

Coordination Compounds of Monoborane–Lewis Base Adducts: Syntheses and Structures of $[M(CO)_5(\eta^1-BH_3 \cdot L)]$ ($M = Cr, Mo, W; L = NMe_3, PMe_3, PPh_3$)

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Abstract: Photolysis of $[M(CO)_6]$ ($M = Cr, W$) in the presence of $BH_3 \cdot L$ ($L = NMe_3, PMe_3, PPh_3$) gave isolable borane complexes $[M(CO)_5(\eta^1-BH_3 \cdot L)]$ (**1a**, $M = Cr, L = PMe_3$; **1b**, $M = Cr, L = PPh_3$; **1c**, $M = Cr, L = NMe_3$; **2a**, $M = W, L = PMe_3$; **2b**, $M = W, L = PPh_3$; **2c**, $M = W, L = NMe_3$). In products **1** and **2**, the monoborane–Lewis base adduct coordinates to the metal center through a B–H–M three-center two-electron bond, which was confirmed by X-ray structural analyses of **1a**, **2a**, and **2b** at low temperature. The X-ray crystal structural analysis of **1c** at ambient temperature also showed the same coordination mode, although the positions of hydrogen atoms on the boron were not determined. The 1H NMR spectra of **1** and **2** exhibit only one BH signal at -2 to -3 ppm with an intensity of 3H in the temperature range of -80 °C to room temperature. This indicates that the coordinated BH and terminal BH's are rapidly exchanging in solution even at low temperature. When $[Mo(CO)_6]$ was used as a precursor, the formation of the corresponding molybdenum–borane complexes, $[Mo(CO)_5(\eta^1-BH_3 \cdot L)]$ (**3a**, $L = PMe_3$; **3b**, $L = PPh_3$; **3c**, $L = NMe_3$), was observed by NMR spectroscopy, but the complexes could not be isolated because of their thermal instability. Complexes of pyridineborane $[M(CO)_5(\eta^1-BH_3 \cdot NC_5H_5)]$ (**1d**, $M = Cr$; **2d**, $M = W$) were also observable by NMR spectroscopy. Fenske–Hall MO calculations for the model compound $[Cr(CO)_5(\eta^1-BH_3 \cdot PH_3)]$ (**1e**) demonstrated that the bonding between the borane and metal can be described as donation of the bonding electron pair of BH to the a_1 orbital of $[Cr(CO)_5]$, and that π back-donation from the metal d orbital to the antibonding σ^* orbital of BH is negligible. Compounds **1–3** can be regarded as model compounds of the methane complex $[M(CO)_5(CH_4)]$, which is observed in the photolyses of $[M(CO)_6]$ in methane matrixes. Structural and spectroscopic features of the ligated borane are discussed and compared with those of related compounds.

Introduction

The photolysis of $M(CO)_6$ (where $M = Cr, Mo, W$) in inert media such as a liquid alkane (i.e., CH_4 at low temperature) or a liquid noble gas has been shown to give $M(CO)_5$ and CO. The resulting $M(CO)_5$ is extremely reactive and reacts even with CH_4 or with a noble gas atom within 1 ps to produce $[M(CO)_5(\text{solv})]$ ($\text{solv} = CH_4$ or noble gas atom). The coordinated alkane or noble gas atom in such complexes is extremely labile and can be very easily displaced. $[M(CO)_5(\text{solv})]$ can be detected in low-temperature matrixes by spectroscopic techniques.^{1,2} At room temperature, its lifetime is reported to be of microsecond order.³ The alkane-coordinated species is of considerable interest because of its possible role in the catalytic activation of the

CH bond. Zarić and Hall have proposed a C–H–M single bridge for the bonding between methane and metal in $[W(CO)_5(CH_4)]$, based on a theoretical study.⁴ However, owing to the extreme instability of $[M(CO)_5(CH_4)]$, little is known of its detailed structure and chemistry. A closely related and more stable molecular species could be helpful in understanding coordination of alkanes.

The BH_4^- ion is isoelectronic with the CH_4 molecule and is known to form relatively stable borohydride compounds containing metal–hydrogen–boron three-center two-electron bonds.⁵ For group 6 metal carbonyl complexes of BH_4^- , however, only the bidentate complexes $[M(CO)_4(\eta^2-BH_4)]^-$ are known,⁶ so a direct comparison with $[M(CO)_5(\text{alkane})]$ is impossible. The first

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unidentate borohydride complex was reported by Bommer et al.⁷ They prepared $[\text{Cu}(\eta^1\text{-BH}_3\text{OAc})(\text{PMePh}_2)_3]$, to which they assigned a unidentate structure on the basis of spectroscopic evidence. The compound was the first to contain a definite single, unsupported metal–hydrogen–boron bond. They then synthesized $[\text{Cu}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3]$; the structure of this molecule has been determined unequivocally by X-ray^{8,9} and neutron diffraction⁹ methods.

The reality of a metal–hydrogen–boron three-center covalent bond stabilizing the borohydride complexes was subjected to some questions because of the charges on the metal (1+) and the BH_4^- (1-). Were these charges necessary to provide an ionic contribution for the formation of the stable structures? A neutral borane ligand was required in order to test this point. The neutral compound, $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$, was prepared,¹⁰ and it was demonstrated that it could serve as a bidentate ligand using three-center metal–hydrogen–boron bonds.¹¹ Compounds prepared and subjected to X-ray structural verification included $[\text{ZnCl}_2(\eta^2\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$,¹¹ $[\text{Ni}(\text{CO})_2(\eta^2\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$,¹² and several others.¹³ While $\text{Ni}(\text{CO})_4$ reacts with $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$ at room temperature under mild conditions, the reaction stops unless the liberated CO is removed during the reaction. Other metal carbonyls were even less reactive. Group 6 metal complexes $\text{M}(\text{CO})_6$ did not react with $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$ when they were combined.

With the additional step of photolyzing $\text{M}(\text{CO})_6$ (M = Cr, W) in the presence of $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$, we synthesized two types of chromium and tungsten complexes of $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$.¹⁴ The first complexes appear to derive from $\text{M}(\text{CO})_5$ and involve a unidentate $[\text{M}(\text{CO})_5(\eta^1\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$. These compounds are heat-sensitive (as is the monodentate copper–borohydride complex, $[\text{Cu}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3]$) and liberate another molecule of CO to give $[\text{M}(\text{CO})_4(\eta^2\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$, in which the borane ligand is bidentate. The process may be represented as in Scheme 1. This reaction sequence appears to occur more readily with molybdenum than it does with chromium or tungsten, since no unidentate molybdenum complex was ever isolated; only the bidentate molybdenum complex was isolated.

