

# Boryls Bound to Iron Carbonyl. Structure of a Rare Bis(boryl) Complex, Synthesis of the First Anionic Boryl, and Reaction Chemistry That Includes the Synthetic Equivalent of Boryl Anion Transfer

Xiaoming He and John F. Hartwig\*

Department of Chemistry, Yale University, P.O. Box 208107,  
New Haven, Connecticut 06520-8107

Received June 8, 1995<sup>Ⓢ</sup>

The synthesis, structure, and reaction chemistry of iron carbonyl boryl complexes are described. Bis(boryl) complexes were prepared by reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  with chlorocatecholborane and substituted chlorocatecholboranes. An X-ray diffraction study of  $[\text{Fe}(\text{CO})_4(\text{BCat}^*)_2]$  ( $\text{BCat}^* = -\text{BO}_2\text{C}_6\text{H}_3-4-t\text{Bu}$ ) was performed and showed significant distortions from octahedral geometry. These bis(boryl) complexes underwent exchange reactions with alcohols, amines, and silylamides. They were converted to anionic compounds by reaction with  $\text{LiN}(\text{SiMe}_3)_2$ , and these anionic boryls are the first such examples. The anionic character allowed for nucleophilic substitutions. These complexes reacted with  $\text{ClSnMe}_3$  to yield a mixed boryl–stannyl compound in high yield. In contrast, reaction with methyl iodide or methyl triflate did not lead to an isolable alkylboryl complex. Instead, rapid formation of  $\text{MeBCat}$  occurred, a rare transformation that substitutes a boryl group for halide.

## Introduction

$\text{We}^{1-3}$  and others<sup>4-12</sup> have been pursuing the fundamental chemistry of transition-metal boryl complexes. This class of compounds is important as intermediates in transition-metal-catalyzed hydroboration with catecholborane and analogs<sup>8,13-26</sup> as well as diboration with catecholate-substituted diboron compounds.<sup>27,28</sup> They can impart electrophilic character to low-valent metal

complexes and may participate in metal–ligand multiple bonding through weak  $\pi$ -interactions that result from the similarity of the frontier orbitals to carbene ligands.<sup>29-32</sup> The existence of the free boryl fragment has been controversial,<sup>33-36</sup> and examples of two-coordinate boron-centered radicals are limited.<sup>37,38</sup> Transition metals, thus, stabilize these reactive main-group fragments as they often stabilize organic reactive intermediates. Few examples of well-characterized boryl complexes exist, and even fewer examples of bis(boryl) compounds are known.<sup>8,12</sup> Anionic boryl transition-metal complexes were unknown prior to this work.

We have prepared transition-metal boryl complexes with metal ligand fragments that have existed as classic systems for studying the organometallic chemistry of metal–carbon bonds. Published examples include the boryl complexes  $\text{CpFe}(\text{CO})_2(\text{BCat})(\text{Fp})$ ,<sup>1</sup>  $\text{Cp}_2\text{W}(\text{H})(\text{BCat})$ , and  $\text{Cp}_2\text{Nb}(\text{H})_2(\text{BCat})$ .<sup>2</sup> Others have studied similar

<sup>Ⓢ</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1995.

(1) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.

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

(3) Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.

(4) Schmid, G. *Angew. Chem.* **1970**, *9*, 819.

(5) Baker, 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.

(6) 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.

(7) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930.

(8) Baker, R. T.; Joseph, C. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367.

(9) Nguyen, P.; Blom, H. P.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329.

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

(11) Lantero, D. R.; Motry, D. H.; Ward, D. L.; Smith, M. R., III. *J. Am. Chem. Soc.* **1994**, *116*, 10811.

(12) Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 4403.

(13) The first example of catalytic hydroboration with catecholborane: Mannig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878.

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

(15) Dorigo, A. E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 115.

(16) Brands, K. M. J.; Kende, A. S. *Tetrahedron Lett.* **1992**, *33*, 5887.

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

(18) Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1992**, *114*, 6679.

(19) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

(20) Brown, J. M.; Lioyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866.

(21) Kocienski, P.; Jarowicki, K.; Marczak, S. *Synthesis* **1991**, 1191.

(22) Hayashi, T.; Matsumoto, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 601.

(23) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.

(24) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 5351.

(25) For rhodium-catalyzed hydroboration with carboranes see: Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757.

(26) For catalytic hydroboration with polyboranes see: Davan, T.; Corcoran, E. W.; Sneddon, L. G. *Organometallics* **1982**, *2*, 1693 and references within.

(27) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.

(28) Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336.

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

(30) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: Sons: New York, 1988.

(31) Cardin, D. J.; Cetinkaya, B.; Dotle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99.

(32) Petz, W. *Iron-Carbene Complexes*; Springer-Verlag: Berlin, 1993.

(33) Auten, R. W.; Kraus, C. *J. Am. Chem. Soc.* **1952**, *74*, 3398.

(34) Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117.

(35) Eisch, J. J.; Boleslawski, M. P.; Tamao, K. *J. Org. Chem.* **1989**, *54*, 1627.

(36) Wagner, M.; van Eikema Hommes, N. J. R.; Nöth, H.; Schleyer, P. v. R. *Inorg. Chem.* **1995**, *34*, 607.

(37) Nelson, W.; Gordy, W. *J. Chem. Phys.* **1969**, *51*, 4710.

(38) Franzi, R.; Geoffroy, M.; Lucken, E. A. *J. Chem. Phys.* **1983**, *78*, 708.

tantalocene complexes,<sup>11</sup> a variety of complexes involving iridium and rhodium,<sup>6,7,9,10</sup> and complexes of platinum.<sup>12</sup> The metal–boryl bond is very strong, relative to other metal–ligand covalent bonds,<sup>39</sup> but boryl compounds have reaction pathways that are kinetically accessible. It is this kinetic lability that leads to their catalytic chemistry.

In this report we describe the boryl chemistry derived from the classic metal–carbonyl system (CO)<sub>2</sub>Fe<sup>2+</sup>. Substitution reactions of this metal fragment with haloboranes yield bis(boryl) complexes. These complexes have proven to be extremely reactive, but an X-ray structure of one example has been obtained. The boryl complexes can be converted to other transition-metal main-group compounds such as Fe(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>. The presence of two boryl ligands allowed for the synthesis of a five-coordinate anionic boryl complex by the removal of one boryl ligand with LiN(SiMe<sub>3</sub>)<sub>2</sub>. This anion allows for preparation of a complex containing one boryl and one stannyl ligand. In addition, the reaction of this anionic boryl complex with electrophilic alkylating reagents such as MeI and MeOTf gives alkylborane products and is the first metal-mediated reaction that provides formal addition of a boryl anion.

