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Polytertiary Phosphines and Arsines. III. Metal Complexes of the Tritertiary Phosphine Bis(2-diphenylphosphinoethyl)phenylphosphine[1]

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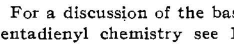
Metal complexes of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (Pf-Pf-Pf) are discussed. This tritertiary phosphine can bond to transition metals in all six possible ways (monoligate monometallic, biligate monometallic, triligate monometallic, biligate bimetallic, triligate bimetallic, and triligate trimetallic). Reactions of chlorides of nickel, palladium, and platinum with Pf-Pf-Pf in ethanol give the yellow-orange to colorless cations (Pf-Pf-Pf)MCl$^+$ (M = Ni, Pd, or Pt) which can be isolated as hexafluorophosphate salts. Reaction of cobalt(II) chloride with Pf-Pf-Pf in boiling ethanol gives orange (Pf-Pf-Pf)$CoCl_2$ which readily decomposes in solution. Reactions of rhodium and iridium chlorides with Pf-Pf-Pf give the yellow to white nonelectrolytes (Pf-Pf-Pf)MCl_3 (M = Rh and Ir). Reactions of ruthenium and osmium chlorides with Pf-Pf-Pf in boiling ethanol give the yellow ruthenium(II) derivative (Pf-Pf-Pf)$RuCl_2$ and the yellow osmium(IV) derivative (Pf-Pf-Pf)$OsCl_4$, respectively. Reaction of the rhodium(I) derivative $[(C_6H_5)_3P]_3RhCl$ with Pf-Pf-Pf in boiling toluene gives the yellow rhodium(I) derivative (Pf-Pf-Pf)RhCl. The hydrides (Pf-Pf-Pf)IrH_3 and [(Pf-Pf-Pf)PtH][PF_6] can be prepared by conventional methods. Reactions of the metal hexacarbonyls or their norbornadiene or cycloheptatriene derivatives with Pf-Pf-Pf give either the yellow bidentate derivatives (Pf-Pf-Pf)$M(CO)_4$ (M = Cr and Mo) or the yellow tridentate derivatives (Pf-Pf-Pf)$M(CO)_3$ (M = Cr, Mo, and W) depending upon the reaction conditions. Reaction of $CH_3Mn(CO)_5$ with Pf-Pf-Pf in boiling benzene gives the pale yellow bidentate derivative $CH_3Mn(CO)_3$(Pf-Pf-Pf). However, reaction of $Mn(CO)_5Br$ with Pf-Pf-Pf in boiling benzene gives the yellow tridentate derivative (Pf-Pf-Pf)$Mn(CO)_2Br$. Reaction of $Fe_2(CO)_9$ with Pf-Pf-Pf at room temperature gives the yellow-orange monodentate derivative (Pf-Pf-Pf)$Fe(CO)_4$. Reaction of $Ni(CO)_4$ with Pf-Pf-Pf at room temperature gives the bidentate derivative (Pf-Pf-Pf)$Ni(CO)_2$ which readily goes to the yellow tridentate derivative (Pf-Pf-Pf)NiCO upon chromatography or heating. Reaction of $CH_3Mo(CO)_3C_5H_5$ with Pf-Pf-Pf in acetonitrile at room temperature gives the pale yellow triligate trimetallic acetyl derivative (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$. Reaction of $C_5H_5Mo(CO)_3Cl$ with Pf-Pf-Pf in benzene at room temperature gives the yellow-brown cation $C_5H_5Mo(CO)_2$(Pf-Pf-Pf)$^+$ with bidentate Pf-Pf-Pf; this cation can be isolated as the chloride or hexafluorophosphate. However, ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with Pf-Pf-Pf in benzene gives red carbonyl-free tridentate C_5H_5Mo(Pf-Pf-Pf)Cl. Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with Pf-Pf-Pf in boiling methanol gives the orange triligate bimetallic derivative $[(C_5H_5)_2Mn_2(CO)(NO)_2$(Pf-Pf-Pf)]$[PF_6]_2$. Reaction of $[C_5H_5Fe(CO)_2]_2$ with Pf-Pf-Pf in boiling toluene gives the green biligate bimetallic derivative (Pf-Pf-Pf)$Fe_2(CO)_2(C_5H_5)_2$. Reaction of $CH_3Fe(CO)_2C_5H_5$ with Pf-Pf-Pf in boiling acetonitrile gives the yellow-brown monodentate acetyl derivative $CH_3COFe(CO)$(Pf-Pf-Pf)(C_5H_5). Ultraviolet irradiation of $C_5H_5Fe(CO)_2Br$ with Pf-Pf-Pf in benzene gives the yellow cation C_5H_5Fe(Pf-Pf-Pf)$^+$ with tridentate Pf-Pf-Pf; this cation can be isolated as the bromide or hexafluorophosphate. The infrared spectra, proton nmr spectra, conductances, and magnetic susceptibilities of some of the new complexes are discussed.

Introduction

During the last few years metal complexes of various chelating ditertiary phosphines, particularly $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, have been extensively investigated. Corresponding studies with metal complexes of chelating tritertiary phosphines have been limited to the ligands $CH_3C[CH_2P(C_6H_5)_2]_3$ (I)$^{4-8}$ and $[o\text{-}(C_6H_5)_2PC_6H_4]_2PC_6H_5$ (II)[9] since appropriate methods for the preparation of other potentially chelating tritertiary phosphines were not available until development of the new synthetic techniques discussed in the first paper of this series.[10] Furthermore, only in recent years has the chemistry of certain metal carbonyl and cyclopentadienylmetal carbonyl derivatives[11] been sufficiently well understood to make such derivatives useful for the preparation of metal carbonyl and cyclopentadienyl derivatives also containing tertiary phosphine ligands.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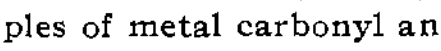
II

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[1] For Part II of this series see R. B. King, *J. Coord. Chem.*, in press.

[2] Postdoctoral research associate, 1968–1969.

[3] Postdoctoral research associate, 1967–1970

[4] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).

[5] R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, **8**, 1042 (1969).

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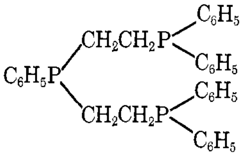
[8] R. Davis and J. E. Fergusson, *ibid.*, **4**, 16 (1970).

[9] J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 3930 (1963).

[10] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **93**, 4158 (1971).

[11] For a discussion of the basic principles of metal carbonyl and metal cyclopentadienyl chemistry see R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

This paper presents a survey of the metal complexes of the chelating tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (III, abbreviated as Pf-Pf-Pf), now readily available[10] through the base-catalyzed addition of phenylphosphine to diphenylvinylphosphine. This tritertiary phosphine III has similar two-carbon bridges between phosphorus atoms as the frequently studied ditertiary phosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. However, the tritertiary phosphine III can complex with metal atoms in a variety of ways such as the following: (1) monoligate monometallic (IVa or less likely[12] IVb), (2) biligate monometallic (IVc), (3) triligate monometallic (IVd), (4) biligate bimetallic (IVe or IVf[12]), (5) triligate bimetallic (IVg), and (6) triligate trimetallic (IVh). All six of these possible modes of coordination of the tritertiary phosphine III have been found in actual complexes described in this paper.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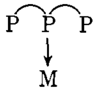
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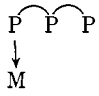
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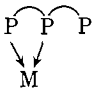
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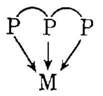
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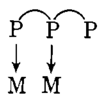
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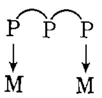
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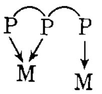
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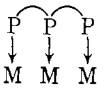
IVh

Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) admitting to evacuated vessels containing organometallic compounds. Ultraviolet irradiations were carried out using a jacketed Engelhard-Hanovia 450-W mercury ultraviolet lamp immersed into the reaction mixture. All reactions described in this paper were carried out with magnetic stirring.

Materials.—The ligand bis(2-diphenylphosphinoethyl)phenylphosphine (III, Pf-Pf-Pf) was prepared by the base-catalyzed reaction of phenylphosphine with diphenylvinylphosphine as discussed in the first paper of this series.[10] Platinum metal compounds were generally purchased from Engelhard Industries, Newark, N. J. The following metal carbonyls were purchased from the indicated commercial sources: $M(CO)_6$ (M = Cr, Mo, and W) (Pressure Chemical Co., Pittsburgh, Pa.), $C_5H_5Mn(CO)_3$ (Ethyl Corp., New York, N. Y.), $Fe(CO)_5$ ((General Aniline and Film, New York, N. Y.), and $Ni(CO)_4$ (Matheson Co., East Rutherford, N. J.). Rhenium trichloride was purchased from Shattuck Chemical Co., Denver, Colo. The remaining transition metal organometallic compounds were prepared by published procedures.[13]

Preparation of [(Pf-Pf-Pf)NiCl][PF$_6$].—A mixture of 0.5 g (2.1 mmol) of $NiCl_2\cdot6H_2O$, 1.1 g (2.1 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 100 ml of ethanol was boiled under reflux until no further color changes occurred. Solvent was removed from the reaction mixture at 25° (40 mm) to give a yellow-green solid (0.9 g) which was recrystallized once from a mixture of acetone and ethanol to give yellow crystals, probably impure [(Pf-Pf-Pf)NiCl]Cl or a hydrate thereof. *Anal.* Calcd for [(Pf-Pf-Pf)NiCl]Cl: C, 61.5; H, 5.0; Cl, 10.7. Calcd for [(Pf-Pf-Pf)NiCl]Cl·3H$_2$O: C, 56.9; H, 5.4; Cl, 10.0. Found: C, 57.8; H, 4.8; Cl, 11.4. This compound was converted to the more readily purified hexafluorophosphate salt by treatment of an acetone solution with an aqueous solution containing excess ammonium hexafluorophosphate followed by slow removal of the acetone at 25° (40 mm). The yellow-orange precipitate was purified by recrystallization from a mixture of acetone and benzene to give [(Pf-Pf-Pf)NiCl][PF$_6$] in ~70% yield.

