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## A Phosphido-Bridged Cluster Synthesis with Metal-Coordinated Diphosphine. 1. Synthesis and Characterization of $\text{FeCo}_2(\mu\text{-CO})(\text{CO})_7(\mu\text{-PPh}_2)_2$

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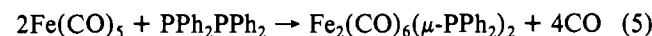
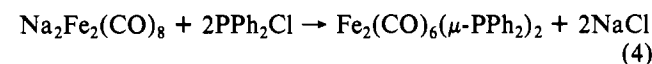
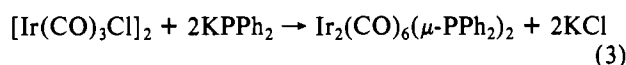
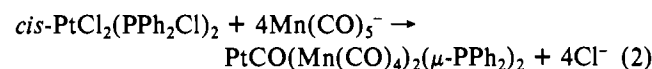
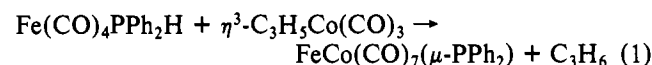
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A new cluster  $\text{FeCo}_2(\mu\text{-CO})(\text{CO})_7(\mu\text{-PPh}_2)_2$  was synthesized in 71% yield by the reaction of  $\text{Fe}(\text{CO})_4(\text{PPh}_2\text{PPh}_2)$  with  $\text{Co}_2(\text{CO})_8$ . Structural characterization by single-crystal X-ray diffraction determined the following: space group  $P\bar{1}$  (No. 2) with  $Z = 4$  and unit cell dimensions  $a = 14.694$  (4) Å,  $b = 20.599$  (5) Å,  $c = 10.715$  (3) Å,  $\alpha = 90.36$  (2)°,  $\beta = 94.83$  (2)°,  $\gamma = 87.62$  (2)°, and  $V = 3228.7$  Å<sup>3</sup>. Diffraction data ( $0^\circ < 2\theta < 45^\circ$ ) were collected with an Enraf-Nonius CAD4 automated diffractometer by using graphite-monochromated Mo  $K\alpha$  radiation, and the structure was refined to  $R_1 = 0.068$  and  $R_2 = 0.079$  for 3759 independent reflections. The unit cell contains two stereoisomeric pairs of molecules designated A and B. Each contains a triangular core of  $\text{FeCo}_2$  with a  $\text{PPh}_2$  ligand bridging each Fe-Co bond. One of the  $\text{PPh}_2$  bridging ligands is above and the other below the  $\text{FeCo}_2$  plane. Two terminal carbonyls are bound to the Fe, three to one Co, and two to the other Co. A semibringing carbonyl bridges the Co-Co bond and resides closer to the Co with the two terminal carbonyls. A low-temperature <sup>13</sup>C NMR study (on a <sup>13</sup>CO-enriched sample) and a <sup>31</sup>P NMR study demonstrated a carbonyl-exchange process which we postulate contains four distinct steps. Cyclic voltammetry showed three one-electron reduction waves for the complex at -1.01, -1.45, and -1.75 V vs. a Ag (0.10 N  $\text{AgNO}_3$ ) reference electrode in acetonitrile solution. Whereas the first and third waves appear to be reversible at slow scan rates, the second appears reversible only at high scan rates. Reduction of the complex with sodium amalgam gave a new anionic derivative. Protonation of this derivative with  $\text{H}_3\text{PO}_4$  returned the neutral starting complex in high yield.

### Introduction

Interest in the chemical applications of transition-metal cluster complexes has been growing at a prodigious rate. The development of high yield, specific syntheses of metal complexes is thus of increasing importance. We wish to report a new synthesis of a heteronuclear cluster of iron and cobalt, the structural and chemical characterization of the complex, and the relationship it bears to some similar complexes of iron and cobalt.

Complexes containing dialkylphosphido ligands bridging two metals have been prepared previously by several routes. For example, the reaction of a complex bearing a dialkylphosphine ligand with a complex having an appropriate leaving group ligand has given bridged heteronuclear derivatives, reaction 1,<sup>1</sup> as has the nucleophilic displacement of halide from metal-coordinated chlorodiphenylphosphine with metal anions, reaction 2.<sup>2</sup> Homonuclear metal complexes containing dialkylphosphido bridges have been prepared by displacing halogen with  $\text{PR}_2^-$ , reaction 3,<sup>3</sup> by displacing halogen from  $\text{PR}_2\text{X}$  with anionic metal complexes, reaction 4,<sup>4</sup> and by scission of the P-P bond in tetraalkyldiphosphines, reaction 5.<sup>3,5</sup>



Suspecting that  $\text{Fe}(\text{CO})_4(\text{PPh}_2\text{PPh}_2)$  (I) might be an intermediate in reaction 5, we decided to explore the reactivity of I with various metal complexes to determine if a new synthetic route to heteronuclear derivatives of iron would result. We were rewarded with a high-yield synthesis of  $\text{FeCo}_2(\mu\text{-CO})(\text{CO})_7(\mu\text{-PPh}_2)_2$  (II) from  $\text{Co}_2(\text{CO})_8$ .

Table I. Crystal Data for  $\text{FeCo}_2(\mu\text{-CO})(\text{CO})_7(\mu\text{-PPh}_2)_2$

|           |              |                       |                               |
|-----------|--------------|-----------------------|-------------------------------|
| <i>a</i>  | 14.694 (4) Å | <i>V</i>              | 3228.7 Å <sup>3</sup>         |
| <i>b</i>  | 20.599 (5) Å | mol wt                | 768.17                        |
| <i>c</i>  | 10.715 (3) Å | $\rho_{\text{calcd}}$ | 1.580 g cm <sup>-3</sup>      |
| $\alpha$  | 90.36 (2)°   | <i>Z</i>              | 4                             |
| $\beta$   | 94.83 (2)°   | space group           | $P\bar{1}$ (No. 2); triclinic |
| $\gamma$  | 87.62 (2)°   |                       |                               |
| $\lambda$ | 0.710 730 Å  |                       |                               |

### Experimental Section

All operations were carried out under an argon atmosphere by using either Schlenk techniques or a Vacuum Atmospheres Corp. glovebox. Solvents were dried and deoxygenated by distillation from  $\text{CaH}_2$  under argon.  $\text{Co}_2(\text{CO})_8$  and  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5\text{C}_4\text{H}_8\text{O}_2$  were purchased from Alfa Ventron Corp. and were used without further purification. <sup>13</sup>CO (90%) was purchased from Stohler Isotope Chemicals.  $\text{Fe}(\text{CO})_4\text{PPh}_2\text{PPh}_2$  (I) was prepared by literature methods.<sup>6</sup>

**Spectral Measurements.** Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer with 0.20-mm path length CaF solution cells. <sup>13</sup>C and <sup>31</sup>P NMR spectra were obtained at 22.628 and 36.440 MHz, respectively, with a Bruker HX-90E Fourier transform spectrometer with tetramethylsilane as internal <sup>13</sup>C shift reference and  $\text{H}_3\text{PO}_4$  as external <sup>31</sup>P shift reference. Mass spectra were obtained with a Varian Model 731 field desorption instrument.

