

Binuclear Iron-Manganese Acetyl and Hydride Complexes from the Reactions of $\text{Cp}(\text{CO})_2\text{FePPh}_2$ with $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{HMn}(\text{CO})_5$

Richard P. Rosen,[†] Jeffrey B. Hoke,[†] Robert R. Whittle,[†] Gregory L. Geoffroy,^{*†}
John P. Hutchinson,[‡] and Jon A. Zubieta[‡]

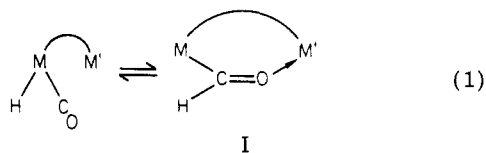
Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and State University of New York at Albany, Albany, New York 12222

Received November 7, 1983

The new heterobimetallic bridging acetyl complex $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_4$ (**1**) has been prepared by the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with $\text{PPh}_2\text{FeCp}(\text{CO})_2$. It has been spectroscopically and structurally characterized. Complex **1** crystallizes in the space group $P\bar{1}$ with $a = 11.485$ (4) Å, $b = 12.989$ (4) Å, $c = 16.932$ (5) Å, $\alpha = 68.22$ (2)°, $\beta = 87.17$ (2)°, $\gamma = 88.88$ (2)°, $V = 2342$ (1) Å³, and $Z = 4$. The structure has been refined to $R = 0.044$ and $R_w = 0.042$ for the 3353 reflections with $I > 3\sigma(I)$. The acetyl ligand bridges the Fe and Mn centers with the acetyl carbon attached to Fe and the oxygen bound to Mn. The nonbonded metals ($\text{Fe}\cdots\text{Mn} = 3.718$ Å) are also bridged by the $\mu\text{-PPh}_2$ ligand. The chemistry of complex **1** has been examined with HBF_4 , $[(\text{CH}_3)_3\text{O}]\text{BF}_4$, $[\text{Ph}_3\text{C}]\text{BF}_4$, H_2 , PPh_2Me , and MeLi , and these reactions are discussed.

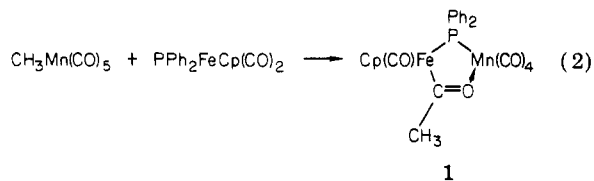
Reaction of $\text{HMn}(\text{CO})_5$ with $\text{PPh}_2\text{FeCp}(\text{CO})_2$ gives the bridging hydride complex $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_4$ (**3**), which has also been structurally characterized. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.795$ (4) Å, $b = 13.931$ (2) Å, $c = 14.497$ (4) Å, $\beta = 102.08$ (3)°, $V = 2132$ (2) Å³, and $Z = 4$. The structure has been refined for the 2412 reflections with $I > 2\sigma(I)$ to $R = 0.057$ and $R_w = 0.063$. The Fe and Mn atoms are separated by 2.806 (1) Å and are bridged by the hydride and the $\mu\text{-PPh}_2$ ligand. The Fe atom is further coordinated by the Cp ligand and one CO, and Mn has four additional CO ligands.

Transition-metal formyl complexes are believed to be key intermediates in the homogeneous reduction of carbon monoxide by hydrogen.¹ However, thermodynamic data² and numerous experimental results^{1a} show that formyl complexes are unstable with respect to the corresponding metal carbonyl hydrides. One potential method for stabilizing the formyl ligand and thus for shifting the unfavorable metal carbonyl hydride \rightleftharpoons metal formyl equilibrium to the right is via coordination of the formyl oxygen to a second metal as in eq 1. While there are no reported

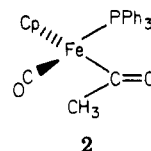


polynuclear formyl complexes of precisely type I, there are some close analogues.³ A large number of bridging acyl complexes of type I are known, but the chemistry of these complexes has been little investigated.⁴

In the course of our studies of polynuclear formyl and acyl complexes⁵ we have prepared the new heterobimetallic μ -acetyl complex $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-PPh}_2)(\mu\text{-C}(\text{O})\text{CH}_3)\text{Mn}(\text{CO})_4$ (**1**) ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) by the reaction shown in eq 2. Complex



1 can be viewed as a derivative of the well-studied terminal acetyl complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{C}(\text{O})\text{CH}_3$ (**2**), and thus it affords the opportunity to compare the chemistry of bridging and terminal acetyl ligands in complexes of sim-



ilar composition. Such experiments are described herein along with the complete spectroscopic and structural characterization of **1**.

Given the successful synthesis of the bridging acetyl complex **1** via the reaction of eq 2, we then wondered whether a bridging formyl complex analogous to **1** would be produced from the reaction of $\text{HMn}(\text{CO})_5$ and $\text{PPh}_2\text{FeCp}(\text{CO})_2$. However, we find that such a complex

(1) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(2) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

(3) (a) Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 2643. (b) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. F. *Ibid.* **1979**, *101*, 218. (c) Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1981**, *103*, 1650.

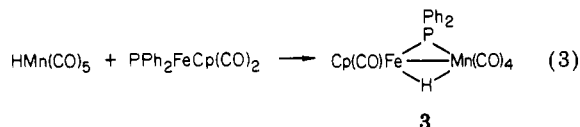
(4) (a) Fischer, E. O.; Kiener, V.; Bunbury, D. St. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *Chem. Commun.* **1968**, 1378. (b) Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279. (c) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *23*, 215. (d) *Ibid.* **1972**, *42*, 447. (e) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2681. (f) Blickensderfer, J. R.; Knobler, C. B.; Kaesz, H. D. *Ibid.* **1975**, *97*, 2686. (g) Merlino, S.; Montagnoli, G.; Braca, G.; Sbrana, G. *Inorg. Chim. Acta* **1978**, *27*, 233. (h) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209. (i) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360. (j) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109. (k) Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91. (l) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56. (m) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (n) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *Ibid.* **1982**, *104*, 4679. (o) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189. (p) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2897. (q) Fischer, E. O.; Weiss, K.; Kreiter, C. G. *Chem. Ber.* **1974**, *107*, 3554. (r) Weiss, K.; Fischer, E. O. *Ibid.* **1976**, *109*, 1120. (s) Sunkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227.

(5) (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Ibid.* **1983**, *105*, 1069.

[†]The Pennsylvania State University.

[‡]State University of New York at Albany.

does not result from this combination of reagents, but instead the bridging hydride complex **3** is produced (eq 3). The synthesis of **3**, its spectroscopic and structural



characterization, and some aspects of its derivative chemistry, including attempts to force CO insertion to give a bridging formyl complex, are presented herein.

Experimental Section

General. The complexes $\text{CH}_3\text{Mn}(\text{CO})_4(\text{PPh}_3)$,⁶ $\text{PPh}_2\text{FeCp}(\text{CO})_2$,⁷ and $[\text{FeCp}(\text{CO})_2]_2$,⁸ were prepared by published procedures. The reagents $[\text{Ph}_3\text{C}]\text{BF}_4$, $\text{HBF}_4 \cdot \text{OEt}_2$ (Aldrich Chemical Corp.), $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ (Alfa Chemical Co.), $\text{Mn}_2(\text{CO})_{10}$, PMePh_2 (Strem Chemical Corp.), and ^{13}CO , 90% (Monsanto Research Corp., Mound Facility) were obtained from commercial sources. Solvents used were dried by standard procedures, and all manipulations were carried out under a purified N_2 atmosphere using normal vacuum and Schlenk line techniques.⁹ ^{13}CO enriched $\text{PPh}_2\text{FeCp}(\text{CO})_2$ (~25%) was prepared from enriched $[\text{FeCp}(\text{CO})_2]_2$, itself prepared from irradiating (366 nm, toluene, 48 h) $[\text{FeCp}(\text{CO})_2]_2$ under 1 atm of ^{13}CO (90%).

IR spectra were obtained on a Perkin-Elmer 580 grating infrared spectrophotometer or an IBM/32 Fourier-transform infrared spectrophotometer, utilizing 0.5-mm NaCl cells for solution samples and KBr disks for solid samples. NMR spectra were recorded on Bruker WP-200, Bruker WM-360, and JEOL PFT-100 spectrometers. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 with downfield chemical shifts reported as positive. ^1H and ^{13}C NMR spectra were externally referenced to tetramethylsilane. $\text{Cr}(\text{acac})_3$ (1.0 mol %) was added to ^{13}C NMR samples as a shiftless relaxation agent.¹⁰ Field-desorption (FD) mass spectra were obtained by R. J. Hale at Tennessee Eastman Company, Kingsport, TN. Electron-impact (EI) mass spectra were recorded on an AEI-MS9 mass spectrometer operated in the electron-impact mode with a source voltage of 70 eV and probe temperatures in the 100–200 °C range.

Preparation of $\text{CH}_3\text{Mn}(\text{CO})_5$. The complex $\text{CH}_3\text{Mn}(\text{CO})_5$ ¹¹ was prepared by the addition of 2.0 mL of Na/K alloy to a tetrahydrofuran (THF, ~100 mL) solution of $\text{Mn}_2(\text{CO})_{10}$ (5.19 g, 13.3 mmol). After stirring for 1 h at room temperature, the THF was removed in vacuo and ~50 mL of Et_2O was added. Iodomethane (1.73 mL, 27.8 mmol) was then added, and the solution was allowed to stir for ~2 h. The Et_2O was removed in vacuo, and the $\text{CH}_3\text{Mn}(\text{CO})_5$ was sublimed (22 °C, 10^{-5} mmHg) to give 2.5 g of $\text{CH}_3\text{Mn}(\text{CO})_5$ in 44.8% yield. ^{13}CO -enriched (~25%) $\text{CH}_3\text{Mn}(\text{CO})_5$ was prepared by a similar procedure using enriched $\text{Mn}_2(\text{CO})_{10}$, itself prepared by irradiation (366 nm, toluene, 24 h) of $\text{Mn}_2(\text{CO})_{10}$ under 1 atm of ^{13}CO (90%).

