Investigation of the Stability of the M-H-B Bond in Borane σ Complexes [M(CO)$_5$(η^1-BH$_2$R·L)] and [CpMn(CO)$_2$(η^1-BH$_2$R·L)] (M = Cr, W; L = Tertiary Amine or Phosphine): Substituent and Lewis Base Effects

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Abstract: We investigated the influence of a substituent and a Lewis base on boron upon the thermodynamic stability of metal complexes of borane–Lewis base adducts, [M(CO)$_5$(η^1-BH$_2$R·L)] (M = Cr, W) and [CpMn(CO)$_2$(η^1-BH$_2$R·L)], where R = Cl, I, m-C$_6$H$_4$F, Ph, H, Me, Et; L = PMe$_3$, PPh$_3$, NMe$_3$, quinuclidine. In these compounds, the stability of the metal–borane linkage was enhanced by increasing the electron-releasing ability of the substituent on boron. A stronger base L additionally stabilized the complexes. The strength of the borane–metal interaction is thus mainly ascribed to the electron donation from the BH σ orbital to metal rather than the back-donation into the BH σ* orbital. This result supports the bonding model for the B-H-M linkage in the borane complexes suggested by MO calculations, where the borane-to-metal electron donation is predominant while the metal back-donation into the BH σ* orbital is negligible. Such a stability trend of the borane complexes makes a sharp contrast to that of many silane and dihydrogen complexes.

Keywords: boranes · chromium · manganese · sigma complexes · tungsten

Introduction

Much attention is focused currently on transition metal–boron chemistry. In this research area, metallaborane clusters have long been investigated. However, it seems to be difficult to clearly understand the character of the metal–boron interaction of metallaboranes because it is buried in rather complicated cluster cores.[1,2] From such a point of view, we have explored the coordination chemistry of simple boron hydrides, BH$_3$·L (L = NMe$_3$, PMe$_3$, PPh$_3$)[3–8] and B$_2$H$_4$·2PMe$_3$.[9–12] We thought that this work could bring the nature of the metal–boron interaction into light. During the course of study, we have synthesized borane σ complexes [M(CO)$_5$(η^1-BH$_3$·L)] (M = Cr, W; L = PMe$_3$, PPh$_3$, NMe$_3$),[3,4] [CpMn(CO)$_2$(η^1-BH$_3$·L)] (L = PMe$_3$, NMe$_3$),[5] and related compounds.[6,7]

Transition-metal σ complexes, in which an E−H σ bond (E = main group element) acts as a two-electron donor, have been of interest from the bonding- and structure-point of view.[13] Complexation of a σ bond with a metal center is thought to consist of the electron donation from the E−H bonding σ orbital into a vacant metal d$_σ$ orbital as well as the back-donation from a filled d$_π$ orbital to the E–H antibonding σ* orbital (Scheme 1). The balance between these two interactions can be finetuned by incorporation of electron-releasing or -withdrawing groups into the σ ligand.

Efforts of many researchers have clarified the factors that affect the stability of the metal–ligand interaction in σ com-

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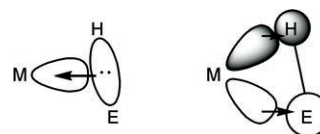
Scheme 1.

plexes. In particular, dihydrogen complexes and silane complexes have been studied extensively.[14] Dihydrogen and hydrosilane ligands are excellent π acceptors. Accordingly, in many cases, the stability of the bonding between the central metal and H_2 or silane ligand is strongly affected by metal back-donation into the H–H or Si–H σ* orbital. For example, while a dihydrogen complex $[M(CO)_5(\eta^2\text{-}H_2)]$ (M = Cr, Mo, W) is observable only in low temperature matrices,[15,16] $[M(CO)_3(PiPr_3)_2(\eta^2\text{-}H_2)]$ has a stability enough to be isolated because of the back-bonding into the H–H σ* orbital enhanced by the strong electron donation of the phosphine ligands.[17] In manganese–silane species $[(MeCp)Mn(CO)_2(\eta^2\text{-}HSiR_3)]$ $(MeCp = \eta^5\text{-}C_5H_4Me)$, silanes having electron-*withdrawing* substituents form more stable complexes because they can undergo effective back-donation from metal.[18–21] Raising the electron density at the metal center can also enhance the back-bonding and stabilize the silane–metal interaction. Indeed, fragments $[Cp*Mn(CO)_2]$ $(Cp* = \eta^5\text{-}C_5Me_5)$ and $[(MeCp)Mn(CO)(PMe_3)]$ bind silanes more strongly than $[(MeCp)Mn(CO)_2]$.[22] Stronger back-donation stretches the Si−H bond and reduces the coupling constant $J(Si,H)$ in NMR. Consequently, the metal–silane interaction becomes close to a complete oxidative addition.[23] An exceptional case is short-lived silane–metal adducts, $[Cr(CO)_5(HSiR_3)]$. In this system, electron-*releasing* substituents on silicon more stabilize the σ complexes.[24] This was attributed to the poor π-donating ability of a $[Cr(CO)_5]$ fragment. As the back-donation is very weak, the stability of the complexes is ascribed to the ligand-to-metal electron donation.

An estimate of the strength of the C-H-M linkage in alkane σ complexes is somewhat difficult owing to their extreme instability. Nonetheless, their lifetimes in solution have been established by means of flash photolysis techniques[25] for $[M(CO)_5(alkane)]$ (M = Cr, Mo, W),[26–28] $[CpM(CO)_2(alkane)]$ (M = Mn, Re),[29,30] and other related species.[31] Those studies elucidated that complexes of larger (electron-rich) alkanes had longer lifetimes. In particular, the rhenium derivatives $[CpRe(CO)_2(cyclo\text{-}C_5H_{10})]$ and $[CpRe(CO)_2(C_5H_{12})]$ have a remarkable stability and have been observed directly by NMR spectroscopy at −100 °C.[32,33] Thus, in many cases, the stability of the metal–alkane interaction is strongly influenced by the extent of electron donation from the C-H σ orbital to metal. However, in highly electron-rich metal systems, alkanes can undergo significant back-donation into the C-H σ* orbital, and oxidative addition (CH activation) takes place to give alkyl-(hydrido) complexes.[34] Thus, alkanes potentially have weak π-accepting ability, and actual extent of back-donation depends on the nature of the central metal. This should originate from high energy of C-H σ* orbitals.

Borane adducts BH₃·L are isoelectronic with alkanes and silanes. Therefore, it is of interest to compare the bonding nature of our borane complexes to those of other σ complexes. Fenske–Hall MO calculations on model compounds $[Cr(CO)_5(\eta^1\text{-}BH_3\cdot PH_3)]$ and $[CpMn(CO)_2(\eta^1\text{-}BH_3\cdot NH_3)]$ showed characteristic features of the B-H-M linkages. The borane–metal interaction is composed of electron donation

from the BH σ bond to metal predominantly while the contribution of the metal back-donation into the BH σ* orbital is negligible.[4] For $[Cr(CO)_5(\eta^1\text{-}BH_3\cdot PH_3)]$, one of the reasons for this should be the fact that $[Cr(CO)_5]$ is a σ acceptor essentially, but is a poor π donor. However, it is still in contrast to the orbital interactions in $[Cr(CO)_5(\eta^2\text{-}H_2)]$ shown by Hoffmann and co-workers, where the H_2 ligand accepts small but significant π back-donation into the antibonding orbital.[35] Furthermore, the borane σ donation also dominates over the π back-donation even in $[CpMn(CO)_2(\eta^1\text{-}BH_3\cdot NH_3)]$, despite the potent π-donating ability of the manganese fragment.[5] The antibonding σ* orbitals of BH are so high in energy that they cannot interact with metal d orbitals.

To experimentally confirm this bonding model, we examined the effect of the substituent R upon the stability of substituted borane complexes, $[M(CO)_5(\eta^1\text{-}BH_2R\cdot L)]$ (M = Cr, W) and $[CpMn(CO)_2(\eta^1\text{-}BH_2R\cdot L)]$. The influence of the Lewis base was also investigated. Based on the aforementioned bonding model, it is expected that the introduction of an electron-releasing substituent enhances the borane σ donation and stabilizes the borane-metal linkage. Here we wish to emphasize that the influence of the substituents upon the stability of σ complexes can be a good indicator that reveals the nature of the σ ligand–metal interaction. Through this work, we show the unique character of borane adducts as a σ ligand, which comes from the lack of low-lying orbitals to accept the metal back donation.

