Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30601

Complexes of Trivalent Phosphorus Derivatives. VI. The Unsymmetrical Cleavage of Binuclear Cyclopentadienylmetal Carbonyls with Chelating Ditertiary Phosphines[1]

By R. B. King,[2,3] K. H. Pannell,[4] C. A. Eggers,[4] and L. W. Houk[4]

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The cyclopentadienylmolybdenum carbonyl $[C_5H_5Mo(CO)_3]_2$ undergoes unsymmetrical cleavage upon reaction with chelating ditertiary phosphines in hydrocarbon solvents at room temperature to give yellow ionic products of the type $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ (diphos = $R_2PCH_2CH_2PR_2$ or *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$; R = CH_3 or C_6H_5). The cyclopentadienyliron carbonyl $[C_5H_5Fe(CO)_2]_2$ undergoes unsymmetrical cleavage upon reaction with the methylated chelating ditertiary phosphine $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in hydrocarbon solvents at room temperature to give orange pyrophoric ionic $[C_5H_5Fe(CO)(CH_3)_2PCH_2CH_2P(CH_3)_2][C_5H_5Fe(CO)_2]$; this is the first solid salt of the very reactive $C_5H_5Fe(CO)_2^-$ anion to be isolated. Other salts of cations of the types $C_5H_5Mo(CO)_2(diphos)^+$ and $C_5H_5Fe(CO)(diphos)^+$ with chloride or hexafluorophosphate anions have also been prepared.

Metal carbonyls react with trivalent phosphorus ligands in two distinctly different manners.[5] In most cases these phosphorus ligands form nonionic products by replacement of one or more carbonyl groups in a substitution reaction. Thus, $Cr(CO)_6$ reacts with tris(dimethylamino)phosphine (tdp) to give the nonionic product $tdpCr(CO)_5$.[6] However, in a few cases binuclear metal carbonyl derivatives, particularly $Co_2(CO)_8$, undergo disproportionation to form ionic products containing a cation with the metal in a formal positive oxidation state and an anion with the metal in a formal negative oxidation state.[7] A good example of this disproportionation reaction is that of $Co_2(CO)_8$ with tris(dimethylamino)phosphine to give the salt $[(tdp)_2Co(CO)_3][Co(CO)_4]$.[6] This type of disproportionation reaction of a binuclear metal carbonyl derivative with a Lewis base such as a tertiary phosphine may be regarded as an unsymmetrical cleavage reaction analogous to the unsymmetrical cleavage of diborane, B_2H_6, with Lewis bases to give ionic products of the type $[L_2BH_2][BH_4]$.[8] The unsymmetrical cleavage of binuclear metal carbonyls with tertiary phosphines contrasts with the familiar symmetrical cleavage of binuclear metal carbonyls with reagents such as the halogens or the alkali metals to give mononuclear products such as the corresponding metal carbonyl halides or anions.

The reactions of cyclopentadienylmetal carbonyls with trivalent phosphorus ligands have been much less investigated. The mononuclear cyclopentadienylmetal carbonyls $C_5H_5V(CO)_4$, $C_5H_5Mn(CO)_3$, and $C_5H_5Co(CO)_2$ (or their simple derivatives) react with tertiary phosphines to give substitution products of the types $C_5H_5V(CO)_n(PR_3)_{4-n}$,[6,9] $C_5H_5Mn(CO)_n(PR_3)_{3-n}$,[10] or $C_5H_5Co(CO)(PR_3)$,[11] respectively. The binuclear cyclopentadienylmetal carbonyl $[C_5H_5Mo(CO)_3]_2$ when treated with triphenylphosphine in boiling tetrahydrofuran undergoes a substitution reaction without cleavage of the metal–metal bond giving the binuclear derivative $(C_5H_5)_2Mo_2(CO)_5P(C_6H_5)_3$.[12] All of these reported reactions of cyclopentadienylmetal carbonyls may be regarded as simple substitution reactions. This paper reports some disproportionation (unsymmetrical cleavage) reactions of the binuclear cyclopentadienylmetal carbonyls $[C_5H_5Mo(CO)_3]_2$ and $[C_5H_5Fe(CO)_2]_2$. After completion of this work, a paper appeared by Haines, Nyholm, and Stiddard,[13] which described the similar unsymmetrical cleavage of $[C_5H_5Mo(CO)_3]_2$ with various tertiary phosphines to give the similar salts $[C_5H_5Mo(CO)_2L_2][C_5H_5Mo(CO)_3]$ (L = $(C_2H_5)_3P$, $(C_4H_9)_3P$, and $(C_6H_5)_3P$ or L_2 = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$).

