Metal Complexes of Fluorophosphines. II. The Use of Tetrakis(trifluorophosphine)nickel as a Source of Trifluorophosphine in the Synthesis of Metal–Trifluorophosphine Complexes[1–3]

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Abstract: Reactions of transition metal derivatives with $Ni(PF_3)_4$ in boiling toluene provide a new method for the synthesis of trifluorophosphine–metal complexes. The reaction of $[(CH_3)_5C_5RhCl_2]_2$ with $Ni(PF_3)_4$ gives orange $(CH_3)_5C_5Rh(PF_3)_2$. The analogous reaction of $[(CH_3)_5C_5IrCl_2]_2$ with $Ni(PF_3)_4$ gives a mixture of pale yellow $(CH_3)_5C_5Ir(PF_3)_2$ and pale yellow $(CH_3)_5C_5IrF(PF_2)(PF_3)$. Reaction of $Mn(CO)_5Br$ with $Ni(PF_3)_4$ results in debromination to give a yellow mixture of the composition $Mn_2(CO)_{10-x}(PF_3)_x$ (x = 0.5–1.5). However the corresponding reaction of $Re(CO)_5Br$ with $Ni(PF_3)_4$ gives a colorless mixture of $Re(CO)_3(PF_3)_2Br$ isomers without debromination. Reaction of $C_5H_5Mo(CO)_3Cl$ with $Ni(PF_3)_4$ results in dechlorination to give either dark red $(C_5H_5)_2Mo_2(CO)_5(PF_3)$ or dark red $[C_5H_5Mo(CO)_2PF_3]_2$, depending upon the reaction conditions. Reaction of $C_5H_5Fe(CO)_2I$ with $Ni(PF_3)_4$ gives brown $C_5H_5Fe(CO)(PF_3)I$ without deiodination. Reactions of the methyl–transition metal derivatives $CH_3M(CO)_3C_5H_5$ (M = Mo and W) with $Ni(PF_3)_4$ give yellow $CH_3M(CO)_2(PF_3)(C_5H_5)$ (M = Mo and W). The infrared, proton, fluorine nmr, and, in some cases, mass spectra of the new compounds are described.

During the last few years metal complexes of trifluorophosphine (phosphorus trifluoride) have received considerable attention.[5,6] Such complexes are of particular interest because of the similarly high π-acceptor strengths of both the trifluorophosphine and the carbonyl groups combined with the higher metal–ligand bond strength in metal–trifluorophosphine complexes relative to the corresponding metal–carbonyl complexes. This makes many metal–trifluorophosphine complexes more stable than the corresponding metal carbonyls. Furthermore, the extensive known chemistry of metal carbonyls[7] makes analogous chemistry of metal–trifluorophosphine derivatives of considerable interest.[5,6]

Investigation of the chemistry of metal–trifluorophosphine complexes first requires the development of efficient methods for forming metal–trifluorophosphine bonds. Known syntheses of metal–trifluorophosphine complexes employ the following two general methods: (1) reactions of free metals, metal halides, metal–olefin complexes, or other carbonyl-free metal derivatives (*e.g.*, dibenzenechromium[8]) with phosphorus trifluoride under pressure often in the presence of copper metal as an added reducing agent;[5,6] (2) reactions of metal carbonyls with phosphorus trifluoride under relatively mild conditions, often in the presence of ultraviolet irradiation.[6,9–13] Both of these preparative methods require use of the very volatile (bp 101°) phosphorus trifluoride and are thus subject to various inconveniences and limitations associated with the use of a gaseous reagent with such physical properties. Methods for forming metal–trifluorophosphine bonds which do not require the use of free phosphorus trifluoride are thus of some interest.

The following two categories of synthetic methods potentially can give metal–trifluorophosphine complexes without requiring the use of free phosphorus trifluoride: (1) fluorination of a metal complex of another trivalent phosphorus ligand (*e.g.*, trichlorophosphine);[6] (2) transfer of a PCl_3 group from a readily available metal–trifluorophosphine complex to other transition metals. The fluorination method has been employed in the synthesis of $Ni(PF_3)_4$ by fluorination of $Ni(PCl_3)_4$ with potassium fluorosulfinate.[14] The scope of this fluorination method for the preparation of metal–trifluorophosphine complexes is limited by the instability of many transition metal systems, particularly those in lower oxidation states, toward the necessary fluorinating agents. The trifluorophosphine transfer method had not been employed when this work was started because no trifluorophosphine complex was sufficiently readily available to serve as a practical source of trifluorophosphine groups for other transition metals. However, when tetrakis(trifluorophosphine)nickel, $Ni(PF_3)_4$, became commercially available in research quantities, its use as a source of trifluorophosphine groups in the synthesis of other metal–trifluorophosphine complexes appeared feasible. This paper describes some exploratory reactions of $Ni(PF_3)_4$ with various transition metal halides which clearly demonstrate the value of this nickel compound in the synthesis of novel metal–trifluorophosphine complexes.

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(1) For part I of this series, see R. B. King, W. C. Zipperer, and M. Ishaq, *Inorg. Chem.*, 11, 1361 (1972).

(2) For a preliminary communication of some of this work, see R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **93**, 5260 (1971).

(3) Portions of this work were presented to the Division of Fluorine Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

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In some cases the zerovalent nickel derivative $Ni(PF_3)_4$ served both as a reducing and trifluorophosphinating agent. In other cases $Ni(PF_3)_4$ served only as a trifluorophosphinating agent. This work enabled us to extend significantly the known range of cyclopentadienylmetal–trifluorophosphine complexes, since the only previously reported compounds of this type appeared to be $C_5H_5M(PF_3)_2$ (M = Co[15] and Rh[16]) and the series $RC_5H_4Mn(CO)_{3-x}(PF_3)_x$ (R = H or CH_3; x = 1, 2, and 3).[17] The use of $Ni(PF_3)_4$ as a trifluorophosphinating agent in this work resembles the use of $Fe(CO)_5$ as a carbonylating agent in reported preparations of $W(CO)_6$[18] and $Rh_6(CO)_{16}$.[19]

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Meade Microanalytical Laboratory, Amherst, Mass. Melting points were taken in capillaries and are uncorrected. Infrared and nmr data on the new complexes are summarized in Tables I and II, respectively. A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions; (b) handling filtered solutions of metal complexes; and (c) admitting to evacuated vessels.

