

# Tricarbonyl(phosphine)ferrates(2-), $\text{Fe}(\text{CO})_3(\text{PR}_3)^{2-}$ , and Their Derivatives<sup>1</sup>

John E. Ellis\* and Yu-Sen Chen

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received August 18, 1988

A two-step synthesis of  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PR}_3)]$  ( $\text{PR}_3 = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{and } \text{PMe}_3$ ) from the corresponding  $\text{Fe}(\text{CO})_4(\text{PR}_3)$  has been developed. Treatment of  $\text{Fe}(\text{CO})_4(\text{PR}_3)$  with a methanolic solution of  $[\text{Et}_4\text{N}]\text{OH}$  provided the corresponding monohydrides  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$ . Deprotonation of monohydrides by  $\text{K}[\text{sec-Bu}_3\text{BH}]$  in refluxing tetrahydrofuran gave 50–70% isolated yields (based on  $\text{Fe}(\text{CO})_4(\text{PR}_3)$ ) of the thermally stable but exceedingly air-sensitive salts  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PR}_3)]$ , which were characterized by elemental analysis, infrared spectra, and reactivity patterns. These are the first isolated salts containing (phosphine)carbonylmetalate dianions and are extremely reactive. They quickly deprotonated acetonitrile to give essentially quantitative yields of  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$  and reacted with triphenylstannyl chloride to provide  $\text{Ph}_3\text{SnFe}(\text{CO})_3(\text{PR}_3)^-$ . Ligand exchange reactions of  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PPh}_3)]$  with CO and  $\text{P}(\text{OMe})_3$  readily occurred at room temperature and gave 80–90% isolated yields of  $\text{K}_2[\text{Fe}(\text{CO})_4]$  and  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{P}(\text{OMe})_3)]$ . The latter salt contains the first isolated (phosphite)carbonylmetalate dianion and was characterized by elemental analyses and infrared spectra as a triphenyltin derivative,  $(\text{Ph}_3\text{Sn})\text{Fe}(\text{CO})_3(\text{P}(\text{OMe})_3)^-$ . Treatment of  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PPh}_3)]$  with hot ethanol provided low yields (ca. 10%) of the bridging phosphide salt  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]$ . Full details on the molecular structure of this anion, which has been mentioned previously in the scientific literature (Kyba, E. P.; Davis, R. E.; Clubb, C. N.; Liu, S. T.; Palacios, H. A. O.; McKennis, J. S., *Organometallics* 1986, 5, 869), are reported for the first time. Crystal data: triclinic, space group  $P\bar{1}$  (No. 2);  $a = 11.140$  (1) Å,  $b = 13.982$  (4) Å,  $c = 10.161$  (3) Å;  $\alpha = 105.30$  (2)°,  $\beta = 103.33$  (2)°,  $\gamma = 77.21$  (2)°,  $V = 1464$  (1) Å<sup>3</sup>;  $Z = 2$ ;  $R = 0.034$ ;  $R_w = 0.039$ .

## Introduction

Countless mononuclear substituted metal carbonyls of the general formula  $\text{M}(\text{CO})_x\text{L}_y$  have been prepared over the years, where  $z = 1+, 0,$  and  $1-$  and  $\text{L} = \text{NR}_3, \text{PR}_3, \text{AsR}_3, \text{RNC}, \text{NO}, \text{C}_5\text{H}_5,$  allyl, olefin, arene, H, and alkyl.<sup>2</sup> However, when this work was initiated in 1980, only three examples of dianions of this sort containing a transition metal in a formally negative oxidation state had been reported, viz.,  $(\eta^2\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3^{2-},$ <sup>3</sup>  $\text{V}(\text{CO})_5(\text{CN})^{2-},$ <sup>4</sup> and  $(\eta^4\text{-C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3^{2-}.$ <sup>5</sup> Our general interest in the synthesis and chemistry of substituted metal carbonyl anions and highly reduced metal carbonyls led us to investigate whether it might be possible to prepare dianionic iron species of the type  $\text{Fe}(\text{CO})_3(\text{PR}_3)^{2-}.$  We felt that the synthetic methodologies developed in this research could be applicable to numerous other systems. Also, it was thought that such materials would be of considerable interest in view of their very electron-rich nature and possible use as intermediates in chemical synthesis. While this work was in progress, N. J. Cooper and co-workers reported on a distinctly different route to a related tungsten compound,  $\text{W}(\text{CO})_4\text{P}(\text{iPr})_3^{2-},$  the first such phosphine dianion of a group 6 metal.<sup>6</sup> A portion of the research presented herein has been the subject of a preliminary communication.<sup>7</sup> Since 1982, several other mononuclear substituted

carbonyl dianions containing metals in formally negative oxidation states have been reported from our laboratory and that of Cooper. Some of the most interesting of these are the following:  $\text{Mn}(\text{CO})_3\text{NO}^{2-},$ <sup>8</sup>  $\text{XM}(\text{CO})_5^{2-}$  ( $\text{M} = \text{V}, \text{Nb}, \text{Ta}; \text{X} = \text{SnPh}_3,$ <sup>9</sup> and  $\text{H}^{10}$ ),  $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3^{2-}$  ( $\text{M} = \text{Nb}, \text{Ta},$ <sup>11</sup>  $\text{Cr}(\text{C}_4\text{Ph}_4)(\text{C}_2\text{Ph}_2)(\text{CO})_2^{2-},$ <sup>12</sup>  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2^{2-},$ <sup>13</sup>  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2^{2-},$ <sup>14</sup> and  $\text{XM}(\text{CO})_4^{2-}$  ( $\text{M} = \text{Mn}, \text{Re}; \text{X} = \text{SnPh}_3, \text{H}, \text{Me}).$ <sup>15</sup> Lindner and co-workers have also described  $\text{Mn}(\text{CO})_4(\text{PPh}_2)^{2-},$ <sup>16</sup> a formal derivative of  $\text{Mn}(\text{CO})_4^{3-}.$ <sup>17</sup>

In this paper is presented the first full account of the syntheses and isolation of salts containing dianions of the general formula  $\text{Fe}(\text{CO})_3(\text{PR}_3)^{2-}$  and  $\text{Fe}(\text{CO})_3(\text{P}(\text{OR})_3)^{2-}.$  Significantly, these remain the only isolated compounds of this type for any metal.

## Experimental Section

**General Procedure and Starting Materials.** A summary of the general procedures used in this study have been described previously.<sup>1,8</sup> The following reactants were obtained from commercial sources and used without further purification: triphenylphosphine, dimethylphenylphosphine, trimethylphosphine, iron pentacarbonyl, glacial acetic acid, K-Selectride (Aldrich) ( $\text{K}[\text{sec-Bu}_3\text{BH}]$ , 0.50 and 1.0 M THF solutions), L-Selectride (Aldrich) ( $\text{Li}[\text{sec-Bu}_3\text{BH}]$ , 1.0 M THF solution), Superhydride

(8) Chen, Y. S.; Ellis, J. E. *J. Am. Chem. Soc.* 1983, 105, 1689.

(9) Warnock, G. F. P.; Sprague, J.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* 1983, 105, 672.

(10) Warnock, G. F. P.; Ellis, J. E. *J. Am. Chem. Soc.* 1984, 106, 5016.

(11) Pfahl, K. M.; Ellis, J. E. *Organometallics* 1984, 3, 230, 948.

(12) Wink, D. J.; Fox, J. R.; Cooper, N. J. *J. Am. Chem. Soc.* 1985, 107, 5012. (The formal oxidation state assignment of chromium in this complex is uncertain since the coordinated cyclobutadiene could be considered to be dianionic or neutral.)

(13) Leong, V. S.; Cooper, N. J. *Organometallics* 1987, 6, 2000.

(14) Leong, V. S.; Cooper, N. J. *Organometallics*, in press.

(15) Warnock, G. F. P.; Cammarano, L.; Ellis, J. E., submitted for publication.

(16) Lindner, E.; Starz, K. A.; Eberle, H. J.; Hiller, W. *Chem. Ber.* 1983, 116, 1209.

(17) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* 1977, 99, 1801.

(18) Lin, J. T.; Ellis, J. E. *J. Am. Chem. Soc.* 1983, 105, 6252.

(1) Part 26 of Highly Reduced Organometallics. For previous papers in this series see: (a) Chi, K. M.; Frerichs, S. R.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* 1988, 1013. (b) Blackburn, D. W.; Chi, K. M.; Frerichs, S. R.; Tinkham, M. L.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 437.

(2) Wilkinson, G.; Stone, F. G. A.; Abel, E. A., Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982.

(3) Fischer, E. O.; Vigoureaux, S. *Chem. Ber.* 1958, 91, 2205.

(4) Rehder, D. *J. Organomet. Chem.* 1972, 37, 303.

(5) (a) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R.; Poliner, B. S. *J. Am. Chem. Soc.* 1975, 97, 5951. (b) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* 1983, 105, 6314. (c) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* 1987, 26, 420.

(6) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* 1982, 1, 215.

(7) Chen, Y. S.; Ellis, J. E. *J. Am. Chem. Soc.* 1982, 104, 1143.

(Aldrich) ( $\text{Li}[\text{Et}_3\text{BH}]$ , 1.0 M THF solution). Trimethyl phosphite was sparged with nitrogen and then distilled from sodium metal immediately before use. Methanolic solutions of tetraethylammonium hydroxide (25%) were degassed by three or more freeze-thaw cycles on the vacuum line prior to use. Modifications of literature procedures were used in the syntheses of  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ ,  $\text{Fe}(\text{CO})_4(\text{PMe}_2\text{Ph})$ , and  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$ .<sup>19</sup> Details of the  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$  preparation are given later in this section. Solutions for proton and <sup>31</sup>P NMR spectra were prepared under  $\text{N}_2$  and sealed inside 5-mm glass tubes. Varian FT 80 and Nicolet NT-300 WB NMR spectrometers were employed. Elemental analyses were carried out at Analytische Laboratorien (Engelskirchen, Germany) and Galbraith Laboratories (Knoxville, TN). Melting points were determined on samples sealed under nitrogen in capillaries and were uncorrected.

**Preparation of  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$ .** Sodium benzophenone ketyl was prepared by dissolving small pieces of sodium metal (0.040 g, 1.7 mmol) and benzophenone (0.36 g, 2.0 mmol) in 20 mL of THF. This solution was added by cannula to a mixture of  $\text{PMe}_3$  (1.0 mL, 10 mmol) and  $\text{Fe}(\text{CO})_5$  (3.5 mL, 27 mmol). The blue color of the ketyl was discharged immediately on contact with  $\text{Fe}(\text{CO})_5$ . The reaction mixture was stirred and refluxed under nitrogen for 5 h. During this time the solution quickly developed the deep red-brown color characteristic of polynuclear ferrates. Volatiles were removed in vacuo. Heptane, 100 mL, was added to the residue, and the mixture was boiled in a container open to air until the solution color changed from red-brown to a yellowish hue. The hot mixture was then quickly filtered under a blanket of nitrogen, and the resulting filtrate was cooled (under  $\text{N}_2$ ) to  $-30^\circ\text{C}$  for about 12 h. Off-white crystals formed that were rinsed with cold pentane ( $-30^\circ\text{C}$ ) and dried in vacuo to provide 1.35 g (57%) of  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$ : IR (THF)  $\nu(\text{CO})$  2050 (m), 1975 (m), 1935 (s)  $\text{cm}^{-1}$ ; IR (Nujol mull)  $\nu(\text{CO})$  2040 (m), 1975 (m), 1935 (s br)  $\text{cm}^{-1}$ . Similar procedures provided 70% and 45% isolated yields of spectroscopically pure  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  and  $\text{Fe}(\text{CO})_4(\text{PMe}_2\text{Ph})$ , respectively.

**Synthesis of  $\text{K}_2[\text{Fe}(\text{CO})_4]$  by the Reduction of  $\text{Fe}(\text{CO})_4\text{PPh}_3$  with  $\text{K}[\text{sec-Bu}_3\text{BH}]$ .** A yellow solution of  $\text{Fe}(\text{CO})_4\text{PPh}_3$  (1.61 g, 3.75 mmol) in 30 mL of THF was treated with a 0.50 M THF solution of  $\text{K}[\text{sec-Bu}_3\text{BH}]$  (25 mL, 12 mmol). After being stirred for a few minutes at ambient temperature, the reaction mixture was heated to reflux. A white precipitate was produced almost instantly. Forty minutes later heating was stopped. After the solution was cooled to room temperature, the white precipitate was collected by filtration, rinsed with THF (2  $\times$  20 mL), and dried in vacuo. This extremely air-sensitive white powder was characterized as  $\text{K}_2[\text{Fe}(\text{CO})_4]$  by its Nujol mull IR spectrum, which in the  $\nu(\text{CO})$  region exhibits an extremely broad intense band at about 1730  $\text{cm}^{-1}$ . The latter is superimposable on that of an authentic sample of  $\text{K}_2[\text{Fe}(\text{CO})_4]$ . The latter was prepared from the reduction of  $\text{Fe}(\text{CO})_5$  by  $\text{K}[\text{sec-Bu}_3\text{BH}]$  under the same conditions;<sup>27</sup> yield 0.83 g (90%).

**$[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PPh}_3)]$  (1).** Thirty milliliters of an oxygen-free 25% methanolic solution of  $[\text{Et}_4\text{N}][\text{OH}]$  (51 mmol) was added to solid  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  (3.20 g, 7.44 mmol). After the solution was stirred for 20 min, methanol was slowly removed in vacuo. After about 25 mL of  $\text{CH}_3\text{OH}$  had been removed, all solid  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  suddenly dissolved completely, yielding a viscous yellow oil. Further evaporation of solvent resulted in vigorous gas evolution. Ten hours later gas evolution had ceased. A bright yellow slurry was present. It was rinsed with ethanol (2  $\times$  30 mL), hexanes (30 mL), and THF (30 mL). Recrystallization from acetone-Et<sub>2</sub>O afforded air-sensitive bright yellow crystals of 1: yield 3.55 g (89%); mp 180  $^\circ\text{C}$  dec; IR ( $\text{CH}_3\text{CN}$ )  $\nu(\text{CO})$  1930 (m), 1865 (w), 1820 (vs br); IR (HMPA)  $\nu(\text{CO})$  1925 (s), 1860 (w), 1820 (vs)  $\text{cm}^{-1}$ ; IR (Nujol mull) 1910 (s), 1890 (w), 1810 (vs br)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.14–7.90 (m, 15 H, phenyl), 3.46 (q, 8 H,  $\text{CH}_2$  of  $\text{Et}_4\text{N}^+$ ), 1.36 (t of t, 12 H,  $\text{CH}_3$  of  $\text{Et}_4\text{N}^+$ ), -9.02 (d, 1 H,  $J_{\text{P-H}} = 6.4$  Hz); <sup>31</sup>P NMR (acetone-*d*<sub>6</sub>)  $\delta$  87.1 (d,  $J_{\text{P-H}} = 6.4$  Hz). Anal. Calcd for  $\text{C}_{29}\text{H}_{36}\text{FeNO}_3\text{P}$ : C, 65.33; H, 6.75; N, 2.63; Fe, 10.48. Found: C, 65.23; H, 6.84; N, 2.51; Fe, 10.61.

Interestingly, no detectable reaction occurred when a slurry of  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  in methanol was stirred with a large excess of

$[\text{Et}_4\text{N}]\text{OH}$  (30 equiv) for 48 h at room temperature under a nitrogen atmosphere. However, on removal of solvent as described above, product formation commenced.