**X-ray Crystallographic Study.** The structure of  $\text{FeCo}_2(\mu\text{-CO})(\text{CO})_7(\mu\text{-PPh}_2)_2$  was determined by Molecular Structure Corp., College Station, Texas. A suitable prism-shaped crystal with the dimensions  $0.25 \times 0.3 \times 0.35$  mm was grown from a diethyl ether/hexane mixed-solvent solution. The crystal was embedded in epoxy with random orientation. With the use of an Enraf-Nonius CAD4 diffractometer with Mo  $K\alpha$  radiation, a total of 8702 reflections, of which 8336 were independent, were collected. The structure was solved by direct methods. Final values of  $R_1 = 0.068$  and  $R_2 = 0.079$  were obtained for 3759 reflections having  $F_o^2 > 3\sigma(F_o^2)$ .<sup>19</sup> Crystal data

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup>

| atom | x          | y           | z           | B(1,1)     | B(2,2)      | B(3,3)     | B(1,2)      | B(1,3)      | B(2,3)      |
|------|------------|-------------|-------------|------------|-------------|------------|-------------|-------------|-------------|
| Co1  | 0.6887 (1) | 0.8611 (1)  | 0.4401 (2)  | 0.0046 (1) | 0.00240 (6) | 0.0096 (2) | 0.0013 (1)  | 0.0016 (3)  | 0.0014 (2)  |
| Co2  | 0.6302 (1) | 0.7532 (1)  | 0.5309 (2)  | 0.0040 (1) | 0.00271 (6) | 0.0100 (2) | -0.0001 (1) | 0.0024 (3)  | -0.0009 (2) |
| Co3  | 0.8677 (1) | 0.2743 (1)  | 0.0087 (2)  | 0.0039 (1) | 0.00219 (6) | 0.0123 (3) | -0.0004 (1) | 0.0016 (3)  | 0.0004 (2)  |
| Co4  | 0.7853 (2) | 0.2968 (1)  | 0.2149 (2)  | 0.0060 (1) | 0.00215 (6) | 0.0110 (3) | -0.0003 (2) | 0.0004 (3)  | 0.0003 (2)  |
| Fe1  | 0.8012 (1) | 0.78480 (9) | 0.5640 (2)  | 0.0031 (1) | 0.00169 (5) | 0.0071 (2) | 0.0005 (1)  | 0.0013 (2)  | -0.0003 (2) |
| Fe2  | 0.6985 (1) | 0.30927 (9) | -0.0056 (2) | 0.0033 (1) | 0.00149 (5) | 0.0093 (2) | 0.0002 (1)  | -0.0001 (3) | 0.0004 (2)  |
| P1   | 0.7585 (3) | 0.8796 (2)  | 0.6269 (4)  | 0.0041 (2) | 0.0018 (1)  | 0.0118 (5) | 0.0008 (3)  | 0.0021 (6)  | -0.0001 (4) |
| P2   | 0.7494 (3) | 0.7026 (2)  | 0.4563 (4)  | 0.0039 (2) | 0.0021 (1)  | 0.0076 (4) | 0.0001 (3)  | 0.0006 (5)  | -0.0004 (4) |
| P3   | 0.7518 (3) | 0.2137 (2)  | -0.0558 (4) | 0.0044 (2) | 0.0019 (1)  | 0.0090 (4) | -0.0004 (3) | 0.0014 (5)  | 0.0007 (4)  |
| P4   | 0.7260 (3) | 0.3879 (2)  | 0.1260 (4)  | 0.0044 (2) | 0.0021 (1)  | 0.0106 (5) | -0.0003 (3) | 0.0034 (5)  | -0.0008 (4) |

| atom | x          | y          | z         | B, Å <sup>2</sup> | atom | x          | y          | z          | B, Å <sup>2</sup> |
|------|------------|------------|-----------|-------------------|------|------------|------------|------------|-------------------|
| O1   | 0.9770 (8) | 0.8048 (6) | 0.470 (1) | 7.5 (3)           | O9   | 0.6787 (8) | 0.3706 (5) | -0.248 (1) | 6.9 (3)           |
| O2   | 0.8707 (8) | 0.7290 (6) | 0.799 (1) | 7.6 (3)           | O10  | 0.5100 (9) | 0.2829 (6) | 0.024 (1)  | 8.8 (4)           |
| O3   | 0.5768 (8) | 0.7985 (5) | 0.246 (1) | 6.6 (3)           | O11  | 0.9760 (7) | 0.3634 (5) | 0.165 (1)  | 5.9 (3)           |
| O4   | 0.8210 (8) | 0.8831 (6) | 0.259 (1) | 7.4 (3)           | O12  | 1.0020 (8) | 0.1675 (6) | 0.000 (1)  | 8.1 (3)           |
| O5   | 0.5821 (8) | 0.9821 (6) | 0.428 (1) | 8.1 (3)           | O13  | 0.9098 (8) | 0.3465 (6) | -0.207 (1) | 7.6 (3)           |
| O6   | 0.5086 (7) | 0.8525 (5) | 0.633 (1) | 5.4 (2)           | O14  | 0.8734 (8) | 0.1691 (5) | 0.265 (1)  | 6.6 (3)           |
| O7   | 0.6360 (9) | 0.6772 (6) | 0.757 (1) | 8.7 (4)           | O15  | 0.6197 (8) | 0.2593 (6) | 0.321 (1)  | 7.9 (3)           |
| O8   | 0.4888 (9) | 0.6795 (6) | 0.400 (1) | 8.1 (3)           | O16  | 0.8756 (9) | 0.3537 (6) | 0.438 (1)  | 8.4 (3)           |