Results and Discussion

Preparation of monosubstituted borane complexes: First we confirmed photochemical formation of σ complexes of monosubstituted boranes. Photolyses of $[M(CO)_6]$ (M = Cr, W) in the presence of mono-organylboranes BH₂R·L (R = m-C₆H₄F, Ph, Me, Et; L = PMe₃, NMe₃) in [D₆]benzene gave yellow solutions. In the ¹H NMR spectra, the resulting solutions revealed a characteristic broad resonance coupled with boron with 2H intensity at δ −5 to −7 ppm (M = Cr) or −2 to −3.5 ppm (M = W). These are assigned to the BH protons of borane complexes, $[M(CO)_5(\eta^1\text{-}BH_2R\cdot L)]$ (**1–4**, see Scheme 2). The intrinsically inequivalent BH protons are observed as a single resonance at ambient temperature owing to the fast exchange between equivalent structures via migration of the $[M(CO)_5]$ moiety between the two BH hydrogen atoms. These resonances appear at substantially higher field in comparison to that of parent borane complexes $[M(CO)_5(\eta^1\text{-}BH_3\cdot L)]$, because the chemical shift value of the latter is the weighted average of one bridging and two terminal BH protons (e.g. $[Cr(CO)_5(\eta^1\text{-}BH_3\cdot PMe_3)]$ reveals the BH resonance at −3.8 ppm).[4] The fluxional process was frozen on cooling, and the ¹H NMR spectra showed distinct signals for the coordinated and terminal BH protons. Details of the temperature-dependent NMR spectra will be discussed later. In the ¹¹B NMR spectra, the ligated borane resonates at higher field relative to free boranes by
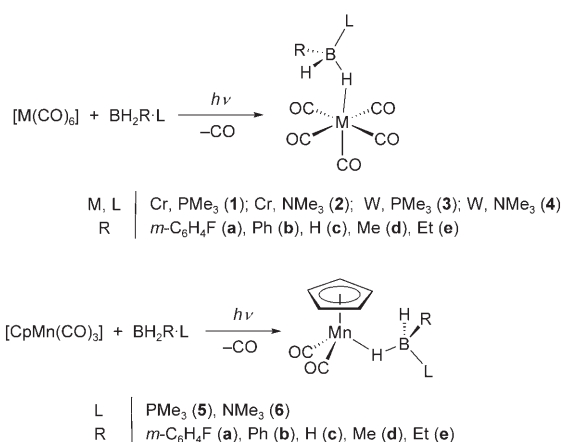
Scheme 2.

5–10 ppm similarly to other borane complexes. Likewise, formation of manganese complexes, $[CpMn(CO)_2(\eta^1\text{-}BH_2R\cdot L)]$ (**5**: L = PMe$_3$, **6**: L = NMe$_3$) was confirmed by NMR spectroscopy (Scheme 2). In every metal system, no evidence for the formation of haloborane complexes was provided when BH$_2$Cl·L and BH$_2$I·L were employed. NMR data of the new complexes obtained in this work are listed in Table 1.

Among the complexes obtained, $[Cr(CO)_5(\eta^1\text{-}BH_2Ph\cdot PMe_3)]$ (**1b**), $[Cr(CO)_5(\eta^1\text{-}BH_2Me\cdot PMe_3)]$ (**1d**), and $[CpMn(CO)_2(\eta^1\text{-}BH_2Me\cdot NMe_3)]$ (**6d**) were structurally authenticated by the X-ray diffraction method. Their structures are illustrated in Figures 1–3, and key structural parameters are listed in Tables 2–4. The structures of these compounds embody those of alkane complexes coordinated with a secondary CH moiety while the parent borane complexes manifest the primary CH-bound derivatives. However, the structural features are essentially similar to the non-
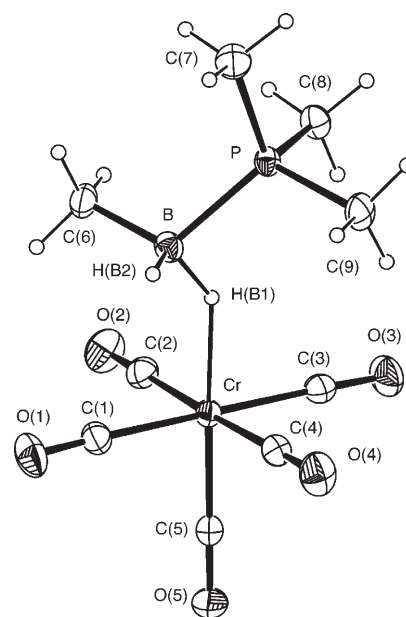

Figure 2. ORTEP drawing of $[Cr(CO)_5(\eta^1\text{-}BH_2Me\cdot PMe_3)]$ (**1d**).
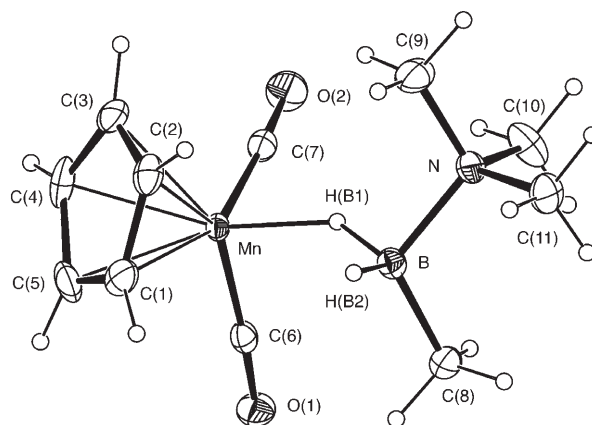

Figure 3. ORTEP drawing of $[CpMn(CO)_2(\eta^1\text{-}BH_2Me\cdot NMe_3)]$ (**6d**).

substituted borane derivatives $[Cr(CO)_5(\eta^1\text{-}BH_3\cdot PMe_3)]$ (**1c**) and $[CpMn(CO)_2(\eta^1\text{-}BH_3\cdot NMe_3)]$ (**6c**) except for the presence of a substituent on boron. The borane ligand coordinates to the central metal through a B-H-M single bridge. The metal–boron separations are sufficiently long (2.769–2.791 Å) that this linkage is best described as an end-on coordination. The B-H-Mn bond angle of **6d** (143(2)°) are much wider than the Si-H-Mn bond angles of $[(MeCp)Mn(CO)_2(\eta^2\text{-}HSiR_3)]$ (88–93°), which include a side-on silane ligand.[19] The metal-coordinated B–H bond is stretched only marginally relative to the terminal B–H bonds, indicating that these are classified as unstretched σ complexes. This suggests little back-donation into the BH σ* orbitals. Indeed, in compound **6d**, the coordinated BH bond adopts an orientation in which the σ* orbital does not match the HOMO of the $[CpMn(CO)_2]$ fragment in symmetry.[5]

In compound **1d**, a steric interaction is found between the methyl group on boron and two of the *cis* carbonyl ligands.

Figure 1. ORTEP drawing of $[Cr(CO)_5(\eta^1\text{-}BH_2Ph\cdot PMe_3)]$ (**1b**).

Table 1. ^{1}H, ^{11}B, and ^{31}P NMR data for new borane complexes.[a]