## Experimental Section

**General Considerations.** Unless otherwise noted, all manipulations were performed by standard Schlenk or drybox techniques under N<sub>2</sub>. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. *n*-Pentane (technical grade) was distilled from sodium/benzophenone ketyl made soluble by addition of tetraglyme to the still. Benzene, toluene, THF, and ether were distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents for use in NMR experiments were dried as their protiated analogs but were vacuum-transferred from the drying agent. Na<sub>2</sub>Fe(CO)<sub>4</sub><sup>40</sup> and [B(3,5-*t*-Bu<sub>2</sub>-Cat)<sub>2</sub>]<sub>2</sub> (Cat = 1,2-C<sub>6</sub>H<sub>2</sub>R<sub>2</sub>O<sub>2</sub>)<sup>41–43</sup> were prepared by methods similar to literature procedures. UV photolyses were conducted with a 450-W medium-pressure Conrad-Hanovia mercury arc lamp with an Ace 7830-60 power supply and a double-jacketed Pyrex immersion well with cooling water.

**Spectroscopic Studies.** <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectra were obtained on a GE QE300 or Ω300 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded relative to residual protiated solvent. <sup>119</sup>Sn, <sup>11</sup>B, and <sup>7</sup>Li NMR chemical shifts were recorded in units of parts per million downfield from neat Me<sub>4</sub>Sn, BF<sub>3</sub>·OEt<sub>2</sub>, and LiCl/D<sub>2</sub>O external standards. Sealed NMR tubes were prepared by attaching the sample tube via Cajon Ultra Torr adapters directly to a high-vacuum valve. IR spectra were recorded on a MIDAC M1200 FTIR spectrometer using a Perkin-Elmer NaCl cell. Mass spectra were obtained on a Hewlett-Packard 5989A mass spectrometer. Isobutane was selected as the chemical ionization source and the CI flow had manifold pressures of ~1.0 × 10<sup>-4</sup> Torr and 300 V for emission.

**X-ray Crystallographic Studies.** Crystals were removed from Schlenk tubes under a stream of N<sub>2</sub> and placed into a layer of hydrocarbon oil. A suitable crystal was selected,

**Table 1. Summary of X-ray Crystallography Data for Fe(CO)<sub>4</sub>(B(4-*t*-Bu-Cat))<sub>2</sub> (2)**

empirical formula	C <sub>24</sub> H <sub>24</sub> O <sub>8</sub> B <sub>2</sub> Fe
<i>a</i> , Å	11.991(7)
<i>b</i> , Å	32.509(7)
<i>c</i> , Å	6.352(9)
α, deg	90
β, deg	90
γ, deg	90
<i>V</i> , Å <sup>3</sup>	2476(4)
<i>Z</i>	4
fw	517.92
cryst syst	orthorhombic
space group	<i>Pnma</i>
diffractometer	Rigaku AFC5S
temp, °C	-90
λ, Å	0.710 69
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.389
μ, cm <sup>-1</sup>	6.50
no. of observns	1137 ( <i>I</i> > 3.00σ( <i>I</i> ))
no. of variables	166
<i>R</i>	0.051
<i>R</i> <sub>w</sub>	0.054

**Table 2. Important Atom Coordinates for Fe(CO)<sub>4</sub>(B(4-*t*-Bu-Cat))<sub>2</sub> (2)**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq), Å <sup>2</sup>
Fe	0.01617(9)	1/4	0.0498(2)	2.00(5)
O1	-0.1578(3)	0.3154(1)	-0.0390(6)	2.6(2)
O2	-0.0530(3)	0.3025(1)	-0.3318(6)	2.6(2)
O3	0.12108(3)	0.3199(1)	0.2733(7)	3.4(2)
O4	-0.1281(5)	1/4	0.322(1)	2.9(3)
O5	0.1703(5)	1/4	-0.311(1)	3.8(3)
C11	0.0827(4)	0.2926(2)	0.188(1)	2.3(3)
C12	-0.1043(7)	1/4	0.218(1)	2.2(4)
C13	0.1120(7)	1/4	-0.169(1)	2.4(4)
B1	-0.0716(5)	0.2912(2)	-0.123(1)	2.1(3)

**Table 3. Important Bond Distances (Å) and Angles (deg) for 2**

(a) Interatomic Distances			
Fe–C11	1.823(6)	Fe–C12	1.795(9)
Fe–C13	1.803(9)	Fe–B1	2.028(7)
C11–O3	1.136(6)	C12–O4	1.146(9)
C13–O5	1.141(9)	O1–B1	1.404(7)
O2–B1	1.393(8)		
(b) Interatomic Angles			
C11–Fe–C11A	99.0(4)	C11–Fe–C12	93.8(2)
C11–Fe–C13	95.2(3)	C11–Fe–B1	89.1(3)
C12–Fe–C13	166.0(4)	C12–Fe–B1	84.5(3)
C13–Fe–B1	85.0(3)	B1–Fe–B1A	82.8(4)

attached to a glass fiber, and placed into the low-temperature nitrogen stream.

X-ray data for **2** and **6** were collected at 183 and 153 K on a Rigaku AFC5S diffractometer with Mo Kα radiation (λ = 0.710 69 Å). Details of the data collections and refinements are provided in Table 1. Further details are available in the Supporting Information. The structure of **2** was solved by Patterson methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1137 observed reflections (*I* > 3.00(*σ*)) and 166 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted agreement factors. Hydrogen atoms were included with fixed positions. Attempts were made to solve the structure of **6** by direct and Patterson methods. Unfortunately, the structure could not be refined well enough for us to draw any conclusions on bond lengths and angles, presumably due to poor crystal quality.<sup>44</sup> Bond distances and angles for **2** are provided in Tables 2 and 3.

(44) Cell parameters for LiFe(CO)<sub>4</sub>B(3,5-di-*tert*-Bu-Cat)·Et<sub>2</sub>O: *P*2/*m*; *a*, 8.217(2) Å; *b*, 14.955(3) Å; *c*, 20.17(1) Å; α, 90°; β, 91.63°; γ, 90°; *V*, 2477(2) Å<sup>3</sup>; *Z*, 4; temp, -120 °C.

(39) Hartwig, J. F.; Bhandari, S.; Rablen, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 1839.

(40) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.

(41) Brotherton, R. J.; McCloskey, A. L.; Boone, J. L.; Manasevit, H. M. *J. Am. Chem. Soc.* **1960**, *82*, 6245.

(42) Moezzi, A.; Olmstead, M. M.; Bartlett, R. A.; Power, P. P. *Organometallics* **1992**, *11*, 2383.

(43) Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N. L.; Clegg, W.; Elsegood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623.

**Synthesis of Fe(CO)<sub>4</sub>(BCat)<sub>2</sub> (1).** To a rapidly stirred suspension of Na<sub>2</sub>Fe(CO)<sub>4</sub> (0.482 g, 2.25 mmol) in toluene (20 mL) was added slowly at room temperature a solution of ClBCat (0.616 g, 4.00 mmol) in toluene (2 mL). The reaction mixture was stirred for 12 h, during which time a brown suspension formed. After removal of volatile materials under reduced pressure, the residue was extracted with pentane (3 × 20 mL). Filtration of the resulting slurry, reduction of the volume of the resulting filtrate, and cooling at -35 °C for 12 h afforded colorless needles of **1**. This compound is air-sensitive and thermally unstable. However, it was stored at -35 °C in the drybox for more than 3 weeks with only slight decomposition. Yield: 0.593 g, 73%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.87 (m, 2H), 6.61 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 204.3, 202.2, 149.5, 122.3, 111.8. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ 45. IR (pentane): 2116.8 (s), 2050.2 (vs), 2036.5 (vs), 1999.8 (w) cm<sup>-1</sup>.