Compound 1 was also prepared in about 70% yields from the reaction of  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  with an equimolar mixture of NaOH and  $[\text{Et}_4\text{N}]\text{Br}$  in methanol. Exactly the same workup procedure as described above was used in purifying the product.

**$[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PMe}_2\text{Ph})]$  (2).** Solid  $\text{Fe}(\text{CO})_4(\text{PMe}_2\text{Ph})$  (1.20 g, 3.92 mmol) was treated with an oxygen-free 25% methanolic solution of  $[\text{Et}_4\text{N}]\text{OH}$  (15 mL, 26 mmol). There was no apparent reaction at room temperature after several hours. Methanol was then slowly removed under vacuum. After about 10 mL of  $\text{CH}_3\text{OH}$  had been removed, vigorous gas evolution occurred. As evolution of gas ceased, the vacuum was released, yielding an oily mixture. Extraction with THF and addition of ether gave a yellow oil: IR (THF)  $\nu(\text{CO})$  1920 (m), 1875 (w), 1815 (s), 1800 (sh), 1675 (m)  $\text{cm}^{-1}$ . The band at 1675  $\text{cm}^{-1}$  was attributed to methanolic  $[\text{Et}_4\text{N}][\text{OH}]$ . Extraction of this oil with 100 mL of hot toluene (ca. 90  $^\circ\text{C}$ ), filtration, and subsequent cooling provided a product free of the methanolic tetraethylammonium hydroxide. However, this air-sensitive yellow oil, which appeared to be reasonably pure 2 on the basis of its spectroscopic properties, could not be induced to crystallize; IR ( $\text{CH}_3\text{CN}$ )  $\nu(\text{CO})$  1925 (m), 1807 (vs)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.27–7.66 (m, 5 H, phenyl), 3.17 (q, 8 H,  $\text{CH}_2$  of  $\text{Et}_4\text{N}^+$ ), 1.67 (d, 6 H,  $J_{\text{P-H}} = 7.3$  Hz), 1.25 (t of t, 12 H,  $\text{CH}_3$  of  $\text{Et}_4\text{N}^+$ ), -9.40 (d, 1 H,  $J_{\text{P-H}} = 5.2$  Hz); <sup>31</sup>P NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  46.9 (m).

A combination of equimolar amounts of NaOH and  $[\text{Et}_4\text{N}]\text{Br}$  can also be used in lieu of  $[\text{Et}_4\text{N}]\text{OH}$  for this preparation.

**$[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PMe}_3)]$  (3).** An oxygen-free 25% methanolic solution of  $[\text{Et}_4\text{N}][\text{OH}]$  (20 mL, 34 mmol) was syringed into a flask containing solid  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$  (1.00 g, 4.10 mmol). No apparent reaction was observed after 2 days of stirring at 25  $^\circ\text{C}$ . Methanol was then slowly removed under vacuum. Initially, some pale yellow crystals separated from solution. When most of the  $\text{CH}_3\text{OH}$  had been removed, all of the reactants suddenly redissolved, yielding a viscous pale yellow oil. Further evaporation of solvent turned the yellow oil into a yellow-green oil, accompanied by vigorous gas evolution. The vacuum was released when gas evolution completely stopped (in ca. 8 h). The resulting oily solid mixture was dissolved in THF and filtered. Addition of ether to the filtrate provided an extremely air-sensitive yellow oil which did not crystallize even after this operation was repeated. Spectroscopically, the oil appeared to be substantially pure 3: IR (THF)  $\nu(\text{CO})$  1920 (m), 1815 (bs br), 1800 (sh)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  3.19 (q, 8 H,  $\text{CH}_2$  of  $\text{Et}_4\text{N}^+$ ), 1.38 (d, 9 H,  $J_{\text{P-H}} = 8.0$  Hz), 1.23 (t of t, 12 H,  $\text{CH}_3$  of  $\text{Et}_4\text{N}^+$ ), -9.66 (d, 1 H,  $J_{\text{P-H}} = 3.9$  Hz); <sup>31</sup>P NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  32.9 (d of decets,  $J_{\text{P}(\text{Fe-H})} = 3.9$  Hz,  $J_{\text{P}(\text{Me})} = 8.0$  Hz) ppm.

A combination of equimolar amounts of NaOH or KOH and  $[\text{Et}_4\text{N}]\text{Br}$  could also be used instead of  $[\text{Et}_4\text{N}]\text{OH}$  in this preparation. Trituration of 3 with ether or pentane did not induce crystallization. Although, the resulting oil appeared to be spectroscopically free of impurities, it seems very likely that unsolvated 3 must be a solid in its most stable form, particularly in view of a recent report on the isolation of solid  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PEt}_3)]$ .<sup>33</sup>

**Synthesis of  $\text{Fe}(\text{CO})_3(\text{Ph}_3\text{P})_2$  by the Reaction of  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PPh}_3)]$  with Acetic Acid in the Presence of  $\text{PPh}_3$ .** Glacial acetic acid (1.2 mL, 2.6 mmol) was added dropwise into a solution of  $\text{PPh}_3$  (1.72 g, 6.6 mmol) and 1 (0.70 g, 1.3 mmol) in 60 mL of toluene with vigorous stirring. A reaction occurred immediately as evidenced by gas evolution and gradual disappearing of solid 1. After filtration the yellow filtrate was concentrated. Addition of hexanes caused precipitation of yellow crystals whose infrared spectrum in THF displayed in the  $\nu(\text{CO})$  region only one band at 1880 (s)  $\text{cm}^{-1}$ , diagnostic of  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ : mp 270  $^\circ\text{C}$  dec (lit.<sup>19b</sup> (THF)  $\nu(\text{CO})$  1887  $\text{cm}^{-1}$ ; mp 272  $^\circ\text{C}$  dec); yield 0.822 g (95%).

**$[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]$  (4).** To 0.70 g of solid 1 (1.3 mmol) in a flask was added 100 mL of absolute ethanol. It was then heated to reflux. A reaction occurred within minutes to give a yellow precipitate and dark brownish red solution. After 6 h the mixture was cooled to room temperature and filtered through a medium-porosity frit. The yellow solids collected were further recrystallized from toluene-hexanes and THF-hexanes,

(19) (a) Butts, S. B.; Shriver, D. F. *J. Organomet. Chem.* 1979, 169, 191. (b) Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* 1966, 8, 185.

giving yellow crystals [IR (THF)  $\nu(\text{CO})$  1880 (vs)  $\text{cm}^{-1}$ ; mp 270 °C dec] characterized as  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$  (vide supra), yield 0.191 g (20%). The red filtrate was evaporated to dryness, and the resulting yellowish red residue was rinsed with toluene ( $2 \times 50$  mL). Two recrystallizations from acetone-hexanes and THF-Et<sub>2</sub>O afforded a shiny red crystalline solid characterized as **4** by elemental analysis, by IR and NMR spectra, and by a single-crystal X-ray diffraction analysis: yield 0.051 g (13%); IR (THF)  $\nu(\text{CO})$  2010 (m), 1965 (vs), 1935 (s), 1920 (s), 1705 (w br); IR (Nujol mull)  $\nu(\text{CO})$  2010 (s), 1965 (s), 1910 (bs br), 1865 (s), 1735 (s br)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.21–7.80 (m, 10 H, phenyl), 3.47 (q, 8 H, CH<sub>2</sub> of Et<sub>4</sub>N<sup>+</sup>), 1.39 (t of t, 12 H, CH<sub>3</sub> of Et<sub>4</sub>N<sup>+</sup>); mp 122 °C dec. Anal. Calcd for C<sub>27</sub>H<sub>30</sub>Fe<sub>2</sub>NO<sub>7</sub>P: C, 52.06; H, 4.82; N, 2.25; Fe, 17.93. Found: C, 54.23; H, 5.44; N, 2.80; Fe, 17.45.

Interestingly, [Et<sub>4</sub>N][HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] was stable toward decomposition in refluxing CH<sub>3</sub>CN.

**K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (5).** A suspension of **1** (1.00 g, 1.88 mmol) in 120 mL of THF was treated with 1.0 M K[*sec*-Bu<sub>3</sub>BH] (29 mL, 29 mmol). The solid reactant gradually disappeared with gas evolution. No precipitate was produced. The infrared spectrum of the resultant gold solution of K[HFe(CO)<sub>3</sub>PPh<sub>3</sub>] in the  $\nu(\text{CO})$  region showed the following bands: 1930 (m), 1865 (w), 1825 (s), 1810 (sh)  $\text{cm}^{-1}$ . (Treatment of dry [Et<sub>4</sub>N]Br with K[*sec*-Bu<sub>3</sub>BH] under the same conditions also resulted in rapid gas evolution.) The reaction mixture was then heated to reflux with vigorous stirring (glass stir bar) for 5 h; during this time a yellow precipitate formed. After the solution was cooled to room temperature, the solid yellow product was collected by filtration, rinsed with THF ( $2 \times 30$  mL) and hexanes (30 mL), and vacuum dried. Analytically pure **5** was obtained as an extremely air-sensitive yellow solid: yield 0.74 g (82%); mp 186 °C dec; IR (Nujol mull)  $\nu(\text{CO})$  1789 (m), 1692 (s), 1637 (s)  $\text{cm}^{-1}$ ; IR (HMPA) brownish-red solution  $\nu(\text{CO})$  1784 (m), 1700 (s br)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>21</sub>H<sub>15</sub>FeK<sub>2</sub>O<sub>3</sub>P: C, 52.50; H, 3.12; Fe, 11.63; K, 16.29. Found: C, 52.22; H, 3.22; Fe, 11.61; K, 16.46.

**Synthesis of [Et<sub>4</sub>N][HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (1) by the Reaction of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (5) with Excess Acetonitrile.** Dry acetonitrile (60 mL) was syringed into a flask containing **5** (0.40 g, 0.83 mmol). After 30 min of stirring all of **5** was consumed. An infrared spectrum of the resulting gold solution in the  $\nu(\text{CO})$  region exhibited the following bands: 1930 (m), 1865 (w), 1825 (s), 1810 (sh)  $\text{cm}^{-1}$ , superimposable with that of K[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] prepared previously from the reaction of **1** and K[*sec*-Bu<sub>3</sub>BH] at 25 °C. Addition of a solution of [Et<sub>4</sub>N]Br (0.26 g, 1.25 mmol) in 15 mL of CH<sub>3</sub>CN caused the clear solution to turn turbid immediately. One hour later the solution was evaporated to dryness. The residue was dissolved in acetone and filtered. Slow evaporation of acetone under vacuum followed by addition of Et<sub>2</sub>O gave an oily, crystalline solid. It was washed with THF (15 mL) and further recrystallized from acetone-hexanes to give brilliant yellow crystals of **1**. This product gave IR and NMR spectra identical with that of an authentic sample of compound **1** prepared previously from the reaction of Fe(CO)<sub>4</sub>PPh<sub>3</sub> and [Et<sub>4</sub>N][OH]; yield 0.40 g (90%).

**Synthesis of K<sub>2</sub>[Fe(CO)<sub>4</sub>] by the Reaction of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (5) with Carbon Monoxide.** Carbon monoxide gas was bubbled through a slurry of **5** (0.40 g, 0.83 mmol) in 30 mL of THF. A reaction occurred immediately. All of the yellow slurry reacted completely in 15 min to form a white precipitate. The clear solution was decanted, and the white precipitate was rinsed with THF (30 mL) and dried under vacuum: IR (Nujol mull)  $\nu(\text{CO})$  ca. 1730 (vs br)  $\text{cm}^{-1}$ , diagnostic of K<sub>2</sub>[Fe(CO)<sub>4</sub>]; yield 0.17 g (83%).

This product was further characterized as a triphenyltin derivative. Treatment of a slurry of this white solid (0.17 g, 0.69 mmol) in 30 mL of THF with a solution of Ph<sub>3</sub>SnCl (0.27 g, 0.69 mmol) in 15 mL of THF, followed by cation exchange with excess [Et<sub>4</sub>N]Br (0.29 g, 1.4 mmol) in 30 mL of CH<sub>3</sub>CN and recrystallization from THF-Et<sub>2</sub>O provided white crystals of [Et<sub>4</sub>N][Fe(CO)<sub>4</sub>(SnPh<sub>3</sub>)]: yield 0.31 g (70%); IR (THF)  $\nu(\text{CO})$  1995 (s), 1905 (m), 1880 (vs)  $\text{cm}^{-1}$ ; IR (Nujol mull) 1990 (s), 1900 (s), 1865 (vs)  $\text{cm}^{-1}$  (lit.<sup>96</sup> (Nujol mull)  $\nu(\text{CO})$  2001, 1897, and 1887  $\text{cm}^{-1}$ ).

**Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (6).** a. **From the Reduction of 1 by Li[Et<sub>3</sub>BH].** To a suspension of **1** (0.30 g, 0.56 mmol) in 15 mL of THF was added a 1.0 M THF solution of Li[Et<sub>3</sub>BH] (11 mL, 11 mmol). Gas evolution readily occurred while the crystals of

**1** dissolved. An IR spectrum of the resulting clear yellow solution showed bands in the  $\nu(\text{CO})$  region at 1925 (s), 1840 (sh), 1820 (vs), and 1760 (m)  $\text{cm}^{-1}$ , suggesting the formation of Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)]. The reaction mixture was then heated to reflux for 3 h. No precipitate was produced. Inspection of the IR spectrum of the brownish red solution exhibited bands in the  $\nu(\text{CO})$  region at 1930 (m), 1850 (m), 1835 (s), 1770 (m), 1695 (m), and 1655 (m)  $\text{cm}^{-1}$ , indicating the presence of both Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] and Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)].

b. **From the Reduction of 1 with Li[*sec*-Bu<sub>3</sub>BH].** A suspension of **1** (0.70 g, 1.31 mmol) in 30 mL of THF was treated with a 1.0 M THF solution of Li[*sec*-Bu<sub>3</sub>BH] (26 mL, 26 mmol). All crystals of **1** gradually disappeared, accompanied by gas evolution. An infrared spectrum of the resulting yellow solution in the  $\nu(\text{CO})$  region displayed the following bands 1925 (s), 1840 (sh), 1820 (vs), and 1760 (m)  $\text{cm}^{-1}$ , indicating the formation of Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)]. It was then heated to reflux. A dark brownish red color immediately developed. Fifteen hours later the solution was cooled to room temperature. No precipitate formed. The solution was evaporated to dryness. After the mixture was washed with hexanes ( $3 \times 30$  mL) to remove unreacted Li[*sec*-Bu<sub>3</sub>BH], the resulting oily residue was redissolved in THF. The IR spectrum showed bands in the  $\nu(\text{CO})$  region at 1815 (w), 1770 (w), 1750 (w), 1695 (s), and 1655 (s br)  $\text{cm}^{-1}$ , suggesting the formation of Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)]. Addition of a THF solution of Ph<sub>3</sub>SnCl (0.35 g, 0.92 mmol) gave an immediate reaction. The IR spectrum of this solution in the  $\nu(\text{CO})$  region showed bands at 1930 (m), 1840 (sh), 1820 (s, br), and 1760 (m)  $\text{cm}^{-1}$ . After filtration, THF was removed under vacuum. The residue was redissolved in 30 mL of CH<sub>3</sub>CN and metathesized with [Et<sub>4</sub>N]Br (0.55 g, 2.6 mmol). The solvent was removed and followed by two recrystallizations from acetone-Et<sub>2</sub>O to give pale yellow crystals, which had an infrared spectrum superimposable on that of genuine [Et<sub>4</sub>N][(Ph<sub>3</sub>Sn)Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (**12**) (vide infra), yield 0.50 g (43%, based on [Et<sub>4</sub>N][HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)]).

