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UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601Polytertiary Phosphines and Arsines. IV. Metal Complexes
of Two Isomeric Tetratertiary Phosphines¹By R. B. KING,* RAMESH N. KAPOOR,² MOHAN SINGH SARAN,³ AND PRAMESH N. KAPOOR⁴

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Metal complexes of the two isomeric tetratertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf-Pf-Pf) and $[(C_6H_5)_2PCH_2CH_2]_3P$ (abbreviated as P(-Pf)₃) are discussed. Reactions of the chlorides of nickel, palladium, and platinum with the linear tetratertiary phosphine Pf-Pf-Pf-Pf give red-brown to pale yellow derivatives of the type $(Pf-Pf-Pf-Pf)MCl_2$ which react with ammonium hexafluorophosphate to give the hexafluorophosphate salts of the square-planar $(Pf-Pf-Pf-Pf)M^{2+}$ cations. Nickel chloride reacts with the tripod tetratertiary phosphine P(-Pf)₃ in boiling ethanol to form the deep blue five-coordinate $P(-Pf)_3NiCl^+$ cation, isolated as its hexafluorophosphate salt. Reactions of cobalt(II) chloride with either tetratertiary phosphine in boiling ethanol give the brown five-coordinated (tetraphos)- $CoCl^+$ cations, best isolated as their hexafluorophosphate salts. Reactions of hydrated rhodium trichloride with either tetratertiary phosphine in boiling ethanol give the yellow tridentate rhodium(III) derivatives (tetraphos) $RhCl_3$. Reactions of $[(C_6H_5)_3P]_3RhCl$ with either tetratertiary phosphine in boiling toluene followed by treatment with ammonium hexafluorophosphate give the yellow rhodium(I) derivatives $[(tetraphos)Rh][PF_6]$. Reaction of ferrous chloride with the tripod tetratertiary phosphine P(-Pf)₃ in boiling ethanol gives the violet cation $P(-Pf)_3FeCl^+$, isolated as its hexafluorophosphate salt. Reactions of rhenium trichloride with either tritertiary phosphine in 2-methoxyethanol give the green rhenium(III) derivatives (tetraphos) $ReCl_3$. Reactions of the metal hexacarbonyls with the tetratertiary phosphines in boiling xylene give yellow tridentate derivatives of the type (tetraphos) $M(CO)_3$ ($M = Cr$ and Mo). Reactions of the olefinmetal carbonyls $C_7H_8M(CO)_4$ ($C_7H_8 =$ norbornadiene; $M = Cr$ and Mo), $C_7H_8Mo(CO)_3$ ($C_7H_8 =$ cycloheptatriene), and $(1,3-C_6H_5)_2M(CO)_2$ ($M = Mo$ and W) with the tetratertiary phosphines give the yellow bidentate derivatives (tetraphos) $M(CO)_4$ ($M = Cr$ and Mo), the yellow tridentate derivatives (tetraphos) $Mo(CO)_3$, and the yellow tetradentate derivatives $P(-Pf)_3M(CO)_2$ ($M = Mo$ and W), respectively. Reactions of $CH_3Mn(CO)_5$ with the tetratertiary phosphines give the yellow bidentate methyl derivative $CH_3Mn(CO)_5(Pf-Pf-Pf-Pf)$, the light brown tridentate methyl derivative $CH_3Mn(CO)_2P(-Pf)_3$, or the pale yellow bidentate acetyl derivative $CH_3COMn(CO)_3P(-Pf)_3$ depending upon the tetratertiary phosphine and the reaction conditions. Reaction of $Mn(CO)_5Br$ with either tetratertiary phosphine in boiling benzene gives the yellow tridentate (tetraphos) $Mn(CO)_2Br$. Reactions of $CH_3Mo(CO)_5C_6H_5$ with either tetratertiary phosphine in acetonitrile at room temperature give the yellow tetraligand tetrametallic derivatives (tetraphos) $[Mo(CO)_2(COCH_3)(C_6H_5)]_4$. Ultraviolet irradiation of $C_6H_5Mn(CO)_3$ with either tetratertiary phosphine in benzene solution gives the orange to brown bidentate $C_6H_5Mn(CO)(tetraphos)$. Reaction of $[C_6H_5Mn(CO)_2NO][PF_6]$ with the linear tetratertiary phosphine Pf-Pf-Pf-Pf in boiling methanol gives orange triligand bimetallic $[(C_6H_5)_2Mn_2(CO)(NO)_2(Pf-Pf-Pf-Pf)][PF_6]$. However, the reaction of $[C_6H_5Mn(CO)_2NO][PF_6]$ with the tripod tetratertiary phosphine P(-Pf)₃ under the same conditions gives the orange biligand monometallic $[C_6H_5Mn(NO)P(-Pf)_3][PF_6]$. Reactions of $[C_6H_5Fe(CO)_2]_2$ with either tetratertiary phosphine in boiling toluene give the green tetraligand tetrametallic (tetraphos) $[Fe_2(CO)_2(C_6H_5)_2]_2$ derivatives. Reaction of $CH_3Fe(CO)_2C_6H_5$ with Pf-Pf-Pf-Pf in boiling acetonitrile gives orange monodentate monometallic $CH_3COFe(CO)(Pf-Pf-Pf-Pf)(C_6H_5)$. Ultraviolet irradiation of $C_6H_5Fe(CO)_2I$ with Pf-Pf-Pf-Pf followed by treatment with ammonium hexafluorophosphate gives yellow tridentate $[(C_6H_5)_2Fe(Pf-Pf-Pf)][PF_6]$. Reaction of $C_6H_5Fe(CO)_2I$ with P(-Pf)₃ in boiling benzene gives yellow-orange $[C_6H_5Fe(CO)P(-Pf)_3]I$. The infrared spectra, electronic spectra (ultraviolet and visible), molar conductances, and magnetic susceptibilities of many of the new complexes have been determined and are discussed.