The tetrakis(trifluorophosphine)nickel, $Ni(PF_3)_4$, was purchased from Ozark-Mahoning, Co., and used as received. The following transition metal derivatives were prepared by the cited published procedures: $[(CH_3)_5C_5MCl_2]_2$ (M = Rh[20] and Ir[20]), $M(CO)_5Br$ (M = Mn[21] and Re[22]), $C_5H_5Fe(CO)_2I$,[23] $C_5H_5Mo(CO)_3Cl$,[24] and $CH_3M(CO)_3C_5H_5$ (M = Mo[24,25] and W).[24]

Reaction of $[(CH_3)_5C_5RhCl_2]_2$ with $Ni(PF_3)_4$. A mixture of 8.40 g (13.6 mmol) of $[(CH_3)_5C_5RhCl_2]_2$, 20 ml (36 g, 87.5 mmol) of tetrakis(trifluorophosphine)nickel, and 250 ml of toluene was boiled under reflux for 40 hr. The reaction mixture was cooled to room temperature and filtered. Solvent was removed from the filtrate at 50° (35 mm). The residue was sublimed at 30° (0.01 mm) to give 6.5 g (58% yield) of a deep orange crystalline sublimate of $(CH_3)_5C_5Rh(PF_3)_2$, mp 88–89°.

Anal. Calcd for $C_{10}H_{15}F_6P_2Rh$: C, 29.0; H, 3.6; F, 27.5; P, 15.0; Rh, 24.8. Found: C, 29.5; H, 3.6; F, 27.4; P, 14.9; Rh, 24.7.

Reaction of $[(CH_3)_5C_5IrCl_2]_2$ with $Ni(PF_3)_4$. A mixture of 2.0 g (2.5 mmol) of $[(CH_3)_5C_5IrCl_2]_2$, 8 ml (14.4 g, 35 mmol) of tetrakis(trifluorophosphine)nickel, and 100 ml of toluene was boiled under reflux for 28 hr. Because of the apparent sensitivity of the iridium–trifluorophosphine derivatives to water and other hydroxylic solvents, the $[(CH_3)_5C_5IrCl_2]_2$ for this reaction was dried at 70–80° (0.01 mm) for 24 hr prior to use and the toluene was freshly distilled over metallic sodium. After the reaction period was over, the reaction mixture was cooled to room temperature and filtered in a nitrogen atmosphere. Solvent was removed from the filtrate at 50° (35 mm). The residue was sublimed at 25° (0.01 mm) for 12–14 hr to give 0.5 g (20% yield) of pale yellow $(CH_3)_5C_5Ir(PF_3)_2$, mp 90–92°. After removal of the $(CH_3)_5C_5Ir(PF_3)_2$ the residue was sublimed further at 75–80° (0.01–0.05 mm) to give 0.19 g (8% yield) of pale yellow $(CH_3)_5C_5IrF(PF_2)(PF_3)$, mp ~140°. Both iridium compounds were handled as much as possible in a nitrogen-filled glove bag because of their apparent moisture sensitivity.

Anal. Calcd for $C_{10}H_{15}F_6IrP_2$: C, 23.8; H, 3.0; F, 22.6; Ir, 38.2; P, 12.3; O, 0.0; mol wt, 503. Found for $(CH_3)_5C_5Ir(PF_3)_2$: C, 24.0; H, 3.2; F, 22.6; Ir, 38.1; P, 12.4; O, 0.0; mol wt, 494 (osmometer in chloroform). Found for $(CH_3)_5C_5IrF(PF_2)(PF_3)$: C, 23.8; H, 3.2; F, 22.6; Ir, 38.1; P, 12.4; O, 0.0; mol wt, 517 (osmometer in chloroform).

Reaction of $Mn(CO)_5Br$ with $Ni(PF_3)_4$. A mixture of 5.0 g (18.2 mmol) of $Mn(CO)_5Br$, 10 ml (18 g, 43.8 mmol) of tetrakis(trifluorophosphine)nickel, and 100 ml of toluene was boiled under reflux for 27 hr. Solvent was removed from the filtered reaction mixture at 40–50° (35 mm). The yellow residue was dissolved in 60 ml of pentane and the pentane solution cooled to −78° to give 1.02 g of yellow crystals, mp 67–68°, after filtration of the cold solution. Further purification of this product by sublimation at 25° (0.05 mm) gave 0.85 g (18% yield) of a yellow solid, mp 70–71°. Analytical data on this yellow solid indicated it to be a mixture. However, bromine was clearly absent.

Anal. Calcd for $Mn_2(CO)_{8.5}(PF_3)_{1.5}$: C, 21.2; H, 0.0; Br, 0.0; F, 17.7; Mn, 23.0; P, 9.7. Found: C, 21.7, 22.8; H, 0.0; Br, 0.0; F, 20.3, 19.0; Mn 22.5, 23.0; P, 8.7, 8.3.

Reaction of $Re(CO)_5Br$ with $Ni(PF_3)_4$. A mixture of 2.0 g (4.9 mmol) of $Re(CO)_5Br$, 5.5 ml (9.9 g, 24 mmol) of $Ni(PF_3)_4$, and 100 ml of toluene was boiled under reflux for 2 hr. Solvent was removed from the filtered reaction mixture at 40–50° (35 mm). The residue was sublimed at 25° (0.01 mm). After removal of trace quantities of the initial oily sublimate, further sublimation at 25° (0.01 mm) for 48 hr gave 0.65 g (25% yield) of colorless crystalline $Re(CO)_3(PF_3)_2Br$. The analytical sample, mp 40–41°, was purified by low-temperature crystallization from pentane.

Anal. Calcd for $C_3BrF_6O_3P_2Re$: C, 6.8; Br, 15.2; F, 21.6; P, 11.8. Found: C, 6.4; Br, 17.0; F, 20.5; P, 11.3.

Reaction of $C_5H_5Mo(CO)_3Cl$ with $Ni(PF_3)_4$. A mixture of 2.5 g (8.9 mmol) of $C_5H_5Mo(CO)_3Cl$, 3.2 ml (5.8 g, 14 mmol) of tetrakis(trifluorophosphine)nickel, and 80 ml of toluene was boiled under reflux for 14 hr. Solvent was removed from the filtered reaction mixture at 40–50° (35 mm). The residue was sublimed twice at 115–125° (0.1 mm) to give 0.13 g (15% yield) of dark red crystalline $(C_5H_5)_2Mo_2(CO)_5(PF_3)$, mp 159–160°. Extensive decomposition occurred during each sublimation.