Preparation of [(Pf-Pf-Pf)PdCl][PF$_6$].—A mixture of 0.5 g (2.8 mmol) of palladium(II) chloride, 0.3 g (5.1 mmol) of sodium chloride, and 20 ml of water was heated until the palladium(II) chloride dissolved to form a red-brown solution. This solution was treated with 2.0 g (3.7 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ and 20 ml of ethanol. The resulting mixture was stirred for 20 hr at room temperature and then filtered. Solvent was removed from the yellow-orange filtrate at ~40° (40 mm). The residue was dissolved in acetone and the filtered solution was treated with an aqueous solution containing excess ammonium hexafluorophosphate. The reaction mixture was then evaporated (40° (40 mm)) to dryness. The residue was washed with water and then recrystallized from a mixture of acetone and ethanol to give 2.1 g (91% yield) of orange-yellow crystalline [(Pf-Pf-Pf)PdCl][PF$_6$].

Preparation of [(Pf-Pf-Pf)PtCl]Cl and [(Pf-Pf-Pf)PtCl][PF$_6$].—A mixture of 0.3 g (0.72 mmol) of potassium tetrachloroplatinate(II), 0.4 g (0.83 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, 50 ml of water, and 50 ml of ethanol was stirred at room temperature for 30 hr. Solvents were removed at ~40° (40 mm). The yellowish residue was washed with several portions of acetone to give 0.4 g (77% yield) of white [(Pf-Pf-Pf)PtCl]Cl, mp >300°. A portion of this chloride was converted to the analogous hexafluorophosphate [(Pf-Pf-Pf)PtCl][PF$_6$] using ammonium hexafluorophosphate in aqueous acetone similar to the procedure used for the nickel and palladium analogs discussed above.

Preparation of (Pf-Pf-Pf)CoCl$_2$.—A mixture of 0.25 g (1.05 mmol) of $CoCl_2\cdot6H_2O$, 0.6 g (1.13 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 50 ml of ethanol was boiled for 3 hr under reflux. After cooling to room temperature, the orange solid which precipitated was removed by filtration and dried to give 0.65 g (94% yield) of (Pf-Pf-Pf)CoCl$_2$, dec pt 220–224°. An attempt to convert this compound to the corresponding hexafluorophosphate led instead to decomposition.

If the reaction between cobalt(II) chloride and the tritertiary phosphine III is performed as described above but using excess cobalt chloride, the red-orange solid which separates from the ethanol at the boiling point becomes blue upon cooling.

Preparation of (Pf-Pf-Pf)RhCl$_3$.—A mixture of 0.3 g (1.16 mmol) of commercial hydrated rhodium trichloride (40% rhodium), 0.7 g (1.31 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 50 ml of ethanol was boiled under reflux for 16 hr. After cooling to room temperature, the yellow solid which precipitated was removed by filtration and dried to give 0.7 g (81% yield) of (Pf-Pf-Pf)RhCl$_3$. This compound was too insoluble in benzene or chloroform to be recrystallized from either or both of these solvents. The analytical sample, dec pt 355°, was obtained by recrystallization from a mixture of dimethylformamide and diethyl ether.

Preparation of (Pf-Pf-Pf)RhCl.—A mixture of 1.0 g (1.27 mmol) of $[(C_6H_5)_3P]_3RhCl$,[14] 0.6 g (1.13 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 100 ml of toluene was boiled under reflux for 30 min. The resulting clear yellow solution was kept for ~12 hr in a freezer at −15°. The yellow crystals which separated were filtered and dried to give 0.75 g (99% yield) of (Pf-Pf-Pf)RhCl, dec pt 240°.

Preparation of (Pf-Pf-Pf)IrCl$_3$.—A 0.3-g (0.54-mmol) sample of $Na_2IrCl_6\cdot6H_2O$ was dissolved in 50 ml of ethanol containing 1 ml of concentrated hydrochloric acid and the resulting mixture was heated until it became brown. At this point 0.4 g (0.75 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ was added. A white solid separated. The reaction mixture was boiled under reflux for 20

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[12] The end phosphorus atoms in the tritertiary phosphine III have two aromatic substituents and one aliphatic substituent whereas the center phosphorus atom in the tritertiary phosphine III has two aliphatic substituents and only one aromatic substituent. The center phosphorus atom would be expected to be more basic than the outer phosphorus atoms in III and hence should bond more readily from the outer phosphorus atoms to transition metals. However, currently available data on the metal complexes of the tritertiary phosphine III do not permit unequivocal differentiation between structures IVa and IVb for the monoligate monometallic complexes of the tritertiary phosphine III.

[13] Except where otherwise indicated, the transition metal organometallic compounds used in this work were prepared as described by R. B. King, "Organometallic Synthesis," Vol. I, Academic Press, New York, N. Y., 1965.

[14] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

hr. The white crystalline precipitate was then removed by filtration and dried to give 0.4 g (89% yield) of (Pf-Pf-Pf)$IrCl_3$, mp 250–255°.

Preparation of (Pf-Pf-Pf)$RuCl_2$.—A mixture of 0.3 g (1.16 mmol) of commercial hydrated ruthenium(III) chloride (39% ruthenium), 0.8 g (1.50 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, 100 ml of ethanol, and 2 ml of concentrated hydrochloric acid was boiled under reflux for ~3 hr. Solvent was then removed at 40° (40 mm). The residue was crystallized from a mixture of chloroform and hexane to give 0.8 g (98% yield) of yellow crystalline (Pf-Pf-Pf)$RuCl_2$, mp 225–228°.

Preparation of (Pf-Pf-Pf)$OsCl_4$.—An osmium stock solution was prepared by dissolving the contents of a 1-g (3.94 mmol) ampoule of osmium tetroxide in 3 ml of concentrated hydrochloric acid and diluting to 50 ml with ethanol. A 10-ml aliquot of this stock solution (0.79 g-atom of osmium) was boiled under reflux with 0.5 g (0.94 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ and 2 ml of concentrated hydrochloric acid. A clear orange solution first formed which deposited a yellow solid upon continued boiling. After ~4 hr the heating was stopped, the reaction mixture was allowed to cool to room temperature, and the resulting yellow precipitate was removed by filtration and dried to give 0.65 g (95% yield) of (Pf-Pf-Pf)$OsCl_4$, mp 270–275° dec.

Reaction of Rhenium Trichloride with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 0.3 g (1.03 mmol as $ReCl_3$) of commercial rhenium trichloride, 0.6 g (1.13 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 100 ml of acetonitrile was boiled under reuflx for 8 hr. A red-brown solid separated. After cooling to room temperature, this solid was removed by filtration, washed with several portions of acetonitrile and benzene, and then dried to give 0.5 g (75% yield) of a red-brown insoluble solid, mp 250–255° dec, identified by analysis as (Pf-Pf-Pf)$_2Re_3Cl_9$. The original acetonitrile filtrate was green, but no identifiable rhenium complex could be isolated from this filtrate.

A similar reaction between rhenium trichloride and $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, but in boiling 2-methoxyethanol rather than acetonitrile, gave a dark green crystalline solid, mp 122–125°, which was readily soluble in dichloromethane. Analytical data, although not entirely definitive, suggested formulation as [(Pf-Pf-Pf)$ReCl_3]_n$. *Anal.* Calcd: Cl, 12.8. Found: Cl, 13.0.

Preparation of (Pf-Pf-Pf)IrH_3.—A suspension of 0.6 g (0.72 mmol) of (Pf-Pf-Pf)$IrCl_3$ in 100 ml of redistilled tetrahydrofuran was stirred with excess (~2 g) lithium aluminum hydride at room temperature. After boiling under reflux for 2 hr the reaction mixture was treated with ~100 ml of water followed by ~200 ml of benzene. Solvent was removed from the dried (Na_2SO_4) benzene layer at 25° (40 mm). The residue was recrystallized from a mixture of benzene and petroleum ether (bp 60–80°) to give ~0.2 g (~38% yield) of white crystalline (Pf-Pf-Pf)IrH_3, mp 93–96°.

Preparation of [(Pf-Pf-Pf)PtH][PF_6].—A mixture of 0.3 g (0.72 mmol) of potassium tetrachloroplatinate(II), 0.4 g (0.75 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 50 ml of 50% aqueous ethanol was boiled under reflux until a clear solution was obtained (~1 hr). The reaction mixture was then treated with 2 ml of 95% hydrazine and boiled 1 additional hr. The ethanol was then removed at 25° (40 mm). The remaining aqueous suspension was neutralized with dilute hydrochloric acid. The white precipitate of crude [(Pf-Pf-Pf)PtH]Cl (0.4 g, 73% yield) was removed by filtration. It was converted to the corresponding hexafluorophosphate salt by treatment with ammonium hexafluorophosphate in a mixture of ethanol, acetone, and water. The white [(Pf-Pf-Pf)PtH][PF_6], dec pt 280°, obtained in 73% yield (based on K_2PtCl_4), was purified by crystallization from a mixture of ethanol and acetone.

Preparation of (Pf-Pf-Pf)$Cr(CO)_4$.—A mixture of 0.5 g (1.96 mmol) of norbornadienetetracarbonylchromium, 1.04 g (1.95 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 60 ml of hexane was boiled under reflux for 5.5 hr. The yellow precipitate which separated was filtered off and purified further by recrystallization from a mixture of benzene and hexane to give 1.2 g (88% yield) of yellow crystalline (Pf-Pf-Pf)$Cr(CO)_4$, mp 111–112°.

Preparation of (Pf-Pf-Pf)$Mo(CO)_4$.—A mixture of 0.5 g (1.90 mmol) of hexacarbonylmolybdenum, 1.00 g (1.87 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 100 ml of methylcyclohexane was boiled under reflux for 42 hr. The reaction mixture was filtered hot. A yellow solid immediately began to separate from the hot filtrate. After cooling to room temperature, this solid was removed by filtration and dried to give 0.8 g (58% yield) of yellow crystalline (Pf-Pf-Pf)$Mo(CO)_4$, mp 128–130°.

A similar reaction between the less reactive[15] $W(CO)_6$ and $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ in boiling methylcyclohexane resulted in the recovery of unchanged starting materials without formation of significant quantities of (Pf-Pf-Pf)$W(CO)_n$ derivatives.