Preparation of $\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_5\text{Cp}$ (1**).** A 20-mL THF solution of $\text{CH}_3\text{Mn}(\text{CO})_5$ (0.87 g, 4.14 mmol) was added dropwise to a 20-mL THF solution of $\text{FeCp}(\text{PPh}_2)(\text{CO})_2$ (1.5 g, 4.14 mmol) at 22 °C. The resultant red solution was stirred for 48 h, the solvent was removed in vacuo, and the reaction mixture was extracted with CH_2Cl_2 . Chromatography on a preparative thin-layer chromatography plate using silica gel as the support and 30% $\text{CH}_2\text{Cl}_2/70\%$ hexane as the eluant gave a faint yellow band of $\text{Mn}_2(\text{CO})_{10}$, an unidentified yellow band, a purple band of $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_5$, and a large orange band containing $\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_5\text{Cp}$ (**1**). Removal of

the latter from the plate, dissolution of the complex into CH_2Cl_2 , filtration to remove the SiO_2 , and evaporation of solvent gave **1** as a red oil in ~17% yield (0.38 g, 0.70 mmol). **1**: IR ν_{CO} (hexane), 2080 (m), 2002 (s), 1993 (s), 1950 (s) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (22 °C, benzene- d_6) δ 106.4 (s); ^1H NMR (22 °C, benzene- d_6) δ 6.9–7.5 (Ph) 4.1 (s, 5 H, Cp), 2.5 (s, 3 H, C-CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (22 °C, benzene/benzene- d_6) δ 319.3 (d, C(O)CH₃, $J_{^{13}\text{C}-^{31}\text{P}} = 11.9$ Hz), 220.1 (s, br), 218.7 (d, $J_{^{13}\text{C}-^{31}\text{P}} = 19.0$ Hz), 213.3 (s, br, M-CO), 212.2 (s, br, M-CO), 86.1 (s, Cp), 51.3 (s, C(O)CH₃).

Preparation of $[\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_5]$ (3**).** $\text{FeCp}(\text{PPh}_2)(\text{CO})_2$ (0.25 g, 0.69 mmol) in THF (20 mL) was added dropwise via a transfer needle to a THF solution (50 mL) of $\text{HMn}(\text{CO})_5$, the latter prepared by in situ acidification of $[\text{Li}[\text{Mn}(\text{CO})_5]^{12}]$ (0.56 mmol) at 22 °C. The resultant red solution was stirred at 22 °C for 24 h, the solvent removed in vacuo, and the reaction mixture extracted with methylene chloride. Chromatography was conducted on a preparative-scale thin-layer chromatography plate using silica gel as the support and 30% $\text{CH}_2\text{Cl}_2/70\%$ hexane as the eluant. An unidentified yellow band eluted first, followed by a large purple band containing $[\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_5]$ (**3**). The latter band was removed from the plate, the complex dissolved into CH_2Cl_2 , and the solution filtered to remove the SiO_2 . Evaporation of solvent and recrystallization with hexane gave **3** as purple microcrystals in 35% yield (0.099 g, 0.196 mmol). Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{FeMnO}_5$: C, 52.62; H, 3.21. Found: C, 52.84; H, 3.40. **3**: IR ν_{CO} (hexane), 2069 (s), 1995 (s), 1974 (s), 1952 (s) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (22 °C, benzene/benzene- d_6) δ 176.7 (s, br); ^1H NMR (22 °C, benzene- d_6) δ 6.9–7.8 (Ph), 4.0 (s, Cp), -18.1 (d, H, $J_{\text{H}-^{31}\text{P}} = 34.9$ Hz); MS (EI), m/z 502 (M^+), 474 ($\text{M}^+ - \text{CO}$), 418 ($\text{M}^+ - 3\text{CO}$), 390 ($\text{M}^+ - 4\text{CO}$), 362 ($\text{M}^+ - 5\text{CO}$).

Reaction of **1 with PMePh_2 .** Methyl-diphenylphosphine (0.03 mL, 0.16 mmol) was added dropwise via syringe to a THF solution (15 mL) of **1** (0.085 g, 0.16 mmol) at 22 °C. This solution was stirred for 24 h as the color changed from red to orange. The solvent was removed in vacuo and the reaction mixture extracted with 40% $\text{CH}_2\text{Cl}_2/60\%$ hexane. Chromatography was conducted on a silica gel column using 40% $\text{CH}_2\text{Cl}_2/60\%$ hexane as the eluant. A faint yellow band of an unidentified compound eluted first, followed by an orange band containing $\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_4(\text{PMePh}_2)\text{Cp}$ (**4**). Evaporation of solvent gave **4** as an orange powder in 62.2% yield (0.074 g, 0.10 mmol). **4**: IR ν_{CO} (hexane) 2020 (m), 1950 (s), 1927 (w), 1902 (m) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (22 °C, benzene/benzene- d_6) δ 112.7 (d, $J_{^{31}\text{P}-^{31}\text{P}} = 34.5$ Hz), 44 (s, br); ^1H NMR (22 °C, benzene- d_6) δ 6.9–8.2 (Ph), δ 4.18 (s, Cp, 5 H), 2.55 (s, C(O)CH₃, 3 H), 1.81 (d, PCH_2Ph_2 , $J_{\text{H}-^{31}\text{P}} = 8.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene/benzene- d_6) δ 315 (d, C(O)CH₃, $J_{^{13}\text{C}-^{31}\text{P}} = 6.6$ Hz), 86.1 (s, Cp), 50.7 (s, CH₃), 217.0 (s, br, M-CO), 219 (d, M-CO, $J_{^{13}\text{C}-^{31}\text{P}} = 18.6$ Hz), 217 (s, br, M-CO); MS (FD) m/z 716 (M^+).

Reaction of **1 with MeLi.** MeLi (1.3 M, 0.15 mL, 0.20 mmol) was added dropwise via syringe to a 20-mL THF solution of **1** (0.069 g, 0.13 mmol), and the solution was allowed to stir at room temperature for 0.5 h. A deepening of the color was observed, and an IR spectrum after 0.5 h showed new IR bands at 1996 (m), 1935 (s, br), 1960 (s), 1871 (s), 1540 (m) cm^{-1} . The THF was concentrated to 2 mL and ~20 mL of petroleum ether added to deposit $[\text{Li}[\text{FeMn}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-PPh}_2)(\text{CO})_4\text{Cp}(\text{C}(\text{O})\text{CH}_3)] \cdot 2\text{THF}$ (**6**) as a red oil. **6**: IR ν_{CO} (THF) 1996 (m), 1935 (s, br), 1900 (s), 1871 (s), 1540 (m) cm^{-1} ; ^1H NMR (22 °C, acetone- d_6) δ 7.3–7.4 (Ph) 4.4 (s, Cp, 5 H), 2.9 (s, C(O)CH₃, 3 H), 2.5 (s, C(O)CH₃, 3 H), 3.6, 1.8 (THF); $^{13}\text{C}\{^1\text{H}\}$ NMR (22 °C, acetone- d_6) δ 323.8 (d, $\mu\text{-C}(\text{O})\text{CH}_3$, $J_{^{13}\text{C}-^{31}\text{P}} = 12.2$ Hz), 309.7 (d, C(O)CH₃, $J_{^{13}\text{C}-^{31}\text{P}} = 9.8$ Hz), 87.2 (s, Cp), 219.9 (d, M-CO, $J_{^{13}\text{C}-^{31}\text{P}} = 20.0$ Hz), 210 (br, s, M-CO), 208.5 (s, M-CO), 207.4 (s, M-CO); $^{31}\text{P}\{^1\text{H}\}$ NMR (22 °C, acetone- d_6) δ 93.3 (s).

Thermolysis of **1.** A sample of **1** (0.139 g, 0.256 mmol) was dissolved in 25 mL of THF and allowed to reflux for 4 h. The THF was removed in vacuo and the reaction mixture dissolved in a minimal amount of CH_2Cl_2 . Chromatography was conducted on silica gel using 10% $\text{CH}_2\text{Cl}_2/90\%$ hexane as the eluant and with the percentage of CH_2Cl_2 gradually increased as the separation progressed. Seven products were isolated, all in very low

(6) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 5043.

(7) Burckett-St. Laurent, J. C. T. R.; Haines, R. J.; Nolte, C. R.; Steen, N. D. C. T. *Inorg. Chem.* **1980**, *19*, 577.

(8) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.

(9) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(10) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

(11) King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1, p 147.

(12) Gladysz, J. A.; Tam, W.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163.

Table I. Experimental Details of the X-ray Diffraction Study of $\text{FeMn}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_2$ (1) and $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_2$ (3)

	1	3
(A) Crystal Parameters		
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a , Å	11.485 (4)	10.795 (4)
b , Å	12.989 (4)	13.931 (2)
c , Å	16.932 (5)	14.497 (4)
α , deg	68.22 (2)	
β , deg	87.17 (2)	102.08 (3)
γ , deg	88.88 (2)	
V , Å ³	2342 (1)	2132 (2)
Z	4	4
d_{calcd} , g cm ⁻³	1.542	1.564
T , °C	21	22 (2)
abs coeff., cm ⁻¹	12.1	13.5
(B) Measurement of Intensity Data		
diffractometer	Nicolet R3M	Enraf-Nonius CAD4
radiation	Mo K α , $\lambda = 0.71073$ Å	Mo K α , $\lambda = 0.71073$ Å
monochromator	graphite crystal	graphite crystal
scan type	coupled $\theta-2\theta$	coupled $\theta-2\theta$
scan speed	variable from 7–30° min ⁻¹ in θ	1.0–3.5° min ⁻¹
scan range	symmetrical, over $[1.0 + \Delta(\alpha_1 - \alpha_2)]$	$(1.4^\circ + 0.347 \tan \theta)^\circ$ below and above K α_1 and K α_2 , respectively
reflcs measd	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
std. reflns	3 measd after every 197	3 measd every h
data limits	$3^\circ < 2\theta \leq 45^\circ$	$2.8^\circ < 2\theta \leq 46.14^\circ$
obsd data	3353 [$I > 3\sigma(I)$]	2412 [$I > 2\sigma(I)$]
R	0.0436	0.0571
R_w	0.0417	0.0629
esd	1.223	2.552
drift corrections		
empirical		1.000–1.010
anisotropic		0.978–1.054

yield, four of which were characterized. A yellow band of an unidentified compound eluted first, followed by a purple band of 3, an orange band of $\text{MnH}(\text{CO})_3(\text{PMePh}_2)_2$,¹³ a yellow unidentified band, a green unidentified band, an orange band of 4, and finally a red band containing $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$.