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Combustion analyses for carbon, hydrogen, and oxygen on some of the products gave erratic results. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated vessels. In addition, the metal carbonyl anion salts were filtered under a nitrogen atmosphere and the pyrophoric salts containing both metal carbonyl anions and 1,2-bis(dimethylphosphino)ethanemetal carbonyl cations were transferred in a nitrogen-filled polyethylene glove bag.

Reagents.—The chelating ditertiary phosphine ligands were

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[1] Part V: R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 1510 (1968).

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] Author to whom inquiries should be addressed at the University of Georgia.

[4] Postdoctoral fellows supported by the Air Force Office of Scientific Research at various times during the period Nov 1966–Aug 1968.

[5] For a review of the reactions of metal carbonyls with trivalent phosphorus ligands, see T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

[6] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[7] For a review article containing many examples of disproportionation reactions of this type, see W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

[8] R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959); G. Kodama and R. W. Parry, *ibid.*, **81**, 3534 (1959); **82**, 6250 (1960).

[9] E. O. Fischer and R. J. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 569 (1967).

[10] (a) J. Lewis, R. S. Nyholm, A. G. Osborne, S. S. Sandhu, and M. H. B. Stiddard, *Chem. Ind.* (London), 1398 (1963); (b) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

[11] (a) R. B. King, *Inorg. Chem.*, **5**, 82 (1966); (b) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

[12] K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

[13] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, *A*, 43 (1968).

TABLE I

NEW COMPOUNDS PREPARED IN THIS WORK

				Analyses, %											
				C		H		O		P		Halogen		Metal	
Compound[a,b]	Color	Prepn[c]	Yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(C_5H_5Mo(CO)_2$-$(Pm—Pm)]Cl \cdot H_2O$	Yellow	A	Good	37.2	37.6	5.5	5.5	11.4	11.7	14.7	15.4	8.4 (Cl)	7.9 (Cl)		
$[C_5H_5Mo(CO)_2$-$(Pm—Pm)][PF_6]$	Yellow	B	Good	30.4	30.2	4.1	4.1			18.1	17.8	22.2 (F)	22.1 (F)		
$[C_5H_5Mo(CO)_2$-$(Pm—Pm)][C_5H_5Mo(CO)_3]$	Yellow	C	77%	41.2	40.7	4.3	4.2	13.1	13.1	10.1	10.5	...	...	31.1 (Mo)	31.2 (Mo)
$[C_5H_5Mo(CO)_2$-$(Pf—Pf)][PF_6]$	Yellow	B	100%							12.2	11.8	15.0 (F)	14.8 (F)		
$[C_5H_5Mo(CO)_2$-$(Pf—Pf)][C_5H_5Mo(CO)_3]$	Yellow	C	90%	57.2	57.3	4.0	4.2	9.3	11.3	7.2	7.2	...	...	22.3 (Mo)	20.5 (Mo)
$[C_5H_5Mo(CO)_2$-$(Pf{=}Pf)]Cl \cdot H_2O$	Yellow	A	98%	59.4	59.6	4.3	4.4	7.2	7.6	9.3	10.0	5.3 (Cl)	5.1 (Cl)		
$[C_5H_5Mo(CO)_2$-$(Pf{=}Pf)][PF_6]$	Yellow	B	100%							12.3	11.8	15.0 (F)	14.8 (F)	12.6 (Mo)	12.1 (Mo)
$[C_5H_5Mo(CO)_2$-$(Pf{=}Pf)][C_5H_5Mo(CO)_3]$	Yellow	C	95%	57.3	55.3	3.7	4.1			7.2	7.0	...	...	22.4 (Mo)	20.6 (Mo)
$[C_5H_5Fe(CO)$-$(Pm—Pm)][PF_6]$	Pale yellow	*d*	43%	32.5	32.6	4.7	4.7			20.8	20.9	25.7 (F)	26.6 (F)		
$[C_5H_5Fe(CO)$-$(Pm—Pm)][C_5H_5Fe(CO)_2]$	Orange	C	72%	47.9	47.2	5.5	6.3			13.0	13.8	...	...	23.4 (Fe)	23.3 (Fe)