Preparation of the (Pf-Pf-Pf)$M(CO)_3$ (M = Cr, Mo, and W) Derivatives from the Corresponding Hexacarbonyls.—A mixture of 0.5–1.0 g of the metal hexacarbonyl, the stoichiometric amount of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (1:1 mole ratio), and xylene (weight ratio xylene:$M(CO)_6$ = 100:1) was boiled under reflux for periods ranging from 55 hr (M = Cr) to 150 hr (M = W). The reaction mixture was filtered while hot. The filtrate deposited yellow crystals of the (Pf-Pf-Pf)$M(CO)_3$ derivative upon cooling. These crystals were removed by filtration, washed with several portions of hexane, and dried to give ~90% yields of the (Pf-Pf-Pf)$M(CO)_3$ (M = Cr, Mo, and W) derivatives.

Reaction of the Cycloheptatriene Complex $C_7H_8Mo(CO)_3$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 0.5 g (1.84 mmol) of cycloheptatrienetricarbonylmolybdenum, 1.02 g (1.91 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 150 ml of benzene was stirred for 4 hr at room temperature. Solvent was removed from the filtered solution at 25° (40 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give yellow (Pf-Pf-Pf)$Mo(CO)_3$, mp 241–242°, identical with the material obtained from $Mo(CO)_6$ and $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ in boiling xylene as discussed above.

Reaction of $CH_3Mn(CO)_5$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 0.5 g (2.38 mmol) of $CH_3Mn(CO)_5$, 1.28 g (2.40 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 50 ml of benzene was boiled under reflux for 67 hr. Solvent was removed from the filtered reaction mixture at 25° (40 mm) to give 1.5 g (92% yield) of pale yellow crude $CH_3Mn(CO)_3$(Pf-Pf-Pf). The analytical sample, mp 100–101°, was purified by recrystallization from a mixture of dichloromethane and hexane.

Preparation of (Pf-Pf-Pf)$Mn(CO)_2Br$.—A mixture of 1.0 g (3.64 mmol) of $Mn(CO)_5Br$, 1.94 g (3.64 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and 60 ml of benzene was boiled under reflux for 41 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give 2.6 g (99% yield) of crude (Pf-Pf-Pf)$Mn(CO)_2Br$. The analytical sample, mp 219–220° dec, was purified by chromatography on an alumina column in dichloromethane–hexane solution followed by recrystallization from a mixture of dichloromethane and hexane.

Reaction of $Fe_2(CO)_9$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 1.0 g (2.75 mmol) of $Fe_2(CO)_9$, 1.46 g (2.74 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and ~100 ml of benzene was stirred at room temperature for 40 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give a yellow spongy solid which became pasty upon standing. Attempts to crystallize this material from mixtures of dichloromethane with hexane, ethanol, or diethyl ether were unsuccessful. However, treatment of the yellow pasty solid with petroleum ether (bp 60–90°) and evaporation of the filtered solution in a stream of nitrogen gave 1.5 g (78% yield) of yellow-orange crystalline (Pf-Pf-Pf)-$Fe(CO)_4$, mp 67–68°.

Reaction of $C_8H_8Fe(CO)_3$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 0.5 g (2.05 mmol) of cyclooctatetraenetricarbonyliron, 1.05 g (1.97 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and ~100 ml of benzene was boiled under reflux for 21 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give 1.3 g (98% yield) of crude yellow (Pf-Pf-Pf)$Fe(CO)_3$. This crude sample was purified somewhat by recrystallization from mixtures of dichloromethane and petroleum ether or from hexane and petroleum ether, but such recrystallizations did not yield completely pure product apparently owing to instability in solution like other $(R_3P)Fe(CO)_3$ derivatives.[16] *Anal.* Calcd for (Pf-Pf-Pf)$Fe(CO)_3$: C, 65.9; H, 4.9. Found: C, 63.7; H, 5.4.

Reaction of $Ni(CO)_4$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$.—A mixture of 0.5 ml (0.66 g, 3.86 mmol) of tetracarbonylnickel, 1.6 g (3.00 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and ~100 ml of benzene was stirred for 41 hr at room temperature. Evaporation of the filtered reaction mixture at ~25° (40 mm) gave 1.8 g of a yellowish solid identified as (Pf-Pf-Pf)$Ni(CO)_2$ by comparison of the positions of its two ν(CO) frequencies (Table I) with those of authentic $(R_3P)_2Ni(CO)_2$ derivatives. Attempts to separate this material from unreacted ligand by crystallization were un-

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(15) For a discussion of the relative reactivities of the metal hexacarbonyls see R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

(16) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 273 (1968).

TABLE I

INFRARED SPECTRA OF SOME BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE DERIVATIVES IN THE 2000-CM^{-1} REGION[a]

A. Metal Carbonyl and Cyclopentadienylmetal Carbonyl Derivatives

Compound[b]	Medium[c]	ν(CO), cm^{-1}	Ref
(Pf-Pf-Pf)Cr(CO)$_4$	CH	2017 m, 1923 m, 1896 vs, 1870 m, sh	*d*
(Pf-Pf-Pf)Mo(CO)$_4$	CH$_2$Cl$_2$	2026 m, 1942 m, sh, 1923 s, sh, 1902 vs	*d*
(cPf=Pf)Cr(CO)$_4$	C$_6$H$_6$	2009 m, 1914 m, sh, 1899 s, 1877 s	*e*
(Pf-Pf-Pf)Cr(CO)$_3$	CH$_2$Cl$_2$	1929 s, 1834 s, br	*d*
(Pf-Pf-Pf)Mo(CO)$_3$	CH$_2$Cl$_2$	1942 s, 1848 s, br	*d*
(Pf-Pf-Pf)W(CO)$_3$	CH$_2$Cl$_2$	1935 s, 1840 s, br	*d*
cis-[(C$_6$H$_5$)$_3$P]$_3$Mo(CO)$_3$	V	1934 s, 1835 s	*f*
(π-CH$_3$C$_6$H$_5$)W(CO)$_3$	CH	1984 s, 1910 s	*g*
CH$_3$Mn(CO)$_3$(Pf-Pf-Pf)	CH	1999 s, 1921 s, 1865 m	*d*
(Pf-Pf-Pf)Mn(CO)$_2$Br	CH$_2$Cl$_2$	1936 s, 1864 s	*d*
(Pf-Pf-Pf)Fe(CO)$_4$	CH	2054 s, 1975 s, 1940 vs, 1903 m	*d*
(C$_6$H$_5$)$_3$PFe(CO)$_4$	CHCl$_3$	2059 s, 1978 s, 1938 vs	*h*
(Pf-Pf-Pf)Fe(CO)$_3$	CH$_2$Cl$_2$	1984 s, 1912 s, 1889 s	*d*
(cPf=Pf)Fe(CO)$_3$	CH$_2$Cl$_2$	1988 s, 1920 s, sh, 1897 s	*e*
(Pf-Pf-Pf)Ni(CO)$_2$	CH$_2$Cl$_2$	2004 s, 2001 s, 1938 s	*d*
[(C$_6$H$_5$)$_2$PC$_4$H$_9$]$_2$Ni(CO)$_2$	CHCl$_3$	1998 s, 1934 s	*i*
(Pf-Pf-Pf)NiCO	CH$_2$Cl$_2$	1913 s	*d*
[(CH$_3$)$_3$P]$_3$NiCO	C$_{16}$H$_{34}$	1917 s	*j*
C$_5$H$_5$V(CO)$_2$(Pf-Pf-P)	CH	1878 s, 1813 s	*d*
C$_5$H$_5$V(CO)$_2$(Pf-Pf)	CH$_2$Cl$_2$	1864 vs, 1787 vs	*k*
(Pf-Pf-Pf)[Mo(CO)$_2$(COCH$_3$)(C$_5$H$_5$)]$_3$	CH$_2$Cl$_2$	1934 m, 1852 s, 1597 w[l]	*d*
[C$_5$H$_5$Mo(CO)$_2$(Pf-Pf-Pf)]Cl	CH$_2$Cl$_2$	1982 s, 1914 s	*d*
[C$_5$H$_5$Mo(CO)$_2$(Pf-Pf-Pf)][PF$_6$]	KBr	1980 s, 1909 s	*d*
[(C$_5$H$_5$)$_2$Mn$_2$(CO)(NO)$_2$(Pf-Pf-Pf)]-[PF$_6$]	CH$_2$Cl$_2$	2046 s, 1798 s,[o] 1754 s[o]	*d*
(Pf-Pf-Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$	CH$_2$Cl$_2$	1672 s[m]	*d*
(cPf=Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$	CCl$_4$	1691 s[m]	*n*
CH$_3$COFe(CO)(Pf-Pf-Pf)(C$_6$H$_5$)	CH$_2$Cl$_2$	1913 s, 1591 m[l]	*d*

B. Metal Hydride Derivatives

Compound[b]	Medium	ν(MH), cm^{-1}	Ref
(Pf-Pf-Pf)IrH$_3$	KBr	2030 m, br, 1975 m, br	*d*
[(Pf-Pf-Pf)PtH][PF$_6$]	KBr	1978 m	*d*

[a] These spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 infrared spectrometer. [b] The following abbreviations are used: Pf-Pf-Pf, [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$; cPf=Pf, *cis*-(C$_6$H$_5$)$_2$PCH=CHP(C$_6$H$_5$)$_2$. [c] CH, cyclohexane solution; KBr, potassium bromide pellet; V, vaseline. [d] Data from this work. [e] Data from R. B. King and C. A. Eggers, *Inorg. Chim. Acta*, **2**, 33 (1968). [f] Data from R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962). [g] Data from R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966). [h] Data from F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960). [i] Data from G. R. vanHecke and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966). [j] Data from M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1986 (1960). [k] Data from H. Behrens and H. Brandl, *Z. Naturforsch. B.*, **22**, 1353 (1967). Pf-Pf = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$. [l] Acyl ν(CO) frequency. [m] Bridging ν(CO) frequency. [n] Data from R. J. Haines and A. L. duPreez, *J. Organometal. Chem.*, **21**, 181 (1970). [o] ν(NO) frequency.

promising. Upon chromatography on alumina a pale yellow band was obtained which gave a pale yellow solid upon elution and evaporation of the eluate. However, this yellow solid had only one strong ν(CO) frequency in its infrared spectrum and was shown to be (Pf-Pf-Pf)NiCO by comparison of the position of this ν(CO) frequency with that reported for [(CH$_3$)$_3$P]$_3$NiCO (Table I). A purer sample of (Pf-Pf-Pf)NiCO, mp 207–208°, was obtained directly from the reaction between Ni(CO)$_4$ and [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$ in boiling benzene or toluene without the need to decarbonylate an intermediate dicarbonyl by chromatography. *Anal.* Calcd for (Pf-Pf-Pf)NiCO: C, 67.7; H, 5.3; P, 15.0. Found: C, 65.3; H, 5.2; P, 13.6. However, we were unable to obtain completely pure (Pf-Pf-Pf)NiCO apparently owing to some instability in solution.