Anal. Calcd for $C_{15}H_{10}F_3Mo_2O_5P$: C, 33.0; H, 1.8; F, 10.3; P, 5.5. Found: C, 34.0; H, 1.9; F, 9.6; P, 5.5.

If the reaction between $C_5H_5Mo(CO)_3Cl$ and $Ni(PF_3)_4$ was carried out under more vigorous conditions using a greater amount of $Ni(PF_3)_4$ relative to $C_5H_5Mo(CO)_3Cl$, the product was $[C_5H_5Mo(CO)_2PF_3]_2$ rather than $(C_5H_5)_2Mo_2(CO)_5(PF_3)$. Thus a mixture of 6.0 g (21.3 mmol) of $C_5H_5Mo(CO)_3Cl$, 15 ml (27 g, 65.6 mmol) of tetrakis(trifluorophosphine)nickel, and 125 ml of toluene was boiled under reflux for 24 hr. Solvent was removed from the filtered reaction mixture at 40–50° (35 mm). A pentane solution of the residue was cooled to −78° to give 0.58 g (9% yield) of deep red $[C_5H_5Mo(CO)_2PF_3]_2$, dec >175°.

Anal. Calcd for $C_{14}H_{10}F_6Mo_2O_4P_6$: C, 27.5; H, 1.6; F, 18.7; Cl, 0.0. Found: C, 27.8; H, 1.7; F, 17.0; Cl, 0.0.

Reaction of $C_5H_5Fe(CO)_2I$ with $Ni(PF_3)_4$. A mixture of 1.0 g (3.29 mmol) of $C_5H_5Fe(CO)_2I$, 2.0 ml (3.6 g, 8.8 mmol) of tetrakis(trifluorophosphine)nickel, and 75 ml of toluene was boiled under reflux for 12 hr. Solvent was removed from the filtered reaction mixture at 40° (30 mm). The residue was dissolved in ~70 ml of hexane. The filtered hexane solution was cooled to −78° to give a dark crystalline precipitate. This was removed by filtration and sublimed at 25° (0.1 mm) for 12 hr to give 0.93 g (77% yield) of brown crystalline $C_5H_5Fe(CO)(PF_3)I$, mp 102–103°.

Anal. Calcd for $C_6H_5F_3FeIOP$: C, 19.9; H, 1.4; F, 15.7; Fe, 15.4; P, 8.5. Found: C, 20.2; H, 1.5; F, 15.5; Fe, 15.1; P, 8.1.

Reaction of $CH_3Mo(CO)_3C_5H_5$ with $Ni(PF_3)_4$. A mixture of 1.0 g (3.85 mmol) of $CH_3Mo(CO)_3C_5H_5$, 4.0 ml (7.2 g, 17.6 mmol) of tetrakis(trifluorophosphine)nickel, and 50 ml of toluene was boiled under reflux for 19 hr. Solvent was removed from the filtered reaction mixture at 50° (35 mm). The residue was sublimed at 25° (0.05 mm). The infrared spectrum of the sublimate indicated it to be a mixture of $CH_3Mo(CO)_3C_5H_5$ and $CH_3Mo(CO)_2(PF_3)C_5H_5$. This sublimate was chromatographed on a 2 × 30 cm Florisil column. The yellow band of product was eluted with hexane. Evaporation of the eluate gave 0.3 g (24% yield) of yellow waxy $CH_3Mo(CO)_2(PF_3)(C_5H_5)$. This compound was rather air sensitive both in solution and in the solid state. Upon prolonged standing even in vacuum it decomposed. Because of the limited stability of this compound, it was necessary to carry out its chromatographic purification as rapidly as possible.

Anal. Calcd for $C_8H_8F_3MoO_2P$: C, 30.0; H, 2.5; F, 17.8;

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Table I. Infrared Spectra of Metal–Trifluorophosphine Complexes Prepared in This Work^{a}

Compound	ν(CO),^{b} cm^{-1}	ν(PF),^{c} cm^{-1}	Other,^{c} cm^{-1}
$Me_5C_5Rh(PF_3)_2$		905 (vs), 836 (vs)	1073 (w), 1033 (w)
$Me_5C_5IrF(PF_2)(PF_3)$		866 (m), 844 (s)	2131 (w), 1102 (w), 1033 (w), 733 (m)
$Re(CO)_3(PF_3)_2Br$	2085 (s), 2068 (s), 2025 (s), 2012 (s) 1982 (s) 1963 (s)	916 (s), 894 (m), 886 (s), 872 (s), 863 (s), 853 (m)	
$Cp_2Mo_2(CO)_5PF_3$	1986 (m) 1957 (s) 1895 (vs), 1843 (vs)^{d}	847 (s), 837 (s), 823 (s), 807 (s)	1060 (w), 1018 (vw), 1011 (w), 1004 (w)
$[CpMo(CO)_2PF_3]_2$	1988 (w), 1913 (s), 1898 (s)^{d}	866 (m), 843 (s), 824 (s)	1063 (w), 1020 (w), 1008 (vw)
$CpFe(CO)(PF_3)I$	2021 (s)	888 (m), 868 (m), 848 (m)	1062 (vw), 1013 (w, sh), 1006 (w)
$MeMo(CO)_2(PF_3)Cp$	1997 (s), 1938 (s)	886 (w), 857 (s), 842 (sh), 828 (w), 818 (m)	1013 (vw)
$MeW(CO)_2(PF_3)Cp$	1990 (s), 1933 (s)	863 (s), 847 (w, sh), 825 (m)	1010 (vw)

^{a} These infrared spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. The spectra were calibrated against the 1601-cm^{-1} band of polystyrene film. ^{b} Unless otherwise indicated, the ν(CO) frequencies were measured in saturated hydrocarbon solvents such as pentane or hexane. ^{c} These frequencies were obtained from spectra taken in Nujol mulls. ^{d} Nujol mull.

