

# Monoborane NHC Adducts in the Coordination Sphere of Transition Metals

Philipp Bissinger, Holger Braunschweig,\* Thomas Kupfer, and Krzysztof Radacki

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Irradiation of various carbonyl complexes in the presence of 1,3-dimethylimidazol-2-ylideneborane (IMe·BH<sub>3</sub>) afforded the new borane complexes [CpMn(CO)<sub>2</sub>( $\eta^1$ -H<sub>3</sub>B–IMe)] and [M(CO)<sub>5</sub>( $\eta^1$ -H<sub>3</sub>B–IMe] (M = Cr, Mo, W). With the exception of [Mo(CO)<sub>5</sub>( $\eta^1$ -H<sub>3</sub>B–IMe], which was detected only in solution, the solid-state structures of all species were validated by single-crystal X-ray diffraction. The NHC–BH<sub>3</sub> moiety was found to be coordinated to the metal center through a B–H–M three-center two-electron bond presumably without any B–M interaction.  $\pi$ -Back-donation from the metal center to the boron-containing ligand is most likely negligible.

## Introduction

The introduction of N-heterocyclic carbenes (NHCs) in organometallic chemistry has led to a plethora of new species over the past decades showing enhanced and interesting reactivity patterns. The steric and electronic properties of NHCs allow for the stabilization of highly reactive and unique compounds.<sup>1</sup> It was also shown that NHCs readily form stable adducts with unsaturated, highly Lewis acidic group 13 derivatives, which is a result of the distinct electron-pair donor capabilities of the carbenes.<sup>2</sup>

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# **Results and Discussion**

1,3-Dimethylimidazol-2-ylideneborane (IMe $\cdot$ BH<sub>3</sub>; 1) was isolated from the reaction of the free carbene 1,3-dimethylimidazol-2-ylidene and monoborane methylsulfide complex BH<sub>3</sub> $\cdot$ SMe<sub>2</sub> in quantitative yield according to Scheme 1. An alternative synthetic access to 1 is given by the thermal decarboxylation of 1,3-dimethylimidazolium-2-carboxylate (IMe $\cdot$ CO<sub>2</sub>).<sup>6</sup> NHC carboxylates are prone to extrude carbon dioxide at elevated temperatures depending on the steric requirements of the nitrogen-bound substituents. Thermally induced decarboxylation of IMe $\cdot$ CO<sub>2</sub> might thus lead to *in situ* generation of the free carbene and subsequent trapping with

<sup>\*</sup>To whom correspondence should be addressed. E-mail: h. braunschweig@mail.uni-wuerzburg.de. Fax: (+049)931-3184623. Tel: (+049)931-3185260.

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Figure 1. Molecular structure of 1 in the solid state. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths [Å] and angles [deg]: B-C1 1.600(4), B-C1-N1 129.0(2), N1-C1-N2 105.2(2), N2-C1-B 125.7(2).

#### Scheme 1. Synthesis of 1



borane in the formation of 1. Thus, heating a toluene solution of  $IMe \cdot CO_2$  and  $BH_3 \cdot SMe_2$  at 110 °C smoothly resulted in the formation of 1 in good yields, which is in stark contrast to earlier results; thermogravimetric analysis of  $IMe \cdot CO_2$  indicated a high stability up to 162 °C followed by decomposition at higher temperatures.<sup>7</sup>

Colorless crystals of **1** suitable for X-ray diffraction were grown from saturated toluene solutions at room temperature. The molecular structure of **1** in the solid state is in agreement with the data obtained in solution and is depicted in Figure 1 together with important geometrical parameters.<sup>8</sup>



Figure 2. Molecular structure of 2 in the solid state. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths [Å] and angles [deg]: B-C1 1.587(2), B-H1 1.252(19), B-H2 1.106(19), B-H3 1.14(2), Mn-H1 1.67(2), Mn-C2 1.7677(17), Mn-C3 1.7640(19), Mn-H1-B 127.09, Mn-H1-B-C1 84.04.