Reaction of C$_5$H$_5$V(CO)$_4$ with [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$.—A mixture of 0.64 g (2.81 mmol) of C$_5$H$_5$V(CO)$_4$, 1.5 g (2.82 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and 125 ml of toluene was boiled under reflux for 22 hr. During this time the originally yellow solution became a dark red-brown. After the reaction period was over, the reaction mixture was allowed to cool to room temperature. Solvent was removed from the filtered solution at 25° (0.1 mm) to give 1.5 g (76% yield) of a red-brown solid shown to be C$_5$H$_5$V(CO)$_2$(Pf-Pf-Pf) from the two ν(CO) frequencies in its infrared spectrum. Because of its instability and air sensitivity, particularly in solution, this complex could not be obtained completely pure. The sample used for analysis, an orange solid, mp 86–88°, was purified by chromatography on alumina under nitrogen in a 70:30 mixture of dichloromethane and hexane. *Anal.* Calcd for C$_5$H$_5$V(CO)$_2$(Pf-Pf-Pf): C, 69.7; H, 5.4; O, 4.5. Found: C, 67.0; H, 5.6; O, 5.6.

Preparation of (Pf-Pf-Pf)[Mo(CO)$_2$(COCH$_3$)(C$_5$H$_5$)]$_3$.—A mixture of 0.5 g (1.93 mmol) of CH$_3$Mo(CO)$_3$C$_5$H$_5$, 1.03 g (1.93 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and ~100 ml of acetonitrile was stirred for 60 hr at room temperature. The pale yellow solid which separated was removed by filtration, washed with acetonitrile, and dried to give 0.6 g (71% yield based on CH$_3$Mo(CO)$_3$C$_5$H$_5$) of pale yellow (Pf-Pf-Pf)[Mo(CO)$_2$(COCH$_3$)(C$_5$H$_5$)]$_3$, mp 123–125°.

Preparation of [C$_5$H$_5$Mo(CO)$_2$(Pf-Pf-Pf)]Cl and [C$_5$H$_5$Mo(CO)$_2$(Pf-Pf-Pf)][PF$_6$].—A mixture of 0.7 g (2.50 mmol) of C$_5$H$_5$Mo(CO)$_3$Cl, 1.33 g (2.49 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and 100 ml of benzene was stirred for 28 hr at room temperature. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give 1.4 g (71% yield) of yellow-brown solid [C$_5$H$_5$Mo(CO)$_2$(Pf-Pf-Pf)]Cl, mp 71°. A portion of this chloride was converted to the corresponding hexafluorophosphate by treatment with ammonium hexafluorophosphate by a procedure similar to that described above for the conversion of [(Pf-Pf-Pf)PtCl]Cl to [(Pf-Pf-Pf)PtCl][PF$_6$].

Preparation of C$_5$H$_5$Mo(Pf-Pf-Pf)Cl.—A mixture of 0.5 g (1.79 mmol) of C$_5$H$_5$Mo(CO)$_3$Cl, 0.95 g (1.78 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and ~250 ml of benzene was exposed to ultraviolet irradiation for 41 hr. An infrared spectrum of the solution after 22 hr showed that all carbonyl groups had been lost. Solvent was removed from the filtered reaction mixture at 25° (40 mm). During this process a red solid separated. Removal of this solid by filtration gave 1.2 g (92%) yield of red C$_5$H$_5$Mo(Pf-Pf-Pf)Cl. The analytical sample, dec pt 260°, was purified by recrystallization from a mixture of dichloromethane and hexane. Because of the limited solubility of C$_5$H$_5$Mo(Pf-Pf-Pf)Cl, a relatively large amount of dichloromethane was necessary for its recrystallization.

Preparation of [(C$_5$H$_5$)$_2$Mn$_2$(CO)(NO)$_2$(Pf-Pf-Pf)][PF$_6$]$_2$.—A mixture of 1.0 g (2.85 mmol) of [C$_5$H$_5$Mn(CO)$_2$NO][PF$_6$],[17] 0.76 g (1.43 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and 50 ml of methanol was boiled under reflux for 21 hr. The reaction mixture was filtered from a yellow solid (~0.2 g) which had separated. Solvent was removed from the orange filtrate at ~40 mm. The orange solid which separated was removed by filtration and washed with several portions of benzene. It was then crystallized from a mixture of dichloromethane and ethanol to give 0.8 g (49% yield) of orange [(C$_5$H$_5$)$_2$Mn$_2$(CO)(NO)$_2$(Pf-Pf-Pf)][PF$_6$]$_2$, mp 192–194°. The analytical sample was purified further by recrystallization from hot methanol. Attempted purification of this compound by chromatography on alumina led to decomposition.

Reaction of [C$_5$H$_5$Fe(CO)$_2$]$_2$ with [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$.—A mixture of 0.5 g (1.42 mmol) of [C$_5$H$_5$Fe(CO)$_2$]$_2$, 1.5 g (2.81 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and ~100 ml of toluene was boiled under reflux for 21 hr. Solvent was removed from the filtered reaction mixture at ~25° (0.1 mm) to give 1.8 g of crude green (Pf-Pf-Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$ containing much excess [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$. This material was purified by chromatography in 1:1 dichloromethane–hexane on a 2 × 40 cm alumina column. Development of the chromatogram led to a weak yellow band of ferrocene followed by an intense green band of the (Pf-Pf-Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$; the filtered eluate from the latter band gave pure green (Pf-Pf-Pf)Fe$_2$(CO)$_2$(C$_5$H$_5$)$_2$, mp 132–134°, upon evaporation.

Preparation of CH$_3$COFe(CO)(Pf-Pf-Pf)(C$_5$H$_5$).—A mixture of 0.5 g (2.60 mmol) of CH$_3$Fe(CO)$_2$C$_5$H$_5$, 1.4 g (2.63 mmol) of [(C$_6$H$_5$)$_2$PCH$_2$CH$_2$]$_2$PC$_6$H$_5$, and ~50 ml of acetonitrile was

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(17) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

boiled under reflux for 76 hr. Solvent was removed from the filtered solution at ~25° (40 mm) to give 1.75 g (93% yield) of yellow-brown crude $CH_3COFe(CO)(Pf\text{-}Pf\text{-}Pf)(C_5H_5)$. The analytical sample, mp 62–64°, was purified by one recrystallization from a mixture of benzene and petroleum ether (bp 90–120°) followed by a second recrystallization from a mixture of dichloromethane and hexane.

Preparation of $[C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)]Br$ and $[C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)][PF_6]$.—A mixture of 1.0 g (3.89 mmol) of $C_5H_5Fe(CO)_2Br$,[18] 2.07 g (3.88 mmol) of $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$, and ~250 ml of benzene was exposed to ultraviolet irradiation for 15 hr. Solvent was removed at 25° (40 mm) from the filtered black reaction mixture to give a black pasty solid. A dichloromethane solution of this solid was passed through a 2 × 50 cm alumina column and the chromatogram was developed with dichloromethane. The originally black band did not move but instead become yellow on the column. The yellow band was eluted with acetone. Solvent was removed from the filtered acetone eluate at ~25° (40 mm) to give a yellow oil which crystallized upon trituration with a mixture of benzene and petroleum ether (bp 90–120°). This yellow solid was then recrystallized from a mixture of dichloromethane and hexane to give 1.5 g (52% yield) of yellow $[(C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)]Br$, mp 240–242° dec. A portion of this $[C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)]Br$ was converted to the corresponding hexafluorophosphate by treatment of its acetone solution with an aqueous solution containing excess ammonium hexafluorophosphate followed by concentration at 25° (40 mm). The solid which separated was removed by filtration and then purified further by recrystallization from a mixture of acetone and benzene to give yellow $[C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)][PF_6]$, mp 253–255° dec.

Infrared Spectra.—Far-infrared spectra (400–100 cm^{-1}) of the metal chloride complexes (Table II) were obtained in Nujol mulls pressed between polyethylene plates and recorded on a Beckman IR-11 spectrometer. Assignments of the ν(M–Cl) frequencies were based on comparison with known spectra of related compounds[19–22] and must be regarded as tentative until far-infrared data on corresponding bromides and iodides become available.

TABLE II

FAR-INFRARED SPECTRA OF METAL CHLORIDE COMPLEXES OF BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE[a]

Complex[b]	ν(M–Cl), cm^{-1}	Other bands, cm^{-1}
Pf-Pf-Pf		257 vvw, 231 vvw
$[(Pf\text{-}Pf\text{-}Pf)NiCl][PF_6]$	344 m	386 w,[c] 363 vw,[c] 285 vw
$[(Pf\text{-}Pf\text{-}Pf)PdCl][PF_6]$	318 s	366 w,[c] 357 w,[c] 288 w, 274 vvw
$[(Pf\text{-}Pf\text{-}Pf)PtCl][PF_6]$	314 m	369 m,[c] 275 vw, 220 w
$[(Pf\text{-}Pf\text{-}Pf)PtCl]Cl$	324 m, 318 m	375 w,[c] 360 m,[c] 335 sh,[c] 275 vvw, 249 m, 233 m
$(Pf\text{-}Pf\text{-}Pf)CoCl_2$	338 s, 322 s	393 w,[c] 248 s, 223 s, 172 m, 147 m
$(Pf\text{-}Pf\text{-}Pf)RhCl_3$	302 s, 278 sh, 269 s	221 m
$(Pf\text{-}Pf\text{-}Pf)RhCl$	274 vw	
$(Pf\text{-}Pf\text{-}Pf)IrCl_3$	314 w	
$(Pf\text{-}Pf\text{-}Pf)RuCl_2$	284 sh, 279 vw	233 vw, 229 vw
$(Pf\text{-}Pf\text{-}Pf)OsCl_4$	317 m, 313 m, 301 m	232 w
$(Pf\text{-}Pf\text{-}Pf)_2Re_3Cl_9$	358 s, 331 w, br	204 w

[a] These spectra (400–100 cm^{-1}) were run in Nujol mulls pressed between polyethylene plates and recorded on a Beckman IR-11 spectrometer. Frequencies are given in cm^{-1}. [b] Pf-Pf-Pf = $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$. [c] Probably ν(M–P).