In view of the foregoing facts, it seemed that, by using the photolysis technique, it should be possible to synthesize group 6 metal carbonyl complexes containing $\text{BH}_3\cdot\text{L}$ as a ligand. Here we report the synthesis and the molecular structure of borane complexes of the type $[\text{M}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{L})]$. The Lewis bases L are PMe_3 , PPh_3 , and NMe_3 . These complexes have great importance as a model system of the methane complexes since $\text{BH}_3\cdot\text{L}$ is isoelectronic with methane. The properties of the B–H–M bond in solution and the results of MO calculations are also discussed. A part of this work has been published already.¹⁵

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(8) (a) Atwood, J. L.; Rogers, R. D.; Kutal, C.; Grutsch, P. A. *J. Chem. Soc., Chem. Commun.* **1977**, 593. (b) Kutal, C.; Grutsch, P. A.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558. This study indicated a linear metal–hydrogen–boron bond. Two subsequent X-ray studies and a neutron diffraction study support a bent M–H–B bond.⁹

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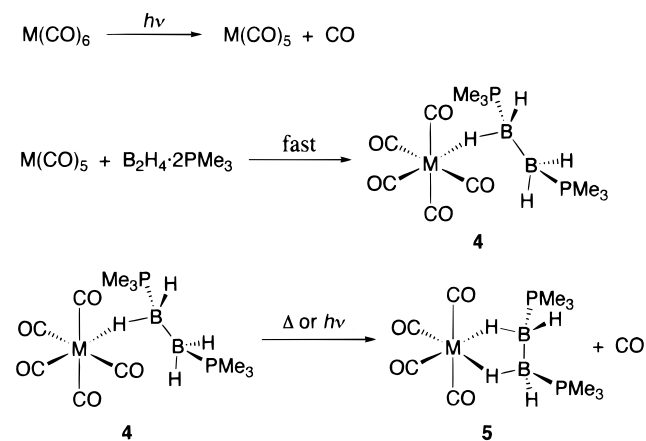
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(b) Shimoi, M.; Katoh, K.; Ogino, H. *J. Chem. Soc., Chem. Commun.* **1990**, 811.

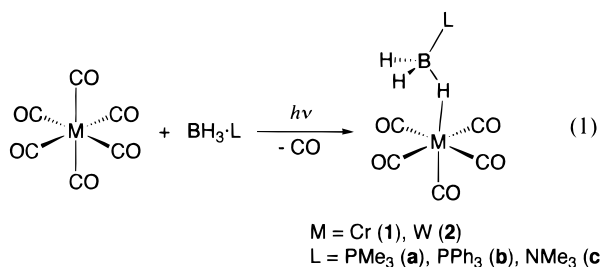
Scheme 1



Results

Syntheses and Crystal Structures of Borane Complexes.

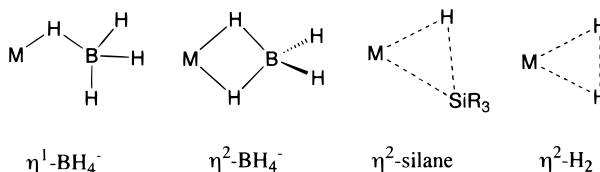
When chromium or tungsten hexacarbonyl was photolyzed in the presence of $\text{BH}_3\cdot\text{L}$ (L = PMe_3 , PPh_3 , NMe_3) in toluene or hexane using a medium-pressure Hg lamp, solid $[\text{M}(\text{CO})_6]$ gradually dissolved and a yellow color developed, accompanied by evolution of CO. Removal of the solvent and subsequent recrystallization of the residue afforded novel borane complexes $[\text{M}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{L})]$ (**1a**, M = Cr, L = PMe_3 ; **1b**, M = Cr, L = PPh_3 ; **1c**, M = Cr, L = NMe_3 ; **2a**, M = W, L = PMe_3 ; **2b**, M = W, L = PPh_3 ; **2c**, M = W, L = NMe_3) as yellow crystals in good yields (eq 1).¹⁶ These are the first metal complexes of



neutral monoborane–Lewis base adducts with an unsupported M–H–B bond.^{17,18} They are also the second examples of fully characterized σ complexes of binary $[\text{M}(\text{CO})_5]$, following $[\text{M}(\text{CO})_5(\eta^1\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$ (**4**). When $[\text{Mo}(\text{CO})_6]$ was used as a precursor, formation of the corresponding molybdenum complexes $[\text{Mo}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{L})]$ (**3a**, L = PMe_3 ; **3b**, L = PPh_3 ;

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(16) Representation of σ complexes is somewhat confusing. The geometries of the M–H–B linkage in boron hydride complexes are essentially “end-on”, and M···B distances are sufficiently long, particularly in unidentate complexes (bidentate BH_4^- complexes necessarily involve close contact between metal and boron).⁵ Thus, $\eta^1\text{-BH}_4$ and $\eta^2\text{-BH}_4$ represent unidentate and bidentate BH_4^- ligands, respectively, where one and two BH σ bonds interact with the metal. On the other hand, silanes coordinate to metals in “side-on” fashion through a single Si–H σ bond, which is represented as “ $\eta^2\text{-silane}$ ”. Similarly, “ $\eta^2\text{-H}_2$ ” means a side-on dihydrogen ligand coordinating through a single σ bond. Throughout this paper, the unidentate borane ligands in complex **1–3** are represented as “ $\eta^1\text{-BH}_3\cdot\text{L}$ ”.



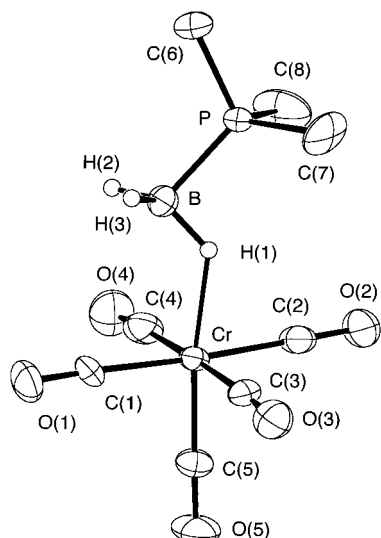


Figure 1. ORTEP diagram of $[\text{Cr}(\text{CO})_5(\text{BH}_3 \cdot \text{PMe}_3)]$ (**1a**) (thermal ellipsoids at 30% probability).

3c, $L = \text{NMe}_3$) was confirmed by NMR spectroscopy. However, isolation of **3** was not successful due to rapid decomposition. This is attributable to the particular lability of the molybdenum complexes among group 6 metal compounds.¹⁹ Also, in the $\text{B}_2\text{H}_4 \cdot 2\text{PMe}_3$ system, the unidentate molybdenum complex $[\text{Mo}(\text{CO})_5(\eta^1\text{-B}_2\text{H}_4 \cdot 2\text{PMe}_3)]$ was not isolated.¹⁴ Even in the Cr and W systems, the complexes of pyridineborane, $[\text{M}(\text{CO})_5(\eta^1\text{-BH}_3 \cdot \text{NC}_5\text{H}_5)]$ (**1d**, $\text{M} = \text{Cr}$; **2d**, $\text{M} = \text{W}$), were not stable enough to be isolated. We note that even prolonged photolysis did not give bidentate complexes of formula $[\text{M}(\text{CO})_4(\eta^2\text{-BH}_3 \cdot \text{L})]$. This contrasts with the group 6 metal–tetrahydroborate compounds, for which only the bidentate complexes $[\text{M}(\text{CO})_4(\eta^2\text{-BH}_4)]^-$ are obtained.⁶ Characterization of the new complexes was accomplished by NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction, by which the coordination mode of the borane ligand in the complexes was unequivocally established. We present the crystal structures of the compounds first, and the spectroscopic features will be discussed later.

ORTEP diagrams of **1a**, **1c**, **2a**, and **2b** are provided in Figures 1–4, respectively, with the atomic numbering schemes. Tables 4–7 summarize key geometrical parameters for **1a**, **1c**, **2a**, and **2b**, respectively. As evident in the figures, the borane–Lewis base adduct coordinates to the metal center through a B–H–M single bridge in these compounds. Each metal atom in the complexes has five carbonyl ligands, and the geometry around the central atom is approximately octahedral when the BH is regarded as one ligand. The positions of the hydrogen atoms attached to boron were determined by difference Fourier synthesis for **1a**, **2a**, and **2b**, for which the data collection was carried out at low temperature. The conformations around the B–P axis are all staggered. For **1c**, the reflection data were collected at ambient temperature, and the coordinates of the hydrogen atoms were calculated assuming a staggered conformation around the B–N bond. As the structural features of **1a**,

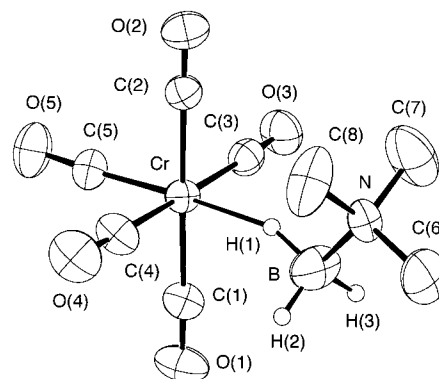


Figure 2. ORTEP diagram of $[\text{Cr}(\text{CO})_5(\text{BH}_3 \cdot \text{NMe}_3)]$ (**1c**) (thermal ellipsoids at 30% probability).

