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Dehydrocoupling Reactions of Secondary and Primary Amine–Borane Adducts Catalyzed by Half-sandwich Carbonyl Complexes, [CpMn(CO)$_3$], [(η^6-C$_6$H$_6$)Cr(CO)$_3$], and [CpV(CO)$_4$]

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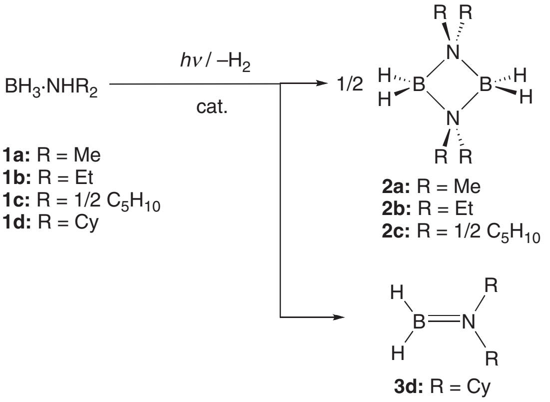
Dehydrocoupling reactions of amine–borane adducts catalyzed by half-sandwich carbonyl complexes are described. Secondary amine–borane adducts released H_2 with catalytic action of [CpMn(CO)$_3$] (Cp: η^5-C$_5$H$_5$), [(η^6-C$_6$H$_6$)Cr(CO)$_3$], and [CpV(CO)$_4$] under photoirradiation to produce dimeric or monomeric aminoboranes. These results were parallel to the [M(CO)$_6$]-catalyzed system (M = Cr, Mo, and W); however, the reactions were considerably slower. Dehydrocoupling of $BH_3{\cdot}NH_2Me$ afforded an aminoborane polymer, [BH$_2$NHMe]$_n$.

Intense attention is currently focused on transition-metal-catalyzed dehydrocoupling reactions of amine–borane adducts.[1] This reaction provides aminoboranes and borazines, which are potential precursors of BN ceramics. Moreover, this type of reaction has been developed toward utilization of amine–boranes (in particular ammonia–borane) as chemical hydrogen storage materials because of the large hydrogen content and its effective release.[2] To date, it has been reported that borane dehydrocoupling can be catalyzed by Sc, Y,[3] Ti,[4] Zr,[4b] Re,[5] Ru,[6,7] Rh,[7–9] Ir,[10,11] and Ni[12] complexes.[13]

Recently, we reported dehydrocoupling of secondary and primary amine–borane adducts catalyzed by group 6 metal carbonyls, [M(CO)$_6$] (M = Cr, Mo, and W).[14] Non-bulky secondary amine adducts, $BH_3{\cdot}NHR_2$ (R = Me, Et, 1/2 C$_4$H$_8$, and 1/2 C$_5$H$_{10}$), undergo the catalytic dehydrogenation under photoirradiation to afford dimeric aminoboranes [BH$_2$NR$_2$]$_2$, while the reaction of bulky derivatives (R = *i*-Pr and Cy; Cy: *cyclo*-C$_6$H$_{11}$) provides monomeric $BH_2{=}NR_2$. Furthermore, primary amine adducts, $BH_3{\cdot}NH_2R$ (R = Me and Et), release two equivalents of H_2 through the action of the metal carbonyl catalyst to give borazine derivatives [BHNR]$_3$.

DFT calculations predicted a crucial role of an intermediate involving a three-center two-electron interaction between the metal atom and BH_3 moiety in the catalytic cycle.[14] This suggests that metal fragments capable of interacting with a BH_3 moiety can catalyze borane dehydrocoupling reactions. Based on such an idea, we examined dehydrogenation of secondary and primary amine–boranes using half-sandwich carbonyls [CpMn(CO)$_3$] and [(η^6-C$_6$H$_6$)Cr(CO)$_3$], which are known to react with tertiary amine–boranes under photoirradiation to yield σ complexes, [CpMn(CO)$_2$(η^1-BH$_3{\cdot}$L)] and [(η^6-C$_6$H$_6$)Cr(CO)$_3$(η^1-BH$_3{\cdot}$L)] (L = NMe$_3$ and N(CH$_2$CH$_2$)$_3$CH).[15,16] We also employed a structurally relevant vanadium complex, [CpV(CO)$_4$] as a precatalyst. In fact, these trials resulted in occurrence of catalytic borane dehydrocoupling reactions. In this paper, we describe the results of this study. We also discuss the reaction mechanism on the basis of DFT calculations.