Infrared spectra of the metal carbonyl and metal hydride derivatives in the 2200–1600-cm^{-1} region (Table I) were obtained in the indicated media and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics.

Ultraviolet Spectra.—The following ultraviolet spectra were obtained on a Cary Model 14 spectrometer in ethanol solution (unless otherwise indicated): (A) $[(Pf\text{-}Pf\text{-}Pf)NiCl][PF_6]$, maxima at 419 m$\mu$ (ϵ 3900) and 289 mμ (ϵ 22,000); (B) $[(Pf\text{-}Pf\text{-}Pf)PdCl][PF_6]$, maxima at 328 m$\mu$ (ϵ 14,000) and 266 mμ (ϵ 16,000); (C) $[(Pf\text{-}Pf\text{-}Pf)PtCl][PF_6]$, maximum at 267 m$\mu$ (ϵ 23,000); (D) $(Pf\text{-}Pf\text{-}Pf)CoCl_2$, maxima at 273 m$\mu$ (ϵ 3300), 265 mμ (ϵ 3900), and 259 mμ (ϵ 2900); (E) (Pf-Pf-Pf)RhCl, maximum at 258 mμ (ϵ 15,000); (F) $(Pf\text{-}Pf\text{-}Pf)RuCl_2$, maximum at 360 m$\mu$ (ϵ 2300); (G) $(Pf\text{-}Pf\text{-}Pf)OsCl_4$, maxima at 425 m$\mu$ (ϵ 560), 376 mμ (ϵ 2800), and 340 mμ (ϵ 5600); (H) $(Pf\text{-}Pf\text{-}Pf)ReCl_3$ (CH_2Cl_2 solution), maximum at 626 mμ (ϵ 250).

Proton Nmr Spectra.—The proton nmr spectra listed in Table III were obtained on a Varian HA-100 nmr spectrometer in the indicated solvents. Attempts to obtain nmr spectra of the hydrides $(Pf\text{-}Pf\text{-}Pf)IrH_3$ and $[(Pf\text{-}Pf\text{-}Pf)PtH][PF_6]$ in the high-field metal hydride region failed because of insufficient solubility.

TABLE III

PROTON NMR SPECTRA OF METAL COMPLEXES OF BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE ALSO CONTAINING π-CYCLOPENTADIENYL, METHYL, OR ACETYL GROUPS[a]

		Chemical shifts,[d] τ	
Compound[b]	Solvent	π-C_5H_5	CH_3
$CH_3Mn(CO)_3(Pf\text{-}Pf\text{-}Pf)$	C_6H_6	. . .	9.62 s
$C_5H_5V(CO)_2(Pf\text{-}Pf\text{-}Pf)$	$CDCl_3$	6.02 s	. . .
$(Pf\text{-}Pf\text{-}Pf)[Mo(CO)_2(COCH_3)(C_5H_5)]_3$	$CDCl_3$	~5.2[c]	[c]
$[C_5H_5Mo(CO)_2(Pf\text{-}Pf\text{-}Pf)]Cl$	$CDCl_3$	5.21 s	. . .
$C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)Cl$	$CDCl_3$	6.34 m, br	. . .
$[(C_5H_5)_2Mn_2(CO)(NO)_2(Pf\text{-}Pf\text{-}Pf)][PF_6]_2$	$(CD_3)_2CO$	~4.5 br, ~5.1 br	. . .
$(Pf\text{-}Pf\text{-}Pf)Fe_2(CO)_2(C_5H_5)_2$	$CDCl_3$	5.87 s	. . .
$CH_3COFe(CO)(Pf\text{-}Pf\text{-}Pf)(C_5H_5)$	$CDCl_3$	5.83 d (1)	7.59 d (6)
$[C_5H_5Fe(Pf\text{-}Pf\text{-}Pf)][PF_6]$	$CDCl_3$	5.77	. . .

[a] The proton nmr resonances arising from the Pf-Pf-Pf ligand are not listed although they were observed in all of these spectra at positions similar to the corresponding protons in the free ligand.[8] Thus strong phenyl resonances were observed around τ ~2.7 and broad not always discernible methylene resonances around τ 8. [b] The following abbreviations are used: Pf-Pf-Pf, bis(2-diphenylphosphinoethyl)phenylphosphine; s, singlet; d, doublet; m, multiplet; br, broad. [c] The solubility of this compound was too low for unambiguous determination of the fine structure of the cyclopentadienyl resonance or for observation of the methyl resonance. [d] Coupling constants in hertz are given in parentheses.

Molar Conductance Measurements.—The molar conductances listed in Table IV were determined in ~0.0007–0.003 *M* acetone or nitromethane solutions at room temperature (~25°) using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. The values given in Table IV for the electrolytes represent average values of three or more measurements in the indicated solvent in the above concentration range in the solid state.

Magnetic Susceptibility Measurements.—The following magnetic susceptibilities were measured at room temperature in the solid state on an Alpha Scientific Model 9500 magnetic balance using the Faraday method: (A) $[(Pf\text{-}Pf\text{-}Pf)NiCl][PF_6]$, $\chi_{mol}{}^{27°} = -281 \times 10^{-6}$ cm^3/mol; (B) $(Pf\text{-}Pf\text{-}Pf)CoCl_2$, $\chi_{mol}{}^{27°} = +1419 \times 10^{-6}$ cm^3/mol corresponding to a magnetic moment of 2.11 BM after making a correction of -416×10^{-6} cm^3/mol for the diamagnetism of the ligands; (C) $(Pf\text{-}Pf\text{-}Pf)OsCl_4$, $\chi_{mol}{}^{27°} = +382 \times 10^{-6}$ cm^3/mol corresponding to a magnetic moment of 1.42 BM after making a correction of -452×10^{-6} cm^3/mol for the diamagnetism of the ligands; (D) $(Pf\text{-}Pf\text{-}Pf)_2Re_3Cl_9$, $\chi_{mol}{}^{27°} = -597 \times 10^{-6}$ cm^3/mol.

Discussion

(A) Metal Halide Complexes.—Reactions of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ with metal(II) chlorides of nickel, palladium, and platinum give the cations $(Pf\text{-}Pf\text{-}Pf)MCl^+$ best isolated as hexafluorophosphates. These appear to be square-planar complexes analogous to other known $(R_3P)_3MX^+$ com-

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[20] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970, pp 213–216.

[21] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **90**, 2259 (1968).

[22] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. A*, 1674 (1969).

TABLE IV

METAL COMPLEXES OF BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE

Compound[a]	Color	Mp,[b] °C	Analyses,[c] %										Molar conductance[d]
			C		H		X or O		P		Other		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
A. Metal Chloride Derivatives													
[(Pf-Pf-Pf)NiCl][PF$_6$]	Yellow-orange	260–264	52.8	52.9	4.3	4.4	14.7 (F)	15.1 (F)	16.0	16.1			A, 110; N, 82
[(Pf-Pf-Pf)PdCl][PF$_6$]	Yellow-orange	266–269 dec	49.7	49.8	4.0	4.2	13.7 (F)	14.1 (F)	15.1	15.2	4.3 (Cl)	4.3 (Cl)	A, 107; N, 78
[(Pf-Pf-Pf)PtCl]Cl	White	>300	51.1	50.2	4.1	4.3	8.8 (Cl)	8.5 (Cl)					
[(Pf-Pf-Pf)PtCl][PF$_6$]	White	300–304	44.8	44.4	3.6	3.6	12.5 (F)	12.8 (F)					A, 108; N, 75
(Pf-Pf-Pf)CoCl$_2$	Orange	220–224 dec	61.5	61.0	5.0	5.2	10.7 (Cl)	10.7 (Cl)	14.0	14.0			A, dec; N, dec
(Pf-Pf-Pf)RhCl$_3$	Yellow	355 dec	54.9	55.0	4.5	4.5	14.3 (Cl)	14.1 (Cl)	12.5	12.6			A, 2.7
(Pf-Pf-Pf)RhCl	Yellow	240 dec	60.7	60.7	4.9	5.0	5.3 (Cl)	5.3 (Cl)	13.8	13.9			
(Pf-Pf-Pf)IrCl$_3$	White	250–255	49.0	49.6	4.0	4.1	12.8 (Cl)	13.2 (Cl)					A, 4.6
(Pf-Pf-Pf)RuCl$_2$	Yellow	225–228	57.8	58.5	4.7	4.9	10.0 (Cl)	9.8 (Cl)	13.1	13.2			A, 25
(Pf-Pf-Pf)OsCl$_4$	Yellow	270–275 dec	47.1	45.9	3.8	3.9	16.4 (Cl)	16.9 (Cl)	10.7	10.5	21.9 (Os)	21.5 (Os)	A, 13
(Pf-Pf-Pf)$_2$Re$_3$Cl$_9$	Red-brown	250–255 dec	41.9	42.1	3.4	3.4	16.4 (Cl)	16.1 (Cl)	9.5	9.9			A, 8.5
B. Metal Hydride Derivatives													
(Pf-Pf-Pf)IrH$_3$	White	93–96	56.0	56.1	5.0	5.0			12.7	11.9			
[(Pf-Pf-Pf)PtH][PF$_6$]	White	280 dec	46.6	46.0	3.9	4.3	13.0 (F)	13.0 (F)					A, 110; N, 88
C. Metal Carbonyl Derivatives													
(Pf-Pf-Pf)Cr(CO$_4$)	Yellow	111–112	65.3	64.7	4.8	5.0	9.2 (O)	9.5 (O)					
(Pf-Pf-Pf)Cr(CO)$_3$	Yellow	230–232	66.4	66.3	5.0	5.0	7.2 (O)	7.3 (O)					
(Pf-Pf-Pf)Mo(CO)$_4$	Yellow	128–130	61.5	60.4	4.5	4.4	8.6 (O)	8.9 (O)					
(Pf-Pf-Pf)Mo(CO)$_3$	Yellow	241–243	62.2	61.9	4.6	4.7	6.7 (O)	7.0 (O)					
(Pf-Pf-Pf)W(CO)$_3$	Pale yellow	266–268	55.4	55.5	4.1	4.2	6.0 (O)	6.3 (O)					
CH$_3$Mn(CO)$_3$(Pf-Pf-Pf)	Pale yellow	100–101	66.3	66.1	5.3	5.4	7.0 (O)	7.2 (O)					
(Pf-Pf-Pf)Mn(CO)$_2$Br	Yellow	219–220 dec	59.6	59.4	4.6	4.7	4.4 (O)	4.2 (O)			11.8 (Br)	11.1 (Br)	
(Pf-Pf-Pf)Fe(CO)$_4$	Yellow-orange	67–68	65.0	63.4	4.7	5.2	9.1 (O)	9.5 (O)					
D. Metal Cyclopentadienyl Derivatives													
(Pf-Pf-Pf)[Mo(CO)$_2$-(COCH$_3$)(C$_5$H$_5$)]$_3$	Pale yellow	123–125	55.7	55.8	4.4	4.7	10.9 (O)	10.0 (O)					
[C$_5$H$_5$Mo(CO)$_2$-(Pf-Pf-Pf)]Cl	Yellow brown	71	62.6	63.9	4.9	5.1	4.5 (O)	4.3 (O)					A, 51; N, 49
[C$_5$H$_5$Mo(CO)$_2$-(Pf-Pf-Pf)][PF$_6$]	Yellow-brown	197–200	54.9	55.4	4.3	4.3	12.7 (F)	13.3 (F)	13.8	13.7	10.7 (Mo)	10.8 (Mo)	A, 100; N, 63
C$_5$H$_5$Mo(Pf-Pf-Pf)Cl	Red	260 dec	64.1	64.0	5.2	5.4	4.9 (Cl)	4.7 (Cl)					
[(C$_5$H$_5$)$_2$Mn$_2$(CO)(NO)$_2$-(Pf-Pf-Pf)][PF$_6$]$_2$	Orange	192–194	46.9	47.0	3.8	3.9	19.8 (F)	19.2 (F)			2.4 (N)	2.4 (N)	N, 167
(Pf-Pf-Pf)Fe$_2$(CO)$_2$-(C$_5$H$_5$)$_2$	Green	132–134	66.4	66.6	5.2	5.2	3.8 (O)	3.8 (O)			13.4 (Fe)	12.4 (Fe)	
CH$_3$COFe(CO)-(Pf-Pf-Pf)(C$_5$H$_5$)	Yellow-brown	62–64	69.4	69.4	5.7	5.8	4.4 (O)	4.5 (O)					
[C$_5$H$_5$Fe(Pf-Pf-Pf)]Br	Yellow	240–242 dec	63.7	63.0	5.2	5.3	10.9 (Br)	11.1 (Br)					A, 93; N, 59
[C$_5$H$_5$Fe(Pf-Pf-Pf)]-[PF$_6$]	Yellow	253–255 dec	58.5	57.8	4.8	4.9	14.2 (F)	14.3 (F)	15.5	15.7	7.0 (Fe)	6.9 (Fe)	A, 138; N, 87