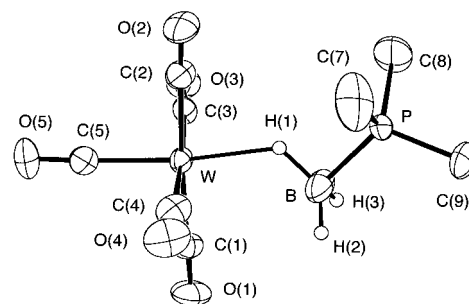


Figure 3. ORTEP diagram of $[\text{W}(\text{CO})_5(\text{BH}_3 \cdot \text{PMe}_3)]$ (**2a**) (thermal ellipsoids at 30% probability).

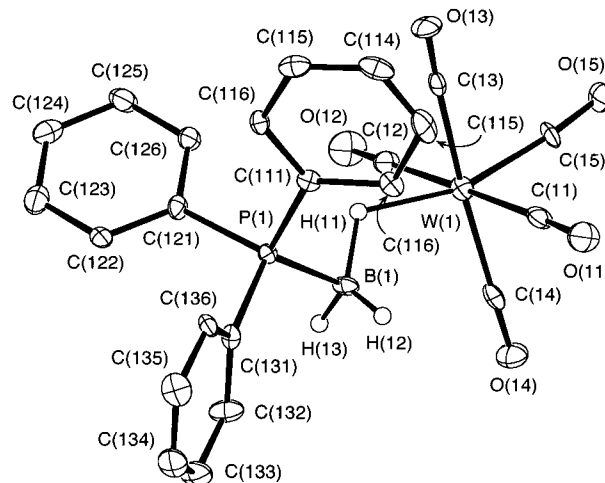


Figure 4. ORTEP diagram of molecule A of $[\text{W}(\text{CO})_5(\text{BH}_3 \cdot \text{PPh}_3)]$ (**2b**) (thermal ellipsoids at 30% probability). Hydrogen atoms on aromatic rings are omitted for clarity.

1c, **2a**, and **2b** are almost identical except for the Lewis base on the boron atom, the details of the structure of **1a**, which has smaller standard deviations, are primarily described below.

When the C(5)–Cr axis is extended beyond the Cr atom, it crosses the midpoint of the B–H(1) bond. Although the Cr–H(1)–B bridge is tilted with a bond angle of $130(8)^\circ$, the coordination mode of $\text{BH}_3 \cdot \text{PMe}_3$ is essentially “end-on”. This clearly indicates that the bonding between the chromium and the borane is a three-center two-electron bond. The bond angle of Cr–H(1)–B is roughly comparable to the corresponding M–H–B angles in the η^1 -tetrahydroborate complexes, $[(\text{Ph}_2\text{MeP})_3\text{Cu}(\eta^1\text{-BH}_4)]$ (121.7°)⁹ and $[\text{V}(\eta^1\text{-BH}_4)_2(\text{dmpe})_2]$ (140°) ($\text{dmpe} = \text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2$).²⁰ An η^1 -borohydride complex

(17) Two complexes with a BH_3 -inner base adduct coordinating to the metal center, $[(\text{Me}_3\text{P})_2(\text{OC})\text{Fe}\{\text{CH}(\text{SMe})\text{S}\cdot\text{BH}_3\}]$ (**6**)^{17a} and $[\text{Cp}(\text{CO})_2\text{Mo}(\text{P}(\text{BH}_3)\text{Ph}\{\text{N}(\text{SiMe}_3)_2\})]$ (**7**),^{17b} have been reported. (a) Khasnis, D. V.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1987**, 230. (b) McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kollé, P.; Nöth, H. *Organometallics* **1986**, *5*, 380.

(18) Quite recently, coordination of a BH_3 -inner base adduct to Rh in a bidentate fashion was reported: Macias, R.; Rath, N. P.; Barton, L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 162.

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(20) Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4450.

Table 1. NMR Spectral Data for Borane Complexes^a

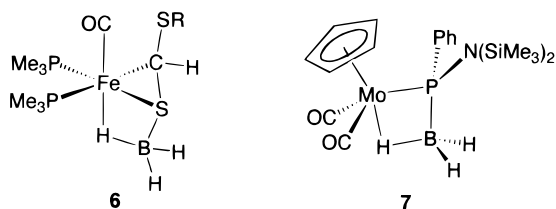
compound [M(CO) ₅ (BH ₃ ·L)]	¹ H NMR (200 MHz)		¹¹ B{ ¹ H} NMR (28.8 MHz)
	BH ₃ ·L	BH ₃ ·L	
[Cr(CO) ₅ (BH ₃ ·PMe ₃)] (1a)	0.34 (d, <i>J</i> (PH) = 11.1 Hz)	−3.8 (br q, <i>J</i> (BH) = 85 Hz)	−42.8 (d, <i>J</i> (BP) = 71 Hz)
[Cr(CO) ₅ (BH ₃ ·PPh ₃)] (1b)	6.8–7.1, 7.2–7.4 (m)	−2.8 (br, <i>J</i> (BH) = 80 Hz)	−41.9 (br)
[Cr(CO) ₅ (BH ₃ ·NMe ₃)] (1c)	1.60 (s)	−3.3 (br q, <i>J</i> (BH) = 86 Hz)	−13.4 (br)
[Cr(CO) ₅ (BH ₃ ·NC ₅ H ₅)] (1d)	7.64 (d, <i>J</i> = 5.2 Hz, 2-CH) 6.5–6.7 (m, 4-CH) 6.1–6.3 (m, 3-CH)	−2.0 (br q, <i>J</i> (BH) = 84 Hz)	−18.2 (br)
[W(CO) ₅ (BH ₃ ·PMe ₃)] (2a)	0.30 (d, <i>J</i> (PH) = 11.2 Hz)	−2.1 (br q, <i>J</i> (BH) = 82 Hz)	−47.0 (d, <i>J</i> (BP) = 74 Hz)
[W(CO) ₅ (BH ₃ ·PPh ₃)] (2b)	6.8–7.1, 7.2–7.4 (m)	−1.2 (br, <i>J</i> (BH) = 80 Hz)	−46.3 (br)
[W(CO) ₅ (BH ₃ ·NMe ₃)] (2c)	1.60 (s)	−1.5 (br q, <i>J</i> (BH) = 81 Hz)	−17.7 (br)
[W(CO) ₅ (BH ₃ ·NC ₅ H ₅)] (2d)	7.64 (d, <i>J</i> = 5.4 Hz, 2-CH) 6.5–6.7 (m, 4-CH) 6.1–6.3 (m, 3-CH)	−0.1 (br q, <i>J</i> (BH) = 86 Hz)	
[Mo(CO) ₅ (BH ₃ ·PMe ₃)] (3a)	0.40 (d, <i>J</i> (PH) = 11.1 Hz)	−2.0 (br q, <i>J</i> (BH) = 87 Hz)	
[Mo(CO) ₅ (BH ₃ ·PPh ₃)] (3b)	6.8–7.1, 7.2–7.5 (m)	−1.0 (br, <i>J</i> (BH) = 85 Hz)	
[Mo(CO) ₅ (BH ₃ ·NMe ₃)] (3c)	1.60 (s)	−1.4 (br q, <i>J</i> (BH) = 86 Hz)	−15.4

^a NMR spectra were recorded in C₆D₆.