Introduction

The base-catalyzed addition of phosphorus-hydrogen compounds to the vinyl double bond in diphenylvinylphosphine makes two new isomeric tetratertiary phosphines readily available in sufficient quantities for the study of their coordination chemistry.^{5,6} Thus the base-catalyzed addition of both phosphorus-hydrogen bonds in 1,2-bis(phenylphosphino)ethane, $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$, to the vinyl double bonds in 2 equiv of diphenylvinylphosphine gives the linear tetratertiary phosphine hexaphenyl-1,4,7,10-tetraphosphadecane $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (I, abbreviated as Pf-Pf-Pf-Pf), the next homolog of the series containing the frequently studied ditertiary phosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and the tritertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_3PC_6H_5$ discussed in the previous paper of this series.¹ Similarly the base-catalyzed addition of the three phos-

phorus-hydrogen bonds in phosphine, PH_3 , to the vinyl double bonds in 3 equiv of diphenylvinylphosphine gives the branched tetratertiary phosphine tris(2-diphenylphosphinoethyl)phosphine $[(C_6H_5)_2PCH_2CH_2]_3P$ (II, abbreviated as P(-Pf)₃), a tripod ligand closely related to several ligands studied by Venanzi and co-workers⁷ but with aliphatic rather than aromatic bridges between phosphorus atoms. Also, several workers have reported various aspects of the coordination chemistry of the related tripod tetradentate ligands $[(CH_3)_2ECH_2CH_2CH_2]_3E'$ ($E = E' = As$,^{8,9} $E = As$, $E' = P$ ¹⁰) which have three-carbon $CH_2CH_2CH_2$ bridges between the donor atoms. In addition, some metal complexes of the tripod tetradentate ligand $[(C_6H_5)_2PCH_2CH_2]_3N$, a nitrogen analog of II, have been prepared.¹¹ This paper describes a comparative study of the reactions of the two isomeric tetratertiary phosphines I and II with various transition metal compounds with the objective of observing the effects of the different relative arrangements of the donor phosphorus

(1) For part III of this series see R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).

