

Supplementary Material Available: A listing of crystallographic data processing formulas and observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

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Migration of Triphenylboron from Iron to an η^5 -Cyclopentadienyl Ligand

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Triphenylborane and $(C_2H_5)_4N^+(\eta^5-C_5H_5)Fe(CO)_2^-$ form a 1:1 adduct $Ph_3BFe(CO)_2Cp^-NEt_4^+$, **1**. Analyses of spectroscopic data (IR, 1H NMR, and ^{11}B NMR) from **1** and the analogous $(n-C_4H_9)_4N^+$ salt, including comparisons with $Ph_3BOCH_3^-NEt_4^+$ and $Ph_3AlFe(CO)_2Cp^-NEt_4^+$, strongly indicate the presence of an iron-to-boron bond and suggest that the negative charge is localized on the boron atom. In dilute tetrahydrofuran solutions, **1** spontaneously converted to $Ph_3BC_5H_4Fe_2(CO)_4Cp^-NEt_4^+ \cdot 1/2 THF$, **2**, and $Ph_3BH^-NEt_4^+$, **3**. From X-ray diffraction analysis, the crystal structure of **2** was refined to $R = 0.097$ in $C2/c$ with $a = 40.357$ (6) \AA , $b = 9.943$ (2) \AA , $c = 20.453$ (2) \AA , and $\beta = 111.72$ (1)° with $Z = 8$. Partial disorder in the cation required two-state parameterization. The anion consists of a central di- μ -carbonyl-diiron unit ($Fe-Fe = 2.540$ (2) \AA) with a terminal carbonyl and an η^5 -cyclopentadienyl ligand on each metal atom; the configuration of the rings is *cis*. The nearly tetrahedral Ph_3B group is η^1 bonded to one of the rings at the position farthest from the other ring. The bonding geometry around the iron atoms is essentially that found in *cis*- $[CpFe(CO)_2]_2$. In acetone, the conductivity of **2** is similar to that of $Ph_4B^-NEt_4^+$. The IR spectra of **2** in dimethyl sulfoxide and in methylene chloride show different intensities of corresponding $\nu(CO)$, indicative of a *cis*-*trans* isomer distribution. Compound **3** is identical with $Ph_3BH^-NEt_4^+$ prepared from Ph_3B and KH followed by metathesis with $Et_4N^+Br^-$. The single B-H bond in **3** was identified from the stretching frequency of $2198 \pm 1 \text{ cm}^{-1}$, observed by Raman and infrared spectroscopy and from 1H and ^{11}B NMR spectroscopy. A prominent absorption at 2136 cm^{-1} seen only in the infrared was assigned as a combination band. A mechanism is proposed for the conversion of **1** to **2** and **3** via an intramolecular nucleophilic attack on the Cp ring by Ph_3B^- , followed by hydride elimination.

Introduction

Aromatic substitution of a π -bonded ligand by a group already bonded to the same metal has been limited to a few cases mainly involving organic groups. McCleverty and Wilkinson reported the migration of the σ -bonded ethyl group of $EtMoCp(CO)_3$ ($Cp = \eta^5-C_5H_5$) to the cyclopentadienyl ring with formation of $[(\eta^5-C_5H_4Et)Mo(CO)_3]_2$.¹ Subsequently Nesmeyanov and co-workers described analogous behavior for $PhMoCp(CO)_3$.² Phenyl migration has been promoted by nucleophiles; Schrock, Guggenberger, and English showed that the phenyl group of $PhM(C_8H_8)_2$ ($M = Nb$ or Ta) migrated to one cyclooctatetraene ligand upon treatment with chelating phosphines or arsines.³ Similarly, the reaction of $PhVCp_2$ with carbon monoxide gave $[CpV(\eta^5-C_5H_4Ph)(CO)]_2$.⁴ Examples wherein a migrating phenyl, trimethylsilyl, or trimethylgermyl group substitutes an incoming olefin have been described by Stone and co-workers.⁵

The present work originated with a study of the reaction of $(\eta^5\text{-cyclopentadienyl})\text{dicarbonylferrate}(-I)$, $FeCp(CO)_2^-$, with triphenylborane. In tetrahydrofuran (THF) solution the resulting adduct, $Ph_3BFeCp(CO)_2^-$ as the tetraethylammonium salt, **1**, spontaneously converted to tetraethylammonium [di- μ -carbonyl- $(\eta^5\text{-cyclopentadienyl})\text{carbonyliron}(\text{carbonyliron})\text{-}\eta^5\text{-cyclopentadienyl}]$ triphenylborate ($Fe-Fe$) hemikis(tetrahydrofuranate), **2**, and tetraethylammonium hydridotriphenylborate, **3**. The evidence described herein shows that this transformation formally involves a novel metal-to-ring migration and aromatic substitution by the triphenylboron group.

Experimental Section

Unless stated otherwise all operations were carried out under a purified argon atmosphere. The apparatus and techniques employed for handling air-sensitive compounds have been described in detail.⁶ Infrared (IR) spectra were obtained on a Perkin-Elmer Model 337

spectrometer, calibrated with polystyrene. ^1H NMR and ^{11}B NMR spectra were recorded on Varian Associates A-60 and HA-100 instruments, respectively, unless otherwise stated. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane or external $^{11}\text{B}(\text{OCH}_3)_3$, unless otherwise noted. Conductance measurements were carried out in acetone under argon at 25.0 °C with an Industrial Instruments Model RC16B2 conductivity bridge at 1000 Hz and a Freas-type solution cell with bright platinum electrodes ($k = 0.113 \text{ cm}^{-1}$) equipped with a gas adapter. Unless noted, all melting points were determined in sealed argon-filled capillaries using a Büchi melting point apparatus and are corrected. Elemental analyses were carried out by the Pascher Microanalytical Laboratory, Bonn, West Germany.

Reagents. All solvents were reagent grade and were dried and degassed prior to distillation under an argon atmosphere. Tetrahydrofuran and toluene were distilled from potassium- or sodium-benzophenone ketyl, respectively. Methanol was distilled from $\text{Mg}(\text{OMe})_2$; methylene chloride and diethyl ether were distilled from P_4O_{10} and CaH_2 , respectively. Acetone for conductance measurements was distilled twice from activated molecular sieve (Linde, type 4A) and had a specific conductance of $7.86 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$.⁷ The deuterated solvents (acetone- d_6 , dimethyl- d_6 sulfoxide and tetrahydrofuran- d_8) employed for ^1H NMR spectroscopy were purified by trap-to-trap vacuum distillation (TTVD) from activated molecular sieve. Triphenylborane (mp 149–151 °C) was prepared as described by Wittig.⁸ Tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium salts of $[\text{FeCp}(\text{CO})_2]^-$ were prepared according to established procedures.⁹

Preparation of 1. Addition of 20 mL of diethyl ether to 0.355 g (1.47 mmol) of Ph_3B and 0.451 g (1.47 mmol) of $[\text{FeCp}(\text{CO})_2]^- \text{NEt}_4^+$ in a Schlenk reaction vessel (SRV) gave, after stirring for 23 h, a suspension which separated into a light orange supernatant and a beige precipitate. The supernatant at this point did not contain any appreciable concentration of reactants (IR). After removal of 7 mL of the supernatant liquid with a syringe and addition of 12 mL of THF with stirring at 0 °C, the cold mixture was then filtered through a "fine"-porosity frit and the light beige solid was washed with two 5-mL portions of diethyl ether and vacuum dried on the frit, giving 0.676 g (84%) of **1** as an air-sensitive powder, mp 213–216 °C dec. Anal. Calcd for $\text{C}_{33}\text{H}_{40}\text{BFeNO}_2$: C, 72.2; H, 7.35; N, 2.55. Found: C, 71.1; H, 7.39; N, 2.48. IR (Nujol mull): $\nu(\text{CO})$ 1991 (s), 1975 (sh), 1920 (s), 1890 (sh) cm^{-1} .

Reaction of 1 with Pyridine. To a mixture of 0.082 g (0.15 mmol) of $\text{Ph}_3\text{BFc}(\text{CO})_2^- \text{NEt}_4^+$ in THF (5 mL) in a SRV was added 0.012 mL (0.15 mmol) of pyridine at 0 °C. Stirring and warming to room temperature did not cause dissolution of the solid, while addition of a fivefold excess of pyridine (0.06 mL) via syringe and stirring for 30 min yielded a clear red solution. The infrared spectrum of this solution showed mostly $\nu(\text{CO})$ of $[\text{FeCp}(\text{CO})_2]^-$ at 1863 (s) and 1789 (s) cm^{-1} and weaker bands of the starting complex at 1990 and 1922 cm^{-1} ; the latter disappeared completely after stirring the solution for 14 h.