Table 2. IR Spectral and Analytical Data for Isolated Complexes

compd	IR (KBr)/cm ^{−1}		anal. found (calcd)
	ν(BH)	ν(CO)	
1a	2455 (w), 2410 (w)	2065 (m), 1995 (sh), 1950 (sh), 1930 (vs), 1890 (s), 1870 (s), 1840 (sh)	C, 33.78; H, 4.30 (C, 34.08; H, 4.29)
1b	2450 (w), 2405 (w)	2055 (m), 1992 (m), 1980 (m), 1950 (sh), 1920 (vs), 1890 (s)	C, 58.88; H, 4.10 (C, 59.01; H, 3.88)
1c	2460 (w), 2430 (w)	2140 (w), 2060 (m), 1995 (s), 1950 (vs), 1930 (vs), 1895 (s), 1870 (s)	C, 35.15; H, 4.60; N, 5.07 (C, 36.26; H, 4.56; N, 5.29)
2a	2450 (w), 2400 (w)	2075 (m), 1982 (sh), 1940 (sh), 1925 (vs), 1880 (s), 1860 (s)	C, 22.98; H, 2.72 (C, 23.22; H, 2.92)
2b	2460 (w), 2420 (w)	2075 (w), 1990 (m), 1975 (m), 1940 (sh), 1918 (vs), 1885 (m)	C, 45.78; H, 3.14 (C, 46.04; H, 3.02)
2c	2460 (w), 2420 (w)	2070 (m), 1985 (s), 1940 (vs), 1920 (vs), 1880 (s), 1860 (s)	C, 24.26; H, 2.71; N, 3.21 (C, 24.21; H, 3.05; N, 3.53)

[FeH(dppe)₂(η¹-BH₄)] (dppe = PPh₂CH₂CH₂PPh₂), with a significantly large M–H–B angle (162°), has also been reported.²¹ The bond distance of B–H(1) (1.12(11) Å) is longer by ca. 10% than those of B–H(2) and B–H(3) (0.97(17) and 0.94(7) Å, respectively). This is attributed to the decrease of the bond order between B and H(1) due to coordination to the chromium atom. Similar lengthening of the B–H bonds has been observed in the foregoing η¹-BH₄ compounds and the complexes of a borane–inner base adduct, [(Me₃P)₂(OC)Fe{CH(SMe)S·BH₃}] (**6**)^{17a} and [Cp(CO)₂Mo(P(BH₃)Ph{N(SiMe₃)₂})] (**7**),^{17b} although the M–H–B bond angles of **6** and **7**



are much narrower than those of **1** and **2**. The degree of B–H bond extension in **1** and **2** is less pronounced than that of the Si–H bond in many of the η²-hydrosilane complexes (around 20% elongation in [CpMn(CO)₂(η²-HSiR₃)] and related systems)²² but is rather close to those of most η²-dihydrogen

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(22) (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, 30, 151. (b) Schubert, U.; Ackermann, K.; Wörle, B. *J. Am. Chem. Soc.* **1982**, 104, 7378. (c) Schubert, U.; Bahr, K.; Müller, J. *J. Organomet. Chem.* **1987**, 327, 357. (d) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, 6, 469. (e) Colomer, K.; Corriu, R. J. P.; Manzin, C.; Viox, A. *Inorg. Chem.* **1982**, 21, 368. (f) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K.; Wörle, B.; Stansfield, R. F. D. *J. Organomet. Chem.* **1986**, 306, 303.

complexes (around 10%)²³ as well as complexes with an agostic CH bond (<10%).²⁴ Thus, the borane complexes **1** and **2** may be classified as unstretched σ complexes.^{25,26}

The interatomic distance between Cr and C(5) (*trans* carbonyl to the borane ligand) is substantially shorter (1.95 Å) than those between Cr and the carbon atoms of the carbonyl ligands in the *cis* positions (2.03–2.05 Å). This is explained by the enhanced back-donation to the *trans* carbonyl ligand caused by the poor π-acidity of the borane ligand (*vide infra*). Moreover, the carbonyl ligands in the *cis* positions slightly tilt toward BH₃·L. This “umbrella effect” also reflects the σ donor character of the borane ligands in **1** and **2**.²⁷

Spectroscopic Features and Dynamic Behavior of 1–3.

Based on the crystal structures, it could be expected that complexes **1–3** would reveal a signal for the coordinating BH as well as one for the terminal BH atoms in a 1:2 intensity

(23) (a) Kubas, G. *J. Acc. Chem. Res.* **1988**, 21, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, 23, 95. (c) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, 92, 155. (d) Heinkey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, 93, 913.

(24) (a) Green, M. L. H. *J. Organomet. Chem.* **1983**, 205, 395. (b) Schulz, A. *J. Science* **1983**, 220, 197. (c) Brookhart, M.; Green, M. L. H.; Wang, L. L. *Prog. Inorg. Chem.* **1988**, 36, 1.

(25) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 789.

(26) Only a few examples are known for stretched η²-H₂ complexes (e.g., [Re(η²-H₂)H₃{P(*p*-C₆H₄Me)₃}₂]}^{26a} and unstretched η²-silane complexes (e.g., [(OC)₄W=C(NMe₂)SiHMe₂]}^{26b}, [(Cp₂Ti)₂(μ-SiH₂Ph)₂], and [(Cp₂Ti)₂(μ-H)(μ-SiH₂Ph)]^{26c}). (a) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241. (b) Schubert, U.; Schwarz, M.; Müller, F. *Organometallics* **1994**, 13, 1554. (c) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, 108, 4059.

(27) (a) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, 25, 805. (b) Simpson, C. Q., II; Hall, M. B. *J. Am. Chem. Soc.* **1992**, 114, 1641. (c) Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.* **1995**, 128, 831. (d) Weiss, J.; Stetzcamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 70.