**K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)] (7) from [HFe(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)]<sup>-</sup>.** A yellow oil containing **2** was prepared from the reaction of Fe(CO)<sub>4</sub>(PMe<sub>2</sub>Ph) (1.20 g, 3.92 mmol) with a 25% methanolic solution of [Et<sub>4</sub>N]OH (15 mL, 26 mmol). It was dissolved in 50 mL of THF and treated with 1.0 M THF solution of K[*sec*-Bu<sub>3</sub>BH] (78 mL, 78 mmol). After being stirred for 2 h at room temperature (glass stir bar), the reaction mixture was filtered to remove precipitated impurities. The gold filtrate was then heated to reflux for 3 h. During this time a yellow precipitate was produced. After the solution was cooled, to room temperature, the product was collected on a frit, washed with THF ( $2 \times 30$  mL) and hexanes (30 mL), and then dried in vacuo. An extremely air-sensitive, yellow microcrystalline solid which provided satisfactory elemental analysis for unsolvated **7** was thereby obtained: yield 1.05 g (75%, based on Fe(CO)<sub>4</sub>(PMe<sub>2</sub>Ph)); mp 190 °C dec; IR (Nujol mull)  $\nu(\text{CO})$  1780 (m), 1670 (sh), 1650 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>11</sub>H<sub>11</sub>FeK<sub>2</sub>O<sub>3</sub>P: C, 37.10; H, 3.09; Fe, 15.68; K, 21.96. Found: C, 36.88; H, 2.99; Fe, 15.58; K, 21.81.

**K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>3</sub>)] (8) from [HFe(CO)<sub>3</sub>(PMe<sub>3</sub>)]<sup>-</sup>.** A yellow oil containing **3** was prepared from the reaction of Fe(CO)<sub>4</sub>(PMe<sub>3</sub>) (1.00 g, 4.10 mmol) and a 25% methanolic solution of [Et<sub>4</sub>N]OH (20 mL, 34 mmol) as described previously. After addition of 40 mL of THF, it was treated with 40 mL of 1.0 M K[*sec*-Bu<sub>3</sub>BH] in THF. The resulting reaction mixture was then heated to reflux with vigorous stirring (glass stir bar) for 12 h. During this time a white precipitate was produced. After the solution was cooled to room temperature, a pyrophoric, white solid (**8**) was isolated, washed with THF ( $2 \times 30$  mL) and hexanes ( $2 \times 30$  mL), and dried in vacuo. Without further treatment, this material provided satisfactory elemental analysis for the composition K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>3</sub>)]: yield 0.62 g, 51% (based on Fe(CO)<sub>4</sub>(PMe<sub>3</sub>)); mp 212 °C with dec; IR (Nujol)  $\nu(\text{CO})$  1780 (m), 1682 (s), 1650 (sh), and 1619 (s)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>6</sub>H<sub>9</sub>FeK<sub>2</sub>O<sub>3</sub>P: C, 24.50; H, 3.06; P, 10.53. Found: C, 24.27; H, 3.04; P, 10.60.

**K<sub>2</sub>[Fe(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)] (9) from K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (5).** Trimethyl phosphite (1.85 mL, 15.6 mmol) was syringed into a slurry of **5** (0.50 g, 1.0 mmol) in 30 mL of THF with vigorous stirring. Within 2 h all yellow reactant was converted to a white solid. This was collected by filtration, washed with THF ( $3 \times 20$  mL), and dried in vacuo. An extremely air-sensitive, homogeneous white solid formed, which was characterized as compound

9 on the basis of satisfactory elemental analyses, IR spectra, and its conversion to compound 10 (vide infra): IR (Nujol mull)  $\nu(\text{CO})$  1817 (sh), 1803 (m), 1710 (s), 1663 (s)  $\text{cm}^{-1}$ ; yield 0.317 g (89%); mp 181 °C dec. Anal. Calcd for  $\text{C}_6\text{H}_9\text{FeK}_2\text{O}_6\text{P}$ : C, 21.06; H, 2.65; P, 9.05. Found: C, 20.87; H, 2.64; P, 8.84.

**[Et<sub>4</sub>N][Ph<sub>3</sub>SnFe(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)] (10).** To a slurry of 9 (0.250 g, 0.730 mmol) in 10 mL of THF was added a solution of Ph<sub>3</sub>SnCl (0.281 g, 0.730 mmol) in 25 mL of THF. After being stirred for about 12 h, the reaction mixture was filtered and the pale gold filtrate was evaporated to dryness. The residue was redissolved in 30 mL of CH<sub>3</sub>CN and treated with [Et<sub>4</sub>N]Br (0.307 g, 1.46 mmol). The acetonitrile was removed, and recrystallization of the residue from acetone-Et<sub>2</sub>O provided colorless crystals of an air-stable product, which gave satisfactory elemental analyses for 10: yield 0.31 g (58%); mp 142 °C dec; IR (CH<sub>3</sub>CN)  $\nu(\text{CO})$  1835 (vs)  $\text{cm}^{-1}$ ; IR (Nujol mull)  $\nu(\text{CO})$  1925 (vw), 1820 (bs br)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  7.07–7.77 (m, 15 H, phenyl), 3.69 (d, 9 H, P(OMe)<sub>3</sub>,  $J_{\text{PH}} = 12.5$  Hz), 3.11 (q, 8 H, CH<sub>2</sub> of Et<sub>4</sub>N<sup>+</sup>), 1.18 (t of t, 12 H, CH<sub>3</sub> of Et<sub>4</sub>N<sup>+</sup>). Anal. Calcd for C<sub>32</sub>H<sub>44</sub>FeNO<sub>6</sub>PSn: C, 51.65; H, 5.92; N, 1.88. Found: C, 51.85; H, 5.92; N, 1.86.

**[Et<sub>4</sub>N][Ph<sub>3</sub>SnFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (11).** To a slurry of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] (0.32 g, 0.67 mmol) in 40 mL of THF was added a solution of Ph<sub>3</sub>SnCl (0.26 g, 0.67 mmol) in 40 mL of THF dropwise with vigorous stirring. An immediate reaction occurred. After 1.5 h the reaction mixture was filtered, and the gold filtrate was evaporated to dryness. The residue was redissolved and treated with [Et<sub>4</sub>N]Br (0.282 g, 1.34 mmol) in 40 mL of CH<sub>3</sub>CN. After the solvent was removed under vacuum, the product was recrystallized from acetone-hexanes and washed with EtOH (2 × 20 mL). Analytically pure, pale yellow crystalline 11 was obtained after one additional recrystallization from acetone-ether. The product appeared to be stable in air for an indefinite period at room temperature: yield 0.38 g (65%); mp 130 °C dec; IR (CH<sub>3</sub>CN)  $\nu(\text{CO})$  1930 (w), 1820 (vs),  $\text{cm}^{-1}$ ; (Nujol mull) IR  $\nu(\text{CO})$  1910 (w), 1805 (vs)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  7.18–7.81 (m, 30 H, phenyl), 3.14 (q, 8 H, CH<sub>2</sub> of Et<sub>4</sub>N<sup>+</sup>), 1.19 (t of t, 12 H, CH<sub>3</sub> of Et<sub>4</sub>N<sup>+</sup>). Anal. Calcd for C<sub>47</sub>H<sub>50</sub>FeNO<sub>3</sub>PSn: C, 63.98; H, 5.67; N, 1.59; Fe, 6.34. Found: C, 64.04; H, 5.72; N, 1.71; Fe, 6.39.

**[Et<sub>4</sub>N][Ph<sub>3</sub>SnFe(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)] (12).** A solution of Ph<sub>3</sub>SnCl (0.26 g, 0.68 mmol) in 40 mL of THF was added dropwise into a slurry of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)] (0.24 g, 0.68 mmol) in 20 mL of THF with vigorous stirring. All of the solid K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)] reacted quickly leaving a pale yellow solution. Two hours later it was filtered, and the pale yellow filtrate was evaporated to dryness. The resulting residue was redissolved in 40 mL of CH<sub>3</sub>CN and treated with [Et<sub>4</sub>N]Br (0.286 g, 1.36 mmol). After CH<sub>3</sub>CN was removed under vacuum, it was washed with cold THF (30 mL) and ethanol (30 mL). Recrystallization from acetone-hexanes afforded analytically pure 12 as colorless, air-sensitive crystals: yield 0.22 g (43%); mp 138 °C dec; IR (CH<sub>3</sub>CN)  $\nu(\text{CO})$  1810 (vs)  $\text{cm}^{-1}$ ; IR (Nujol mull) 1900 (vw), 1805 (vs), 1790 (sh)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.03–8.14 (m, 20 H, phenyl), 3.49 (q, 8 H, CH<sub>2</sub> of Et<sub>4</sub>N<sup>+</sup>), 1.88 (d, 6 H, methyl,  $J_{\text{PH}} = 8.2$  Hz), 1.40 (t of t, 12 H, CH<sub>3</sub> of Et<sub>4</sub>N<sup>+</sup>). Anal. Calcd for C<sub>37</sub>H<sub>46</sub>FeNO<sub>3</sub>PSn: C, 58.63; H, 6.07; N, 1.85. Found: C, 58.41; H, 5.97; N, 2.03.

**[Et<sub>4</sub>N][Ph<sub>3</sub>SnFe(CO)<sub>3</sub>(PMe<sub>3</sub>)] (13).** To a slurry of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>3</sub>)] (0.150 g, 0.510 mmol) in 10 mL of THF was added dropwise a solution of Ph<sub>3</sub>SnCl (0.196 g, 0.509 mmol) in 20 mL of THF with vigorous stirring. The dianion was consumed rapidly leaving a cloudy, pale yellow solution. One hour later the solution was filtered and the pale yellow filtrate was evaporated to dryness. The resulting residue was dissolved in 25 mL of CH<sub>3</sub>CN and treated with [Et<sub>4</sub>N]Br (0.215 g, 1.02 mmol). After CH<sub>3</sub>CN was removed under vacuum, the product was recrystallized twice from THF-Et<sub>2</sub>O to provide 13 as air-sensitive white crystals: yield 0.233 g (60%); mp 256 °C dec; IR (CH<sub>3</sub>CN)  $\nu(\text{CO})$  1905 (vw), 1810 (vs)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.10–7.98 (m, 15 H, phenyl), 3.36 (q, 8 H, CH<sub>2</sub> of Et<sub>4</sub>N<sup>+</sup>), 1.59 (d, 9 H, methyl,  $J_{\text{PH}} = 8.81$  Hz), 1.31 (t of t, 12 H, CH<sub>3</sub> of Et<sub>4</sub>N<sup>+</sup>). Anal. Calcd for C<sub>32</sub>H<sub>44</sub>FeNO<sub>3</sub>PSn: C, 55.25; H, 6.33; N, 2.01. Found: C, 54.99; H, 6.60; N, 2.00.

**Crystal Preparation and Crystallographic Analysis of [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -CO)( $\mu$ -PPh<sub>2</sub>)] (4).** Suitable crystals of 4 were grown by layering diethyl ether on top of a nearly saturated solution of 4 in THF for 24 h at room temperature and recovered

**Table I. Summary of Crystal Data and Intensity Collection for [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -CO)( $\mu$ -PPh<sub>2</sub>)] (4)**

(A) Crystal Parameters at 23 °C	
space group: $P\bar{1}$	
$a = 11.140$ (1) Å	$V = 1464$ (1) Å <sup>3</sup>
$b = 13.982$ (4) Å	$Z = 2$
$c = 10.161$ (3) Å	mol wt = 623.21 g/mol
$\alpha = 105.30$ (2)°	$\rho(\text{calcd}) = 1.414$ g/cm <sup>3</sup>
$\beta = 103.33$ (2)°	cryst dimens: 0.35 × 0.20 × 0.20
$\gamma = 77.21$ (2)°	
(B) Measurement of Intensity Data	
radiatn: $\lambda(\text{Mo K}\alpha) = 0.71073$ Å	
monochromator: graphite	
abs coeff: 11.163 $\text{cm}^{-1}$	
$2\theta$ limits = 0–50°	
final no. of variables: 343	
unique data used: 3492, $F_o^2 \geq 2.0 \sigma(F_o^2)$	
$R^a = 0.034$	
$R_w^a = 0.039$	
GOF or error in observn of unit wt: 1.481 <sup>b</sup>	

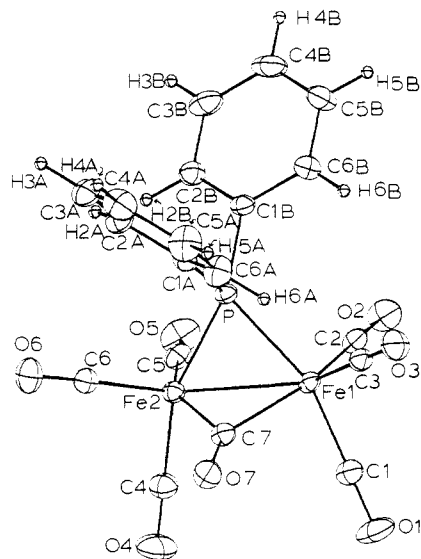
<sup>a</sup>The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ . The unweighted residuals are defined as follows:  $R = (\sum ||F_o - |F_c||) / (\sum |F_o|)$  and  $R_w = [(\sum w(|F_o| - |F_c|)^2) / (\sum |F_o|)^2]^{1/2}$ . <sup>b</sup>The error in an observation of unit weight is  $[\sum w(|F_o| - |F_c|)^2(\text{NO} - \text{NV})]^{1/2}$  where NO and NV are the number of observations and variables, respectively.

by decantation of the solvent and drying in a stream of argon. A clear, red rectangular tablet-shaped crystal of dimensions 0.35 × 0.20 × 0.20 mm was selected and wedged inside a 0.2-mm glass capillary tube which was then flame sealed under argon and mounted on a goniometer head. The crystal was found to belong to the triclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs and by a Delauney reduction calculation.<sup>20</sup> The centrosymmetric space group  $P\bar{1}$  (No. 2) was chosen, and this assignment was verified by the successful refinement of the structure. Data was collected on a CAD 4 Nonius diffractometer. Background counts were measured at both ends of the scan range with the use of an  $\omega$ - $2\theta$  scan equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of measuring background is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was noted. The intensities of 5147 ( $\pm h, \pm k, +l$ ) unique reflections were measured at 23 °C out to  $2\theta = 50^\circ$  by using monochromatized Mo K $\alpha$  radiation. The data were corrected for Lorentz, polarization, and background effects, but not for absorption, using a value of 0.03 for  $p$ .<sup>21</sup> Of the 5147 unique reflections, 3492 have  $F_o^2 \geq 2.0\sigma(F_o^2)$  and were used for the final solution and refinement of the structure. A summary of crystal and intensity collection data is shown in Table I.

**Solution and Refinement of the Structure for 4.** The structure was solved by conventional heavy-atom techniques. The two Fe atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining non-hydrogen atoms.<sup>22</sup> The atomic

(20) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in: Frenz, B. A. in *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, J., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also: *CAD 4 and SDP Users Manual*, Enraf-Nonius: Delft, Holland, 1978.

