N₃)Cr(CO)₃ are consistent with little change in B=N bond order upon coordination. One of the few differences is the shorter M–N1 bond distance (2.142(3) vs 2.217(3) Å) observed for 1 in comparison to $(\eta^6-Me_6B_3N_3)-Cr(CO)_{3,4}^{4}$ which may be attributed to the smaller ionic radius of Mn(I) versus Cr(0).

Although they are structurally similar, borazine adducts of $Cr(CO)_3$ and $Mn(CO)_3^+$ were found to exhibit large differences in reactivity. For instance, competitive ligand displacement studies were conducted in which $(\eta^6 - Me_6B_3N_3)$ - $Cr(CO)_3$ and 1 were titrated with THF and the rate of borazine release was measured. The resulting kinetic profiles (Figure 1 in the Supporting Information) revealed that the borazine unit of 1 displayed a higher substitutional lability (ca. $3\times$) than the chromium analogue. These results can be rationalized by considering the bonding interactions of coordinated borazines, wherein cooperative binding via σ donation from the N atoms and π acceptance by the B atoms is proposed.¹⁴ For the isostructural $Me_6B_3N_3$ complexes, Mn(I) is less electron rich than Cr(0), as quantified by observed A₁ CO bands (2072 and 1947 cm⁻¹ for Mn and Cr, respectively). This likely increases borazine's substitutional lability and is consistent with the observed ligand displacement reactivity (vide supra).

In addition to ligand substitution reactivity, we hypothesized that the electrophilic $Mn(CO)_3^+$ fragment would also facilitate nucleophilic attack at the borazine unit. While uncoordinated Me₆B₃N₃ did not react with excess CH₃MgBr, 1 and 1 equiv of CH₃MgBr were cleanly converted to a new product when a frozen Et₂O solution containing both reactants was warmed to room temperature. The product was isolated in 59% yield and identified as the dearomatized borazine adduct $(\eta^5 - Me_7B_3N_3)$ - $Mn(CO)_3$ (2), by heteronuclear NMR and IR spectroscopy. The ¹¹B NMR spectrum contained resonances at 34.2 and 9.3 ppm, the latter of which appears in the region characteristic of B–N derived tetrahedral boron atoms, which typically appear between –10 and +10 ppm.¹⁵ ¹H NMR spectroscopy further bolstered the assignment by the identification of three unique B-CH₃ groups, observed in a 2:1:1 ratio at 0.66, 0.05, and -0.69 ppm, as well as two N-CH₃ resonances observed in a 2:1 ratio at 2.90 and 2.47 ppm. Finally, the IR spectrum displayed three C=O stretches (2023, 1922, and 1901 cm^{-1}), shifted to lower wavenumbers and consistent with the predicted C_{s} symmetry.

Single crystals suitable for X-ray diffraction were isolated from a concentrated pentane solution at -35 °C, and the solidstate structure of **2** (Figure 2a) was confirmed as (η^{5} -Me₇B₃N₃)Mn(CO)₃. The borazine ring is severely distorted by the introduction of a tetrahedral boron atom (B1), as evidenced by the elongation of the B1–N1 bond (1.599(6) Å) as well as the out-of-plane distortion of B1 (44°) relative to the ring nitrogen atoms. These structural distortions are in good agreement with those previously observed for $[(\eta^{5}-Me_{7}B_{3}N_{3})-Cr(CO)_{3}]MgBr$ and collectively illustrate a general approach for the isolation of dearomatized borazine fragments.⁴

In addition to attack by carbon nucleophiles, reactivity with hydride donors was pursued. Key reactivity differences between analogous arene and borazine $Mn(CO)_3$ compounds were noted. For instance, in contrast to reports of $Mn(arene)-(CO)_3^+$, where two hydride additions to the arene complete C–C bond reduction, ¹⁶ analogous double hydride addition was not observed for 1. Instead, the reaction of 1 with 1–2 equiv of LiAlH₄, in Et₂O at –35 °C, afforded the monohydride $Mn(\mu-H)(Me_6B_3N_3)(CO)_3$ (3) with a κ^2 -N,N'-(μ -H) binding mode, as visualized by solution cell IR spectroscopy (Figure 17 in the Supporting Information). Removal of solvent followed by extraction with pentane allowed for the isolation of 3, and the



