Syntheses and Structures of Trimethylphosphine-complexed Primary Boryl Complexes of Group 8 Metals, $Cp^*M(CO)_2(BH_2{\cdot}PMe_3)$ (M = Fe, Ru)

Takahiro Yasue, Yasuro Kawano,* and Mamoru Shimoi
Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Meguro-ku, Tokyo 153-8902

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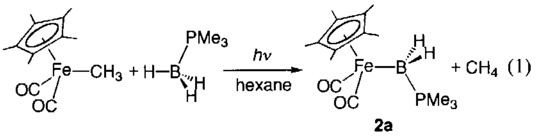
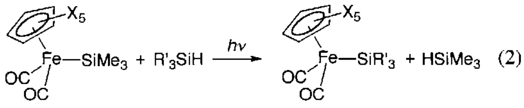
Photolysis of $Cp^*Fe(CO)_2Me$ in the presence of $BH_3{\cdot}PMe_3$ (**1**) produced a boryliron complex $Cp^*Fe(CO)_2(BH_2{\cdot}PMe_3)$ (**2a**). Complex **2a** and the ruthenium analogue $Cp^*Ru(CO)_2(BH_2{\cdot}PMe_3)$ (**3**) were accessible by the salt-elimination reaction between $K[Cp^*M(CO)_2]$ (M = Fe, Ru) and $BH_2Cl{\cdot}PMe_3$.

Recently we described non-substituted boryl complexes of group 6 metals, $Cp^*M(CO)_3(BH_2{\cdot}PMe_3)$ (M = Mo, W). The syntheses of these compounds were accomplished by the photolyses of methyl complexes $Cp^*M(CO)_3Me$ in the presence of $BH_3{\cdot}PMe_3$ (**1**).[1,2] This preparation is remarkable as an example of BH bond activation of a tetra-coordinate (sp^3-type) borane, which is isoelectronic with alkanes. To examine the generality of BH activation of tetra-coordinate boranes by metal complexes and to obtain further knowledge on the properties of non-substituted boryl complexes, we carried out the photolysis of a methyliron complex, $Cp^*Fe(CO)_2Me$ with **1**. Syntheses of boryl complexes by salt-elimination reactions with use of $K[Cp^*M(CO)_2]$ (M = Fe, Ru) and $BH_2Cl{\cdot}PMe_3$ were also examined.

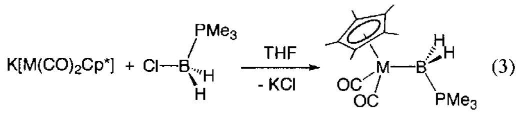
A hexane solution of $Cp^*Fe(CO)_2Me$ and **1** was photolyzed using a medium pressure Hg lamp to produce a new boryliron complex $Cp^*Fe(CO)_2(BH_2{\cdot}PMe_3)$ (**2a**) in low yield (5%).[3] Monitoring of the reaction by NMR spectroscopy showed evolution of methane (eq 1). Although the non-substituted cyclo-pentadienyl derivative $CpFe(CO)_2(BH_2{\cdot}PMe_3)$ (**2b**) was generated by the similar photoreaction of $CpFe(CO)_2Me$ with **1** in C_6D_6, the isolation was not successful due to its thermal instability ($\tau_{1/2} \approx 24$ h).[4] The phenomenon that the Cp derivative is thermally unstable is parallel to the molybdenum and tungsten systems.[1] The photochemical formation of **2** probably proceeds via dissociation of a CO ligand and following interaction between the resulting intermediate $Cp^*Fe(CO)Me$ and **1** through a B–H–Fe 3c2e bond or complete oxidative addition of BH.[1a,5] However, no intermediate was detected spectroscopically during the photolysis. Wrighton *et al.* and Ogino *et al.* have reported the photolysis of $Cp'Fe(CO)_2SiMe_3$ (Cp' = Cp, Cp*) in the presence of hydrosilanes, R'_3SiH, which results in silyl-exchange to give $Cp^*Fe(CO)_2SiR'_3$ and Me_3SiH (eq 2).[6-8] Formation of **2** is apparently akin to the silyl exchange. We also note that the photolysis of $CpFe(CO)_2SiMe_3$ with $RSiH_3$ (R = *t*Bu, CMe_2CMe_2H) produces silylene-bridged diiron complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHR)$, via double activation of Si-H bonds.[8] In this boron system, however, no evidence for the multiple activation of BH bonds was observed.