Scheme 1. Half-sandwich carbonyl-catalyzed dehydrocoupling reactions of secondary amine–boranes. cat. = [CpMn(CO)$_3$], [(η^6-C$_6$H$_6$)-Cr(CO)$_3$], and [CpV(CO)$_4$].

A benzene-d_6 solution of $BH_3{\cdot}NHMe_2$ (**1a**) containing a catalytic amount of [CpMn(CO)$_3$] (5 mol %) was prepared and loaded in a flame-sealed Pyrex NMR tube. Near-UV irradiation to this solution resulted in gentle gas evolution to produce a red-orange solution. After 1 h of photolysis, the ^{1}H and ^{11}B NMR spectra of the resulting mixture indicated 32% conversion of **1a**. The major product was dimethylaminoborane dimer, [BH$_2$NMe$_2$]$_2$ (**2a**, δ^{11}B = 5.0),[17] and a small amount of the monomer $BH_2{=}NMe_2$ (**3a**, δ^{11}B = 37.7) was also detected.[17c] Additional standing for 24 h at room temperature was required for the completion of the reaction. The final yield of **2a** reached 93%, while **3a** almost disappeared at the end of the reaction (Scheme 1 and Table 1, Entries 1 and 2). Thus, the manganese complex has a catalytic ability on the dehydrocoupling of **1a**; however, the reaction was considerably slower than in the [M(CO)$_6$]-catalyzed system (M = Cr, Mo, and W). The hexacarbonyl catalysts complete the hydrogen elimination of **1a** within 1 h of photolysis or 24 h of standing after 5 min irradiation.[14]

After the reaction, minor products (<1%), BH(NMe$_2$)$_2$ and (μ-Me$_2$N)B$_2$H$_5$ were detected along with **2a** by ^{11}B NMR spectroscopy (28.5 and −18.0 ppm, respectively). These products were identified by comparison of their ^{11}B NMR chemical shift values with the literature.[18,19] In addition, a weak resonance appeared at −22.2 ppm in the ^{11}B NMR spectrum after the reaction. We tentatively assigned this signal to a borane σ complex, [CpMn(CO)$_2$(η^1-BH$_3{\cdot}$NHMe$_2$)] (**4**), because it appeared at 9 ppm higher field than free **1a**. Such a high-field-shifted ^{11}B NMR signal has been observed for a structurally characterized manganese–borane complex, [CpMn(CO)$_2$(η^1-BH$_3{\cdot}$NMe$_3$)],[15] and other amine–borane and phosphine–borane complexes.[20]

A benzene chromium complex [(η^6-C$_6$H$_6$)Cr(CO)$_3$] also catalyzed the dehydrogenation of **1a** to afford **2a**. After 1 h of photolysis, the conversion of **1a** was 73%. The reaction was thus rather faster than the Mn-catalyzed case, but still slower than the

Table 1. Manganese-, chromium-, and vanadium-catalyzed dehydrocoupling reactions of scondary amine–borane adducts

Entry	Borane	Catalyst (5 mol %)	Condition[a]	Conversion /%	Product distribution[b]/%	
					$[BH_2NR_2]_2$ (**2**)	$BH_2{=}NR_2$ (**3**)
1	$BH_3{\cdot}NHMe_2$ (**1a**)	$[CpMn(CO)_3]$	$h\nu$ 1 h	32	87	4
2			$h\nu$ 1 h + RT 1 d	100	93	trace
3		$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$	$h\nu$ 1 h	73	75	1
4			$h\nu$ 1 h + RT 1 d	94	96	trace
5			FL[c] 1 d	96	92	trace
6			RT 3 h (dark)	0	—	—
7		$[CpV(CO)_4]$	$h\nu$ 1 h	73	73	3
8			$h\nu$ 1 h + RT 1 d	79	92	trace
9			FL[c] 3 h	81	90	trace
10			FL[c] 1 d	87	96	trace
11			RT 3 h (dark)	0	—	—
12	$BH_3{\cdot}NHEt_2$ (**1b**)	$[CpMn(CO)_3]$	$h\nu$ 1 h + RT 2 d	100	68	6
13		$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$	$h\nu$ 5 m + RT 2 d	95	69	5
14		$[CpV(CO)_4]$	FL[c] 3 h	91	58	5
15	$BH_3{\cdot}NH(CH_2)_5$ (**1c**)	$[CpMn(CO)_3]$	$h\nu$ 1 h + RT 2 d	79	93	trace
16		$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$	$h\nu$ 1 h	92	35	5
17		$[CpV(CO)_4]$	FL[c] 3 h	75	69	trace
18	$BH_3{\cdot}NHCy_2$ (**1d**)	$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$	$h\nu$ 1 h + RT 1 d	5	—	63