**Synthesis of cis-Fe(CO)<sub>4</sub>(B(4-*t*-Bu-Cat))<sub>2</sub> (2).** A procedure similar to the synthesis of **1** was followed, but the reaction mixture was stirred for 2 days and crude product was obtained by crystallization from a concentrated toluene solution. Crystals of the product suitable for an X-ray diffraction analysis were obtained by slow recrystallization in toluene at -20 °C. Yield: 0.525 g, 63%. Although this compound is thermally sensitive, satisfactory microanalytical data were obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.07 (s, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 1.01 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 204.6, 202.4, 149.6, 147.4, 145.7, 119.0, 110.9, 109.4, 34.3, 31.1. <sup>11</sup>B (C<sub>6</sub>D<sub>6</sub>): δ 45 (broad). IR: 2112.7 (m), 2044.3 (vs), 2028.7 (s), 2000.7 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>B<sub>2</sub>FeO<sub>8</sub>: C, 55.66; H, 4.67. Found: C, 55.36; H, 4.58.

**Synthesis of Fe(CO)<sub>4</sub>(B(3,5-*t*-Bu<sub>2</sub>-Cat))<sub>2</sub> (3). (a) By Reaction of ClB(3,5-*t*-Bu<sub>2</sub>-Cat) with Na<sub>2</sub>Fe(CO)<sub>4</sub>.** A procedure similar to that for the preparation of **1** was followed, except the pentane was removed completely from the final filtrate to give a pale yellow oil consisting of **3** that was roughly 80% pure. This compound was used for the preparation of the anion **6** without further purification. Yield: 1.20 g, 77% (80% purity).<sup>45</sup> <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.05 (m, 1H) (two resonances overlap at 7.05 and 7.06), 7.06 (m, 1H), 1.40 (s, 9H), 1.18 (s, 9H). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ 45 (broad). IR: 2110.5 (s), 2046.7 (vs), 2030.5 (vs), 1998.2 (w) cm<sup>-1</sup>.

**(b) By Photolysis of Fe(CO)<sub>5</sub> and B(3,5-*t*-Bu<sub>2</sub>-Cat)<sub>2</sub>.** In the drybox, Fe(CO)<sub>5</sub> (8.5 mg, 5.7 μL, 0.0433 mmol) was weighed into a vial and 0.6 mL of C<sub>6</sub>D<sub>6</sub> was added. To this solution was added [B(3,5-*t*-Bu<sub>2</sub>-Cat)<sub>2</sub>]<sub>2</sub> (20 mg, 0.0433 mmol) and toluene (1 μL) as an internal standard. The resulting solution was transferred to an NMR tube that was sealed under vacuum. The sample was then irradiated at 0 °C for 15 min. Compound **3** was formed in 83% yield, as determined by <sup>1</sup>H NMR spectroscopy.

**Synthesis of Li[Fe(CO)<sub>4</sub>(BCat)] (4).** To a rapidly stirred solution of Fe(CO)<sub>4</sub>(BCat)<sub>2</sub> (0.290 g) in pentane (10 mL) was added dropwise at room temperature a solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.121 g) in pentane (2 mL). A white solid immediately precipitated from solution. The suspension was stirred for an additional 15 min and was then filtered. The white solid was washed several times with pentane and dried under vacuum. Yield: 0.121 g, 58%. This compound is thermally unstable and slowly decomposes in Et<sub>2</sub>O or THF solvent at -35 °C. <sup>1</sup>H NMR (50% C<sub>7</sub>D<sub>8</sub>-50% THF-*d*<sub>8</sub>): δ 6.98 (m, 2H), 6.70 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (30% dioxane-*d*<sub>8</sub>-70% THF): δ 219.5, 150.7, 120.3, 110.3. <sup>11</sup>B NMR (Et<sub>2</sub>O): δ 55. <sup>7</sup>Li NMR (30% C<sub>7</sub>D<sub>8</sub>-70% THF): δ -0.293. IR (Et<sub>2</sub>O): 2016 (s), 1907 (m), 1821 (vs) cm<sup>-1</sup>.

**Synthesis of Li[Fe(CO)<sub>4</sub>(B(4-*t*-Bu-Cat))] (5).** A procedure analogous to that used to prepare **4** was followed, starting with 0.203 g of Fe(CO)<sub>4</sub>[B(4-*t*-Bu-Cat)]<sub>2</sub>. Yield: 0.075 g, 55%. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 219.7, 151.0, 148.6, 143.0, 116.4, 108.8,

107.8, 34.3, 31.3. <sup>11</sup>B NMR (THF-*d*<sub>8</sub>): δ 54.8. <sup>7</sup>Li NMR (THF-*d*<sub>8</sub>): δ -0.32. IR (Et<sub>2</sub>O): 2020 (m), 1931 (w), 1878 (m), 1819 (vs) cm<sup>-1</sup>.

**Synthesis of Li[Fe(CO)<sub>4</sub>(B(3,5-*t*-Bu<sub>2</sub>-Cat))] (6), Li[Fe(CO)<sub>4</sub>(B(3,5-*t*-Bu<sub>2</sub>-Cat))]·0.5Et<sub>2</sub>O (6').** This synthesis was conducted with 1.20 g of crude **3** (by method a) using a procedure analogous to that for **4**. The ether-free white precipitate **6** was washed twice with toluene and dissolved in Et<sub>2</sub>O (3 mL). Filtration, concentration of the resulting filtrate to near dryness, addition of toluene (5 mL), complete mixing of the two solvents, and cooling to -35 °C gave **6'** as a white solid that was washed several times with pentane and dried under vacuum. The crystals most suitable for an X-ray diffraction study were obtained by dissolving this solid in a mixture of Et<sub>2</sub>O (2 mL) and toluene (3 mL), filtering the resulting solution, reducing the volume to about 3 mL, and cooling at -20 °C for 4 days. Yield: 0.402 g, 53%. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 6.96 (s, 1H), 6.83 (s, 1H), 3.38 (q, 2H), 1.45 (s, 9H), 1.30 (s, 9H), 1.11 (t, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (30% C<sub>7</sub>D<sub>8</sub>-70% THF): δ 220.7, 151.6, 147.3, 143.1, 132.8, 114.1, 106.4, 35.1, 34.8, 32.3, 30.2. <sup>11</sup>B NMR (30% C<sub>7</sub>D<sub>8</sub>-70% THF): δ 54.3. <sup>7</sup>Li NMR (30% C<sub>7</sub>D<sub>8</sub>-70% THF): δ -0.35. IR (Et<sub>2</sub>O): 2020.5 (m), 1945.0 (w), 1873.2 (m), 1823.0 (s) cm<sup>-1</sup>.

