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Syntheses and Structures of Manganese Complexes of Borane–Lewis Base Adducts, $[CpMn(CO)_2(\eta^1\text{-}BH_3{\cdot}L)]$ ($L = NMe_3, PMe_3$)

Taeko Kakizawa, Yasuro Kawano,* and Mamoru Shimoi*

Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Meguro-ku, Tokyo 153-8902, Japan

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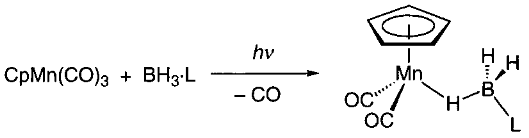
Summary: Photolysis of $[CpMn(CO)_3]$ *in the presence of* $BH_3{\cdot}L$ ($L = NMe_3, PMe_3$) *produced borane σ complexes,* ***1a*** *and* ***1b****. These compounds were characterized by X-ray crystallography. The bonding between the borane ligand and metal is considerably different from those of other σ complexes. It consists of electron donation from the BH σ orbital to metal exclusively, and back-donation into the BH σ* orbital is negligible.*

Much attention has been focused on transition metal σ complexes.[1] In particular, alkane–metal complexes are of interest in relation to metal-catalyzed alkane activation.[2] However, details of their properties are not clear because of their extreme instability. Borane–Lewis base adducts $BH_3{\cdot}L$ are isoelectronic with alkanes and are electronically neutral. We previously reported the syntheses of group 6 metal complexes of $BH_3{\cdot}L$, $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}L)]$ ($M = Cr, W$), and showed that their properties embodied those of alkane complexes.[3] Syntheses of borane complexes of other metals are important to better understand the coordination chemistry of borane–Lewis base adducts as well as of alkanes. We report herein borane adduct complexes of manganese, $[CpMn(CO)_2(\eta^1\text{-}BH_3{\cdot}L)]$ (**1a**, $L = NMe_3$; **1b**, $L = PMe_3$). These compounds are new members of σ complexes of a $[Cp'Mn(CO)_2]$ fragment (Cp′ = substituted cyclopentadienyl ligands), for which silane,[4] germane,[5] stannane,[6] and tricoordinate borane complexes[7] have been reported so far. However, detailed investigation of structural and chemical properties of **1** clarified that the bonding nature between the $BH_3{\cdot}L$ ligand and manganese moiety is considerably different from other manganese σ complexes.

The synthesis of **1** was achieved by the photolysis of a toluene solution of $[CpMn(CO)_3]$ and excess $BH_3{\cdot}L$, using a medium-pressure Hg arc lamp (eq 1). Complexes **1a** and **1b** were isolated as red crystals in 23% and 8% yields, respectively.[8,9] Because of the high lability, the coordinated borane is readily displaced by liberated CO in the system, reducing the isolated yield (vide infra).



(1)

1a: L = NMe$_3$
1b: L = PMe$_3$

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An X-ray diffraction study was conducted at 150 K for crystals of **1a** and **1b**, which were grown from a toluene−hexane mixture. The molecular structures of the complexes are displayed in Figure 1.[10,11] In both complexes, the borane ligand binds to the manganese atom through a B−H−M three-center two-electron bond. The mode of coordination for the borane is end-on. The bond angles of Mn−H−B are 142(3)° and 129(3)° in **1a** and **1b**, respectively. These values are close to those found in group 6 metal complexes [M(CO)$_5$(η^1-BH$_3$·PMe$_3$)] (M = Cr, 130(8)°; M = W, 128(7)°). However, at the same time, it makes a sharp contrast to the side-on coordination of borane in tricoordinate borane complexes [(MeCp)Mn(CO)$_2$(HBX$_2$)] (**2**: HBX$_2$ = HBcat, HBpin, HBCy$_2$), reported by Hartwig and co-workers.[7] The Mn···B distances (2.682(3) Å for **1a**, 2.573(2) Å for **1b**) are roughly comparable to those of chromium complexes [Cr(CO)$_5$(η^1-BH$_3$·L)] (L = NMe$_3$, 2.87 (2) Å; L = PMe$_3$, 2.79(1) Å) and considerably longer than those of compounds **2** (2.083(2)−2.187(3) Å). The B−H$_{\mathrm{brid}}$ bond distance is lengthened only marginally relative to the B−H$_{\mathrm{term}}$ bonds, indicating that **1a** and **1b** are classified as unstretched σ complexes.