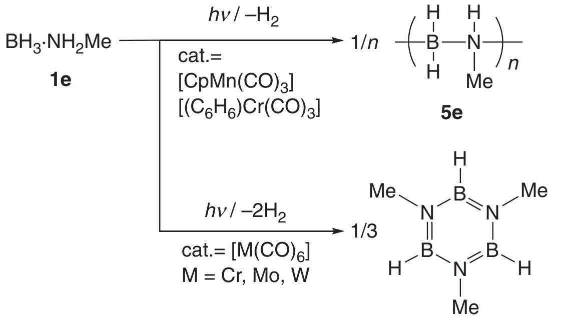
[a]Photolyses were carried out at 8 °C using a 450 W medium pressure Hg lamp. [b]The yields of the products were judged by NMR. [c]Under fluorescent light.

$[M(CO)_6]$-catalyzed reactions. After the irradiation, the solution was allowed to stand for 24 h at room temperature in the dark to complete the dehydrogenation. Interestingly, this Cr-catalyzed reaction proceeds even under fluorescent light. As shown in Table 1 (Entry 5), product **2a** was obtained almost quantitatively by fluorescent light-irradiation for 24 h. Note that no reaction occurred if the sample was kept in the dark throughout, indicating that the photoirradiation was required to generate the active catalyst.

Furthermore, the dehydrocoupling of **1a** was also catalyzed by $[CpV(CO)_4]$. Near-UV photolysis of a benzene-d_6 solution of **1a** and 5 mol % of the vanadium complex led to H_2 evolution with concomitant color change from orange to deep green. The conversion was 73% after 1 h of photolysis, and was 79% after additional standing for 1 d at room temperature. Fluorescent light-induced dehydrocoupling of **1a** took place again even in this V-catalyzed system. Under fluorescent light, H_2 vigorously evolved, and the conversion reached 81% in 3 h. However, the hydrogen release terminated with the conversion of 87% even though the reaction time was prolonged. This is probably because a coordinatively unsaturated vanadium species, a possible active catalyst, dimerizes to produce a deep green dinuclear complex, $[Cp_2V_2(CO)_5]$,[21] losing the catalytic activity.

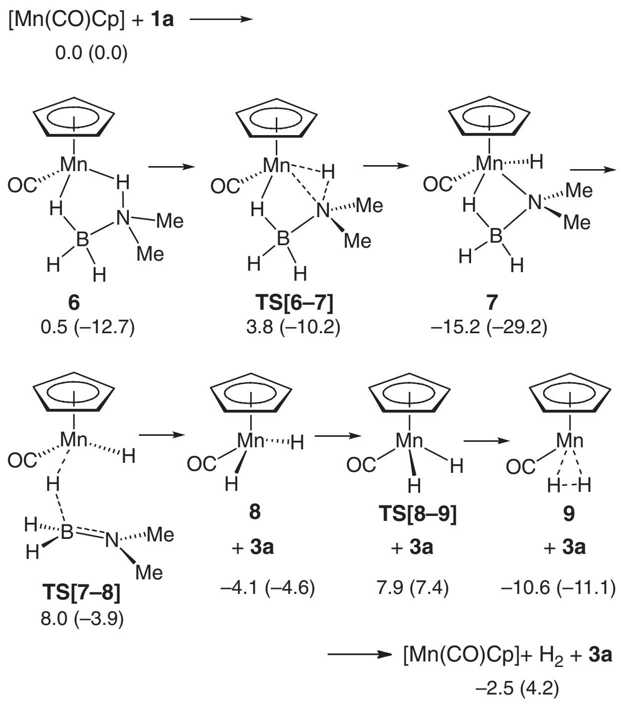
Table 1 summarizes the results of dehydrocoupling reactions of several secondary amine–borane adducts. By the catalytic action of the half-sandwich carbonyl complexes, diethylamine–borane **1b** and piperidine–borane **1c** release H_2 similarly to **1a** to afford $[BH_2NR_2]_2$ (**2b**: R = Et,[17c,22a] **2c**: R = 1/2 C_5H_{10})[22] in moderate to good yields. The dehydrogenation of bulky $BH_3{\cdot}NHCy_2$ (**1d**) was very slow, and monomeric $BH_2{=}NCy_2$ (**3d**)[22a] was produced in low yield only if $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ was employed as a catalyst.