[a] Pm—Pm = 1,2-bis(dimethylphosphino)ethane; Pf—Pf = 1,2-bis(diphenylphosphino)ethane; Pf=Pf = *cis*-1,2-bis(diphenylphosphino)ethylene. [b] These compounds did not exhibit definite melting points; instead gradual darkening occurred upon heating in a capillary. [c] The following general methods of preparation were used: (A) stirring $C_5H_5Mo(CO)_3Cl$ with the ditertiary phosphine at room temperature in a mixture of benzene and hexane; (B) treatment of a solution of the corresponding chloride in aqueous ethanol with ammonium hexafluorophosphate; (C) stirring $[C_5H_5Mo(CO)_3]_2$ or $[C_5H_5Fe(CO)_2]_2$ with the ditertiary phosphine at room temperature in a mixture of benzene and hexane. Further details of these general procedures are presented in the Experimental Section. [d] See the Experimental Section for a description of the preparation of $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$.

prepared by various published methods[14] all based on the reaction of 1,2-dichloroethane or *cis*-1,2-dichloroethylene with the appropriate alkali metal dialkylphosphide, MPR_2, in liquid ammonia (R = CH_3; M = Na) or tetrahydrofuran (R = C_6H_5; M = Li). The solid phenyl derivatives $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (designated as Pf—Pf) and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (designated as Pf=Pf) were purified by crystallization. The very air-sensitive liquid methyl derivative $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (designated as Pm—Pm) was purified by vacuum distillation and stored in the solid state in Schlenk tubes under nitrogen in a freezer at −10°; this ligand Pm—Pm was identified by comparison of its proton nmr spectrum with that reported in the literature.[10b]

The cyclopentadienylmetal carbonyl derivatives $[C_5H_5Mo(CO)_3]_2$ and $[C_5H_5Fe(CO)_2]_2$ were prepared by published procedures[15] using commercial[16] $Mo(CO)_6$ and $Fe(CO)_5$. The chloride $C_5H_5Mo(CO)_3Cl$ was obtained by treatment of a tetrahydrofuran solution of $NaMo(CO)_3C_5H_5$ at 0° with a mixture of carbon tetrachloride and glacial acetic acid.[17]

Reaction of $[C_5H_5Mo(CO)_3]_2$ with Chelating Ditertiary Phosphines.—A filtered benzene solution of 0.5–1.0 g of $[C_5H_5Mo(CO)_3]_2$ was stirred at room temperature with a slight excess of the chelating ditertiary phosphine (Pf—Pf, Pf=Pf, or Pm—Pm, generically indicated as "diphos") and some added hexane. The red-purple color of the $[C_5H_5Mo(CO)_3]_2$ gradually faded with concurrent formation of a yellow precipitate of $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$. After the reaction appeared complete (1–24 hr), the product was filtered under nitrogen, washed liberally with benzene and hexane, and dried under nitrogen.

None of the $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ compounds could be satisfactorily recrystallized. In the cases of the derivatives of the phenylated ditertiary phosphines Pf—Pf and Pf=Pf, the somewhat dirty product which originally precipitated could be purified somewhat by mechanical separation from the darker colored impurities. However, analyses (Table I) indicated this purification process to be incomplete. The compound $[C_5H_5Mo(CO)_2(Pm—Pm)][C_5H_5Mo(CO)_3]$ was obtained directly in a pure state but was so air sensitive that it had to be handled in a nitrogen-filled polyethylene glove bag.

Preparation of Other $[C_5H_5Mo(CO)_2(diphos)]^+$ Salts. (a) **$[C_5H_5Mo(CO)_2(diphos)]Cl$.**—A filtered benzene solution of 0.5–1.0 g of $C_5H_5Mo(CO)_3Cl$ was stirred at room temperature with a slight excess of the chelating ditertiary phosphine (Pf—Pf, Pf=Pf, or Pm—Pm) and some added hexane. The red color of the $C_5H_5Mo(CO)_3Cl$ gradually faded with concurrent formation of a yellow precipitate of $[C_5H_5Mo(CO)_2(diphos)]Cl$. After the reaction appeared complete (3–24 hr), the product was filtered under nitrogen, washed with benzene and hexane, and dried first under nitrogen and then under vacuum.