Scheme 2. Synthesis of 2  

$$[CpMn(CO)_{3}] + 1 \xrightarrow[-CO]{h_{V}} OC^{-Mn} H^{+}_{B} H^{+}_{OC} N^{-N}$$

Scheme 3. Reactivity of 1 toward  $[M(CO)_6]$  (M = Cr, Mo, W)

$$[M(CO)_6] + 1 \xrightarrow[-CO]{toluene} (OC)_5 M^{-H} \xrightarrow[-K]{H} 3: M = Cr$$

$$4: M = Mo$$

$$5: M = W$$

Irradiation of a solution of 1 and  $[CpMn(CO)_3]$  in toluene afforded  $[CpMn(CO)_2(\eta^1-H_3B\cdot IMe)]$  (2) in 86% yield, which was isolated as a red crystalline solid (Scheme 2). The solid-state structure was validated by X-ray diffraction analysis (Figure 2); suitable single crystals could be obtained by crystallization from toluene/hexane (1:1) at -30 °C.

The borane ligand in **2** features an end-on coordination mode to the metal center through a bridging hydrogen atom, whereby the Mn-H1-B bond angle (127.09°) is comparable to those observed in the related systems [CpMn(CO)<sub>2</sub>( $\eta^1$ -H<sub>3</sub>B·L)] (L = NMe<sub>3</sub>, 142(3)°; L = PMe<sub>3</sub>, 129(3)°).<sup>5b</sup> The B-C1 bond distance (1.587(2) Å) is only marginally shorter than in **1** (1.600(4) Å). As anticipated, both terminal hydrogen atoms H2 and H3 are located closer to the B center than the bridging hydrogen atom H1. The B···M separation distance of 2.624 Å is clearly larger than in borane complexes [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Mn(CO)<sub>2</sub>(HBClSi-Me<sub>3</sub>)] (2.183(16) Å), [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Mn(CO)<sub>2</sub>(HBcat)] (2.08(1) Å) and suggests a negligible boron-metal interaction, if present at all.

Related species were obtained by irradiation of the carbonyl complexes  $[M(CO)_6](M=Cr, Mo, W)$  and 1 in toluene solution (Scheme 3). While  $[(CO)_5M(\eta^1-H_3B\cdot IMe)] (M = Cr, 3; M = W, 5)$  were isolated as orange solids in 37% and 73% yield, respectively, the analogous Mo complex  $[(CO)_5Mo(\eta^1-H_3B\cdot IMe)]$ (4) was subject to fast decomposition even at low temperatures and was observed only in solution by <sup>11</sup>B NMR spectroscopy. Decomposition also has been observed for the analogous molybdenum complexes  $[(CO)_5Mo(\eta^1-H_3B\cdot L)] (L = PMe_3, PPh_3, NMe_3).^{5a}$ 

The molecular compositions of **3** and **5** in the solid state were ascertained by X-ray diffraction analysis of crystals obtained from toluene/hexane (1:1) solutions at -30 °C (Figure 3).

