Transition-Metal Boryl Complexes: Structure and Reactivity of $CpFe(CO)_2Bcat$ and $CpFe(CO)_2BPh_2$

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We have initiated studies to understand the structure and reactivity of covalent transition-metal–boron bonds.[1-5] We report results with two transition-metal boryl compounds of the formula $CpFe(CO)_2BR_2$ that reveal the role of metal-boron π-interactions. Our results indicate that π-donation from the metal to the boron in these compounds exists but is weak, resulting in a reactive metal-boron linkage. Few fundamental studies of transition-metal boryl complexes have been conducted, despite the growing interest in transition-metal-catalyzed hydroboration reactions involving metal-boryl intermediates.[6-10] Little information exists concerning the nature of the metal-boron bond, and no studies connect structural data with reactivity.

The chemistry we report is summarized in Scheme I. Addition of *B*-chlorocatecholborane or diphenylboron bromide to a benzene suspension of $Na[CpFe(CO)_2]$ rapidly formed the yellow, hydrocarbon-soluble products $CpFe(CO)_2BR_2$ (**1a**, $R_2 = OC_6H_4O$; **1b**, $R_2 = Ph_2$). Both complexes are air sensitive, and compound **1b** is light sensitive (*vide infra*). X-ray diffraction studies were conducted on the two compounds, and the results of these analyses are displayed in Figure 1.[11] The ^{11}B NMR chemical shift for **1a** is δ 51.8 and for **1b** is δ 121. The value observed for **1b** conflicts with a chemical shift of δ 37.0 reported for a compound formulated previously as $CpFe(CO)_2BPh_2$.[12,13] ^1H and ^{13}C NMR data for both complexes are consistent with η^1-boryl ligands, and we have no proposal for the identity of the compound formulated previously as **1b**.

The most important distinction between the two structures displayed in Figure 1 is the difference in dihedral angles between the Cp centroid–Fe–B and O1–B–O2 or C8–B–C14 planes, 7.9° and 75° for **1a** and **1b**, respectively. The $[CpFe(CO)_2]^+$ (Fp^+) and isoelectronic metal fragments bound to carbenes and olefins typically display geometries dictated by π-interaction of the Fp^+ HOMO with the ligand LUMO.[14,15] The structure of catecholboryl **1a** suggests that a similar π-interaction can occur within boryl complexes, since the catecholboryl ligand is oriented to allow overlap of the boron p-orbital with the Fp^+ HOMO.[14,15] However, the steric requirements of the diphenylboryl substituent override the effect of its greater Lewis acidity. The resulting geometry contains an unusual orientation of the π-acidic ligand, indicating the absence of an interaction with the Fp^+ HOMO. Consistent with less multiple bond character within **1b**, its iron-boron bond length is significantly longer (2.034(3) Å) than that in **1a** (1.959(6) Å).

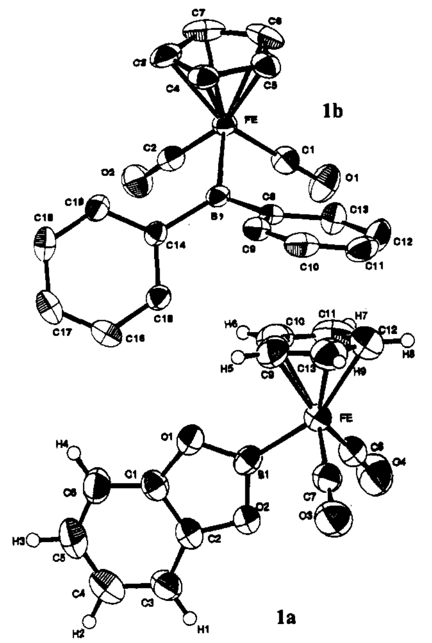
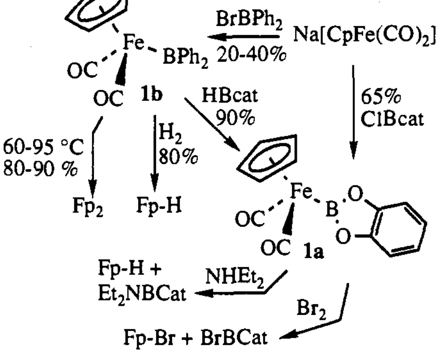


Figure 1. ORTEP drawing of **1a** and **1b**. Selected distances for **1a**: Fe-B1, 1.959(6); Fe-C7, 1.734(5); Fe-C8, 1.728(6); Fe-Cp centroid, 1.7155(7); B1-O1, 1.401(6); B1-O2, 1.420(7). Selected distances for **1b**: Fe-B1, 2.034(3); Fe-C1, 1.755(3); Fe–C2, 1.740(3); Fe-Cp centroid, 1.7294(7) (all bond distances in angstroms).