Reaction of 1 in THF. Isolation of 2 and 3. To a solution of triphenylborane (0.759 g, 3.13 mmol) in THF (30 mL) was added a solution of $[\text{FeCp}(\text{CO})_2]^- \text{NEt}_4^+$ (0.960 g, 3.13 mmol) in 70 mL of THF in a SRV. The mixture was allowed to stand in the dark at room temperature. After two days, dark red, needle-like crystals began to form. The growth of crystals continued for approximately ten days, after which time the supernatant had lightened in color and was decanted and reserved. The crystalline product was washed with two 4-mL portions of THF and dried under a stream of argon to give 0.65 g (54%) of **2**, mp 210–2 °C dec. Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{BFe}_2\text{NO}_{4.5}$: C, 66.26; H, 6.36; Fe, 14.67; N, 1.84; O, 9.54. Found: C, 67.13; H, 6.45; Fe, 14.57; N, 1.79; O, 9.48. IR: $\nu(\text{CO})$ CH_2Cl_2 1985 (8.8), 1946 (4.8), 1790 (1.4), 1760 (10) cm^{-1} ; $\nu(\text{CO})$ Me_2SO 1980 (10.3), 1935 (3.0), 1790 (0.9), 1757 (10) cm^{-1} . Molar conductivity in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (molarity): 119 (1.36×10^{-3}), 124 (6.81×10^{-4}), 149 (3.14×10^{-4}), 163 (6.81×10^{-5}), 160 (3.41×10^{-5}), 165 (5.68×10^{-6}).

The clear red supernatant was seeded with a crystal of **2** and cooled to -80 °C (dry ice/acetone); no further crystallization was observed. Filtration of the mixture and removal of the solvent by TTVD yielded a brown oil, which turned into a rubbery solid upon drying under vacuum. Addition of 50 mL of toluene and stirring at room temperature gave a clear red supernatant over an oily precipitate. The supernatant was decanted into a separate SRV and the oil was washed via syringe with three 10-mL portions of toluene. The residue was

vacuum dried to give a light brown solid (~0.5 g). Redissolution in 20 mL of THF, followed by addition of 13 mL of toluene, gave a clear, light brown solution which upon slow cooling to -68 °C yielded small, tan needle-like crystals of **3** (0.3 g, 26%), mp 105–108 °C (dec). Recrystallization from a tetrahydrofuran-toluene mixture gave light tan crystals, mp 108–109.5 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{BN}$: C, 83.63; H, 9.71; N, 3.75. Found: C, 82.07; H, 9.64; N, 3.67. IR (KBr pellet): 3049 (s), 2995 (sh), 2989 (s), 2198 (m), 2136 (m), 2005 (w), 1580 (w), 1482 (vs), 1435 (m), 1396 (m), 1263 (w), 1169 (m), 1148 (w), 1063 (w), 1011 (s), 998 (m-w), 924 (w), 897 (w), 780 (m-w), 738 (m), 707 (s), 613 (w), 583 (w) cm^{-1} .

The IR spectrum of the clear dark red toluene extract from which **3** was separated contained $\nu(\text{CO})$ at 2002 (7.0), 1960 (6.3), and 1788 (10) cm^{-1} indicative of $[\text{FeCp}(\text{CO})_2]_2$; its concentration was estimated to be $6.4 \times 10^{-3} \text{ M}$ (50 mL, 0.32 mmol) by comparison of the absorbances with standard solutions of $[\text{FeCp}(\text{CO})_2]_2$ in toluene ($\nu(\text{CO})$ 1998 (6.9), 1955 (6.2), and 1783 (10) cm^{-1}). Attempts to crystallize the dimer yielded only oils which, when dissolved in various solvents, showed $\nu(\text{CO})$ having medium-dependent relative absorbances (e.g., $\nu(\text{CO})$ THF 1993 (7.7), 1952 (6.2), 1783 (10) cm^{-1} ; $\nu(\text{CO})$ CH_2Cl_2 1998 (10), 1958 (6.0), 1774 (9.0) cm^{-1}) characteristic of $[\text{FeCp}(\text{CO})_2]_2$.

Preparation of $\text{Ph}_3\text{BH}^- \text{NEt}_4^+$ from Ph_3B and KH. A solution of Ph_3B (0.408 g, 1.68 mmol) in 25 mL of THF was added dropwise to 2 mmol of KH (0.374 g of a 22.5% suspension in mineral oil, Alfa/Ventron) in 17 mL of THF in a SRV with stirring at room temperature. After 7 h, the initially cloudy mixture showed only little residual KH. The clear supernatant was then filtered ("M" frit, Celite) onto 0.63 g (3.0 mmol) of $\text{NEt}_4^+ \text{Br}^-$ which had been dried under vacuum for 12 h. The resultant milky white suspension was stirred for 19 h, followed by filtration ("M" frit, Celite) to give a clear, colorless solution. Addition of toluene (30 mL) and slow cooling to -30 °C caused crystallization of needle-like crystals. The cold supernatant was decanted and the crystals were washed with three 5-mL portions of toluene, followed by vacuum drying, to give 0.349 g (56%) of $\text{Ph}_3\text{BH}^- \text{NEt}_4^+$, mp 112–113.5 °C. A mixture melting point with **3** was 110–112.5 °C. The compound was hygroscopic and was handled under an inert atmosphere. Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{BN}$: C, 83.63; H, 9.72; N, 3.75. Found: C, 83.45; H, 9.73; N, 3.70. IR (KBr pellet): 3043 (s), 2990 (sh), 2979 (s), 2192 (m), 2130 (m), 2000 (w), 1580 (w), 1482 (vs), 1430 (m), 1392 (m), 1260 (m-w), 1170 (m), 1147 (m-w), 1062 (w), 1012 (s), 996 (sh), 781 (m-w), 740 (m), 709 (s), 615 (vw), 586 (w) cm^{-1} .

$\text{Ph}_3\text{BOCH}_3^- \text{NEt}_4^+$. This salt was prepared by combining equimolar quantities of sodium methoxide and Ph_3B in methanol, followed by metathesis with excess $\text{Et}_4\text{N}^+ \text{Br}^-$ in THF. Crystallization from a tetrahydrofuran-toluene mixture gave white, prismatic crystals, mp 351–353 °C (uncor). Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{BNO}$: C, 80.39; H, 9.49. Found: C, 81.69; H, 9.91. IR (Nujol mull): 3043 (m-s), 2790 (m), 1580 (w), 1473 (s), 1429 (m), 1395 (m), 1260 (w, b), 1190 (m-w), 1175 (m), 1139 (m), 1089 (vs), 1063 (m-w), 1032 (w), 1003 (m-w), 922 (w), 890 (w), 873 (m), 863 (m), 848 (m), 782 (m-w), 754 (m), 742 (vs), 710 (vs), 613 (m-s) cm^{-1} . ^1H NMR (CH_2Cl_2): δ 1.35 (t of t, 12 H), 2.96 (q, 8 H), 3.61 (s, 3 H), 7.54 (m, 9 H) and 7.99 (m, 6 H).

Exposure to air radically reduced the melting point of $\text{Ph}_3\text{BOCH}_3^- \text{NEt}_4^+$ by about 150 °C, presumably due to hydrolysis.

$\text{Ph}_4\text{B}^- \text{NEt}_4^+$. This salt was prepared by combining equimolar quantities of Et_4NBr and NaPh_4B in 1:1 methanol-water and was recrystallized from 1:2 DMF-absolute EtOH to give white crystals, mp 363–364 °C (uncor). Anal. Calcd for $\text{C}_{33}\text{H}_{40}\text{BN}$: C, 85.50; H, 8.97; N, 3.12. Found: C, 85.40; H, 8.97; N, 3.19. Molar conductivity in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (molarity): 128 (1.03×10^{-3}), 135 (5.14×10^{-4}), 141 (2.57×10^{-4}), 136 (6.43×10^{-5}), 132 (1.61×10^{-5}), 136 (4.05×10^{-6}), 175 (1.01×10^{-6}).