In tricoordinate borane complexes **2** and silane complexes [CpMn(CO)$_2$(HSiR$_3$)] (**3**), the coordinated B−H or Si−H bond lies in the "horizontal" plane of the complexes (Scheme 1). This geometry is effective to undergo back-donation into the low-lying Si−H σ^* orbital and boron p orbital from the metal HOMO, which also lies in the horizontal plane and is a potent π donor. Notably, the coordinated B−H bond in **1a** adopts the bisectional geometry with respect to the Mn fragment. The dihedral angle between the plane defined by Mn, the midpoint of C(6) and C(7), and the centroid of the Cp ligand and that of Mn−H(B1)−B is 3.6°. The BH σ^* orbital of BH$_3$·L is so high in energy that it cannot interact with the metal-based HOMO, and thus, the borane ligand adopts the bisectional geometry, which minimizes the steric hindrance. The bonding between the borane ligand and metal in **1** is thus described as an exclusive electron donation from the BH σ orbital to metal. This is consistent with the result of Fenske−Hall MO calculations on the model compound [CpMn(CO)$_2$(η^1-BH$_3$·NH$_3$)]. It indicated the absence of stabilization of d orbitals caused by the π back-donation into the BH σ^* orbital.[12] Complex **1b** has a twisted geometry with the dihedral angle of 69.7°. Likewise, this geometry is not suitable to undergo back-bonding since the bridging hydrogen atom is placed on the nodal plane of the metal HOMO.

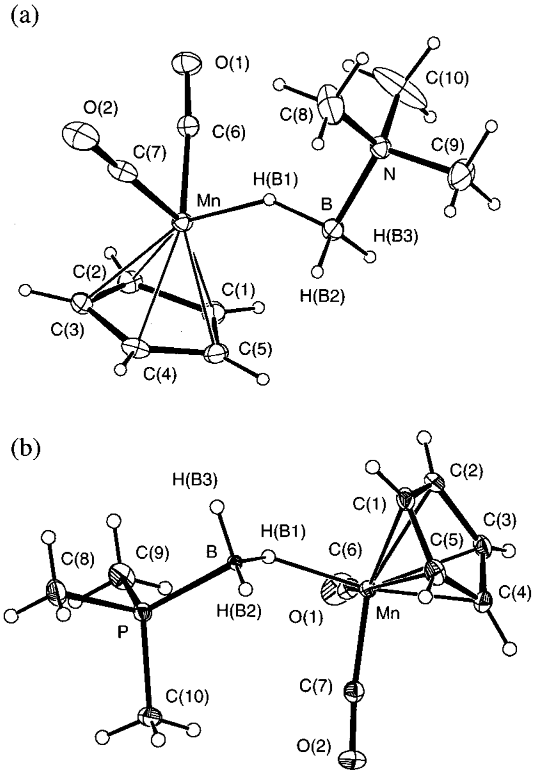
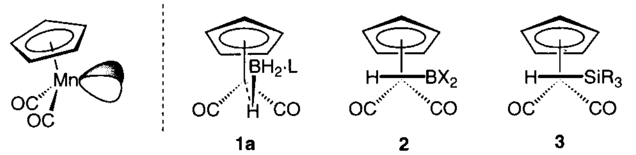


Figure 1. ORTEP diagrams of **1a** (a) and **1b** (b) with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg). **1a**: Mn···B 2.682(3), Mn−H(B1) 1.65(4), B−H(B1) 1.19(4), B−H(B2) 1.14(4), B−H(B3) 0.99(5), Mn−CP 1.774(3), Mn−C(6) 1.768(3), Mn−C(7) 1.779(3), B−N 1.611(4); Mn−H(B1)-B 142(3), N−B−H(B1) 101(2), CP−Mn−HB(1) 127.1(15), CP−Mn−C(6) 123.91(8), CP−Mn−C(7) 124.84(9). **1b**: Mn···B 2.573(2), Mn−H(B1) 1.81(4), B−H(B1) 1.01(4), B−H(B2) 0.84(4), B−H(B3) 1.02(5), Mn−CP 1.772(3), Mn−C(6) 1.778(3), Mn−C(7) 1.770(3), B−P 1.952(2); Mn−H(B1)−B 129(3), N−B−H(B1) 100(2), CP−Mn−H(B1) 121.4(12), CP−Mn−C(6) 122.97(9), CP−Mn−C(7) 123.84(10). CP = the centroid of the Cp ring.

Scheme 1



The ν(CO) bands of **1** appear at lower frequency by ca. 100 cm^{-1} relative to those of [CpMn(CO)$_3$]. This very large red shift of carbonyl bands is attributed to the inherent ability of the BH$_3$·L ligand to be a good σ donor but a very poor π acceptor. Much smaller red shifts of ν(CO) bands were observed for **2** and **3** (20−60 cm^{-1}),

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(8) A solution of CpMn(CO)$_3$ (160 mg, 78 mmol) and BH$_3$·NMe$_3$ (60 mg, 82 mmol) in dry toluene (4 mL) was irradiated at 5 °C using a 450 W medium-pressure Hg arc lamp under high vacuum. After irradiation for 30 min, volatiles were removed under vacuum and the residue was extracted with a toluene−pentane mixture (1:4, 5 mL). The resultant extract was cooled to −25 °C to afford **1a** (45 mg, 18 mmol, 23%) as red needles. Complex **1b** was prepared by a similar procedure with the use of BH$_3$·PMe$_3$. The yield of red crystalline **1b** was 8%.