[a] Pf-Pf-Pf refers to $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$. [b] These melting points were determined in capillaries and are uncorrected. [c] Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Tungsten trioxide was added as a catalyst for the combustions to determine carbon and hydrogen. [d] The molar conductance values are given in the usual ohm^{-1} cm^2/mol. A, acetone solution; N, nitromethane solution; dec, decomposes too rapidly in the indicated solvent for a meaningful measurement to be obtained.

plexes[23] but with the tritertiary phosphine acting as a tridentate ligand. The yellow color and diamagnetism of the nickel derivative both support its formulation as a square-planar rather than tetrahedral derivative.

Reaction of the tritertiary phosphine III with cobalt(II) chloride in boiling ethanol in a 1:1 mole ratio gives orange crystals of composition (Pf-Pf-Pf)CoCl$_2$. The far-infrared spectrum of (Pf-Pf-Pf)CoCl$_2$ exhibits two strong bands at 338 and 322 cm^{-1} which may be tentatively assigned to ν(Co–Cl) frequencies. The presence of two ν(Co–Cl) frequencies in (Pf-Pf-Pf)CoCl$_2$ indicates that both chlorine atoms are covalently bonded to the cobalt atom corresponding to a nonionic formulation. This was supported further by the inability to convert (Pf-Pf-Pf)CoCl$_2$ to a hexafluorophosphate salt by treatment with ammonium hexafluorophosphate. However, attempts to confirm the nonionic nature of (Pf-Pf-Pf)CoCl$_2$ by conductivity measurements were unsuccessful, since the orange solutions of the cobalt complex rapidly became blue. The complex (Pf-Pf-Pf)CoCl$_2$ exhibited a magnetic susceptibility of 2.11 BM corresponding approximately to the one unpaired electron expected for a low-spin cobalt(II) derivative. Furthermore, this observed magnetic susceptibility value for (Pf-Pf-Pf)CoCl$_2$ is relatively close to that found for the red square-pyramidal five-coordinate derivatives[24] $[(C_6H_5)_2PH]_3CoX_2$ (X = Br, 2.43 BM; X = I, 2.23 BM). Accordingly, (Pf-Pf-Pf)-

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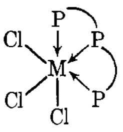
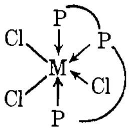
(23) H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, **91**, 596 (1969).

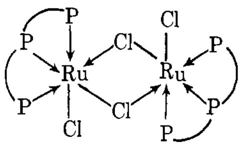
(24) J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 880 (1966).

$CoCl_2$ is formulated as a square-pyramidal five-coordinate nonionic derivative with the tritertiary phosphine III acting as a tridentate ligand.

Reactions of the tritertiary phosphine III with rhodium(III) chloride and with sodium hexachloroiridate(IV) in 1:1 mole ratios in boiling ethanol give (Pf-Pf-Pf)MCl_3 (M = Rh or Ir) derivatives. No evidence of reduction to metal(I) complexes or of formation of carbonyl or hydride derivatives from these reactions was observed. The complexes (Pf-Pf-Pf)MCl_3 (M = Rh or Ir) have a low conductance in acetone solution indicating formulations as nonelectrolytes. Hence, they appear to be octahedral metal(III) complexes with the tritertiary phosphine III occupying three coordination positions. Such complexes can exist as either facial (V) or meridional (VI) isomers. The far-infrared spectrum of the rhodium complex (Pf-Pf-Pf)$RhCl_3$ (Table II) shows three ν(Rh–Cl) frequencies at 302, 278, and 269 cm^{-1} in much closer agreement with the ν(Rh–Cl) frequencies reported[22] for the facial triethylphosphine complex *fac*-$[(C_2H_5)_3P]_3RhCl_3$ (ν(Rh–Cl) = 304 and 274 cm^{-1}) than for the meridional isomer *mer*-$[(C_2H_5)_3P]_3RhCl_3$ (ν(Rh–Cl) = 332, 288, and 256 cm^{-1}). This indicates that (Pf-Pf-Pf)$RhCl_3$ is the facial isomer V (M = Rh).


V


VI


VII

Reaction of the tritertiary phosphine III with $[(C_6H_5)_3P]_3RhCl$ in boiling toluene resulted in displacement of the coordinated triphenylphosphine to give yellow (Pf-Pf-Pf)RhCl. This compound apparently is a square-planar rhodium(I) complex with the tritertiary phosphine III acting as a tridentate ligand. The rhodium(I) complex (Pf-Pf-Pf)RhCl is thus isoelectronic with the palladium(II) cation (Pf-Pf-Pf)-$PdCl^+$ discussed above.

Reaction of the tritertiary phosphine III with commercial ruthenium trichloride in boiling ethanol in the presence of some hydrochloric acid gave a good yield of yellow solid (Pf-Pf-Pf)$RuCl_2$. The tendency for ruthenium(II) to form octahedral six-coordinate rather than five-coordinate complexes suggests formulation of this ruthenium derivative as a dimer $[(Pf\text{-}Pf\text{-}Pf)RuCl_2]_2$ of structure VII with chlorine bridges, but the solubility of this ruthenium complex in organic solvents was too low for a molecular weight determination to be performed. The amount of hydrochloric acid used in the preparation of (Pf-Pf-Pf)$RuCl_2$ appears to be critical, since use of a lesser quantity than that suggested in the Experimental Section appears to result in a different ruthenium complex, still under investigation.

Reaction of the tritertiary phosphine III with osmium tetroxide in the presence of excess hydrochloric acid gave a good yield of the yellow osmium(IV) derivative (Pf-Pf-Pf)$OsCl_4$. This compound exhibited the paramagnetism (~1.4 BM) expected for an octahedral osmium(IV) derivative (reported[25] for $(R_3P)_2OsCl_4$: 1.5–1.6 BM). Its low conductance in acetone indicates it to be a nonelectrolyte; therefore all four chlorine atoms must be bonded to the osmium atom leaving only two coordination positions for the tritertiary phosphine ligand. The tritertiary phosphine in (Pf-Pf-Pf)$OsCl_4$ thus acts as a biligate monometallic ligand. Such a bidentate tritertiary phosphine would be expected to occupy cis positions in an octahedral complex leading to a *cis*-L_2OsCl_4 derivative with C_{2v} symmetry. Group theory predicts such a complex to have four ν(Os–Cl) frequencies ($2\,A_1 + B_1 + B_2$); three of these expected four ν(Os–Cl) frequencies were observed in the far-infrared spectrum of (Pf-Pf-Pf)$OsCl_4$ (Table II). This contrasts with the reported far-infrared spectra of *trans*-$(R_3P)_2OsCl_4$ derivatives[21] which exhibit only one infrared-active ν(Os–Cl) frequency as predicted by group theory.