(b) **$[C_5H_5Mo(CO)_2(diphos)][PF_6]$.**—A sample of the chloride salt $[C_5H_5Mo(CO)_2(diphos)]Cl$ was dissolved in ethanol. Water was added followed by a filtered aqueous solution of ammonium hexafluorophosphate. The yellow precipitate which separated was filtered and recrystallized from a mixture of acetone and benzene to give yellow crystals of $[C_5H_5Mo(CO)_2(diphos)][PF_6]$.

Reaction of $[C_5H_5Fe(CO)_2]_2$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$.—A filtered solution of 0.8 g (2.14 mmol) of $[C_5H_5Fe(CO)_2]_2$ in ~250 ml of benzene was stirred overnight at room temperature with 0.5 g (3.33 mmol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$. The resulting orange precipitate was filtered under nitrogen, washed with hexane, and dried under nitrogen to give 0.73 g (72% yield) of orange, very air-sensitive $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$.

Preparation of $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$.—A sample of orange $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$ was prepared from 0.8 g of $[C_5H_5Fe(CO)_2]_2$ and 0.5 g of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ as described above. It was decomposed to a brown sticky solid by exposure to air. This brown solid was dissolved in a mixture of 10 ml of water and 40 ml of ethanol and the filtered solution was treated with a filtered solution of 4 g of ammonium hexafluorophosphate in aqueous ethanol. The yellow precipitate

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(14) For the preparation of the chelating ditertiary phosphines see the following references: (a) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960); (b) *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$: A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964); (c) $(CH_3)_2PCH_2CH_2P(CH_3)_2$: J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961). However, in this work the $NaP(CH_3)_2$ was obtained by cleavage of $(CH_3)_2P—P(CH_3)_2$ with sodium metal in liquid ammonia.

(15) For the preparation of these cyclopentadienylmetal carbonyls see the following references: (a) $[C_5H_5Mo(CO)_3]_2$: R. B. King, *Organometal. Syn.*, **1**, 109 (1965); (b) $[C_5H_5Fe(CO)_2]_2$: R. B. King, *ibid.*, **1**, 114 (1965).

(16) The following commercial sources were used: (a) $Fe(CO)_5$, Antara Division of General Aniline and Film, New York, N. Y.; (b) $Mo(CO)_6$, Pressure Chemical Corp., Pittsburgh, Pa.

(17) This procedure is a minor modification of that described by T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

TABLE II

ν(CO) FREQUENCIES OF COMPOUNDS REPORTED IN THIS PAPER

Compound	Medium	ν(CO) frequencies, cm^{-1}	
		Cation	Anion
$[(C_2H_5)_4N][C_5H_5Mo(CO)_3]$	KBr		1889 s, 1775 s, 1742 s
$[C_5H_5Mo(CO)_2(Pm—Pm)]Cl$	KBr	1981 s, 1882 s	
$[C_5H_5Mo(CO)_2(Pm—Pm)][PF_6]$	KBr	1984 s, 1912 s	
$[C_5H_5Mo(CO)_2(Pm—Pm)][C_5H_5Mo(CO)_3]$	KBr	1966 s, 1901 s	1876 s, 1786 s, 1743 s
$[C_5H_5Mo(CO)_2(Pf—Pf)]Cl$	KBr	1964 s, 1879 s	
$[C_5H_5Mo(CO)_2(Pf—Pf)][PF_6]$	KBr	1991 s, 1927 s	
$[C_5H_5Mo(CO)_2(Pf—Pf)][C_5H_5Mo(CO)_3]$	KBr	1988 s, 1930 s	1897 s, 1770 s, br
$[C_5H_5Mo(CO)_2(Pf{=}Pf)]Cl$	KBr	1977 s, 1919 s	
$[C_5H_5Mo(CO)_2(P{=}Pf)][PF_6]$	KBr	1994 m, 1936 s	
$[C_5H_5Mo(CO)_2(Pf{=}Pf)][C_5H_5Mo(CO)_3]$	KBr	1989 s, 1939 s	1900 s, 1781 s, 1759 s[a]
$[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$	KBr	1970 s	
$[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$	KBr	1970 s	1858 m, 1770 s

[a] Other ν(CO) frequencies at 1960 (m) and 1820 (w) cm^{-1} probably arise from the presence of an impurity.

was filtered and recrystallized from a mixture of acetone and benzene to give 0.41 g (43% yield) of pale yellow crystalline $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$, mp >300°.