(2) Postdoctoral research associate, 1967-1970.

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(4) Postdoctoral research associate, 1968-1969, 1970-1971.

(5) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **91**, 5191 (1969).

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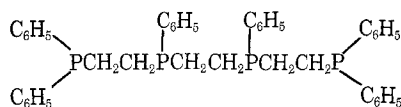
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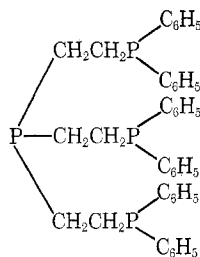
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I



II

atoms in I and II on the nature of the complexes formed.

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.

The sources of the transition metal derivatives used in this work are discussed in the previous paper of this series.¹ The ligand hexaphenyl-1,4,7,10-tetraphosphadecane (I, Pf-Pf-Pf-Pf) was prepared by the base-catalyzed reaction of $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ with diphenylvinylphosphine.^{5,6}

Large-Scale Preparation of Tris(2-diphenylphosphinoethyl)phosphine (II, P(-Pf)₃).—A scaled-up reaction between phosphine and diphenylvinylphosphine at atmospheric pressure in tetrahydrofuran solution in the presence of a potassium *tert*-butoxide catalyst was used to prepare the relatively large quantities of $[(C_6H_5)_2PCH_2CH_2]_3P$ required for this work.

A mixture of 63.6 g (301 mmol) of diphenylvinylphosphine, 2.0 g (17.9 mmol) of potassium *tert*-butoxide, and 250 ml of redistilled tetrahydrofuran (over $LiAlH_4$) was boiled under reflux. Phosphine was generated by dropwise addition of ~50 ml of water to a slurry of 24 g (414 mmol) of aluminum phosphide (Alfa Inorganics, Beverly, Mass.) in ~15 ml of dioxane and passed through the boiling solution of diphenylvinylphosphine for 4 hr in a stream of nitrogen. The effluent nitrogen was passed through a bromine water trap to destroy any unreacted phosphine. After the passage of phosphine through the diphenylvinylphosphine was complete, the tetrahydrofuran was removed from the reaction mixture at ~25° (40 mm). The pale yellow solid residue was washed five times with methanol and dried to give 62.3 g (93% yield) of $[(C_6H_5)_2PCH_2CH_2]_3P$. After two recrystallizations from mixtures of benzene and methanol 47 g (70% yield) of pure $[(C_6H_5)_2PCH_2CH_2]_3P$, mp 128–130° (lit.^{5,6} mp 129–130°), was obtained.

If benzene rather than tetrahydrofuran was used as the solvent in this reaction, no product was obtained.

Reactions of $NiCl_2 \cdot 6H_2O$ with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.26 mmol) of $NiCl_2 \cdot 6H_2O$, 0.9 g (1.34 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and 50 ml of ethanol was boiled under reflux for 42 hr. After cooling to room temperature, the red-brown solid was removed by filtration, washed with hexane, and dried to give 1.0 g (99% yield) of red-brown $(Pf-Pf-Pf-Pf)NiCl_2$. The analytical sample, mp 140–142°, was purified by recrystallization from a mixture of dichloromethane and hexane. A sample of $(Pf-Pf-Pf-Pf)NiCl_2$ was converted to yellow $[(Pf-Pf-Pf-Pf)Ni][PF_6]_2$ by treatment with ammonium hexafluorophosphate in aqueous acetone; the hexafluorophosphate salt was purified by crystallization from a mixture of acetone and ethanol.