Compound	^{1}H NMR	^{11}B{^{1}H} NMR	^{31}P NMR
[Cr(CO)$_5$(η^1-BH$_2$(m-C$_6$H$_4$F)·PMe$_3$)] (**1a**)	−4.93 (q, ^{1}J(B,H) = 103.0 Hz, 2H, BH), 0.32 (d, ^{2}J(P,H) = 11.0 Hz, 9H, PMe$_3$), 6.9–7.4 (m, 5H, ring protons)	−30.0 (J(B,P) = 58.5 Hz)	−7.1 (br)
[Cr(CO)$_5$(η^1-BH$_2$Ph·PMe$_3$)] (**1b**)	−4.83 (q, ^{1}J(B,H) = 100.0 Hz, 2H, BH), 0.41 (d, ^{2}J(P,H) = 11.5 Hz, 9H, PMe$_3$), 7.10, 7.29, 7.6 (m, 5H, ring protons)	−29.3 (J(B,P) = 63.0 Hz)	−7.1 (br)
[Cr(CO)$_5$(η^1-BH$_2$Me·PMe$_3$)] (**1d**)	−6.05 (q, ^{1}J(B,H) = 96.5 Hz, 2H, BH), 0.06 (d, ^{3}J(P,H) = 21.0 Hz, 3H, BMe), 0.68 (d, ^{2}J(P,H) = 11.0 Hz, 9H, PMe$_3$)	−30.9 (J(B,P) = 61.6 Hz)	−3.3 (br, q, J(B,P) = 61.6 Hz)
[Cr(CO)$_5$(η^1-BH$_2$Et·PMe$_3$)] (**1e**)	−5.93 (q, ^{1}J(B,H) = 101.0 Hz, 2H, BH), 0.52 (d, ^{2}J(P,H) = 10.5 Hz, 9H, PMe$_3$), 0.56 (br, 2H, CH$_2$CH$_3$), 1.02 (t, J = 7.0 Hz, 3H, CH$_2$CH$_3$)	−27.9 (J(B,P) = 55.0 Hz)	−5.6 (br)
[Cr(CO)$_5$(η^1-BH$_2$(m-C$_6$H$_4$F)·NMe$_3$)] (**2a**)	−4.92 (br, 2H, BH), 1.45 (s, 9H, NMe$_3$), 7.0–7.4 (m, 5H, ring protons)	−6.2	−
[Cr(CO)$_5$(η^1-BH$_2$Ph·NMe$_3$)] (**2b**)	−4.82 (q, ^{1}J(B,H) = 98.5 Hz, 2H, BH), 1.50 (s, 9H, NMe$_3$), 7.26, 7.37, 7.7 (m, 5H, ring protons)	−5.3	−
[Cr(CO)$_5$(η^1-BH$_2$Me·NMe$_3$)] (**2d**)	−5.69 (br, 2H, BH), −0.02 (br, 3H, BMe), 1.68 (s, 9H, NMe$_3$)	−5.2	−
[Cr(CO)$_5$(η^1-BH$_2$Et·NMe$_3$)] (**2e**)	−5.69 (br, 2H, BH), 0.37 (br, 2H, CH$_2$CH$_3$), 0.97 (br, 3H, CH$_2$CH$_3$), 1.43 (s, 9H, NMe$_3$)	−2.5	−
[W(CO)$_5$(η^1-BH$_2$(m-C$_6$H$_4$F)·PMe$_3$)] (**3a**)	−2.48 (br, 2H, BH), 0.23 (d, ^{2}J(P,H) = 11.5 Hz, 9H, PMe$_3$), 6.9–7.4 (m, 5H, ring protons)	−33.4 (J(B,P) = 72.5 Hz)	−9.8 (br)
[W(CO)$_5$(η^1-BH$_2$Ph·PMe$_3$)] (**3b**)	−2.39 (q, ^{1}J(B,H) = 105.0 Hz, 2H, BH), 0.27 (d, ^{2}J(P,H) = 11.5 Hz, 9H, PMe$_3$), 7.10, 7.23, 7.7 (m, 5H, ring protons)	−33.3 (J(B,P) = 58.5 Hz)	−9.2 (br)
[W(CO)$_5$(η^1-BH$_2$Me·PMe$_3$)] (**3d**)	−3.45 (q, ^{1}J(B,H) = 87.5 Hz, 2H, BH), 0.14 (dt, ^{3}J(P,H) = 21.0 Hz, ^{3}J$_{HH}$ = 5.5 Hz, 3H, BMe), 0.48 (d, ^{2}J(P,H) = 11.0 Hz, 9H, PMe$_3$)	−34.4 (J(B,P) = 74.4 Hz)	−6.1 (br, q, J(B,P) = 74.4 Hz)
[W(CO)$_5$(η^1-BH$_2$Et·PMe$_3$)] (**3e**)	−3.42 (q, ^{1}J(B,H) = 105.0 Hz, 2H, BH), 0.52 (d, ^{2}J(P,H) = 10.5 Hz, 9H, PMe$_3$), 0.55 (br, 2H, CH$_2$CH$_3$), 1.03 (t, J = 6.7 Hz, 3H, CH$_2$CH$_3$)	−31.0 (J(B,P) = 70.0 Hz)	−8.3 (br)
[W(CO)$_5$(η^1-BH$_2$(m-C$_6$H$_4$F)·NMe$_3$)] (**4a**)	−2.51 (br, 2H, BH), 1.49 (s, 9H, NMe$_3$), 7.0–7.4 (m, 5H, ring protons)	−9.6	−
[W(CO)$_5$(η^1-BH$_2$Ph·NMe$_3$)] (**4b**)	−2.40 (q, ^{1}J(B,H) = 109.5 Hz, 2H, BH), 1.62 (s, 9H, NMe$_3$), 7.28, 7.39, 7.7 (m, 5H, ring protons)	−8.7	−
[W(CO)$_5$(η^1-BH$_2$Me·NMe$_3$)] (**4d**)	−3.26 (q, ^{1}J(B,H) = 88.0 Hz, 2H, BH), 0.14 (t, ^{3}J$_{HH}$ = 5.5 Hz, 3H, BMe), 1.50 (s, 9H, NMe$_3$)	−13.3	−
[W(CO)$_5$(η^1-BH$_2$Et·NMe$_3$)] (**4e**)	−3.21 (q, ^{1}J(B,H) = 101.0 Hz, 2H, BH), 0.47 (br, 2H, CH$_2$CH$_3$), 1.04 (br, 3H, CH$_2$CH$_3$), 1.75 (s, 9H, NMe$_3$)	−5.0	−
[CpMn(CO)$_2$(η^1-BH$_2$(m-C$_6$H$_4$F)·PMe$_3$)] (**5a**)	−9.14 (br, 2H, BH), 0.30 (br, 9H, PMe$_3$), 4.31 (s, 5H, Cp), 6.9–7.4 (m, 5H, ring protons)	−33.5 (J(B,P) = 63.8 Hz)	−7.3 (br)
[CpMn(CO)$_2$(η^1-BH$_2$Ph·PMe$_3$)] (**5b**)	−9.53 (br, 2H, BH), 0.26 (br, 9H, PMe$_3$), 4.15 (s, 5H, Cp), 6.7–7.4 (m, 5H, ring protons)	−32.9 (J(B,P) = 59.5 Hz)	−7.2 (br, q, J(B,P) = 59.5 Hz)
[CpMn(CO)$_2$(η^1-BH$_2$Me·PMe$_3$)] (**5d**)	−10.77 (br, 2H, BH), −0.17 (d, ^{3}J(P,H) = 19.5 Hz, 3H, BMe), 0.67 (d, ^{2}J(P,H) = 10.0 Hz, 9H, PMe$_3$), 4.21 (s, 5H, Cp)	−33.8 (J(B,P) = 63.0 Hz)	−9.2 (br, q, J(B,P) = 63.0 Hz)
[CpMn(CO)$_2$(η^1-BH$_2$Et·PMe$_3$)] (**5e**)	−10.69 (br, 2H, BH), 0.26 (br, 2H, CH$_2$CH$_3$), 0.81 (br, 9H, PMe$_3$), 0.96 (br, 3H, CH$_2$CH$_3$), 4.26 (s, 5H)	−30.4 (J(B,P) = 65.3 Hz)	−6.4 (br, q, J(B,P) = 65 Hz)
[CpMn(CO)$_2$(η^1-BH$_2$(m-C$_6$H$_4$F)·NMe$_3$)] (**6a**)	−9.26 (br, 2H, BH), 1.51 (br, 9H, NMe$_3$), 4.04 (s, 5H, Cp), 6.9–7.4 (m, 5H, ring protons)	−8.1	−
[CpMn(CO)$_2$(η^1-BH$_2$Ph·NMe$_3$)] (**6b**)	−9.79 (br, 2H, BH), 1.64 (br, 9H, NMe$_3$), 4.07 (s, 5H, Cp), 7.2–7.7 (m, 5H, ring protons)	−7.3	−
[CpMn(CO)$_2$(η^1-BH$_2$Me·NMe$_3$)] (**6d**)	−0.08 (br, 3H, BMe), 1.82 (s, 9H, NMe$_3$), 4.21 (s, 5H, Cp)[b]	−6.6	−
[CpMn(CO)$_2$(η^1-BH$_2$Et·NMe$_3$)] (**6e**)	0.24, (br, 2H, CH$_2$CH$_3$), 1.20 (br, 3H, CH$_2$CH$_3$), 1.80 (s, 9H, NMe$_3$), 4.23 (s, 5H, Cp)[c]	−2.88	−
[Cr(CO)$_5$(η^1-BH$_3$·quinuclidine)] (**7**)	−3.33 (br, 3H, BH), 0.75 (br, 6H, N(CH$_2$CH$_2$)$_3$CH), 1.01 (br, 1H, N(CH$_2$CH$_2$)$_3$CH), 2.21 (t, J = 7.5 Hz, 6H, N(CH$_2$CH$_2$)$_3$CH)	−15.6	−
[W(CO)$_5$(η^1-BH$_3$·quinuclidine)] (**8**)	−1.60 (br, 3H, BH), 0.70 (br, 6H, N(CH$_2$CH$_2$)$_3$CH), 0.90 (br, 1H, N(CH$_2$CH$_2$)$_3$CH), 2.19 (t, J = 7.8 Hz, 6H, N(CH$_2$CH$_2$)$_3$CH)	−19.8	−
[CpMn(CO)$_2$(η^1-BH$_3$·quinuclidine)] (**9**)	−6.24 (br, 3H, BH), 0.82 (br, 6H, N(CH$_2$CH$_2$)$_3$CH), 1.03 (br, 1H, N(CH$_2$CH$_2$)$_3$CH), 2.37 (br, 6H, N(CH$_2$CH$_2$)$_3$CH), 4.31 (s, 5H, Cp)	−18.0	−

[a] NMR spectra were recorded in [D$_6$]benzene unless stated. [b] The BH resonance was not observed at ambient temperature. At −90°C, separated BH signals appeared at −22.6 and 1.62 ppm in [D$_8$]toluene. [c] The separated BH resonances were observed at −24.8 ppm and 2.3 ppm at −70°C in [D$_8$]toluene.

The interatomic distances C(6)···C(1) and C(6)···C(2) are 3.505(4) and 3.368(4) Å, respectively. These values are substantially shorter than the minimal nonbonding approach between the relevant atoms.[36] On the other hand, in the phenylborane complex **1b**, there is no steric repulsion between the phenyl group and [Cr(CO)$_5$] moiety in the orientation of the phenyl ring in crystal. The closest separations between the phenyl ring and *cis* carbonyl ligands, C(14)···C(3) and H(14)···C(3) are 3.678(3) and 3.06(2) Å, respectively. In manganese complex **6d**, the methyl group C(8) approaches a carbonyl carbon C(6) to 3.247(3) Å, closer than the van der Waals contact.