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<sup>(8)</sup> Crystal data were collected at a Bruker X8Apex diffractometer with CCD area detector and multilayer mirror monochromated Mo Ka radiation. The structures were solved using direct methods, refined with the Shelx software package (Sheldrick, G. Acta Crystallogr. 2008, A64, 112-122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Boron-bound hydrogen atoms were located on the Fourier difference map and refined. Other hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for 1:  $C_5H_{11}BN_2$ ,  $M_r = 109.97$ , colorless plate,  $0.13 \times 0.115 \times 0.05 \text{ mm}^3$ , monoclinic space group  $P_{2_1/m}$ ,  $a = 6.9795(4)^{\circ}$ Å, b = 6.8312(5)Å, c = 7.2125(4)Å,  $\beta = 105.428(4)^{\circ}$ , V = 331.49(4)Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.102$  g·cm<sup>-3</sup>,  $\mu = 0.066$  mm<sup>-1</sup>, F(000) = 120, T = 100(2) K,  $R_1 = 0.0728$ ,  $wR_2 = 0.1946$ , 884 independent reflections  $[2\theta \le 56.56^\circ]$  and 49 parameters. Crystal data for **2**: C<sub>12</sub>H<sub>16</sub>BMnN<sub>2</sub>O<sub>2</sub>,  $M_r$  = 286.02, red plate,  $0.30 \times 0.28 \times 0.13$  mm<sup>3</sup>, monoclinic space group  $P2_1/c$ ,  $\begin{array}{l} & a = 8.1688(15) \ \ \dot{A}, \ b = 8.2410(15) \ \ \dot{A}, \ c = 20.076(3) \ \ \dot{A}, \ \beta = 94.821(7)^\circ, \ V = 1346.7(4) \ \ \dot{A}^3, \ Z = 4, \ \rho_{calcd} = 1.411 \ \ g \cdot cm^{-3}, \ \mu = 0.974 \ mm^{-1}, \ F(000) = 592, \ T = 1346.7(4) \ \ \dot{A}^3, \ Z = 4, \ \rho_{calcd} = 1.411 \ \ g \cdot cm^{-3}, \ \mu = 0.974 \ mm^{-1}, \ F(000) = 592, \ T = 1346.7(4) \ \ \dot{A}^3, \ Z = 4, \ \rho_{calcd} = 1.411 \ \ g \cdot cm^{-3}, \ \mu = 0.974 \ \ mm^{-1}, \ F(000) = 592, \ T = 1346.7(4) \ \ \dot{A}^3, \ Z = 4, \ \rho_{calcd} = 1.411 \ \ g \cdot cm^{-3}, \ \mu = 0.974 \ \ \ mm^{-1}, \ F(000) = 592, \ T = 1346.7(4) \ \ \dot{A}^3, \ \ \dot{A} = 1.411 \ \ \dot{A}^3, \ \dot{A} = 1.411 \ \dot{A}^3, \ \dot{A} = 1.411$ 100(2) K,  $R_1 = 0.0298$ ,  $wR_2 = 0.0964$ , 2668 independent reflections  $[2\theta \le 52.22^\circ]$ and 174 parameters. Crystal data for 3:  $C_{10}H_{11}BCrN_2O_5$ ,  $M_r = 302.02$ , orange and 1/7 planticels. Clystal data 10.5. Clystal planticels,  $W_1^- = 50.25$ ,  $W_1^- = 50.25$ parameters. Crystal data for 5:  $C_{10}H_{11}BN_2O_5W$ ,  $M_r = 433.87$ , orange needle, 0.30 × 0.15 × 0.06 mm<sup>3</sup>, monoclinic space group  $P_{21}/n$ , a = 7.2065(3) Å, b = 12.2074(5) Å, c = 15.3582(6) Å,  $\beta = 97.076(2)^\circ$ , V = 1340.81(9) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 2.149$  g·cm<sup>-3</sup>,  $\mu = 8.631$  mm<sup>-1</sup>, F(000) = 816, T = 100(2) K,  $R_1 = 100(2)$  K,  $R_2 = 100(2)$  K,  $R_1 = 100(2)$  K,  $R_2 = 100(2)$  K,  $R_1 = 100(2)$  K,  $R_1 = 100(2)$  K,  $R_2 = 100(2)$  K,  $R_1 = 100$ 0.0145,  $wR_2 = 0.0358$ , 2640 independent reflections  $[2\theta \le 52.08^\circ]$  and 183 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-782754 (1), CCDC-782755 (2), CCDC-782756 (3), and CCDC-782757 (5). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.



**Figure 3.** Molecular structures of **3** and **5** in the solid state. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths [Å] and angles [deg]: **3**: B-Cr 2.838, B-C1 1.591(2), B-H1 1.15(2), B-H2 1.13(2), B-H3 1.09(2), Cr-H1 1.83(2), Cr-C2 1.8530(17), Cr-C3 1.9031(17), Cr-C4 1.9088(17), Cr-C5 1.9179(18), Cr-C6 1.9042(17), Cr-H1-B 143.27, Cr-H1-B-C1 70.88. **5**: B-W 2.898, B-C1 1.589(4), B-H1 1.149(19), B-H2 1.138(19), B-H3 1.135(19), W-H1 1.90(2), W-C2 1.973(3), W-C3 2.052(3), W-C4 2.048(3), W-C5 2.037(3), W-C6 2.043(3), W-H1-B 142.94, Cr-H1-B-C1 69.66.

Table 1. NMR Spectroscopic Parameters of 1-5

	1	2	3	4	5
$\frac{\delta^{1} \mathrm{H} (\mathrm{B} \mathrm{H})^{a}}{\delta^{11} \mathrm{B}^{a}}$	1.95 (q)	-5.55 (br)	-3.16 (br q)	n.d. <sup>b</sup>	-1.45 (br q)
	-37.2 (q)	-47.0 (q)	-42.5 (q)	-44.3 (q)	-47.1 (q)

<sup>*a*</sup> Chemical shift  $\delta$  in ppm. <sup>*b*</sup> Not determined.