(21) The intensity data were processed as described: *CAD 4 and SDP Users Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity  $I = (K/\text{NPI})(C - 2B)$ , where  $K = 20.1166x$  (attenuator) factor, NPI = ratio of fastest possible scan rate to scan rate for the measurement,  $C$  = total count, and  $B$  = total background count. The standard deviation in the net intensity is given by  $\sigma^2(I) = (K/\text{NPI})^2[C + 4B + (pI)^2]$ , where  $p$  is a factor used to down-weight intense reflections. The observed structure factor amplitude  $F_o$  is given by  $F_o = (I/Lp)^{1/2}$ , where  $Lp$  = Lorentz and polarization factors. The  $\sigma(I)$ 's were converted to the estimated errors in the relative structure factors  $\sigma(F_o)$  by  $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$ .



**Figure 1.** ORTEP drawing of the anion in  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]$  showing the labeling scheme. Thermal ellipsoids are drawn with 50% probability boundaries. Selected interatomic distances (Å) and angles (deg):  $\text{Fe}(1)\text{-Fe}(2) = 2.601(1)$ ,  $\text{Fe}(1)\text{-P} = 2.211(1)$ ,  $\text{Fe}(2)\text{-P} = 2.209(1)$ ,  $\text{Fe}(1)\text{-C}(1) = 1.778(3)$ ,  $\text{Fe}(1)\text{-C}(2) = 1.796(3)$ ,  $\text{Fe}(1)\text{-C}(3) = 1.763(3)$ ,  $\text{Fe}(1)\text{-C}(7) = 1.951(3)$ ,  $\text{Fe}(2)\text{-C}(4) = 1.773(3)$ ,  $\text{Fe}(2)\text{-C}(5) = 1.802(3)$ ,  $\text{Fe}(2)\text{-C}(6) = 1.755(3)$ ,  $\text{Fe}(2)\text{-C}(7) = 1.976(3)$ ,  $\text{C}(1)\text{-O}(1) = 1.135(3)$ ,  $\text{C}(2)\text{-O}(2) = 1.140(3)$ ,  $\text{C}(3)\text{-O}(3) = 1.144(3)$ ,  $\text{C}(4)\text{-O}(4) = 1.146(4)$ ,  $\text{C}(5)\text{-O}(5) = 1.147(3)$ ,  $\text{C}(6)\text{-O}(6) = 1.149(4)$ ,  $\text{C}(7)\text{-O}(7) = 1.178(3)$ ;  $\text{Fe}(1)\text{-P-Fe}(2) = 72.09(3)$ ,  $\text{Fe}(1)\text{-C}(7)\text{-Fe}(2) = 82.9(1)$ ,  $\text{Fe}(1)\text{-C}(1)\text{-O}(1) = 178.7(3)$ ,  $\text{Fe}(1)\text{-C}(2)\text{-O}(2) = 178.7(3)$ ,  $\text{Fe}(1)\text{-C}(3)\text{-O}(3) = 178.3(1)$ ,  $\text{Fe}(1)\text{-C}(7)\text{-O}(7) = 139.8(2)$ ,  $\text{Fe}(2)\text{-C}(4)\text{-O}(4) = 178.0(3)$ ,  $\text{Fe}(2)\text{-C}(5)\text{-O}(5) = 177.6(3)$ ,  $\text{Fe}(2)\text{-C}(6)\text{-O}(6) = 176.4(3)$ .

scattering factors were taken from the usual tabulation,<sup>23</sup> and the effects of anomalous dispersion were included in  $F_c$  for all atoms using Cromers and Ibers values of  $\Delta f'$  and  $\Delta f''$ .<sup>23</sup> Non-hydrogen atoms were refined anisotropically. Positions of H atoms were calculated and included in structure factor calculations. The H atoms were assigned isotropic thermal parameters such that  $B(\text{H}_i) = [B(\text{C}_i) + 1.0]$ . In the final difference Fourier maps no chemically significant peaks were observed. A table of observed and calculated structure factors for 4 is available.<sup>24</sup> The final positional parameters for the atoms in 4 are in Table II, while selected interatomic distances and angles with esds are provided in the caption for Figure 1, which shows the labeling scheme for the anion. The final thermal parameters of all atoms and a table of interatomic distances and angles are available as supplementary data.<sup>24</sup>

## Results and Discussion

**Development of a Route to  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$ .** Several years ago a variety of possible routes to dianions of the general formula  $\text{M}(\text{CO})_x(\text{PR}_3)_y^{2-}$  were considered in this laboratory (vide infra).<sup>25</sup> Although these were unknown substances at the time, the existence of the homoleptic  $\text{PF}_3$  complexes  $\text{M}(\text{PF}_3)_4^{2-}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{and Os}$ )<sup>26</sup> as well as numerous carbonyl(phosphine)metalate monoanions suggested that the dianionic analogs should be accessible.

(22) The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ . The unweighted and weighted residuals are defined as  $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$  and  $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|]^2$ . The error in the observation of unit weight is  $[\sum w|F_o| - |F_c|]^2 / (\text{NO} - \text{NV})^{1/2}$  where NO and NV are the number of observations and variables, respectively.

(23) Cromers, D. T.; Weber, J. T. *Internal Tables for X-ray Crystallography*; Kynock Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromers, D. T.; Ibers, J. A. *Ibid.* Table 2.3.1.

(24) See paragraph at the end of paper regarding supplementary material.

(25) Ellis, J. E. *J. Organomet. Chem.* 1975, 86, 1.

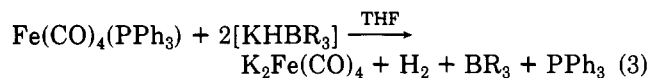
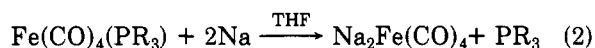
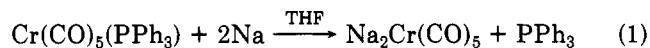
(26) Kruck, T. *Angew. Chem., Int. Ed. Engl.* 1967, 6, 53.

**Table II. Positional Parameters and Their Estimated Standard Deviations for  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]$  (4)<sup>a</sup>**

atom	x	y	z	B, Å <sup>2</sup>
Fe(1)	0.21132 (4)	0.34491 (3)	0.11730 (4)	2.77 (2)
Fe(2)	0.25210 (4)	0.14954 (3)	0.04139 (4)	2.77 (2)
P	0.34128 (7)	0.25275 (6)	-0.02103 (8)	2.64 (3)
O(1)	0.0207 (2)	0.3962 (3)	0.2900 (3)	6.5 (1)
O(2)	0.4185 (2)	0.3817 (2)	0.3521 (3)	6.5 (1)
O(3)	0.1374 (2)	0.5247 (2)	0.0055 (3)	4.9 (1)
O (4)	0.0786 (3)	0.0850 (2)	0.1624 (3)	6.4 (1)
O(5)	0.4724 (3)	0.0852 (2)	0.2427 (3)	6.5 (1)
O(6)	0.2201 (3)	0.0101 (2)	-0.2271 (3)	7.0 (1)
O(7)	0.0075 (2)	0.2527 (2)	-0.0816 (2)	4.9 (1)
N	0.7735 (3)	0.2501 (2)	-0.4336 (3)	4.2 (1)
C(1)	0.0960 (3)	0.3760 (3)	0.2240 (3)	3.9 (1)
C(2)	0.3390 (3)	0.3667 (3)	0.2600 (3)	3.8 (1)
C(3)	0.1659 (3)	0.4533 (3)	0.0480 (3)	3.4 (1)
C(4)	0.1484 (3)	0.1099 (3)	0.1168 (4)	4.1 (1)
C(5)	0.3883 (3)	0.1105 (3)	0.1628 (3)	3.8 (1)
C(6)	0.2363 (3)	0.0634 (3)	-0.1197 (4)	3.9 (1)
C(7)	0.1078 (3)	0.2518 (2)	-0.0115 (3)	3.2 (1)
C(1A)	0.3115 (3)	0.2516 (2)	-0.2070 (3)	3.2 (1)
C(2A)	0.3741 (3)	0.1736 (3)	-0.2941 (3)	4.1 (1)
C(3A)	0.3555 (4)	0.1702 (3)	-0.4353 (4)	5.0 (2)
C(4A)	0.2744 (4)	0.2447 (3)	-0.4901 (4)	5.3 (2)
C(5A)	0.2127 (4)	0.3221 (3)	-0.4054 (4)	5.8 (2)
C(6A)	0.2300 (4)	0.3262 (3)	-0.2645 (4)	4.7 (2)
C(1B)	0.5085 (3)	0.2607 (2)	0.0236 (3)	3.0 (1)
C(2B)	0.6001 (3)	0.1768 (3)	0.0211 (4)	4.0 (1)
C(3B)	0.7257 (3)	0.1874 (4)	0.0474 (4)	5.3 (2)
C(4B)	0.7574 (3)	0.2795 (4)	0.0748 (4)	5.5 (2)
C(5B)	0.6659 (3)	0.3642 (3)	0.0796 (4)	5.2 (2)
C(6B)	0.5418 (3)	0.3544 (3)	0.0543 (4)	4.1 (1)
C(10)	0.7397 (4)	0.3197 (3)	-0.3017 (4)	6.0 (2)
C(11)	0.6008 (4)	0.3590 (4)	-0.3048 (4)	6.1 (2)
C(12)	0.9137 (4)	0.2209 (4)	-0.4086 (5)	7.2 (2)
C(13)	0.9668 (4)	0.1513 (4)	-0.5319 (6)	9.0 (3)
C(14)	0.7299 (5)	0.3028 (5)	-0.5522 (4)	8.7 (3)
C(15)	0.7868 (7)	0.3996 (5)	-0.5280 (7)	11.4 (3)
C(16)	0.7112 (5)	0.1610 (4)	-0.4714 (6)	9.1 (3)
C(17)	0.7388 (7)	0.0985 (5)	-0.3667 (8)	12.6 (4)
H(2A)	0.4315 (0)	0.1202 (0)	-0.2557 (0)	5.1*
H(3A)	0.4025 (0)	0.1154 (0)	-0.4939 (0)	5.8*
H(4A)	0.2627 (0)	0.2413 (0)	-0.5880 (0)	6.2*
H(5A)	0.1533 (0)	0.3737 (0)	-0.4453 (0)	6.8*
H(6A)	0.1850 (0)	0.3817 (0)	-0.2043 (0)	5.9*
H(2B)	0.5769 (0)	0.1105 (0)	-0.0002 (0)	5.1*
H(3B)	0.7913 (0)	0.1295 (0)	0.0473 (0)	6.4*
H(4B)	0.8432 (0)	0.2887 (0)	0.0905 (0)	6.5*
H(5B)	0.6892 (0)	0.4311 (0)	0.1027 (0)	6.1*
H(6B)	0.4763 (0)	0.4137 (0)	0.0577 (0)	5.1*
H(10A)	0.7833 (0)	0.3764 (0)	-0.2794 (0)	7.5*
H(10B)	0.7719 (0)	0.2850 (0)	-0.2264 (0)	7.5*
H(11A)	0.5837 (0)	0.4028 (0)	-0.2196 (0)	7.2*
H(11B)	0.5671 (0)	0.3954 (0)	-0.3776 (0)	7.2*
H(11C)	0.5557 (0)	0.3040 (0)	-0.3246 (0)	7.2*
H(12A)	0.9417 (0)	0.1861 (0)	-0.3310 (0)	8.5*
H(12B)	0.9532 (0)	0.2806 (0)	-0.3769 (0)	8.5*
H(13A)	1.0555 (0)	0.1351 (0)	-0.5155 (0)	9.6*
H(13B)	0.9317 (0)	0.0920 (0)	-0.5637 (0)	9.6*
H(13C)	0.9432 (0)	0.1864 (0)	-0.6096 (0)	9.6*
H(14A)	0.6399 (0)	0.3267 (0)	-0.5671 (0)	9.9*
H(14B)	0.7509 (0)	0.2632 (0)	-0.6369 (0)	9.9*
H(15A)	0.7603 (0)	0.4365 (0)	-0.5990 (0)	11.3*
H(15B)	0.7670 (0)	0.4492 (0)	-0.4412 (0)	11.3*
H(15C)	0.8780 (0)	0.3856 (0)	-0.5110 (0)	11.3*
H(16A)	0.7337 (0)	0.1162 (0)	-0.5549 (0)	10.0*
H(16B)	0.6215 (0)	0.1800 (0)	-0.4876 (0)	10.0*
H(17A)	0.7040 (0)	0.0410 (0)	-0.3865 (0)	12.1*
H(17B)	0.8336 (0)	0.0752 (0)	-0.3416 (0)	12.1*
H(17C)	0.7214 (0)	0.1391 (0)	-0.2743 (0)	12.1*

<sup>a</sup> Parameters with an asterisk were refined isotropically. <sup>b</sup> Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(1/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)(2,3)]$ .

Further, it was felt that such materials would be quite useful as intermediates in the synthesis of new families of organometallic compounds including metal clusters. All attempts to synthesize such materials by "one-step" reductions of carbonyl(phosphine)metal(0) species failed due to the preferential loss of organophosphines during these reactions as shown in the following equations:



For example,  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  was reduced by 2 or more equiv of potassium-*tri-sec*-butylborohydride in refluxing THF to provide nearly quantitative (90%) isolated yields of  $\text{K}_2[\text{Fe}(\text{CO})_4]$ , which was previously obtained from a similar reduction of  $\text{Fe}(\text{CO})_5$ .<sup>27</sup> Several years ago the reduction of  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  by excess  $\text{K}[\text{HB}(\text{OMe})_3]$  was also reported to give a product tentatively identified as  $\text{K}_2[\text{Fe}(\text{CO})_4]$ .<sup>28</sup> We found this material to be identical with bona fide dipotassium tetracarbonylferrate.

Of substantial importance in our quest was the report of D. Darensbourg and Froelich that carbonyl oxygen exchange with water in  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  was catalyzed by hydroxide ion under phase-transfer conditions.<sup>29</sup> They proposed that the metalcarboxylic acid anion  $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_3(\text{CO}_2\text{H})^-$  was a key intermediate in this exchange process.<sup>29</sup> Significantly, the intermediate did not tend to rapidly lose triphenylphosphine in solution, unlike the closely related formyl anion  $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_3(\text{CHO})^-$ . The latter easily decomposed to provide only  $\text{HFe}(\text{CO})_4^-$  and  $\text{PPh}_3$ .<sup>30-33</sup> Since the late Professor Roland Pettit and his co-workers had shown that metalcarboxylic acids such as  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{CO}_2\text{H})$  underwent smooth decarboxylation to form the corresponding hydride,<sup>34</sup> we believed that under appropriate conditions, phosphine-substituted iron carbonyls of the general formula  $\text{Fe}(\text{CO})_x(\text{PR}_3)_y$  might also react with  $\text{OH}^-$  to ultimately provide the hydride monoanions  $\text{HFe}(\text{CO})_{x-1}(\text{PR}_3)_y^-$ . It was hoped that the latter could be deprotonated to form the desired dianions.

Although triaryl phosphite substituted derivatives of  $\text{HFe}(\text{CO})_4^-$  had been noted in the scientific<sup>32</sup> and thesis literature<sup>35</sup> prior to 1982, our initial report<sup>7</sup> appears to have been the first published account of the synthesis of corresponding organophosphine-substituted monohydrides  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$ , where R = aryl or alkyl.