Reaction of $\text{Ph}_3\text{BFc}(\text{CO})_2^- \text{Na}^+$ in THF. A clear, red, filtered solution containing ~1 mmol of $[\text{FeCp}(\text{CO})_2]^- \text{Na}^+$, prepared from 0.216 g (0.60 mmol) of $[\text{FeCp}(\text{CO})_2]_2$ and excess 0.59% sodium amalgam (4.35 mg-atoms of Na) in 18 mL of THF, was added to a solution of 0.242 g (1 mmol) of Ph_3B in 9 mL of THF at 0 °C. The IR spectrum of the resulting tan solution had $\nu(\text{CO})$ 1992 (s) and 1925 (s) cm^{-1} , characteristic of $\text{Ph}_3\text{BFc}(\text{CO})_2^-$. Upon being stirred at room temperature, the solution darkened to a burgundy red color. After 110 h no further changes were observed in the appearance of the mixture or its IR solution spectrum ($\nu(\text{CO})$ 1988 (s), 1970 (sh), 1938 (m), 1780 (w), 1765 (s) cm^{-1}). Attempts to isolate a solid product

from mixtures of THF, toluene, and hexane by slow cooling and/or solvent removal yielded dark red oils.

Reaction of $\text{Ph}_3\text{BFeCp}(\text{CO})_2\text{NBu}_4^+$ in THF. Spectroscopic Study. Addition of 2.0 mL of THF to 0.208 g (0.3 mmol) of $\text{Ph}_3\text{BFeCp}(\text{CO})_2\text{NBu}_4^+$ in a SRV at room temperature gave a clear, light red solution. A 0.8-mL aliquot for ^1H NMR spectroscopy was withdrawn from the mixture with an airtight syringe and injected into a sample tube, which contained a sealed capillary with Me_4Si and which was equipped with a septum. The remaining solution was diluted with THF to 5 mL, and aliquots were withdrawn from the solution at various times for IR spectroscopy. The samples were kept at room temperature for 22 h and then heated to 50 °C (oil bath) until no further changes were observed in their ^1H NMR and IR spectra (cf. Results and Discussion).

Recovery of the products from the reaction of $\text{Ph}_3\text{BFeCp}(\text{CO})_2\text{NBu}_4^+$ in THF was attempted in a separate experiment. Solutions of 0.751 g (1.79 mmol) of $\text{FeCp}(\text{CO})_2\text{NBu}_4^+$ in 15 mL of THF and 0.433 g (1.79 mmol) of Ph_3B in 12 mL of THF were mixed and stirred with heating (53 °C, oil bath) in a SRV for 1 week. Solvent removal from the deep red mixture by TTVD gave a dark brown oil which foamed under vacuum. Addition of CH_2Cl_2 and toluene (15 mL each) formed a dark red solution. Cooling to -65 °C caused precipitation of a small amount of a brown solid which was recovered by filtration, washed with toluene, and vacuum dried. The amount of the material was sufficient for spectroscopic analysis which indicated the presence of $[\text{Ph}_3\text{BC}_5\text{H}_4\text{Fe}_2\text{Cp}(\text{CO})_4\text{NBu}_4^+]$ analogous to **2**: IR (Nujol): $\nu(\text{CO})$ 1975 (s), 1929 (m), 1779 (w), 1763 (w), 1748 (s) cm^{-1} . ^1H NMR (acetone- d_6): δ 0.75–1.17 (m), 1.28–1.98 (m), 3.08–3.48 (m), 4.04–4.25 (m), 4.75 (s), 4.71–4.92 (m), 6.78–7.12 (m), 7.21–7.56 (m) (12:16:8:2:5:2:9:6). Attempts to isolate a solid from the supernatant failed; only a dark red oil was obtained from various solvent mixtures as the major product fraction.

X-ray Diffraction Data of **2.** A somewhat irregular parallelepiped of approximate dimensions $0.40 \times 0.33 \times 0.38$ mm was cut from a needle-shaped crystal of **2**. Weissenberg and precession X-ray photography and Delauney reduction analysis revealed a C-centered monoclinic lattice with a glide plane parallel to the *c* axis. The possible space groups were Cc (C_2^2) and $C2/c$ (C_{2h}^2); statistical analyses of intensity distributions and the absence of a measurable piezoelectric effect were consistent with the choice of the centric group $C2/c$, and this choice was confirmed by the structure analysis. Twelve reflections with $2\theta \geq 40^\circ$ for Cu $K\alpha$ were automatically centered on a Picker FACS-I four-circle diffractometer, and least-squares refinement of the results produced lattice parameters of $a = 40.357$ (6) Å, $b = 9.943$ (2) Å, $c = 20.453$ (2) Å, and $\beta = 111.72$ (1)°. For $Z = 8$, this gives $D_x = 1.326$ g cm^{-3} for one-half molecule of THF per asymmetric unit; $D_m = 1.321$ g cm^{-3} was determined by flotation of several well-formed crystals in a carbon tetrachloride/hexane solution.

Diffracted intensities were measured for a total of 6079 reflections with $(\sin \theta)/\lambda \leq 0.5475$ in θ - 2θ scan mode with Ni-filtered Cu $K\alpha$ radiation incident at a takeoff angle of 3°. The scan rate was 1° $2\theta/\text{min}$ over a minimum range of 1.8° with systematic allowance for spectra dispersion; 40-s background counts were taken at both ends of each scan. Of the 5234 reflections found to be independent and not systematically absent, 4607 were regarded as objectively observed with $|F_o| \geq 1.96\sigma_F$, where $|F_o| = k[(C - tB)/Lp]^{1/2}$ and $\sigma_F = k[(C + t^2B)^{1/2}/(2|F_o|Lp) + 0.02|F_o|]$; C is the total count recorded during the scan, t is the ratio of the scanning time to the total time for the background B , and L and p are the Lorentz and polarization corrections, respectively. Correction for absorption of X-rays was made through the value of k , which was computed for each reflection using a linear mass absorption coefficient $\mu = 6.62$ mm^{-1} by an algorithm^{9,10} for a crystal of arbitrary shape bounded by plane faces. Three standard reflections periodically monitored with each 50 data throughout the 20-day experiment showed a standard deviation of about 2%.

X-ray Structure Determination and Refinement of **2.** The coordinates of the iron atoms were determined from a Patterson synthesis but the resulting phased Fourier maps calculated with the acceptance criterion $|F_o|/|F_c| \geq 0.5$ were uninterpretable. It became clear that the phasing was unacceptable for about half of the data because of the proximity of the phasing atoms to the plane $y = 1/4$. Stringent acceptance conditions were imposed by weighting phased reflections in accordance with Woolfson's analysis¹² of the probability of correct phasing. A total of 1400 phased reflections with probability greater than 0.90 yielded a Fourier map from which the structure could be deduced and refined.

Full-matrix, isotropic least-squares refinement and subsequent anisotropic, block-diagonal refinement reduced the standard residual R to about 0.12. A difference Fourier synthesis revealed significant disorder in the tetraethylammonium ion and strong anisotropy in the THF molecule. A two-state model was adopted for the α carbons of the ethyl groups with occupancies of $1/3$ and $2/3$, as suggested by the electron density map. At this point, the thermal parameters of the anion were fixed; full-matrix refinement of the positional parameters and the anisotropic temperature factors for the cation and solvent molecule was continued until convergence. The total number of parameters thus varied was 493, including a scale factor.

The quantity minimized in the least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ with σ as defined above. Scattering factors were those of Cromer and Mann¹³ and anomalous dispersion corrections applied to the iron form factors were those of Cromer.¹⁴ The final conventional residual was $R_1 = 0.097$ and the weighted residual $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.118 with a data-to-parameter ratio of 9.4 to 1. The final difference Fourier synthesis displayed a maximum residual density of 0.32 $e/\text{Å}^3$ in a position consistent with that of a phenyl hydrogen atom. The final structural parameters are listed in Tables I and II; selected anion distances and angles are given in Table III.