Table 3. Crystal Data for **1a**, **1c**, **2a**, and **2b**

	1a	1c	2a	2b
sample formula	[Cr(CO) ₅ (η ¹ -BH ₃ ·PMe ₃)]	[Cr(CO) ₅ (η ¹ -BH ₃ ·NMe ₃)]	[W(CO) ₅ (η ¹ -BH ₃ ·PMe ₃)]	[W(CO) ₅ (η ¹ -BH ₃ ·PPh ₃)]
fw	C ₈ H ₁₂ BCrO ₅ P	C ₈ H ₁₂ BCrO ₅ N	C ₈ H ₁₂ BO ₅ PW	C ₂₃ H ₁₈ BO ₅ PW
color of crystal	yellow	yellow	yellow	yellow
temp/°C	-60	20	-50	-90
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group		<i>P</i> 2 ₁ / <i>n</i> (variant of no. 14)		<i>P</i> 1 (no. 2)
system absence		(<i>h</i> 0 <i>l</i>): <i>h</i> + <i>l</i> = 2 <i>n</i> + 1; (0 <i>k</i> 0): <i>k</i> = 2 <i>n</i> + 1		
<i>a</i> /Å	12.540(5)	12.596(6)	12.629(3)	10.491(2)
<i>b</i> /Å	10.065(2)	9.785(2)	10.195(3)	24.302(7)
<i>c</i> /Å	12.387(5)	12.014(5)	12.363(4)	9.261(2)
α/deg	90.0	90.0	90.0	90.33(2)
β/deg	118.62(3)	117.46(6)	118.02(2)	101.27(2)
γ/deg	90.0	90.0	90.0	94.43(2)
<i>V</i> /Å ³	1372.1(9)	1314.0(7)	1405.1(7)	2308.0(9)
<i>Z</i>	4	4	4	4
<i>d</i> _{calcd} /g cm ⁻³	1.36	1.34	1.96	1.73
μ (Mo Kα)	9.84	9.10	88.2	54.0
crystal size/mm	0.43 × 0.20 × 0.13	0.20 × 0.15 × 0.10	0.20 × 0.13 × 0.10	0.30 × 0.20 × 0.10
radiation		Mo Kα (λ = 0.710 69 Å)		
monochromator		graphite		
reflens measd	± <i>h</i> , + <i>k</i> , + <i>l</i>	± <i>h</i> , + <i>k</i> , + <i>l</i>	± <i>h</i> , + <i>k</i> , + <i>l</i>	± <i>h</i> , ± <i>k</i> , + <i>l</i>
2θ range/deg	3–60	3–50	3–60	3–50
scan mode			2θ – ω	
ω scan width/deg	1.575 + 0.30 tan θ	1.1 + 0.30 tan θ	0.84 + 0.30 tan θ	1.2 + 0.30 tan θ
ω-scan rate/deg min ⁻¹	2.0	2.0 (3–40°), 1.0 (40–50°)	2.0	8.0
no. of unique data	4290	2465	4300	7143
no. of data used with <i>F</i> _o > 3σ(<i>F</i> _o)	1541	1193	2510	5527
no. of params refined	158	158	158	560
<i>R</i>	0.087	0.063	0.049	0.050
<i>R</i> _w	0.098	0.106	0.057	0.063
GOOF	2.38	0.81	2.52	1.70
largest shift/esd, final cycle	0.16	0.10	0.089	0.060
max resid electron dens/Å ³	0.62	0.40	1.32	1.66

Table 4. Key Geometrical Parameters for [Cr(CO)₅(BH₃·PMe₃)] (**1a**)

Distances (Å)			
Cr–H(1)	1.94(10)	Cr···B	2.79(1)
B–H(1)	1.12(11)	B–H(2)	0.97(17)
B–H(3)	0.94(7)	B–P	1.85(1)
Cr–C(1)	1.90(1)	Cr–C(2)	1.89(1)
Cr–C(3)	1.90(1)	Cr–C(4)	1.89(2)
Cr–C(5)	1.84(1)		
Angles (deg)			
Cr–H(1)–B	130(8)	P–B–H(1)	95(5)
H(1)–Cr–C(1)	94(3)	H(1)–Cr–C(2)	82(3)

Table 5. Key Interatomic Distances (Å) for [Cr(CO)₅(BH₃·NMe₃)] (**1c**)

Cr···B	2.873(15)	B–N	1.534(14)
Cr–C(1)	1.91(1)	Cr–C(2)	1.89(1)
Cr–C(3)	1.92(1)	Cr–C(4)	1.88(2)
Cr–C(5)	1.82(1)		

ratio in the ¹H NMR spectra. In the actual spectra, however, **1–3** show only one BH signal at –1.0 to –3.8 ppm with integral intensity of three protons (Table 1). The observed chemical shifts of the BH signals are considered to be the weighted average of typical values of chemical shifts for the terminal BH protons and that for the metal-coordinating BH proton (in general, hydrogen atoms terminally bound to boron resonate at 1–2 ppm, while signals of BH atoms coordinated to transition metals are found around –10 ppm). This clearly indicates that the bridging hydrogen atom and the terminal hydrogen atoms in **1–3** are exchanging their positions faster than the NMR time scale in solution (Scheme 2). This process is so fast that it is not frozen out, even at low temperature. The ¹H NMR spectrum (the BH

Table 6. Key Geometrical Parameters for [W(CO)₅(BH₃·PMe₃)] (**2a**)

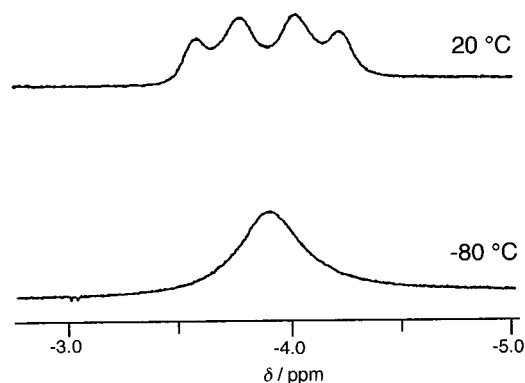
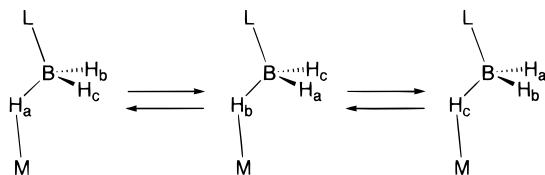
Distances (Å)			
W–H(1)	2.01(9)	W···B	2.86(2)
B–H(1)	1.14(10)	B–H(2)	1.14(28)
B–H(3)	0.92(12)	B–P	1.85(1)
W–C(1)	2.05(1)	W–C(2)	2.04(1)
W–C(3)	2.05(2)	W–C(4)	2.05(2)
W–C(5)	1.97(1)		
Angles (deg)			
W–H(1)–B	128(7)	P–B–H(1)	92(5)
H(1)–W–C(1)	96(2)	H(1)–W–C(2)	80(2)

region) of **1a** is shown in Figure 5. The broad quartet of the BH protons does not decoalesce, even at –80 °C, although it is sharpened by quadrupole-induced thermal decoupling.²⁸ The activation energy Δ*G*[‡] for the hydrogen exchange process at 193 K is estimated to be less than 30 kJ mol⁻¹, assuming conventional values for the original chemical shifts for the bridging BH and the terminal BH's in **1–3**. This value is much lower than the energy expected for dissociation of the borane ligand (see later section). Thus, the BH scrambling proceeds through the concerted site exchange of the hydrogen atoms in the coordination sphere rather than a dissociation–recombination mechanism. At the transition state, the borane ligand should interact in an η²-fashion with the metal center. Fluxional behavior due to the exchange between the bridging and terminal hydrogen atoms was also observed for the unidentate B₂H₄·

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Table 7. Key Geometrical Parameters for $[\text{W}(\text{CO})_5(\text{BH}_3\cdot\text{PPh}_3)]$ (**2b**)

	molecule A	molecule B		molecule A	molecule B
Distances (Å)					
W–H(1)	1.91	1.75	W...B	2.845(13)	2.812(14)
B–H(1)	1.38	1.19	B–H(2)	0.87	1.10
B–H(3)	1.05	0.97	B–P	1.900(15)	1.936(14)
W–C(1)	2.030(14)	2.054(13)	W–C(2)	2.065(13)	2.055(15)
W–C(3)	2.052(12)	2.041(12)	W–C(4)	2.080(13)	2.034(11)
W–C(5)	1.953(11)	1.984(12)			
Angles (deg)					
W–H(1)–B	119.0	146.3	P–B–H(1)	96.5	109.5
H(1)–W–C(3)	79.9	101.0	H(1)–W–C(4)	87.2	92.8

**Figure 5.** BH region in the ^1H NMR spectrum of **1a**.**Scheme 2**

2PMe₃ complex $[\text{M}(\text{CO})_5(\eta^1\text{-B}_2\text{H}_4\cdot 2\text{PMe}_3)]$ (**4**), in which the exchange took place not only between geminal hydrogens but also with vicinal hydrogens.¹⁴