A mixture of 0.2 g (0.84 mmol) of $NiCl_2 \cdot 6H_2O$, 0.6 g (0.89 mmol) of the tripod tetratertiary phosphine P(-Pf)₃ (II), and 50 ml of ethanol was boiled under reflux for 6 hr. After cooling to room temperature, the precipitate was removed by filtration and dried to give 0.6 g of a deep blue solid, possibly impure $[P(-Pf)_3NiCl_2][NiCl_4]$ or a hydrate thereof. *Anal.* Calcd for $[P(-Pf)_3NiCl_2][NiCl_4]$: C, 58.3; H, 4.9; Cl, 12.3. Calcd for $[P(-Pf)_3$

$NiCl_2][NiCl_4] \cdot 8H_2O$: C, 53.8; H, 5.3; Cl, 11.4. Found: C, 53.5; H, 5.6; Cl, 11.3. A 0.2-g sample of this blue solid was converted to the hexafluorophosphate by treatment with ammonium hexafluorophosphate in aqueous acetone. The crude hexafluorophosphate was purified by crystallization from a mixture of acetone and benzene to give 0.2 g (79% yield based on $NiCl_2 \cdot 6H_2O$) of shining violet plates of $[P(-Pf)_3NiCl_2][PF_6]$.

Reaction of Na_2PdCl_4 with the Linear Tetratertiary Phosphine Pf-Pf-Pf-Pf.—A mixture of 0.3 g (1.69 mmol) of palladium(II) chloride, 0.2 g (3.42 mmol) of sodium chloride, and 20 ml of water was heated until a dark red-brown solution was obtained. This solution was stirred for 69 hr with 1.14 g (1.70 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) in 20 ml of ethanol. The color of the reaction mixture immediately changed to lemon yellow and a clear yellow solution was slowly formed. Solvent was removed from the filtered reaction mixture at ~25° (40 mm). The precipitate which separated was removed by filtration and purified by crystallization from a mixture of ethanol and dichloromethane to give ~1.0 g of yellow crystals, mp 215–217°. Analyses on two independent preparations of this material did not correspond to a simple formula but instead to the peculiar composition $(Pf-Pf-Pf-Pf)(PdCl_2)_{1.2}$. *Anal.* Calcd: C, 57.1; H, 4.8; Cl, 9.7. Found: C, 57.1, 56.9; H, 5.2, 5.2; Cl, 9.9, 9.6. A sample of this yellow solid $(Pf-Pf-Pf-Pf)(PdCl_2)_{1.2}$ was converted to the hexafluorophosphate salt $[(Pf-Pf-Pf-Pf)Pd][PF_6]_2$, dec pt 210°, by treatment with ammonium hexafluorophosphate in aqueous acetone followed by recrystallization from a mixture of acetone and ethanol.

Reactions of K_2PtCl_4 with the Tetratertiary Phosphines.—A mixture of 0.3 g (0.72 mmol) of potassium tetrachloroplatinate(II), 0.5 g (0.75 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), 50 ml of ethanol, and 50 ml of water was stirred for 54 hr at room temperature. Removal of solvent from the filtered reaction mixture gave a precipitate which was removed by filtration to give 0.5 g (74% yield) of pale yellow $(Pf-Pf-Pf-Pf)PtCl_2$. The analytical sample was purified by recrystallization from a mixture of dichloromethane and hexane. The filtrate after removal of the $(Pf-Pf-Pf-Pf)PtCl_2$ was treated with aqueous ammonium hexafluorophosphate to give 0.2 g (24% yield) of dirty yellow $[(Pf-Pf-Pf-Pf)Pt][PF_6]_2$.

A similar reaction of potassium tetrachloroplatinate(II) with the tripod tetratertiary phosphine P(-Pf)₃ (II) gave a 96% yield of yellow $P(-Pf)_3PtCl_2$, mp 271–272°, purified by recrystallization from a mixture of dichloromethane and hexane. A portion of this chloride was converted to the white hexafluorophosphate $[P(-Pf)_3Pt][PF_6]_2$ by treatment with ammonium hexafluorophosphate in aqueous ethanol followed by recrystallization from a mixture of acetone and ethanol.