Infrared Spectra (KBr Pellets). **A. $[C_5H_5Mo(CO)_2(Pm—Pm)]Cl \cdot H_2O$.**—$\nu$(CH) bands at 3094 (vvw), 3040 (vvw), 2970 (vw), 2955 (vw), 2927 (vw), 2900 (vw), and 2813 (vw) cm^{-1}; see Table II for ν(CO) bands; other bands at 1417 (m), 1397 (w, sh), 1298 (vw), 1287 (w), 1280 (vw), 1237 (w), 1127 (w), 1085 (vw), 1022 (m), 989 (w), 947 (m, sh), 940 (m), 920 (w), 906 (w), 825 (m), 795 (w), 731 (w), 703 (m), and 646 (w) cm^{-1}.

B. $[C_5H_5Mo(CO)_2(Pm—Pm)][PF_6]$.—$\nu$(CH) bands at 3118 (w) and 2913 (vw) cm^{-1}; see Table II for ν(CO) bands; ν(PF) band at 830 (s) cm^{-1}; other bands at 1422 (m), 1395 (w, sh), 1308 (vw), 1290 (w), 1238 (vw), 1128 (vw), 1005 (vw), 940 (m), 915 (vw), 898 (w), 870 (m, sh), 855 (m, sh), 807 (s), 732 (w), 705 (w), and 645 (w) cm^{-1}.

C. $[C_5H_5Mo(CO)_2(Pm—Pm)][C_5H_5Mo(CO)_3]$.—$\nu$(CH) bands at 3112 (w), 3087 (vw), 2996 (vw), and 2912 (vw) cm^{-1}; see Table II for ν(CO) bands; other bands at 1423 (m), 1408 (w), 1303 (w), 1289 (m), 1233 (vw), 1095 (vw), 1085 (vw), 1055 (vw), 1001 (vw), 990 (vw), 946 (w, sh), 940 (m), 925 (w), 910 (w), 825 (m), 772 (m), 736 (vw), 703 (vw), and 631 (w) cm^{-1}.

D. $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$.—$\nu$(CH) bands at 3115 (vw), 2974 (vw), and 2906 (vw) cm^{-1}; see Table II for ν(CO) band; ν(PF) band at 835 (s) cm^{-1}; other bands at 1420 (m) 1306 (w), 1292 (m), 1240 (vvw), 1105 (w, br), 1008 (vvw), 936 (m), 904 (w), 868 (m, sh), 820 (s), 735 (w), 706 (w), 658 (w), 610 (vw), 579 (w), and 547 (s) cm^{-1}.

Discussion

A. Molybdenum Complexes.—The three chelating ditertiary phosphines used in this work each reacted readily with $[C_5H_5Mo(CO)_3]_2$ in benzene solution at room temperature with fading of the red color and deposition of a yellow precipitate. These yellow precipitates were unambiguously identified as the salts $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ by comparison of the ν(CO) frequencies in their infrared spectra of KBr pellets (Table II) with those of the salts $[(C_2H_5)_4N][C_5H_5Mo(CO)_3]$[18] and $[C_5H_5Mo(CO)_2(diphos)]X$ (X = Cl or PF_6) as authentic representatives of the $C_5H_5Mo(CO)_3^-$ anion and $C_5H_5Mo(CO)_2(diphos)^+$ cations, respectively.[19-21] The $[C_5H_5Mo(CO)_2(diphos)]Cl$ salts were obtained by reaction of $C_5H_5Mo(CO)_3Cl$ with the chelating ditertiary phosphines in benzene solution at room temperature, an extension of the preparative methods of Treichel, Barnett, and Shubkin.[21] Simple metathesis with ammonium hexafluorophosphate converted the chlorides to the corresponding more readily purified hexafluorophosphates. The $[C_5H_5Mo(CO)_2(diphos)][PF_6]$ salts were identified by elemental analyses and by their proton nmr spectra which exhibited triplet π-C_5H_5 resonances owing to coupling of the π-C_5H_5 protons with the two phosphorus atoms attached to the same molybdenum atom. The ν(CO) frequencies of the $C_5H_5Mo(CO)_2(diphos)^+$ salts were similar to those of previously reported[13,21] $C_5H_5Mo(CO)_2L_2^+$ salts.