The transition metal centers in 3 and 5 feature nearly ideal octahedral coordination environments. The NHC-B fragments adopt an almost parallel arrangement with respect to the planes formed by the metal centers and the carbonyl ligands cis to the borane ligand (8.62° and 8.15° for 3 and 5, respectively). Both complexes show M-H1-B angles (3, 143.27°; 5, 142.94°) that unambiguously confirm an end-on coordination mode of the borane NHC adducts. The differences in bond lengths for the bridging and terminal B-H bonds are much less visible for 3 and 5 than those found for 2. Again, the B-C1 bond distances (3, 1.591(2) Å; 5, 1.589(4) Å) remain nearly unaffected by the metal coordination and are similar to that observed in free IMe  $\cdot$  BH<sub>3</sub> (1, 1.600(4) A). The B  $\cdot \cdot \cdot$  M separation distances of 2.838 Å (3) and 2.898 Å (5) indicate once again the absence of any interaction between boron and the metal center. It should be noted that the geometrical parameters discussed above are similar to those of  $[(CO)_5Cr(\eta^1-H_3B\cdot PMe_3)]$  and  $[(CO)_5W (\eta^1 - H_3 B \cdot PMe_3)].^{5a}$ 

The metal carbonyl distances *trans* to boron (**3**, Cr-C2 = 1.8530(17) Å; **5**, W-C2 = 1.973(3) Å) are notably shortened with respect to those in *cis* positions (**3**, average Cr-CO = 1.9085 Å; **5**, average W-CO = 2.045 Å), which can be rationalized by the missing  $\pi$ -acceptor capabilities of the borane ligand. Hence, the binding mode in complexes **2**-**5** is best described as an open three-center two-electron bond. Fenske-Hall MO calculations performed by Shimoi et al. on related systems, i.e., [(CO)<sub>5</sub>Cr( $\eta^1$ -H<sub>3</sub>B·PH<sub>3</sub>)] and [CpMn(CO)<sub>2</sub>( $\eta^1$ -H<sub>3</sub>B·NH<sub>3</sub>)], revealed that the ligand acts predominately as a  $\sigma$ -donor, while  $\pi$ -back-donation from the metal center is most likely negligible, <sup>5a,b</sup> which is supported by IR spectroscopy. IR spectra of **2**, **3**, and **5** feature  $\nu$ (CO) bands that are red-shifted by about 50 to 70 cm<sup>-1</sup> in comparison to those of the starting materials.

In addition to solid-state structures and IR spectroscopy, borane complexes **2**, **3**, and **5** were characterized by elemental analysis and NMR spectroscopy (Table 1). The <sup>11</sup>B NMR spectra show quartet signals ( $\delta$  –47.1 to  $\delta$  –42.5) shifted toward higher field by 6 to 10 ppm relative to those of **1** ( $\delta$  –37.2). The



**Figure 4.** <sup>1</sup>H NMR spectra of **5** (B*H* region) at (a) 298 K, (b) 273 K, (c) 223 K, and (d) 183 K.

Scheme 4. Reactivity of  $2^a$ 



<sup>a</sup> Reaction conditions: (i) SiPh<sub>2</sub>H<sub>2</sub>; (ii) HBcat; (iii) 4-methylpyridine.

NHC and Cp ring hydrogen atoms give rise to sharp resonances in the <sup>1</sup>H NMR spectra of 2, 3, and 5 and are easily assigned, whereas the boron-bound hydrogen atoms show only one broad signal in the range  $\delta$  -5.55 to -1.45. While the latter signal of **2** exhibits no visible splitting pattern at ambient temperature, the corresponding signals of 3 and 5 are best described as broad quartets. The broad nature of these resonances clearly indicates fast scrambling between the terminal and bridging boron-bound hydrogen atoms. However, low-temperature NMR experiments (rt to -90 °C) did not result in separated signals for the bridging (expected at higher field) and terminal hydrogen atoms, thus indicating that scrambling is fast on the NMR time scale. The low-temperature <sup>1</sup>H NMR spectra (BH region) of 5 in toluene $d_8$  are depicted in Figure 4. Coalescence cannot be observed. The sharpening of the signal can be ascribed to quadrupole-induced thermal decoupling.<sup>10</sup>