Reactions of $CoCl_2 \cdot 6H_2O$ with the Tetratertiary Phosphines.—A mixture of 0.25 g (1.05 mmol) of $CoCl_2 \cdot 6H_2O$, 0.71 g (1.06 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and 50 ml of ethanol was boiled under reflux for about 60 hr. The original blue color rapidly changed to brown but no further color changes occurred past about 2 hr of heating. The filtered reaction mixture was concentrated to ~15 ml at 25° (40 mm). The precipitate which separated was removed by filtration and dried to give 0.15 g (25% yield) of green-gray crystalline $[P(-Pf)_3CoCl_2][CoCl_4]$, mp 190–192°. The ethanol filtrate after removal of the chloride salt was treated with excess aqueous ammonium hexafluorophosphate. The resulting precipitate was filtered and washed several times with 15-ml portions of hot water. After purification by crystallization from a mixture of ethanol and acetone, 0.66 g (73% yield) of brown $[(Pf-Pf-Pf-Pf)CoCl_2][PF_6]_2$, mp 265–267°, was obtained.

An entirely analogous procedure was used to prepare the compounds $[P(-Pf)_3CoCl_2][CoCl_4]$ and $[P(-Pf)_3CoCl_2][PF_6]_2$ from $CoCl_2 \cdot 6H_2O$ and the tripod tetratertiary phosphine P(-Pf)₃ (II).

Reactions of Hydrated Rhodium Trichloride with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.16 mmol) of commercial hydrated rhodium trichloride (40% rhodium), 0.9 g (1.34 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and 50 ml of ethanol was boiled under reflux for 17 hr. A clear yellow-orange solution was obtained. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give 1.0 g (98% yield) of yellow $(Pf-Pf-Pf-Pf)RhCl_3$, mp >300°. The analytical sample was purified by recrystallization from a mixture of dichloromethane and hexane.

A similar reaction between the commercial hydrated rhodium trichloride and the tripod tetratertiary phosphine P(-Pf)₃ (II) in boiling ethanol gave yellow $P(-Pf)_3RhCl_3$ in 98% yield; some

of the product precipitated during the reaction and the remainder of the product was obtained upon evaporation of some of the ethanol. The analytical sample of $P(-Pf)_3RhCl_3$, mp 220–224°, was purified by recrystallization from a mixture of dimethylformamide and diethyl ether.

Reactions of $[(C_6H_5)_3P]_3RhCl$ with the Tetratertiary Phosphines.—A mixture of 0.7 g (0.76 mmol) of $[(C_6H_5)_3P]_3RhCl$, 0.5 g (0.75 mmol) of the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I), and 50 ml of toluene was boiled under reflux for 4 hr. Upon cooling to room temperature a yellow solid (0.18 g) precipitated; additional quantities of this material were obtained by concentrating the solution at 25° (1 mm) and cooling to –10°. This yellow solid (probably crude $[(Pf-Pf-Pf-Pf)Rh]Cl$) was converted to the corresponding hexafluorophosphate salt $[(Pf-Pf-Pf-Pf)Rh][PF_6]$ by treatment with ammonium hexafluorophosphate in aqueous acetone; the crude hexafluorophosphate was purified by recrystallization from a mixture of acetone and ethanol.

A similar procedure was used to prepare $[(P(-Pf)_3Rh)][PF_6]$ in ~40% yield from $[(C_6H_5)_3P]_3RhCl$ and the tripod tetratertiary phosphine $P(-Pf)_3$ (II).