Similar fluxionality has been reported for an η^1 -silylborohydride complex $[\text{Cp}_2\text{Ta}(\text{PMe}_3)\{\eta^1\text{-BH}_3(\text{SiHt-Bu}_2)\}]$ ($\Delta G^\ddagger = 34.7$ kJ mol⁻¹ at 215 K).²⁹ Similarly, only a coalesced BH signal was observed for the η^1 -tetrahydroborate complex, $[(\text{MePh}_2\text{P})_3\text{-Cu}(\eta^1\text{-BH}_4)]$,⁷ and the iron complex of a borane–inner base adduct, **6**.^{17a} On the other hand, in another borane–inner base complex, **7**, the bridging hydrogen and the terminal hydrogen atoms are separately observed.^{17b} Exchange between bridging and terminal hydrogen atoms has also been found for bidentate BH₄⁻ complexes, but the barriers to bridging–terminal interchange are generally larger than those of **1–3**.⁵ For example, the free energy of activation for the H_t–H_b interchange in $[\text{Mo}(\text{CO})_4(\eta^2\text{-BH}_4)]^-$ was reported to be 42 kJ mol⁻¹ at 231 K.⁶ Kubas and co-workers recently reported an η^2 -SiH₄ complex $[\text{Mo}(\text{depe})_2(\text{CO})(\eta^2\text{-SiH}_4)]$ (depe = PEt₂CH₂CH₂PEt₂), which is in equilibrium with a silyl(hydrido) complex.^{16,30,31} Interconversion between an η^2 -H₂ complex and a dihydrido complex is also occasionally found in polyhydride compounds.^{23,32} Likewise, a niobocene derivative, Cp₂Nb(H₂Bcat), is known to exist

(29) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177.

(30) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.

(31) Lin et al. suggested a possibility that Kubas's complex $[\text{Mo}(\text{depe})_2(\text{CO})(\eta^2\text{-SiH}_4)]$ is in equilibrium not with the hydrido(silyl) complex but with an isomer generated by the rotation of the silane ligand: Fan, M.-F.; Jia, G.; Lin, Z. *J. Am. Chem. Soc.* **1996**, *118*, 9915.

as an equilibrium mixture of the Nb(III) η^2 -borohydrido complex and the Nb(V) boryl(dihydrido) complex.³³ However, a similar equilibrium (between borane complexes and boryl(hydrido) complexes) is not observed in **1–3**.

The apparent coupling constants $^1J(\text{BH})$ of **1–3** are 80–87 Hz, which are smaller by ca. 10 Hz than those of free BH₃·L. Since the $^1J(\text{BH}_b)$ and $^1J(\text{BH}_t)$ values are averaged by the fast scrambling of BH's, the real values of $^1J(\text{BH}_b)$ can be estimated to be around 60 Hz on the assumption that the value of $^1J(\text{BH}_t)$ is the same as that of free BH₃·L. This value corresponds to ca. 65% of $^1J(\text{BH})$ of free BH₃·L (95.0 Hz for BH₃·PMe₃, 92.5 Hz for BH₃·PPh₃, 91.5 Hz for BH₃·NMe₃) and falls into the range of the reduction percentage of the J values of unstretched σ complexes (e.g., $J(\text{HD})$ values in most η^2 -HD complexes are 22–35 Hz, whereas that of free HD is 43 Hz: $J_{\text{coord}}/J_{\text{free}} = 50\text{--}80\%$).²³ For $[\text{CpRe}(\text{CO})_2(\text{cyclo-C}_5\text{H}_{10})]$, the alkane complex directly observed by NMR,³⁴ the coupling constant of the coordinating CH was observed to be 96 Hz, which is reduced by 74% from that of free cyclopentane. In the ¹¹B NMR spectra, the coordinated boranes in **1–3** resonate at higher field than free boranes.

In the IR spectra of **1** and **2**, two bands assignable to the terminal BH stretching are observed at 2400–2460 cm⁻¹. These frequency values are slightly higher than those for free BH₃·L. We were not able to identify the $\nu(\text{BH}_{\text{brid}})$ bands, probably because they are overlapped by the strong $\nu(\text{CO})$ bands. The average position of the $\nu(\text{CO})$ bands (1950–1870 cm⁻¹) is ca. 30 cm⁻¹ lower in frequency than that for $[\text{M}(\text{CO})_6]$. This also reflects the weak π -accepting ability of the BH₃·L ligand.

Coordination of BH₃·L to the metal in **1–3** is very weak, and the boranes readily dissociate in solution. When solid $[\text{M}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{L})]$ (M = Cr, W) was dissolved in C₆D₆ under vacuum, an intractable brown precipitate gradually formed, and the signals of free BH₃·L appeared in the NMR spectra. Complexes **1a** and **2a** liberate the BH₃·PMe₃ ligand under high vacuum even in the solid state. This is attributable to the volatility of BH₃·PMe₃. Dissociation of borane ligands from the complexes is more significant in the presence of other ligands. When a solution of **1a** or **2a** was photolytically generated in a sealed NMR tube and left at room temperature, growth of the signal of free BH₃·PMe₃ and decrease of that of the complex were observed with concomitant precipitation of $[\text{M}(\text{CO})_6]$. This demonstrates that BH₃·PMe₃ in the complex is replaced by CO in the closed system, which is the reverse reaction of eq 1. Irradiation of the resulting mixture reproduces complex **1a** or **2a**. In the Mo system, the borane complexes are

(32) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(33) Hartwig, J. F.; De Gala, R. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

(34) Recently, a rhenium alkane complex, CpRe(CO)₂(cyclopentane), was directly observed by NMR: Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.

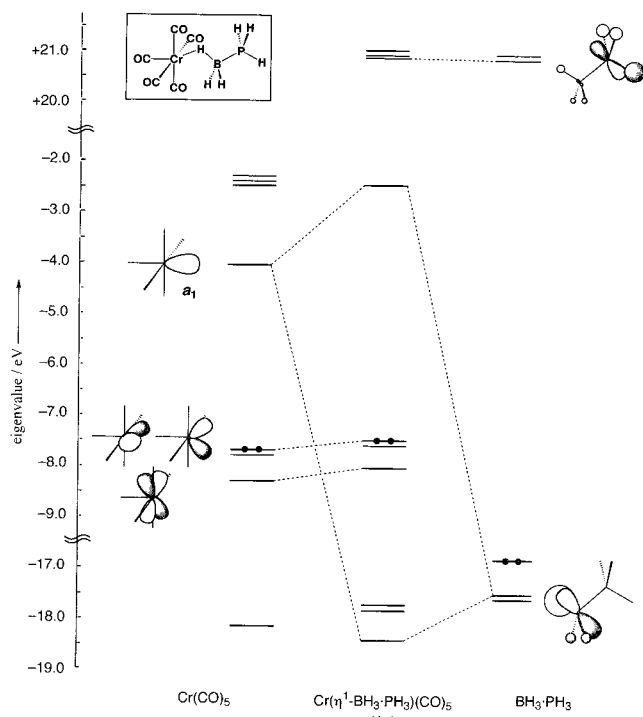


Figure 6. Correlation diagram of $[\text{Cr}(\text{CO})_5]$ with $\text{BH}_3\cdot\text{PH}_3$ obtained by Fenske–Hall MO calculations.

extremely labile and the coordinated $\text{BH}_3\cdot\text{L}$ is rapidly replaced by CO in the system, so **3** could not be isolated.