The salts $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ were stable in the solid state in the absence of air but decomposed rapidly when dissolved in acetone or chlorinated solvents; reliable nmr spectra of these salts could not be obtained. Recrystallization of these salts was not possible. However, analyses indicated that the product $[C_5H_5Mo(CO)_2(Pm—Pm)][C_5H_5Mo(CO)_3]$ originally precipitated from the reaction mixture was pure. On the other hand, analyses indicated the other two $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ (diphos = Pf—Pf and Pf=Pf) compounds to be somewhat impure when originally precipitated from the reaction mixture. Our observations suggest that the phenylated chelating ditertiary phosphines Pf—Pf and Pf=Pf do not react as readily with metal carbonyls as the methylated chelating ditertiary phosphine Pm—Pm. Possibly more side reactions involving decomposition to insoluble materials occur in the slower reactions of $[C_5H_5Mo(CO)_3]_2$ with Pf—Pf and Pf=Pf than in the faster reaction of $[C_5H_5Mo(CO)_3]_2$ with Pm—Pm.

B. Iron Complexes.—A comparison of the reactions of $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Mo(CO)_3]_2$ with tetrakis(dimethylamino)ethylene[22] suggests a much greater difficulty in converting $[C_5H_5Fe(CO)_2]_2$ to $C_5H_5Fe(CO)_2^-$ than in converting $[C_5H_5Mo(CO)_3]_2$ to $C_5H_5Mo(CO)_3^-$. This is consistent with our present

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(18) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), **5**, 341 (1966).

(19) Analyses of the chloride salts were in best agreement with formulations as the monohydrates $[C_5H_5Mo(CO)_2(diphos)]Cl \cdot H_2O$. Other examples of monohydrate formation by chloride salts of complex cyclopentadienylmetal carbonyl cations have been previously noted (*e.g.*, $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl \cdot H_2O$).[20] In the cases of the $[C_5H_5Mo(CO)_2(diphos)]Cl \cdot H_2O$ salts the scales of their preparations were sufficiently small that the absorption of 0.02–0.05 g of water from the solvent or from the atmosphere would be sufficient to form the monohydrate.

(20) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 293 (1966).

(21) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.* (Amsterdam), **7**, 449 (1967).

(22) R B .King, *Inorg. Chem.*, **4**, 1518 (1965).

observation that all three of the chelating ditertiary phosphines studied (Pf—Pf, Pf=Pf, and Pm—Pm) convert $[C_5H_5Mo(CO)_3]_2$ to $[C_5H_5Mo(CO)_2(\text{diphos})][C_5H_5Mo(CO)_3]$ whereas only the most reactive (Pm—Pm) converts $[C_5H_5Fe(CO)_2]_2$ to $[C_5H_5Fe(CO)(\text{diphos})][C_5H_5Fe(CO)_2]$. Although the anion $C_5H_5Fe(CO)_2^-$ has been known since 1956[23] and has been extensively[24] used in solution as a reagent for the preparation of many $RFe(CO)_2C_5H_5$ compounds, the salt $[C_5H_5Fe(CO)(\text{Pm—Pm})][C_5H_5Fe(CO)_2]$ is the first derivative of the *anion* $C_5H_5Fe(CO)_2^-$ to be isolated in the solid state.

Kinetic studies by electrochemical techniques[25] have shown the anion $C_5H_5Fe(CO)_2^-$ to have very high relative nucleophilicity of 70,000,000 compared to the anion $C_5H_5Mo(CO)_3^-$ with a relative nucleophilicity of only 67. This high nucleophilicity of $C_5H_5Fe(CO)_2^-$ is consistent with the air sensitivity of $[C_5H_5Fe(CO)(\text{Pm—Pm})][C_5H_5Fe(CO)_2]$. Treatment of this iron salt with air destroyed the $C_5H_5Fe(CO)_2^-$ anion but not the $C_5H_5Fe(CO)(\text{Pm—Pm})^+$ cation as demonstrated by the ability to isolate appreciable amounts of the hexafluorophosphate $[C_5H_5Fe(CO)(\text{Pm—Pm})][PF_6]$ by treatment of a filtered solution of completely decomposed $[C_5H_5Fe(CO)(\text{Pm—Pm})][C_5H_5Fe(CO)_2]$ with ammonium hexafluorophosphate. Thus, the anion $C_5H_5Fe(CO)_2^-$ and not the cation $C_5H_5Fe(CO)(\text{Pm—Pm})^+$ is the "unstable" part of the salt $[C_5H_5Fe(CO)(\text{Pm—Pm})][C_5H_5Fe(CO)_2]$.