**Synthesis and Properties of  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$ .** Surprisingly, treatment of  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  with 15–20 equiv of  $\text{Et}_4\text{N}^+\text{OH}^-$  in methanol did not lead to any apparent

reaction after 24–48 h at room temperature. Decomposition occurred on heating a portion of the solution to provide  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$  and uncharacterized carbonylferrates, but after most of the methanol was removed under vacuum, at or slightly below room temperature, the sparingly soluble  $\text{Fe}(\text{CO})_4\text{PPh}_3$  rapidly dissolved with simultaneous evolution of  $\text{CO}_2$ . The now viscous solution was homogeneous and bright yellow. From this reaction, air-sensitive, yellow, crystalline, and quite pure  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PPh}_3)]$  was isolated in high yields (80–90%). By essentially identical procedures, bright yellow and spectroscopically pure oils containing  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PMe}_2\text{Ph})]$  and  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PMe}_3)]$  were prepared. No concerted attempts to crystallize these materials were made since our principle objective in this study was to prepare and examine the properties of their conjugate bases. However, subsequently in superb work, M. Darensbourg and co-workers isolated crystalline samples of  $[\text{PPN}][\text{HFe}(\text{CO})_3(\text{P}(\text{OMe})_3)]$ ,<sup>36</sup>  $[\text{PPN}][\text{HFe}(\text{CO})_3(\text{P}(\text{OEt})_3)]$ ,<sup>36</sup>  $[\text{PPN}][\text{HFe}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ ,<sup>37</sup> and  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{PEt}_3)]$ .<sup>38</sup> These were obtained by essentially the same synthetic procedure. On the basis of Darensbourg's efforts it appears that  $\text{PPN}^+$  is generally a better cation for the isolation of these anions than  $\text{Et}_4\text{N}^+$ . X-ray structural characterizations have been carried out on  $[\text{Et}_4\text{N}][\text{trans-HFe}(\text{CO})_3(\text{PPh}_3)]$ <sup>38</sup> and  $[\text{PPN}][\text{cis-HFe}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ .<sup>37</sup>

In these reactions equimolar amounts of KOH or NaOH and  $\text{Et}_4\text{NBr}$  or other tetralkylammonium chlorides or bromides also provided essentially the same yields of products. High concentrations of hydroxide ion are clearly necessary to facilitate formation of the hydrides since suspension of  $\text{Fe}(\text{CO})_4(\text{PR}_3)$  (R = alkyl, aryl) react only very slowly with saturated methanolic solutions of NaOH. However, slurries of the more soluble KOH in methanol have been successfully used to synthesize  $\text{HFe}(\text{CO})_3(\text{PPh}_3)^-$ .

Infrared spectra of  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$  in the  $\nu(\text{CO})$  region are shown in the Experimental Section and consist of two intense bands in solution or as a Nujol mull for R = Ph. On this basis, assignment of  $\text{C}_{3v}$  or trans trigonal-bipyramidal geometry seemed most reasonable. The <sup>1</sup>H NMR spectra of the  $\text{Et}_4\text{N}^+$  salts in acetone or acetonitrile show hydride resonances which range from  $\delta$  -9.0 ( $\text{PPh}_3$ ) to -9.7 ( $\text{PMe}_3$ ). These are shifted upfield relative to the hydride resonance of  $\text{HFe}(\text{CO})_4^-$  ( $\delta$  -8.7). The corresponding  $J_{\text{P-H}}$  values range from 6.4 to 3.9 Hz and were unexpectedly small compared to that of  $\text{HCo}(\text{CO})_3(\text{PPh}_3)$ ,  $J_{\text{P-H}} = 51$  Hz, which has been assigned a trans geometry.<sup>39</sup> Phosphorus-31 NMR spectra of the  $\text{Et}_4\text{N}^+$  salts are presented in the Experimental Section and vary from  $\delta$  +87.1 ( $\text{PPh}_3$ )

(27) Gladysz, J. A.; Tam, W. *J. Org. Chem.* **1978**, *43*, 2279.  
 (28) Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* **1977**, *133*, 339.  
 (29) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 338.  
 (30) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.  
 (31) It is interesting to note, however, that the corresponding triphenyl phosphite complex  $(\text{PhO})_3\text{PFe}(\text{CO})_3(\text{CHO})^-$  was reported to decompose in THF at 65 °C to provide a 3:1 mixture of  $\text{HFe}(\text{CO})_4^-$  and  $\text{HFe}(\text{CO})_3[\text{P}(\text{OPh})_3]^-$ .<sup>32,33</sup> As far as we can determine, Casey's mention of  $\text{HFe}(\text{CO})_3[\text{P}(\text{OPh})_3]^-$  was the first report of a complex of this type in the scientific literature. Unfortunately, however, no spectroscopic data in support of this formulation was presented in the original (ref 32) or follow-up paper (Ref 33).

(32) Casey, C. P.; Neumann, S. M. *Adv. Chem. Ser.* **1979**, *No. 173*, 131.  
 (33) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Cesa, I. G.; Haller, K. J. *Organometallics* **1985**, *4*, 143.

(34) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1127.  
 (35) Doctoral students of R. Pettit examined the reaction of alkali-metal hydroxides with  $\text{Fe}(\text{CO})_4(\text{PR}_3)$  in the 1970's. While their two-phase THF/KOH-H<sub>2</sub>O reaction medium was reportedly unsuccessful in converting the relatively electron-rich  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$  or corresponding trialkylphosphine complexes to the desired monohydrides, they discovered that the more reactive triaryl phosphite complexes did work. Mauldin (Mauldin, C. H. Ph.D. Dissertation, University of Texas, Austin, 1976) first showed that  $\text{Fe}(\text{CO})_4(\text{P}(\text{OPh})_3)$  reacted with THF/KOH-H<sub>2</sub>O to provide  $\text{HFe}(\text{CO})_3(\text{P}(\text{OPh})_3)^-$  while Edens (Edens, M. W. Ph.D. Dissertation, University of Texas, Austin, 1978) later extended this procedure to the synthesis and isolation of the substituted phosphite complex  $[\text{PPN}][\text{HFe}(\text{CO})_3(\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{F})_3)]$ . Fortunately, we were unaware of these studies before 1982 or this project may never have been initiated! This is yet another example of where ignorance can be bliss in research!

(36) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.  
 (37) Ash, C. E.; Kim, C. M.; Darensbourg, M. Y.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1357.

(38) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

(39) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2933.

to  $\delta +32.9$  (PMe<sub>3</sub>), relative to external 85% H<sub>3</sub>PO<sub>4</sub>. The proton-coupled <sup>31</sup>P NMR spectrum of HFe(CO)<sub>3</sub>(PMe<sub>3</sub>)<sup>-</sup> showed a well-resolved doublet of decets where  $J_{P-H(Fe-H)} = 3.9$  Hz and  $J_{P-H(CH_3)} = 8.0$  Hz. During our limited spectral studies on these materials, we did not appreciate the remarkable temperature, cation, and solvent dependence of  $J_{P-H}$  values, which Marcetta Darensbourg and co-workers discovered and studied in some detail.<sup>40</sup> In related work,  $\nu(\text{CO})$  IR band analyses were also carried out for these complexes, as well as phosphite- and triethylphosphine-substituted hydrides. In this manner, the nature of cation-anion interactions for these compounds in acetonitrile ether and THF were established.<sup>38</sup>

Darensbourg and co-workers have examined the reactivity patterns of HFe(CO)<sub>3</sub>P<sup>-</sup> and have compared these with corresponding reactions of group 6 analogues.<sup>41</sup> Particularly nice work has been carried out and recently reviewed on studies of the reactions of these materials with a variety of organic halides.<sup>42,43</sup> Also, they established that HFe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>-</sup> resemble other carbonylphosphine-metalates in that the phosphine or phosphite substituents are readily substituted by better acceptor groups.<sup>38</sup> Similar behavior has been observed for [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> and other electron-rich phosphinometalates (vide infra).

While the major objective of this study was not to examine the chemical properties of the hydride ions HFe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>-</sup>, we did observe that protonation of HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> by glacial acetic acid in the presence of 5 equiv of PPh<sub>3</sub> in toluene caused immediate gas evolution and gave a practically quantitative yield of *trans*-Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>. It seems very likely that protonation of HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> initially provided the thermally unstable H<sub>2</sub>Fe(CO)<sub>3</sub>(PPh<sub>3</sub>), which has been reported to react with PPh<sub>3</sub> in this fashion.<sup>44</sup> While [Et<sub>4</sub>N][HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] did not quickly decompose in refluxing acetonitrile, when it was refluxed in absolute ethanol, a rapid and complex reaction ensued. Workup of the products provided a 20% yield of insoluble Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and a 13% yield of the dinuclear species [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>7</sub>( $\mu$ -PPh<sub>2</sub>)]. How HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> was converted into the bridging diphenylphosphide species is unknown. However, transformation of coordinated PPh<sub>3</sub> units to bridging PPh<sub>2</sub> groups is a well-precedented reaction in organometallic chemistry and represents one important way in which triphenylphosphine-based transition-metal catalysts degrade in situ.<sup>45</sup> Darensbourg and co-workers have also examined the reaction of HFe(CO)<sub>3</sub>P<sup>-</sup> with weak acids and provisionally characterized a product as "HFe<sub>3</sub>(CO)<sub>8</sub>P<sub>3</sub>"<sup>-</sup>.<sup>38</sup> Perhaps it is an intermediate of this type that is involved in the formation of Fe<sub>2</sub>(CO)<sub>7</sub>(PPh<sub>2</sub>)<sup>-</sup>.

Although IR and especially <sup>1</sup>H NMR spectra (cf. Experimental Section) were compatible with this dinuclear formulation, rather inconclusive elemental analyses were obtained, so an X-ray analysis was carried out to verify its formulation. When this work was completed in 1981, the anionic species was apparently a new material. Subsequently, we learned that Osterloh had prepared the same anion by an independent (and far superior) route.<sup>46</sup> Al-

though an ORTEP plot of the anion from Osterloh's thesis was depicted in a recent publication,<sup>47</sup> as far as we can determine, no interatomic distances or other details of the molecular structure have been reported in the scientific literature. For this reason we felt it appropriate to provide a full account of our crystallographic structural determination in this report. Recently, Baker and co-workers have examined in some detail the properties of corresponding 33-electron neutral analogues, Fe<sub>2</sub>(CO)<sub>7</sub>( $\mu$ -PR<sub>2</sub>).<sup>48</sup>

**X-ray Crystallographic Characterization of Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -CO)( $\mu$ -PPh<sub>2</sub>)<sup>-</sup>.** An ORTEP drawing of the anion showing the labelling scheme of [Fe<sub>2</sub>(CO)<sub>7</sub>PPh<sub>2</sub>]<sup>-</sup> is shown in Figure 1 along with selected distances and angles. The compound [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>7</sub>PPh<sub>2</sub>] consists of discrete cations and anions with no unusually short interionic contacts. The anion contains two approximately octahedrally coordinated iron atoms, each of which is bound to three terminal carbonyl ligands, one bridging carbonyl ligand, one bridging diphenylphosphide group, and the other iron atom. Both iron atoms in the monoanion attain an 18-electron configuration by virtue of their formal charge of 1/2<sup>-</sup>, with the PPh<sub>2</sub> group functioning as a three-electron donor and all carbonyl groups as two-electron donors.

The PPh<sub>2</sub> group bridges the metal atoms symmetrically, and the Fe-P distances [2.211 (1), 2.209 (1) Å] are similar to those found in related bridging diphenylphosphide systems: Fe<sub>2</sub>(CO)<sub>6</sub>(Cl)(PPh<sub>2</sub>) [2.238 (1) Å],<sup>49</sup> Fe<sub>2</sub>(NO)<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub> [2.232 (2), 2.229 (2) Å],<sup>50</sup> and Fe<sub>2</sub>(CO)<sub>6</sub>[CH<sub>2</sub>C(Ph)(NMe)](PPh<sub>2</sub>) [2.222 (2), 2.194 (2) Å].<sup>51a</sup> The Fe-P(bridge)-Fe angle of 72.09 (3)° is unexceptional and similar to the corresponding value of 74.1 (1)° in Fe<sub>2</sub>(CO)<sub>5</sub>( $\mu$ -O=CMe)(PPh<sub>2</sub>)(PPh<sub>2</sub>Me).<sup>51b</sup> Also, the asymmetric carbonyl bridge has a Fe-C(bridge)-Fe angle of 82.9 (1)°, which is only slightly larger than corresponding values in HFe<sub>2</sub>(CO)<sub>8</sub><sup>-</sup> and Fe<sub>2</sub>(CO)<sub>9</sub> of 79.6 (5)° and 77.6 (1)°, respectively.<sup>52,53</sup> The metal-metal distance in this anion, 2.601 (1) Å, is in good agreement with the distances between bridged iron atoms in [HFe<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup> [2.577 (3) Å],<sup>54</sup> Fe<sub>3</sub>(CO)<sub>12</sub> [2.560 (6) Å],<sup>55</sup> and Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub> [2.623 (2) Å]<sup>56</sup> and is significantly shorter than that in the nonbridged anion [Fe<sub>2</sub>(CO)<sub>8</sub>]<sup>2-</sup> [2.787 (2) Å].<sup>57</sup>

The Fe-CO(terminal) distances, ranging between 1.755 (3) and 1.802 (3) Å, are typical of those found in other anionic iron carbonyls such as [HFe<sub>2</sub>(CO)<sub>8</sub>]<sup>-</sup>,<sup>52</sup> [HFe(CO)<sub>4</sub>]<sup>-</sup>,<sup>58</sup> and [Fe<sub>3</sub>(CO)<sub>11</sub>]<sup>2-</sup>.<sup>59</sup> The observed C-O distances and FeCO angles are also typical of those found in other systems. Within the two phenyl rings the C-C distances and angles were reasonable, averaging 1.38 (3) Å and 120.0 (24)°, respectively. The distances from the P atom to its point of attachment on the phenyl rings [1.838 (3), 1.834

(47) Kyba, E. P.; Davis, R. E.; Clubb, C. N.; Liu, S. T.; Palacios, H. A. O.; McKennis, J. S. *Organometallics* **1986**, *5*, 869.

(48) Baker, R. T.; Krusic, P. J.; Calabrese, J. C.; Roe, D. C. *Organometallics* **1986**, *5*, 1506.

(49) Taylor, N. J.; Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1980**, *19*, 560.

(50) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626.

(51) (a) Carty, A. J.; Mott, G. N.; Taylor, N. J. *J. Organomet. Chem.* **1979**, *182*, C69. (b) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

(52) Chin, H. B.; Bau, R. *Inorg. Chem.* **1978**, *17*, 2314.

(53) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans* **1974**, 800.

(54) Dahl, L. F.; Blout, J. F. *Inorg. Chem.* **1965**, *4*, 1373.

(55) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351.

(56) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Munch, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 7381 (footnote 10).

(57) Chin, H. B.; Smith, M. B.; Wilson, R. D.; Ban, R. *J. Am. Chem. Soc.* **1974**, *96*, 5285.

(58) Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388.

(59) Lo, F.; Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 7691.

(40) Ash, C. E.; Darensbourg, M. Y.; Hall, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 4173.

(41) Arndt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2617.

(42) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.

(43) Darensbourg, M. Y.; Ash, C. E.; Kao, S. C.; Silva, R.; Springs, J. *Pure. Appl. Chem.* **1988**, *60*, 131.

(44) Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 2741.

(45) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

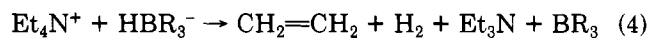
(46) Osterloh, W. T. Ph.D. Dissertation, University of Texas, Austin, 1982.