Discussion

Molecular Orbitals of the Borane Complexes. To better understand the bonding in the borane complexes **1–3**, Fenske–Hall MO calculations were carried out for a model compound $[\text{Cr}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{PH}_3)]$ (**1e**).³⁵ Figure 6 illustrates the correlation diagram of the molecular orbitals of **1e**. The bonding orbital between Cr and the borane ligand is generated by the overlap of the empty a_1 orbital of $[\text{Cr}(\text{CO})_5]$ with one of the degenerate next HOMOs, which has the character of a BH bonding orbital, of $\text{BH}_3\cdot\text{PH}_3$ (the HOMO of $\text{BH}_3\cdot\text{PH}_3$ is essentially a bonding orbital of BP). The almost triply degenerate HOMOs of **1e** are derived from the “ t_{2g} ” set of $[\text{Cr}(\text{CO})_5]$. They are completely nonbonding and scarcely include components of the atomic orbitals of the bridging hydrogen and boron. In other words, there is almost no back-donation from the filled d orbital of chromium to the $\text{BH}\sigma^*$ orbital. One of the reasons should be the fact that $[\text{Cr}(\text{CO})_5]$ is predominantly a σ acceptor and only a weak π donor.³⁶ However, it is still in contrast to the orbital interactions in $[\text{Cr}(\eta^2\text{-H}_2)(\text{CO})_5]$ shown by Saillard and Hoffmann, where Cr back-donation into the H_2 σ^* orbital is small but significant.³⁷ The doubly degenerate LUMOs of $\text{BH}_3\cdot\text{PH}_3$ are essentially of $\text{PH}\sigma^*$ character, in which the coefficients of the AOs of the BH's and the boron atom are very small. The antibonding σ^* orbital of BH is energetically so high (93.0 eV, not depicted in Figure 6) that it cannot interact with the d_{xz} orbital of Cr, even though it has allowed symmetry. Thus, we can describe the bonding between the metal and the borane

ligand in **1–3** as donation of the bonding electron pair of BH to the vacant a_1 orbital of $[\text{M}(\text{CO})_5]$. This is consistent with the end-on coordination mode of the borane ligand in **1–3**. It also accounts well for the fact that the BH is not stretched so much during the complexation, and the bond distance between Cr and C(5) is significantly shorter than those between Cr and carbon atoms of *cis* carbonyls in **1a**, **1c**, **2a**, and **2b**. Finally, the bonding orbital generated by the a_1 of $[\text{Cr}(\text{CO})_5]$ and the next HOMOs of $\text{BH}_3\cdot\text{PH}_3$ is strongly characterized by the latter. This can explain the lability of the borane ligand and the fluxional behavior found in the complexes.

Recently, the σ complexes of tricoordinate catecholborane (HBcat), $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$ and $[\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{HBcat})]$, were reported by Hartwig and co-workers.^{38–40} In these compounds, HBcat ligands bind to Ti(II) in side-on fashion. The MO calculation for $[\text{Cp}_2\text{Ti}\{\text{HB}(\text{OH})_2\}_2]$ (a model compound of $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$) showed that HBcat ligands function as an acceptor with the empty p orbital of the boron atom.^{38,40} Our study demonstrates that tricoordinate boranes and tetracoordinate borane–Lewis base adducts are quite different in their manner of coordination to a metal.

Complexes 1–3 as Model Compounds of Alkane Complexes. Coordination of an alkane to an unsaturated metal center has been one of the most interesting interactions in organometallic chemistry.^{41–43} The first evidence for the existence of such interactions came from studies on photochemically generated $[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in alkane matrixes. Turner and co-workers demonstrated that $[\text{M}(\text{CO})_5(\text{alkane})]$ and $[\text{M}(\text{CO})_5(\text{noble gas})]$ complexes are produced after the photolyses of $[\text{M}(\text{CO})_6]$ in alkane and noble gas matrixes, respectively.⁴⁴ A dihydrogen complex $[\text{M}(\text{CO})_5(\text{H}_2)]$ has also been reported as the short-lived product of photolysis of $[\text{M}(\text{CO})_6]$ in an inert medium containing H_2 .^{3,45} These species are, however, extremely labile, so structural details are not clear. Concerning the bonding between the alkane and metal in $[\text{M}(\text{CO})_5(\text{alkane})]$, it is possible to suppose a C–H–M three-center two-electron bond as found in intramolecular agostic interactions.²⁴ Indeed, a recent theoretical study indicates that the most stable geometry of $[\text{W}(\text{CO})_5(\text{CH}_4)]$ has a bent C–H–M linkage.⁴ The borane complexes **1–3** are closely related to the methane complexes $[\text{M}(\text{CO})_5(\text{CH}_4)]$, since $\text{BH}_3\cdot\text{L}$ is isoelectronic with CH_4 .

For **1–3**, the structural features (lengthening of the BH bond on coordination is small and the M–H–B angle is wide) and spectroscopic data (reduction of the $^1J_{\text{BH}}$ coupling constants is also small) indicate that the borane complexes correspond to an earlier stage on the reaction coordinate of oxidative addition if we adopt the notion that the bonding in σ complexes is “incomplete oxidative addition”. This is very similar to most $\eta^2\text{-H}_2$ complexes and complexes with an agostic C–H–M interaction. Moreover, as described in the previous section, π

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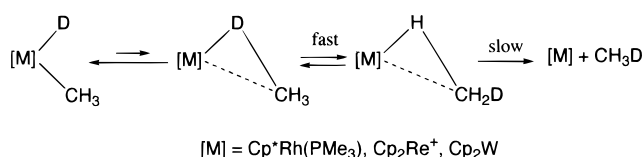
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Scheme 3



back-donation from the metal d orbital to the BH σ^* orbital of the borane ligand is negligible in **1–3**. This is in sharp contrast to the η^2 -silane and η^2 -H₂ complexes, in which these σ ligands have been shown to be π -acceptors (it is particularly significant for η^2 -silanes) theoretically^{37,46} and experimentally.⁴⁷ Thus, the π -acidities of the σ ligands are in the following order: silanes > H₂ > BH₃·L. It is presumed that the poor accepting ability of BH₃·L is very similar to those of alkanes. A question arises here: Why does BH₃·L form more stable complexes with [M(CO)₅] than H₂ despite its poor π -acidity? A possible explanation is that, because BH is more basic than H₂ (and CH), the BH bonding orbitals are higher than those of H₂ and CH in energy, and the BH bond is polarized in a B(+)-H(-) fashion. This idea is supported by the fact that complexes of less basic pyridineborane, **1d** and **2d**, are not stable enough to be isolated. For the [Cr(R₃SiH)(CO)₅] system, silanes possessing electron-releasing groups bind more strongly to [Cr(CO)₅].³⁶ This trend is similar to the case for the borane complexes and is opposed to other metal–silane systems.

In the ¹H NMR spectrum of the alkane complex [CpRe(CO)₂-(cyclo-C₅H₁₀)], the coordinating hydrogen atom is observed as a coalesced signal with the geminal hydrogen atom at -100 °C.³⁴ Theoretical work has also shown that the activation energy for the scrambling of the hydrogen atoms in [W(CO)₅(CH₄)] is very small.⁴ These properties of the alkane complexes are similar to the fluxional character of the borane complexes **1–3**. The dynamic behavior of **1–3** is also closely related to the isotope exchange in intermediate methane complexes, which proceeds faster than elimination of CH₃D (Scheme 3).^{48–50} Periana and Bergman first proposed the role of a methane σ complex as an intermediate for the rhodium system based on careful labeling experiments.⁴⁸ In all cases, HD site exchange was shown to be faster than methane elimination. Similar hydrogen scrambling has been observed by ¹H NMR for a methyl-osmium complex, [Cp*Os(H)Me(dmpm)]⁺ (dmpm = PMe₂CH₂PMe₂).⁵¹ Although the borane ligand in **1–3** readily dissociates as described above, the interchange of the BH's is much faster than its dissociation.