The infrared spectrum (Table II) of $[C_5H_5Fe(CO)(\text{Pm—Pm})][C_5H_5Fe(CO)_2]$ exhibits $\nu(CO)$ frequencies at 1970, 1858, and 1770 cm^{-1}. The $\nu(CO)$ frequency at 1970 cm^{-1} also appears in the salt $[C_5H_5Fe(CO)(\text{Pm—Pm})][PF_6]$ indicating that it arises from the cation. This leaves the two frequencies of 1858 and 1770 cm^{-1} for the $C_5H_5Fe(CO)_2^-$ anion. These compare with the frequencies of 2028 and 1967 cm^{-1} for the isostructural $C_5H_5Co(CO)_2$.[26] Except for the expected shift[27] to lower frequencies and for minor changes in the separation between the two bands, the $\nu(CO)$ frequencies of the isostructural species $C_5H_5Fe(CO)_2^-$ and $C_5H_5Co(CO)_2$ are quite similar. Furthermore, the general region of the $\nu(CO)$ frequencies in $C_5H_5Fe(CO)_2^-$ is similar to that in $C_5H_5Mo(CO)_3^-$ indicating similar carbon–oxygen bond orders and hence similar charges on the metal atoms[27] in these similar cyclopentadienylmetal carbonyl anions.

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[23] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[24] For a review including a discussion of numerous derivatives prepared from the $C_5H_5Fe(CO)_2^-$ anion, see R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964), especially pp 229–234.

[25] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966).

[26] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[27] For a discnssion of the relationship between $\nu(CO)$ frequencies and bonding in metal carbonyls see F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30601

Complexes of Trivalent Phosphorus Derivatives. VII. Some Triphenyl Phosphite Derivatives of Cyclopentadienylmolybdenum Carbonyls[1,2]

By R. B. King[3] and K. H. Pannell[4]

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Ultraviolet irradiation of $[C_5H_5Mo(CO)_3]_2$ with triphenyl phosphite in benzene solution gives red-violet, insoluble $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$. Reduction of this compound with dilute sodium amalgam in tetrahydrofuran solution gives the sodium salt $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ which reacts with various organic halides to give pale yellow derivatives of the type $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ (R = methyl, ethyl, allyl, or benzyl). The proton nmr spectra of these four compounds indicate each compound to be a mixture of two stereoisomers. Reaction of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with isopropyl bromide or *t*-butyl chloride gives the hydride $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. The sparingly soluble mercury derivative $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$ and tin derivative $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ were prepared from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and mercury(II) cyanide or trimethyltin chloride, respectively. A second more soluble isomer of the tin derivative was prepared by ultraviolet irradiation of $(CH_3)_3SnMo(CO)_3C_5H_5$ with triphenyl phosphite. Treatment of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ with iodine gives the red iodide $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ which may also be obtained from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and iodine or 2-iodoheptafluoropropane. This iodide reacts with silver trifluoroacetate to give the corresponding red trifluoroacetate $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.

Introduction

Recently we reported reactions of trivalent phosphorus ligands with cyclopentadienyliron carbonyl derivatives containing iron–silicon or iron–tin bonds.[5] We have also investigated reactions between trivalent phosphorus ligands and other compounds with metal–metal bonds including $[C_5H_5Mo(CO)_3]_2$. Thus chelating ditertiary phosphines such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ react with $[C_5H_5Mo(CO)_3]_2$ breaking the molybdenum–molybdenum bond to give yellow salts

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[1] Part VI: R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).

[2] Portions of this work were presented at the Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, Italy, Sept 1968.

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] Postdoctoral Research Associate supported by Grant GP-7081 of the National Science Foundation from June to Dec 1967.

[5] R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 1510 (1968).