Results and Discussion

Isolation and Characterization of **1.** Equimolar quantities of triphenylborane and $\text{Et}_4\text{N}^+\text{FeCp}(\text{CO})_2^-$ in diethyl ether form a light tan Lewis acid-base adduct which is much less thermally stable than analogous complexes of $\text{FeCp}(\text{CO})_2^-$ with triphenyl derivatives of aluminum, gallium, or indium.⁹ The adduct nature of **1** was verified by complete displacement of $\text{FeCp}(\text{CO})_2^-$ with pyridine.¹⁵ That **1** contains a boron-iron bond is inferred from the qualitative similarity of its infrared spectrum to that of $\text{Ph}_3\text{AlFeCp}(\text{CO})_2\text{NEt}_4^+$, **4**, known from a single-crystal X-ray analysis to incorporate an Fe-Al link.¹⁶ Observation of two, strong, high-frequency, carbonyl stretching vibrations at 1991 and 1920 cm^{-1} for **1** is consistent with a structure of C_1 local symmetry similar to that of **4**. The C-O stretching frequencies in **1** are about 50 cm^{-1} higher than those of **4** ($\nu(\text{CO})$ 1940 and 1871 cm^{-1})^{9,16} indicative of greater transfer of charge from iron to boron. A more direct measure of the negative charge density on boron in $\text{Ph}_3\text{BFeCp}(\text{CO})_2^-$ as the tetra-*n*-butylammonium salt¹⁷ in THF is the high-field shift of the ^{11}B NMR resonance from -42.1 ppm for Ph_3B to +28.8 ppm upon complexation. The latter is typical of anionic boron complexes,¹⁸ e.g., $\Delta(^{11}\text{B}) + 14.7$ ppm for $\text{Ph}_3\text{BOCH}_3\text{NEt}_4^+$ and +7.7 ppm for **3**.

The ^1H NMR spectrum of the adduct resulting from an equimolar mixture of Ph_3B and $\text{FeCp}(\text{CO})_2\text{NBu}_4^+$ in THF contained a singlet cyclopentadienyl resonance at δ 4.75 consistent with the postulated decrease in electron density of the $\text{FeCp}(\text{CO})_2$ unit (compare δ 4.36 for $\text{FeCp}(\text{CO})_2\text{NEt}_4^+$ in THF).¹⁹ The phenyl resonances of the adduct appeared as a broad multiplet at δ 7.6 (ortho) and a finely split multiplet at δ 7.15 (meta and para) with a combined intensity 3 times that of the Cp resonance in accord with the 1:1 stoichiometry postulated for the complex.²⁰

The effect of adduct formation on the IR spectrum of the Ph_3B moiety in **1** was observed as a decrease in the intensity and a 10- cm^{-1} shift to lower frequency of the symmetrical phenyl "breathing" mode $\nu(\text{C}-\text{C})_a$ of Ph_3B (1590 cm^{-1}),²¹ with the appearance of a second stronger C-C stretching mode at 1473 cm^{-1} . Similar spectra have been reported for other triphenylborates.²²

Isolation and Characterization of **2.** By employment of concentrations of Ph_3B and $\text{Et}_4\text{N}^+\text{FeCp}(\text{CO})_2^-$ at levels just below that at which **1** would precipitate from THF solution, red acicular crystals of **2** formed during several days in ~60% yield. The air-stable crystals were sparingly soluble in common donor solvents. In a mineral oil mull **2** had $\nu(\text{CO})$ bands in its IR spectrum consistent with the presence of terminal and bridging CO's (vide infra). In the $\nu(\text{C}-\text{C})$ region, bands at

Table I. Fractional Atomic Coordinates for 2^a

	10 ⁴ x	10 ⁴ y	10 ⁴ z
Fe ₁	4768.4 (3)	2397 (1)	4239.4 (6)
Fe ₂	4204.7 (3)	2092 (1)	3155.6 (5)
C ₁	4599 (2)	2173 (9)	4880 (4)
O ₁	4486 (2)	2012 (9)	5332 (3)
C ₂	3910 (2)	1817 (8)	3557 (4)
O ₂	3718 (2)	1644 (8)	3857 (3)
C ₃	4385 (2)	3581 (9)	3765 (4)
O ₃	4300 (2)	4720 (6)	3818 (3)
C ₄	4527 (2)	825 (8)	3745 (4)
O ₄	4580 (2)	-347 (6)	3785 (3)
B	3428 (2)	768 (9)	1865 (4)
Cyclopentadienyl Rings			
C ₁ (1)	5211 (2)	1833 (10)	3955 (5)
C ₂ (1)	5297 (2)	1632 (11)	4688 (5)
C ₃ (1)	5264 (2)	2923 (12)	4986 (5)
C ₄ (1)	5169 (2)	3918 (10)	4452 (5)
C ₅ (1)	5126 (2)	3206 (10)	3799 (5)
C ₁ (2)	3813 (2)	1545 (8)	2133 (3)
C ₂ (2)	3868 (2)	3012 (8)	2213 (4)
C ₃ (2)	4242 (2)	3301 (11)	2325 (4)
C ₄ (2)	4417 (2)	2025 (10)	2355 (4)
C ₅ (2)	4157 (2)	962 (9)	2227 (4)
Phenyl Rings			
C ₁ (3)	3451 (2)	-808 (7)	2096 (4)
C ₂ (3)	3164 (2)	-1682 (8)	1713 (4)
C ₃ (3)	3152 (3)	-3039 (9)	1900 (5)
C ₄ (3)	3433 (3)	-3564 (9)	2472 (6)
C ₅ (3)	3722 (3)	-2750 (9)	2867 (5)
C ₆ (3)	3729 (2)	-1357 (8)	2679 (4)
C ₁ (4)	3140 (2)	1567 (7)	2116 (3)
C ₂ (4)	3014 (2)	2876 (8)	1854 (4)
C ₃ (4)	2774 (2)	3578 (8)	2084 (4)
C ₄ (4)	2643 (2)	3006 (9)	2572 (4)
C ₅ (4)	2773 (2)	1708 (8)	2838 (4)
C ₆ (4)	3016 (2)	1016 (8)	2611 (4)
C ₁ (5)	3297 (2)	775 (7)	983 (4)
C ₂ (5)	3537 (2)	436 (9)	666 (4)
C ₃ (5)	3429 (3)	333 (9)	-87 (5)
C ₄ (5)	3078 (3)	612 (9)	-501 (4)
C ₅ (5)	2827 (3)	954 (10)	-202 (4)
C ₆ (5)	2937 (2)	1052 (9)	545 (4)
Tetraethylammonium Cation (Two-State)			
N	3404 (2)	4723 (6)	4918 (3)
C ₅	3295 (4)	4795 (15)	4113 (6)
C ₅ '	3081 (8)	5783 (31)	4711 (21)
C ₅ a	2992 (3)	5923 (11)	3803 (5)
C ₆	3092 (4)	4523 (15)	5165 (8)
C ₆ '	3211 (9)	3285 (18)	4585 (14)
C ₆ a	2890 (3)	3124 (13)	4816 (7)
C ₇	3683 (4)	3569 (15)	5157 (7)
C ₇ '	3513 (7)	4746 (35)	5712 (12)
C ₇ a	3828 (3)	3437 (13)	5995 (5)
C ₈	3576 (3)	6068 (13)	5286 (7)
C ₈ '	3688 (8)	4863 (31)	4574 (18)
C ₈ a	3901 (3)	6409 (14)	5037 (8)
Tetrahydrofuran			
C ₉	109 (8)	1685 (23)	2081 (13)
C ₁₀	54 (10)	3072 (16)	2269 (12)
O ₅	0	862 (15)	1/4

^a Estimated standard deviations in parentheses refer to the last significant digit.

1580 and 1482 cm⁻¹ were consistent with four-coordinate triphenylborate. The conductivity of **2** in acetone compared closely with that of Ph₃B⁻NEt₄⁺ and the data are well within the range for uni-univalent electrolytes.⁷

Crystal Structure of 2. A perspective view of the complete anion of **2** is presented in Figure 1. It is most simply described as a derivative of *cis*-[FeCp(CO)₂]₂,²³ **5**, in which a Ph₃B group is σ bonded to one of the cyclopentadienyl ligands. To a good approximation, the underlying geometry of the *cis* dimer unit is virtually unaltered by the presence of the Ph₃B group in **2**.

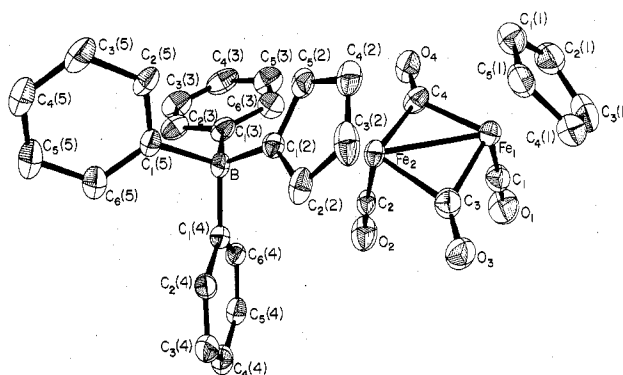


Figure 1. Perspective view of the anion.