Attempted Reaction of 1 with $[\text{Ph}_3\text{C}]\text{BF}_4$, HBF_4 , $[(\text{C}-\text{H}_3)_3\text{O}]\text{BF}_4$, and H_2 . In separate experiments compound 1 was stirred with $[\text{Ph}_3\text{C}]\text{BF}_4$ (1.1 equiv, CH_2Cl_2 , 22 °C, 12 h), $\text{HBF}_4\cdot\text{OEt}_2$ (1 equiv, THF, 22 °C, 2 days), $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ (1 equiv, CH_2Cl_2 , 22 °C, 500 psi of CO, 5 h), and H_2 (50 psi, 22 °C, 24 h), but IR and ¹H NMR spectral monitoring indicated that in each case no reaction occurred.

Attempted Reaction of 3 with CO. A 10-mL THF solution of 0.01 M 3 was placed in a Parr Model 4753 stainless steel reactor vessel with 4316 Gauge Block assembly and charged with 1000 psi of CO. The reaction was allowed to stir overnight at room temperature. The IR spectrum of the solution recorded after releasing the CO pressure showed only bands due to 3. Similar results were obtained when the reaction was conducted at 55 °C.

X-ray Diffraction Study of 1. Slow evaporation of a petroleum ether solution of 1 led to the formation of red crystals suitable for an X-ray crystallographic study. Pertinent crystal and intensity data are collected in Table I. All calculations were performed using an in-house Syntex SHELXTL structure-determination system at the State University of New York at Albany. The analytical scattering factors compiled by Cromer and Weber,^{14a} the absorption coefficients in terms of 10^{-24} cm²,^{14b} and both real and imaginary components of anomalous dispersion were used.^{14c} The positions of the heavy atoms were determined using the direct-methods program SOLV which indicated the presence of two molecules per asymmetric unit. The location of all subsequent atoms was accomplished through a series of difference-Fourier maps.

Refinement of all positional and anisotropic thermal parameters (with hydrogen atoms included in constrained, delayed positions with thermal parameters set to 1.2 times the attached carbon thermal parameter) led to convergence with $R = 0.0436$ and $R_w = 0.0417$ and "goodness of fit" = 1.223. R and R_w are defined as $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. No unusual features were observed on a final difference Fourier map. No significant features were observed as a function of parity group, $(\sin \theta) / \lambda$, ideality, or parity of Miller indices. The weighting scheme was thus deemed satisfactory. Final positional parameters for molecules 1 and 2 are listed in Tables II and III. Relevant bond distances and bond angles are set out in Tables IV and V. Tables of thermal parameters and the structure factors are given as supplementary material.

X-ray Diffraction Study of 3. Dark red crystals of 3 were grown by slow cooling to 0 °C of a hot hexane solution of the complex. A crystal measuring 0.27 × 0.36 × 0.49 mm was mounted in an arbitrary orientation on a glass fiber which was then fixed into an aluminum pin and mounted onto a eucentric goniometer. Diffraction data were collected on an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP 8a computer at the Pennsylvania State University. The Enraf-Nonius program SEARCH was employed to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide cell dimensions.¹⁵ Details of the data collection and reduction procedures have been described previously.¹⁶ Pertinent crystal and intensity data are listed in Table I.

Iron, manganese, and phosphorus atoms were located by Patterson-heavy-atom techniques. The coordinates of the remaining non-hydrogen atoms and the hydride position were determined by successive least-squares refinements and difference Fourier maps. Phenyl hydrogens were fixed at idealized positions

(13) Laing, M.; Singleton, E.; Kruger, G. J. *Organomet. Chem.* 1973, 54, C30.

(14) (a) Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974, Vol. IV, pp 99–101. (b) *Ibid.*; pp 149–150. (c) *Ibid.*; pp 55–60.

(15) All programs used in this study are part of the Enraf-Nonius Structure Determination Package (SDP plus, version 1); Enraf-Nonius: Delft, Holland, 1982.

(16) Horrocks, W. DeW.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.* 1982, 21, 3265.

Table II. Atomic Positional Parameters for Molecule 1 of $[\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-C}(\text{O})\text{Me})(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$

atom	x	y	z	atom	x	y	z
Fe1	0.7111 (1)	0.7367 (1)	0.3076 (1)	C12	0.9650 (7)	0.5933 (7)	0.2278 (5)
Mn1	0.9291 (1)	0.7281 (1)	0.1403 (1)	C13	1.0822 (6)	0.7599 (7)	0.1248 (4)
P1	0.8902 (2)	0.7972 (1)	0.2519 (1)	C14	0.9051 (7)	0.8600 (7)	0.0500 (5)
O1B	0.7538 (4)	0.7097 (4)	0.1494 (3)	C15	0.9356 (7)	0.6540 (7)	0.0653 (5)
O11	0.7590 (5)	0.5034 (4)	0.3660 (3)	C16(Me1)	0.5551 (6)	0.7097 (7)	0.1787 (5)
O12	0.9956 (5)	0.5150 (5)	0.2776 (4)	C101	0.5543 (8)	0.821 (1)	0.3146 (6)
O13	1.1786 (4)	0.7821 (5)	0.1111 (3)	C102	0.6447 (9)	0.8847 (7)	0.3140 (6)
O14	0.8935 (5)	0.9374 (5)	-0.0096 (4)	C103	0.7063 (8)	0.834 (1)	0.3837 (7)
O15	0.9430 (7)	0.6081 (6)	0.0199 (4)	C104	0.658 (1)	0.7317 (9)	0.4308 (5)
C1B	0.6786 (6)	0.7201 (5)	0.2028 (4)	C105	0.5606 (8)	0.7231 (8)	0.3841 (8)
C11	0.7451 (6)	0.5997 (6)	0.3420 (4)	C111	0.9024 (5)	0.9493 (5)	0.2177 (4)

Table III. Atomic Positional Parameters for Molecule 2 of $[\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-C}(\text{O})\text{Me})(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$

atom	x	y	z	atom	x	y	z
Fe2	0.5451 (1)	0.2832 (1)	0.3197 (1)	C22	0.3109 (7)	0.5087 (6)	0.2206 (5)
Mn2	0.3468 (1)	0.4345 (1)	0.1474 (1)	C23	0.1935 (7)	0.4093 (6)	0.1494 (5)
P2	0.3833 (2)	0.2623 (1)	0.2593 (1)	C24	0.3681 (7)	0.3696 (6)	0.0659 (4)
O2B	0.5227 (4)	0.4447 (4)	0.1528 (3)	C25	0.3415 (7)	0.5695 (7)	0.0581 (5)
O21	0.4604 (5)	0.4584 (4)	0.3746 (4)	C26(Me2)	0.1711 (6)	0.4208 (6)	0.1835 (5)
O22	0.0958 (5)	0.3921 (5)	0.1523 (4)	C201	0.5433 (7)	0.1441 (6)	0.4370 (4)
O23	0.3733 (5)	0.3349 (4)	0.0141 (3)	C202	0.5755 (6)	0.1101 (5)	0.3698 (4)
O24	0.3323 (5)	0.6516 (5)	0.0046 (4)	C203	0.6787 (6)	0.1651 (6)	0.3290 (5)
O25	0.2782 (6)	0.5604 (5)	0.2580 (4)	C204	0.7089 (7)	0.2337 (6)	0.3725 (5)
C2B	0.5898 (6)	0.3904 (6)	0.2094 (4)	C205	0.6257 (7)	0.2239 (6)	0.4371 (5)
C21	0.4900 (6)	0.3893 (6)	0.3492 (4)	C211	0.2655 (6)	0.2026 (5)	0.3398 (4)

Table IV. Selected Bond Distances (Å) in $[\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-C}(\text{O})\text{Me})(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$

Molecule 1			
Fe1...Mn1	3.718 (1)	Mn1-C13	1.799 (7)
Fe1-P1	2.249 (2)	Mn1-C14	1.851 (7)
Fe1-C18	1.919 (8)	Mn1-C15	1.854 (11)
Fe1-C11	1.698 (8)	P1-C111	1.847 (7)
Fe1-C101	2.108 (10)	P1-C121	1.849 (7)
Fe1-C102	2.093 (10)	C1B-O1B	1.262 (9)
Fe1-C103	2.112 (15)	C1B-Me1	1.518 (10)
Fe1-C104	2.112 (15)	C11-O11	1.173 (9)
Fe1-C105	2.078 (11)	C12-O12	1.117 (9)
Mn1-P1	2.395 (2)	C13-O13	1.140 (8)
Mn1-O1B	2.024 (5)	C14-O14	1.141 (9)
Mn1-C12	1.881 (7)	C15-O15	1.134 (13)

Molecule 2			
Fe2...Mn2	3.713 (1)	Mn2-C24	1.793 (8)
Fe2-P2	2.234 (2)	Mn2-C25	1.870 (9)
Fe2-C2B	1.923 (6)	Mn2-C22	1.845 (7)
Fe2-C21	1.729 (9)	P2-C211	1.835 (6)
Fe2-C201	2.132 (6)	P1-C221	1.843 (8)
Fe2-C202	2.117 (6)	C2B-O2B	1.249 (8)
Fe2-C203	2.119 (8)	C2B-Me2	1.522 (9)
Fe2-C204	2.109 (8)	C21-O21	1.169 (11)
Fe2-C205	2.102 (8)	C22-O22	1.130 (12)
Mn2-P2	2.380 (2)	C23-O23	1.144 (16)
Mn2-O2B	2.036 (5)	C24-O24	1.124 (16)
Mn2-C23	1.859 (10)	C25-O25	1.121 (9)

Table V. Selected Bond Angles (deg) in $[\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-C}(\text{O})\text{Me})(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$