The isolated species **2**, **3**, and **5** are stable at room temperature and can be stored under an inert gas atmosphere for an enhanced period of time. Preliminary reactivity studies are in full agreement with the anticipated weak coordination of the NHC-borane adduct. Thus, reaction of **2** with SiH<sub>2</sub>Ph<sub>2</sub> or HBcat is accompanied by the loss of NHC-borane and the concomitant formation of the previously reported sideon-coordinated silane (**6**) and borane (**7**) complexes, respectively, which were clearly identified by NMR spectroscopy (Scheme 4).<sup>11,5b</sup> Conversion is not quantitative and requires

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several hours, whereas the corresponding reaction of [CpMn-(CO)<sub>2</sub>( $\eta^1$ -H<sub>3</sub>B·NMe<sub>3</sub>)] is completed within one hour.<sup>5b</sup> Use of excess silane or borane does not lead to higher yields. Reaction of **2** with 4-methylpyridine affords the manganese- $\eta^1$ -*N*-picoline derivative **8** quantitatively within 30 min.<sup>12</sup>

In summary, we showed that NHC·BH<sub>3</sub> adducts can be incorporated in the coordination sphere of different transition metals to afford  $\eta^1$ -end-on-coordinated borane complexes. Several species, namely, [CpMn(CO)<sub>2</sub>( $\eta^1$ -H<sub>3</sub>B·IMe)] (2), [(CO)<sub>5</sub>Cr( $\eta^1$ -H<sub>3</sub>B·IMe)] (3), and [(CO)<sub>5</sub>W( $\eta^1$ -H<sub>3</sub>B· IMe)] (5) were isolated and fully characterized both in solution and in the solid state, while the analogous molybdenum congener [(CO)<sub>5</sub>Mo( $\eta^1$ -H<sub>3</sub>B·IMe)] (4) was much more labile and could be detected only by NMR spectroscopy. The results of the X-ray diffraction analyses, as well as preliminary reactivity studies, confirm the presence of only weak interactions between the metal centers and the borane substituent.

### **Experimental Section**

All manipulations were conducted either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Solvents (toluene and hexane) were purified by distillation from Na/K alloy under dry argon, immediately prior to use. Deuterated solvents ( $C_6D_6$ ,  $C_7D_8$ ) were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. Reagents were dried and purified by standard procedures. IR spectra were recorded as toluene solutions between KBr plates on a Bruker Vector 22 FT-IR spectrometer. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to external TMS via the residual protons of the solvent (<sup>1</sup>H) or the solvent itself (<sup>13</sup>C). <sup>11</sup>B NMR spectra were referenced to external  $BF_3 \cdot OEt_2$ . Microanalyses (C, H, N) were performed on a Leco Instruments elemental analyzer, type CHNS 932. A Hg/Xe arc lamp (400-550 W) equipped with IR filters, irradiating at 210-600 nm, was used as a light source.

**IMe**•**BH**<sub>3</sub> (1) from **IMe**. **B**H<sub>3</sub>•**S**Me<sub>2</sub> (2 M in Et<sub>2</sub>O; 4.54 mL, 9.07 mmol) was added dropwise to a solution of IMe (0.87 g, 9.07 mmol) in hexane (20 mL). A white solid precipitated immediately. After 1 h the solid was filtered off and washed with hexane. Removal of all volatiles *in vacuo* afforded analytically pure, colorless IMe•BH<sub>3</sub> (1) (yield 1.00 g, 9.05 mmol, 99%). <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.62 (s, 2H, NCHCHN), 3.10 (s, 6H, CH<sub>3</sub>), 1.95 (q, <sup>1</sup>J<sub>HB</sub> = 87.7 Hz, 3H, BH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  118.95 (NCHCHN), 35.30 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.46 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -37.2 (q, <sup>1</sup>J<sub>BH</sub> = 87.7 Hz) ppm.

**IMe**•**BH**<sub>3</sub> (1) from **IMe**•**CO**<sub>2</sub>. A suspension of IMe•CO<sub>2</sub> (0.90 g, 6.42 mmol) and BH<sub>3</sub>•**SMe**<sub>2</sub> (2 M in Et<sub>2</sub>O; 5.00 mL, 10.0 mmol) in toluene was refluxed for 1.5 h. The mixture was cooled to room temperature, and remaining insolubilities were removed. Hexane (15 mL) was added, whereupon colorless IMe•BH<sub>3</sub> (1) precipitated. The product was filtered, washed with hexane, and dried *in vacuo* (yield 0.46 g, 4.14 mmol, 64%).