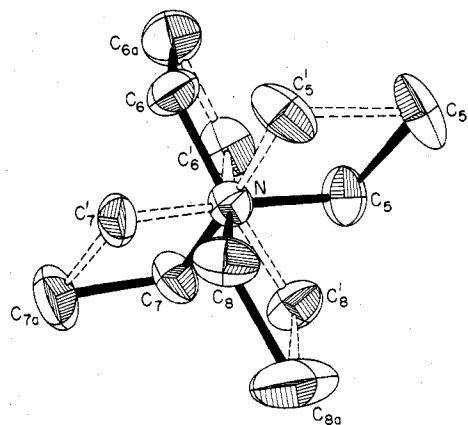


Figure 2. Perspective view of the disordered cation.

Moreover, although there has been no prior report of a Ph₃B(η⁵-C₅H₄) ligand, there are no unexpected features either in the geometry of the ligand itself or in its π-bonding interaction with the iron atom labeled Fe₂. Of the two terminal carbonyl groups, the one at the Ph₃B(η⁵-C₅H₄) end of the anion is somewhat shorter (1.167 (8) vs. 1.184 (9) Å); the average bridging carbonyl distance is 1.19 (1) Å. In **5**, the average value for terminal carbonyls is 1.154 (7) Å while the bridging CO's average 1.181 (6) Å.²³

The Fe-Fe distance (2.540 (2) Å) in **2** is nearly identical with that in **5** (2.531 (2) Å). A doubly negative analogue of **5** also has been reported,²⁴ [(3)-1,2-B₂C₂H₁₁Fe(CO)₂]₂²⁻, **6**, wherein the cyclopentadienyl ligands are replaced by 1,2-dicarbonyl groups; the metal-metal distance in this compound is 2.591 (5) Å.²⁵ The fact that the Fe-Fe bond length in the singly charged anion much more closely approximates that in the neutral dimer suggests that the charge is localized in the Ph₃B unit rather than near the metal atoms. The spectroscopic data (vide infra) are consistent with this interpretation.

Two examples of tetraphenylboron ligands have been reported; in Rh[P(OMe)₃]₂Ph₄B²⁶ and Ru(C₅H₅)Ph₄B,²⁷ the overall average B-C distance is 1.648 (4) Å and the average C-C bond length is 1.388 (2) Å for all phenyl rings not directly involved in π bonding to the metal atoms. In **2**, the equivalent averages are 1.650 (6) and 1.412 (2) Å, respectively. In all three cases, the average angular deviations from tetrahedral geometry about the boron atoms are modest. However, in **2** the boron atom does subtend an 8.2° angle from the cyclopentadienyl plane, as measured at the bridgehead carbon atom, and lies in a direction away from the metal atom. While this might be due to steric effects, it is the single largest deviation and could reflect a feature of the bonding.

A perspective view of the cation structure is presented in Figure 2, wherein the two-state parameterization of the α carbons is indicated. The disorder was parameterized from Fourier syntheses with occupancies of 2/3 for unprimed α-

Table II. Thermal Parameters for 2^a

	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃	B, Å ²
Fe ₁	7.5 (1)	122 (2)	19.3 (4)	0.1 (4)	2.7 (2)	-2.3 (8)	3.96
Fe ₂	7.2 (1)	107 (2)	17.4 (4)	-1.7 (4)	3.2 (2)	-0.2 (7)	3.57
C ₁	7.4 (9)	169 (17)	26 (3)	4 (3)	4 (1)	-10 (6)	4.76
O ₁	14.6 (10)	333 (20)	28 (3)	-5 (4)	11 (1)	-8 (6)	7.11
C ₂	6.3 (8)	150 (15)	18 (3)	-5 (3)	5 (1)	-8 (5)	3.70
O ₂	11.2 (8)	291 (18)	27 (2)	-14 (3)	8 (1)	-15 (5)	6.18
C ₃	8.5 (10)	117 (14)	31 (4)	-1 (3)	2 (2)	-3 (6)	4.81
O ₃	13.3 (9)	109 (10)	47 (3)	10 (2)	-2 (1)	-18 (5)	6.06
C ₄	9.5 (10)	101 (13)	21 (3)	0 (3)	5 (1)	3 (5)	4.00
O ₄	13.3 (9)	102 (10)	32 (3)	3 (2)	0 (1)	5 (4)	5.41
B	6.6 (9)	90 (13)	17 (3)	-1 (3)	3 (1)	0 (5)	3.27
C ₁ (1)	8.6 (10)	168 (18)	30 (4)	0 (3)	4 (2)	14 (7)	5.28
C ₂ (1)	8.7 (11)	188 (20)	40 (4)	2 (4)	5 (2)	1 (8)	6.08
C ₃ (1)	5.8 (9)	266 (25)	33 (4)	-9 (4)	0 (1)	3 (8)	5.64
C ₄ (1)	8.0 (10)	161 (18)	46 (5)	-4 (3)	6 (2)	-11 (8)	5.81
C ₅ (1)	5.6 (8)	182 (18)	35 (4)	-3 (3)	3 (1)	-6 (7)	5.01
C ₁ (2)	7.4 (8)	105 (12)	16 (3)	1 (3)	3 (1)	-3 (5)	3.45
C ₂ (2)	11.2 (10)	88 (12)	17 (3)	-7 (3)	2 (1)	12 (5)	3.72
C ₃ (2)	9.0 (10)	220 (21)	19 (3)	-18 (4)	2 (1)	12 (6)	4.75
C ₄ (2)	10.7 (11)	177 (18)	18 (3)	-7 (4)	6 (1)	4 (6)	4.68
C ₅ (2)	8.7 (10)	171 (17)	14 (3)	-1 (3)	4 (1)	-4 (5)	4.11
C ₁ (3)	9.6 (10)	75 (11)	25 (3)	1 (3)	6 (1)	-1 (5)	3.78
C ₂ (3)	11.1 (11)	96 (13)	36 (4)	-5 (3)	10 (2)	-11 (6)	4.65
C ₃ (3)	15.7 (15)	100 (15)	45 (5)	-5 (4)	14 (2)	-4 (7)	5.71
C ₄ (3)	18.7 (17)	92 (14)	54 (5)	-3 (4)	20 (3)	-7 (7)	5.90
C ₅ (3)	15.3 (15)	110 (15)	41 (4)	10 (4)	10 (2)	17 (7)	5.83
C ₆ (3)	11.1 (11)	95 (13)	34 (4)	3 (3)	6 (2)	12 (6)	4.84
C ₁ (4)	5.8 (7)	91 (11)	16 (3)	0 (2)	2 (1)	-4 (4)	3.09
C ₂ (4)	7.6 (9)	89 (12)	24 (3)	1 (3)	1 (1)	-1 (5)	3.92
C ₃ (4)	7.9 (9)	104 (13)	29 (3)	-1 (3)	2 (1)	-9 (5)	4.40
C ₄ (4)	7.1 (9)	138 (15)	29 (3)	-6 (3)	3 (1)	-14 (6)	4.59
C ₅ (4)	8.0 (9)	114 (14)	26 (3)	-6 (3)	3 (1)	-8 (5)	4.31
C ₆ (4)	6.3 (8)	117 (13)	23 (3)	-3 (3)	5 (1)	-8 (5)	3.73
C ₁ (5)	8.8 (9)	80 (11)	18 (3)	-4 (3)	2 (1)	-5 (5)	3.56
C ₂ (5)	11.8 (11)	135 (15)	20 (3)	-1 (3)	8 (2)	-11 (5)	4.38
C ₃ (5)	15.8 (15)	127 (16)	28 (4)	-5 (4)	8 (2)	-4 (6)	5.56
C ₄ (5)	15.8 (15)	139 (16)	23 (3)	-10 (4)	5 (2)	-8 (6)	5.48
C ₅ (5)	12.2 (12)	173 (18)	21 (3)	-6 (4)	2 (2)	-4 (6)	5.39
C ₆ (5)	10.4 (11)	128 (15)	23 (3)	-5 (3)	2 (2)	0 (6)	4.81
N	8.4 (8)	110 (11)	26 (3)	2 (2)	5 (1)	-6 (4)	4.24
C ₅ ¹	12 (1)	176 (22)	20 (4)	1 (4)	5 (2)	-8 (7)	5.12
C ₅ ²	10 (3)	124 (41)	91 (18)	22 (9)	-4 (6)	-32 (22)	6.17
C _{5a}	16 (2)	168 (20)	31 (4)	8 (5)	-3 (2)	8 (7)	6.66
C ₆ ¹	9 (1)	174 (22)	45 (6)	-7 (4)	11 (2)	3 (9)	5.54
C ₆ ²	16 (4)	115 (35)	35 (10)	-10 (9)	8 (5)	-32 (15)	5.32
C _{6a}	12 (1)	246 (27)	61 (6)	-20 (5)	7 (2)	15 (11)	7.87
C ₇	10 (1)	157 (20)	36 (5)	13 (4)	3 (2)	9 (8)	5.74
C ₇ ¹	10 (3)	293 (56)	13 (7)	17 (10)	2 (4)	12 (16)	4.83
C _{7a}	15 (2)	253 (26)	33 (4)	18 (5)	4 (2)	31 (9)	7.21
C ₈ ¹	8 (1)	114 (17)	46 (5)	-7 (3)	6 (2)	-33 (8)	4.82
C ₈ ²	12 (3)	170 (45)	65 (15)	-16 (10)	18 (6)	-13 (20)	6.17
C _{8a}	10 (1)	266 (31)	113 (11)	-16 (5)	16 (3)	4 (15)	9.01
C ₉	65 (6)	375 (48)	150 (16)	60 (15)	74 (9)	61 (21)	17.12
C ₁₀	79 (7)	209 (25)	129 (19)	-21 (3)	67 (9)	-7 (16)	16.18
O ₅	60 (5)	181 (24)	78 (9)	0	25 (5)	0	13.92