Table II. Nmr Spectra of Metal–Trifluorophosphine Complexes Prepared in This Work

	Proton nmr spectrum^{a,b}		Fluorine nmr spectrum^{b,c}		
Compound	R_5C_5^{d}	Other	$\phi(PF_3)$	$^{1}J_{PF}$	Other coupling constants
$Me_5C_5Rh(PF_3)_2$	7.97 (t, 4)^{e}		10.8 (dtd)	1335	$^{2}J_{PP} = 178$, $^{2}J_{RhF} \approx 30$, $^{3}J_{PF} \approx 6$
$Me_5C_5Ir(PF_3)_2$	7.87 (t, 4)^{e}		16.6 (dt)	1250	$^{2}J_{PP} = 90$, $^{3}J_{PF} \approx 2$
$Me_5C_5IrF(PF_2)(PF_3)$	7.83 (q, 4)^{e}		PF_3 20.5 (d)	1280	
			PF_2 4.4 (d)	1180	
$Re(CO)_3(PF_3)_2Br$			A 10.2 (d)	1237	
			B 11.9 (d)	1262	
			C 24.6 (d)	1309	
			D 25.8 (d)	1313	
$CpFe(CO)(PF_3)I$	5.88 (s)		4.5 (d)^{f}	1325	
$CpW(CO)_2(PF_3)CH_3$	5.29 (t, 3)	CH_3 9.61	A 4.9 (d)	1245	
			B 12.7 (d)	1260	

^{a} Unless otherwise indicated, the proton nmr spectra were taken in C_6D_6 solution at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane as an internal standard. ^{b} Unless otherwise indicated, the fluorine nmr spectra were taken in CH_2Cl_2 solution at 56.456 MHz on a Hitachi Perkin-Elmer R-20 spectrometer with 1,2-difluoro-1,1,2,2-tetrachloroethane (ϕ 67.8) as an internal standard. The ϕ scale is used as reported by G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). ^{c} The following abbreviations are used: s = singlet; d = doublet; t = apparent triplet (not necessarily 1:2:1); q = quartet. Coupling constants are given in hertz. ^{d} Coupling constants are given in parentheses. ^{e} CH_2Cl_2 solution. ^{f} C_6D_8 solution.

Mo, 30.0; P, 9.7. Found: C, 29.7; H, 2.6; F, 18.5; Mo, 30.5; P, 10.5.

Reaction of $CH_3W(CO)_3C_5H_5$ with $Ni(PF_3)_4$. A mixture of 3.0 g (8.62 mmol) of $CH_3W(CO)_3C_5H_5$, 7.0 ml (12.6 g, 30.4 mmol) of tetrakis(trifluorophosphine)nickel, and 60 ml of toluene was boiled under reflux for 27 hr. Solvent was removed from the resulting reaction mixture at 40–50° (35 mm). The residue was dissolved in ~50 ml of pentane. The filtered pentane solution was cooled in a −78° bath. The crystals which separated were removed by filtration and sublimed at 25° (0.05 mm) to give 1.3 g (37% yield) of yellow hygroscopic $CH_3W(CO)_2(PF_3)(C_5H_5)$, mp 119–121°. This compound decomposed rapidly in solution. It was best kept in a sealed evacuated tube at 0°.

Anal. Calcd for $C_8H_8F_3O_2PW$: C, 23.5; H, 2.0; F, 14.0; P, 7.6. Found: C, 25.3; H, 2.0; F, 14.3; P, 6.2.

Mass Spectra. The mass spectra listed below were taken at 70 eV on a Hitachi Perkin-Elmer RMU-6 mass spectrometer with a chamber temperature of 220°. The spectra of the pentamethylcyclopentadienyliridium compounds were relatively complex because of the tendency for ions such as $(CH_3)_5C_5Ir^+$ to undergo dehydrogenation and loss of individual carbon atoms to give a large variety of ions of the type $C_mH_nIr^+$. In this case only the pentamethylcyclopentadienyliridium ions with a complete pentamethylcyclopentadienyl ($C_{10}H_{15}$) unit are listed below. Relative intensities and sample temperatures are given in parentheses with the designation D in place of a relative intensity value indicating ions that are found mixed with dehydrogenation products.

(A) $(CH_3)_5C_5Rh(PF_3)_2$ (~100°). $C_{10}H_{15}Rh(PF_3)_2^+$ (19), $C_{10}H_{15}Rh(PF_3)(PF_2)^+$ (2), $C_{10}H_{15}RhPF_3^+$ (16), $C_{10}H_{15}RhPF_2^+$ (2), $C_{10}H_{15}Rh^+$ (100), $C_{10}H_{13}Rh^+$ (25), $C_9H_{12}Rh^+$ (2), $C_9H_{10}Rh^+$ (2.5), $C_9H_8Rh^+$ (1.4), $C_9H_7Rh^+$ (2.3), $C_9H_8Rh^+$ (1.3), $C_8H_9Rh^+$ (0.8), $C_8H_8Rh^+$ (1.3), $C_8H_7Rh^+$ (1.5), $C_8H_8Rh^+$ (2.5), $C_8H_5Rh^+$ (2.4), $RhPF_3^+$ (4.4), $C_6H_7Rh^+$ (0.7), $C_6H_8Rh^+$ (1.2), $C_6H_5Rh^+$ (1.7), $C_6H_4Rh^+$ (0.8), $C_5H_5Rh^+$ (1.0), $C_{10}H_{15}RhPF_3^{2+}$ (1.6), $C_4H_5Rh^+$ (1.2), $C_4H_4Rh^+$ (1.5), $C_4H_3Rh^+$ (2.1), $C_4H_2Rh^+$ (1.0), $C_3H_3Rh^+$ (1.2), $C_3H_2Rh^+$ (0.9), $C_{10}H_{15}^+$ (0.3), $C_{10}H_{13}^+$ (0.5), $C_{10}H_{10}^+$ (0.7), $C_{10}H_9^+$ (1.0), $C_{10}H_{15}Rh^{2+}$ (14), $C_9H_7^+$ (1.6), $C_8H_9^+$ (1.3), Rh^+ (9), $C_7H_7^+$ (1.9), PF_3^+ (1.2), $C_8H_5^+$ (1.3), PF_2^+ (1.9), $C_5H_5^+$ (0.8), $C_5H_3^+$ (0.3), $C_4H_5^+$ (1.0), $C_4H_3^+$ (0.9), $C_3H_5^+$ (2.0), $C_3H_3^+$ (1.3); metastable ions at *m/e* 256.5 (s) ($C_{10}H_{15}$-$Rh(PF_3)_2^+ \rightarrow C_{10}H_{15}RhPF_3^+ + PF_3$) and 173.5 (s) ($C_{10}H_{15}RhPF_3^+ \rightarrow C_{10}H_{15}Rh^+ + PF_3$).