Molecule 1			
P1-Fe1-C18	88.5 (2)	O18-Mn1-C13	173.8 (3)
P1-Fe1-C11	95.7 (2)	O1B-Mn1-C14	86.5 (3)
P1-Fe1-C101	132.4 (3)	O1B-Mn1-C15	88.4 (3)
P1-Fe1-C102	98.4 (3)	C12-Mn1-C13	88.7 (3)
P1-Fe1-C103	92.7 (3)	C12-Mn1-C14	175.4 (4)
P1-Fe1-C104	120.3 (3)	C12-Mn1-C15	88.3 (4)
P1-Fe1-C105	156.8 (4)	C13-Mn1-C14	87.4 (3)
C18-Fe1-C11	84.9 (3)	C13-Mn1-C15	93.1 (4)
C18-Fe1-C101	94.8 (4)	C14-Mn1-C15	89.5 (4)
C18-Fe1-C102	112.6 (4)	Fe1-P1-Mn1	106.4 (1)
C18-Fe1-C103	149.7 (3)	Fe1-P1-C111	111.8 (2)
C18-Fe1-C104	151.1 (4)	Fe1-P1-C121	116.1 (2)
C18-Fe1-C105	111.5 (4)	Mn1-P1-C111	114.3 (2)
P1-Mn1-O1B	82.5 (2)	Mn1-P1-C121	107.7 (3)
P1-Mn1-C12	85.7 (3)	C111-P1-C121	101.7 (3)
P1-Mn1-C13	96.8 (3)	C1B-O1B-Mn1	131.0 (5)
P1-Mn1-C14	97.1 (3)	Fe1-C1B-O1B	125.7 (5)
P1-Mn1-C15	168.3 (3)	Fe1-C1B-Me1	122.0 (5)
O1B-Mn1-C12	97.4 (3)	Me1-C1B-O1B	112.2 (7)

Molecule 2			
P2-Fe2-C2B	85.6 (2)	O2B-Mn2-C23	173.6 (3)
P2-Fe2-C21	95.1 (3)	O2B-Mn2-C24	90.2 (3)
P2-Fe2-C201	103.8 (2)	O2B-Mn2-C25	91.9 (3)
P2-Fe2-C202	91.8 (2)	C22-Mn2-C23	88.2 (4)
P2-Fe2-C203	116.0 (2)	C22-Mn2-C24	94.2 (3)
P2-Fe2-C204	154.4 (3)	C22-Mn2-C15	87.0 (4)
P2-Fe2-C205	141.2 (2)	C23-Mn2-C24	87.3 (4)
C2B-Fe2-C21	89.4 (3)	C23-Mn2-C25	173.0 (3)
C2B-Fe2-C201	163.3 (3)	C24-Mn2-C25	88.0 (4)
C2B-Fe2-C202	129.0 (3)	Fe2-P2-Mn2	107.1 (1)
C2B-Fe2-C203	98.6 (3)	Fe2-P2-C211	110.9 (2)
C2B-Fe2-C204	101.4 (3)	Fe2-P2-C221	114.1 (2)
C2B-Fe2-C205	133.2 (3)	Mn2-P2-C211	117.7 (2)
P2-Mn2-O2B	80.0 (1)	Mn2-P2-C221	105.7 (2)
P2-Mn2-C22	94.1 (2)	C211-P2-C221	101.4 (3)
P2-Mn2-C23	93.9 (2)	C2B-O2B-Mn2	130.3 (4)
P2-Mn2-C24	91.3 (2)	Fe2-C2B-O2B	126.5 (5)
P2-Mn2-C25	171.8 (3)	Fe2-C2B-Me2	121.2 (5)
O2B-Mn2-C22	95.1 (3)	Me2-C2B-O2B	112.3 (5)

(C-H bond length 0.97 Å) with fixed isotropic temperature factors of $B = 5.0 \text{ \AA}^2$. In the final cycle, least-squares convergence was achieved upon refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms, and the positional

Table VI. Table of Positional Parameters and Their Estimated Standard Deviations for $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_5$ (3)

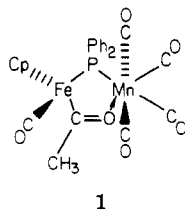
atom	x	y	z	B, Å ² ^a
Fe	0.7039 (1)	0.15963 (8)	0.45621 (8)	3.50 (2)
Mn	0.6763 (1)	0.35904 (8)	0.43343 (8)	3.19 (2)
P	0.5860 (2)	0.2361 (1)	0.3393 (1)	3.25 (4)
O1	0.5065 (6)	0.1222 (5)	0.5585 (5)	6.6 (2)
O2	0.4542 (6)	0.3622 (6)	0.5246 (5)	6.9 (2)
O3	0.8000 (6)	0.4802 (4)	0.5939 (4)	5.4 (2)
O4	0.5730 (7)	0.5141 (5)	0.3022 (5)	6.3 (2)
O5	0.9138 (6)	0.3608 (5)	0.3594 (5)	5.9 (2)
C1	0.5848 (9)	0.1395 (6)	0.5168 (6)	4.6 (2)
C2	0.5375 (8)	0.3597 (6)	0.4893 (6)	4.3 (2)
C3	0.7546 (8)	0.4318 (6)	0.5332 (6)	3.9 (2)
C4	0.6134 (8)	0.4552 (6)	0.3541 (6)	4.2 (2)
C5	0.8228 (8)	0.3577 (6)	0.3859 (6)	4.3 (2)
C1P	0.857 (1)	0.0841 (7)	0.5370 (8)	6.8 (3)
C2P	0.9005 (8)	0.1425 (7)	0.4752 (8)	5.9 (3)
C3P	0.843 (1)	0.1170 (7)	0.3830 (7)	6.2 (3)
C4P	0.762 (1)	0.0412 (7)	0.3904 (7)	6.2 (3)
C5P	0.765 (1)	0.0212 (6)	0.4834 (7)	5.5 (2)
C10	0.4117 (7)	0.2249 (6)	0.3155 (5)	3.7 (2)
C11	0.3552 (8)	0.1371 (7)	0.3204 (6)	5.0 (2)
C12	0.2225 (9)	0.1300 (8)	0.2949 (7)	6.6 (3)
C13	0.1504 (9)	0.2097 (9)	0.2681 (7)	6.7 (3)
C14	0.2053 (9)	0.2965 (8)	0.2653 (8)	6.4 (3)
C15	0.3362 (8)	0.3045 (7)	0.2893 (6)	5.0 (2)
C20	0.6151 (7)	0.2199 (5)	0.2215 (6)	3.3 (2)
C21	0.6837 (8)	0.2824 (6)	0.1785 (6)	4.2 (2)
C22	0.7117 (8)	0.2647 (6)	0.0921 (6)	4.5 (2)
C23	0.6700 (8)	0.1816 (6)	0.0448 (6)	4.3 (2)
C24	0.6003 (8)	0.1185 (6)	0.0846 (6)	4.2 (2)
C25	0.5737 (8)	0.1352 (6)	0.1717 (6)	3.9 (2)
H	0.723 (7)	0.261 (5)	0.504 (5)	5.0

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{1}{3} [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

parameters of the hydride atom (fixed thermal parameter of $B = 5.0 \text{ \AA}^2$). The structure converged to $R = 0.057$ and $R_w = 0.063$ using unit weights. Final positional parameters are listed in Table VI and relevant bond distances and angles are summarized in Table VII. Tables of thermal parameters, least-squares planes, and structure factors are given in the supplementary material.

Results

Preparation of $\text{FeMn}(\mu\text{-PPh}_2)(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_5\text{Cp}$ (1). Complex 1 was isolated in modest yield (~20%) after workup of the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with $\text{PPh}_2\text{FeCp}(\text{CO})_2$ (eq 2). The complex has been characterized spectroscopically and by a single-crystal X-ray diffraction study; the latter showed the structure sketched below.



1

Spectroscopic data for 1 are consistent with the determined structure. The ¹³C NMR spectrum shows the acetyl carbon resonance at δ 319.3 (d). This ¹³C NMR resonance for 1 is further downfield than the usual resonances of terminal acyl complexes, and it is in the region normally associated with carbene ligands.¹⁷ It is quite close to the δ 317.3 resonance for the bridging acetyl ligand in $\text{ZrMo}(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_2\text{Cp}_3$ ⁴ⁱ for which spectroscopic and structural data imply that this ligand has considerable oxycarbene character. An oxycarbene description may also be relevant for 1. The IR spectrum of 1 shows five bands at 2080 (m), 2002 (s), 1993 (s), 1976 (w), and 1950 (s) cm⁻¹. The four higher energy bands we attribute to the Mn-CO's. They compare favorably in position to the four bands of $\text{Mn}(\text{CO})_4\{\text{P}(\text{OCH}_2\text{CH}_3)_3\}\{\text{C}(\text{O})\text{CH}_3\}$ at 2071 (w), 2009 (m), 1988 (s), and 1975 (s) cm⁻¹.¹⁸ The 1950-cm⁻¹ band is assigned to Fe-CO; it compares to the 1910-cm⁻¹ band of $\text{FeCp}(\text{CO})\{\text{PPh}_3\}\{\text{C}(\text{O})\text{CH}_3\}$.^{4m}

(17) Mann, B. E.; Taylor, B. F. ¹³C NMR Data for Organometallic Compounds; Academic Press: London, 1981.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) in $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_5$ (3)

Bond Distances			
Fe-Mn	2.806 (1)	Mn-C2	1.846 (6)
Fe-P	2.174 (2)	Mn-C3	1.823 (5)
Fe-C1	1.724 (7)	Mn-C4	1.803 (6)
Fe-H	1.56 (5)	Mn-C5	1.852 (6)
Mn-P	2.278 (1)	Mn-H	1.72 (6)
Bond Angles			
Mn-Fe-P	52.59 (4)	P-Mn-C5	93.5 (2)
Mn-Fe-C1	98.6 (2)	P-Mn-H	78 (2)
Mn-Fe-H	33 (2)	C2-Mn-C3	86.1 (2)
P-Fe-C1	95.7 (2)	C2-Mn-C4	92.5 (3)
P-Fe-H	85 (2)	C2-Mn-C5	175.9 (3)
C1-Fe-H	88 (2)	C2-Mn-H	85 (2)
Fe-Mn-P	49.30 (4)	C3-Mn-C4	98.2 (2)
Fe-Mn-C2	91.7 (2)	C3-Mn-C5	90.6 (2)
Fe-Mn-C3	115.9 (2)	C3-Mn-H	87 (2)
Fe-Mn-C4	145.8 (2)	C4-Mn-C5	90.4 (3)
Fe-Mn-C5	87.5 (2)	C4-Mn-H	174 (2)
Fe-Mn-H	30 (2)	C5-Mn-H	93 (2)
P-Mn-C2	89.0 (2)	Fe-P-Mn	78.10 (5)
P-Mn-C3	164.3 (2)	Fe-H-Mn	117 (3)
P-Mn-C4	96.9 (2)		