A primary amine–borane adduct $BH_3{\cdot}NH_2Me$ (**1e**) also liberated H_2 catalyzed by half-sandwich carbonyl complexes under photolytic conditions. Notably, the product of this reaction was an aminoborane polymer, $[BH_2NHMe]_n$ (**5e**, Scheme 2). When $[CpMn(CO)_3]$ was employed as a catalyst, the solution color changed from yellow to red-brown with gentle gas evolution with progress of the reaction. After 12 h of photolysis, polymer **5e** precipitated out as a white viscous material. Likewise, $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ also catalyzed hydrogen elimination of **1e** to provide a similar precipitate almost quantitatively after 3 h of photolysis. Product **5e** was insoluble in benzene, but moderately soluble in chloroform. The ^1H and ^{11}B NMR spectral data of the product in chloroform-d well accorded with the literature values reported by Manners ($\delta^{11}B$ = 0–10, broad).[10] Polymer **5e** formed a highly viscous gel-like material to frustrate complete removal of residual solvent.



Scheme 2. Transition-metal carbonyl complex-catalyzed dehydrocoupling reactions of methylamine–borane **1e**.

Formation of the polymeric product contrasts the $[M(CO)_6]$-catalyzed dehydrocoupling reaction of **1e**, in which the polymeric borane is first generated, but it undergoes further dehydrogenation to ultimately yield trimethylborazine $[BHNMe]_3$.[14] The lower activity of the half-sandwich carbonyls should prevent the



Scheme 3. The reaction pathway of the Mn-catalyzed dehydrocoupling of **1a** predicted by DFT calculations (MPW1K). Relative free energies are given in kcal mol^{-1}. Zero point-corrected electronic energies are also given in parentheses.

borazine formation. This makes possible selective preparation of either a borazine derivative or an aminoborane polymer by the proper choice of a catalyst ([M(CO)$_6$] or half-sandwich carbonyls).

The reaction mechanism of the Mn-catalyzed dehydrocoupling of **1a** was studied by DFT calculations with use of the MPW1K functional (Scheme 3).[23,24] Presumably, the active catalyst of this reaction is a 14 electron species, [Mn(CO)Cp]. Borane **1a** coordinates to the manganese center through the BH and NH hydrogen atoms to form a chelate intermediate **6**. This complex then undergoes NH activation via a transition state **TS[6–7]**, generating an amido(borane) species **7**. This step is followed by BH activation (through **TS[7–8]**) to release **3a**. The resulting dihydride **8** liberates H$_2$ through a dihydrogen adduct **9**, regenerating the active catalyst, while liberated aminoborane dimerizes to produce **2a**. The BH activation step has the highest barrier, 23.2 kcal mol^{-1} (in free energy), in the reaction sequence. This value is significantly larger than the activation energy for the [Cr(CO)$_6$]-catalyzed dehydrocoupling of **1a** ($\Delta G^{\ddagger} = 13.3$ kcal mol^{-1}).[14] This well accounts for the lower activity of the manganese catalyst. The active species [Mn(CO)Cp] can be generated via disproportionation of [Mn(CO)$_2$Cp], which is formed by the photolysis of [CpMn(CO)$_3$] or borane dissociation from the σ complex **4** (See Supporting Information).[25] Another reaction pathway, concerted H$_2$ elimination that occurs on 16 electron [Mn(CO)$_2$Cp], was shown to have an even higher activation barrier.

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References and Notes

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1 a) T. J. Clark, K. Lee, I. Manners, *Chem.—Eur. J.* **2006**, *12*, 8634. b) C. A. Jaska, I. Manners, in *Inorganic Chemistry in Focus II*, ed. by G. Meyer, D. Naumann, L. Wesemann, Wiley-VCH, Weinheim, **2005**, pp. 53–64. c) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279.

2 a) W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283. b) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613.

3 M. S. Hill, G. Kociok-Köhn, T. P. Robinson, *Chem. Commun.* **2010**, *46*, 7587.

4 a) T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.* **2006**, *128*, 9582. b) D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2007**, 3297.