X = H, Me; $SiR'_3 = SiEt_2Me$, $SiEt_3$, $SiH_2{}^tBu$, $SiH_2(CMe_2CMe_2H)$

During the photochemical synthesis of **2a**, a large amount of $[Cp^*Fe(CO)_2]_2$ precipitated (47–89% recovery) and obstructed the light, reducing the efficiency of the photolysis. Alternatively, **2a** was obtained in better yield (14%) by the conventional salt-elimination method with the use of $K[FeCp^*(CO)_2]$ and $BH_2Cl{\cdot}PMe_3$.[9] The Ru analogue $Cp^*Ru(CO)_2(BH_2{\cdot}PMe_3)$ (**3**) was also prepared by the similar reaction (eq 3).[10] Similar methods have also been employed for the syntheses of boryliron and ruthenium complexes with a tri-coordinate boryl group.[12,13]



2a: M = Fe; **3**: M = Ru

Precise structural data of **2a** were not obtained due to crystal twinning problems. We therefore determined the crystal structure of the ethyltetramethylcyclopentadienyl derivative, $(\eta^5\text{-}C_5Me_4Et)Fe(CO)_2(BH_2{\cdot}PMe_3)$ (**2c**).[14] An ORTEP diagram of **2c** is shown in Figure 1. Owing to the steric effect, the Fe–B axis adopts an *anti* conformation with respect to Cp* and PMe_3 ligands. The Fe–B bond distance of 2.195(14) Å is slightly longer than the sum of the half of the Fe–Fe interatomic distance in $[CpFe(CO)_2]_2$ (2.531(2) Å)[15] and half of the boron–boron bond length in $B_2H_4{\cdot}2PMe_3$ (1.740(7) Å).[16] It is also the longest Fe–B σ bond among structurally authenticated iron(II) boryl complexes. The Fe–B bond distances of $CpFe(CO)_2Bcat$ (cat = $1,2\text{-}O_2C_6H_4$),[12] $CpFe(CO)_2BPh_2$,[12] $CpFe(CO)_2B(NMe_2)B(Cl)NMe_2$,[13a] and $[Fe(CO)_4(Bcat^*)_2]$[17] (cat* = $1,2\text{-}O_2\text{-}4\text{-}{}^tBuC_6H_3$) are 1.959(6), 2.034(3), 2.090(3), and 2.028(7) Å, respectively. Those of the iron-substituted borazine, $[(\eta\text{-}C_5H_4Me)Fe(CO)_2]_2(B_3ClN_3H_3)$, are 2.041(1) and 2.045(1) Å.[18] Figure 2 illustrates the molecular structure of **3**.[19] The overall geometry is similar to that of **2c**. The Ru–B bond length (2.243(8) Å) is likewise substantially longer than those of $CpRu(CO)_2B(NMe_2)B(Cl)NMe_2$ (2.173(3) Å) and $CpRu(CO)_2BClN(SiMe_3)BCl\{N(SiMe_3)_2\}$ (2.115(2) Å).[13b,c]

For boryliron complexes, we can find a good correlation between the Fe–B bond distances and the positions of the CO stretching bands. The short Fe–B bond in $CpFe(CO)_2Bcat$ is caused by the significant back-bonding from iron to the *p* orbital of boron.[12] The back-bonding reduces the electron density on the iron atom, and consequently, the ν(CO) bands

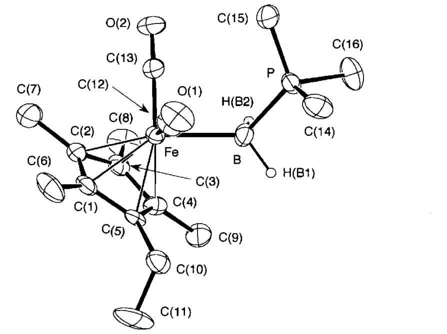


Figure 1. Molecular structure of **2c**. Selected interatomic distances (Å) and angles(°): Fe–B 2.195(14), B–P 1.924(15); Cp*(centroid)–Fe–B 119.7 (4), Fe–B–P 120.7(8), B–Fe–C(12) 88.3(6), B–Fe–C(13) 88.1(5).