(B) $(CH_3)_5C_5Ir(PF_3)_2$ (~140°). $C_{10}H_{15}Ir(PF_3)_2^+$ (100), $C_{10}H_{15}Ir(PF_3)(PF_2)^+$ (14), $C_{10}H_{15}IrPF_3^+$ (D), $C_{10}H_{15}IrPF_2^+$(D), $Ir(PF_3)_2^+$ (0.7), $C_{10}H_{15}IrF^+$ (3), $C_{10}H_{15}Ir^+$ (D), $C_{10}H_{15}Ir(PF_3)_2^{2-}$ (5), $C_{10}H_{15}IrPF_3^{2+}$ (7), $C_{10}H_{15}Ir^{2+}$ (D); metastable ions at *m/e* 343.5 ($C_{10}H_{15}Ir(PF_3)_2^+ \rightarrow C_{10}H_{15}IrPF_3^+ + PF_3$), 258 ($C_{10}H_{15}IrPF_3^+ \rightarrow C_{10}H_{15}Ir^+ + PF_3$), and 172 ($C_{10}H_{15}Ir(PF_3)_2^{2+} \rightarrow C_{10}H_{15}IrPF_3^{2+} + PF_3$).

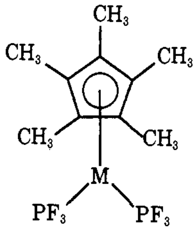
(C) $(CH_3)_5C_5IrF(PF_2)(PF_3)$ (~150°). $C_{10}H_{15}IrF(PF_3)(PF_2)^+$ (100), $C_{10}H_{15}Ir(PF_3)(PF_2)^+$ (5), $C_{10}H_{15}IrPF_3^+$ (D), $C_{10}H_{15}IrF^+$ (32), $C_{10}H_{14}$-IrF^+ (24), $C_{10}H_{15}Ir^+$ (D), $IrPF_3^+$ (7), $C_{10}H_{15}IrPF_3^{2+}$ (10), and $C_{10}H_{15}$-Ir^{2+} (D); metastable ions at *m/e* 343 ($C_{10}H_{15}Ir(PF_3)_2^+ \rightarrow C_{10}H_{15}$-$IrPF_3^+ + PF_3$), 258 ($C_{10}H_{15}IrPF_3^+ \rightarrow C_{10}H_{15}Ir^+ + PF_3$), and 288 ($C_{10}H_{15}IrPF_3^+ \rightarrow C_{10}H_{15}IrF^+ + PF_2$).

(D) $CH_3W(CO)_2(PF_3)(C_5H_5)$ (~100°). $CH_3W(CO)_2(PF_3)(C_5H_5)^+$ (69), $C_5H_5W(CO)_2PF_3^+$ (26), $CH_3W(CO)(PF_3)(C_5H_5)^+$ (50), C_5H_5W-$(CO)(PF_3)^+$ (7), $CH_3W(CO)(PF_2)(C_5H_5)^+$ (7), $CH_3W(PF_3)C_5H_5^+$ (17), $C_6H_6WPF_3^+$ (~28), $C_5H_5WPF_3^+$ (15), $CH_3W(CO)_2C_5H_5^+$ (44), $C_5H_5W(CO)_2^+$ (50), $CH_3W(CO)C_5H_5^+$ (62), $C_8H_6WCO^+$ (37), $C_5H_5WCO^+$ (~50), $C_6H_8W^+$ (~160), $C_6H_6W^+$ (~50), $C_5H_5W^+$ (100), $C_4H_2W^+$ (~30), C_4HW^+ (~30), $C_3H_2W^+$ (~50), C_3HW^+ (~50), $C_2H_2W^+$ (~25), C_2HW^+ (~25), CHW^+ (10), W^+ (~7), $CH_3W(CO)(PF_3)C_5H_5^{2+}$ (~7), $CH_3W(CO)_2C_5H_5^{2+}$ (~1), C_8H_8W-$(CO)_2^{2+}$ (~1), $CH_3WCOC_5H_5^{2+}$ (~1), $C_8H_6WCO^{2+}$ (~1), $C_6H_8W^{2+}$ (~12), $C_6H_4W^{2+}$ (~12), $C_5H_5W^{2+}$ (~3), $C_5H_3W^{2+}$ (~8), $C_4H_4W^{2+}$ (~3), $C_4H_2W^{2+}$ (~6), $C_3H_3W^{2+}$ (~1), PF_3^+ (125), $C_6H_8^+$ (10),

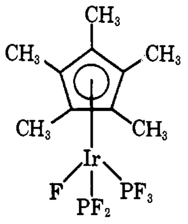
$C_8H_7^+$ (14), $C_6H_6^+$ (5), $C_6H_5^+$ (9), PF_2^+ (140), $C_5H_8^+$ (190), $C_5H_5^+$ (90), $C_4H_3^+$ (35), $C_4H_2^+$ (31), $C_3H_4^+$ (56) and $C_3H_3^+$ (78).

Discussion

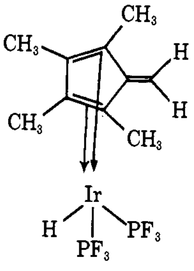
The reaction between $[(CH_3)_5C_5RhCl_2]_2$ and $Ni(PF_3)_4$ resulted in both dehalogenation and trifluorophosphination of the rhodium derivative to give orange crystalline $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh). This compound is clearly the trifluorophosphine analog of the recently prepared[26] $(CH_3)_5C_5Rh(CO)_2$. The proton nmr spectrum of $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh) exhibits a triplet arising from the 15 equivalent pentamethylcyclopentadienyl protons split by the two phosphorus atoms of the PF_3 groups. The fluorine nmr spectrum of $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh) exhibits an $X_3AA'X_3'$ pattern[27] which is doubled because of additional coupling with the spin $^1/_2$ rhodium atom. The mass spectrum of $(CH_3)_5C_5Rh(PF_3)_2$ exhibits a fairly intense molecular ion which undergoes stepwise loss of its two trifluorophosphine groups. This stepwise loss of PF_3 groups from $C_{10}H_{15}Rh(PF_3)_2^+$ was supported by the presence of strong metastable ions at the appropriate *m/e* values and resembles the well-established stepwise loss of carbonyl groups in numerous metal carbonyls.[28] The fluorine nmr spectra and the mass spectra thus both unequivocally indicate the presence of two trifluorophosphine ligands attached to the rhodium atom in $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh).