**Synthesis of Na[Fe(CO)<sub>4</sub>(BCat)] (7).** To a rapidly stirred suspension of Na<sub>2</sub>Fe(CO)<sub>4</sub> (0.214 g) in THF (10 mL) was added dropwise at room temperature a solution of ClBCat (0.154 g) in toluene (2 mL). The resulting solution was then stirred for 15 min and filtered through glass wool. This procedure yielded a dark red solution of **7**, which was unstable at room temperature. <sup>11</sup>B NMR (THF): δ 54.3. IR (THF): 2016 (vs), 1907 (s), 1821 (vs) cm<sup>-1</sup>.

**Synthesis of ClB(3,5-*t*-Bu<sub>2</sub>-Cat).** A 500 mL Schlenk tube, equipped with a magnetic stirrer and submerged in an ice bath, was charged with 3,5-di-*tert*-butylcatchol (5.55 g) and pentane (100 mL). Into this flask was added slowly by cannula a heptane solution of BCl<sub>3</sub> (25.5 mL, 1.0 M). The resulting solution was stirred for 2 h. After removal of low-boiling compounds under reduced pressure at 25 °C, the product was distilled at 10<sup>-3</sup> Torr/100-110 °C onto a condenser cooled to -78 °C. The white solid collected on the condenser was then allowed to melt into a collection flask. This air- and moisture-sensitive product is a colorless liquid at room temperature. Yield: 6.12 g, 92%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.11 (d, 1H), 7.00 (d, H), 1.37 (s, 9H), 1.18 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 148.4, 146.4, 143.9, 135.0, 116.8, 107.9, 34.7, 34.2, 31.4, 29.5. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ 28.4.

**Synthesis of ClB(4-*t*-Bu-Cat).** This colorless liquid was synthesized by methods similar to the synthesis of compound ClB(3,5-*t*-Bu<sub>2</sub>-Cat). Yield: 89%. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>): δ 6.69 (d, *J*<sub>2</sub> = 2 Hz, 1H), 6.81 (dd, *J* = 8.4, 2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 1.12 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>): δ 148.8, 147.6, 146.6, 120.6, 112.2, 110.5, 35.2, 32.0. <sup>11</sup>B NMR (pentane): δ 28.6.

**Synthesis of Fe(CO)<sub>4</sub>[B(3,5-*t*-Bu<sub>2</sub>-Cat)](SnMe<sub>3</sub>) (9).** In the drybox, compound **6** (60 mg, 0.13 mmol) was weighed into a vial and 2 mL of toluene was added. While the mixture was rapidly stirred, Me<sub>3</sub>SnCl (25 mg, 0.125 mmol) in toluene was added. After 10 min, the volatile species were removed under reduced pressure and the tan residue was extracted several times with pentane. Removal of the solvent under reduced pressure gave the yellowish oil **9**. Yield: 63 mg, 90%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.11 (m, 1H), 7.09 (m, 1H), 1.47 (s, 9H), 1.20 (s, 9H), 0.41 (m, 9H). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ 47. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 207.4, 206.7, 204.4, 150.1, 145.7, 145.6, 134.4, 116.3, 107.6, 35.0, 34.6, 31.8, 29.9, -4.1. <sup>119</sup>Sn NMR: δ -75.3. IR (toluene): 2082, 2054, 2026, 2004, 1976 cm<sup>-1</sup>. MS [*m*(M + H<sup>+</sup>)]/*z* (intensity): 559 (0.85%), 560 (14.65%), 561 (52.20%), 562 (53.40%), 563 (88.69%), 564 (65.87%), 565 (100%), 566 (29.06%), 567 (20.29%), 568 (5.38%), 569 (16.37%). Anal. Calcd for C<sub>21</sub>H<sub>29</sub>O<sub>6</sub>BSnFe: C, 44.82; H, 5.19. Found: C, 44.75; H, 5.30.

**Reaction of 2 with HOEt and HNEt<sub>2</sub>.** In the drybox, bis(boryl) complex **2** (5.0 mg, 0.0097 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub>,

(45) The 20% impurity is B<sub>2</sub>Cat\*<sub>3</sub>, whose analog B<sub>2</sub>Cat<sub>3</sub> has been characterized previously in ref 43.

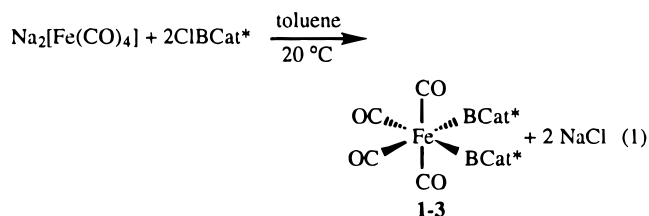
a small amount of 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> was added as internal standard, and the sample was placed into an NMR sample tube capped with a rubber septum. After an initial <sup>1</sup>H NMR spectrum was obtained, 3 equiv of EtOH or Et<sub>2</sub>NH was added by syringe, and the sample was rapidly mixed. After 5–10 min, a second <sup>1</sup>H NMR spectrum was obtained, as well as a <sup>11</sup>B NMR spectrum. Yields were calculated by comparing integrations of the final spectra to those of spectra taken before addition of alcohol or amine.

**Reaction of 1 with (Et<sub>2</sub>N)SiMe<sub>3</sub>.** In the drybox, bis(boryl) complex **1** (14 mg, 0.034 mmol) was weighed into a vial equipped with a Teflon-lined septum, and 0.6 mL of C<sub>7</sub>D<sub>8</sub> containing 1 μL of C<sub>7</sub>H<sub>8</sub> internal standard was added. The vial was then placed in an ice bath and stirred rapidly, and (Et<sub>2</sub>N)SiMe<sub>3</sub> (26 μL, 0.138 mmol) was added by syringe. The resulting solution was warmed to room temperature and was stirred for 3 h. The sample was then transferred to an NMR sample tube for measurements. Infrared spectroscopic measurements were conducted with the same sample. All IR, <sup>1</sup>H NMR, and <sup>13</sup>C{<sup>1</sup>H} NMR spectral data were identical with those of the known compound Fe(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>.<sup>46</sup> Yield: 75%.

**Reaction of 4 with MeI and MeOTf.** In the drybox, the ionic species **4** (15 mg, 0.051 mmol) was weighed into a vial and 0.6 mL of a cold (–30 °C) mixture of C<sub>7</sub>D<sub>8</sub> (50%) and THF-d<sub>8</sub> (50%) was added, along with 1 μL of C<sub>7</sub>H<sub>8</sub> as internal standard. The resulting solution was transferred quickly to a screw-top NMR tube with a Teflon-lined septum and was then frozen in liquid nitrogen. At this low temperature, 3.2 μL of MeI (0.051 mmol) or 5.8 μL of MeOTf was added by syringe. NMR measurements of reaction with MeI were conducted periodically over the course of 1 h in a spectrometer probe cooled to –35 °C. Roughly 50% conversion had occurred after that time. The sample was then warmed to room temperature to complete the reaction, and a 30% yield of MeBCat was observed. Reaction with MeOTf was monitored for 20 min in a spectrometer probe that was maintained at –35 °C, and complete conversion of the product had occurred during this time. The yield of MeBCat was 60% for this reaction. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ 35. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.02 (m, 2H), 6.85 (m, 2H), 0.52 (s, 3H).