(O)CH₃)(CO)₂Cp₃⁴ⁱ for which spectroscopic and structural data imply that this ligand has considerable oxycarbene character. An oxycarbene description may also be relevant for 1. The IR spectrum of 1 shows five bands at 2080 (m), 2002 (s), 1993 (s), 1976 (w), and 1950 (s) cm⁻¹. The four higher energy bands we attribute to the Mn-CO's. They compare favorably in position to the four bands of $\text{Mn}(\text{CO})_4\{\text{P}(\text{OCH}_2\text{CH}_3)_3\}\{\text{C}(\text{O})\text{CH}_3\}$ at 2071 (w), 2009 (m), 1988 (s), and 1975 (s) cm⁻¹.¹⁸ The 1950-cm⁻¹ band is assigned to Fe-CO; it compares to the 1910-cm⁻¹ band of $\text{FeCp}(\text{CO})\{\text{PPh}_3\}\{\text{C}(\text{O})\text{CH}_3\}$.^{4m}

The ν_{CO} bands of the μ -acetyl ligand of 1 and its derivatives (see below) have not been located. IR bands associated with the μ -PPh₂ ligand dominate the 1400–1500-cm⁻¹ spectral region where this band is expected to appear. A range of CO stretching frequencies have been reported for μ -acetyl complexes⁴ with the lowest energy bands associated with a dominant oxycarbene character of the ligand. For example, the acetyl ν_{CO} stretch in $\text{MnIr}(\mu\text{-C}(\text{O})\text{CH}_3)(\mu\text{-C}(\text{O})\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_3\text{Cp}$ is at 1508 cm⁻¹^{4e} whereas in $\text{ZrMo}(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_2\text{Cp}_3$ it appears at 1339 cm⁻¹.⁴ⁱ The IR spectrum of ¹³C enriched 1, prepared from enriched $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{FeCp}(\text{CO})_2\text{PPh}_2$, also did not reveal any significant band shifts in the 1400–1500-cm⁻¹ region.

A surprising aspect of the spectroscopic data for 1 is the downfield chemical shift of the ³¹P NMR resonance for the μ -PPh₂ ligand, even though the crystal structure clearly shows the absence of a metal-metal bond {Fe...Mn = 3.718 (molecule 1) and 3.713 (molecule 2)} in 1. The usual correlation that has been made is that *upfield* chemical shifts for μ -PPh₂ ligands are expected when they bridge two metals not joined by a metal-metal bond, whereas downfield chemical shifts generally correlate with the presence of a metal-metal bond.¹⁹ However, exceptions to this correlation have recently appeared and thus it must be used with caution.²⁰ Furthermore, the Fe-P-Mn angles of 106.4 (1)° and 107.1 (1)° for the two independent

(18) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* 1968, 7, 1806.

(19) (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* 1980, 19, 186. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* 1981, 204, C27. (c) Carty, A. J. *Adv. Chem. Ser.* 1982, No. 196, 163. (d) Garrou, P. *Chem. Rev.* 1981, 81, 229. (e) Johannsen, G.; Stelzer, O. *Chem. Ber.* 1977, 110, 3438.

(20) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* 1983, 2, 470.

molecules of 1 are among the largest M-P_n-M angles known, and Carty's^{19c} chemical shift-M-P-M angle correlation shows signs of reversing at large M-P-M angles. The downfield position of the μ -PPh₂ resonance of 1 does agree with the "ring-effect" noted by Garrou²¹ in which unusual downfield shifts have been observed for phosphorus nuclei that are incorporated in 5-membered ring systems, as is the μ -PPh₂ ligand in 1.

Experiments Relevant to the Mechanism of Formation of 1. The formation of 1 from CH₃Mn(CO)₅ and FeCp(CO)₂PPh₂ is surprising since the acetyl carbon was initially anticipated to be bound to Mn, given the fact that Mn bound acyl complexes generally result from the reaction of CH₃Mn(CO)₅ with tertiary phosphines. Several experiments were conducted in an attempt to probe the mechanism of formation of 1. The IR spectral changes which occur during the reaction of CH₃Mn(CO)₅ with FeCp(CO)₂PPh₂ are complex but do indicate the formation of at least one reasonably stable intermediate. After 30-min reaction time at 22 °C, a new band appears at 2052 cm⁻¹ which is not due to either of the starting reagents or to product 1. After 1 h, another weak band appears at 2042 cm⁻¹, and after 3 h the 2074-cm⁻¹ band of 1 grows in. The initial 2052-cm⁻¹ band disappears after 20-h reaction time while the 2042- and 2074-cm⁻¹ bands both increase in intensity. We attribute the 2052-cm⁻¹ band to an intermediate en route to the formation of 1 while the 2042-cm⁻¹ band is either that of another intermediate or a second product which decomposes during workup.

The ³¹P NMR spectra of the reaction mixtures also show the formation of at least one intermediate. After 2-h reaction time, ³¹P NMR resonances were observed at δ 63.5 (s) and 54.3 (s) in a ~1:7 intensity ratio. After 21 h, this ratio had changed to ~1:4 but the δ 106.3 (s) resonance of 1 was not yet apparent. Upon warming of the solution to ~35 °C for 0.5 h, the latter resonance grew in such that the relative intensities of the δ 106.3, 63.5, and 54.3 resonances was ~1:5:5. After 5 days reaction time only the δ 106.3 resonance of 1 and the δ 63.5 resonance were apparent.

Carbon-13 NMR monitoring of the reaction proved particularly informative. Reaction of 25% ¹³CO enriched CH₃Mn(CO)₅ with FeCp(CO)₂PPh₂ in THF/benzene-*d*₆ for 1 h at 22 °C gave a spectrum showing a doublet at δ 269.1 ($J_{^{13}\text{C},^{31}\text{P}} = 17.1$ Hz). This resonance is between the δ 265.3 and 277.0 resonances of Mn(CO)₄(PPh₃)|C(O)-CH₃^{22a} and FeCp(CO)(PPh₃)|C(O)CH₃^{22b} and is in the range expected for a terminal acyl ligand. After 22 h, the doublet at δ 319 due to 1 grew in, and after 34 h, the δ 319 (d) resonance was about 30% as intense as the δ 269.1 doublet.

Several ¹³C NMR experiments were conducted to try to determine which metal the acetyl carbonyl comes from, but these were unsuccessful. Essentially the same ¹³C NMR spectrum was obtained when ¹³CO-enriched CH₃Mn(CO)₅ was allowed to react with unenriched FeCp(CO)₂PPh₂ as when unenriched CH₃Mn(CO)₅ reacted with ¹³CO-enriched FeCp(CO)₂PPh₂, indicating that ¹³CO exchange readily occurs in this system. We also attempted the reaction of CH₃Mn(CO)₄(PPh₃) with FeCp(CO)₂PPh₂, anticipating that ¹³C-³¹P coupling would allow us to pinpoint the metal to which the intermediate acetyl is bound, but this combination of reagents did not lead to an acetyl containing product.

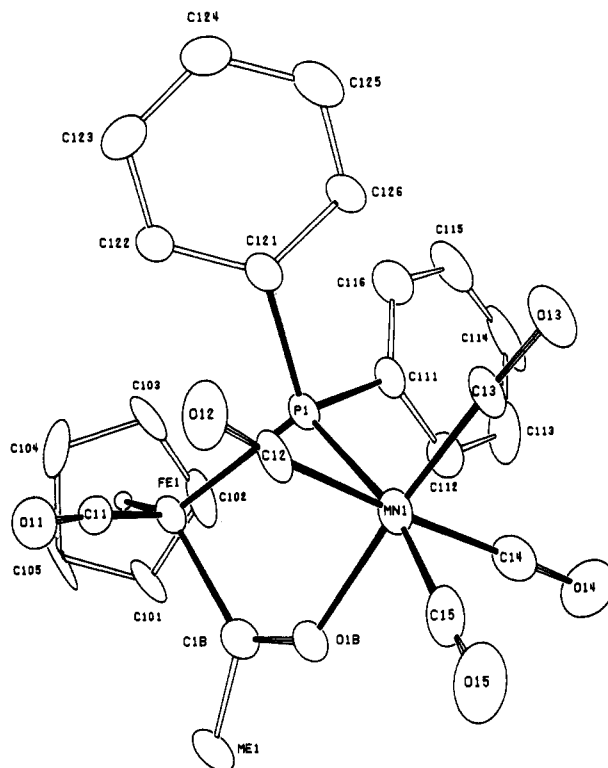
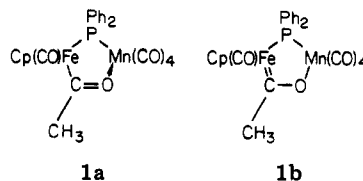


Figure 1. ORTEP drawing of Cp(CO)Fe(μ -C(O)CH₃)(μ -PPh₂)Mn(CO)₄ (1).

Crystal and Molecular Structure of 1. Complex 1 crystallizes in the space group $P\bar{1}$ with two crystallographically independent molecules per unit cell. These are essentially identical with minor differences in bond lengths and bond angles. An ORTEP drawing of molecule 1 is given in Figure 1 which also illustrates the atom numbering scheme. Relevant bond lengths and bond angles for both molecules are given in Tables IV and V.