I



II



III

The reaction of $Ni(PF_3)_4$ with the iridium derivative $[(CH_3)_5C_5IrCl_2]_2$ was considerably more complex than the corresponding reaction of $Ni(PF_3)_4$ with the rhodium analog $[(CH_3)_5C_5RhCl_2]_2$ discussed above. Two pale yellow isomeric products of composition $C_{10}H_{15}IrP_2F_6$ were obtained. Both of these isomers $C_{10}H_{15}IrP_2F_6$ were very hygroscopic and thus were handled in a nitrogen-filled glove bag to prevent hydrolysis. In both cases the compositions $C_{10}H_{15}IrP_2F_6$ were established by elemental analyses, solution molecular weight determinations, and the observation of the ion $C_{10}H_{15}IrP_2F_6^+$ as the highest *m/e* ion in the mass spectrum.

The more volatile $C_{10}H_{15}IrP_2F_6$ isomer exhibited a characteristic $X_3AA'X_3'$ pattern[27] in its fluorine nmr spectrum, indicating it to be $(CH_3)_5C_5Ir(PF_3)_2$ (I, M = Ir) similar to the rhodium compound $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh) discussed above. The iridium compound $(CH_3)_5C_5Ir(PF_3)_2$ (I, M = Ir) underwent hydrolysis in moist air much more rapidly than its rhodium analog. Even in the absence of moisture, the iridium compound $(CH_3)_5C_5Ir(PF_3)_2$ readily changed on prolonged standing into the less volatile isomer of $C_{10}H_{15}IrP_2F_6$.

The formation of two $C_{10}H_{15}IrP_2F_6$ isomers from the reaction of $[(CH_3)_5C_5IrCl_2]_2$ and $Ni(PF_3)_4$ was completely unexpected. The less volatile $C_{10}H_{15}IrP_2F_6$ isomer can be formulated either as $(CH_3)_5C_5IrF(PF_2)(PF_3)$ (II), in which one of the phosphorus–fluorine bonds of one of the trifluorophosphine ligands has broken, forming PF_2 and F fragments, or as the fulvene complex $(CH_3)_4C_5CH_2IrH(PF_3)_2$ (III), in which one of the carbon–hydrogen bonds of one of the methyl groups of the pentamethylcyclopentadienyl ligand has broken, forming $(CH_3)_4C_5CH_2$ and H fragments. Both possible formulations of the less volatile $C_{10}H_{15}IrP_2F_6$ isomer II and III are derived from $(CH_3)_5C_5Ir(PF_3)_2$ by an internal oxidative-addition reaction involving either a trifluorophosphine ligand (II) or the pentamethylcyclopentadienyl ligand (III).

The spectroscopic properties of the less volatile $C_{10}H_{15}IrP_2F_6$ isomer strongly suggest its formulation as $(CH_3)_5C_5IrF(PF_2)(PF_3)$ (II) rather than as $(CH_3)_4C_5CH_2IrH(PF_3)_2$ (III). The following observations are particularly pertinent: (1) the presence of two doublet fluorine nmr resonances of approximate 2:3 relative intensities (the coupling constant of the less intense lower field doublet is only 1180 cps which is clearly outside the 1245–1360-cps range observed in both this work and previous[29] work on metal–trifluorophosphine complexes; this lower field doublet nmr resonance can be assigned to the PF_2 fluorines in $(CH_3)_5C_5IrF(PF_2)(PF_3)$), (2) the absence of olefinic proton nmr resonances which would be required for the structure III because of the presence of an olefinic $=CH_2$ group (also no high-field proton nmr resonance was observed corresponding to a hydrogen directly bonded to iridium), (3) the much higher abundance of the ion $C_{10}H_{15}IrF^+$ in the mass spectrum of the less volatile $C_{10}H_{15}IrP_2F_6$ isomer (the presumed $(CH_3)_5C_5IrF(PF_2)(PF_3)$) than in the mass spectrum of the isomeric $(CH_3)_5C_5Ir(PF_3)_2$ (I, M = Ir). Furthermore, the more volatile $C_{10}H_{15}IrP_2F_6$ isomer $(CH_3)_5C_5Ir(PF_3)_2$ exhibits a detectable $Ir(PF_3)_2^+$ ion, whereas this ion is completely absent in the mass spectrum of the less volatile $C_{10}H_{15}IrP_2F_6$ isomer. Two spectroscopic properties of the less volatile isomer of $C_{10}H_{15}IrP_2F_6$ which do not relate to its formulation as II are the presence of a weak infrared band at 2131 (w) cm^{-1}, which could be a ν(Ir–H) frequency, which would be expected for III but not II, and the failure to observe the fluorine nmr resonance arising from the single fluorine directly bonded to the iridium atom. However, a small amount of $(CH_3)_4C_5CH_2IrH(PF_3)_2$ (III) impurity in $(CH_3)_5C_5IrF(PF_2)(PF_3)$ could be sufficient to give a weak ν(Ir–H) frequency without being enough to give reliably detectable nmr resonances. The failure to observe a fluorine nmr resonance arising from the single fluorine atom in $(CH_3)_5C_5IrF(PF_2)(PF_3)$ apparently arises from excessive broadening of this resonance by coupling of this fluorine atom with two nonequivalent phosphorus atoms and with the 15 protons of the pentamethylcyclopentadienyl ring.

This work thus suggests that the iridium(I) derivative $(CH_3)_5C_5Ir(PF_3)_2$ (I, M = Ir) undergoes oxidative addition reactions much more readily than the corresponding rhodium(I) derivative $(CH_3)_5C_5Rh(PF_3)_2$

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(I, M = Rh). Previous work[30] has analogously demonstrated that tertiary phosphine derivatives of iridium(I) (*e.g.*, $[(C_6H_5)_3P]_3IrCl$) undergo oxidative-addition reactions much more readily than corresponding tertiary phosphine derivatives of rhodium(I).