Table 2. Important interatomic distances [Å] and angles [°] for [Cr(CO)$_5$(η^1-BH$_2$Ph·PMe$_3$)] (**1b**).

Bond length			
Cr−H(B1)	1.77(2)	Cr⋯B	2.791(3)
B−H(B1)	1.26(2)	B−H(B2)	1.07(3)
B−C(9)	1.602(3)	B−P	1.935(2)
Cr−C(1)	1.899(2)	Cr−C(2)	1.917(2)
Cr−C(3)	1.911(2)	Cr−C(4)	1.897(2)
Cr−C(5)	1.843(2)	C(1)−O(1)	1.138(2)
C(2)−O(2)	1.133(3)	C(3)−O(3)	1.138(3)
C(4)−O(4)	1.139(3)	C(5)−O(5)	1.154(3)

Nonbonding distances			
C(3)⋯C(14)	3.678(3)	C(3)⋯H(14)	3.058(2)

Bond angles			
Cr-H(B1)-B	133(2)	H(B1)-Cr-C(1)	97.0(9)
H(B1)-Cr-C(2)	83.6(9)	H(B1)-Cr-C(3)	85.9(9)
H(B1)-Cr-C(4)	94.8(9)	H(B1)-Cr-C(5)	171.8(8)
P-B-C(9)	108.45(13)	P-B-H(B1)	100.5(13)
P-B-H(B2)	104.7(16)	C(9)-B-H(B1)	110.3(13)
C(9)-B-H(B2)	120.5(15)	H(B1)-B-H(B2)	110.4(18)

Table 3. Important interatomic distances [Å] and angles [°] for [Cr(CO)$_2$(η^1-BH$_2$Me·PMe$_3$)] (**1d**).

Bond lengths			
Cr−H(B1)	1.78(3)	Cr⋯B	2.806(3)
B−H(B1)	1.21(3)	B−H(B2)	1.08(3)
B−C(6)	1.602(4)	B−P	1.936(3)
Cr−C(1)	1.913(3)	Cr−C(2)	1.912(3)
Cr−C(3)	1.903(3)	Cr−C(4)	1.908(3)
Cr−C(5)	1.839(3)	C(1)−O(1)	1.130(3)
C(2)−O(2)	1.129(4)	C(3)−O(3)	1.135(4)
C(4)−O(4)	1.135(4)	C(5)−O(5)	1.149(4)

Nonbonding distances			
C(1)⋯C(6)	3.505(4)	C(2)⋯C(6)	3.368(4)

Bond angles			
Cr-H(B1)-B	138.4(16)	H(B1)-Cr-C(1)	93.5(9)
H(B1)-Cr-C(2)	87.7(9)	H(B1)-Cr-C(3)	86.5(9)
H(B1)-Cr-C(4)	90.9(9)	H(B1)-Cr-C(5)	175.8(9)
P-B-C(6)	112.1(2)	P-B-H(B1)	95.5(14)
P-B-H(B2)	105.5(18)	C(6)-B-H(B1)	112.5(14)
C(6)-B-H(B2)	113.9(18)	H(B1)-B-H(B2)	116(2)

Table 4. Important interatomic distances [Å] and angles [°] for [CpMn(CO)$_2$(η^1-BH$_2$Me·NMe$_3$)] (**6d**).

Bond lengths			
Mn−H(B1)	1.67(2)	Mn⋯B	2.769(2)
B−H(B1)	1.24(2)	B−H(B2)	1.15(2)
B−C(8)	1.591(3)	B−N	1.637(2)
Mn−C(6)	1.765(2)	Mn−C(7)	1.776(2)
C(6)−O(1)	1.165(2)	C(7)−O(2)	1.161(2)

Nonbonding distances		
C(6)⋯C(8)		3.247(3)

Bond angles			
CNT-Mn-C(6)[a]	124.48(8)	CNT-Mn-C(7)[a]	123.67(8)
CNT-Mn-H(B1)[a]	123.87(8)	Mn-H(B1)-B	143.4(17)
C(6)-Mn-C(7)	91.89(8)	C(6)-Mn-H(B1)	94.6(7)
C(7)-Mn-H(B1)	88.6(7)	Mn-C(6)-O(1)	176.23(15)
Mn-C(7)-O(2)	176.8(2)	C(8)-B-N	133.09(14)
N-B-H(B1)	96.5(10)	N-B-H(B2)	106.0(10)
C(8)-B-H(B1)	112.2(10)	C(8)-B-H(B2)	115.8(11)
H(B1)-B-H(B2)	111.6(15)		

[a] CNT: the centroid of the cyclopentadienyl ring.
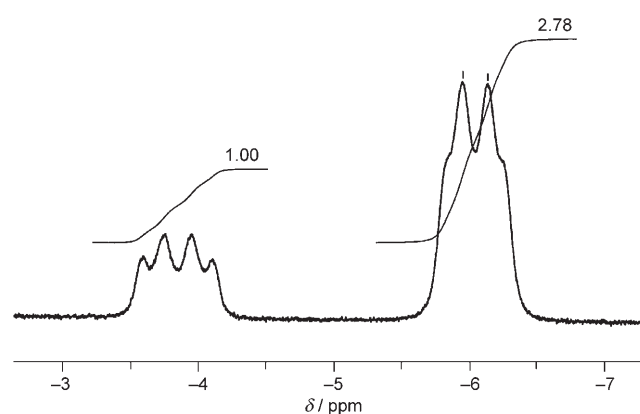
Figure 4. ^{1}H NMR spectrum (M-H-B region) of a mixture containing [Cr(CO)$_5$(η^1-BH$_3$·PMe$_3$)] (**1c**) and [Cr(CO)$_5$(η^1-BH$_2$Me·PMe$_3$)] (**1d**).

Relative stability of Group 6 metal–borane complexes [M(CO)$_5$(η^1-BH$_2$R·EMe$_3$)]: An excess amount of BH$_2$Me·PMe$_3$ was added to a [D$_6$]benzene solution of [Cr(CO)$_5$(η^1-BH$_3$·PMe$_3$)] (**1c**), and the ^{1}H and ^{11}B NMR spectra were recorded immediately. The resulting spectra exhibited the formation of a mixture which consists of [Cr(CO)$_5$(η^1-BH$_2$Me·PMe$_3$)] (**1d**), free BH$_3$·PMe$_3$, a small amount of **1c**, and excess BH$_2$Me·PMe$_3$, indicating ready exchange between the free borane and coordinated one. Separately, the photolysis of [Cr(CO)$_6$] in the presence of a 1:1 mixture of BH$_3$·PMe$_3$ and BH$_2$Me·PMe$_3$ in [D$_6$]benzene produced a yellow solution. This solution contained **1c** and **1d**, the latter of which was more abundant as evidenced by NMR spectroscopy. The B*H* region of the ^{1}H NMR spectrum is displayed in Figure 4. Because of the substantially different chemical shifts, the BH resonances of the two

borane complexes are observed distinctly without overlap. The relative abundance of the two species did not change after 2 h of standing at room temperature. Because of this fact and the aforementioned easy exchange of boranes, the thermal equilibrium described in Equation (1) is attained in this solution. The equilibrium constant K and Gibbs free energy ΔG_{298} are then readily provided based on the relative quantity of each component in the ^{1}H NMR spectrum, and the thermodynamic stability of the borane complexes generated can be estimated. For the [Cr(CO)$_5$(η^1-BH$_2$Me·PMe$_3$)]/ [Cr(CO)$_5$(η^1-BH$_3$·PMe$_3$)] system, the K and ΔG_{298} values were 4.2 and −3.5 kJ mol^{-1}, respectively.

$$[M(CO)_5(\eta^1\text{-}BH_3 \cdot L)] + BH_2R \cdot L \overset{K}{\rightleftharpoons}$$
$$[M(CO)_5(\eta^1\text{-}BH_2R \cdot L)] + BH_3 \cdot L \quad (1)$$
$$M = \text{Cr, W; L} = PMe_3, NMe_3$$
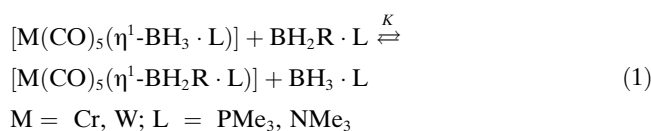
In similar manners, [Cr(CO)$_6$] or [W(CO)$_6$] was irradiated with a 1:1 mixture of BH$_3$·PMe$_3$ and various monosubstitut-

ed boranes BH$_2$R·PMe$_3$, and the relative stability of the resulting borane complexes was evaluated. Table 5 summarizes the results of the photolyses. As shown in this Table, the ability of phosphineboranes to form the stable complex increases in the following order, BH$_2$Cl·PMe$_3$ ≈ BH$_2$I·PMe$_3$ < BH$_2$(*m*-C$_6$H$_4$F)·PMe$_3$ < BH$_2$Ph·PMe$_3$ < BH$_3$·PMe$_3$ < BH$_2$Me·PMe$_3$, for both the Cr and W systems. Complexes of BH$_2$Et·PMe$_3$ were slightly unstable relative to the BH$_2$Me·PMe$_3$ derivatives. Quite a similar trend was found for the stability of amineborane complexes [M(CO)$_5$(η^1-BH$_2$R·NMe$_3$)].