The μ -PPh₂ ligand bridges the Mn and Fe atoms which are also bridged by the μ -acetyl ligand with the carbon attached to Fe and the oxygen to Mn. The Fe is further coordinated by the Cp ligand and one CO and the Mn by four additional CO's. The Mn and Fe atoms are clearly nonbonded with separations of 3.718 Å and 3.713 Å for the two molecules. The coordination geometry about Mn closely approximates an octahedral ligand arrangement whereas that about Fe is the usual distorted tetrahedral ligand arrangement commonly found for CpFe(CO)L(X) derivatives. Thus the acetyl ligand conveniently fits into the preferred coordination geometries for the two metal centers. The absence of a metal-metal bond in 1 is predicted by the effective atomic number rule in that each metal attains an 18-valence-electron configuration without the necessity of a metal-metal bond.

The key feature of 1 is the bridging acetyl ligand. A priori, two resonance forms for this ligand must be considered—the acetyl and oxycarbene forms respectively drawn in 1a and 1b. Unfortunately, the structural data



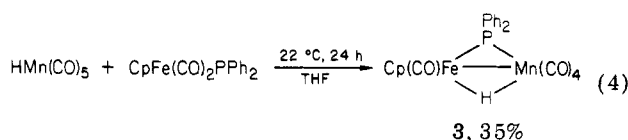
does not allow a clear distinction between them to be made. The Fe-C1B(acetyl) distances of 1.919 (8) and 1.923 (6) Å are slightly shorter than the Fe-C(acyl) bond lengths

(21) Garrou, P. E. *Inorg. Chem.* 1975, 14, 1435.

(22) (a) From the spectrum of an authentic sample prepared according to ref 6. (b) Reger, D. L.; Fauth, D. J.; Dukes, M. D. *Synth. React. Inorg. Met.-Org. Chem.* 1977, 7, 151.

of related terminal acyl complexes. For example, $\text{FeCp}(\text{CO})(\text{PPh}_3)(\text{C}(\text{O})\text{Ph})^{23}$ and $\text{Fe}(\text{HB}(\text{C}_3\text{H}_5\text{N}_2)_3)(\text{CO})_2(\text{C}(\text{O})\text{C}-\text{H}_3)^{24}$ both have Fe–C(acyl) distances of 1.968 (5) Å. This data implies some degree of Fe–C double bond character in the Fe–acetyl bond of 1. The acyl C–O distances of 1.262 (9) and 1.249 (8) Å for the two molecules fall between the values expected for acyl and oxycarbene ligands. The two terminal acyl complexes mentioned above, for example, have acyl C–O distances of 1.22 (3) and 1.193 Å, respectively. In contrast, the acetyl ligand in $\text{ZrMo}(\mu\text{-C}(\text{O})\text{CH}_3)(\text{CO})_2\text{Cp}_3$,⁴¹ which has considerable oxycarbene character, has a much longer C–O distance of 1.285 (3) Å. From the X-ray data, complex 1 appears to be intermediate between the two formal descriptions 1a and 1b, a conclusion also indicated by the ¹³C NMR data discussed above.

Synthesis and Spectroscopic Characterization of $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_5$ (3). The new binuclear bridging hydride complex 3 was prepared by stirring $\text{MnH}(\text{CO})_5$ with $\text{FeCp}(\text{CO})_2(\text{PPh}_2)$ in THF for 24 h at 22 °C (eq 4). Complex 3 was characterized spectroscopically



and by a single-crystal X-ray diffraction study. Its IR spectrum in the ν_{CO} region (see the Experimental Section) shows terminal but no bridging ν_{CO} bands. Its ¹H NMR spectrum exhibits a singlet at δ 4.0 assigned to the Cp ligand on Fe, a doublet at δ –18.1 ($J_{31\text{P}-1\text{H}} = 34.9$ Hz) due to the bridging hydride which couples to the bridging phosphorus atom, and resonances in the δ 6.9–7.7 region attributable to the PPh₂ phenyl hydrogens. The ³¹P{¹H} NMR spectrum of 3 at room temperature shows a broad singlet at δ 176.7 assigned to the $\mu\text{-PPh}_2$ ligand. The downfield ³¹P chemical shift of this resonance is consistent with this ligand bridging two metals joined by a metal–metal bond (Fe–Mn = 2.806 (1) Å).¹⁹ Complex 3 shows a parent ion in its mass spectrum (EI) at m/z 502 with fragment ions corresponding to subsequent loss of the five carbonyl ligands.

X-ray Diffraction Study of $\text{FeMn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{-Cp}(\text{CO})_5$, 3. An ORTEP drawing of 3 is shown in Figure 2. Relevant bond lengths and angles are listed in Table VII. The PPh₂ ligand bridges the two metal atoms that are also bridged by the hydride ligand. The latter was located and refined. The Mn is further coordinated by four CO's and the Fe by the Cp ligand and a carbonyl. The Mn–Fe bond distance is 2.806 (1) Å, well within the range reported for other MnFe single bonds: $\text{FeMn}(\mu\text{-PPh}_2)(\text{CO})_8$ (2.825 (5) Å),²⁵ $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ (2.80, 2.82 Å),²⁶ and $\text{MnFeCp}(\text{CO})_7$ (2.843 (4) Å).²⁷ As found for other hydride bridged complexes, the Fe–Mn–H interaction appears to be best described as a two-electron, three-center bond,²⁸ with the electron density localized within the M–H bonds rather than along the Fe–Mn vector.

(23) (a) Chapovskii, Yu. A.; Semion, V. A.; Andrianov, V. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* 1968, 9, 1100. (b) Semion, V. A.; Struchkov, Yu. T. *Ibid.* 1969, 10, 664.

(24) Cotton, F. A.; Frenz, B. A.; Shaver, A. *Inorg. Chem. Acta* 1973, 7, 161.

(25) Vahrenkamp, H. *Z. Naturforsch. Anorg. Chem., Org. Chem.* 1975, 30B, 814.

(26) Agron, P. A.; Ellison, R. D.; Levy, H. A. *Acta Crystallogr.* 1967, 23, 1079.

(27) Hansen, P. J.; Jacobson, R. A. *J. Organomet. Chem.* 1966, 6, 389.

(28) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* 1979, 12, 176.

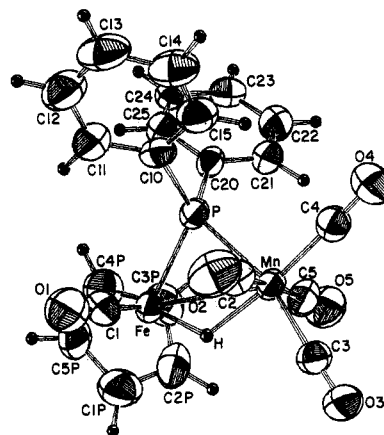
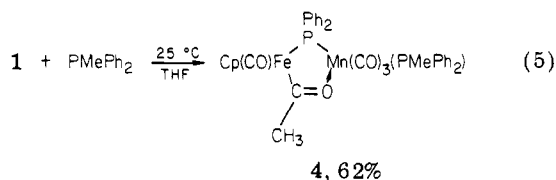


Figure 2. ORTEP drawing of $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_4$ (3).

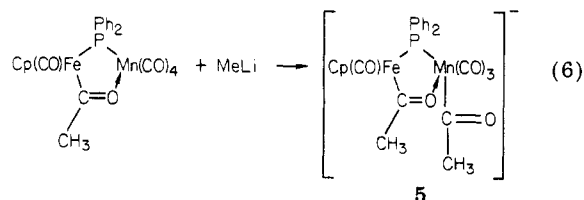
Reaction of 1 with PMePh_2 . A PMePh_2 -substituted derivative of complex 1 was prepared by stirring a THF solution of 1 with 1 equiv of PMePh_2 at 25 °C for 12 h (eq 5). Complex 4 has been spectroscopically characterized.



It shows a parent ion at m/z 716 in its field-desorption mass spectrum, consistent with the indicated stoichiometry. Its ³¹P{¹H} NMR spectrum shows a doublet at δ 112.7 ($J_{31\text{P}-31\text{P}} = 34.5$ Hz) attributed to the $\mu\text{-PPh}_2$ ligand of 4 and a very broad singlet at δ 44.5 assigned to the terminal PMePh_2 ligand on Mn. The breadth of this resonance is presumably due to the quadrupolar Mn nucleus and supports the contention that the PMePh_2 is bound to Mn. The relatively small ³¹P–³¹P coupling constant for 4 suggests that the two phosphorus ligands are mutually cis.

The ¹³C{¹H} NMR spectrum of 4 shows a doublet at δ 315.1 ($J_{13\text{C}-31\text{P}} = 6.6$ Hz) due to the bridging acetyl ligand. The doublet pattern implies that the PMePh_2 ligand is not bound to the same metal as the acetyl carbon. Since acyl isomerization seems unlikely, the PMePh_2 is presumed to be attached to Mn as indicated in eq 5. The ¹H NMR spectrum of 4 shows a singlet at δ 4.2 assigned to the cyclopentadienyl ligand, a singlet at δ 2.5 attributed to the acetyl group, and a doublet at δ 1.8 ($J_{1\text{H}-31\text{P}} = 8.0$ Hz) which is assigned to the methyl group on the PMePh_2 ligand. These integrate in the expected 5:3:3 intensity ratio.

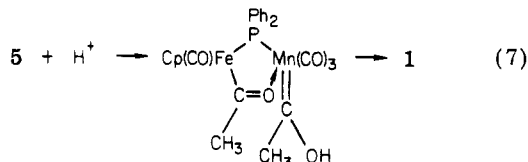
Reaction of 1 with MeLi. Slow addition of MeLi to a THF solution of 1 at room temperature or at –78 °C results in the synthesis of the bis(acetyl) anion 5 (eq 6).