Scheme I



Variable-temperature NMR studies demonstrated that interaction of the catecholboryl substituent with the Fp^+ HOMO is weak. ^1H and $^{13}C\{^1H\}$ NMR spectra of **1a** at −90 °C showed no signs of hindered rotation about the metal-boron bond. The rotational barrier in these systems is not a direct indication of the π-bond energy, since the second-highest occupied orbital with π-symmetry is orthogonal to the HOMO, but does suggest an overall weak interaction. The presumably more electrophilic carbon center in $[CpFeL_2{=}CH_2]^+$ compounds provides a 10.8 kcal/mol barrier to rotation.[16]

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(1) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 880–941.

(2) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 819.

(3) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.

(4) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304.

(5) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.

(6) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.

(7) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863–8869.

(8) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350–9359.

(9) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671–6679.

(10) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679–6685.

(11) Crystallographic data for Mo Kα radiation: **1a**, T = 296 K; orthorhombic $P2_12_12_1$, a = 9.5178(6) Å, b = 9.608(1) Å, c = 13.713(2) Å, V = 1254.0(4) Å^3, Z = 4; 948 data with $I > 3.00\sigma(I)$, R = 0.030; **1b**, T = 199.5 K; monoclinic $P2_1/c$, a = 9.053(1) Å, b = 13.667(2) Å, c = 13.168(7) Å, β = 97.66(2)°, V = 1615(1) Å^3, Z = 4; 2505 data with $I > 3.00\sigma(I)$, R = 0.031.

(12) Noth, H.; Schmidt, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 623.

(13) Several other ^{11}B chemical shifts in the range of δ 28–46 were attributed to diphenylboryl complexes: Noth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1978; Vol. 14, p 271.

(14) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(15) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(16) Studabaker, W. B.; Brookhart, M. *J. Organomet. Chem.* **1986**, *310*, C39.

0002-7863/93/1515-4908$04.00/0

Although the X-ray diffraction and NMR spectroscopic studies indicate a modest π-interaction, the high CO stretching frequencies for **1a** (2024 and 1971 cm^{-1}) and **1b** (2021 and 1951 cm^{-1}) relative to those reported for Fp–alkyl complexes (1999–2005 and 1938–1944 cm^{-1})[17] corroborate its existence. The decrease in electron density at the metal center is due most likely to π-acceptance by the boryl substituent rather than weaker σ-donation by these more electropositive substituents. The similar values for **1a** and **1b** suggest that the strongly Lewis acidic diphenylboryl substituent acts as a π-acceptor to the Fp$^+$ orbital which is orthogonal to the Fp$^+$ HOMO.

Reactivity studies were consistent with a weak metal-boron π-bond, particularly in complex **1b**. We observed rapid and quantitative reactivity of complex **1a** with amine N-H bonds to provide the Fp-H[18,19] and the corresponding aminoborane, an observation which contrasts a lack of reactivity of Fp-alkyls toward amines. However, **1a** reacted with bromine to provide Fp-Br and bromocatecholborane in a similar fashion to reactions of halogens with Fp alkyls.

Complex **1b** displayed a wider range of chemistry. It reacted with hydrogen (2 atm) over the course of 30 min at ambient temperature to provide Fp-H (**3**). Organoboranes undergo hydrogenolysis reactions, but at considerably higher temperatures (*ca.* 200 °C).[20–23] Diphenylborane was presumably the first-formed product containing boron, but a disproportionation formed triphenylboron and diborane, which were observed by ^{11}B NMR spectroscopy. Borane B-D resonances and the high-field Fp-D signal (δ –11.8) were observed by ^{2}H NMR spectroscopy upon addition of D_2. Compound **1b** reacted immediately with CO. The products have not been characterized, but this reactivity ruled out kinetic studies of H_2 addition in the presence of added CO. Nevertheless, the absence of CO reaction products observed during the addition of H_2 makes a CO dissociation pathway unlikely.