|     |             |             |            |          |     |             |             |            |          |
|-----|-------------|-------------|------------|----------|-----|-------------|-------------|------------|----------|
| C1  | 0.9054 (11) | 0.7971 (8)  | 0.509 (2)  | 5.6 (4)  | O33 | 0.7578 (13) | 0.5086 (9)  | 0.569 (2)  | 8.0 (5)  |
| C2  | 0.8426 (10) | 0.7516 (7)  | 0.704 (1)  | 5.0 (4)  | O34 | 0.7277 (12) | 0.5723 (9)  | 0.520 (2)  | 7.2 (5)  |
| C3  | 0.6184 (11) | 0.8132 (8)  | 0.338 (2)  | 5.6 (4)  | C35 | 0.7545 (10) | 0.6929 (7)  | 0.286 (1)  | 4.4 (3)  |
| C4  | 0.7699 (11) | 0.8745 (8)  | 0.335 (2)  | 5.6 (4)  | C36 | 0.6902 (12) | 0.6530 (8)  | 0.225 (2)  | 6.2 (4)  |
| C5  | 0.6211 (12) | 0.9324 (8)  | 0.435 (2)  | 6.5 (4)  | C37 | 0.6933 (11) | 0.6485 (8)  | 0.086 (2)  | 6.1 (4)  |
| C6  | 0.5609 (10) | 0.8166 (7)  | 0.593 (1)  | 4.5 (4)  | C38 | 0.7568 (12) | 0.6797 (9)  | 0.030 (2)  | 7.1 (5)  |
| C7  | 0.6377 (11) | 0.7066 (8)  | 0.666 (2)  | 6.1 (4)  | C39 | 0.8200 (14) | 0.7144 (10) | 0.092 (2)  | 8.3 (5)  |
| C8  | 0.5446 (11) | 0.7114 (8)  | 0.450 (1)  | 5.3 (4)  | C40 | 0.8199 (11) | 0.7229 (8)  | 0.229 (2)  | 5.8 (4)  |
| C9  | 0.6854 (11) | 0.3466 (8)  | -0.147 (2) | 6.2 (4)  | C41 | 0.7353 (10) | 0.1877 (7)  | -0.216 (1) | 3.9 (3)  |
| C10 | 0.5865 (13) | 0.2932 (9)  | 0.014 (2)  | 7.4 (5)  | C42 | 0.7963 (12) | 0.2021 (9)  | -0.302 (2) | 6.6 (4)  |
| C11 | 0.9217 (11) | 0.3283 (8)  | 0.118 (1)  | 5.4 (4)  | C43 | 0.7783 (13) | 0.1808 (9)  | -0.431 (2) | 8.2 (5)  |
| C12 | 0.9493 (12) | 0.2102 (8)  | 0.006 (2)  | 6.4 (4)  | C44 | 0.7021 (12) | 0.1464 (8)  | -0.466 (2) | 6.4 (4)  |
| C13 | 0.8903 (12) | 0.3190 (8)  | -0.119 (2) | 6.3 (4)  | C45 | 0.6448 (12) | 0.1318 (8)  | -0.382 (2) | 6.3 (4)  |
| C14 | 0.8376 (11) | 0.2194 (7)  | 0.233 (1)  | 5.1 (4)  | C46 | 0.6574 (11) | 0.1518 (8)  | -0.253 (1) | 5.2 (4)  |
| C15 | 0.6864 (11) | 0.2741 (8)  | 0.275 (2)  | 5.9 (4)  | C47 | 0.7299 (9)  | 0.1404 (7)  | 0.029 (1)  | 3.9 (3)  |
| C16 | 0.8382 (12) | 0.3330 (9)  | 0.346 (2)  | 6.6 (5)  | C48 | 0.6607 (10) | 0.1384 (7)  | 0.106 (1)  | 4.2 (3)  |
| C17 | 0.6944 (10) | 0.8920 (7)  | 0.768 (1)  | 4.3 (3)  | C49 | 0.6494 (10) | 0.0802 (7)  | 0.176 (1)  | 4.8 (4)  |
| C18 | 0.6524 (11) | 0.9552 (8)  | 0.779 (2)  | 5.7 (4)  | C50 | 0.7098 (11) | 0.0261 (8)  | 0.159 (2)  | 5.8 (4)  |
| C19 | 0.5993 (13) | 0.9631 (9)  | 0.887 (2)  | 7.7 (5)  | C51 | 0.7805 (11) | 0.0292 (8)  | 0.077 (2)  | 5.7 (4)  |
| C20 | 0.5908 (12) | 0.9160 (9)  | 0.971 (2)  | 6.9 (5)  | C52 | 0.7883 (10) | 0.0856 (7)  | 0.009 (1)  | 4.2 (3)  |
| C21 | 0.6352 (12) | 0.8554 (9)  | 0.959 (2)  | 6.7 (5)  | C53 | 0.7958 (10) | 0.4556 (7)  | 0.100 (1)  | 4.2 (3)  |
| C22 | 0.6878 (11) | 0.8438 (8)  | 0.852 (1)  | 5.2 (4)  | C54 | 0.8352 (11) | 0.4898 (8)  | 0.203 (1)  | 5.4 (4)  |
| C23 | 0.8413 (11) | 0.9424 (8)  | 0.649 (1)  | 5.3 (4)  | C55 | 0.8943 (11) | 0.5406 (8)  | 0.187 (2)  | 5.6 (4)  |
| C24 | 0.8452 (13) | 0.9885 (9)  | 0.553 (2)  | 7.7 (5)  | C56 | 0.9126 (11) | 0.5559 (8)  | 0.068 (2)  | 5.6 (4)  |
| C25 | 0.9184 (16) | 1.0379 (11) | 0.579 (2)  | 10.8 (7) | C57 | 0.8754 (11) | 0.5251 (8)  | -0.039 (2) | 6.1 (4)  |
| C26 | 0.9670 (14) | 1.0372 (10) | 0.694 (2)  | 9.0 (6)  | C58 | 0.8139 (11) | 0.4714 (8)  | -0.021 (1) | 5.2 (4)  |
| C27 | 0.9629 (16) | 0.9931 (11) | 0.790 (2)  | 10.8 (7) | C59 | 0.6302 (10) | 0.4297 (7)  | 0.193 (1)  | 4.8 (4)  |
| C28 | 0.8960 (14) | 0.9403 (10) | 0.763 (2)  | 8.8 (6)  | C60 | 0.6143 (16) | 0.4199 (11) | 0.319 (2)  | 10.7 (7) |
| C29 | 0.7866 (10) | 0.6213 (7)  | 0.513 (1)  | 4.1 (3)  | C61 | 0.5351 (16) | 0.4567 (11) | 0.370 (2)  | 10.5 (7) |
| C30 | 0.8794 (10) | 0.6111 (8)  | 0.545 (1)  | 5.1 (4)  | C62 | 0.4815 (15) | 0.4961 (10) | 0.289 (2)  | 9.6 (6)  |
| C31 | 0.9120 (11) | 0.5470 (8)  | 0.588 (2)  | 6.1 (4)  | C63 | 0.5132 (19) | 0.5164 (14) | 0.184 (3)  | 16.9 (9) |
| C32 | 0.8497 (12) | 0.5003 (8)  | 0.603 (2)  | 6.2 (4)  | C64 | 0.5868 (18) | 0.4765 (13) | 0.128 (2)  | 14.1 (8) |

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$ .