This result demonstrates that a more electron-*releasing* substituent on boron more stabilizes the M-H-B linkage of the borane complexes. Steric factor does not look to be important except for the ethylborane derivatives **1–4e**. In the crystal structure of **1b**, severe steric repulsion is not found between the phenylborane ligand and metal fragment as mentioned above. Therefore, relative instability over **1–4c** of **1–4b** is thought to mainly come from the less donating ability of a phenyl group rather than from its bulkiness. Also, because a *m*-C$_6$H$_4$F group and a Ph group are similar in the steric demand, **1–4a** should be destabilized more than **1–4b** by the electron-withdrawing character of a *m*-C$_6$H$_4$F group. Furthermore, despite the steric repulsion found in the X-ray structure of **1d**, the methylborane complexes **1–4d** are more stable than **1–4c**. This is reasonably ascribed to the donating ability of a methyl group. An electron-releasing substituent raises the energy level of the BH bonding orbitals, and thereby enhances the electron donation to stabilize the borane–metal linkage.

An ethyl group has electron-releasing ability similar to or slightly greater than that of a methyl group. Nonetheless, in every series, the ethyl derivatives [M(CO)$_5$(η^1-BH$_2$Et·L)] (**1–4e**) are slightly destabilized in comparison to the methylborane complexes, **1–4d**. This is probably due to the steric hindrance of the bulkier substituent. Based on the most stable conformation of BH$_2$Et·L, it is inferred that the tip of the ethyl group points toward the M(CO)$_5$ moiety, generating a steric interaction. Unfortunately, X-ray quality crystals of **1–4e** could not be obtained.

When [Cr(CO)$_6$] is irradiated with SiHR$_3$, silane adducts [Cr(CO)$_5$(HSiR$_3$)] are generated. Although this species is unstable, it can be observed by NMR at low temperature.[37] Moreover, their lifetimes at ambient temperature have been measured by a fast spectroscopy method by Brown and co-workers.[24] In this system, despite its excellent π-accepting character, silanes with electron-releasing substituents form more stable complexes in contrast to other many silane–metal adducts. The authors attributed this result to the character of [Cr(CO)$_5$], predominantly a σ acceptor, but a weak π donor. Taking this into consideration, at present, we cannot rule out yet a possibility that the above stability trend of the Group 6 metal–borane complexes came just from the poor π donating ability of a [M(CO)$_5$] moiety. Accordingly, we then examined the stability of a series of manganese derivatives [CpMn(CO)$_2$(η^1-BH$_2$R·L)], whose metal fragment [CpMn(CO)$_2$] is known to be a potent π donor, in order to know whether the relative stability reflects the character of borane adducts as a σ ligand.

Relative thermodynamic stability of manganese borane complexes [CpMn(CO)$_2$(η^1-BH$_2$R·L)]: Photolyses of [CpMn(CO)$_3$] in the presence of a 1:1 mixture of BH$_3$·L and BH$_2$R·L gave a red solution, which consists of an equilibrium mixture containing [CpMn(CO)$_2$(η^1-BH$_3$·L)] and [CpMn(CO)$_2$(η^1-BH$_2$R·L)] {see Equation (2)}. The equilibrium constant K and Gibbs free energy ΔG_{298} for Equation (2) were estimated by the same method as that used for the Cr and W 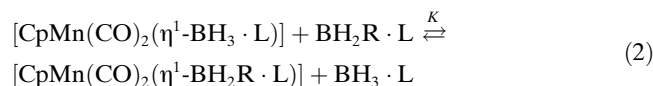systems. Table 6 lists the obtained thermodynamic parameters. As shown in this Table, the stability of the borane complexes increases again with increase of the electron-releasing ability of the substituent on boron. The degree of change of the ΔG value by the difference of the substituent is comparable to that in the Group 6 metal sys-

Table 6. Relative stability of manganese–borane complexes [CpMn(CO)$_2$(η^1-BH$_2$R·L)] (L = NMe$_3$, PMe$_3$).

| Substituent R | L = PMe$_3$ | | L = NMe$_3$ | |
in BH$_2$R·PMe$_3$	K	ΔG_{298}	K	ΔG_{298}
Cl	–[a]	–	–[a]	–
I	–[a]	–	–[a]	–
m-C$_6$H$_4$F	0.28	3.2	< 0.01	–
Ph	0.38	2.4	< 0.01	–
H (standard)	1.0	0.0	1.0	0.0
Me	1.3	−0.72	1.4	−0.83
Et	0.57	1.4	0.27	3.3

[a] Formation of a stable complex was not observed.

Table 5. Relative stability of borane complexes [M(CO)$_5$(η^1-BH$_2$R·L)] (M = Cr, W; L = PMe$_3$, NMe$_3$).

| Substituent R | BH$_2$R·PMe$_3$ complexes | | | | BH$_2$R·NMe$_3$ complexes | | | | Electron-releasing | Stability of |
| in BH$_2$R·L | M = Cr | | M = W | | M = Cr | | M = W | | ability of R | the complex |
	K	ΔG_{298}	K	ΔG_{298}	K	ΔG_{298}	K	ΔG_{298}		
Cl	–[a]	–	–[a]	–	–[a]	–	–[a]	–		
I	–[a]	–	–[a]	–	–[a]	–	–[a]	–		
m-C$_6$H$_4$F	0.10	5.8	0.08	6.1	0.02	9.9	0.02	9.2		
Ph	0.27	3.3	0.30	3.0	0.09	5.9	0.02	9.2		
H (standard)	1.0	0.0	1.0	0.0	1.0	0.0	1.0	0.0		
Me	4.1	−3.5	4.2	−3.5	2.1	−1.7	2.6	−2.4		
Et	2.5	−2.3	2.9	−2.6	0.30	3.0	0.35	2.6		

[a] Formation of a stable complex was not observed.

tems, implying that their steric effect should also not be crucial in this system, except for the case of ethyl derivatives **5e** and **6e**. Furthermore, we found that the permethylated cyclopentadienyl derivatives $[Cp*Mn(CO)_2(\eta^1\text{-}BH_3\text{·}L)]$ (L = NMe_3, PMe_3) were less stable than the Cp congeners. They were observed by NMR spectroscopy, but too labile to be isolated. These findings represent that the major contribution to the complexation of borane adducts is the borane-to-metal electron donation even in the manganese complexes.
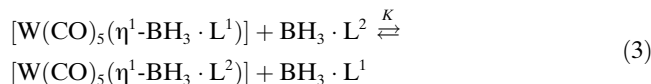
$$[CpMn(CO)_2(\eta^1\text{-}BH_3 \cdot L)] + BH_2R \cdot L \overset{K}{\rightleftharpoons}$$
$$[CpMn(CO)_2(\eta^1\text{-}BH_2R \cdot L)] + BH_3 \cdot L \qquad (2)$$

As already mentioned, in the silane complexes $[Cp'Mn(CO)_2(HSiR_3)]$ (Cp' = substituted cyclopentadienyl; R = various substituents), the metal–ligand interaction is more stabilized by electron-withdrawing groups on silicon as well as by a strongly donating Cp* ligand on manganese. Because the silane ligands undergo effective back-bonding from the central metal into the Si-H σ* orbital, the extent of the back-bonding strongly influences the strength of the silane–metal linkage.

Hartwig and co-workers have prepared manganese complexes of tricoordinate boranes, $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2\text{-}(HBX_2)]$ (HBX_2 = dicyclohexylborane, catecholborane, pinacolborane).[38] These compounds undergo substitution of the borane ligand by diphenylacetylene through a dissociative mechanism. Kinetic studies were undertaken to obtain the activation parameters for the borane dissociation. In the enthalpy of activation, which provides upper limit for the metal–borane binding energies, the reaction of the electron-rich dicyclohexylborane complex is roughly 16 kJ mol^{-1} lower than that of the catecholborane derivative. These tricoordinate boranes undergo back-bonding into the free p orbital of boron.

For the complexes of tetracoordinate borane adducts reported here, the substituent effect was opposite to the silane and tricoordinate borane derivatives. As the energy level of the BH σ* orbital is very high, its slight lowering by an electron withdrawing substituent is not so effective for the back-bonding from the metal center. Furthermore, the boron p orbital is not available to accept electron density from the central metal since it is completely filled by the coordination of the lone electron pair of the Lewis base. The metal–borane interaction is consequently dominated by the BH-to-metal electron donation, and therefore, the complex is stabilized by raise in energy of the BH σ orbital through the incorporation of an electron-releasing substituent. Lack of back-donation to the borane ligand is also consistent with the geometry of **6d**, in which the coordinated BH does not adopt an orientation proper to achieve such an interaction.