[CpMn(CO)<sub>2</sub>( $\eta^{-1}$ H<sub>3</sub>B·IMe)] (2). A solution of [CpMn(CO)<sub>3</sub>] (0.45 g, 2.18 mmol) and IMe·BH<sub>3</sub> (0.24 g, 2.18 mmol) in toluene (20 mL) was irradiated at room temperature. Gaseous CO was removed after 18 h by three freeze–pump–thaw cycles. The resulting slurry was filtered, and the dark red solution was layered with hexane (10 mL). Cooling to -30 °C for 12 h afforded **2** as red crystals (yield 0.54 g, 1.87 mmol, 86%). IR: 1947 (s), 1858 (s) cm<sup>-1</sup> ( $\nu$ (CO)). <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.74 (s, 2H, NCHCHN), 4.39 (s, 5H, CpH), 3.21 (s, 6H, CH<sub>3</sub>), -5.55 (br, 3H, BH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  225.38 (CO), 119.97 (NCHCHN), 81.15 (CCp), 35.33 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.46 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -47.0 (q, <sup>1</sup>J<sub>BH</sub> = 83.1 Hz) ppm. Anal. Calcd (%) for C<sub>12</sub>H<sub>16</sub>BMnN<sub>2</sub>O<sub>2</sub>: C 50.39, H 5.64, N 9.79. Found: C 50.71, H 5.66, N 10.14.

[(CO)<sub>5</sub>Cr( $\eta^{1}$ -H<sub>3</sub>B·IMe)] (3). A mixture of [Cr(CO)<sub>6</sub>] (0.250 g, 1.14 mmol) and IMe·BH<sub>3</sub> (0.13 g, 1.14 mmol) was irradiated for 20 h at room temperature in toluene (20 mL). Gaseous CO was removed by three freeze–pump–thaw cycles, and the dark red solution was filtered and layered with hexane (10 mL). After 2 days at -30 °C, **3** was isolated as orange crystals (yield 0.13 g, 0.43 mmol, 37%). IR: 1933 (s), 1905 (m), 1874 (w), 1857 (m) cm<sup>-1</sup> ( $\nu$ (CO)). <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.48 (s, 2H, NCHCHN), 2.89 (s, 6H, CH<sub>3</sub>), -3.16 (br q, <sup>1</sup>J<sub>HB</sub> = 81.3 Hz, 3H, BH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  230.92 (CO), 217.38 (CO), 120.35 (NCHCHN), 35.18 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.46 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -42.5 (q, <sup>1</sup>J<sub>BH</sub> = 84.8 Hz) ppm. Anal. Calcd (%) for C<sub>10</sub>H<sub>11</sub>CrN<sub>2</sub>O<sub>5</sub>: C 39.77, H 3.67, N 9.42. Found: C 40.25, H 3.76, N 9.28.

[(CO)<sub>5</sub>W(η<sup>1</sup>-H<sub>3</sub>B·IMe)] (5). A mixture of [W(CO)<sub>6</sub>] (0.40 g, 1.14 mmol) and IMe·BH<sub>3</sub> (0.13 g, 1.14 mmol) was irradiated for 4 h at room temperature in toluene (20 mL). Gaseous CO was removed by three freeze–pump–thaw cycles, and the dark red solution was filtered and layered with hexane (10 mL). After 2 days at –30 °C, **5** was isolated as orange crystals (yield 0.36 g, 0.83 mmol, 73%). IR: 2072 (m), 1923 (s), 1900 (s), 1857 (m) cm<sup>-1</sup> (ν(CO)). <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.45 (s, 2H, NCHCHN), 2.87 (s, 6H, CH<sub>3</sub>), –1.45 (br q, <sup>1</sup>J<sub>HB</sub> = 78.8 Hz, 3H, BH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>): δ 199.01 (CO), 191.17 (CO), 120.28 (NCHCHN), 35.20 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160.46 MHz, C<sub>6</sub>D<sub>6</sub>): δ –47.1 (q, <sup>1</sup>J<sub>BH</sub> = 83.7 Hz) ppm. Anal. Calcd (%) for C<sub>10</sub>H<sub>11</sub>WN<sub>2</sub>O<sub>5</sub>: C 27.68, H 2.56, N 6.46. Found: C 28.16, H 2.60, N 6.63.

**Supporting Information Available:** X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(12)</sup> Giordano, P. J.; Wrighton, M. S. Inorg. Chem. 1977, 16, 160-166.