5 Y. Jiang, O. Blacque, T. Fox, C. M. Frech, H. Berke, *Organometallics* **2009**, *28*, 5493.

6 a) M. Käß, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem., Int. Ed.* **2009**, *48*, 905. b) A. Friedrich, M. Drees, S. Schneider, *Chem.—Eur. J.* **2009**, *15*, 10339. c) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 14034.

7 a) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424. b) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Commun.* **2001**, 962.

8 M. E. Sloan, T. J. Clark, I. Manners, *Inorg. Chem.* **2009**, *48*, 2429.

9 a) Y. Chen, J. L. Fulton, J. C. Linehan, T. Autrey, *J. Am. Chem. Soc.* **2005**, *127*, 3254. b) J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.* **2007**, *129*, 11936.

10 A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem., Int. Ed.* **2008**, *47*, 6212.

11 M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048.

12 R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844.

13 It has been documented that Co nanoparticles can be an active catalyst on the ammonia–borane dehydrocoupling. T. J. Clark, G. R. Whittell, I. Manners, *Inorg. Chem.* **2007**, *46*, 7522. The Pd/C-catalyzed dehydrocoupling of ammonia–borane has also been reported. S.-K. Kim, W.-S. Han, T.-J. Kim, T.-Y. Kim, S. W. Nam, M. Mitoraj, L. Piekoś, A. Michalak, S.-J. Hwang, S. O. Kang, *J. Am. Chem. Soc.* **2010**, *132*, 9954.

14 Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa, H. Ogino, *J. Am. Chem. Soc.* **2009**, *131*, 14946.

15 T. Kakizawa, Y. Kawano, M. Shimoi, *Organometallics* **2001**, *20*, 3211.

16 Photolysis of [(η^6-C$_6$H$_6$)Cr(CO)$_3$] in the presence of BH$_3$•L (L = NMe$_3$, N(C$_2$H$_4$)$_3$CH, and PMe$_3$) produces the corresponding borane complex, [(η^6-C$_6$H$_6$)Cr(CO)$_2$(η^1-BH$_3$•L)]. T. Kakizawa, Y. Kawano, M. Shimoi, unpublished results.

17 a) A. B. Burg, C. L. Randolph, Jr., *J. Am. Chem. Soc.* **1949**, *71*, 3451. b) W. Haubold, R. Schaeffer, *Chem. Ber.* **1971**, *104*, 513. c) H. Nöth, H. Vahrenkamp, *Chem. Ber.* **1967**, *100*, 3353.

18 a) A. B. Burg, C. L. Randolph, Jr., *J. Am. Chem. Soc.* **1951**, *73*, 953. b) E. C. Ashby, R. A. Kovar, R. Culbertson, *Inorg. Chem.* **1971**, *10*, 900.

19 W. D. Phillips, H. C. Miller, E. L. Muetterties, *J. Am. Chem. Soc.* **1959**, *81*, 4496.

20 a) M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, H. Ogino, *J. Am. Chem. Soc.* **1999**, *121*, 11704. b) Y. Kawano, K. Yamaguchi, S. Miyake, T. Kakizawa, M. Shimoi, *Chem.—Eur. J.* **2007**, *13*, 6920. c) T. Yasue, Y. Kawano, M. Shimoi, *Angew. Chem., Int. Ed.* **2003**, *42*, 1727. d) Y. Kawano, M. Hashiva, M. Shimoi, *Organometallics* **2006**, *25*, 4420.

21 W. A. Herrmann, J. Plank, *Chem. Ber.* **1979**, *112*, 392.

22 a) L. Pasumansky, D. Haddenham, J. W. Clary, G. B. Fisher, C. T. Goralski, B. Singaram, *J. Org. Chem.* **2008**, *73*, 1898. b) A. Storr, B. S. Thomas, A. D. Penland, *J. Chem. Soc., Dalton Trans.* **1972**, 326. c) H. Nöth, B. Wrackmeyer, *Chem. Ber.* **1974**, *107*, 3070.

23 a) B. J. Lynch, P. L. Fast, M. Harris, D. G. Truhlar, *J. Phys. Chem. A* **2000**, *104*, 4811. b) B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2001**, *105*, 2936.

24 Basis sets. Geometry optimization and frequency analysis: SDD (Mn), 6-31++G(d,p) (B, N, BH and NH hydrogen atoms), 6-31G(d) (C, H, O); Single point energy (SCRF calculation, CPCM model (in benzene)): SDD (Mn), aug-cc-pVDZ (other atoms).

25 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.