Figure 2. Direct synthesis and X-ray crystal structures of complexes (a) 2 and (b) 3. Thermal ellipsoids are shown at the 35% probability level. Hydrogen atoms, with the exception of the bridging hydride (H1), were omitted for clarity.

structural assignment was confirmed by ¹¹B NMR spectroscopy which featured two resonances in a 2:1 ratio at 40.6 and 5.9 ppm, similar to the shifts of **2**.¹⁷ A hydride resonance in the ¹H spectrum was also noted at -3.7 ppm, consistent with a bridging hydride unit.¹⁸ This species exhibited solvent-dependent behavior, and analysis of Et₂O solutions containing **3** showed ¹¹B NMR resonances at 31.1 and 5.9 ppm (Figure 3).



Figure 3. (top) Synthetic scheme for the generation of **3** from stepwise reduction and protonation. (bottom) Overlay of ¹¹B NMR spectra (-30 °C) of **3** generated (a) using LiAlH₄ and (b) using Na/ $C_{10}H_8$ followed by HOAc^F. Legend: (*a) free Me₆B₃N₃; (*b) proposed borazine ring coupling product;²¹ (*c) Na or LiBAr' used as internal standard.

The IR spectrum of 3 revealed three C=O stretches (2023, 1935, and 1906 cm⁻¹) at energies similar to those observed for 2. Further structural confirmation was made possible from single crystals of 3

The X-ray structure (Figure 2b) reveals a hydride, located from the difference map, that bridges the borazine and $Mn(CO)_3$ fragments. As observed for 2, the B1–N1 bond is significantly elongated (1.508(4) Å) and B1 is distorted out of the N1–N2–N3 plane (32°). Notably, 3 also exhibits an elongation of the Mn–C bond trans to H1 (0.016 Å), consistent with the large trans influence of the hydride ligand. Although the structural metrics indicate similarities between Mn and Cr structures, their solution behaviors were distinct. While the Cr hydride ($[Cr(\mu-H)(Me_6B_3N_3)(CO)_3]Li$) decomposed above $-20 \ ^\circ C$, ⁴ **3** was moderately stable at room temperature both in the solid state and as a solution in pentane or cyclohexane, which facilitated more complete spectroscopic characterization than was possible with Cr.

The marked stability of 3, as noted above, suggested that hydride adducts of 1 might also be generated by alternative means. For instance, in addition to direct addition of exogenous hydride donors, metal hydrides can also be generated by protonation of a low-valent metal center. We therefore sought to explore whether such reactivity could be mediated by 1. As an initial step, the reductive electrochemistry of 1 was interrogated to probe the stability of reduced adducts, as well as the potential at which reduction occurred. A cyclic voltammetry experiment in 0.1 M ["Bu₄N]PF₆ in CH₂Cl₂ (Figure 1c and Figures 21 and 22 in the Supporting Information) revealed a quasi-reversible reductive event at -1.38 V in addition to an irreversible reduction at -1.88 V (vs Fc^{0}/Fc^{+}). The first reduction event was minimally solvent dependent; voltammetry experiments in Et₂O (Figure 23 in the Supporting Information) displayed a redox event at -1.34 V, with the second event at -2.00 V (vs Fc^{0/+}; 0.05 M $[^{n}Bu_{4}N]BAr'$ as electrolyte). However, the couple at -1.34 V was irreversible in Et₂O at room temperature and an unrelated return wave at -0.92 V (vs Fc^{0/+}) was observed.

The reversible reduction events noted in the voltammetry studies suggested that reduction of 1 should be chemically accessible. We hypothesized that, if sufficiently long-lived, the reduced adduct could be intercepted by a proton donor to furnish a metal hydride capable of transfer to the borazine unit. Addition of 2 equiv of $Na/C_{10}H_8$ to a thawing solution of 1 in Et₂O afforded a new complex, 4. EPR spectroscopy conducted on frozen solutions of 4 immediately after preparation showed no signals which could be attributed to a d^7 paramagnetic species.¹⁹ 4 was characterized using in situ IR spectroscopy at -30 °C (Figure 18 in the Supporting Information), where a single new set of C=O stretches was visualized immediately after the addition of $Na/C_{10}H_8$, at significantly lower energy $(2006 \text{ and } 1901 \text{ cm}^{-1})$ than for the starting material. The combined spectroscopic characterization suggests that reduction proceeds cleanly through a 2e⁻ pathway. Unfortunately, the reduced adduct was thermally unstable at temperatures greater than -30 °C, which precluded further detailed analyses.