Table III. Selected Bond Lengths (Å) and Bond Angles (Deg) for IIA, IIB, FeCo<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-PPh)<sup>13</sup> and Co<sub>3</sub>(μ-CO)(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub><sup>14</sup>

| IIA       |            | IIB         |            | FeCo <sub>2</sub> (CO) <sub>9</sub> (μ <sub>3</sub> -PPh) |           | Co <sub>3</sub> (μ-CO)(CO) <sub>6</sub> (μ-PPh <sub>2</sub> ) <sub>2</sub> |              |
|-----------|------------|-------------|------------|---|-----------|--|--------------|
| Co1-Co2   | 2.636 (2)  | Co3-Co4     | 2.637 (2)  | Co1-Co2   | 2.632 (2) | Co1-Co2  | 2.571 (3)    |
| Fe1-Co1   | 2.530 (2)  | Fe2-Co3     | 2.552 (2)  | Fe1-Co1   | 2.616 (2) | Co2-Co3  | 2.584 (3)    |
| Fe1-Co2   | 2.615 (2)  | Fe2-Co4     | 2.597 (2)  | Fe1-Co2   | 2.621 (2) | Co3-Co1  | 2.482 (3)    |
| Fe1-P1    | 2.148 (3)  | Fe2-P3      | 2.169 (3)  | Fe1-P1  | 2.162 (3) | Co1-P1   | 2.163 (4)    |
| Fe1-P2    | 2.172 (3)  | Fe2-P4      | 2.169 (3)  |   |           | Co2-P1   | 2.174 (4)    |
| Co1-P1    | 2.209 (4)  | Co3-P3      | 2.214 (3)  | Co1-P1  | 2.120 (2) | Co2-P2   | 2.170 (4)    |
| Co2-P2    | 2.206 (3)  | Co4-P4      | 2.220 (3)  | Co2-P1  | 2.122 (2) | Co3-P2   | 2.210 (4)    |
| Co1-C3    | 1.766 (13) | Co3-C11     | 1.768 (13) |   |           | Co1-C4   | 1.823 (15)   |
| Co2-C3    | 2.405 (13) | Co4-C11     | 2.448 (12) |   |           | Co3-C4   | not reported |
| Co2-C6    | 1.782 (12) | Co4-C14     | 1.746 (13) |   |           |  |              |
| Co1-C6    | 2.780 (11) | Co3-C14     | 2.743 (12) |   |           |  |              |
| Co1-C3-O3 | 158 (1)    | Co3-C11-O11 | 161 (1)    |   |           |  |              |
| Co2-C3-O3 | 126 (1)    | Co4-C11-O11 | 123.8 (9)  |   |           |  |              |

are given in Table I. Positional and thermal parameters are given in Table II and selected bond distances and angles in Table III. Other details relating to the structure determination are given in the sup-

plementary materials (see paragraph at the end of the text).

**Electrochemical Study.** Cyclic voltammograms of II were obtained in acetonitrile solvent by using 0.20 M tetraethylammonium tetra-

fluoroborate supporting electrolyte with a PAR Model 170 electrochemistry system. A Kemula-type hanging mercury-drop electrode was used for the reduction experiments, and a platinum electrode was used for oxidation experiments with a Ag (0.10 N AgNO<sub>3</sub>) reference electrode in both cases.

**Preparation of FeCo<sub>2</sub>(μ-CO)(CO)<sub>7</sub>(μ-PPh<sub>2</sub>)<sub>2</sub> (II).** To a slurry of 6.85 g (12.7 mmol) of I in 350 mL of hexane was added 4.50 g (13.2 mmol) of Co<sub>2</sub>(CO)<sub>8</sub>. The mixture was heated at reflux and stirred for 30 min; the resultant black solution was then cooled. An infrared spectrum of the solution contained the carbonyl bands of I, Co<sub>4</sub>(CO)<sub>12</sub>, and a new product. None of the Co<sub>2</sub>(CO)<sub>8</sub> bands were present. An additional 1.0 g of Co<sub>2</sub>(CO)<sub>8</sub> was added, and refluxing was continued for 10 min. An infrared spectrum showed the absence of the carbonyl bands of I. The solution was stripped free of hexane under vacuum and left a black, crystalline solid. The solid residue was dissolved in 75 mL of toluene and chromatographed over a 2 × 28 in. column of deoxygenated silica gel with hexane as the eluant. The first two bands removed contained small amounts of Co<sub>4</sub>(CO)<sub>12</sub> and FeCo(CO)<sub>7</sub>(μ-PPh<sub>2</sub>) (III).<sup>1</sup> The band containing II was then eluted with toluene. The toluene solution was stripped to dryness under vacuum. The resultant black crystalline (II) was dissolved in 100 mL of diethyl ether. This solution was then diluted with 100 mL of hexane, vacuum stripped to 70 mL volume, and chilled. The resultant shiny black, air-stable crystals were filtered off and dried under vacuum to give 6.98 g of II; 71% yield, mp 165–166 °C (under argon). An analytical sample was chromatographed as before and gave product with mp 168–169 °C. Anal. Calcd for C<sub>32</sub>H<sub>20</sub>Co<sub>2</sub>FeO<sub>8</sub>P<sub>2</sub>: C, 50.03; H, 2.62. Found: C, 49.99; H, 2.72. Mass spectrum *m/e* (based on <sup>56</sup>Fe and <sup>59</sup>Co) (relative intensity): P, 768 (1.00); P – CO, 740 (0.10). The isotope pattern fit that calculated for FeCo<sub>2</sub>.

**Reaction of II with Sodium Amalgam and Subsequent Reaction with H<sub>3</sub>PO<sub>4</sub>.** To a solution of 0.50 g (0.65 mmol) of II in 100 mL of THF was added a solution of 0.68 g (30 mmol) of sodium in 90 g of mercury. The mixture was stirred for 3 h as the initial black color became red-brown. An infrared spectrum of the THF solution showed the absence of the carbonyl bands of II; new bands were observed at 1988 w, 1940 w sh, 1922 m sh, 1900 vs sh, 1889 vs, 1858 s, 1795 m, and 1760 w sh cm<sup>-1</sup>. After the solution was stirred for 2 h more, the spectrum consisted of the above bands, with the exception that the 1795 m band had become a 1790 s band, and a new 1710 w band appeared. Stirring an additional 18 h produced no further change in the spectrum. A 40-mL portion of the THF solution was filtered off and stripped free of THF under vacuum; 100 mL of hexane and 5 mL of concentrated H<sub>3</sub>PO<sub>4</sub> were added to the brown residue, and 20 mL each of diethyl ether and water were then added. The black organic layer was separated and stripped free of solvent under vacuum, and the residue was chromatographed as described earlier; 0.16 g of II, 80% of theory, was recovered.

**Exchange of II with <sup>13</sup>CO.** A 0.25-g sample of II was dissolved with 0.10 g of Cr(acac)<sub>3</sub> in 4 mL of THF-*d*<sub>8</sub> on a vacuum line and stirred for 20 h under an atmosphere of <sup>13</sup>CO, 90% enriched, at 25 °C. An infrared spectrum of the resultant solution indicated that about 40% enrichment had occurred. This solution and a similar one without Cr(acac)<sub>3</sub> were used for the <sup>13</sup>C NMR study.