(3) Å] are comparable to those in other metal carbonyl diphenylphosphide complexes.<sup>60-62</sup>

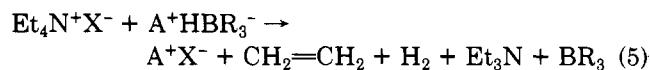
The coordination about each Fe is approximately octahedral, and the terminal carbonyl groups are not collinear with the bridging atoms, as evidence by the C(t)-Fe-C(b) and C(t)-Fe-P angles of 149.9 (1) and 159.3 (1)°, respectively. The bridging CO and PPh<sub>2</sub> groups are situated closer to the Fe-Fe bond than they would be if the above angles were 180°. This is consistent with the general pattern of ligands found in Fe<sub>2</sub>(CO)<sub>9</sub> [C(t)-Fe-C(b) = 172.1 (1)°]<sup>53</sup> and [HFe<sub>2</sub>(CO)<sub>8</sub>]<sup>-</sup> [C(t)-Fe-C(b) = 164 (1)°, C(t)-Fe-H(b) = 164 (3)°].<sup>52</sup> The tetraethylammonium cation shows no unusual features. The mean N-C and C-C distances are 1.50 (2) and 1.52 (3) Å, respectively, and are in reasonable agreement with previously observed bond lengths for this cation.<sup>63</sup>

The Nujol mull spectrum of [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>7</sub>PPh<sub>2</sub>] (2010 (m), 1965 (s), 1925 (sh), 1910 (vs), 1865 (sh), 1735 (s) cm<sup>-1</sup>) resembles the compound's THF solution spectrum (2010 (m), 1965 (vs), 1935 (m), 1920 (s), 1705 (w br) cm<sup>-1</sup>). Both spectra show the presence of a bridging carbonyl, and, thus, it seems likely that the structure described above also persists in solution.

**Synthesis, Isolation, and IR Spectral Properties of Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>2-</sup>.** Tetraethylammonium salts of HFe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>-</sup> readily reacted with K-Selectride (K[sec-Bu<sub>3</sub>BH]), L-Selectride (Li[sec-Bu<sub>3</sub>BH]), or Superhydride (Li[Et<sub>3</sub>BH]) in THF at room temperature with gas evolution to provide solutions of K[HFe(CO)<sub>3</sub>(PR<sub>3</sub>)] or Li[HFe(CO)<sub>3</sub>(PR<sub>3</sub>)]. The latter anions are very soluble in THF. While the IR spectrum in the ν(CO) region of the potassium salt (1930 (m), 1865 (w), 1825 (s), 1810 (sh) cm<sup>-1</sup>) in THF was quite similar to that of the Et<sub>4</sub>N<sup>+</sup> salt in CH<sub>3</sub>CN or HMPA (see Experimental Section), the lithium salt exhibited also a band at 1760 cm<sup>-1</sup> of medium intensity. Darenbourg and co-workers recently reported a very similar spectrum for this material and considered the low energy band to arise from a direct Li<sup>+</sup>-carbonyl oxygen interaction.<sup>38</sup> No reduction of HFe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>-</sup> by HBR<sub>3</sub><sup>-</sup> was observed even after long stirring (~24 h) at room temperature. Similar treatment of dry [Et<sub>4</sub>N]Br with solutions of HBR<sub>3</sub><sup>-</sup> resulted in rapid gas evolution and the formation of triethylamine, which does not interact appreciably with the quite bulky BR<sub>3</sub> product. Although the gaseous products of these reactions were not identified, it is reasonable to propose that a Hoffman elimination reaction occurred, i.e.

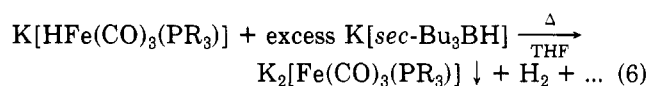


Cooke and Parklman have previously observed similar reactions.<sup>64</sup> We note that this reaction represents an excellent and rapid in situ method for the conversion of tetraethylammonium salts to corresponding alkali-metal compounds as long as the anion does not react with HBR<sub>3</sub><sup>-</sup> or any of the by products of the reaction, i.e.



A = alkali metal

In refluxing THF, K[HFe(CO)<sub>3</sub>(PR<sub>3</sub>)] was deprotonated by K-Selectride with evolution of H<sub>2</sub> to produce dipotassium salts of the dianions K<sub>2</sub>[Fe(CO)<sub>3</sub>(PR<sub>3</sub>)]. These materials precipitated from solution as yellow (PPh<sub>3</sub>, PMe<sub>2</sub>Ph) or colorless (PMe<sub>3</sub>) extremely air-sensitive solids of high thermal stability (mp with dec 186 °C (R = Ph) to 212 °C (R = Me)). Fortunately, these solids proved to be quite pure and provided excellent elemental analyses without further purification. They appear to be indefinitely stable under a nitrogen atmosphere at room temperature. Since we had no luck in growing single crystals of these rather difficult to handle materials, potassium and iron analyses were obtained for two of the salts to provide additional support for our assigned compositions. Carbon and hydrogen (and phosphorus for R = Me) analyses were also entirely consistent with their formulations as unsolvated K<sub>2</sub>[Fe(CO)<sub>3</sub>(PR<sub>3</sub>)]. The isolated yields of these substances range from outstanding (70%, R = Ph) to moderate (51%, R = Me), based on Fe(CO)<sub>4</sub>(PR<sub>3</sub>). A summary of these results are shown in eq 6. Our study



also established that Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] was quantitatively reduced by L-Selectride in refluxing THF, but in this case a brownish red solution of Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] was obtained. Interestingly, treatment of Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] with Superhydride in refluxing THF led instead to an incomplete reduction, producing a mixture of Li[HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)] and Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)]. It would appear that Superhydride is a weaker reducing agent than K-Selectride or L-Selectride toward [HFe(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>-</sup> under these conditions. Although this dilithium salt has not been isolated, its IR spectrum (vide infra) and chemical properties are entirely consistent with the proposed formulation. No attempts have been made to prepare other Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PR<sub>3</sub>)] (R = alkyl), by this route. Since the corresponding hydrides are expected to be more weakly acidic, however, more forcing conditions may be required for their synthesis.

IR spectra of K<sub>2</sub>[Fe(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)] and K<sub>2</sub>[Fe(CO)<sub>3</sub>(PMe<sub>3</sub>)] as mineral oil mulls are shown in Figure 2, while solution IR spectra of K<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] in HMPA and Li<sub>2</sub>[Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)] in THF are depicted in Figure 3. All spectra of [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sup>2-</sup> show basically a two-band pattern where one or both bands are further split or broadened in the solid state or in solution. The band positions are reasonable for tetrahedral substances of the general formula [M(CO)<sub>3</sub>L]<sup>z</sup>, where z = 2- for a given L. For example, the IR spectra of Ni(CO)<sub>3</sub>(PPh<sub>3</sub>) [ν(CO) 2070 (m), 2000 (s) cm<sup>-1</sup> in cyclohexane],<sup>66</sup> Co(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>-</sup> [ν(CO) 1928 (m), 1834 (s) cm<sup>-1</sup> as the Et<sub>4</sub>N<sup>+</sup> salt in CH<sub>3</sub>CN],<sup>67</sup> and Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>2-</sup> [ν(CO) 1784 (m), 1700 (s) as the K<sup>+</sup> salt in HMPA] show similar two-band patterns which are more or less consistent with the presence of molecules of C<sub>3v</sub> geometry. A given band (A<sub>1</sub> or E mode) of M(CO)<sub>3</sub>(PPh<sub>3</sub>)<sup>z</sup> is observed to decrease in energy by 150 (±15) cm<sup>-1</sup> as z decreases by 1 unit. For the parent tetracarbonyls, M(CO)<sub>4</sub><sup>z</sup>, the decline in the ν(CO) value (T<sub>2</sub> mode) is about the same (ca. 160 cm<sup>-1</sup>) as z decreases by 1 unit: Ni(CO)<sub>4</sub>, 2044 cm<sup>-1</sup> in CCl<sub>4</sub>,<sup>68</sup> Co(CO)<sub>4</sub><sup>-</sup>, 1887 cm<sup>-1</sup>

(60) Burt, J. C.; Boese, R.; Schmid, G. *J. Chem. Soc., Dalton Trans.* 1978, 1387.

(61) Braunstein, P.; Matt, D.; Bars, O.; Grandjean, D. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 797.

(62) Breen, M. J.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A. *Organometallics* 1982, 1, 1008.

(63) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Organometallics* 1984, 3, 1288.

(64) Cooke, M. P.; Parklman, R. M. *J. Org. Chem.* 1975, 40, 531.

(65) Lindner, E.; Schauss, E.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 711.

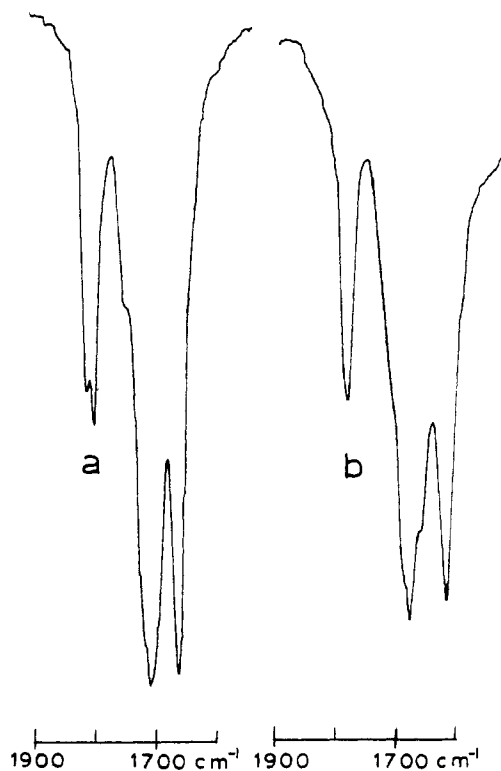
(66) Meriwether, L. S.; Fiene, L. *J. Am. Chem. Soc.* 1959, 81, 4200.

(67) Winzenburg, M. L. Ph.D. Thesis, University of Minnesota, Minneapolis, 1979, p 119.

(68) Bouquet, G.; Bigorgne, M. *Spectrochim. Acta* 1971, 27A, 139.

(69) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* 1971, 93, 6403.





**Figure 2.** Mineral oil mull infrared spectra of  $K_2[Fe(CO)_3(P(OMe)_3)]$  (a) and  $K_2[Fe(CO)_3(PMe_3)]$  (b) in the  $\nu(CO)$  region. Position of bands: for a, 1817 (sh), 1803 (m), 1710 (s), 1663 (s)  $cm^{-1}$ ; for b 1780 (m), 1682 (s), 1650 (sh), 1619 (s)  $cm^{-1}$ .

as  $Na^+$  salt in THF;  $Fe(CO)_4^{2-}$ , 1729  $cm^{-1}$  as  $Na^+$  salt in HMPA.<sup>70</sup> We feel these IR spectral observations represent excellent independent evidence for the existence of  $Fe(CO)_3(PR_3)_2^{2-}$  in solution and in the solid state. It is apparent that the E mode  $\nu(CO)$  band, i.e., the one of lowest energy, of  $K_2[Fe(CO)_3(PPh_3)]$  in HMPA is significantly broader and less symmetric than corresponding bands of the less highly reduced Ni and Co species. This observation indicates that even in the very polar solvent HMPA, the basic  $C_{3v}$  geometry of  $Fe(CO)_3(PPh_3)_2^{2-}$  is strongly perturbed by ion pairing with  $K^+$ .<sup>71</sup> The highly reduced nature of the latter anion is also indicated by its very low  $\nu(CO)$  values, which are actually in the range of those of the presently known first-row carbonyl trianion salts: e.g.,  $K_3[V(CO)_5]$ , 1812 (m), 1600 (vs, br)  $cm^{-1}$  (Nujol mull);<sup>72</sup>  $Na_3[Mn(CO)_4]$ , 1792 (w), 1665 (vs, br)  $cm^{-1}$  (HMPA);<sup>73</sup> and  $Na_3[Co(CO)_3]$ , 1757 (w), 1614 (vs, br)  $cm^{-1}$  (Nujol mull).<sup>74</sup> Finally the  $\nu(CO)$  values of  $K_2[Fe(CO)_3(PR_3)]$  decrease as the basicity of the coordinated phosphines increase, a trend which is expected on the basis of enhanced metal-carbon monoxide back-bonding<sup>75</sup> and is also observed for corresponding nickel and cobalt complexes.

**Reaction of  $[Fe(CO)_3(PR_3)_2]^{2-}$ : Brønsted Acids.** While the dianions are protonated by water or ethanol to generate  $HFe(CO)_3(PR_3)_2^-$ , quantitative yields (by IR spectra) of the monohydrides are also provided by the

(70) Ellis, J. E.; Hentges, S. G.; Faltynek, R. A., unpublished research.

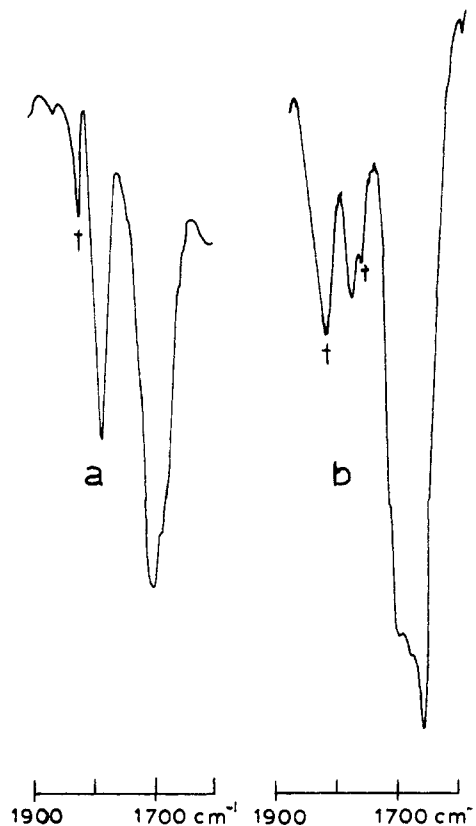
(71) An excellent review that discusses the effect of ion pairing of cations and carbonyl anions has recently appeared: Darendsbourg, M. Y., *Prog. Inorg. Chem.* **1985**, *33*, 221.

(72) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

(73) Warnock, G. F. P.; Cammarano, L.; Ellis, J. E., submitted for publication.

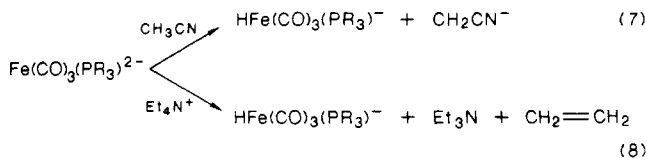
(74) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977** 686. A full paper on this work is in preparation.

(75) Abel, E. W.; Stone, F. G. A. *Q. Rev., Chem. Soc.* **1969**, *23*, 325.