## Results and Discussion

**Synthesis.** The bis(boryl) complexes **1–3** were prepared by addition of the iron dianion Na<sub>2</sub>[Fe(CO)<sub>4</sub>]<sup>40</sup> to parent and substituted chlorocatecholboranes (eq 1). It



BCat\* = B(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**1**), B(O<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>3</sub>) (**2**),

B(O<sub>2</sub>-3,5-di-*t*-BuC<sub>6</sub>H<sub>2</sub>) (**3**)

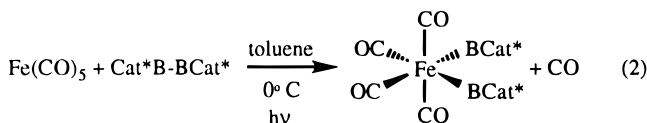
was necessary to conduct the reactions in hydrocarbon solvents in order to obtain boryl products. The yields of these reactions depended heavily on the purity of the metal dianion and the amount of THF contained in the solid Collman reagent, since the presence of THF led to significant decomposition of the product. The bis(boryl) compounds were all soluble in hydrocarbon solvents. The compounds **1** and **2** were obtained in pure form by crystallization of the crude product from

**Table 4. CO Stretching Frequencies for Fe(CO)<sub>4</sub>X<sub>2</sub> Complexes**

compd	ν <sub>CO</sub> (cm <sup>-1</sup> )
Fe(CO) <sub>4</sub> (BCat) <sub>2</sub>	2117, 2050, 2036, 2000
Fe(CO) <sub>4</sub> (SiMe <sub>3</sub> ) <sub>2</sub> <sup>46</sup>	2069, 2006, 2000, 1979
Fe(CO) <sub>4</sub> (SnMe <sub>3</sub> ) <sub>2</sub> <sup>54</sup>	2059, 2001, 1989, 1972
Fe(CO) <sub>4</sub> Br <sub>2</sub> <sup>47,48</sup>	2151, 2109, 2099, 2075
Fe(CO) <sub>4</sub> I <sub>2</sub> <sup>47,48</sup>	2132, 2086, 2081, 2063
Fe(CO) <sub>4</sub> H <sub>2</sub> <sup>69</sup>	2121, 2111, 2053, 2042, 2029, 2010

toluene/pentane solvent mixtures at –30 °C. All three compounds are thermally sensitive, but compound **2** was stable enough to allow a satisfactory microanalysis.

The bis(boryl) complexes were also formed by photochemical reactions of diboron complexes with iron pentacarbonyl (eq 2). These oxidative-addition reactions



of the diborane(4) reagents,<sup>43</sup> presumably to photochemically generated Fe(CO)<sub>4</sub>, were rapid. Full conversion of Fe(CO)<sub>5</sub> to provide an 83% yield of **3** by <sup>1</sup>H NMR spectroscopy with an internal standard was achieved with a 450-W mercury arc lamp in 20 min.

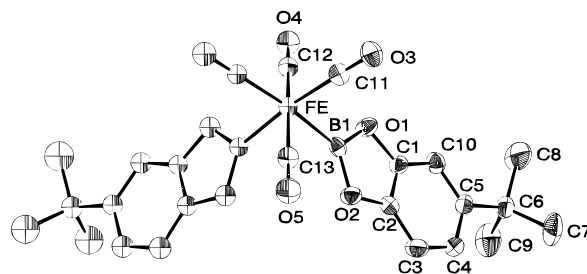
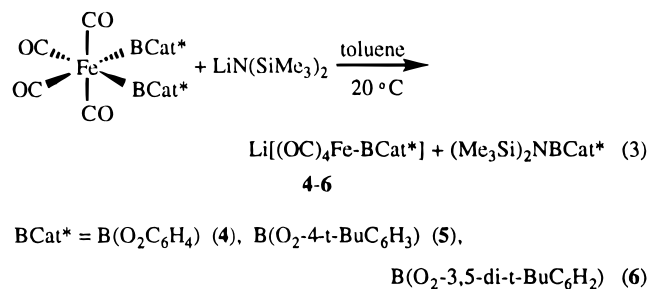
Spectroscopic data for **1–3** clearly identified the reaction products as cis-disposed bis(boryl) complexes. <sup>11</sup>B NMR spectra for all three compounds showed chemical shifts at δ 45, which are characteristic for catecholboryl complexes. The shifts for **1–3** were significantly downfield of that for RhCl(BCat)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub><sup>8</sup> (δ 35.9) and upfield of that for the iron complex CpFe(CO)<sub>2</sub>BCat<sup>1</sup> (δ 51.8). Importantly, <sup>13</sup>C{<sup>1</sup>H} NMR spectra at room temperature showed two distinct chemical shifts, one at δ 204 (w<sub>1/2</sub> = 10 Hz) and one at δ 202 (w<sub>1/2</sub> = 5 Hz). We assign the broader resonance at δ 204 to the CO ligand located trans to the boryl group. No distinct coupling to the boron was resolved, but one resonance was presumably broadened more than the other as a result of stronger quadrupolar effects toward the ligand located trans to the boryl. The infrared spectrum of **3** in pentane solvent showed the best resolution and included CO stretching frequencies at 2112 (m), 2046 (vs), 2031 (vs), and 1999 (w) cm<sup>-1</sup>, consistent with the C<sub>s</sub> symmetry observed in the solid state (vide infra). The spectra for **1** and **2** were similar, but the bands were broader and less well resolved. These data are included in the Experimental Section. The stretching frequencies for **1–3** were similar to those for other (CO)<sub>4</sub>FeX<sub>2</sub> compounds such as Fe(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>, Fe(CO)<sub>4</sub>(SnMe<sub>3</sub>)<sub>2</sub>, Fe(CO)<sub>4</sub>H<sub>2</sub>, Fe(CO)<sub>4</sub>I<sub>2</sub>, and Fe(CO)<sub>4</sub>Br<sub>2</sub> provided in Table 4.<sup>47,48</sup>

Reaction of **1–3** with **1** equiv of lithium bis(trimethylsilyl)amide in toluene solvent afforded the white solid anionic complexes **4–6** that were free of solvents capable of coordinating the lithium cation (eq 3). These compounds are thermally sensitive and adopt a reddish color within minutes at room temperature. The presence of THF or Et<sub>2</sub>O also caused significant decomposition of **4** and **5**, even at low temperature. The di-*tert*-butyl derivative **6** was the most stable ionic boryl complex.

(47) Nyholm, R. S. *Proc. Chem. Soc., London* **1961**, 273.

(48) Butler, I. S.; Spendjian, H. K. *J. Organomet. Chem.* **1969**, *18*, 145–152.

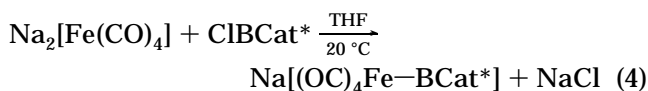
(46) Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 897.



**Figure 1.** ORTEP drawing of **2**. Hydrogen atoms were omitted for clarity.

The etherated species **6'** was generated by dissolving the complex in ether, concentrating the solution, adding toluene, and removing the remainder of the ether solvent. Cooling of the resulting solution at  $-35^\circ\text{C}$  gave **6'** as a white solid that could be stored at  $-35^\circ\text{C}$  in the drybox for weeks or in toluene solution for days.