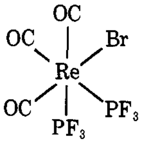
Reactions between the two metal carbonyl bromides $M(CO)_5Br$ (M = Mn and Re) and tetrakis(trifluorophosphine)nickel were investigated in attempts to use this new synthetic method for the preparation of mixed trifluorophosphine-metal carbonyls. However, pure products could be obtained from neither of these reactions. This relates to the analogous difficulty to obtain pure products from reactions of metal carbonyls with trifluorophosphine[8-13] owing to the similar π-accepting properties of the carbonyl and trifluorophosphine ligands which tend to give most possible isomers an approximately equal ease of formation.

The reaction between $Mn(CO)_5Br$ and $Ni(PF_3)_4$ resulted in debromination to give yellow crystalline products in the composition range $Mn_2(CO)_{9.5}(PF_3)_{0.5}$ to $Mn_2(CO)_{8.5}(PF_3)_{1.5}$. The fluorine nmr spectra of these clearly impure products exhibited two doublets (J = ~1300 cps) centered around ϕ −1.5, which differed slightly in relative intensities from sample to sample. The approximate chemical shift difference between these doublets was 0.3 ppm. The lack of fluorine nmr data on pure samples of the $Mn_2(CO)_{10-x}(PF_3)_x$ derivatives[12] prevents a detailed interpretation on the nmr spectrum of this $Mn(CO)_5Br$–$Ni(PF_3)_4$ reaction product at the present time.

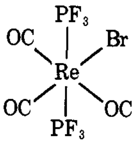
The reaction between $Re(CO)_5Br$ and $Ni(PF_3)_4$, unlike the corresponding reaction between $Mn(CO)_5Br$ and $Ni(PF_3)_4$, did not result in debromination of the rhenium derivative. This is consistent with the well-established higher stability of higher oxidation states of heavier transition metals relative to corresponding lighter transition metals in similar systems. The colorless crystalline product from $Re(CO)_5Br$ and $Ni(PF_3)_4$ had the consistent composition $Re(CO)_3(PF_3)_2Br$. Its fluorine nmr spectrum exhibited two pairs of doublets. In each pair of doublets, each resonance had approximately the same relative intensity. At the present time the precise interpretation of this nmr spectrum is not clear. However, three geometrical isomers for $Re(CO)_3(PF_3)_2Br$ (IVa, IVb, and IVc) are possible.

Several reactions of cyclopentadienylmetal carbonyl halides with $Ni(PF_3)_4$ were investigated in attempts to extend the range of known cyclopentadienylmetal carbonyl trifluorophosphine derivatives. The reaction between $C_5H_5Mo(CO)_3Cl$ and $Ni(PF_3)_4$ resulted in dechlorination to give either the monosubstituted cyclopentadienylmolybdenum tricarbonyl dimer $(C_5H_5)_2Mo_2(CO)_5(PF_3)$ or the disubstituted cyclopentadienylmolybdenum tricarbonyl dimer $[C_5H_5Mo(CO)_2PF_3]_2$. Both of these compounds were red, rather unstable solids. Their instability in solution prevented reliable nmr spectra from being obtained. The infrared spectra of $(C_5H_5)_2Mo_2(CO)_5(PF_3)$ and $[C_5H_5Mo(CO)_2PF_3]_2$ were distinctly different from each other in the ν(CO) region. Furthermore, the infrared spectrum of $[C_5H_5Mo(CO)_2PF_3]_2$ in the ν(CO) region resembled that of related compounds such as $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$.[31]

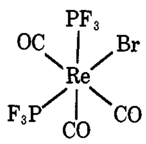
The reaction between $C_5H_5Fe(CO)_2I$ and $Ni(PF_3)_4$, unlike the reaction between $C_5H_5Mo(CO)_3Cl$ and $Ni(PF_3)_4$, did not result in dehalogenation. Instead, the reaction between $C_5H_5Fe(CO)_2I$ and $Ni(PF_3)_4$ gave the iodo derivative $C_5H_5Fe(CO)(PF_3)I$ (V). A pure sample of V could readily be obtained from this reaction, since no other cyclopentadienyliron iodides containing both carbonyl and trifluorophosphine groups are possible. The infrared spectrum of $C_5H_5Fe(CO)(PF_3)I$ (V) exhibited the expected single ν(CO) frequency. Similarly, the fluorine nmr spectrum exhibited the expected doublet PF_3 resonance. An attempt to obtain the mass spectrum of $C_5H_5Fe(CO)(PF_3)I$ using the conditions described in the Experimental Section including a chamber temperature of 220° resulted instead in pyrolytic decomposition to ferrocene in the mass spectrometer.



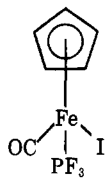
IVa



IVb



IVc



V

There appears to be a relationship between the ease of dehalogenation of a metal carbonyl halide derivative with $Ni(PF_3)_4$ and the nucleophilicity of the corresponding metal carbonyl anion.[32] Metal carbonyl halides which are dehalogenated by $Ni(PF_3)_4$ correspond to metal carbonyl anions of relatively low nucleophilicity. Similarly, metal carbonyl halides which are not dehalogenated by $Ni(PF_3)_4$ correspond to metal carbonyl anions of relatively high nucleophilicity. This relationship is not surprising, since the nucleophilicity of a metal carbonyl anion relates to its tendency to form an additional bond, whereas the dehalogenation of a metal carbonyl halide relates to its tendency to break the metal-halogen bond.