**Figure 3.** Solution infrared spectra of a nearly saturated solution of  $K_2[Fe(CO)_3(PPh_3)]$  in HMPA (a) and  $Li_2[Fe(CO)_3(PPh_3)]$  in THF (b). Position of bands: for a, 1784 (m), 1700 (s)  $cm^{-1}$ ; for b, 1770 (w), 1695 (sh), 1655 (s)  $cm^{-1}$ . The bands with a dagger (†) in a and b are due to small amounts of  $K[HFe(CO)_3(PPh_3)]$  at 1824  $cm^{-1}$  and  $Li[HFe(CO)_3(PPh_3)]$  at 1815 and 1753 (sh)  $cm^{-1}$ , respectively.

reactions of  $K_2[Fe(CO)_3(PR_3)]$  with anhydrous acetonitrile and dry  $[Et_4N]Br$  in HMPA at room temperature. These reactions presumably proceed by the following equations; however, none of the organic products have been unequivocally identified:



Since acetonitrile is an exceptionally weak acid ( $K_{\text{autoprotolysis}} = 3 \times 10^{-29}$ ),<sup>76</sup> it follows that the dianions are quite strong Brønsted bases. From the reaction of  $K_2[Fe(CO)_3(PPh_3)]$  with neat  $CH_3CN$ , followed by metathesis, a 90% yield of pure  $[Et_4N][HFe(CO)_3(PPh_3)]$  was isolated. In contrast,  $K_2[Fe(CO)_4]$  appears to be inert to acetonitrile. It has been reported that the dianions  $(C_5H_5)_2M(CO)_3^{2-}$  ( $M = V, Nb$ , and  $Ta$ ), are also sufficiently basic to deprotonate acetonitrile.<sup>77-79</sup>

Clearly for many highly reduced carbonylmetalates, acetonitrile is an inappropriate medium for the determination of the  $pK_a$ 's of their conjugate acids. In view of HMPA's pronounced chemical inertness toward carbonyl

(76) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

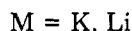
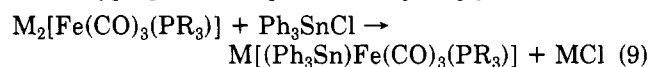
(77) Nümann, F.; Rehder, D.; Pank, V. *J. Organomet. Chem.* **1982**, *240*, 363 ( $(C_5H_5)_2V(CO)_3^{2-}$ ).

(78) Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219 ( $(C_5H_5)_2Nb(CO)_3^{2-}$ ).

(79) Pfahl, K. M.; Ellis, J. E. *Organometallics* **1984**, *3*, 230 ( $(C_5H_5)_2M(CO)_3^{2-}$ ,  $M = Nb, Ta$ ).

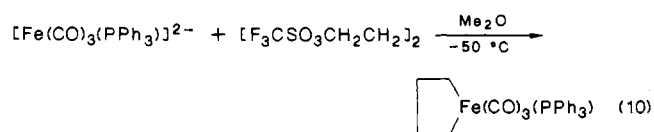
anions, its high polarity and dielectric constant, and its fairly low absorptivity in the  $\nu(\text{CO})$  region (above 1550  $\text{cm}^{-1}$ ), it may well prove to be an attractive medium for the determination of kinetic and thermodynamic acidities of hydrido transition-metal complexes,<sup>80</sup> when acetonitrile cannot be used. HMPA's principle disadvantages include its toxicity (potential carcinogen),<sup>81</sup> fairly high viscosity, and relatively high melting point (+7 °C) and normal boiling point (235 °C).<sup>82</sup>

**Reactions with  $\text{Ph}_3\text{SnCl}$ : Synthesis of *trans*- $\text{Ph}_3\text{SnFe}(\text{CO})_3(\text{PR}_3)^-$ .** Slurries of  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PR}_3)]$  or solutions of  $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PPh}_3)]$  in THF react rapidly with 1 equiv of  $\text{Ph}_3\text{SnCl}$  to give apparently new anionic species of the type [*trans*- $(\text{Ph}_3\text{Sn})\text{Fe}(\text{CO})_3(\text{PR}_3)^-$ ].



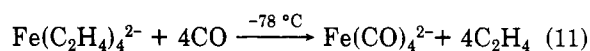
The reaction in THF is faster than the corresponding reaction of the quite insoluble  $\text{K}_2[\text{Fe}(\text{CO})_4]$  under similar conditions, which takes about 10 h to go to completion. This difference is possibly because  $[\text{Fe}(\text{CO})_3(\text{PR}_3)]^{2-}$  is a stronger nucleophile but also perhaps because  $[\text{Fe}(\text{CO})_3(\text{PR}_3)]^{2-}$  has a higher solubility in THF (although this solubility is still very small for the potassium salts). Although the reactions appeared to be quantitative by infrared spectroscopy, the isolated pure salts  $[\text{Et}_4\text{N}][(\text{Ph}_3\text{Sn})\text{Fe}(\text{CO})_3(\text{PR}_3)]$  were obtained in about 40–65% yields as colorless ( $\text{PMe}_2\text{Ph}$ ,  $\text{PMe}_3$ ,  $\text{P}(\text{OMe})_3$ ) or pale yellow ( $\text{PPh}_3$ ) crystals. They are fairly stable for minutes to hours in air as crystalline materials, but the air stabilities decrease as the relative basicities of the phosphine substituents increase. Infrared spectra of these species are summarized in the Experimental Section and show sharp two band patterns in the  $\nu(\text{CO})$  region, which are consistent with the presence of *trans*- $[(\text{Ph}_3\text{Sn})\text{Fe}(\text{CO})_3(\text{PR}_3)]^-$  units. Qualitatively very similar IR spectra have been previously reported for neutral iridium analogues, *trans*- $(\text{R}_3\text{Sn})\text{Ir}(\text{CO})_3(\text{PPh}_3)$  ( $\text{R} = \text{Me}, \text{Ph}$ ).<sup>83</sup>

**Reactions with Other Electrophiles.** General studies on the reactivity patterns of the dianions  $\text{Fe}(\text{CO})_4(\text{PR}_3)^{2-}$  with transition-metal, organic, and other main-group electrophiles have not been carried out but promise to be of considerable interest. One indication of the utility of such species in synthesis of unusual materials involves Lindner's recent report on the use of  $[\text{Fe}(\text{CO})_3(\text{PPh}_3)]^{2-}$  in the syntheses of a very thermally robust ferracyclopentane (mp 79 °C)<sup>65</sup> (eq 10).

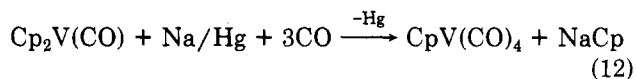


**Ligand Exchange Reactions of  $\text{Fe}(\text{CO})_3(\text{PR}_3)^{2-}$ .** A characteristic reaction of highly reduced and especially anionic organometallics containing relatively poor or non-acceptor ligands is substitution of the latter for better acceptor groups, provided the incoming group is not too bulky. One of the most spectacular reactions of this type

was demonstrated by K. Jonas and co-workers several years ago (eq 11).<sup>84</sup> All coordinated ethylenes were readily

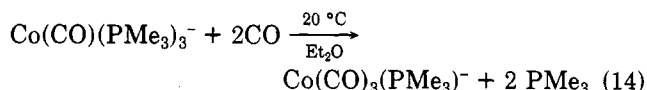
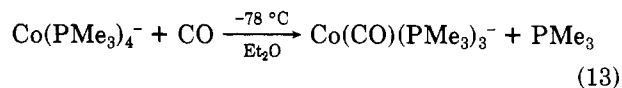


shed in the presence of CO to provide quantitative yields of the long known  $\text{Fe}(\text{CO})_4^{2-}$ . Even earlier Floriani had shown that a cyclopentadienide group could be displaced by carbon monoxide in the presence of an equivalent of alkali metal, i.e.<sup>85</sup>

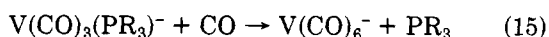


On the basis of the existence of derivatives of the type  $\text{CpV}(\text{CO})_3\text{R}^-$ , where R is a  $\sigma$ -bound hydrocarbyl, and Casey's recent demonstration that  $\text{Cp}^-$  can be a good leaving group in  $\eta^1\text{-C}_5\text{H}_5$  complexes,<sup>86</sup> it seems very likely that an intermediate of the formula  $\text{CpV}(\text{CO})_3(\eta^1\text{-C}_5\text{H}_5)^-$  is involved in Floriani's reaction, which is an example of reductive labilization (vide infra).

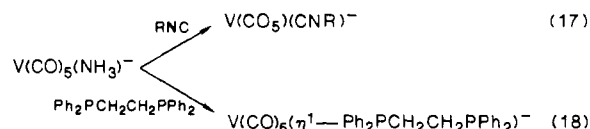
Facile substitution of coordinated phosphines by CO in metalates appears to have been observed initially by Hammer and Klein with  $\text{Co}(\text{PMe}_3)_4^-$ .<sup>87</sup> The latter readily reacts with CO to provide  $\text{Co}(\text{CO})(\text{PMe}_3)_3^-$  or  $\text{Co}(\text{CO})_3(\text{PMe}_3)^-$ , i.e., eq 13 and 14. More recent work has indi-



cated that related  $\text{Co}(\text{CO})_3(\text{PR}_3)^-$  species are slowly converted to  $\text{Co}(\text{CO})_4^-$  in the presence of excess CO.<sup>88</sup> As mentioned previously, M. Darensbourg has shown the same basic reaction occurs for  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$ .<sup>83</sup> Earlier, her group examined qualitatively similar reactions of  $\text{V}(\text{CO})_5(\text{PR}_3)^-$ .<sup>89</sup>



Important contributions from these studies included the determination that rate-limiting steps involved dissociation of phosphines (or phosphites) and were dependent on the nature of leaving group and ion pairing; i.e., the solvent and cation. The related  $\text{V}(\text{CO})_5(\text{NH}_3)^-$  was found to be exceptionally labile and a useful precursor to previously inaccessible materials, e.g.<sup>90–92</sup>



(84) Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 550.

(85) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1976, 1046.

(86) Casey, C. P.; O'Connor, J. M.; Haller, R. J. *J. Am. Chem. Soc.* 1987, 107, 1241.

(87) Hammer, R.; Klein, H. F. *Z. Naturforsch., B* 1977, 32B, 138.

(88) (a) Reeb, P.; Mugnier, Y.; Moise, C.; Laviron, E. *J. Organomet. Chem.* 1984, 273, 247. (b) Ungvary, F.; Wojcicki, A. *J. Am. Chem. Soc.* 1987, 109, 6848.

(89) Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* 1982, 1, 82.

(90) Ellis, J. E.; Fjare, K. L. *J. Organomet. Chem.* 1981, 214, C33 (b).

(91) Ellis, J. E.; Fjare, K. L. *Organometallics* 1982, 1, 898.

(92) Fjare, K. L.; Ellis, J. E. *Organometallics* 1982, 1, 1373.

(80) Eddin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* 1987, 109, 3945 and references therein.

(81) Zapp, J. A. *Science (Washington, D.C.)* 1976, 190, 422.

(82) Fujinaga, T.; Izutsu, K.; Sakura, S. In *Recommended Methods for Purification of Solvents*; Coetzee, J. F., Ed.; Pergamon: Oxford, 1982; pp 38–43.

(83) Collman, J. P.; Vastine, F. D.; Roper, W. R. *J. Am. Chem. Soc.* 1968, 90, 2282.

Similar materials were obtained from  $M(\text{CO})_5\text{L}^-$ ,<sup>93</sup> where  $M = \text{Nb}$  and  $\text{Ta}$  and  $\text{L} = \text{NH}_3$  and  $\text{THF}$ , and the related substitutionally labile species  $V(\text{CO})_5\text{L}^-$ , where  $\text{L} = \text{THF}$ ,<sup>94</sup>  $\text{DMSO}$ ,<sup>95</sup> and other poor or nonacceptor groups.

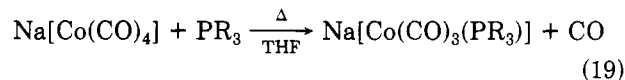
For the foregoing reasons, our original discovery that the organophosphine groups in  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$  were quite labile no longer seems remarkable. It appears that the phosphines are strongly repelled by the negative charge on the dianionic tricarbonyliron unit. Other acceptor groups readily substitute for  $\text{PR}_3$ , but the reaction proceeds to completion only if the incoming ligand is a significantly better  $\pi$ -acceptor than  $\text{PR}_3$ . A suspension of  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PPh}_3)]$  reacted with  $\text{CO}$  rapidly in  $\text{THF}$  at room temperature, despite its poor solubility in this medium. The yellow color of the reactant changed within minutes to colorless  $\text{K}_2[\text{Fe}(\text{CO})_4]$ . The product was isolated in 80% yield and characterized by comparison of its infrared spectrum with that of a genuine sample of  $\text{K}_2[\text{Fe}(\text{CO})_4]$  and by its reaction with  $\text{Ph}_3\text{SnCl}$  to provide bona fide  $\text{Ph}_3\text{SnFe}(\text{CO})_4^-$ .<sup>96</sup>

Similarly, treatment of  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PPh}_3)]$  with excess  $\text{P}(\text{OMe})_3$  in  $\text{THF}$  at room temperature in 2 h produced  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{P}(\text{OMe})_3)]$  as a white solid in 89% isolated yield. This new dianion had a mull infrared spectrum which was similar to that of the other  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PR}_3)]$  described previously except all  $\nu(\text{CO})$  bands were shifted to higher energies due to the greater electron-accepting ability of  $\text{P}(\text{OMe})_3$ . No bands due to starting material were evident in this spectrum. Satisfactory elemental analyses were obtained for this substance. Further confirmation of its nature was provided by its conversion in good yield to *trans*- $[\text{Ph}_3\text{SnFe}(\text{CO})_3(\text{P}(\text{OMe})_3)]^-$  (vide supra) and *trans*- $[\text{HFe}(\text{CO})_3(\text{P}(\text{OMe})_3)]^-$ .<sup>38</sup> By comparison, 15 equiv of  $\text{PPh}_3$  showed no evidence of reacting with a  $\text{THF}$  slurry of white  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PMe}_3)]$  at room temperature after 10 h. However, after the mixture was stirred for 3 h at reflux, the solid had changed to a pale yellow hue. The mull IR spectrum of the product clearly showed  $\nu(\text{CO})$  bands due to both  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PMe}_3)]$  and  $\text{K}_2[\text{Fe}(\text{CO})_3(\text{PPh}_3)]$ , in roughly equal amounts.

Although it has been established that  $\text{CO}$  and  $\text{P}(\text{OMe})_3$  react readily with  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2^-$ , the scope of this reaction remains poorly explored. Of particular interest in future work would be to determine whether appropriately substituted isocyanides, alkenes, alkynes, or bis(phosphines) react cleanly with  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$  since dianions of the type  $\text{Fe}(\text{CO})_3(\text{CNR})_2^-$ ,  $\text{Fe}(\text{CO})_3(\text{alkene})_2^-$ ,  $\text{Fe}(\text{CO})_3(\text{alkyne})_2^-$ , and  $\text{Fe}(\text{CO})_3(\eta^1\text{-R}_2\text{P}(\text{CH}_2)_n\text{PR}_2)_2^-$  are unknown. Such species may not be available by other routes, particularly if the corresponding  $\text{Fe}(\text{CO})_4\text{L}$  is unavailable or cannot be converted to  $\text{HFe}(\text{CO})_3\text{L}^-$  (e.g., because coordinated  $\text{L}$  reacts with  $\text{OH}^-$ ) or when  $\text{HFe}(\text{CO})_3\text{L}^-$  cannot be deprotonated.