Complex 5 can be isolated as an air-sensitive red oil. Its IR spectrum shows 4 bands at 1966 (m), 1935 (s), 1871 (s) cm^{-1} , significantly red shifted (50–100 cm^{-1}) from the bands of 1, consistent with their assignment as terminal carbonyl ligands on an anionic complex. A medium intensity band at 1540 cm^{-1} is also observed, attributed to a terminal

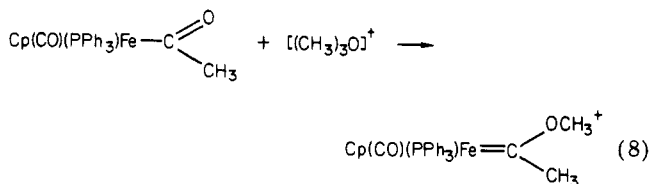
acetyl ligand. The ^1H NMR spectrum of **5** shows a singlet at δ 4.4 assigned to the Cp ligand and two singlets at δ 2.9 and δ 2.5 which are assigned to the two acetyl ligands. These integrate in the expected 5:3:3 intensity ratio. Two downfield resonances at δ 323.8 (d, $J_{^{13}\text{C}-^{31}\text{P}} = 12.2$ Hz) and δ 309.7 (d, $J_{^{13}\text{C}-^{31}\text{P}} = 9.8$ Hz) are observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5**. The doublet at δ 323.8 is assigned to the bridging acetyl ligand as it is close to the doublet observed for the bridging acetyl ligand of **1** at δ 319.3. The δ 309.7 doublet is attributed to the terminal acetyl ligand, although it falls outside the normal terminal acetyl range.¹⁷

The exact structure of **5** is unknown, but the structure indicated in eq 6 appears most consistent with the spectral and chemical data. It is unlikely that both acetyl ligands are in bridging positions. First, the 1540-cm^{-1} band of **5** implies the presence of a terminal acetyl ligand. Also consistent with a terminal acetyl is the observation that upon protonation with 20% H_3PO_4 , complex **5** decomposes to generate compound **1** (eq 7). Protonation of terminal



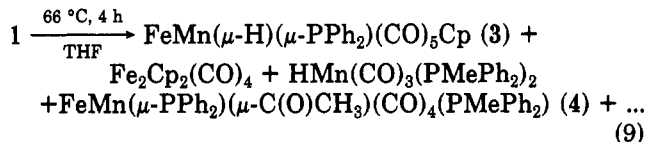
acetyl complexes generally leads to unstable hydroxycarbene complexes which readily decompose,^{5b,29} and such is also likely with **5**. Protonation of $[\text{W}(\text{CO})_5\{\text{C}(\text{O})\text{Ph}\}]^-$, for example, has been reported to yield PhCHO and substantial quantities of $\text{W}(\text{CO})_6$.^{29a}

Other Attempted Reactions of 1. Terminal acyl complexes generally can be alkylated or protonated to give carbene derivatives, e.g., eq 8.³⁰ However, complex **1** does



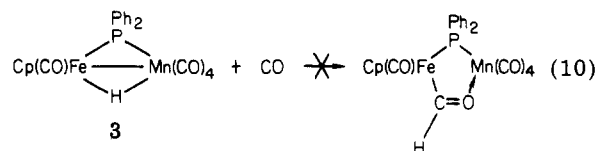
not react with HBF_4 nor with $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ when stirred with these reagents at room temperature. We suspected that perhaps if the acetyl oxygen of **1** could be released from Mn, creating a terminal acetyl intermediate, reaction might occur. We thus carried out the reaction of **1** with $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ under 500 psi of CO pressure, hoping to substitute CO for the acyl oxygen, but again no reaction was observed. Complex **1** also does not react with H_2 (50 psi, 22 °C) nor with $[\text{Ph}_3\text{C}]\text{BF}_4$. It was anticipated that the latter reagent might abstract hydride from the acetyl methyl group, but this does not occur.

Thermolysis of 1. Although complex **1** is not reactive toward the reagents discussed above, it is not particularly stable. When heated at 66 °C for 4 h under N_2 , complete decomposition occurs to give a complex mixture of at least seven different compounds. The five products shown in eq 9 were identified by comparison of their IR spectra to those reported in the literature or given herein. None of these were isolated in yields in excess of 10%. The formation of $\text{HMn}(\text{CO})_3(\text{PMePh}_2)_2$ and **4** is particularly sig-



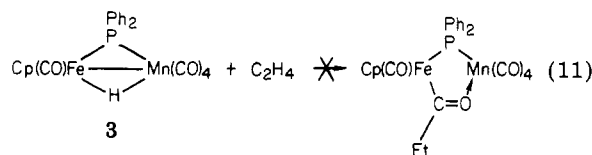
nificant since the PMePh_2 ligand in these compounds presumably arises from coupling of the $\mu\text{-PPh}_2$ ligand with the acetyl methyl group. This decomposition could proceed through CH_3 migration to one of the metal centers, followed by reductive coupling of the CH_3 and $\mu\text{-PPh}_2$ ligands, a type of reaction that we have observed with other $\mu\text{-PPh}_2$ bridged complexes.³¹

Attempted Reaction of 3 with CO and C_2H_4 . The reaction of **3** with CO was examined to determine if a bridging formyl complex might result, eq 10, analogous to



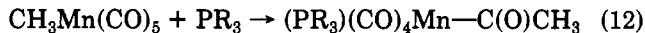
the stable bridging acetyl complex **1**. However, **3** shows no net reaction with CO, even at pressures up to 1000 psi, and it is recovered unchanged. A formyl complex such as that indicated in eq 10 should be stable, given the stability of the bridging acetyl complex **1**. Thus if it were to form from **3**, it should not readily deinsert and should thereby be detected upon releasing the CO pressure. Failure to observe such a product implies that a $\mu\text{-CHO}$ ligand does not form.

Kaes et al. recently reported the reaction of the bridging hydride clusters $\text{Ru}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_{10}$ with C_2H_4 to yield the bridging acyl derivatives $\text{Ru}_3(\mu\text{-C}(\text{O})\text{C}_2\text{H}_5)(\mu\text{-X})(\text{CO})_9$.^{4p} An analogous reaction of **3** with C_2H_4 would yield a μ -propionyl complex similar to the stable μ -acetyl complex **1** (eq 11). The reaction of **3** with C_2H_4 (500 psi) and CO (500 psi) together at 100 °C was carried out, but no reaction was detected by IR spectral monitoring.



Discussion

The method employed for the synthesis of complex **1** derives from the known reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with tertiary phosphines which generally yields PR_3 -substituted acyl complexes (eq 12).⁶ Such reaction is believed to



proceed by addition of PR_3 to a coordinatively unsaturated $(\text{CO})_4\text{Mn}\{\text{C}(\text{O})\text{CH}_3\}$ intermediate, itself formed by the reversible migration of CH_3 to CO. By simply employing a metallo-substituted phosphine such as $\text{Cp}(\text{CO})_2\text{FePPh}_2$ in the reaction, a bimetallic acyl complex such as **1** should and does result. This reaction should prove to be a general method for the preparation of bi- and polymetallic acyl complexes. A number of other alkyl complexes could be employed, including $\text{CH}_3\text{Co}(\text{CO})_4$, $\text{CH}_3\text{MoCp}(\text{CO})_3$, $\text{CH}_3\text{FeCp}(\text{CO})_2$, and $\text{CH}_3\text{Re}(\text{CO})_5$, and a large number of mono- and polynuclear metallophosphines exist, since these are readily derived by deprotonation of PPh_2H

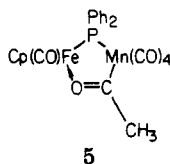
(29) (a) Fischer, E. O.; Maasbol, A. *Chem. Ber.* 1967, 100, 2445. (b) Fischer, E. O.; Riedel, A. *Ibid.* 1968, 101, 156.

(30) (a) Green, M. L. H.; Mitchard, L. C.; Swanwich, M. G. *J. Chem. Soc. A* 1971, 794. (b) Casey, C. P.; Cyr, C. R.; Boggs, R. A. *Synth. React. Inorg. Met.-Org. Chem.* 1973, 3, 249. (c) Johnson, M. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, Chapter 31.2.

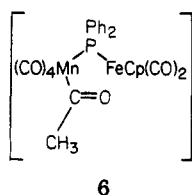
(31) (a) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* 1983, 2, 53. (b) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* 1984, 106, 1519.

substituted derivatives (e.g., $[\text{Fe}(\text{CO})_4\text{PPh}_2]^-$, $[\text{W}(\text{CO})_5\text{PPh}_2]^-$, etc.).³²

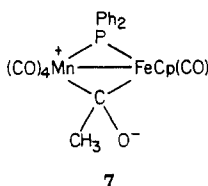
Concerning the formation of complex 1 from the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with $\text{FeCp}(\text{CO})_2\text{PPh}_2$, it would be important to know how the acetyl ligand ends up with its carbon atom attached to Fe rather than Mn. Although a Mn-carbon bound acyl product such as 5 might have been



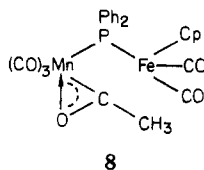
anticipated on kinetic grounds, formation of the actual product 1 is probably driven by thermodynamic considerations since the oxygen atom is bound to the more oxophilic metal Mn. We have tried to probe the mechanism of formation 1 but with limited success. Spectroscopic monitoring of the reaction clearly shows the formation of at least one reasonably stable intermediate, which must decompose upon workup since we have not been able to isolate this species. Complex 6 is consistent with the



spectroscopic data, particularly since the ^{13}C NMR resonance for the acetyl ligand in this intermediate (δ 269.1) is close to that of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\{\text{C}(\text{O})\text{CH}_3\}$ (δ 265.3), a mononuclear analogue of 6. This would also be the expected intermediate based on the known PR_3 derivative chemistry of $\text{CH}_3\text{Mn}(\text{CO})_5$ (eq 12). Formation of 1 from 6 requires loss of a CO ligand and migration of the acyl carbon to Fe. Carbon monoxide loss could occur from Fe, followed by addition of the coordinatively unsaturated Fe center to the acetyl carbon, possibly via π -coordination of the acetyl group. This could yield an oxycarbene intermediate such as 7 which could then rearrange to 1. Loss

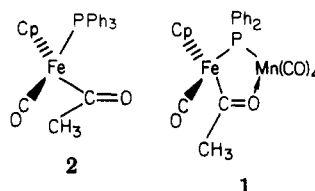


of CO from Mn could also occur to yield a transient η^2 -acyl complex such as 8. Nucleophilic addition of Fe to the acyl carbon of 8 followed by CO migration to Mn would also yield 1.