Reactions of $FeCl_2 \cdot 4H_2O$ with the Tetratertiary Phosphines.—A mixture of 0.32 g (1.61 mmol) of $FeCl_2 \cdot 4H_2O$, 1.20 g (1.79 mmol) of the tripod tetratertiary phosphine $P(-Pf)_3$ (II), and 50 ml of ethanol was boiled under reflux for 2 hr. The light yellow solution immediately turned to deep violet. After the reaction period was over, the reaction mixture was cooled to room temperature and then concentrated at 25° (40 mm). The crystals which separated were removed by filtration and purified by crystallization from a mixture of dichloromethane and hexane to give 0.67 g (72% yield) of violet needles of $[P(-Pf)_3FeCl_2][FeCl_4]$, mp 106–107°. The filtrate from the crystallization of this iron derivative was evaporated to dryness at 40 mm and the residue was dissolved in ethanol. Addition of excess aqueous ammonium hexafluorophosphate gave a violet precipitate. This was removed by filtration, washed with hot water, and dried. After recrystallization of this material from a mixture of acetone and ethanol, 0.23 g (16% yield) of violet $[P(-Pf)_3FeCl_2][PF_6]$, mp 278–280°, was obtained.

Under similar conditions $FeCl_2 \cdot 4H_2O$ failed to react with the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I).

Reaction of Rhenium Trichloride with the Tripod Tetratertiary Phosphine in Acetonitrile Solution.—A mixture of 0.3 g (1.03 mmol) of $ReCl_3$ of commercial rhenium trichloride, 0.69 g (1.03 mmol) of the tripod tetratertiary phosphine $P(-Pf)_3$ (II), and 50 ml of acetonitrile was boiled under reflux for 12 hr. The original pink color of the reaction mixture soon became dark green. After the reaction period was over, solvent was removed from the reaction mixture at ~25° (40 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give 0.39 g (51% yield) of green $[P(-Pf)_3ReCl_3]$, mp 241–242° dec.

Reaction of Rhenium Trichloride with the Tetratertiary Phosphines in 2-Methoxyethanol.—A mixture of 0.3 g (1.03 mmol) of $ReCl_3$ of commercial rhenium trichloride, 0.69 g (1.03 mmol) of the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I), and 50 ml of 2-methoxyethanol was boiled under reflux for 2 hr. Solvent was removed from the filtered deep green reaction mixture at 25° (0.1 mm). Crystallization of the residue from a mixture of dichloromethane and hexane gave ~0.5 g (50% yield) of deep green crystalline $(Pf-Pf-Pf-Pf)ReCl_3$, mp 169–172°.

A similar reaction between the commercial rhenium trichloride and tripod tetratertiary phosphine $P(-Pf)_3$ (II) on the same scale gave 0.56 g (56% yield) of green crystalline $P(-Pf)_3ReCl_3$, mp 119–121°, after purification by precipitation from benzene solution with excess hexane.

Reactions of the Norbornadiene Complexes $C_7H_8M(CO)_4$ ($M = Cr$ and Mo) with the Tetratertiary Phosphines.—Equimolar quantities of the $C_7H_8M(CO)_4$ derivative and the tetratertiary phosphine were boiled under reflux in hexane solution (50 ml for ~1 mmol of each reactant) for about 40 hr. Solvent was then removed from the reaction mixture at ~25° (40 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give the corresponding (tetraphos) $M(CO)_4$ derivative in 40–80% yield.

Reactions of the Cycloheptatriene Complex $C_7H_8Mo(CO)_3$ with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.10 mmol) of $C_7H_8Mo(CO)_3$, 0.74 g (1.10 mmol) of the tetratertiary phosphine (I or II), and 50 ml of benzene was stirred for ~20 hr at room temperature. The characteristic red color of the $C_7H_8Mo(CO)_3$ became yellow-brown almost immediately. Removal of the solvent at 25° (40 mm) gave the yellow (tetraphos) $Mo(CO)_3$

derivative in 45–90% yield. Further purification could be accomplished by reprecipitating from benzene solution with excess hexane.