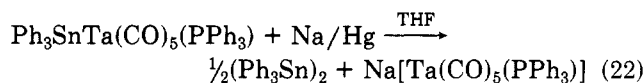
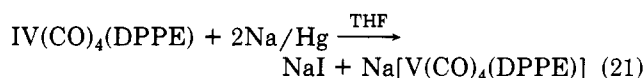
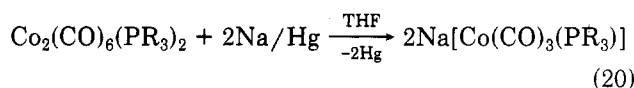
**Other Possible Routes to  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$ .** Alternative pathways to the dianions  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$ , which work for the synthesis of various substituted metalate monoanions, were also under consideration in case the hydroxide route did not succeed. These included (1) "direct" substitution of  $\text{PR}_3$  into  $\text{Fe}(\text{CO})_4^{2-}$ ; (2) reduction of  $\text{I}_2\text{Fe}(\text{CO})_3(\text{PR}_3)$ ,  $\text{E}[\text{Fe}(\text{CO})_3\text{PR}_3]$ , where  $\text{E} = \text{Zn}$ ,  $\text{Cd}$ , or  $\text{Hg}$ ,

$\text{Fe}(\text{CO})_3(\text{PR}_3)\text{L}$ , where  $\text{L} = \text{PR}_3$ ,  $\text{NR}_3$ , or other poor or nonacceptor ligands, and other derivatives containing a preformed  $\text{Fe}(\text{CO})_3\text{PR}_3$  unit; (3) deprotonation of the (then unknown) dihydrides  $\text{H}_2\text{Fe}(\text{CO})_3(\text{PR}_3)$ . Route one was believed to be the most problematic entry, since no precedent existed for the direct substitution of any ligand for  $\text{CO}$  in  $\text{Fe}(\text{CO})_4^{2-}$ . However, alkali metal cations have been reported recently to promote thermal substitution reactions of the isoelectronic  $\text{Co}(\text{CO})_4^-$  (eq 19).<sup>97</sup> Since the



metal-carbon bonds in  $\text{Fe}(\text{CO})_4^{2-}$  are expected to be appreciably more robust than those in  $\text{Co}(\text{CO})_4^-$ , the possibility of such a thermally induced process working for  $\text{Fe}(\text{CO})_4^{2-}$  under strictly anaerobic conditions seems doubtful. But photopromoted substitution of phosphines and other groups into carbonylmetalate monoanions such as  $\text{V}(\text{CO})_6^-$ ,<sup>4,98</sup> and  $\text{Mn}(\text{CO})_5^-$ ,<sup>99</sup> is a well-established and important route to substituted carbonylmetalates(1-). While no reports on extensions of this procedure to the corresponding dianions  $\text{M}(\text{CO})_x^{2-}$  have yet appeared, it might be anticipated that under the right conditions such photoinitiated substitutions of carbonyl dianions will succeed, particularly if ion-pairing interactions can be employed to weaken the metal carbonyl carbon bonds.<sup>71</sup>

Phosphine-substituted carbonyl monoanions have also been obtained by reduction of corresponding metal carbonyl dimers, e.g.,  $\text{Co}_2(\text{CO})_8(\text{PR}_3)_2$ ,<sup>100</sup> metal carbonyl halides, e.g.,  $\text{IV}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ ,<sup>101</sup> or mixed main-group transition-metal species such as  $(\text{Ph}_3\text{Sn})\text{Ta}(\text{CO})_5(\text{PPh}_3)$ <sup>102</sup> (eq 20-22). Attempts to extend these



routes to the synthesis of the dianions  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^-$ , however, were either unsuccessful in the case of the previously known  $\text{I}_2\text{Fe}(\text{CO})_3\text{P}(\text{C}_6\text{H}_{11})_3$ ,<sup>103,104</sup> or impractical due to the unavailability of suitable precursors containing  $\text{Fe}(\text{CO})_3(\text{PR}_3)$  units. For example,  $\text{Fe}_2(\text{CO})_6(\text{PPh}_3)_2^-$ , isoelectronic with the known  $\text{Co}_2(\text{CO})_8(\text{PPh}_3)_2$ ,<sup>100</sup>  $(\text{Ph}_3\text{Sn})\text{Fe}(\text{CO})_3(\text{PPh}_3)^-$ , and phosphine derivatives of the known  $[\text{EFe}(\text{CO})_4]_4$ , where  $\text{E} = \text{Zn}$ ,  $\text{Cd}$ , or  $\text{Hg}$ ,<sup>105</sup> were unknown when this study was initiated.

(97) See ref 67 and 88b.

(98) (a) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* 1971, 31, 239.

(b) Wrighton, M. S.; Handeli, D. I.; Morse, D. L. *Inorg. Chem.* 1976, 15, 434.

(99) (a) Ellis, J. E.; Fennell, R. W.; Flom, E. A. *Inorg. Chem.* 1976, 15, 2031. (b) Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* 1978, 100, 2701.

(100) Hieber, W.; Lindner, E. *Chem. Ber.* 1961, 94, 1417.

(101) Davidson, A.; Ellis, J. E. *J. Organomet. Chem.* 1972, 36, 131.

(102) Ellis, J. E.; Faltynek, R. A. *Inorg. Chem.* 1976, 15, 3168.

(103) Cohen, I. A.; Basolo, F. *J. Inorg. Nucl. Chem.* 1966, 28, 511.

(104) For example, treatment of  $\text{I}_2\text{Fe}(\text{CO})_3\text{P}(\text{C}_6\text{H}_{11})_3$  with  $\text{Na-Ph}_2\text{CO}$  in  $\text{THF}$  provided low yields of  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ , but no  $\text{Na}_2[\text{Fe}(\text{CO})_3\text{PR}_3]$ .

(105) (a)  $\text{E} = \text{Zn}$ : Neustadt, R. J.; Cymbaluk, T. H.; Ernst, R. D.; Cagle, F. W. *Inorg. Chem.* 1980, 19, 2375. (b)  $\text{M} = \text{Cd}$ ;  $\text{Hg}$ : Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* 1977, 99, 2090 and references therein.

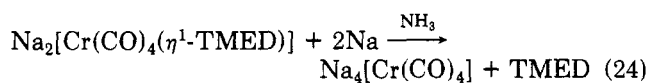
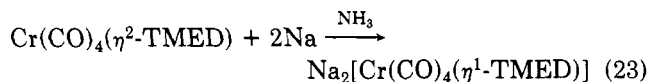
(93) Warnock, G. F. P.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* 1983, 105, 672.

(94) (a) Ihmels, K.; Rehder, D. *Chem. Ber.* 1985, 118, 895. (b) Ihmels, K.; Rehder, D. *Organometallics* 1985, 4, 1340.

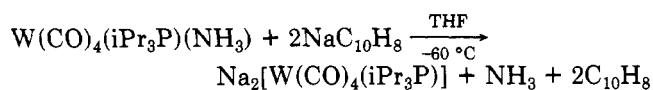
(95) Ihmels, K.; Rehder, D. *Organometallics* 1985, 4, 1334, and references cited therein. Also Rehder has investigated related labile  $\text{V}(\text{CO})_5\text{L}^-$  complexes where  $\text{L} = \text{N}_2$ , alkene, alkyne,  $\text{SO}_2$ ,  $\text{CS}_2$ , and acetone.<sup>94</sup>

(96) (a) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* 1975, 88, 237. (b) Kruck, T.; Herber, B. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 679.

One of the most useful and general routes to substituted carbonyl anions utilizes mononuclear metal complexes containing coordinated carbon monoxide and poor or non  $\pi$ -acceptor ligands. Reduction of these materials usually causes preferential loss of the poorest or nonacceptor ligand.<sup>106</sup> One of the earliest applications of this useful principle in the synthesis of an unusual carbonylmetalate involved the reduction of  $\text{Cr}(\text{CO})_4(\eta^2\text{-TMED})$ , where  $\text{TMED} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ , a process which was assumed to proceed in a stepwise fashion as follows:<sup>107</sup>

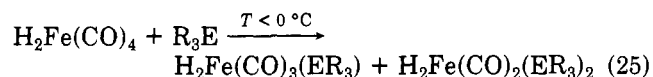


In an important variation of this theme, Cooper and co-workers used a mixed ammine phosphine carbonyl complex to synthesize  $\text{W}(\text{CO})_4(\text{iPr}_3\text{P})_2$ ,<sup>6</sup> i.e.



More recently, Leong and Cooper have found pyridine to be an especially effective leaving group in such reductions.<sup>13,14</sup> While corresponding iron compounds of the type  $\text{Fe}(\text{CO})_3(\text{PR}_3)\text{L}$ , where L is an amine, are apparently unknown, reduction of the bis(phosphine) complexes  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ <sup>108</sup> could provide a useful alternative route to corresponding dianions  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^{2-}$  if the phosphine ligand is not readily reduced.<sup>109</sup>

Deprotonation of the dihydrides  $\text{H}_2\text{Fe}(\text{CO})_3(\text{PR}_3)$  would appear to be a straight forward route to corresponding dianions. While related ruthenium and osmium dihydrides had been reported before 1970,<sup>110</sup> when this study began, complexes of the type  $\text{H}_2\text{Fe}(\text{CO})_3(\text{PR}_3)$  were unknown. However, shortly thereafter in 1981, two groups independently reported on syntheses of these materials from  $\text{H}_2\text{Fe}(\text{CO})_4$ ,<sup>111,112</sup> i.e.



( $\text{R}_3\text{E} = \text{Ph}_3\text{P}$ ,<sup>111</sup>  $(\text{MeO})_3\text{P}$ ,<sup>111,112</sup>  $(\text{PhO})_3\text{P}$ ,<sup>112</sup>  $\text{Ph}_3\text{As}$ ,<sup>112</sup>  $\text{Ph}_3\text{Sb}$ ,<sup>112</sup>  $\text{EtC}(\text{CH}_2\text{O})_3\text{P}$ <sup>112</sup>). Also, somewhat earlier, a bis(triphenyl phosphite) complex,  $\text{H}_2\text{Fe}(\text{CO})_2(\text{P}(\text{OPh})_3)_2$ , had been prepared by a different route.<sup>113</sup> Although the

disubstituted species  $\text{H}_2\text{Fe}(\text{CO})_2\text{P}_2$  were reported to be thermally stable at room temperature, especially for  $\text{P} = \text{EtC}(\text{CH}_2\text{O})_3\text{P}$ , the monosubstituted analogues and phosphites tended to be quite thermally unstable, difficult to separate from other products and were not obtained in good yields. On this basis, complexes of the type  $\text{H}_2\text{Fe}(\text{CO})_3(\text{PR}_3)$  would not appear to be good precursors to corresponding  $\text{HFe}(\text{CO})_3(\text{PR}_3)^-$  or  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^{2-}$ ; however, the latter may prove to be useful in the synthesis of the neutral dihydrides! In contrast,  $\text{H}_2\text{Fe}(\text{CO})_3(\text{Ph}_3\text{As})$  and  $\text{H}_2\text{Fe}(\text{CO})_3(\text{Ph}_3\text{Sb})$  were fairly stable materials and available in good yields (after 3–24 days) from  $\text{H}_2\text{Fe}(\text{CO})_4$ .<sup>112</sup> Although, no attempts to prepare heavier group 15 anions of the type  $\text{HFe}(\text{CO})_3\text{L}^-$  or  $\text{Fe}(\text{CO})_3\text{L}^{2-}$ , where  $\text{L} = \text{R}_3\text{As}$  or  $\text{R}_3\text{Sb}$ , have been reported to our knowledge, Berke's dihydrides may prove to be excellent precursors to the corresponding  $\text{Ph}_3\text{As}$  or  $\text{Ph}_3\text{Sb}$  complexes. Alternatively, these may be available more readily by the reaction of  $\text{OH}^-$  and the respective  $\text{Fe}(\text{CO})_4\text{L}$ .

### Concluding Remarks

The two-step process described herein for converting  $\text{Fe}(\text{CO})_4(\text{PR}_3)$  to  $\text{Fe}(\text{CO})_3(\text{PR}_3)_2^{2-}$  may be of general importance for the conversion of other substituted mononuclear carbonyls,  $\text{M}(\text{CO})_x\text{L}_y$  to the corresponding  $\text{M}(\text{CO})_{x-1}\text{L}_y^{2-}$ , provided  $\text{M}(\text{CO})_x\text{L}_y$  reacts with  $\text{OH}^-$  to give a reasonably acidic and thermally stable monohydride,  $\text{HM}(\text{CO})_{x-1}\text{L}_y^-$ , where L does not readily dissociate from the anion and is reasonably inert toward reduction or base attack. The scope of this general reaction remains to be determined. In at least one class of compounds,  $(\text{C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_3$  ( $\text{R} = \text{H}, \text{CH}_3$ ), the reaction fails to provide  $(\text{C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2\text{H}^-$  or  $(\text{C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2^{2-}$  since decarboxylation does not readily occur in the presence of excess  $\text{OH}^-$ . Instead thermally stable, isolable and satisfactorily pure dipotassium salts of the corresponding metallacarboxylate dianions,  $(\text{C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2(\text{CO}_2)^{2-}$ , are obtained in good yield.<sup>114</sup>

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE85-06710 and CHE88-13314) for continued funding of this research on highly reduced organometallics and Professor Marcetta Darensbourg for helpful discussions. Special thanks go the Ruth K. Granheim and Kelly V. Beamer for expert assistance with the manuscript.

**Registry No.** 1, 80612-33-5; 2, 80612-36-8; 3, 98942-60-0; 4, 116783-71-2; 5, 80612-34-6; 6, 119655-77-5; 7, 80612-37-9; 8, 119655-78-6; 9, 80630-31-5; 10, 80630-30-4; 11, 80612-39-1; 12, 80630-28-0; 13, 119655-80-0;  $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ , 35679-07-3;  $\text{Fe}(\text{CO})_4(\text{PMe}_2\text{Ph})$ , 37410-37-0;  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$ , 18475-02-0;  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{K}[\text{HFe}(\text{CO})_4]$ , 16182-63-1; *trans*- $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ , 21255-52-7;  $\text{K}[\text{HFe}(\text{CO})_3\text{PPh}_3]$ , 119655-81-1;  $[\text{Et}_4\text{N}][\text{Fe}(\text{CO})_4(\text{SnPh}_3)]$ , 55703-22-5;  $\text{Li}[\text{HFe}(\text{CO})_3(\text{PPh}_3)]$ , 99031-94-4;  $\text{Ph}_3\text{SnCl}$ , 639-58-7;  $\text{Fe}$ , 7439-89-6.

**Supplementary Material Available:** Tables of final thermal parameters and their esd's for the non-hydrogen atoms, bond distances and angles, and weighted least-squares planes for 4 (4 pages); a listing of observed and calculated structure factors for 4 (15 pages). Ordering information is given on any current masthead page.

(113) Grant, S. M.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* 1979, 1789.

(114) Ellis, J. E., unpublished research, 1982.

(106) First discussed in: Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* 1978, 100, 3605.

(107) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* 1983, 105, 2296.

(108) (a) Strohmeier, W.; Muller, F. *J. Chem. Ber.* 1969, 102, 3613. (b) Condor, H. L.; Darensbourg, M. Y. *J. Organomet. Chem.* 1974, 67, 93.

(109) For example, phosphines of the following type  $\text{R}_n\text{PX}_{3-n}$ , where  $n = 0-2$ ,  $\text{R} = \text{alkyl}$ , and  $\text{X} = \text{aryl}, \text{H}$ , or halogen, are easily reduced, particularly when coordinated to a metal. See: McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McLeverly, J. A., Eds.; Pergamon: London, 1987; Vol. 2, pp 989–1006.

(110) (a) Ru: Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. A* 1968, 2162. (b) Os: L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* 1967, 6, 2092.

(111) Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* 1981, 20, 2743. Unfortunately, no spectroscopic or analytical data were presented in support of these formulations, which were based on "unpublished observations".

(112) (a) Berke, H.; Bankhardt, W.; Huttner, G.; Seyerl, J.; Zsolnai, L. *Chem. Ber.* 1981, 114, 2754. (b) Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* 1981, 114, 3549.