Some reactions of σ-methyl derivatives of transition metals with $Ni(PF_3)_4$ were investigated in attempts to insert a PF_3 group into the methyl-metal bond to prepare a derivative with a CH_3PF_3 group bonded to a transition metal similar to the insertion of CO into the methyl-metal bond to prepare an acetyl derivative.[33] Reaction of $CH_3W(CO)_3C_5H_5$ with $Ni(PF_3)_4$ in boiling toluene gave a relatively unstable yellow solid, indicated by its elemental analyses and mass spectrum to have the composition $CH_3W(CO)_2(PF_3)(C_5H_5)$. The proton nmr spectrum of this compound exhibited a methyl resonance at τ 9.61, indicating that the methyl group has remained bonded to tungsten rather than migrating to phosphorus or carbon. The fluorine nmr spectrum of $CH_3W(CO)_2(PF_3)(C_5H_5)$ exhibited two separate doublet resonances of approximately the same relative intensities. These spectroscopic properties of $CH_3W(CO)_2(PF_3)(C_5H_5)$ are consistent with its formulation as a mixture of isomers VIa and VIb (M = W). The reaction of $CH_3W(CO)_3C_5H_5$ with $Ni(PF_3)_4$

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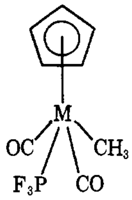
[30] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[31] (a) R. J. Haines, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc. A*, 43 (1968); (b) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).

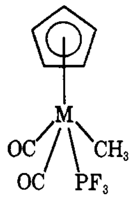
[32] R. E. Dessy, R. L. Pohl and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

[33] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, 10, 101 (1967).

in boiling toluene thus resulted in the replacement of one carbonyl group with a trifluorophosphine ligand without any migration of the methyl group[33] from tungsten to either phosphorus or carbon.



VIa



VIb

The analogous reactions of $CH_3Mo(CO)_3C_5H_5$ and $CH_3Fe(CO)_2C_5H_5$ with $Ni(PF_3)_4$ were also investigated. The reaction between $CH_3Mo(CO)_3C_5H_5$ and $Ni(PF_3)_4$ in boiling toluene gave a yellow crystalline solid of composition $CH_3Mo(CO)_2(PF_3)(C_5H_5)$. Its infrared spectrum was similar to that of the tungsten analog $CH_3W(CO)_2(PF_3)(C_5H_5)$ (VI, M = W), suggesting analogous structures (VI, M = Mo). The reaction between $CH_3Fe(CO)_2C_5H_5$ and $Ni(PF_3)_4$ in boiling toluene gave after chromatography on Florisil an unstable liquid. The infrared spectrum of this liquid in the ν(CO) region exhibited ν(CO) frequencies at 2018 and 1960 cm^{-1}, corresponding to unreacted $CH_3Fe(CO)_2C_5H_5$ (lit.[34] ν(CO) for $CH_3Fe(CO)_2C_5H_5$, 2010 and 1955 cm^{-1}) and an additional stronger ν(CO) frequency at 1982 cm^{-1}, consistent with the presence of a monocarbonyl derivative $CH_3Fe(CO)(PF_3)(C_5H_5)$. The instability of this product precluded attempts to purify it further.

The work described in this paper shows that tetrakis(trifluorophosphine)nickel can serve as a source of trifluorophosphine in the synthesis of metal–trifluorophosphine complexes. In some cases the tetrakis(trifluorophosphine)nickel also acts as a dehalogenating agent. The reactions of metal carbonyls with tetrakis(trifluorophosphine)nickel proceed similarly to their reactions with phosphorus trifluoride[8–13] in that a wide range of closely related and difficultly separable mixed metal carbonyl trifluorophosphine derivatives can be formed. Tetrakis(trifluorophosphine)nickel appears to be unsuited for the insertion of a PF_3 group into an alkyl–metal bond.

Acknowledgment. We are indebted to the National Institute of General Medical Sciences for partial support of this work under Grant No. GM-14664-03.

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Pentamethylcyclopentadienyl Derivatives of Transition Metals. II. Synthesis of Pentamethylcyclopentadienyl Metal Carbonyls from 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene[1–3]

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Abstract: Reactions of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, $(CH_3)_5C_5COCH_3$, with metal carbonyls provide a convenient route to various pentamethylcyclopentadienyl metal carbonyl derivatives. Thus the reaction of $Cr(CO)_6$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives green $[(CH_3)_5C_5Cr(CO)_2]_2$. The reaction of $Mo(CO)_6$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives a mixture of yellow $CH_3Mo(CO)_3C_5(CH_3)_5$ and red $[(CH_3)_5C_5Mo(CO)_2]_2$. Reaction of $(CH_3CN)_3W(CO)_3$ with acetylpentamethylcyclopentadiene in boiling methylcyclohexane gives yellow $CH_3W(CO)_3C_5(CH_3)_5$. Reaction of $Mn_2(CO)_{10}$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives pale yellow $(CH_3)_5C_5Mn(CO)_3$. Reaction of $Fe(CO)_5$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives red-violet $[(CH_3)_5C_5Fe(CO)_2]_2$. However, the reaction of $Fe_2(CO)_9$ with acetylpentamethylcyclopentadiene in pentane at room temperature gives a mixture of the yellow waxy diene complex $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ and the pale yellow crystalline σ-acetyl derivative $CH_3COFe(CO)_2C_5(CH_3)_5$. Reaction of $Co_2(CO)_8$ with acetylpentamethylcyclopentadiene in boiling cyclohexane gives red crystalline $(CH_3)_5C_5Co(CO)_2$. The infrared, proton nmr, and mass spectra of the new pentamethylcyclopentadienyl metal carbonyl derivatives are described.

Several years ago[1] we reported the preparations of several pentamethylcyclopentadienyl metal carbonyls by reactions of pentamethylcyclopentadiene (I) with various metal carbonyls. Of particular interest was the reaction of pentamethylcyclopentadiene with hexacarbonylmolybdenum which gave a red compound $[(CH_3)_5C_5Mo(CO)_2]_2$ with a different type of stoichiometry than that of the molybdenum carbonyl derivative $[C_5H_5Mo(CO)_3]_2$ obtained in an analogous reaction of unsubstituted cyclopentadiene with hexacarbonylmolybdenum.

This relatively early observation on pentamethylcyclopentadienylmolybdenum carbonyl chemistry demonstrated that the chemistry of the pentamethylcyclo-

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(1) The paper, R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 8, 287 (1967), should be considered as part I of this series since it serves as an introduction to our work with pentamethylcyclopentadienyl derivatives of transition metals.

(2) For a preliminary communication of this work, see R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93, 4950 (1971).

(3) Portions of this work were presented at the Fifth International Conference on Organometallic Chemistry, Moscow, U. S. S. R., August 1971, paper 235, abstracts, Vol. II, p 14.

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