As mentioned above, the properties of **1–3** are very similar to those of alkane complexes. The alkane in [M(CO)₅(alkane)] is occasionally termed a “token ligand”.⁵² This work has visualized the “token ligand” by the use of isoelectronic borane–Lewis base adducts.

Experimental Section

All manipulations were carried out under high vacuum or a dry nitrogen atmosphere. Reagent-grade pentane, hexane, toluene, and THF were distilled under a nitrogen atmosphere from sodium-benzophenone ketyl just before use. Benzene-*d*₆ and toluene-*d*₈ were dried over potassium mirrors before use and transferred into NMR tubes under

vacuum. BH₃·PMe₃, BH₃·PPh₃, BH₃·NMe₃, and BH₃·NC₅H₅ were prepared by treatment of B₂H₆ with the corresponding bases under vacuum.⁵³ [Cr(CO)₆] and [Mo(CO)₆] (Strem) and [W(CO)₆] (Aldrich) were used as purchased. ¹H NMR spectra were recorded on Varian XL-200 and JEOL GX-400 spectrometers. ¹¹B and ³¹P NMR spectra were recorded on JEOL FX-90Q and JEOL α -500 spectrometers. IR spectra were recorded on JASCO IR-810, JASCO FTIR-350, and Bruker IFS66v spectrometers. NMR data of the new complexes obtained in this work are listed in Table 1. IR and analytical data for the isolated compounds are listed in Table 2.

Synthesis of [Cr(CO)₅(η^1 -BH₃·PMe₃)] (1a). A Pyrex glass tube (22 mm o.d.) was charged with [Cr(CO)₆] (67 mg, 0.30 mmol) and BH₃·PMe₃ (27 mg, 0.30 mmol). Toluene (8 mL) was transferred to the sample tube by conventional trap-to-trap distillation. The resulting suspension was photolyzed using a 450-W medium-pressure Hg lamp with stirring at 0 °C under high vacuum. During the photolysis, a yellow color developed, and evolution of CO was observed. After irradiation of the suspension for 1 h, the evolved CO in the reaction vessel was completely removed by freeze–pump–thaw cycles, and then the mixture was irradiated again for 1 h. The resulting solution was evaporated to dryness at -15 °C. Recrystallization of the yellow residue from pentane at -20 °C afforded **1a** (70 mg, 0.25 mmol, 88%) as air- and moisture-sensitive yellow crystals.

Other borane complexes were prepared by a similar procedure. The yields were as follows: [Cr(CO)₅(η^1 -BH₃·PPh₃)] (**1b**), 94%; [Cr(CO)₅(η^1 -BH₃·NMe₃)] (**1c**), 87%; [W(CO)₅(η^1 -BH₃·PMe₃)] (**2a**), 93%; [W(CO)₅(η^1 -BH₃·PPh₃)] (**2b**), 88%; [W(CO)₅(η^1 -BH₃·NMe₃)] (**2c**), 24%. Mass spectra of these compounds gave poor data, probably due to their easy fragmentation. Therefore, only the mass spectral data of **1c** and **2c** are given. **1c** (EI, 25 eV): *m/z* 265 (0.7, M⁺ based on ¹⁸⁴W), 237 (1.7, M⁺ - CO), 209 (5.7, M⁺ - 2CO), 153 (M⁺ - 4CO), 125 (26.4, M⁺ - 5CO), 192 (8.8, Cr(CO)₅⁺), 164 (10.4, Cr(CO)₄⁺), 136 (9.5, Cr(CO)₃⁺), 108 (33.0, Cr(CO)₂⁺), 80 (100, Cr(CO)⁺), 52 (85.2, Cr⁺), 72 (32.0, BH₂·NMe₃⁺). **2c** (EI, 25 eV): *m/z* 369 (9.9, M⁺ - CO based on ¹⁸⁴W), 352 (100, W(CO)₆⁺), 341 (3.2, M⁺ - 2CO), 324 (13.3, W(CO)₅⁺).

Formation of [Mo(CO)₅(η^1 -BH₃·PMe₃)] (3a). A Pyrex NMR tube equipped with a high-vacuum stopcock was charged with [Mo(CO)₆] (ca. 0.05 mmol) and BH₃·PMe₃ (0.05 mmol) and evacuated. Benzene-*d*₆ (0.5 mL) was introduced into the NMR tube. The resulting suspension was irradiated at ca. 5 °C using a 450-W medium-pressure Hg lamp, with removal of the evolved CO every 1 h. After 3 h of photolysis, the NMR tube was flame-sealed, and a ¹H NMR spectrum was quickly recorded. The signals assignable to **3a** were observed at positions close to those of **1a** and **2a**. The formation of [Mo(CO)₅(η^1 -BH₃·PPh₃)] (**3b**) was confirmed by a similar method.

Attempted Synthesis of [Mo(CO)₅(η^1 -BH₃·NMe₃)] (3c). Photolysis of a hexane suspension of [Mo(CO)₆] and BH₃·NMe₃ was carried out using a procedure similar to that for **1a**. After photolysis (4 h irradiation), the resulting yellow solution was filtered and cooled at -20 °C to provide **3c** (61 mg, 0.20 mmol, 46%) as a yellow solid. However, the product rapidly decomposed to give a brown solid.

Observation of [M(CO)₅(η^1 -BH₃·NC₅H₅)] (1d, M = Cr; 2d, M = W). The photoreaction of [M(CO)₆] (M = Cr or W) with BH₃·NC₅H₅ was monitored by ¹H NMR spectroscopy. Signals assignable to **1d** and **2d** were observed in the NMR spectra. However, intensities of the signals reached the upper limit where they were smaller than those of free BH₃·NC₅H₅. Attempts to isolate the complexes were not successful.

X-ray Crystal Structure Determination. Crystals of **1a**, **1c**, **2a**, and **2b** were obtained by cooling their pentane solutions at -20 °C. The intensity data for the complexes were collected on a Rigaku AFC-5 (for **1a**, **2a**, and **2b**) and Rigaku AFC-6A (for **1c**) four-circle diffractometers using graphite-monochromated Mo K α radiation (λ = 0.710 73 Å). Data collection for **1a**, **2a** and **2b** was carried out at -60, -50, and -90 °C, respectively. That for **1c** was carried out at 20 °C. The reflection data were corrected with Lorentz and polarization factors but not for absorption and extinction. The space groups were determined from the systematic absence. Crystallographic and experimental data for these crystals are listed in Table 3.

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The structures of all complexes were solved by the heavy atom method. All the non-hydrogen atoms were located and refined applying anisotropic temperature factors. For **1a** and **2a**, the coordinates of the hydrogen atoms bound to the boron atom were determined by difference Fourier synthesis and refined isotropically. For **2b**, the hydrogen atoms bound to the boron atom were found and then fixed. For **1c**, the positions of hydrogen were calculated assuming B–H distances of 1.09 Å and a staggered conformation around the B–N axis and then fixed. Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from refs 54 and 55, respectively. Calculations were performed using the program UNICS III.⁵⁶

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The Fenske–Hall Molecular Orbital Calculation. The molecular orbitals were calculated for [Cr(CO)₅(η¹-BH₃·PH₃)] (**1e**) by Fenske–Hall methods.³⁵ The geometry of **1e** was idealized to the C_s symmetry. Calculations for BH₃·PH₃ were performed assuming the C_{3v} symmetry. For the required parameters of the atoms, the values given by R. F. Fenske et al. were used as presented.

Supporting Information Available: Tables of positional parameters, anisotropic temperature factors, bond distances, and bond angles for **1a**, **1c**, **2a**, and **2b**; positional parameters of the model compound **1e** for the Fenske–Hall MO calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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