Although the reduction of 1 at low temperature afforded a species with limited stability, the addition of acid immediately following reduction provided a means to effectively capture the reduced adduct. For instance, when an ethereal solution of 4 was treated with 1 equiv of $HOAc^{F}$, conversion to 3 in 75% yield was observed.²⁰ The product was confirmed by spectroscopic comparison with Et₂O solutions of the independently prepared sample (vide supra). The ¹¹B NMR spectrum exhibited new resonances at 32.2 and 7.1 ppm (Figure 3), and solution-cell IR spectroscopy (Figure 17 in the Supporting Information) revealed nearly identical C=O stretching bands for 3 prepared by both pathways.²² To the best of our knowledge, the formation/delivery of a boron hydride derived from sequential reduction and protonation is an unprecedented, yet noteworthy, metal-mediated reaction to consider for spent B-N fuel regeneration.

In this communication, we have demonstrated a key transformation relevant to borazine reduction, which is an archetypal B-N spent fuel. Although isoelectronic with benzene, the reactivity of metal-coordinated borazines is distinct, and while some parallels exist between redox transformations at both fragments, reactivity differences imposed by the more polar B=N bonds have been largely unexplored. Using carefully selected reaction conditions, the $Mn(CO)_{3}^{+}$ fragment was found to coordinate and activate a borazine for nucleophilic addition reactions of H⁻ and Me⁻. In addition to direct reaction with a hydride source, stepwise reduction/protonation reactions were also found to provide a hydride equivalent to the borazine unit, which is the thermodynamically most demanding step of borazine reduction.⁷ The demonstration of this reaction solely from electrons and protons clearly illustrates how metal coordination may be used to promote reduction reactions of B=N units, which is an important step toward the development of systems that can regenerate useful hydrogen storage materials via low-energy pathways. We are currently investigating multistep reduction and protonation reactions, as well as coulometry experiments to adapt this method for the reduction of multiple B=N bonds.

ASSOCIATED CONTENT

S Supporting Information

Experimental details and crystallographic (CCDC 975657–975659) data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*N.K.S.: e-mail, nszym@umich.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Chelsea D. Cates for initial experimental work, Jeff W. Kampf for the collection of X-ray data, and Prof. Anne McNeil for use of the in situ IR equipment. This work was supported by the University of Michigan Department of Chemistry, a Dow Corning Assistant Professorship, and by NSF Grant CHE-0840456 for X-ray instrumentation.

REFERENCES

(1) http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/ hstt_roadmap_june2013.pdf.

(2) (a) Stephens, F. H.; Pons, V.; Baker, R. T. Dalton Trans. 2007, 2613. (b) Smythe, N. C.; Gordon, J. C. Eur. J. Inorg. Chem. 2010, 2010, 509. (c) Staubitz, A.; Robertson, A. P. M.; Manners, I. Chem. Rev. 2010, 110, 4079. (d) Huang, Z.; Autrey, T. Energy Environ. Sci. 2012, 5, 9257. (e) Luo, W.; Campbell, P. G.; Zakharov, L. N.; Liu, S. Y. J. Am. Chem. Soc. 2011, 133, 19326.

(3) (a) Davis, B. L.; Rekken, B. D.; Michalczyk, R.; Garner, E. B.; Dixon, D. A.; Kalviri, H.; Baker, R. T.; Thorn, D. L. Chem. Commun.
2013, 49, 9095. (b) Davis, B. L.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Matus, M. H.; Scott, B.; Stephens, F. H. Angew. Chem., Int. Ed.
2009, 48, 6812. (c) Sutton, A. D.; Burrell, A. K.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Nakagawa, T.; Ott, K. C.; Robinson, J. P.; Vasiliu, M. Science 2011, 331, 1426. (d) Summerscales, O. T.; Gordon, J. C. Dalton Trans. 2013, 42, 10075. (e) Ramachandran, P. V.; Gagare, P. D. Inorg. Chem. 2007, 46, 7810. (f) Campbell, P. G.; Zakharov, L. N.; Grant, D. J.; Dixon, D. A.; Liu, S. Y. J. Am. Chem. Soc. 2010, 132, 3289. (g) Reller, C.; Mertens, F. O. R. L. Angew. Chem., Int. Ed. 2012, 51, 11731. (4) Carter, T. J.; Kampf, J. W.; Szymczak, N. K. Angew. Chem., Int. Ed. 2012, 51, 13168.