^a The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23})]$. The isotropic equivalent of the anisotropic thermal parameters was obtained from $B = 4.0[V^2 \det(\beta_{ij})]^{1/3}$ and are in the form $\exp[-B(\sin^2 \theta)/\lambda^2]$. Estimated standard deviations in parentheses correspond to the last significant digit.

carbon atoms and $1/3$ for the primed ones. The results display relatively large deviations from accepted bond lengths and angles, especially in the $1/3$ occupancy model; this probably indicates a more complex disorder problem than can be modeled with the data.

The solvent of crystallization consists of a molecule of THF situated upon a twofold axis in the unit cell. The thermal coefficients for these atoms are unusually high, especially for the components out of the plane of the ring. It would appear that the molecules are quite loosely held in columns running through the lattice, although there is no evidence of solvent loss from the crystals on standing.

Figure 3 details the packing of the ions in the unit cell as viewed down the b axis. The structure can be viewed as alternating irregular layers, the first containing the iron dimer

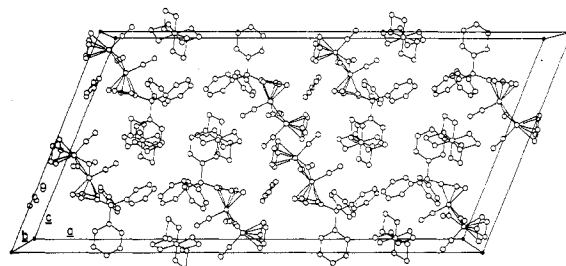


Figure 3. Packing of ions in the unit cell.

units and the second, the triphenylboron moieties and the cations. The closest intermolecular contacts are those between terminal carbonyls and ethyl carbons (3.32, 3.36 Å) and

Table III. Selected Anion Distances and Angles^a

Distances (Å)			
Fe ₁ -Fe ₂	2.540	C ₁ -O ₁	1.184 (9)
Fe ₁ -C ₁	1.703 (9)	C ₂ -O ₂	1.167 (8)
Fe ₁ -C ₃	1.899 (9)	C ₃ -O ₃	1.199 (10)
Fe ₁ -C ₄	1.922 (8)	C ₄ -O ₄	1.182 (9)
Fe ₂ -C ₂	1.698 (7)		
Fe ₂ -C ₃	1.898 (9)		
Fe ₂ -C ₄	1.890 (8)		
Angles (deg)			
C ₁ -Fe ₁ -C ₃	89.6 (4)	O ₁ -C ₁ -Fe ₁	179.1 (8)
C ₁ -Fe ₁ -C ₄	91.6 (4)	O ₂ -C ₂ -Fe ₂	177.4 (9)
C ₁ -Fe ₁ -Fe ₂	99.8 (3)	O ₃ -C ₃ -Fe ₁	138.1 (7)
C ₁ -Fe ₁ -CG (ring 1)	125.8 (4)	O ₃ -C ₃ -Fe ₂	138.0 (7)
Fe ₂ -Fe ₁ -CG (ring 1)	134.4 (4)	O ₄ -C ₄ -Fe ₁	136.3 (6)
C ₃ -Fe ₁ -C ₄	94.4 (3)	O ₄ -C ₄ -Fe ₂	140.0 (6)
C ₃ -Fe ₁ -Fe ₂	48.0 (2)	Fe ₁ -C ₃ -Fe ₂	84.0 (4)
C ₄ -Fe ₁ -Fe ₂	47.7 (2)	Fe ₁ -C ₄ -Fe ₂	83.6 (3)
C ₂ -Fe ₂ -C ₃	88.6 (4)	C ₁ (2)-B-C ₁ (3)	114.2 (6)
C ₂ -Fe ₂ -C ₄	91.3 (4)	C ₁ (2)-B-C ₁ (4)	111.2 (6)
C ₂ -Fe ₂ -Fe ₁	99.1 (2)	C ₁ (2)-B-C ₁ (5)	103.9 (6)
C ₂ -Fe ₂ -CG (ring 2)	125.5 (4)	C ₁ (3)-B-C ₁ (4)	110.4 (6)
Fe ₁ -Fe ₂ -CG (ring 2)	135.2 (4)	C ₁ (3)-B-C ₁ (5)	106.0 (6)
C ₃ -Fe ₂ -C ₄	95.5 (4)	C ₁ (4)-B-C ₁ (5)	110.8 (6)
C ₃ -Fe ₂ -Fe ₁	48.0 (3)		
C ₄ -Fe ₂ -Fe ₁	48.8 (2)		

^a CG refers to the center of gravity of the cyclopentadienyl ring. Estimated standard deviations in parentheses correspond to the last significant digit.

Table IV. Infrared Spectra of **2** and Other Compounds^a

	$\nu(\text{CO})$ terminal	$\nu(\text{CO})$ bridging
<i>cis</i> -[FeCp(CO) ₂] ₂ ²³	1970 vs.	1800 m,
	1933 vs	1765 vs
[Ph ₃ BC ₅ H ₄ Fe ₂ Cp(CO) ₂ NEt ₄ ⁺]	1989 vs. b,	1795 m-w,
	1936 s	1755 vs. b
[(3)-1,2-B ₉ C ₂ H ₁₁ Fe(CO) ₂ NEt ₄ ⁺] ₂ ^{24,25}	1959 s,	1738 s
	1919 m	

^a Nujol mulls

between bridging carbonyls and cyclopentadienyl rings (3.24, 3.26 Å).

Spectroscopic Properties of 2. The infrared spectrum of **2** in the solid state is remarkably similar to that of **5** and the dicarbollide analogue,²⁴ **6** (Table IV), and is consistent with C_{2v} local carbonyl symmetry giving rise to four IR-active vibrational modes (2a₁ + b₁ + b₂). Following previous analyses of the spectrum of **5**,^{23,28} the bands of **2** at 1989 and 1936 cm⁻¹ are assigned to the symmetric and asymmetric stretches of the terminal CO groups, and the bands at 1795 and 1755 cm⁻¹ are assigned to the symmetric and asymmetric stretches of the bridging CO groups, respectively. The low intensity of the 1795-cm⁻¹ band further supports this assignment.²⁸ Corresponding carbonyl frequencies of **2** and **5** are similar and are higher than those of **6**.²⁴ Since the average carbonyl frequency is usually considered to be a sensitive probe of the charge state of a metal carbonyl,²⁹ it is apparent that the negative charge in **2** does not reside at the metal centers. This is consistent with the observation of similar iron-iron bond lengths for **2** and **5**, as discussed above. The most likely site is the triphenylcyclopentadienylborate group. Infrared spectra of **2** in solution exhibited solvent-dependent variations in relative intensities of $\nu(\text{CO})$ analogous to those observed for [FeCp(CO)₂]₂²⁸ and indicative of cis-trans isomerization in solution. From the ratio of the peak heights of the terminal carbonyl bands (using an average Fe-Fe-CO angle of 97.5°) the cis:trans isomer distribution of **2** was estimated as 78:22 in dimethyl sulfoxide and 65:35 in methylene chloride.³⁰

Analysis of the ¹H NMR spectrum of **2** in dimethyl-d₆ sulfoxide follows directly from its crystal structure. Thus, two

multiplets at δ 7.19 (6 H) and 6.91 (9 H) are assigned to phenyl protons. A sharp singlet at δ 4.81 (5 H) is due to the η^5 -C₅H₅ ligand. Protons of the BC₅H₄ unit give two triplets δ 4.64 (2 H) and δ 4.22 (2 H) in an A₂X₂ pattern ($J_{\text{AX}} = 4$ Hz); the former triplet is assigned to the protons on carbons C₂(2) and C₅(2) shown in Figure 1. The tetraethylammonium protons gave rise to a quadruplet at δ 3.21 (8 H) and a triplet of triplets at δ 1.17 (N-CH₃) (12 H). Weak multiplet resonances centered around δ 3.63 (2 H) and 1.78 (2 H) are due to THF of crystallization.