## Results and Discussion

**Synthesis.** The (tetraphenyldiphosphine)iron complex (I) reacted under relatively mild conditions with Co<sub>2</sub>(CO)<sub>8</sub> to produce II in high yield. The minor byproducts were Co<sub>4</sub>(CO)<sub>12</sub>, presumably from the thermal decarbonylation of Co<sub>2</sub>(CO)<sub>8</sub>, and the previously reported FeCo(CO)<sub>7</sub>(μ-PPh<sub>2</sub>).<sup>1,7</sup>

**Structure.** The unit cell of II contains four molecules which are two stereoisomeric pairs designated molecule A, comprised of Fe1, Co1, and Co2, and molecule B, comprised of Fe2, Co3, and Co4 (Figure 1). Each molecule contains a triangular core of one iron and two cobalt atoms. One PPh<sub>2</sub> ligand bridges each iron-cobalt bond. In each molecule one of the two PPh<sub>2</sub> ligands is located above and the other below the trimetal plane. The most unusual features of II are the semibringing carbonyl between the cobalt atoms and the inequality of the Fe-Co bond

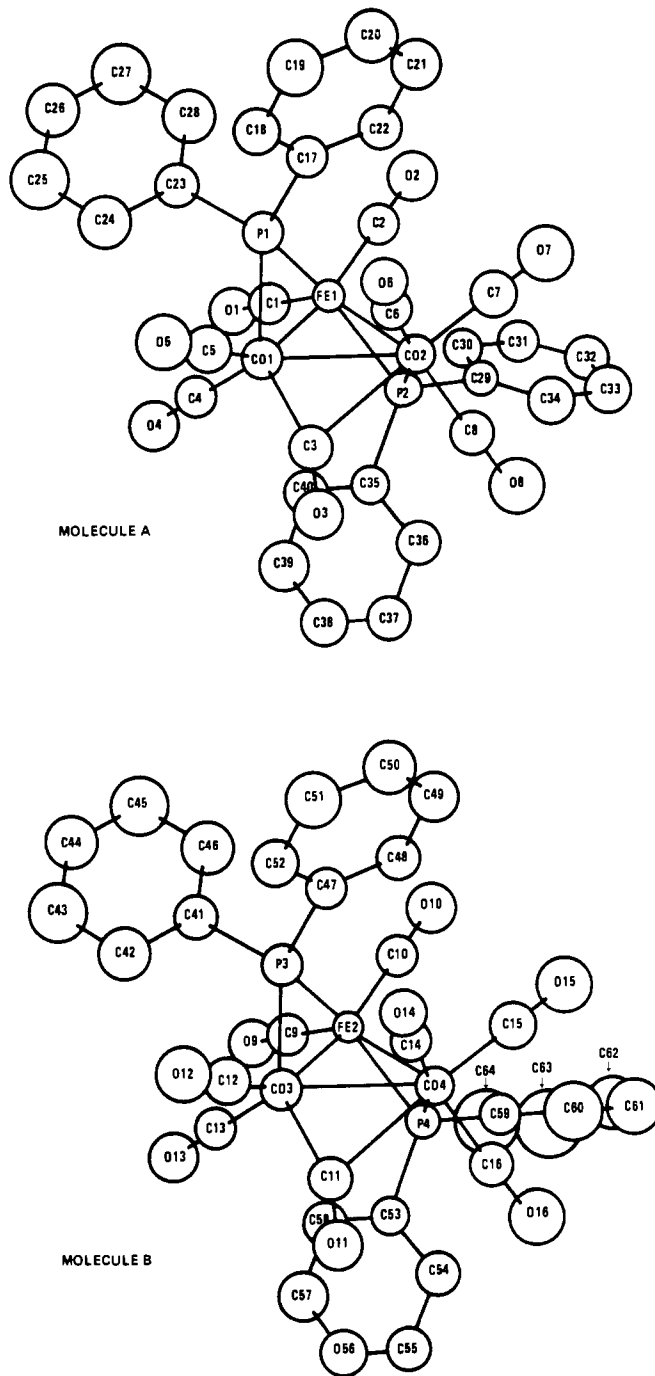


Figure 1. Molecular structure and atomic numbering scheme of FeCo<sub>2</sub>(μ-CO)(CO)<sub>7</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>: IIA (above) and IIB (below). The spheres or ellipsoids include 40% of the electron density.

lengths (Table III). In addition, the plane containing Fe1, C1, and C2 (or Fe2, C9, and C10) is rotated with respect to the trimetal plane and bisects the angle formed by Fe1, P1, and P2 (or Fe2, P3, and P4). This feature maintains a distorted octahedral geometry around the iron.

Molecules A and B differ mainly by the rotation angle of the phenyl ring (containing C29 or C59) on P2 or P4 and by slight differences in the Fe-Co and Co-carbonyl bridge bond lengths. The difference between the two Fe-Co bond lengths in A is 0.085 Å; the difference is 0.045 Å in B.

The carbonyl groups containing C6 and C14 have orientations which produce relatively short nonbonded distances to Co1 and Co6, 2.780 and 2.743 Å, respectively. Moreover, the Co-C-O bond angles in these carbonyls are 172 (1) and 170 (1)°, significantly less than the 175 (1)–178 (1)° angles ob-

(7) The reaction of I with Ru<sub>3</sub>(CO)<sub>12</sub> has produced what we believe is FeRu<sub>3</sub>(CO)<sub>13</sub>(μ-PPh<sub>2</sub>)<sub>2</sub> along with small amounts of FeRu(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>, Fe<sub>2</sub>(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>, Ru<sub>2</sub>(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>, and Ru(CO)<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>.

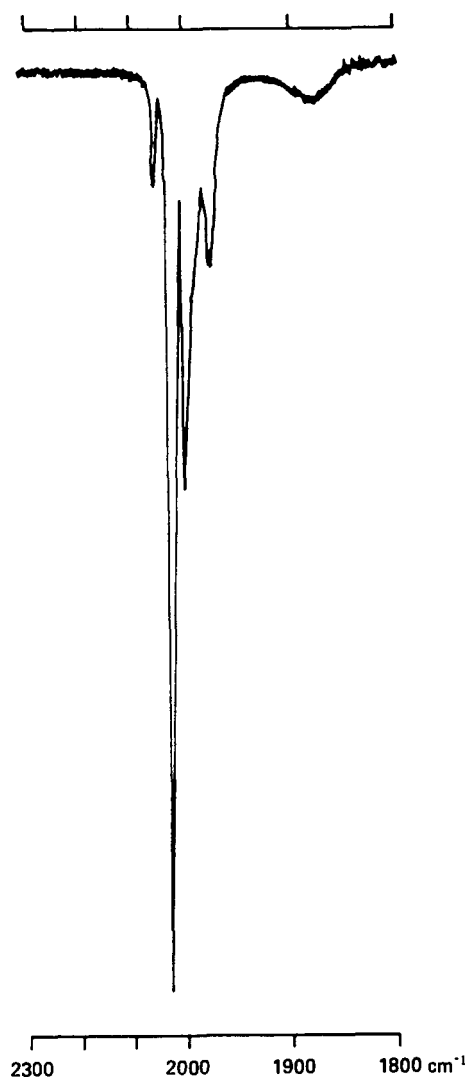


Figure 2. Infrared spectrum of the carbonyl region of II in cyclohexane solution.

served for the other Co-bound terminal carbonyls. Because of these values, we are inclined to consider the two carbonyls bearing C6 and C14 as "incipient semibridging". This interpretation will become important in our discussion later of the observed  $^{13}\text{C}$  NMR spectra.