The ionic species with sodium counterion was generated directly from Collman's reagent in THF solvent by using a 1:1 stoichiometry of dianion and chloroborane as shown in eq 4. However, selectivity for the monobor-



ryl anion could only be achieved in THF solvent, presumably due to the greater solubility of Collman's reagent and the anionic product in this medium. Since the anionic boryl complex decomposes in THF, complex **7** that was generated in this manner could not be isolated from the reaction solution in pure form.

In addition to the low solubility in hydrocarbon solvents and the reaction chemistry described below, the anionic boryl complexes **4-6** were identified by spectroscopic data. Most indicative of the anionic character were low-frequency CO bands in the infrared spectra of **4-6** in diethyl ether solutions. The compounds showed a strong CO band near  $1821\text{ cm}^{-1}$ , and the highest energy band was located near  $2020\text{ cm}^{-1}$ . These values are typical of monoanionic complexes of the  $\text{Fe}(\text{CO})_4$  fragment.  $^7\text{Li}$  NMR spectra showed a resonance at  $\delta -0.3$ , indicating the presence of lithium counterion.

$^{11}\text{B}$  NMR spectra of **4-6** each showed a single resonance at a chemical shift that was characteristic of catecholboryl complexes ( $\delta$  55). This chemical shift is located downfield of those for neutral **1-3**. Although one might expect an upfield shift for the anionic species, the chemical shifts of atoms directly bound to transition-metal centers are dominated by paramagnetic shielding effects of the metal, and these effects are difficult to predict. In a fashion similar to the trends in  $^{11}\text{B}$  NMR chemical shifts for **1-6**, the  $^{13}\text{C}$  NMR chemical shifts corresponding to the carbonyl groups of anionic compounds **4-6** were 15–20 ppm downfield of those for neutral **1-3**. Such downfield shifts of the  $^{13}\text{C}$  resonances of carbonyl groups in other anionic complexes relative to their neutral counterparts have been observed.<sup>49,50</sup> The presence of a single resonance shows that the carbonyl groups are undergoing rapid site exchange, a process that is characteristic of five-

coordinate compounds.<sup>51-53</sup> At  $-80^\circ\text{C}$  in toluene solvent, the resonance for **6** broadened but was not resolved into two separate signals.

**Structural Descriptions.**  $\text{Fe}(\text{CO})_4(\text{B}(4\text{-}t\text{-Bu-Cat}))_2$  (**2**). Crystals of compound **2** that were suitable for an X-ray diffraction analysis were obtained by recrystallization from toluene at  $-20^\circ\text{C}$ . The structure of **2** is illustrated in Figure 1 and consists of well-separated monomeric units with iron in a distorted-octahedral geometry. The coordination sphere of the iron contains four carbonyl groups and two cis-disposed boron atoms of the boryl ligands. There is a mirror plane containing the iron center and the two trans carbonyl groups (C12 and O4; C13 and O5) that bisect the mutually cis CO and boryl ligands. The axial carbonyl groups are bent toward the two boron atoms, giving a C–Fe–C angle of  $166.0(4)^\circ$ . This distortion of trans CO ligands has been observed in  $\text{Fe}(\text{CO})_4(\text{SiMe}_3)_2$ <sup>46</sup> and  $\text{Fe}(\text{CO})_4(\text{SnR}_3)_2$ <sup>54</sup> with C–Fe–C angles of  $141.2(1)$  and  $159.6(4)^\circ$ , respectively. The B–Fe–B angle is smaller than would be found in a regular octahedron ( $82.8(4)^\circ$ ), while the E–Fe–E angles of  $\text{Fe}(\text{CO})_4(\text{SiMe}_3)_2$  ( $111.8(1)^\circ$ ) and  $\text{Fe}(\text{CO})_4(\text{SnR}_3)_2$  ( $95.94(4)^\circ$ ) are larger. The Fe–B distance is  $2.028(7)\text{ \AA}$ , measurably longer than the Fe–B bond length of  $1.959(6)\text{ \AA}$  in the closely related  $\text{CpFe}(\text{CO})_2\text{BCat}$ . The average Fe–C<sub>eq</sub> distance is  $1.82\text{ \AA}$ , and the average Fe–C<sub>ax</sub> distance is  $1.80\text{ \AA}$ . Typically, the metal–carbon distances for mutually trans carbonyl ligands are measurably longer than the metal–carbon distances of those located trans to hydrocarbyl and hydride ligands.<sup>55-59</sup> This effect, presumably due to the strong  $\sigma$  donation and absent  $\pi$  acceptance of these ligands, is not observed in **2**.

$\text{Li}[\text{Fe}(\text{CO})_4\text{B}(3,5\text{-}t\text{-Bu}_2\text{-Cat})]\cdot 0.5\text{Et}_2\text{O}$  (**6'**). We have made extensive attempts to obtain accurate crystal structure data for **6'**. A data set was collected on several different crystals, and in one case a rough structure was obtained. Although the connectivity of the molecule was deduced from this study, the refinement was poor. This structure did fit the spectroscopic data and suggested

(51) Cotton, F. A. *J. Organomet. Chem.* **1975**, *100*, 29.

(52) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 1320–1321.

(53) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305.

(54) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508.

(55) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A. *J. Organomet. Chem.* **1991**, *409*, 367–376.

(56) LaPlaca, S. J.; Hamilton, W. C.; Ibers, J. A.; Davison, A. *Inorg. Chem.* **1969**, *8*, 1928.

(57) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S.-F.; Liu, R.-S. *Organometallics* **1989**, *8*, 1106–1111.

(58) Lindner, E.; Pabel, M.; Fawzi, R.; Mayer, H. A.; Wurst, K. *J. Organomet. Chem.* **1992**, *435*, 109–121.

(59) Masters, A. P.; Richardson, J. F.; Sorensen, T. S. *Can. J. Chem.* **1990**, *68*, 2221.

(49) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* **1977**, *99*, 7381.

(50) Hanson, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 974.

that the boryl ligand resided in an axial position. However, our inability to refine this structure made it impossible to draw any firm conclusions concerning the structure of this compound. We therefore base our structural assignment on spectroscopic data and hesitate to define the precise geometry.

**Relationship between the Structure of 2 and Its Spectroscopic Properties.** The longer Fe–B distance in **2**, relative to that in its iron counterpart CpFe(CO)<sub>2</sub>BCat noted above, may be attributed to two main factors. The longer distance in **2**, most likely, results from the absence of a strongly donating Cp ligand and the presence of additional  $\pi$ -accepting carbonyl groups. These factors may lead to weaker  $\sigma$  bonding and certainly will lead to weakening any potential  $\pi$  bonding between the metal center and the boryl ligand.