Lewis Base effect: Another interest is the influence of a Lewis base on boron upon the stability of the complexes. Photolysis of $[W(CO)_6]$ in the presence of a 1:1 mixture of BH_3·PMe_3 and BH_3·NMe_3 in [D_6]benzene produced an equilibrium mixture containing $[W(CO)_5(\eta^1\text{-}BH_3\text{·}PMe_3)]$ (**3c**) and $[W(CO)_5(\eta^1\text{-}BH_3\text{·}NMe_3)]$ (**4c**) [Eq. (3)].

$$[W(CO)_5(\eta^1\text{-}BH_3 \cdot L^1)] + BH_3 \cdot L^2 \overset{K}{\rightleftharpoons}$$
$$[W(CO)_5(\eta^1\text{-}BH_3 \cdot L^2)] + BH_3 \cdot L^1 \qquad (3)$$

In this mixture, the amineborane complex **4c** was more abundant than the phosphineborane derivative **3c** as determined by ^1H and ^{11}B NMR spectroscopy. The K and ΔG_{298} values for Equation (3) were 2.6 and −2.4 kJ mol^{-1}, respectively. Likewise, irradiation of $[CpMn(CO)_3]$ with a mixture of the two kinds of boranes gave an amineborane complex-rich mixture. Thus, BH_3·NMe_3 better stabilizes the complex than BH_3·PMe_3. Trimethylamine is more basic than trimethylphosphine (pK_a of the conjugate acid: 10.0 for NHMe_3$^+$; 8.7 for PHMe_3$^+$).[36,39] Incorporation of a stronger base brings an effect equivalent to that of an electron-releasing substituent. Table 7 lists the relative stability of Cr, W, and Mn complexes of four kinds of borane adducts. The ability to form a stable complex increases in the order, BH_3·PPh_3 < BH_3·PMe_3 < BH_3·NMe_3 < BH_3·quinuclidine, for every metal series. Additionally, the less basic pyridineborane does not give the complexes stable enough to be isolated.[4] These clearly show that a borane with a stronger Lewis base stabilizes its complexes.

Site exchange of BH protons: Borane complexes prepared in this work all show a dynamic behavior due to exchange between the metal-coordinated and terminal BH protons. It was found that the activation barrier for this process correlated with the thermodynamic stability of the compounds. For example, $[Cr(CO)_5(\eta^1\text{-}BH_3\text{·}quinuclidine)]$ (**7**) showed a single ^1H NMR resonance of the BH protons at δ −3.3 ppm at room temperature. This resonance collapsed into the base line at 218 K. Further cooling to 183 K revealed two distinct signals, which were assigned to the bridging and terminal BH hydrogen atoms, at −13.8 and 2.0 ppm. The ΔG^+ value was evaluated to be 35 kJ mol^{-1} at 218 K. For less stable $[Cr(CO)_5(\eta^1\text{-}BH_3\text{·}NMe_3)]$ (**2c**), the lower activation energy, 34 kJ mol^{-1} was found for the same fluxional process. In the case of $[Cr(CO)_5(\eta^1\text{-}BH_3\text{·}PMe_3)]$ (**1c**), split of the BH resonance is not observed down to 193 K, and the activation barrier has been estimated to be less than 28 kJ mol^{-1}.[4] Thus,

Table 7. Influence of the Lewis base L upon the relative stability of complexes $[ML'_n(\eta^1\text{-}BH_3\text{·}L)]$.

Lewis-base L in BH_3·L	ML'_n=[Cr(CO)_5]		ML'_n=[W(CO)_5]		ML'_n=[CpMn(CO)_2]		pK_a value of the conjugate acid LH$^+$
	K	ΔG_{298}	K	ΔG_{298}	K	ΔG_{298}	
PPh_3	0.39	2.4	0.20	4.0	< 0.01	–	2.73
PMe_3 (standard)	1.0	0.0	1.0	0.0	1.0	0.0	8.7
NMe_3	3.2	−2.9	2.6	−2.4	1.6	−1.2	10.0
quinuclidine	8.6	−5.3	6.5	−4.6	2.6	−2.4	11.0[a]

[a] pK_a value of structurally similar NEt_3.

the order of the $\Delta G^{\pm}$ value is parallel to that of the thermodynamic stability of **1c**, **2c**, and **7**. Similar relationship was found between the activation barrier for the dynamic process and thermodynamic stability of the manganese species, [CpMn(CO)$_2$(η^1-BH$_3$·L)] (L = PMe$_3$ (**5c**), NMe$_3$ (**6c**), quinuclidine (**9**); see Table 8).

Table 8. The coalescence temperature of the BH resonances T_c [K] and activation free energy $\Delta G^{\pm}$ [kJ mol^{-1}] for the BH exchange of borane complexes.

Compound	T_c	$\Delta G^{\pm}$
[Cr(CO)$_5$(η^1-BH$_2$Ph·NMe$_3$)] (**2b**)	213	34
[Cr(CO)$_5$(η^1-BH$_3$·NMe$_3$)] (**2c**)	213	34
[Cr(CO)$_5$(η^1-BH$_2$Me·NMe$_3$)] (**2d**)	243	39
[W(CO)$_5$(η^1-BH$_2$Ph·NMe$_3$)] (**4b**)	< 178	< 28
[W(CO)$_5$(η^1-BH$_3$·NMe$_3$)] (**4c**)	< 174	< 28
[W(CO)$_5$(η^1-BH$_2$Me·NMe$_3$)] (**4d**)	193	31
[CpMn(CO)$_2$(η^1-BH$_2$Ph·PMe$_3$)] (**5b**)	208	33
[CpMn(CO)$_2$(η^1-BH$_3$·PMe$_3$)] (**5c**)	213	30
[CpMn(CO)$_2$(η^1-BH$_2$Me·PMe$_3$)] (**5d**)	228	36
[CpMn(CO)$_2$(η^1-BH$_2$Ph·NMe$_3$)] (**6b**)	268	43
[CpMn(CO)$_2$(η^1-BH$_3$·NMe$_3$)] (**6c**)	253	40
[CpMn(CO)$_2$(η^1-BH$_2$Me·NMe$_3$)] (**6d**)	293	47
[Cr(CO)$_5$(η^1-BH$_3$·PMe$_3$)] (**1c**)	< 193	< 28
[Cr(CO)$_5$(η^1-BH$_3$·NMe$_3$)] (**2c**)	213	34
[Cr(CO)$_5$(η^1-BH$_3$·quinuclidine)] (**7**)	218	35
[CpMn(CO)$_2$(η^1-BH$_3$·PMe$_3$)] (**5c**)	213	30
[CpMn(CO)$_2$(η^1-BH$_3$·NMe$_3$)] (**6c**)	253	40
[CpMn(CO)$_2$(η^1-BH$_3$·quinuclidine)] (**9**)	258	41

The site exchange of the BH hydrogen atoms proceeds through the transition state (TS) that involves an η^2-interacting borane ligand, where the metal–hydrogen separations are much longer than in the equilibrium structures.[40] Based on such a deformation to the TS, we have pointed out that the activation barrier virtually corresponds to the energy to weaken the bridging hydrogen–metal interaction. Consequently, as the strength of the bonding between the metal and coordinated BH hydrogen is increased, the activation barrier for the BH exchange should become greater.

Likewise, the $\Delta G^{\pm}$ values for the BH exchange were reasonably higher in [M(CO)$_5$(η^1-BH$_2$Me·NMe$_3$)] (M = Cr (**2d**), W (**4d**)) than in [M(CO)$_5$(η^1-BH$_2$Ph·NMe$_3$)] (**2b**, **4b**) and [M(CO)$_5$(η^1-BH$_3$·NMe$_3$)] (**2c**, **4c**). However, in a series of [CpMn(CO)$_2$(η^1-BH$_2$R·EMe$_3$)] (E = N, P), both **5b**, **6b** (R = Ph) and **5d**, **6d** (R = Me) showed higher $\Delta G^{\pm}$ values than **5c**, **6c** (R = H). This is probably due to the raise in energy of the TS, which is caused by the steric repulsion between the phenyl group and cyclopentadienyl ligand in the four-membered structure (Scheme 3).
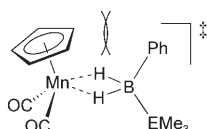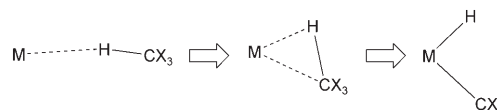

Scheme 3.

Conclusion

This work clarified factors that affect the stability of borane σ complexes. Introduction of an electron-releasing substituent and stronger Lewis base unto boron is effective to stabilize the B-H-M interaction in Group 6 complexes, [M(CO)$_5$(η^1-BH$_2$R·L)]. Importantly, the same trend was found about the substituent and Lewis base effects for the manganese system, [CpMn(CO)$_2$(η^1-BH$_2$R·L)]. This makes a sharp contrast to the stability of silane complexes, [CpMn(CO)$_2$(HSiR$_3$)]. These findings are in accordance with the bonding scheme for the borane–metal interaction, where the borane-to-metal electron donation dominates over the back-donation into the BH σ* orbitals. Such a bonding nature obviously originates from the high energy of the B-H σ* orbitals. Borane adducts BH$_3$·L are thus considerably different as a σ ligand from other species including H$_2$, silanes, and tricoordinate boranes, whose coordination to metal involves significant back-donation to the σ* (for H$_2$ and silanes) or vacant p (for tricoordinate boranes) orbital. Hence, complexes of borane–Lewis base adducts make a unique family among transition metal σ complexes.