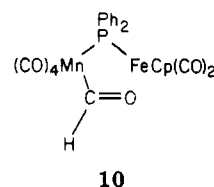
One important aspect of this study is that it allows a comparison of the reactivity of bridging and terminal acetyl ligands in similar complexes. The derivative chemistry of the terminal acetyl complex $\text{Cp}(\text{CO})(\text{PPh}_2)\text{FeC}(\text{O})\text{CH}_3$ (2)

has been extensively studied,³⁰ and as the drawings of 1 and 2 illustrate, this complex bears a structural relationship



to 1. Of course, the significant difference is that the acetyl oxygen is free in 2 but is bound to Mn in 1. We wished to know how strongly the acetyl oxygen is bound to Mn and if the acetyl bridge can be readily opened. As the experiments described herein clearly show, this bonding is extremely strong. Neither PMePh_2 nor CO will displace the oxygen ligand, and the acetyl group cannot be methylated or protonated in 1, although the latter reactions readily occur with 2 to give carbene derivatives. This observation strongly suggests that bridging formyl and acyl complexes of type I, eq 1, may have limited utility in CO reduction chemistry since, even with late transition metals, the oxygen-metal bond is not easily broken.

It is interesting that the reaction of $\text{HMn}(\text{CO})_5$ with $\text{PPh}_2\text{FeCp}(\text{CO})_2$ does not yield a μ -CHO complex analogous to 1 but instead the bridging hydride complex 3. Why does the reaction of $\text{HMn}(\text{CO})_5$ with $\text{PPh}_2\text{FeCp}(\text{CO})_2$ not yield a bridging formyl complex? Basolo and Pearson³³ and Byers and Brown³⁴ have suggested that $\text{HMn}(\text{CO})_5$ undergoes phosphine substitution via the intermediacy of the formyl species $(\text{PR}_3)(\text{CO})_4\text{Mn}(\text{CHO})$, which rapidly decarbonylates and deinserts to give substituted $(\text{PR}_3)(\text{CO})_4\text{MnH}$ derivatives. Recent work by Pearson, Ford, and co-workers supports this suggestion.³⁵ Thus, if $\text{HMn}(\text{CO})_5$ reacts with $\text{PPh}_2\text{FeCp}(\text{CO})_2$ in a similar fashion, a formyl intermediate such as 10 should form. Com-



plex 10 is analogous to 6, the suggested intermediate en route to 1. In order for a bridging formyl complex analogous to 1 to form from 10, CO loss must occur to give an open coordination site on one of the metals. The production of the bridging hydride complex 3 rather than a μ -CHO complex would be rationalized by hydride migration to this open site with a faster rate than capture of the formyl ligand by the second metal. Alternatively, a formyl intermediate may never form, and the synthesis of 3 could proceed via initial dissociation of CO from $\text{HMn}(\text{CO})_5$ to yield coordinatively unsaturated $\text{HMn}(\text{CO})_4$ which then adds $\text{PPh}_2\text{FeCp}(\text{CO})_2$.

If a bridging formyl complex analogous to 1 could be produced from some reaction, we expect that it should be reasonably stable, given the stability of the bridging acetyl complex 1. However, such a species does not form when 3 is allowed to react with CO, one potential route to the desired complex. Another route would be the reaction of $[\text{BHR}_3]^-$ reagents with the presently unknown cationic complex $[\text{FeMn}(\mu\text{-PPh}_2)\text{Cp}(\text{CO})_6]^+$. Efforts are underway

(33) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions" Wiley: New York, 1967; Chapter 7.

(34) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* 1977, 127, 181.

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

in our laboratory to synthesize this reagent and to determine if a μ -CHO product will derive from it.

Acknowledgment. This research was supported by the Department of Energy, Office of Basic Energy Sciences. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978-1983) and the John Simon Guggenheim Foundation for a fellowship (1982-1983). Dr. Michael Breen is thanked for useful discussions at the early stages of this research and Dr. R. J. Hale (Tennessee-Eastman Co.) for obtaining

field desorption mass spectra.

Registry No. 1, 89438-28-8; 3, 89438-29-9; 4, 89438-30-2; 5, 89438-32-4; $\text{MnH}(\text{CO})_3(\text{PMePh}_2)_2$, 42965-72-0; $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$, 11117-09-2; $\text{CH}_3\text{Mn}(\text{CO})_5$, 13601-24-6; $\text{FeCp}(\text{PPh}_2)(\text{CO})_2$, 38816-40-9; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{HMn}(\text{CO})_5$, 16972-33-1; MeLi , 917-54-4; $[\text{Ph}_3\text{C}]\text{BF}_4$, 341-02-6; HBF_4 , 16872-11-0; $[(\text{CH}_3)_3\text{O}]\text{BF}_4$, 420-37-1; H_2 , 1333-74-0; CO , 630-08-0.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and structure factors for the X-ray crystallographic studies of 1 and 3 (41 pages). Ordering information is given on any current masthead page.

Acid-Base Chemistry of the Methylrhodium(III) Derivative $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$

A. R. Siedle* and R. A. Newmark

Science Research Laboratory, 3M Central Research Laboratories, St. Paul, Minnesota 55144

L. H. Pignolet

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

Received November 16, 1983

Reaction of excess methyl iodide with the 14-electron Rh(I) salt $(\text{Ph}_3\text{P})_3\text{Rh}^+\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ produces green $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$, λ_{max} 500 and 610 nm. Crystal data: monoclinic (centric), $C2/c$, $a = 23.982$ (5) Å, $b = 9.828$ (3) Å, $c = 16.063$ (6) Å, $\beta = 114.73$ (3)°, $Z = 4$, and $V = 3439$ (4) Å³. The structure, solved by using 2618 reflections for which $F_o^2 > 1.0 \sigma(F_o^2)$, converged at $R = 0.022$ and $R_w = 0.034$. The coordination geometry of rhodium(III) is flattened square pyramidal with a C_2 axis through rhodium and the methyl carbon. The metal is displaced 0.25 Å toward the apical methyl group from the least-squares plane containing two trans iodines and two trans phosphorus atoms, which comprise the base of the pyramid. Important bond distances are $d(\text{Rh}-\text{C}) = 2.06$ (1) Å, $d(\text{Rh}-\text{I}) = 2.635$ (1) Å, and $d(\text{Rh}-\text{P}) = 2.365$ (2) Å. $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$ has an extensive acid-base chemistry. It is converted by excess carbon monoxide to *cis*- and *trans*- $\text{CH}_3\text{CORhI}_2(\text{PPh}_3)_2\text{CO}$ from which reversible dissociation of the terminal carbonyl ligand leads to $\text{CH}_3\text{CORhI}_2(\text{PPh}_3)_2$. This acetylrhodium(III) compound decomposes by reductive elimination of methyl iodide to form $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{I}$. Trimethylphosphine and trimethyl phosphite displace triphenylphosphine to yield *mer*- $\text{CH}_3\text{RhI}_2\text{L}_3$ ($\text{L} = (\text{CH}_3\text{O})_3\text{P}$, $(\text{CH}_3)_3\text{P}$). Migratory insertion of sulfur dioxide into the CH_3 bond provides $\text{CH}_3\text{SO}_2\text{RhI}_2(\text{PPh}_3)_2$.

Introduction

During the course of a systematic examination of the chemistry of $(\text{Ph}_3\text{P})_3\text{Rh}^+\text{HC}(\text{SO}_2\text{CF}_3)_2^-$, we found that this 14-electron rhodium(I) compound reacted with methyl iodide to form the methylrhodium(III) derivative $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$.¹ Since alkylrhodium(III) materials are not common, a structural and chemical study was undertaken. The metal center behaves as a soft Lewis acid, and in this paper, we describe the acid-base chemistry of $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$ as probed by vibrational and NMR spectroscopy.

Results

Reaction of $(\text{Ph}_3\text{P})_3\text{Rh}^+\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ with excess methyl iodide in dichloromethane at room temperature provides green crystals, compositionally defined by NMR data and elemental analyses as $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$, 1, in 58% yield. Electronic and NMR spectra indicate that this material is similar to $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2\text{-CH}_3\text{I}$ first described by Wilkinson and co-workers.² However, the nature of

the "extra" methyl iodide in Wilkinson's compound remains unresolved and the only other reference to this curious substance is a report of its X-ray photoelectron spectrum.³ In the ¹H NMR spectrum of 1, the protons of the methylrhodium group appear as a doublet of triplets, δ 2.86, with $^2J_{\text{H-C-Rh}} = 2.7$ Hz and $^3J_{\text{H-C-Rh-P}} = 5.3$ Hz. The three-bond coupling constant is twice that of the two-bond coupling, but a similar pattern has been noted in $\text{CH}_3\text{Rh}(\text{PPh}_3)_3$.³ The ¹³C NMR spectrum of ¹³CH₃RhI₂(PPh₃)₂, prepared from $(\text{Ph}_3\text{P})_3\text{Rh}^+\text{HC}(\text{SO}_2\text{CF}_3)_2^-$ and 99 atom % ¹³CH₃I, reveals a multiplet at δ -3.2 for the methyl group with $^1J_{\text{C-Rh}} = 24.6$ Hz, $^1J_{\text{C-H}} = 143$ Hz, and $^2J_{\text{C-Rh-P}} = 5.9$ Hz. The infrared spectrum (KBr disk) shows a sharp, weak band at 2910 cm⁻¹ that is attributed to C-H stretching in the CH₃Rh unit. It is found at 2120 cm⁻¹ in CD₃RhI₂(PPh₃)₂.

Structure of $\text{CH}_3\text{RhI}_2(\text{PPh}_3)_2$. The solid-state molecular structure of 1 is depicted in Figure 1. There are no unusually short intermolecular contacts. In general, the structure resembles that of a benzene solvate described in a preliminary communication by Skapski et al.⁵ The

(1) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* 1984, 106, 1510.

(2) (a) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* 1966, 1733. (b) Douek, I. C.; Wilkinson, G. *J. Chem. Soc. A* 1969, 2604.

(3) Hamer, A. D.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* 1973, 116.

(4) Keim, W. *J. Organomet. Chem.* 1968, 14, 179.