(5) Savéant, J.-M. Chem. Rev. 2008, 108, 2348.

(6) (a) Chen, J.; Lalancette, R. A.; Jäkle, F. *Chem. Commun.* **2013**, *49*, 4893. (b) Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, J. *Can. J. Chem.* **2001**, *79*, 857. (c) Amendola, M. C.; Stockman, K. E.; Hoic, D. A.; Davis, W. M.; Fu, G. C. *Angew. Chem., Int. Ed.* **1997**, *36*, 267.

(7) (a) Lisovenko, A. S.; Timoshkin, A. Y. Inorg. Chem. 2010, 49, 10357. (b) Nutt, R. W.; McKee, M. L. Inorg. Chem. 2007, 46, 7633.
(8) (a) Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. J. Am. Chem. Soc. 1966, 88, 471. (b) Dai, W.; Kim, S. B.; Pike, R. D.; Cahill, C. L.; Sweigart, D. A. Organometallics 2010, 29, 5173. (c) Neto, C. C.; Baer, C. D.; Chung, Y. K.; Sweigart, D. A. J. Chem. Soc. Chem. Commun. 1993, 816.

(9) Cambridge Structural Database, version 5.34, November 2013; Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

(10) (a) Prinz, R.; Werner, H. Angew. Chem., Int. Ed. 1967, 6, 91.
(b) Werner, H.; Prinz, R.; Deckelmann, E. Chem. Ber. 1969, 102, 95.
(c) Lagowski, J. J. Coord. Chem. Rev. 1977, 22, 185.

(11) (a) Jackson, J. D.; Villa, S. J.; Bacon, D. S.; Pike, R. D.; Carpenter, G. B. Organometallics **1994**, 13, 3972. (b) Kündig, E. P. Transition metal arene π -complexes in organic synthesis and catalysis; Springer-Verlag: Berlin, 2004.

(12) (a) Anton, K.; Fußstetter, H.; Nöth, H. Chem. Ber. **1981**, 114, 2723. (b) Gemünd, B.; Günther, B.; Nöth, H. ARKIVOC **2008**, 136.

(13) (a) Deckelmann, E.; Werner, H. *Helv. Chim. Acta* 1969, *52*, 892.
(b) Scotti, M.; Werner, H.; Brown, D. L. S.; Cavell, S.; Connor, J. A.; Skinner, H. A. *Inorg. Chim. Acta* 1977, *25*, 261.

(14) (a) Bridgeman, A. J. Polyhedron **1998**, 17, 2279. (b) Kang, H. S. J. Phys. Chem. A **2005**, 109, 1458.

(15) (a) Narula, C. K.; Janik, J. F.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. *Inorg. Chem.* **1986**, *25*, 3346. (b) Lingam, H. K.; Wang, C.; Gallucci, J. C.; Chen, X.; Shore, S. G. *Inorg. Chem.* **2012**, *51*, 13430.
(c) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. J. Am. Chem. Soc. **2003**, *125*, 9424.

(16) Brookhart, M.; Lamanna, W.; Pinhas, A. R. Organometallics 1983, 2, 638.

(17) Partial decomposition of **3**, to release $Me_6B_3N_3$, occurs during the workup procedure. Due to the nearly identical solubilities that precluded complete separation, **3** was isolated with 25% free $Me_6B_3N_3$. (18) (a) Shimoi, M.; Nagai, S.; Ichikawa, M.; Kawano, Y.; Katoh, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* **1999**, *121*, 11704. (b) Kawano, Y.; Yamaguchi, K.; Miyake, S.; Kakizawa, T.; Shimoi, M. Chem. Eur. J. **2007**, *13*, 6920.

(19) <1% unreacted Na/ $C_{10}H_8$ was observed.

(20) See the Supporting Information for details.

(21) Arene ring coupling is a common side reaction when Mn-arene complexes are chemically reduced. See: Thompson, R. L.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8961.

(22) The spectroscopic characteristics of 3 are dependent on solvent and the presence of residual BAr' salts. When the reaction was monitored in situ in Et₂O, without a workup procedure, negligible differences in the ¹¹B NMR spectrum and $\nu_{\rm CO}$ bands were observed between independently generated 3 and the product from reduction/ protonation.