Infrared stretching frequencies of carbonyl groups are commonly used to compare electron density at a metal center. There are a number of stretching frequencies for **1–3**, and each one is consistently 20–50 cm<sup>-1</sup> higher than its corresponding band for the bis(silyl) and bis(stannyl) compounds. The electronegativity of the elements in these ligands bound to the metal center is similar to that of boron,<sup>60</sup> but the boron center is likely to be more  $\pi$ -accepting. Moreover, the stretching frequencies are higher than those for the related, base-stabilized gallyl compounds (CO)<sub>4</sub>Fe{Ga[(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>](R)}<sub>2</sub>, which should have minimal  $\pi$  effects.<sup>61</sup>

Two different rationalizations for the infrared data can be made. First, the reduced electron density at iron in **1–3** may be due to  $\pi$  acceptance by the boryl ligand. This interaction would be expected to be weaker in these compounds than it would be in CpFe(CO)<sub>2</sub>BCat and would be consistent with the longer Fe–B distance. Alternatively, the presence of oxygen in the catecholborane group may lead to weaker donation through the  $\sigma$  system than the trialkyl-substituted stannyl and silyl groups that have stronger  $\sigma$ -donating alkyl groups. We have not been able to prepare dialkylboryl complexes in this system, and a more complete understanding of the factors controlling metal–boron bonding must await further study.

In sharp contrast to the unusual stereochemical nonrigidity of the six-coordinate compounds Fe(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub><sup>46</sup> and Fe(CO)<sub>4</sub>(SnR<sub>3</sub>)<sub>2</sub>,<sup>54</sup> the neutral boryl complexes **1–3** are stereochemically rigid in solution. <sup>13</sup>C NMR spectra of **1–3** showed two distinct chemical shifts at 204 and 202 ppm for the two chemically inequivalent carbonyl ligands at room temperature. The X-ray diffraction structure of **2** shows that this complex possesses some of the same distortions as the bis(stannyl) and bis(silyl) complexes that are stereochemically nonrigid and rearrange by nondissociative pathways. Most notably, the mutually trans carbonyls are bent toward the covalently bonded ligands. However, there is one distortion that is different from those of the stannyl and silyl compounds. The B–Fe–B bond angle is smaller than the 90° required for an octahedral geometry and is much smaller than the Sn–Fe–Sn or Si–Fe–Si angles in the group 4 analogs.

The mechanism for exchange of the silyl and stannyl compounds invoked by Graham involves isomerization through a bicapped tetrahedron. If this structure is required for rearrangement, then the small B–Fe–B angle would require greater distortion to fully adopt such a structure than would the corresponding silyl and stannyl compounds. Thus, rearrangement rates would be slower, despite distortion of the trans carbonyls in **2** that is similar to those in the bis(silyl) and bis(stannyl) compounds. It should be noted, however, that the opening of the E–Fe–E angle in the bis(stannyl) compound does not enhance the rate of stereochemical exchange relative to the bis(silyl) compounds. Instead, one reviewer suggested that the greater  $\sigma$ -donating ability of the boryl ligand may make the distortion of opening the B–Fe–B angle more disfavored than in the stannyl or silyl compounds. Finally, the distortion<sup>62</sup> of bis(boryl) complexes with cis-disposed boryl ligands toward geometries with small B–M–B angles may suggest a degree of B–B bonding that would slow the site exchange in (CO)<sub>4</sub>Fe(ER)<sub>n</sub><sub>2</sub> compounds.

The synthesis of Fe(CO)<sub>4</sub>(BCat)(SnMe<sub>3</sub>) is described below. This compound is also stereochemically rigid at room temperature. X-ray structural data for this compound have not been obtained, but the presence of a single boryl ligand clearly stops the rapid site exchange that is characteristic of the iron carbonyl compounds bound to heavy group 4 elements. Recently, bis(organogallyl) compounds of iron carbonyl were isolated with base-stabilized gallium centers.<sup>63</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectra also showed a rigid cis geometry, but X-ray data are not available to make comparisons to base-free compounds **1–3**.

**Reactivity of Boryl Complexes.** The isolated compounds **1–3** decomposed over the course of hours in solution and after days as solids. The dominant main-group product was B<sub>2</sub>(Cat)<sub>3</sub> (<sup>11</sup>B  $\delta$  23).<sup>64</sup> The remaining boron was presumably lost in the form of insoluble material, perhaps incorporated into an iron carbonyl cluster. Compounds **4–6** decomposed to form the stable anionic species B(Cat)<sub>2</sub><sup>-</sup> (<sup>11</sup>B  $\delta$  15).<sup>64</sup> These decompositions were accelerated in polar solvents. Again, the remaining boron was not observed in a soluble form. These phenomena are similar to the nucleophile-promoted degradation reactions of HBCat as well as the reaction of RhH(PMe<sub>3</sub>)<sub>4</sub> with HBCat to yield B(Cat)<sub>2</sub><sup>-</sup>.<sup>64</sup> Bis(boryl) complex **1** reacted under photochemical conditions with alkenes, providing alkyl and vinylborane products (<sup>11</sup>B NMR  $\delta$  35, 32), but B<sub>2</sub>-Cat<sub>3</sub> was formed in much higher yields that these organoborane products and further chemistry with alkenes was not pursued.

Compounds **1–6** displayed more tractable reactivity with a number of organic and main-group substrates, and this chemistry is outlined in Scheme 1 for **1–3** and Scheme 2 for **4–6**. Compounds **1–3** were strongly reactive toward heteroatom acids such as alcohols and weak protic substrates such as amines. Compounds **1–3** gave EtOBCat (100% by <sup>1</sup>H NMR spectroscopy) and Et<sub>2</sub>NBCat (100%) upon addition of excess EtOH and Et<sub>2</sub>NH. Iron carbonyl dihydride could be observed im-

(60) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. In *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College: New York, 1993; pp 187–189.

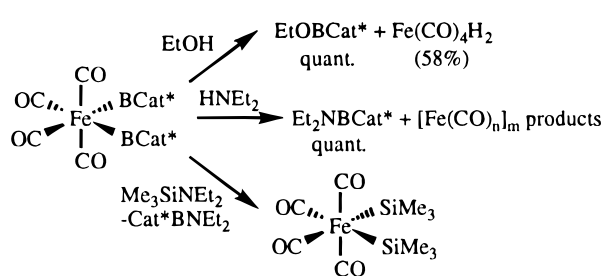
(61) We thank a reviewer for prompting us to compare these numbers.

(62) The B–Pt–B angle in (PPh<sub>3</sub>)<sub>2</sub>Pt(BCat\*)<sub>2</sub> is 77.9(7)°.<sup>12</sup>

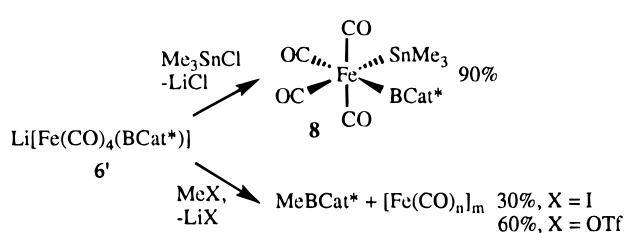
(63) Fischer, R. A.; Schulte, M. M.; Priermeier, T. *J. Organomet. Chem.* **1995**, *493*, 139–142.

(64) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, T. R.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175.