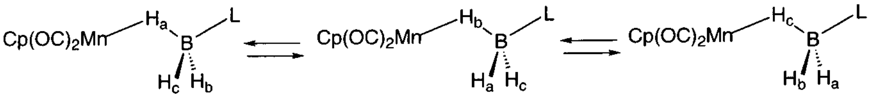
(9) Data for **1a**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) δ 4.26 (s, 5H, Cp), 1.65 (s, 9H, N*Me*$_3$), −6.10 (br, 3H, BH); ^{11}B NMR (160.4 MHz, C$_6$D$_6$, 25 °C) δ −15.9 (q, $^1J_{\mathrm{BH}}$ = 90.6 Hz); IR (KBr) 1927, 1820 (s, ν(CO)), 2456, 2416 (w, ν(BH$_{\mathrm{term}}$)), 2113 (w, ν(BH$_{\mathrm{brid}}$)); MS (EI) *m/z* 176 (4, CpMn(CO)$_2^+$), 148 (16, CpMn(CO)$^+$), 120 (100, CpMn$^+$). Data for **1b**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) δ 4.32 (s, 5H, Cp), 0.54 (d, $^2J_{\mathrm{PH}}$ = 10.5 Hz, 9H, P*Me*$_3$), −6.30 (br, q, $^1J_{\mathrm{BH}}$ = 86.7 Hz, 3H, BH); ^{11}B NMR (160.4 MHz, C$_6$D$_6$, 25 °C) δ −46.6 (br, d, J_{BP} = 74.7 Hz); ^{31}P NMR (202.4 MHz, C$_6$D$_6$, 25 °C) δ 0.5 (br); IR (KBr) 1918, 1839 (s, ν(CO)), 2461, 2383 (w, ν(BH$_{\mathrm{term}}$)), 2022 (w, ν(BH$_{\mathrm{brid}}$)); MS (EI) *m/z* 265 (3, M$^+$), 148 (16, CpMn(CO)$^+$), 120 (100, CpMn$^+$). Owing to the thermal instability, satisfactory elemental analyses could not be obtained.

(10) Crystal data for **1a**: red crystals, monoclinic, space group $P2_1/a$ (variant of No. 14); T = 150 K; a = 12.677(1), b = 15.1950(5), c = 6.194(1) Å; β = 90.2576(1)°, V = 1193.18(4) Å^3; Z = 4; R = 0.0334, wR2 = 0.1098 for 2286 reflections with $|F_o| > 3\sigma(F_o)$, 151 parameters, GooF = 0.286.

(11) Crystal data for **1b**: red crystals, orthorhombic, space group $P2_12_12_1$ (No. 19); T = 150 K; a = 10.7891(3), b = 12.5507(7), c = 9.6149(3) Å; V = 1301.96(9) Å^3; Z = 4; R = 0.0260, wR2 = 0.0624 for 1615 reflections with $|F_o| > 3\sigma(F_o)$, 151 parameters, GooF = 0.822.

(12) The detailed results of the MO calculations will be reported elsewhere.

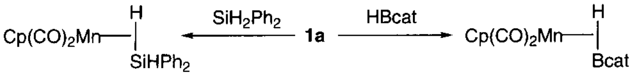
Scheme 2



whose σ ligands are excellent π acceptors. In the ^{1}H NMR spectra at room temperature, complexes **1** show only one BH signal with integral intensity of 3H around −6 ppm. This clearly indicates the existence of fast scrambling between coordinated and terminal BH protons (Scheme 2). For **1a**, this signal collapsed into the baseline at −20 °C, and a new signal (1H intensity) appeared at −22.21 ppm at −60 °C. At this temperature, the fluxional process is frozen, and the metal-coordinated BH is observed as a distinct signal. The signal of terminal BH protons was not detected probably due to its broadness or overlap with the NMe signal. In the case of **1b**, the BH signal was collapsed at −80 °C, but decoalesed peaks were not observed even at −90 °C. The $\Delta G^{\ddagger}$ values for these processes were estimated to be 40 kJ mol^{-1} at 253 K (**1a**) and ca. 30 kJ mol^{-1} at 193 K (**1b**). These values are substantially higher than that for [M(CO)$_5$(η^1-BH$_3$·L)] (<30 kJ mol^{-1}).[3]

The coordinated borane in **1** is highly labile and is easily replaced by other σ ligands. Treatment of **1a** with SiHPh$_3$ or SiH$_2$Ph$_2$ led to clean formation of the corresponding silane complex along with free BH$_3$·NMe$_3$. The reactions were completed within 1 h, and the yields were higher than 90%. Reaction of **1a** with HBcat also took place slowly to produce CpMn(CO)$_2$(HBcat) (Scheme 3).[7]

Scheme 3



Complexation of alkanes is one of the most interesting interactions in organometallic chemistry. [CpM(CO)$_2$(alkane)] (M = Mn, Re) have played a major role in this research area because of the relatively high stability.[13,14] The manganese−borane complexes **1** are important compounds as a model system of alkane complexes, [CpM(CO)$_2$(alkane)].

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Supporting Information Available: Tables furnishing the crystal data, positional parameters, anisotropic thermal parameters of the non-hydrogen atoms, bond distances, and bond angles for **1a** and **1b** and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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