Isolation and Characterization of 3. Evaporation and extraction of the solution from which **2** deposited gave a light tan, crystalline solid identified as **3** by analysis and comparison of its melting point and infrared spectrum with those of an authentic sample. The latter was synthesized by potassium hydride reduction of Ph₃B⁸ in THF followed by metathesis with Et₄N⁺Br⁻. The IR spectrum of **3** contained absorptions at 1580 and 1482 cm⁻¹ typical of four-coordinate triphenylborate²² and a rather complex pattern in the B-H stretching region, viz., 2198, 2136, and 2005 cm⁻¹. A single B-H mode was expected on the basis of the presumed structure and its similarity to salts of hydridotrialkylborates³¹ and of hydridotris(1-pyrazolyl)borate.³² In THF or methylene chloride solution, **3** exhibited two broad bands (2193 and 2130 cm⁻¹) as did the intermediate Ph₃BH⁺K⁺ in THF. The Raman spectrum of solid **3** contained only one strong band in this region (2197 cm⁻¹) and this is assigned to the ¹¹B-H stretching vibration,³³ a shoulder at 2206 cm⁻¹ is assigned to the ¹⁰B-H vibration. The band at 2136 cm⁻¹ in the infrared spectrum may be a resonance-enhanced combination band.

¹H NMR and ¹¹B NMR spectroscopy support a monomeric formulation of Ph₃BH⁺NEt₄⁺ in solution. Its ¹H NMR spectrum in THF-d₈ showed two multiplets centered around δ 7.35 (broad, 6 H) and δ 6.90 (9 H) due to the phenyl protons, and the quadruplet (δ 2.46, 8 H) and triplet of triplets resonances (δ 1.77, 12 H) associated with the tetraethylammonium protons ($J_{\text{CH}_3\text{CH}_2} = 7$ Hz; $J_{\text{N-CN}_3} = 2$ Hz). The BH hydrogen gave rise to a "quadruplet", observed as a series of broad, weak signals at δ 5.42, 4.10, 2.78, and 1.46 ($J_{\text{11B-H}} = 79$ Hz) integrating as approximately one proton. The ¹¹B NMR spectrum³⁴ in THF exhibited a doublet ($J_{\text{11B-H}} = 79 \pm 1$ Hz) at +7.7 ppm indicative of a terminal B-H.

The infrared spectrum of the dark red toluene extract from which **3** was separated showed $\nu(\text{CO})$ coincident with those of [FeCp(CO)₂]₂. Attempts to isolate the dimer yielded only oils but its characteristic $\nu(\text{CO})$ in various solvents²⁸ leaves little doubt about its identity. From absorbance data, the yield of [FeCp(CO)₂]₂ was estimated to be ~20% based on **1**.

Spectroscopic Study of Ph₃BFeCp(CO)₂M⁺ (M = Na and NBU₄) in THF. The high solubility of the sodium and tetrabutylammonium salts allowed monitoring of the migration reaction of Ph₃BFeCp(CO)₂⁻ by ¹H NMR and IR spectroscopy. Both salts gave essentially identical behavior, so only the behavior of the NBU₄⁺ salt will be described here. At ambient temperature under an argon atmosphere the η^5 -Cp proton resonance of Ph₃BFeCp(CO)₂⁻ was gradually replaced by a strong singlet at δ 4.80 and a weak multiplet signal at δ 4.89 due to the η^5 -C₅H₅ and η^5 -C₅H₄ groups of Ph₃BC₅H₄Fe₂Cp(CO)₄⁻, respectively.³⁵ The phenyl multiplet resonances were centered at δ 7.47 and 7.04. A weak singlet at δ 4.99 was assigned to [FeCp(CO)₂]₂. A diluted sample set aside for IR analysis showed $\nu(\text{CO})$ at 1992 (s), 1939 (m), 1785 (sh), and 1768 (s) cm⁻¹ assigned to Ph₃BC₅H₄Fe₂Cp(CO)₄⁻NBU₄⁺ in addition to bands at 1978 (m) and 1755 (m) cm⁻¹ due to an unidentified intermediate.

Heating both samples at 50 °C for 45 h resulted in the appearance of a new strong IR band at 1783 cm⁻¹ associated with the formation of [FeCp(CO)₂]₂ and the simultaneous

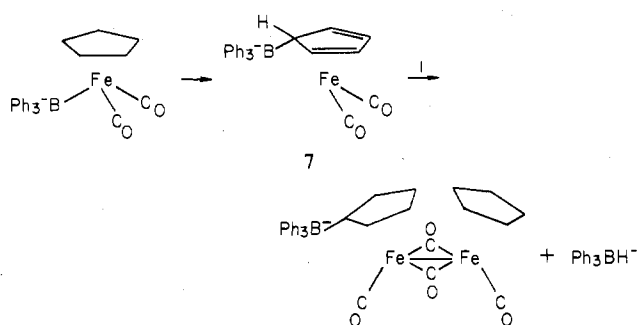
decrease and disappearance of the 1768-cm⁻¹ band. Approximately coinciding with these changes in the IR spectrum, ¹H NMR spectroscopy showed a decrease in the intensity and finally disappearance of the singlet assigned to the Cp group of Ph₃BC₅H₄Fe₂Cp(CO)₄⁻ with the emergence of a strong singlet at δ 4.99 (due to [FeCp(CO)₂]₂) and multiplets at δ 7.23 (3 H) and 7.72 (2 H) due to an unidentified triphenylborate derivative.³⁶ These observations strongly suggest that under the reaction conditions, decomposition of Ph₃BC₅H₄Fe₂Cp(CO)₄⁻ gives [FeCp(CO)₂]₂. The isolation of **2** was made possible by its insolubility in THF under conditions where **1** and **3** were completely soluble.

Possible Mechanism for Migration. Although there appear to be no other reports of metal-to-ring migrations that involve a boron ligand, analogous transformations involving aryl and alkyl groups have been observed and a variety of mechanisms have been proposed. Fachinetti and Floriani⁴ suggested that the conversion of (η⁵-C₅H₅)₂VPh into (η⁵-C₅H₅)(η⁵-C₅H₄Ph)V(CO) was induced by the incoming CO and involved a direct nucleophilic attack of the "phenyl residue" on the Cp ligand. On the other hand, the migration of phenyl from Nb to a C₈H₈ ring of (C₈H₈)₂NbPh, in the presence of a ligand base such as dmpe, was judged³ to proceed via electrophilic attack on the ring, unassisted by coordination of the base; the endo configuration of the phenyl group on the bicyclic C₈H₉ ligand is consistent with such an intramolecular phenyl transfer.

In a case of alkyl migration, McCleverty and Wilkinson¹ postulated homolysis of the C-Mo bond in (η⁵-C₅H₅)Mo(CO)₃C₂H₅ with subsequent attack of the Cp ring by the resulting ethyl radical. The presence of a ligand base appears to be necessary for ethyl migration in the complex (η⁵-C₅H₅)₂MoClEt; with phosphines, the η⁴-1-endo-ethylcyclopentadienyl derivatives (η⁵-C₅H₅)(1-endo-C₅H₄Et)Mo(PR₃)Cl (R₃ = Et₃, MePh₂, and Me₂Ph) were isolated and characterized by IR and NMR spectroscopy.³⁷ Although no particular mode of attack on the Cp ring was postulated, the resulting complex was considered to be a possible intermediate in the conversion by CO of (η⁵-C₅H₅)₂MoClEt to (η⁵-C₅H₅)Mo(CO)₃Cl and EtC₅H₅.³⁷

Stone et al.⁵ showed that migration of MMe₃ ligands from ruthenium to unsaturated hydrocarbons was a general feature of the chemistry of Ru(MMe₃)₂(CO)₄ complexes with M = Si or Ge. A series of rearrangements was postulated⁵ to account for the exo configuration of the migrated Me₃Si group in Ru(SiMe₃)(CO)₂[η⁵-C₇H₇(6-SiMe₃)(7-C₆F₅)] since an endo configuration would be expected from an intramolecular process. It was also noted⁵ that migration of Me₃M could be regarded as an "insertion" of the olefin into Ru-MMe₃ for purposes of comparison with other systems, but no detailed mechanism for such a process was developed.