Reaction of the tritertiary phosphine III with rhenium trichloride gives two different products depending upon the conditions. In boiling acetonitrile a red-brown insoluble diamagnetic solid of stoichiometry $(Pf\text{-}Pf\text{-}Pf)_2Re_3Cl_9$ is obtained. This compound probably contains a triangular rhenium cluster similar to complexes such as the reported[26,27] pale red insoluble $(diphos)_{1.5}Re_3Cl_9$. If the reaction between rhenium trichloride and the tritertiary phosphine III is carried out in boiling 2-methoxyethanol, a dark green solid of approximate stoichiometry (Pf-Pf-Pf)$ReCl_3$ is obtained. The infrared spectrum of this dark green solid shows no ν(Re–O) frequency around 980 cm^{-1} thereby excluding formulation as a rhenium(V) oxyhalide such as (Pf-Pf-Pf)$ReOCl_3$; some known related compounds of this type such as *trans*-$ReOCl_3[P(C_2H_5)_3]_2$ are green.[28] It is possible that (Pf-Pf-Pf)$ReCl_3$ is dimeric and a subtitution product of the dark green $Re_2Cl_8^{2-}$ anion[29] in which two coordinated chloride anions are replaced by tertiary phosphines; known[30] related compounds of the type $[R_3PReCl_3]_2$ are green. However, a formulation of (Pf-Pf-Pf)$ReCl_3$ as an octahedral rhenium(III) derivative with tridentate Pf-Pf-Pf (III) appears preferable for the following reasons: (1) the relative solubility of (Pf-Pf-Pf)$ReCl_3$ in certain organic solvents as contrasted with the insolubility of known[30] $[R_3PReCl_3]_2$ derivatives; (2) the position at 626 mμ (16,000 cm^{-1}) of the maximum in the visible spectrum of (Pf-Pf-Pf)-$ReCl_3$ as contrasted with the 730 mμ (13,700 cm^{-1}) reported maximum in the visible spectrum of $[(C_6H_5)_3PReCl_3]_2$; (3) the failure to obtain similar relatively soluble deep green rhenium(III) tertiary phosphine complexes by analogous reactions in boiling 2-methoxyethanol of rhenium trichloride with the chelating ditertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. In view of various complexities in the chemistry of rhenium(III) derivatives an X-ray crystallographic study on (Pf-Pf-Pf)-$ReCl_3$ is needed before its structure is unambiguously known.

(B) **Metal Hydride Derivatives.**—Two stable metal hydride derivatives of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (III) were prepared containing 5d transition metals which form particularly strong bonds with hydrogen.[31] Lithium aluminum hydride

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(26) F. A. Cotton and R. A. Walton, *Inorg. Chem.*, **5**, 1802 (1966).

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(29) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(30) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *ibid.*, **4**, 1696 (1965).

(31) A. P. Ginsberg, "Progress in Transition Metal Chemistry," Vol. 1, Marcel Dekker, New York, N. Y., 1965, p 112.

reduction of the iridium complex (Pf-Pf-Pf)$IrCl_3$ gave the trihydride (Pf-Pf-Pf)IrH_3 as an air-stable white solid similar to other known[32] $(R_3P)_3IrH_3$ derivatives. The presence of iridium–hydrogen bonds in (Pf-Pf-Pf)-IrH_3 is demonstrated by broad incompletely resolved infrared bands at 2030 and 1975 cm^{-1} (Table I) which can be assigned to ν(Ir–H) frequencies (ν(Ir–H) for *cis*-$[(C_6H_5)_3P]_3IrH_3$ occurs at 2080 cm^{-1}).[32c] The cationic platinum hydride (Pf-Pf-Pf)PtH^+ was obtained by hydrazine reduction of the (Pf-Pf-Pf)$PtCl^+$ cation. It was isolated and characterized as the white hexafluorophosphate salt. The presence of the platinum–hydrogen bond in [(Pf-Pf-Pf)PtH][PF_6] is demonstrated by the infrared band at 1978 cm^{-1} which may be assigned to ν(Pt–H); the ν(Pt–H) frequency for $[(C_6H_5)_3P]_3PtH^+$ is reported[33] to be ~2110 cm^{-1}. Attempts to observe the high-field proton nmr resonances from the metal–hydrogen bonds in (Pf-Pf-Pf)-IrH_3 and [(Pf-Pf-Pf)PtH][PF_6] were unsuccessful apparently for a combination of some of the following reasons: (1) low percentage of hydride hydrogen; (2) predicted complex coupling pattern because of slightly nonequivalent phosphorus atoms in the tritertiary phosphine ligand; (3) insufficient solubility in appropriate organic solvents to overcome the first two problems. For a detailed study of polytertiary phosphine complexes of metal hydrides, polytertiary phosphines with at least some aliphatic groups rather than phenyl rings on the phosphorus atoms appear to be necessary.

(C) **Metal Carbonyl Derivatives.**—The tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (III) can act either as a bidentate or a tridentate ligand in substitution products of the octahedral metal carbonyls.[34] Reaction of the norbornadiene complex $C_7H_8Cr(CO)_4$ with the tritertiary phosphine III results in replacement of the norbornadiene ligand but retention of the four carbonyl groups to give (Pf-Pf-Pf)$Cr(CO)_4$ in which the tritertiary phosphine acts as a bidentate ligand. The molybdenum analog (Pf-Pf-Pf)$Mo(CO)_4$ can be obtained by reaction of the tritertiary phosphine III with hexacarbonylmolybdenum in the saturated hydrocarbon solvent methylcyclohexane at its boiling point. However, reactions of all three metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with the tritertiary phosphine III in the aromatic hydrocarbon solvent xylene at its boiling point give excellent yields of the derivatives (Pf-Pf-Pf)$M(CO)_3$ (M = Cr, Mo, and W) in which the tritertiary phosphine acts as a tridentate ligand. These reactions in xylene probably proceed through an intermediate xylene–metal tricarbonyl derivative.[35] The molybdenum compound (Pf-Pf-Pf)-$Mo(CO)_3$ can also be prepared by displacement of the cycloheptatriene ring in the cycloheptatriene complex $C_7H_8Mo(CO)_3$ with the tritertiary phosphine III by reaction at room temperature in benzene solution.[36]

The infrared spectra in the ν(CO) region (Table I) of the (Pf-Pf-Pf)$M(CO)_4$ and (Pf-Pf-Pf)$M(CO)_3$ derivatives prepared in this work resemble closely the infrared spectra of other similarly substituted tertiary phosphine derivatives of the octahedral metal carbonyls.[34,37]

The iron carbonyl derivatives of the tritertiary phosphine III prepared in this work were much less stable than the octahedral metal carbonyl derivatives of II discussed above and therefore could not be completely purified owing to decomposition in solution during recrystallization. Reaction of $Fe_2(CO)_9$ with the tritertiary phosphine III in benzene at room temperature gives (Pf-Pf-Pf)$Fe(CO)_4$ in which the tritertiary phosphine acts as a monodentate ligand. The same monosubstituted iron carbonyl derivative is also obtained from pentacarbonyliron and the tritertiary phosphine III in boiling toluene, but in this case the product is contaminated with the free tritertiary phosphine III which could not be removed. The disubstituted derivative (Pf-Pf-Pf)$Fe(CO)_3$, in which the tritertiary phosphine acts as a bidentate ligand, is obtained by displacement of the cyclooctatetraene ring in $C_8H_8Fe(CO)_3$ with the tritertiary phosphine III in boiling benzene. The complexes (Pf-Pf-Pf)$Fe(CO)_4$ and (Pf-Pf-Pf)$Fe(CO)_3$ can be identified and differentiated by the ν(CO) frequencies in their infrared spectra (Table I), which correspond to those reported for other $R_3PFe(CO)_4$ and $(R_3P)_2Fe(CO)_3$ derivatives, respectively.

The nickel carbonyl derivatives of the tritertiary phosphine III were also somewhat difficult to purify because of limited stability in solution and were identified mainly by comparison of their ν(CO) frequencies with those of similar known tertiary phosphine substitution products of nickel carbonyl.[38] Reaction of $Ni(CO)_4$ with the tritertiary phosphine III at room temperature gives as the initial product the dicarbonyl (Pf-Pf-Pf)$Ni(CO)_2$ in which the tritertiary phosphine acts as a bidentate ligand. However, upon attempted purification by chromatography on alumina the dicarbonyl (Pf-Pf-Pf)$Ni(CO)_2$ undergoes spontaneous decarbonylation to give the monocarbonyl (Pf-Pf-Pf)-NiCO in which the tritertiary phosphine acts as a tridentate ligand. The monocarbonyl (Pf-Pf-Pf)NiCO is also obtained directly by reaction of $Ni(CO)_4$ with the tritertiary phosphine III in boiling benzene or toluene. Reaction of $[C_5H_5NiCO]_2$ with the tritertiary phosphine III in benzene in room temperature results, as expected,[39] in the displacement of the π-cyclopentadienyl ring to give a mixture of approximately equal quantities of (Pf-Pf-Pf)$Ni(CO)_2$ and (Pf-Pf-Pf)NiCO.

Some manganese carbonyl derivatives of the tritertiary phosphine III were also prepared. Reaction of $Mn(CO)_5Br$ with the tritertiary phosphine III in boiling benzene results in the displacement of three carbonyl groups to give (Pf-Pf-Pf)$Mn(CO)_2Br$ in which the tritertiary phosphine acts as a tridentate ligand. However, a similar reaction of the methyl derivative $CH_3Mn(CO)_5$ with the tritertiary phosphine III results in the displacement of only two carbonyl groups to give $CH_3Mn(CO)_3$(Pf-Pf-Pf) in which the tritertiary phosphine acts only as a bidentate ligand. Formulation of

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[32] (a) R. G. Hayter, *J. Amer. Chem. Soc.*, **83**, 1259 (1961); (b) L. Malatesta, M. Angoletta, A. Araneo, and F. Canziani, *Angew. Chem.*, **73**, 273 (1961); (c) M. Angoletta, *Gazz. Chim. Ital.*, **92**, 811 (1962).

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[35] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Z. Naturforsch. B*, **13**, 458 (1958); *Ber.* **91**, 2763 (1958); B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); G. Natta, R. Ercoli, F. Calderazzo, and S. Santambrogio, *Chim. Ind. (Milan)*, **40**, 1003 (1958).

[36] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

[37] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[38] G. R. van Hecke and W. DeW. Horrocks, Jr., *ibid.*, **5**, 1960 (1966).