Cotton proposed that compounds with semibridging carbonyl groups fall into two classes: those with a compensatory pair, and those with a single semibridging carbonyl or a noncompensatory pair.<sup>8</sup> The latter group was proposed to result from a charge imbalance between the two bridged metal atoms. The more negatively charged metal atom of the pair was proposed to relieve the charge separation by donation of electron density from a filled d orbital into a carbonyl  $\pi^*$  molecular orbital, thus forming the longer metal-carbonyl bridge bond.

With no formal requirement for a charge separation between the two cobalt atoms in II, observation of either no bridging carbonyls, a symmetric bridging pair of carbonyls, or a compensatory semibridging pair would be expected. The observed single semibridging carbonyl and the unequal Fe-Co bond lengths in II imply charge separation. However, we cannot determine to what extent these features result from steric crowding within the molecule or within the crystal lattice.

(8) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1 and references cited therein. A compensatory pair is defined as having the direction of asymmetry of one member of the pair opposite to that of the other. In noncompensatory pairs, both long bridge bonds are directed to the same metal atom.

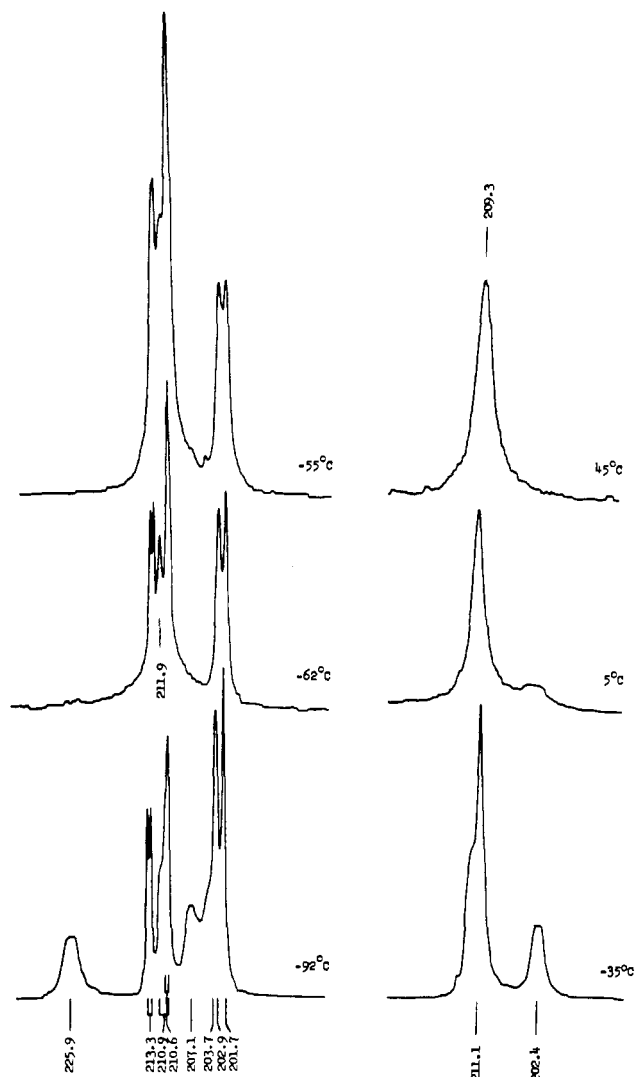


Figure 3.  $^{13}\text{C}$  NMR spectra of the carbonyls of II at 22.628 MHz in  $\text{THF-}d_8$  solution as a function of temperature.

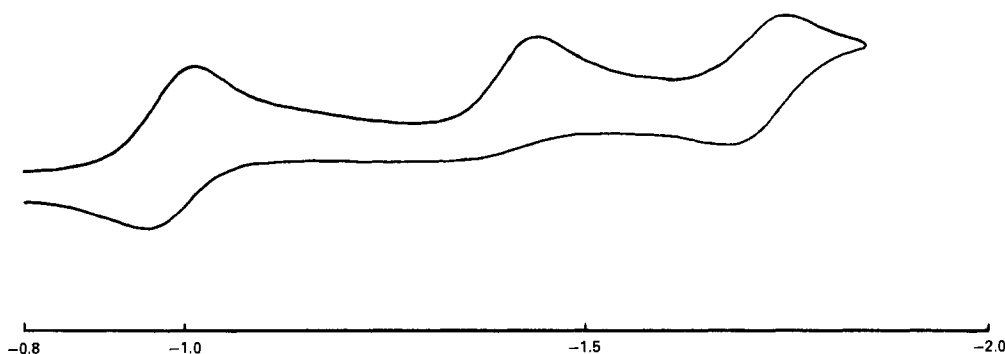
While the latter may be an important factor, the molecular asymmetry persists in solution as evidenced by the  $^{13}\text{C}$  NMR spectra discussed below.

In a recent review article, Colton and McCormick make a distinction between semibridging and asymmetrical bridging carbonyls based on the angle that the C-O bond makes with the M-M bond; an approximate  $90^\circ$  angle is classified as asymmetric, whereas angles other than  $90^\circ$  are semibridging.<sup>9</sup> The angles observed in II are  $85.3^\circ$  for A and  $83.3^\circ$  for B. Thus, although II is best described as having one semibridging carbonyl group, we believe that the structure having a compensatory pair of semibridging carbonyls may be readily energetically accessible.

Calculation of asymmetry constants and  $\theta$  angles for the semibridging carbonyls in IIA and IIB give values consistent with normal two-electron donation; four-electron donation can be ruled out.<sup>10</sup>

(9) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1. This reference also lists the three previously reported complexes that have a semibridging carbonyl group between two cobalt atoms.

(10) Klinger, J. R.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034. The asymmetry constant is defined as  $(D_2 - D_1)/D_1$  where  $D_1$  is the short and  $D_2$  the long metal-carbon bridge bond distance. These values are 0.560 and 0.571 Å for molecules IIA and IIB, respectively. The  $\theta$  angles, angle Co-C-O where the Co-C distance is  $D_1$ , are  $158(1)^\circ$  for IIA and  $161(1)^\circ$  for IIB. The infrared absorption frequency of the bridging carbonyl,  $1878\text{ cm}^{-1}$ , supports the conclusion that it is a two-electron donor.