In the present case, the spectroscopic studies of **1** (especially the ¹¹B NMR data) indicate that, prior to migration, the negative charge of the anion resides largely on the Ph₃B group. The absence of significant negative charge on the iron atom is consistent with the observation that the average ν(CO) of 1955 cm⁻¹ for **1** is at the low end of the range found³⁸ for neutral CpFe(CO)₂X derivatives. Thus, we would expect the Fe(CO)₂ moiety to mildly activate the η⁵-C₅H₅ ring toward nucleophilic attack.³⁹ We suggest that the negatively charged Ph₃B unit acts as a strong nucleophile and that its effectiveness for attack on the η⁵-C₅H₅ ring is enhanced by its proximity to the ring and the intramolecular nature of the reaction. The resulting coordinatively unsaturated anion, **7** (possibly stabilized by the solvent THF), would possess the required endo configuration. Moreover, if the negative charge in **7** were localized on the boron atom, hydride loss from the adjacent carbon atom would provide a reasonable pathway for the



production of Ph₃BH⁻. A plausible, nonconcerted mechanism for this process would include attack by **1** at the coordinatively unsaturated iron atom of **7** giving [η⁴-endo-Ph₃BC₅H₅](CO)₂Fe₂Cp(CO)₂²⁻, **8**, followed by hydride transfer to displaced Ph₃B. Alternatively, hydride transfer from **7** to **1** could occur first, displacing FeCp(CO)₂⁻ which would combine with Ph₃BC₅H₄Fe(CO)₂ to produce **2**. Loss of Ph₃B²⁻ from **8** would provide one route to the observed byproduct [FeCp(CO)₂]₂.

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Registry No. **1**, 69469-64-3; *cis*-**2**, 69469-67-6; *trans*-**2**, 69500-49-8; **3**, 69469-69-8; Ph₃BC₅H₄Fe₂Cp(CO)₄⁻NBu₄⁺, 69515-58-8; Ph₃BFeCp(CO)₂⁻Na⁺, 69469-70-1; Ph₃BFeCp(CO)₂⁻NBu₄⁺, 69469-71-2; Ph₃BOCH₃⁻NEt₄⁺, 69469-73-4; Ph₄B⁻NEt₄⁺, 12099-10-4; FeCp(CO)₂⁻NEt₄⁺, 57812-16-5; FeCp(CO)₂⁻Na⁺, 12152-20-4; Ph₃B, 960-71-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, cyclopentadienyl and phenyl ring bond distances and angles, deviations of atoms from planes in the anion, and bond distances and angles in the cation (27 pages). Ordering information is given on any current masthead page.

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- (34) The ^{11}B NMR spectrum was kindly recorded by Professor S. Shore at The Ohio State University employing side band techniques and a BCl_3 standard (–46.8 ppm).
- (35) The high-field spectrum beyond ca. δ 4.25 was obscured by solvent signals.
- (36) The IR spectrum of the NMR sample (1992 (s), 1951 (m), 1783 (s) cm^{-1}) was identical with that of the final IR sample and with that of a THF solution of $[\text{FeCp}(\text{CO})_2]_2$ ($\nu(\text{CO})$ 1993 (s), 1952 (m), 1783 (s) cm^{-1}). The singlet Cp resonance of $[\text{FeCp}(\text{CO})_2]_2$ in THF was at δ 4.97.
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Molecular Structure of $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$, a Heterobimetallic Complex with a Semibridging Carbonyl

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The structure of the product of the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ with $\text{Co}_2(\text{CO})_8$, $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$, has been determined by X-ray diffraction techniques. Crystals are orthorhombic, with cell parameters $a = 13.821$ (6) Å, $b = 13.352$ (5) Å, $c = 16.142$ (6) Å, space group $Pbca$, and $Z = 8$. The structure was refined to $R = 0.048$ and $R_w = 0.057$ for 3924 unique observed reflections. The molecule contains a semibridged carbonyl group between the Nb and Co atoms with parameters Nb–Co = 2.992 (1) Å, Nb–C_B = 2.531 (4) Å, C_B–Co = 1.792 (4) Å, and Nb–C_B–Co = 85.8 (1)°. Spectral studies indicate an isomeric mixture in solution.

Introduction

As part of our study on the use of early transition metal hydrides in catalytic CO reduction,¹ we have examined the reaction of Cp_2NbH_3 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with $\text{Co}_2(\text{CO})_8$. The product of this reaction turned out to have several interesting structural features, and the results of a single-crystal X-ray structural determination are reported here.

Experimental Section

Synthesis and Characterization. All reactions and manipulations were carried out under inert atmosphere with standard techniques² or otherwise as noted. Infrared spectra were recorded on Perkin-Elmer Infracord and 457 instruments and ^1H NMR on Varian A-60 and XL-100 instruments. Cp_2NbCl_2 was prepared as described elsewhere;³ commercially available $\text{Co}_2(\text{CO})_8$ was used without further purification; solvents were distilled from benzophenone ketyl under argon prior to use.

A benzene solution of Cp_2NbH_3 was prepared by reaction of Cp_2NbCl_2 with LiAlH_4 followed by hydrolysis, as previously described,⁴ and standardized by quantitative NMR measurement. On addition of a slight excess of $\text{Co}_2(\text{CO})_8$ the solution turned dark immediately (room temperature), accompanied by evolution of gas (ca. 1 mol/mol of Cp_2NbH_3). Removal of solvent, followed by extraction with toluene and recrystallization from cold hexane, gave air-sensitive, dark brown to black prisms, in about 70% yield. The ^1H NMR spectrum (C_6D_6) showed three peaks in the Cp region (τ 5.17, 5.34, and 5.47, relative intensities ca. 1:1:2). This pattern was not significantly changed following repeated recrystallization of the sample. No peak in the normal metal hydride region was observed, and no change in the spectrum occurred on adding CDCl_3 , indicating no metal hydride was present. The IR spectrum proved highly medium-dependent; peaks observed in the CO-stretching region are listed in Table I.

Table I. CO-Stretching Absorptions of $\text{Cp}_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$

solvent	ν_{max} , cm^{-1} (intensity)
hexane ^a	2060 vs, 2040 m, sh, 1875 s
THF ^a	2060 vs, 2020 vs, 1940 s, 1880 s
benzene ^a	2080 s, 2040 vs, 1970 s, 1948 m, 1855 m, br
toluene ^a	2060 s, 2020 s, 1960 m, sh, 1940 s, 1850 m
Nujol ^b	2060 vs, 2020 vs, 1980 m, 1870 vs

^a CaF_2 cells. ^b Mull, NaCl plates.

X-ray Crystallographic Data. Suitable crystals were obtained by slow cooling of a solution in hexane. A crystal of dimensions 0.42 × 0.56 × 0.47 mm was selected and mounted in a thin-walled glass capillary. The crystal was found to be orthorhombic, with cell dimensions $a = 13.821$ (6) Å, $b = 13.352$ (5) Å, $c = 16.142$ (6) Å, and $V = 2961$ Å³. The space group was determined as $Pbca$, with $Z = 8$ and a calculated density of 1.89 g/cm^3 .

Diffraction data were collected at 292 K on a Syntex PI diffractometer, by using graphite-monochromated Mo $K\alpha$ radiation. One octant of data was collected by the θ - 2θ scan technique, with scan speeds varying from 2 to 12°/min, to the limit $2\theta < 59^\circ$. The intensities of four standard reflections, monitored at regular intervals, showed no significant fluctuation during the collection procedure. The raw intensity data were corrected for Lorentz, polarization, and absorption ($\mu = 19.34 \text{ cm}^{-1}$) effects. After averaging of equivalent reflections, a total of 3924 independent reflections were used for solution and refinement.

Solution and Refinement of the Structure. The positions of the cobalt and niobium atoms were determined from three-dimensional Patterson functions calculated from intensity data, and the oxygen and carbon atoms were located from a series of difference Fourier maps. Full-matrix least-squares refinement was based on minimization of