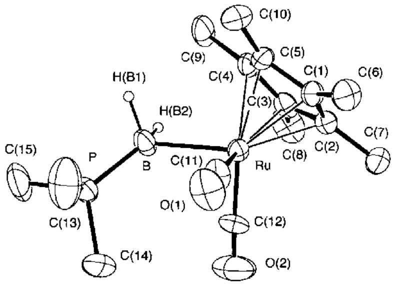


Figure 2. Molecular structure of **3**. Selected interatomic distances (Å) and angles(°): Ru–B 2.243(8), B–P 1.916(9); Cp*(centroid)–Ru–B 116.4 (2), Ru–B–P 122.8(4), B–Ru–C(11) 86.2(4), B–Ru–C(12) 90.7(4).

appear at *higher* wavenumbers than those of $CpFe(CO)_2Me$. A moderate shift to lower wavenumbers of the CO stretching bands ($\Delta\nu(CO)$ = 27 cm^{-1}: average of the shifts of the $\nu(CO)_{sym}$ and $\nu(CO)_{asym}$ bands) relative to those of the methyl complex is found for $CpFe(CO)_2B(NMe_2)B(Cl)NMe_2$, which has a slightly longer Fe–B bond.[13a] In this compound, the boron *p* orbital and the *d* orbital HOMO of $[FeCp(CO)_2]^+$ are perpendicular each other due to the conformation around the Fe–B axis, thus, the π interaction is not pronounced. In complex **2a**, with the longest Fe–B bond in the related systems, the boron *p* orbital is completely filled by coordination of a lone electron pair of PMe_3 so that back-bonding from iron to boron is impossible. Indeed **2a** displays the ν(CO) bands at 1932 and 1869 cm^{-1}, which are much lower in comparison to $Cp^*Fe(CO)_2Me$ ($\Delta\nu(CO)$ = 52 cm^{-1}). In ^{11}B NMR, the boryl group of **2a** resonates at lower field by 12 ppm than $BH_3{\cdot}PMe_3$ (**1**). This infers a polar character of the iron–boron σ bond, M(-)–B(+). The polarization of the Fe–B σ bond also leads to red shift of the ν(CO) bands and elongates the Fe–B bond. Complex **3** also shows low field shifted ^{11}B NMR signal and red shifted ν(CO) bands. Recently, gallyliron complexes with a highly polar Fe–Ga bond, $CpFe(CO)_2(GaX_2{\cdot}NR_3)$ were reported by Fischer *et al.*[20] For thermally unstable $CpFe(CO)_2(GaH_2{\cdot}NMe_3)$, the ν(CO) vibrational frequencies are ca. 60 cm^{-1} lower in avarage than those of $CpFe(CO)_2Me$. The extent of the red shift is similar to that of **2a** and **3**.