**Figure 4.** First scan cyclic voltammogram of  $5 \times 10^{-4}$  M II in acetonitrile containing 0.20 M tetraethylammonium tetrafluoroborate at a hanging mercury drop electrode (electrode potential in V vs. Ag (0.10 N AgNO<sub>3</sub>), scan rate 200 mV s<sup>-1</sup>).

To our knowledge the previously reported FeCo<sub>2</sub> clusters are FeCo<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S),<sup>11</sup> HFeCo<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CR),<sup>12</sup> and FeCo<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-PR).<sup>13</sup> None of these clusters contain bridging carbonyl groups; however, since the last contains a bridging phosphorus atom, we can compare certain features of its structure with II. It is evident from Table III that the Fe-Co bond lengths are somewhat shorter in II relative to those reported for FeCo<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-PPh); the other values are similar.

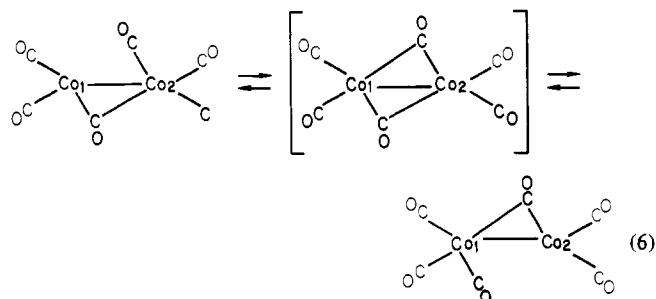
The structure of II is most similar to that reported for Co<sub>3</sub>(μ-CO)(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>,<sup>14</sup> here, the triangle of cobalt atoms has two virtually equal sides and one short side. A semi-bridging carbonyl is located on the short side with an asymmetrically edge bridging PPh<sub>2</sub> group below the trimetal plane and a symmetrically edge bridging PPh<sub>2</sub> group above the plane.

**Spectra.** The infrared spectrum of II in solution exhibits typical terminal carbonyl stretching absorptions at 2060, 2028, 2000, 1992, and 1975 cm<sup>-1</sup> and a weak absorption that is characteristic of a semi-bridging carbonyl at 1878 cm<sup>-1</sup> (Figure 2). The spectrum obtained in the solid state, as a KBr pellet, is virtually the same.

A series of <sup>13</sup>C NMR spectra was obtained as a function of temperature in THF-*d*<sub>8</sub> solution after <sup>13</sup>CO enrichment of II by exchange at 1 atm. The slow exchange-limit spectrum was obtained at -95 °C (Figure 3). We have assigned the semi-bridging carbonyl to the lowest field resonance. The terminal carbonyl assignments are based upon the exchange scheme given below and upon <sup>13</sup>C NMR spectra [ppm (relative intensity)] obtained at 67.88 MHz: 225.9 (1) C3; 213.3 (1) [d, *J*(CP) = 12 Hz] C7 or C8; 210.9 (1) [d, *J*(CP) = 27 Hz] C6; 210.6 (1) [d, *J*(CP) = 10 Hz] C7 or C8; 207.1 (1) C4 or C5; 203.7 (1) C4 or C5; 202.9 (1) C1 or C2; 201.7 (1) C1 or C2.

As the solution is warmed, four distinct processes occur which exchange the carbonyls over various sites in the molecule. These four processes consist of two "turnstile rotations", one on each cobalt atom, bridge-terminal exchange involving the six cobalt-bound carbonyls, and a final process that exchanges all eight carbonyls over all eight sites. At -62 °C, the carbonyls containing C3, C4, and C5 participate in a rapid turnstile rotation through the terminal and bridge sites on Co1 and produce the average resonance observed at 211.9 ppm

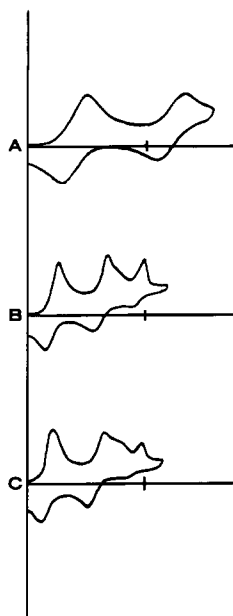
(3).<sup>15</sup> After being warmed to -35 °C, the carbonyl groups containing C6, C7, and C8 participate in a rapid turnstile rotation on Co2 and produce the average resonance observed at 211.1 ppm (3). At this temperature, the iron-bound carbonyls containing C1 and C2 begin to undergo site exchange and produce the average resonance at 202.4 ppm (2). We propose that the last observation results from the onset of bridge-terminal exchange among the cobalt-bound carbonyls. The most reasonable mechanism for this exchange process is the formation of an intermediate with two bridging carbonyl groups between the two cobalt atoms. This process should be facile due to the position of the "incipient semi-bridging" carbonyl discussed earlier. These two carbonyls could be either compensatory semi-bridging (eq 6) or symmetrically disposed



between the cobalt atoms. In either case, the intermediate would have a C<sub>2</sub> axis passing through the iron atom and bisecting the Co-Co bond. As this exchange rate becomes fast on the NMR time scale, the two iron-bound carbonyls become indistinguishable. Because the turnstile rotations occurring on each cobalt are already rapid at this temperature, the bridge-terminal exchange process provides a mechanism for exchange of all six cobalt-bound carbonyls over all six sites.<sup>16</sup> This result was observed on warming the sample to -15 °C; an average resonance at 211.5 ppm (6) was observed for all six cobalt-bound carbonyls. At 25 °C all eight carbonyl

- (11) Khattab, S. A.; Marko, L.; Bor, G.; Marko, B. *J. Organomet. Chem.* **1964**, *1*, 373. Stevenson, D. L.; Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6027.  
 (12) Epstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* **1979**, *18*, 942.  
 (13) Richter, F.; Beurich, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *166*, C5. Burt, J. C.; Schmid, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1385. Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 690.  
 (14) Burt, J. C.; Boese, R.; Schmid, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1387. The possibility that this compound is actually HCo<sub>3</sub>(μ-CO)(CO)<sub>6</sub>(μ-PPh<sub>2</sub>)<sub>2</sub> was not ruled out.

- (15) For a number of examples of this phenomenon, see: Aime, S.; Milone, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 183. It should be emphasized that although this mechanism is considered to be the most probable, it is not the only possibility; see: Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *Inorg. Chem.* **1975**, *14*, 511.  
 (16) There is a fundamental difference between the exchange mechanisms associated with each proposed intermediate. If the bridging carbonyl groups were symmetrically disposed, there would be equal probability of breaking any of the four cobalt-carbon bridge bonds in the exchange process. This would result in the exchange of carbonyl groups from terminal positions on one cobalt atom to terminal positions on the other via turnstile rotation. However, if the carbonyl groups were compensatory semi-bridging and only the two long cobalt-carbon bridge bonds were broken, complete transfer of carbonyl groups between cobalt atoms would not occur. The spectra do not allow a differentiation between these two possibilities; see: Adams, R. D.; Cotton, F. A. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackson, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 12. Also, see ref 9.