During oxidative addition of alkanes, an alkane molecule approaches a metal center along a CH axis (in an end-on fashion), and then the M-H-C angle decreases to transform into a side on geometry and the C–H distance is elongated on further approach (Scheme 4).[13,41] At the latter stage,

Scheme 4.

metal back-donation to the CH σ* orbital becomes strong. The structures of borane complexes [M(CO)$_5$(η^1-BH$_2$R·L)] (**1–4**, **7**, and **8**) and [CpMn(CO)$_2$(η^1-BH$_2$R·L)] (**5**, **6**, and **9**) are featured by the end-on coordination and unstretched BH bond. In addition, the little back-donation into the BH σ* orbital has been demonstrated experimentally in this work. Thus, complexes of borane adducts can be model cases of the earlier stage in the reaction coordinate of alkane oxidative addition. This is complimentary with silane complexes, whose structure and bonding are reminiscent of the latter stage of the described process.

Nikonov pointed out the difference as a σ ligand between the second-row element compounds (e.g. alkanes) and their heavier analogues.[23c] Silicon, germanium, and tin have a propensity to be hypervalent. In a hypothetical donor–acceptor complex L$_n$M→SiHX$_3$, the metal moiety acts as a Lewis base toward the acidic silicon center. If the metal–ligand interaction has any extent of such a character, the compound necessarily involves close contact between the metal and silicon. In actual, most of the non-classical silane ligands coordinate to metal with a side-on fashion. On the other hand, carbon and tetracoordinate boron cannot adopt

such an interaction because of the absence of an acceptor orbital. Both of the borane adduct complexes **1–9** and the theoretically optimized structure of $[W(CO)_5(alkane)]$ include a sufficiently long E···M separation (end-on coordination, E = C or B).[42] In this point, metal complexes of borane–Lewis base adducts are closer, as a model system, to alkane complexes than silane derivatives of the same Group 14. Such a discussion may be expanded to the difference in the bonding situation between borane adduct complexes and tricoordinate borane derivatives (e.g. $[(MeCp)Mn(CO)_2(HBX_2)]$,[37,43] $[Cp_2Ti(HBcat)_2]$,[44] and $[Cp_2Ti(HBcat)(PMe_3)]$,[45] HBcat = catecholborane), the latter of which involve short contact between metal and boron. In these compounds, the boron atom can utilize a free p orbital to accept electron density from metal and thereby expands its coordination number from three to four.

Finally, the results of this work give a guiding principle to synthesize new borane complexes. As BH_3·L ligands bind to metal through the BH-to-metal donation, it is likely that they prefer more electrophilic metal centers. This suggests high affinity of borane adducts with cationic metal fragments. This is being confirmed in our research group.[7]

Experimental Section

All manipulations were carried out under high vacuum or a dry nitrogen atmosphere. Reagent-grade hexane, diethyl ether, and toluene were distilled under a nitrogen atmosphere from sodium/benzophenone just before use. [D$_6$]Benzene and [D$_8$]toluene were dried over potassium mir-

rors before use and transferred into NMR tubes under vacuum. BH_3·PMe_3, BH_3·PPh_3, and BH_3·NMe_3 were prepared by treatment of B_2H_6 with the corresponding bases under vacuum.[46] BH_3·quinuclidine,[47] BH_2Cl·L and BH_2I·L (L = NMe_3, PMe_3) were prepared according to the literature methods.[48] [Cr(CO)6] (Strem), [W(CO)$_6$] (Aldrich), and [CpMn(CO)$_3$] (Strem) were used as purchased. ^1H, ^{11}B, ^{31}P, and ^{13}C NMR spectra were recorded on a JEOL α-500 spectrometer. IR spectra were recorded on a JASCO FTIR-350 spectrometer. Mass spectra were measured on a JEOL JMS-S600H spectrometer.

Syntheses of monosubstituted boranes: Amine-complexed monoorganyl-boranes BH_2R·NMe_3 (R = m-C_6H_4F, Ph, Et) were prepared by modified methods of the synthetic procedure for BH_2Me·NMe_3.[49] Typically, phenylboroxine [PhBO]$_3$ (1.30 g, 4.17 mmol) was heated with LiAlH$_4$ (480 mg, 12.5 mmol) in refluxing diethyl ether (60 mL) in the presence of NMe_3 (21.3 mmol) for 3 h. Hydrolysis (0.81 mL of H_2O), filtration, and evaporation of the resultant mixture gave BH_2Ph·NMe_3 (1.30 g, 9.0 mmol, 72 %) as a colorless crystalline solid. Even when PhB(OH)$_2$ was used instead of [PhBO]$_3$, BH_2Ph·NMe_3 was obtained in similar yield. The syntheses of other amineboranes were carried out by the similar methods using the corresponding boroxines or boronic acids. The yields of BH_2(m-C_6H_4F)·NMe_3 (white crystalline solid) and BH_2Et·NMe_3 (colorless oil) were 47 and 72 %, respectively. Likewise, analogous phosphine-boranes BH_2R·PMe_3 (R = m-C_6H_4F, Ph, Me, Et) were obtained by treatment of the boroxine or boronic acid with LiAlH$_4$ in the presence of excess PMe_3. BH_2(m-C_6H_4F)·PMe_3 (white solid, 86 %), BH_2Ph·PMe_3, (white solid, 48 %), BH_2Me·PMe_3 (colorless crystals that melt around room temperature, 61 %), BH_2Et·PMe_3 (colorless oil, 64 %). ^1H and ^{11}B NMR data of the new boranes are listed in Table 9. ^{13}C NMR, ^{31}P NMR, IR, MS, and analytical data are shown in Table 10.

Photolyses of [M(CO)$_6$] (M = Cr, W) and [CpMn(CO)$_3$] in the presence of substituted boranes: An NMR tube connected to a vacuum line was charged with the carbonyl complexes (about 10 mg) and BH_2R·L (1 equiv), and [D$_6$]benzene (0.5 mL) was introduced. The sample tube was flame-sealed under high vacuum. The sample was then irradiated with a 450 W medium pressure Hg arc lamp for 1 h at 8 °C. ^1H and ^{11}B NMR

Table 9. ^1H and ^{11}B NMR spectral data for new boranes, BH_2R·L.[a]

Compound	^1H NMR (500 MHz)			^{11}B NMR (160.4 MHz)
	BH	R	L	
BH_2(m-C_6H_4F)·PMe_3	2.31 (q of d, ^1J(B,H) = 94.0 Hz, ^2J(P,H) = 15.5 Hz, 2H)	6.67–7.37 (m, 4H, ring H)	0.44 (d, ^2J(P,H) = 10.5 Hz, 9H)	−24.1 (d of t, ^1J(B,P) = 56.0 Hz, ^1J(B,H) = 94.0 Hz)
BH_2Ph·PMe_3	2.44 (q of d, ^1J(B,H) = 90.5 Hz, ^2J(P,H) = 12.5 Hz, 2H)	7.24 (t, ^3J(H,H) = 7.5 Hz, 1H, p-H), 7.41 (t, ^3J(H,H) = 7.0 Hz, 2H, m-H), 7.74 (br, 2H, o-H)	0.49 (d, ^2J(P,H) = 10.0 Hz, 9H)	−23.9 (d of t, ^1J(B,P) = 53.6 Hz, ^1J(B,H) = 90.5 Hz)
BH_2Me·PMe_3	1.67 (q, ^1J(B,H) = 92.0 Hz, 2H)	0.23 (q of d, ^2J(B,H) = 5.5 Hz, ^3J(P,H) = 22.5 Hz, 3H)	0.62 (d, ^2J(P,H) = 10.0 Hz, 9H)	−29.0 (d of t, ^1J(B,P) = 52.0 Hz, ^1J(B,H) = 92.0 Hz)
BH_2Et·PMe_3	1.64 (q, ^1J(B,H) = 94.0 Hz, 2H)	0.85 (br, 2H, CH_2CH$_3$), 1.46 (br, 3H, CH$_2$CH_3)	0.60 (d, ^2J(P,H) = 10.0 Hz, 9H)	−24.5 (d of t, ^1J(B,P) = 51.3 Hz, ^1J(B,H) = 94.0 Hz)
BH_2(m-C_6H_4F)·NMe_3	2.74 (q, ^1J(B,H) = 100.2 Hz, 2H)	6.95–7.48 (m, 4H, ring H)	1.70 (s, 9H)	−1.1 (t, ^1J(B,H) = 100.2 Hz)
BH_2Ph·NMe_3	2.87 (q, ^1J(B,H) = 102.0 Hz, 2H)	7.30 (t, ^3J(H,H) = 8.0 Hz, 1H, p-H) 7.41 (m, 2H, m-H) 7.74 (d, ^3J(H,H) = 7.0 Hz, 2H, o-H)	1.81 (s, 9H)	−0.5 (t, ^1J(B,H) = 102.0 Hz)
BH_2Et·NMe_3	2.20 (q, ^1J(B,H) = 97.0 Hz, 2H)	0.64 (br, 2H, CH_2CH$_3$) 1.37 (t, ^3J(H,H) = 16.1 Hz, CH$_2$CH_3)	1.88 (s, 9H)	−0.9 (t, ^1J(B,H) = 97.0 Hz)
BH_3·quinuclidine	2.23 (q, ^1J(B,H) = 96.2 Hz, 3H)	–	0.92 (br, 6H, N(CH$_2$CH_2)$_3$CH) 1.14 (br, 1H, N(CH$_2$CH$_2$)$_3$CH) 2.65 (t, ^3J(H,H) = 7.8 Hz, 6H, N(CH_2CH$_2$)$_3$CH)	−10.4 (q, ^1J(B,H) = 96.2 Hz)

[a] NMR spectra were recorded in [D$_6$]benzene.