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References and Notes

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3 A hexane (40 mL) solution of $Cp^*Fe(CO)_2Me$ (132 mg, 0.50 mmol) and $BH_3{\cdot}PMe_3$ (**1**) (166 mg, 1.8 mmol) was irradiated using a 450 W medium pressure Hg lamp at 5 °C. After 1 h of photolysis, the solvent and excess **1** were removed under vacuum, and the resulting residue was extracted with pentane (1.2 mL). Cooling of the extract provided $Cp^*Fe(CO)_2(BH_2{\cdot}PMe_3)$ (**2a**) (9 mg, 0.03 mmol, 5%) as amber plates. ^1H NMR (500 MHz, C_6D_6) δ 0.92 (d, $^2J_{PH}$ = 10.0 Hz, 9H, PMe_3), 1.79 (s, 15H, Cp*), the BH signal was too broad to be observed. ^{11}B NMR (160.4 MHz, C_6D_6) δ –25.1 (dt, $^1J_{BH}$ = 110.0 Hz, $^1J_{BP}$ = 63.0 Hz). ^{31}P NMR (202.4 MHz, C_6D_6) δ 0.2 (q,$^1J_{BP}$ = 63.0 Hz). IR (KBr, cm^{-1}) 2316, 2344 (m, ν(BH)), 1932, 1869 (s, ν(CO)). Anal. Found: C, 52.40; H, 7.94%. Calcd for $C_{15}H_{26}BFeO_2P$: C, 53.62; H, 7.80%.

4 NMR data for **2b**: ^1H NMR (500 MHz, C_6D_6) δ 0.82 (d, $^2J_{PH}$ = 12.5 Hz, 9H, PMe_3), 1.88 (br, q, $^1J_{BH}$ = 110.6 Hz, 2H, BH), 4.41 (s, 5H, Cp). ^{11}B NMR (160.4 MHz, C_6D_6) δ -29.2 (dt, $^1J_{BH}$ = 110.6 Hz, $^1J_{BP}$ = 59.3 Hz).

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9 $K[FeCp^*(CO)_2]$ (814 mmol) and $BH_2Cl{\cdot}PMe_3$ (102 mg, 0.82 mmol) were allowed to react in THF at –45 °C - r.t. overnight. Removal of volatiles, extraction of the residue with pentane, and cooling of the extract afforded **2a** (39 mg, 0.12 mmol) in 14% yield. The predominant side-products were $Cp^*Fe(CO)_2Cl$ and $[Cp^*Fe(CO)_2]_2$.

10 Compound **3** was prepared in 9% yield from $BH_2Cl{\cdot}PMe_3$ and $K[RuCp^*(CO)_2]$[11] by the procedure similar to footnote 8. Colorless crystals. ^1H NMR (500 MHz, C_6D_6) δ 0.94 (d, $^2J_{PH}$ = 10.0 Hz, 9H, PMe_3), 1.89 (s, 15H, Cp*), the BH signal was too broad to be observed. ^{11}B NMR (160.4 MHz, C_6D_6) δ -28.9 (dt, $^1J_{BH}$ = 106.3 Hz, $^1J_{BP}$ = 63.8 Hz). ^{31}P NMR (202.4 MHz, C_6D_6) δ 1.7 (q, $^1J_{BP}$ = 63.8 Hz). IR (KBr, cm^{-1}) 2336, 2313 (m, ν(BH)), 1951, 1883 (s, ν(CO)). Anal. Found: C, 47.10; H, 6.68%. Calcd for $C_{15}H_{26}BO_2PRu$: C, 47.26; H, 6.87%.

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14 Complex **2c** was prepared by the salt-elimination method. Spectral features of this compound are similar to those of **2a** except for the C_5EtMe_4 signals in ^1H- and ^{13}C-NMR. Crystal data: amber crystals, orthorhombic, space group $P2_12_12_1$ (No. 19); *a* = 13.088(1), *b* = 15.873(2), *c* = 9.137(1) Å; *V* = 1898.2(3) Å^3; *Z* = 4. *R* = 0.071, *wR2* = 0.107 for 1143 reflections having $|F_o| > 4\sigma(F_o)$, 206 parameters, *GooF* = 1.185.

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19 Crystal data for **3**: colorless crystals, monoclinic, space group $P2_1$ (No. 4); *a* = 11.810(4), *b* = 9.652(2), *c* = 8.3372(8) Å, *ß* = 91.22(1)°; *V* = 950.1(4) Å^3; *Z* = 2. *R* = 0.041, *wR2* = 0.122 for 2857 reflections with $|F_o| > 3\sigma(F_o)$, 189 parameters, *GooF* = 1.14.

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