**Figure 5.** Oscilloscope tracings of first scan cyclic voltammograms of II under the conditions of Figure 4: A,  $x = 0.10 \text{ V cm}^{-1}$ ,  $y = 100 \mu\text{A cm}^{-1}$ , scan rate  $20 \text{ V s}^{-1}$ ; B, same as A except  $x = 0.20 \text{ V cm}^{-1}$ ; C,  $x = 0.20 \text{ V cm}^{-1}$ ,  $y = 200 \mu\text{A cm}^{-1}$ , scan rate  $100 \text{ V s}^{-1}$ . The first and second waves only were scanned in A; all waves were scanned in B and C.

resonances begin to coalesce to an average signal at 210.3 ppm (8). This process probably involves intermediates with bridging carbonyls between iron and cobalt. Further warming to  $45^\circ\text{C}$  produces a sharper average signal at 209.3 ppm, and subsequent cooling shows that all the observed processes are thermally reversible.

The  $^{31}\text{P}$  NMR spectrum of II in THF- $d_8$  solution at  $-55^\circ\text{C}$  consisted of two doublets,  $J(\text{PP}) = 88 \text{ Hz}$ , at 206 and 233 ppm, with respect to external  $\text{H}_3\text{PO}_4$ . On being warmed to  $45^\circ\text{C}$ , these resonances began to broaden. In toluene solution, it was possible to observe the reversible coalescence of these signals at  $75 \pm 10^\circ\text{C}$ . This observation allowed an approximate calculation of  $\Delta F^* = 14.4 \pm 0.5 \text{ kcal mol}^{-1}$  at this temperature for the carbonyl-exchange process that generates a  $\text{C}_2$  axis through the molecule.

**Electrochemistry.** Three one-electron reduction waves were observed for II in acetonitrile solution at  $-1.01$ ,  $-1.45$ , and  $-1.75 \text{ V}$  vs. a Ag ( $0.10 \text{ N AgNO}_3$ ) reference electrode.<sup>17</sup> In

(17) These potentials were observed at  $-0.68$ ,  $-1.20$ , and  $-1.45 \text{ V}$  vs. a saturated calomel reference electrode in acetonitrile.

cyclic voltammograms of II, taken at a scan rate of  $50$  to  $500 \text{ mV s}^{-1}$  (Figure 4), the first and third waves appear to be reversible and the second irreversible. After the scan rate was increased to  $20 \text{ V s}^{-1}$ , the second wave appeared to be reversible (Figure 5). Oscilloscope tracing A is of the first two waves only with  $x = 0.10 \text{ V cm}^{-1}$ . Tracing B is of all three waves with  $x = 0.20 \text{ V cm}^{-1}$ .<sup>18</sup> At a scan rate of  $100 \text{ V s}^{-1}$ , tracing C, a small new wave began to appear at  $-1.6 \text{ V}$  between the second and third waves. We interpret these data as follows: II is most probably reduced to a radical anion reversibly at  $-1.01 \text{ V}$ ; at  $-1.45 \text{ V}$ , the radical anion is reduced to a dianion capable of undergoing a reaction that is fast on the  $50$ – $500 \text{ mV s}^{-1}$  time scale. This reaction may be a structural rearrangement such as the breaking of a M–M bond or a simple protonation by traces of water in the solvent. At this time we cannot say what species undergo reduction in either the third reversible wave at  $-1.75 \text{ V}$  or the small wave observed at  $-1.6 \text{ V}$  at fast scan rates. Attempted oxidation of II in acetonitrile produced only one irreversible wave at  $+0.4 \text{ V}$  vs. a Ag ( $0.10 \text{ N AgNO}_3$ ) reference electrode.

Reduction of II in THF with sodium amalgam was followed by infrared spectroscopy (see Experimental Section). The changes in the metal carbonyl region indicated one or more intermediates were formed before the final limiting spectrum was obtained. It was possible to isolate a new, brown product from these solutions. Treatment of this material with  $\text{H}_3\text{PO}_4$  produced II in high yield, thus indicating a high degree of chemical reversibility. We are continuing to investigate the nature of these anions.

**Acknowledgment.** We wish to thank Dr. P. M. Henrichs, Mr. L. R. Church, and Mr. A. T. Spaugh, Jr., for obtaining the  $^{13}\text{C}$  NMR spectra, Dr. D. A. Payne for obtaining the cyclic voltammograms, and Dr. S. W. Polichnowski, Dr. C. A. Boye, Dr. T. H. Whitesides, and Professor J. R. Norton for valuable discussions.

**Registry No.** I, 41383-38-4; II, 77462-26-1;  $\text{Co}_2(\text{CO})_8$ , 10210-68-1.

**Supplementary Material Available:** Complete structure determination data, including tables of general temperature factor expressions, root-mean-square amplitudes of thermal vibration, bond distances and bond angles, least-squares planes, and intensity data (37 pages). Ordering information is given on any current masthead page.

- (18) The second and third waves appeared smaller than the previous wave in Figure 5B,C due to diffusion limiting effects. With rapid multiple scans, the first and second waves collapsed, while the third grew in size as expected.
- (19)  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ . Scattering factors were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV. Anomalous dispersion effects were included in  $F_c$ ; the values of  $\Delta f'$  and  $\Delta f''$  were those of: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **53**, 1891 (1970).

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## $(\eta^2\text{-Vinylsilane})\text{tetracarbonyliron Complexes}$

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The relatively stable title complexes  $[(\text{CH}_2=\text{CHSiMe}_2\text{Z})\text{Fe}(\text{CO})_4]$  ( $\text{Z} = \text{Me}, \text{Me}_3\text{Si}, \text{OEt}, \text{OPh}, \text{OH}, \text{Cl}, \text{F}, \text{N}_3$ ) have been prepared by reaction of the corresponding vinylsilanes with  $\text{Fe}_2(\text{CO})_9$  and/or by nucleophilic substitution of the chloride complex ( $\text{Z} = \text{Cl}$ ). Spectroscopic characterization is provided. Reactions of these complexes designed to prepare elusive  $(\eta^3\text{-1-silapropenyl})\text{tetra-}$  or  $\text{tricarbonyliron}$  species are described.

### Introduction

Although  $(\eta^4\text{-diene})\text{tricarbonyliron}$  complexes are quite prevalent, stable  $(\eta^2\text{-monoene})\text{tetracarbonyliron}$  complexes are

relatively rare. As a general rule, stability is accorded to only those  $\eta^2\text{-olefin-Fe}(\text{CO})_4$  complexes in which the coordinated double bond either (a) bears highly electronegative substitu-