Table 10. ^{13}C and ^{31}P NMR, IR, and MS spectral data and analytical data for new boranes, $BH_2R\cdot L$[a].

Compound	^{13}C NMR (125 MHz)	^{31}P NMR (202.4 MHz)	IR (ν(BH))	EI MS [%]	elemental analysis found [%] (calcd)
$BH_2(m\text{-}C_6H_4F)\cdot PMe_3$	9.4 (d, ^1J(P,C) = 36.9 Hz, PMe), 111.7 (d of d, J(P,C) = 4.5 Hz, J(F,C) = 20.5 Hz), 122.1 (d of d, J(P,C) = 6.6 Hz, J(F,C) = 16.5 Hz), 128.3 (s), 128.9 (s), 131.8 (d, J = 6.6 Hz, ring-C)	−9.0 (q, ^1J(B,P) = 56.0 Hz)	2340.7, 2329.6	76 (100) [$PMe_3{}^+$], 184 (41) [M^+]	C 58.59 (58.75), H 8.20 (8.22)
$BH_2Ph\cdot PMe_3$	9.6 (d, ^1J(P,C) = 35.2 Hz, PMe), 125.1 (d, J(P,C) = 5.2 Hz), 127.7 (br), 136.4 (d, J(P,C) = 7.2 Hz, ring-C)	−9.8 (q, ^1J(B,P) = 53.6 Hz)	2374.7, 2332.0, 2308.9	166 (100) [M^+]	C 65.00 (65.12), H 9.76 (9.71)
$BH_2Me\cdot PMe_3$	−5.4 (q, ^1J(B,C) = 44.5 Hz, BMe), 9.8 (d, ^1J(P,C) = 34.1 Hz, PMe)	−10.1 (q, ^1J(B,P) = 52.0 Hz)	2379.7, 2305.5	103 (3) [$M^+ - H$], 76 (100) [$PMe_3{}^+$]	C 45.13 (46.22), H 12.58 (13.58)
$BH_2Et\cdot PMe_3$	6.3 (q, ^1J(B,C) = 51.3 Hz, CH_2CH_3), 17.4 (CH_2CH_3), 10.6 (d, ^1J(P,C) = 34.1 Hz, PMe)	−5.4 (q, ^1J(B,P) = 51.3 Hz)	2384.6, 2303.6	76 (100) [$PMe_3{}^+$], 118 (12) [M^+]	C 49.23 (50.91), H 13.16 (13.67)
$BH_2(m\text{-}C_6H_4F)\cdot NMe_3$	51.0 (NMe), 112.8 (d, J(F,C) = 20.0 Hz), 124.0 (d, J(F,C) = 16.6 Hz), 127.6 (s), 128.7 (d, J = 7.3 Hz), 133.6 (s, ring-C)	−	2402.9, 2379.7, 2349.4, 2324.8	166 (100) [$M^+ - H$]	C 64.76 (64.72), H 8.99 (9.05), N 8.39 (8.39)
$BH_2Ph\cdot NMe_3$	51.0 (NMe), 126.2, 127.4, 138.3 (ring-C)	−	2404.3, 2348.4, 2333.0, 2375.9	148 (100) [$M^+ - H$]	C 72.59 (72.53), H 10.74 (10.82), N 9.41 (9.40)
$BH_2Et\cdot NMe_3$	9.5 (q, ^1J(B,C) = 47.5 Hz, CH_2CH_3), 13.1 (s, CH_2CH_3), 51.4 (NMe)	−	2382.6, 2310.7	100 (100) [$M^+ - H$]	C 59.26 (59.46), H 15.43 (15.97), N 12.88 (13.87)
$BH_3\cdot$quinuclidine	20.3 (N(CH$_2$CH$_2$)$_3$CH), 24.8 (N(CH$_2$CH$_2$)$_3$CH), 53.3 (N(CH$_2$CH$_2$)$_3$CH	−	2354.7, 2309.8	124 (100) [$M^+ - H$]	C 67.08 (67.25), H 12.83 (12.90), N 11.23 (11.20)

[a] NMR spectra were recorded in [D_6]benzene.

spectra of the resulting yellow (Cr, W) or red (Mn) solutions exhibited formation of the corresponding borane complexes except when haloboranes were used.

Estimation of the relative thermodynamic stability of various borane complexes: [D_6]Benzene (0.5 mL) solutions containing [M(CO)$_6$] or [CpMn(CO)$_3$] (0.1 mmol), BH$_3$·L, and BH$_2$R·L (R = m-C$_6$H$_4$F, Ph, Me, Et; L = PMe$_3$, NMe$_3$; 0.1 mmol) were prepared in NMR sample tubes. They were photolyzed with a 450 W medium pressure Hg lamp for 1 h at 8 °C. After the photolyses, the ^{1}H NMR spectra were recorded and the thermodynamic parameters were calculated based on the amounts of BH$_3$·L, BH$_2$R·L, and their complexes. Similarly, the metal carbonyls were irradiated in the presence of BH$_3$·PMe$_3$ and BH$_3$·L′ (L′ = PPh$_3$, NMe$_3$, quinuclidine) to evaluate the relative stability of their complexes.

X-ray crystal structure determination: Crystals of **1b**, **1d**, and **6d** were grown by cooling their solutions in hexane/toluene mixture. Intensity data were collected on a Rigaku RAPID imaging plate diffractometer using graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). Data collection was carried out at −120 °C (for **1b**, **1d**) or −123 °C (for **6d**). Crystal data, data collection parameters, and convergence results are listed in Table 11.

Numerical absorption corrections were applied on the crystal shapes. The structures of all complexes were solved by the direct method and refined on F^2. All non-hydrogen atoms were located and refined applying anisotropic temperature factors. Coordinates of hydrogen atoms bound to boron were determined by the difference Fourier syntheses and were refined isotropically. Positions of other hydrogen atoms were idealized with use of riding models. Crystals of **1b** included two molecules of toluene in the lattice, and they disordered over two sites. Calculations were performed using a program package SHELX 97.[50]

CCDC-630 148 (**1b**), -630 149 (**1d**), and -630 150 (**6d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 11. Crystal data for compounds **1b**·$\frac{1}{2}$toluene, **1d**, and **6d**.

	1b·$\frac{1}{2}$toluene	**1d**	**6d**
empirical formula	$C_{17.5}H_{20}BCrO_5P$	$C_9H_{14}BCrO_5P$	$C_{11}H_{19}BMnNO_2$
F_w	404.12	295.98	263.02
crystal color	yellow	yellow	red
T [K]	153(2)	153(2)	153(2)
λ [nm]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	6.5336(19)	7.109(4)	11.3674(8)
b [Å]	19.703(6)	9.990(7)	8.5047(6)
c [Å]	15.510(6)	11.024(6)	13.7194(9)
α [°]	90	86.04(2)	90
β [°]	95.520(15)	83.898(18)	98.257(2)
γ [°]	90	69.80(2)	90
V [Å^3]	1987.3(12)	730.1(7)	1312.6(2)
Z	4	2	4
ρ_{calcd} [Mg m^{-3}]	1.351	1.346	1.331
μ [mm^{-1}]	0.679	0.896	0.990
$F(000)$	836	304	552
crystal size/mm	$0.40 \times 0.35 \times 0.08$	$0.45 \times 0.35 \times 0.08$	$0.45 \times 0.45 \times 0.30$
θ range [°]	3.13 to 27.48	3.07 to 27.47	2.83 to 27.48
index ranges	$0 \leq h \leq 8$	$0 \leq h \leq 9$	$0 \leq h \leq 14$
	$0 \leq k \leq 25$	$-11 \leq k \leq 12$	$0 \leq k \leq 11$
	$-20 \leq l \leq 20$	$-14 \leq l \leq 14$	$-17 \leq l \leq 17$
independent reflns	4552	3332	2700
no. parameters	255	166	157
GoF on F^2	1.100	1.043	0.903
final R indices [$I > 2\sigma(I)$]			
$R1$	0.0386	0.0474	0.0292
$wR2$	0.1299	0.1522	0.0789
R indices (all data)			
$R1$	0.0470	0.0530	0.0300
$wR2$	0.1384	0.1597	0.0798
largest diff. peak and hole [e Å^{-3}]	0.412 and −0.640	0.687 and −0.542	0.382 and −0.260

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