Catecholborane (1–10 equiv) converted **1b** to **1a** in 60–90% yield (^{1}H NMR), depending on the concentration of catecholborane. No diphenylboryl complex **1b** remained. The boron-containing product observed by ^{1}H NMR spectrometry was predominantly triphenylboron from disproportionation of $HBPh_2$. *B*-Phenylcatecholborane was formed slowly from reaction of triphenylboron product and starting catecholborane.[24] Although the disproportionation of diphenylborane prevented the establishment of a simple equilibrium, the shorter metal-boron bond and greater π-interaction of the catecholboryl complex correlates qualitatively with the direction of this transformation.

The difference in thermal and photochemical stabilities of compounds **1a** and **1b** is striking. Compound **1a** is stable in solution for 1 day under room light at 120 °C, but **1b** underwent a formal dinuclear reductive elimination to form the stable dimer **2** upon either thermolysis at 75–95 °C (80–90% yield) in the dark or irradiation with a sunlamp for 30 min (40–60% yield). Triphenylboron was again formed as the main-group product.

Preliminary ^{1}H NMR kinetic studies of the thermolysis of **1b** in C_6D_6 solvent (0.01–0.04 mmol **1b**) indicated that the formally dinuclear reductive elimination occured primarily by a first-order process. Monitoring of the reaction at 75–95 °C showed an initial period (5–10 min) in which typically 20% of the starting complex rapidly formed Fp_2. However, reaction of the remaining material provided linear first-order plots. A linear ($R^2 = 0.998$) Arrhenius plot over the 20-deg temperature range provided activation parameters of $\Delta H^{\ddagger} = 30 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 1.2 \pm 0.1$ eu. Although the temperature range was narrow, it is clear that the $T\Delta S^{\ddagger}$ term is small, and in this case $\Delta H^{\ddagger}$ is close to $\Delta G^{\ddagger}$, typically a reliable measurement. Again, the products observed upon addition of CO were not formed during the thermolysis of **1b**.

The contrast in reactivity between **1a** and **1b** may be due to differences in Lewis acidity that are not compensated by electron donation from the metal center. In addition, the ability of the two boryl substituents to stabilize radical intermediates is likely to be important, since radical processes are common for Fp systems.[19,25] The first-order decomposition and unlikely production of free CO during the thermolysis of **1b**, along with its photochemical instability, suggest the possibility of a homolytic dissociation of the metal–boron bond, although directly observed boron-centered radicals are limited to $^{\bullet}BF_2$ and $^{\bullet}BCl_2$, generated by X- and γ-irradiation of BF_3 and BCl_3.[26,27] The solution chemistry of unligated $^{\bullet}BR_2$ species is unexplored, and the absence of trapping reagent allows recombination of the radicals to compete with formation of the final products. Therefore, the measured $\Delta H^{\ddagger}$ of 30 ± 1 kcal/mol provides an upper limit on the metal-boron bond strength for a homolytic cleavage of compound **1b**. The small entropy of activation is similar to that observed for metal-alkyl bond homolysis.[28] We are in the process of studying systems that are less likely to undergo rearrangements in order to allow a more detailed analysis of these reaction mechanisms.

Initially we considered the possibility that late-metal boryl complexes would be relatively unreactive, in an analogous fashion to early-metal amides. The results presented here indicate that a diverse chemistry of these species is certain to develop.

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Supplementary Material Available: Spectroscopic and analytical data for **1a** and **1b**; tables of positional parameters, anisotropic thermal parameters, intramolecular distances, intramolecular angles, and experimental details for complexes **1a** and **1b** (13 pages). Ordering information is provided on any current masthead page.

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[17] DeLuca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359.

[18] Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch* **1959**, *14B*, 738.

[19] Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248.

[20] Koster, R.; Bruno, G. *Liebigs Ann. Chem.* **1960**, *629*, 89.

[21] Koster, R. *Angew. Chem.* **1958**, *70*, 743.

[22] Koster, R. *Angew. Chem.* **1957**, *69*, 94.

[23] Koster, R. *Angew. Chem.* **1956**, *68*, 383.

[24] We have observed formation of diborane and *B*-phenylcatecholborane from triphenylboron and catecholborane in the absence of metal complex.

[25] Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

[26] Franzi, R.; Geoffroy, M.; Lucken, E. A. C. *J. Chem. Phys.* **1983**, *78*, 708.

[27] Nelson, W.; Gordy, W. *J. Chem. Phys.* **1969**, *51*, 4710.

[28] Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.