[39] R. B. King, *ibid.*, **2**, 936 (1963).

this complex as $CH_3Mn(CO)_3$(Pf-Pf-Pf) rather than the isomeric acetyl derivative $CH_3COMn(CO)_2$(Pf-Pf-Pf) is supported by the following evidence: (1) the apparent absence of an acyl ν(CO) frequency around 1600 cm^{-1} in the infrared spectrum; (2) the similarity between the ν(CO) frequencies found for $CH_3Mn(CO)_3$(Pf-Pf-Pf) (Table I) and those reported[40] for $CH_3Mn(CO)_3$(diphos) derivatives; (3) the presence of an nmr resonance at τ 9.62 in the region corresponding to a methyl group bonded directly to manganese rather than to the acyl carbonyl of an acetyl group.

(D) **Cyclopentadienylmetal Derivatives.**—Reaction of the tritertiary phosphine III with cyclopentadienyltetracarbonylvanadium gives red-brown air-sensitive $C_5H_5V(CO)_2$(Pf-Pf-Pf) in which the tritertiary phosphine acts as a biligate monometallic ligand (IVc) similar to ditertiary phosphines such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)$ in $C_5H_5V(CO)_2$(diphos) complexes.[41] The reaction of the tritertiary phosphine III with $C_5H_5V(CO)_4$ to give $C_5H_5V(CO)_2$(Pf-Pf-Pf) contrasts with the reported[41] reaction of the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ (I) with $C_5H_5V(CO)_4$ to give a $(C_5H_5)_2V_2(CO)_5$(triphos) derivative in which the tritertiary phosphine acts as a triligate dimetallic ligand (IVg).

Reaction of the tritertiary phosphine III with the methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution gives a yellow precipitate of (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$ in which the tritertiary phosphine III acts as a triligate trimetallic ligand as in IVh. This reaction resembles the reported reaction[42] of $CH_3Mo(CO)_3C_5H_5$ with ditertiary phosphines (except for *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$) in acetonitrile solution to give (diphos)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ derivatives. The infrared spectrum of (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$ shows a pattern of metal and acyl ν(CO) frequencies similar to that found in the infrared spectra of the (diphos)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ derivatives indicating similar arrangements of ligands around the molybdenum atom. The trimetallic complex (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$ is very sparingly soluble in organic solvents as might be expected for a trimetallic complex. For this reason a satisfactory nmr spectrum could not be obtained.

The tritertiary phosphine III reacts with $C_5H_5Mo(CO)_3Cl$ in benzene at room temperature to give the $C_5H_5Mo(CO)_2$(Pf-Pf-Pf)$^+$ cation isolated as the chloride and hexafluorophosphate salts. The tritertiary phosphine in the $C_5H_5Mo(CO)_2$(Pf-Pf-Pf)$^+$ cation acts as a bidentate ligand like the chelating ditertiary phosphines in cations of the type $C_5H_5Mo(CO)_2$(diphos)$^+$ obtained from similar reactions of the ligands with $C_5H_5Mo(CO)_3Cl$ at room temperature.[43] Ultraviolet irradiation of the tritertiary phosphine III with $C_5H_5Mo(CO)_3Cl$ in benzene solution results in the eventual displacement of all three carbonyl groups to give the red crystalline carbonyl-free C_5H_5Mo(Pf-Pf-Pf)Cl in which the tritertiary phosphine III acts as a tridentate ligand. This contrasts with the reported[5] ultraviolet irradiation of the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ (I) with $C_5H_5Mo(CO)_3Cl$ for several days to give the monocarbonyl $C_5H_5Mo(CO)$(triphos)Cl in which the tritertiary phosphine acts only as a bidentate ligand. The contrasting tendencies for the tritertiary phosphine I to act as a bidentate ligand upon prolonged irradiation with $C_5H_5Mo(CO)_3Cl$ and for the tritertiary phosphine III to act as a tridentate ligand upon prolonged ultraviolet irradiation with $C_5H_5Mo(CO)_3Cl$ may be a consequence of the greater ease of forming five-membered rather than six-membered rings in chelate systems of this type. The carbonyl-free derivative C_5H_5Mo(Pf-Pf-Pf)Cl is relatively unreactive; thus it remained unchanged upon stirring with methyllithium in diethyl ether at room temperature in an unsuccessful attempt at conversion to a carbonyl-free methyl derivative C_5H_5Mo(Pf-Pf-Pf)CH_3.

Reaction of the tritertiary phosphine III with the salt $[C_5H_5Mn(CO)_2NO][PF_6]$ gives $[(C_5H_5)_2Mn_2(CO)(NO)_2$(Pf-Pf-Pf)$][PF_6]_2$ in which the tritertiary phosphine acts as a triligate bimetallic ligand (IVg) as in a closely related compound obtained from the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ (I) and the same manganese salt.[6] The infrared spectra of both $[(C_5H_5)_2Mn_2(CO)(NO)_2$(triphos)$][PF_6]_2$ compounds in the ν(CO) and ν(NO) regions are nearly identical confirming their similarities. The molar conductance of $[(C_5H_5)_2Mn_2(CO)(NO)_2$(Pf-Pf-Pf)$][PF_6]_2$ in nitromethane solution (Table IV) is consistent with formulation as a 1:2 electrolyte.

Reaction of the tritertiary phosphine III with the binuclear iron derivative $[C_5H_5Fe(CO)_2]_2$ gives green crystals of (Pf-Pf-Pf)$Fe_2(CO)_2(C_5H_5)_2$. The infrared spectrum of this compound exhibits no terminal ν(CO) frequencies and only one bridging ν(CO) frequency indicating that the phosphorus atoms of the tritertiary phosphine ligand III have replaced all of the terminal carbonyl groups but have left intact the bridging carbonyl groups. Similar green compounds with similar infrared spectra in the ν(CO) region were recently[44] obtained by reactions of $[C_5H_5Fe(CO)_2]_2$ with ditertiary phosphines. These data all indicate (Pf-Pf-Pf)$Fe_2(CO)_2(C_5H_5)_2$ to have structure VIII in which the tritertiary phosphine acts as a biligate bimetallic ligand (IVe); this is the only case of biligate bimetallic coordination of the tritertiary phosphine III found in this work.

Reaction of the tritertiary phosphine III with the methyliron derivative $CH_3Fe(CO)_2C_5H_5$ in boiling acetonitrile gives the acetyl derivative $CH_3COFe(CO)$(Pf-Pf-Pf)(C_5H_5) in which the tritertiary phosphine acts as a monodentate ligand. No carbon monoxide is liberated in this reaction since the one carbonyl group replaced by a phosphorus atom of the tritertiary phosphine inserts into the methyliron bond to form an acetyl derivative. The presence of the acetyl group in $CH_3COFe(CO)$(Pf-Pf-Pf)(C_5H_5) is confirmed by the infrared acyl ν(CO) frequency at 1591 cm^{-1} and the position of the methyl resonance at τ 7.75. Similar reactions of $CH_3Fe(CO)_2C_5H_5$ with monotertiary phosphines in polar solvents have been reported.[45] The ultraviolet irradiation of $(CH_3)_3SiFe(CO)_2C_5H_5$ with

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[40] P. K. Maples and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **90**, 6645 (1968).

[41] H. Behrens and H. Brandl, *Z. Naturforsch. B*, **22**, 1353 (1967).

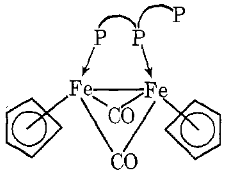
[42] R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

[43] R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *ibid.*, **7**, 2353 (1968).

[44] R. J. Haines and A. L. Du Preez, *J. Organometal. Chem.*, **21**, 181 (1970).

[45] J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966); P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *ibid.*, **5**, 1177 (1966).

the tritertiary phosphine III was also investigated but a pure product was not obtained. Evidence for the presence of a monocarbonyl of the type $RFe(CO)(PR_3)(C_5H_5)$ was obtained from an infrared spectrum of this reaction mixture.



VIII

The photochemical reaction of the tritertiary phosphine III with the iron halide $C_5H_5Fe(CO)_2Br$ follows the peculiar pattern previously[5] observed for the analogous reaction of the tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ (I) with $C_5H_5Fe(CO)_2Br$. After the ultraviolet irradiation of the tritertiary phosphine III with $C_5H_5Fe(CO)_2Br$ has proceeded to the point where ν(CO) frequencies are no longer observed, a black solution is obtained indicative of a nonionic C_5H_5Fe(Pf-Pf-Pf)Br with bidentate tritertiary phosphine III. Chromatography of this black solution on alumina gives a black band which soon turns yellow; the yellow band upon elution gives the ionic $[C_5H_5Fe$(Pf-Pf-Pf)]Br which may be converted to the corresponding hexafluorophosphate salt.

(E) **Conclusion.**—The following complexes characterized in this paper exemplify the six possible coordination modes of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (III): (1) monoligate monometallic (IVa or IVb): (Pf-Pf-Pf)$Fe(CO)_4$ and $CH_3COFe(CO)$(Pf-Pf-Pf)(C_5H_5); (2) biligate monometallic (IVc): (Pf-Pf-Pf)$OsCl_4$, (Pf-Pf-Pf)$M(CO)_4$ (M = Cr and Mo), $CH_3Mn(CO)_3$(Pf-Pf-Pf), and $C_5H_5Mo(CO)_2$(Pf-Pf-Pf)$^+$; (3) triligate monometallic (IVd): (Pf-Pf-Pf)MCl^+ (M = Ni, Pd, and Pt), (Pf-Pf-Pf)$CoCl_2$, (Pf-Pf-Pf)MCl_3 (M = Rh and Ir), (Pf-Pf-Pf)IrH_3, (Pf-Pf-Pf)PtH^+, (Pf-Pf-Pf)$M(CO)_3$ (M = Cr, Mo, and W), (Pf-Pf-Pf)$Mn(CO)_2Br$, C_5H_5Mo(Pf-Pf-Pf)Cl, and C_5H_5Fe(Pf-Pf-Pf)$^+$; (4) biligate bimetallic (IVe or IVf): (Pf-Pf-Pf)$Fe_2(CO)_2(C_5H_5)_2$; (5) triligate bimetallic (IVg): $[(C_5H_5)_2Mn_2(CO)(NO)_2$(Pf-Pf-Pf)]$[PF_6]_2$; (6) triligate trimetallic (IVh): (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$. This work thus demonstrates that a polytertiary phosphine can be made to complex with transition metals in a variety of different ways depending upon the choice of metal atom and the other ligands surrounding the metal atom. In the particular case of the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (III) all of the possible[1] modes of coordination are observed.

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