## Scheme 1



## Scheme 2



mediately after alcohol addition, but no hydride signal was observed 10 min after amine addition. Multiple iron carbonyl products were observed by IR spectroscopy, and further characterization of the iron products was not pursued. Reaction with 1 equiv of alcohol or amine gave mixtures of EtOBCat and HBCat or Et<sub>2</sub>NBCat and HBCat.

Reaction of **1–3** with Et<sub>2</sub>NSiMe<sub>3</sub> gave a  $\sigma$ -bonded ligand exchange to form the aminoborane and the known bis(silyl) compound Fe(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> (**8**) in 75% yield. Literature methods for the synthesis of **8** are not straightforward. It is not formed by the reaction of Na<sub>2</sub>-Fe(CO)<sub>4</sub> with ISiMe<sub>3</sub>,<sup>65</sup> and it is difficult to prepare by photochemical methods starting with Fe(CO)<sub>5</sub>.<sup>66</sup> It is likely that the exchange of boryl and silyl ligands was driven by the B–N bonds in the main-group product being more stable than the Si–N bond in the substrate. Boryl complexes may prove to be useful as precursors for compounds with transition-metal-heavy-element bonds by such exchange reactions driven by the formation of strong B–N bonds.

The generation of the anionic boryl complexes led to methods for the preparation of unusual compounds with covalently bonded ligands located cis to the boryl ligand. Compound **9**, a novel species with one boryl and one stannyl ligand, was prepared by substitution of the [Fe(CO)<sub>4</sub>(BCat\*)]<sup>–</sup> fragment for a chloride in ClSnMe<sub>3</sub>. Compound **9** was isolated as an analytically pure yellowish liquid after filtration and removal of solvent. The identity of the silyl boryl product was readily deduced by its spectroscopic characteristics. The <sup>11</sup>B NMR spectrum displayed a single resonance at  $\delta$  47, which was similar in chemical shift to the neutral bis(boryl) complexes. The <sup>119</sup>Sn NMR spectrum showed a single resonance at  $\delta$  –74.5. The <sup>13</sup>C NMR spectrum showed three resonances,  $\delta$  207.4, 206.6, and 204.4, indicating that complex **9** adopts a cis structure. The structural assignment was also consistent with the infrared spectrum that showed absorptions at 2080, 2054, 2026, 2004, and 1976 cm<sup>–1</sup>, the region characteristic of neutral Fe(CO)<sub>4</sub>XY compounds. Mass spectros-

copy (CI) showed a molecular ion. At elevated temperatures or after extended periods of time in toluene solvent at room temperature, **9** decomposed to form B<sub>2</sub>-Cat\*<sub>3</sub> as the major main-group product in a fashion similar to that for **1–3**. The tin-containing product was not identified, but no coupling of the two electrophilic ligands to form Me<sub>3</sub>SnBCat was observed.

In contrast to the reaction of halostannane that led to observable neutral boryl complexes with an accompanying covalently bonded ligand, the reaction of alkylating reagents led to immediate formation of free alkylborane products. Anion **4** reacted with MeI and MeOTf to yield methylcatecholborane in 30% and 60% yield, respectively. Formally, this reaction involves addition of a boryl anion to an organic electrophile and is a rare example of reactivity that would be characteristic of catecholboryl anion. However, it is unlikely that this reaction involves free catecholboryl anion. As mentioned in the Introduction, the intermediacy of boryl anions, specifically Ph<sub>2</sub>B, has been controversial.<sup>33–36</sup> Further, previous boryl transfer reactions from transition-metal compounds involve species whose identity requires reinvestigation with modern spectroscopic techniques.<sup>67,68</sup>

We conducted the addition of the alkylating agents at low temperature in attempts to observe a potential intermediate that could be an iron alkyl boryl complex, but no such species was detected. Only the metal boryl anion and methylcatecholborane were observed by <sup>11</sup>B NMR spectroscopy. Thus, we cannot distinguish between one pathway in which the organic electrophile attacks directly at the boryl ligand rendered nucleophilic by the anionic charge and another pathway along which the carbon electrophile attacks the metal center, and the resulting neutral alkyl boryl compound undergoes B–C bond-forming reductive elimination. The absence of an observable intermediate makes it necessary that reductive elimination of the alkylborane from such a complex be more rapid than the rate of its formation.

The electronic properties of a potential alkyl boryl intermediate are likely to be different from those of **9**, since it would contain one nucleophilic and one electrophilic covalent ligand located cis to each other. Considering that the tin chloride provided products resulting from addition to the metal center, we favor the mechanism involving addition of the methylating reagent to the metal center followed by B–C bond-forming reductive elimination that is rendered facile by the complementary electronic properties of an alkyl and boryl ligand. Reaction by this pathway would support the requirement for rapid B–C bond-forming reductive elimination in rhodium-catalyzed hydroboration reactions.<sup>13,14</sup>

**Conclusion.** A comparison of the reactivity of the bis(boryl) complexes **1–3** to that of the CpFe(CO)<sub>2</sub>BCat complex and other poly(boryl) complexes indicates that they are unusually reactive. The CpFe(CO)<sub>2</sub>BCat complex, with its single boryl ligand and greater electron density, is very stable thermally, whereas compounds **1–3** are labile. In contrast to these neutral compounds, the full negative charge of **4–6** leads to decomposition that forms the very stable B(Cat)<sub>2</sub><sup>–</sup>. A tris(boryl)

(65) Nasta, M. A.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1971**, *93*, 2813.

(66) Jetz, W.; Graham, W. A. G. *J. Organomet. Chem.* **1974**, *69*, 383.

(67) Schmid, G.; Noth, H. *Chem. Ber.* **1967**, *100*, 2899.

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

(69) Farmery, K.; Kilner, M. *J. Chem. Soc. A* **1970**, 634.

complex of iridium<sup>9</sup> appears to be much more stable than **1–3**, presumably due to its third-row metal center. Bis(boryl) complexes of rhodium are stable enough to isolate but also undergo unusual reaction chemistry. One such example is the apparent insertion of alkenes. The generally greater propensity of rhodium phosphine complexes, rather than iron carbonyl compounds, to undergo alkene insertion reactions is likely to be responsible for the cleaner chemistry with alkenes than was observed with **1**. An understanding of the relative reactivity of boryl complexes of different transition-metal systems toward different organic reagents will emerge with further studies.

**Acknowledgment.** We are grateful for support from the National Science Foundation (Grant No. CHE

1921109 and NYI Award program), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Dreyfus Foundation for a New Faculty Award, Du Pont for a Young Faculty Award, Union Carbide for an Innovative Recognition Award, and Yale University for a Junior Faculty Fellowship.

**Supporting Information Available:** Tables giving full details of crystallographic parameters, bond distances and angles, positional parameters, anisotropic thermal parameters, Cartesian coordinates, and torsion or conformational angles for **2** and figures giving <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C{<sup>1</sup>H}, <sup>7</sup>Li, and <sup>121</sup>Sn NMR and IR spectra of the new compounds **1–6**, **9**, ClB(O<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-4-*t*-Bu), and ClB(O<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-3,5-*t*-Bu<sub>2</sub>) (54 pages). Ordering information is given on any current masthead page.

OM950437T