Reactions of the Hexacarbonyls $M(CO)_6$ ($M = Cr$ and Mo) with the Tetratertiary Phosphines.—Equimolar quantities of the metal hexacarbonyl and the tetratertiary phosphine were boiled under reflux in xylene solution for at least 65 hr using about 50 ml of xylene for each millimole of reactants. After the reaction period was over, the xylene was removed at ~25° (0.1 mm) leaving yellow crystals of the (tetraphos) $M(CO)_3$ derivatives. The $(Pf-Pf-Pf-Pf)M(CO)_3$ derivatives were purified further by crystallization from mixtures of dichloromethane and hexane. The $P(-Pf)_3M(CO)_3$ derivatives were purified by chromatography on alumina columns in a mixture of dichloromethane and hexane as well as by simple recrystallization.

Reactions of the 1,3-Cyclohexadiene Complexes $(C_6H_8)_2M(CO)_2$ ($M = Mo$ and W) with the Tripod Tetratertiary Phosphine $P(-Pf)_3$ (II).—Equimolar quantities of the $(C_6H_8)_2M(CO)_2$ derivative and the tripod tetratertiary phosphine (II) were boiled under reflux in methylcyclohexane solution (~50 ml) for 2 hr ($M = Mo$) or 12 hr ($M = W$). After cooling to room temperature the precipitate was removed by filtration and dried to give yellow crystals of the corresponding $P(-Pf)_3M(CO)_2$ derivative in ~70% yield.

Reactions of $CH_3Mn(CO)_5$ with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.43 mmol) of $CH_3Mn(CO)_5$, 0.96 g (1.43 mmol) of the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I), and 50 ml of benzene was boiled under reflux for 48 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm). The residue was recrystallized first from a mixture of dichloromethane and hexane and then from a mixture of benzene and hexane to give 1.01 g (86% yield) of yellow shining crystals of $CH_3Mn(CO)_3(Pf-Pf-Pf-Pf)$, mp 91–94°.

A mixture of 0.2 g (0.95 mmol) of $CH_3Mn(CO)_5$, 0.64 g (0.95 mmol) of the tripod tetratertiary phosphine $P(-Pf)_3$ (II), and 50 ml of xylene was boiled under reflux for 40 hr. Solvent was then removed at ~25° (0.1 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give 0.62 g (82% yield) of light brown crystals of $CH_3Mn(CO)_2P(-Pf)_3$, mp 131°.

A mixture of 0.2 g (0.95 mmol) of $CH_3Mn(CO)_5$, 0.64 g (0.95 mmol) of the tripod tetratertiary phosphine $P(-Pf)_3$ (II), and 40 ml of redistilled tetrahydrofuran was heated in a sealed tube of 100-ml capacity in an oil bath at 42°. Solvent was removed from the filtered reaction mixture at 25° (40 mm). The sticky residue was extracted with diethyl ether and solvent removed from the filtered extracts at ~25° (40 mm). A similar extraction was then carried out with dichloromethane. The solid remaining upon evaporation of the dichloromethane extracts was washed with hexane and dried to give 0.5 g (62% yield) of pale yellow $CH_3COMn(CO)_3P(-Pf)_3$, mp 60°.

Reactions of $Mn(CO)_5Br$ with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.09 mmol) of $Mn(CO)_5Br$, 0.73 g (1.09 mmol) of the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I), and ~50 ml of benzene was boiled under reflux for 55 hr. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) leaving behind 0.85 g (90% yield) of yellow crystals of crude $(Pf-Pf-Pf-Pf)Mn(CO)_2Br$. Further purification was accomplished by chromatography on alumina in a mixture of dichloromethane and hexane followed by recrystallization from a mixture of dichloromethane and hexane.

A similar reaction between $Mn(CO)_5Br$ and the tripod tetratertiary phosphine $P(-Pf)_3$ (II) on the same scale gave 0.82 g of crude yellow crystals. Further purification of this substance was accomplished by chromatography on alumina in a mixture of dichloromethane and hexane followed by crystallization from a mixture of benzene and ethanol to give yellow crystals, mp 119–121°, with analytical data corresponding to a formula $P(-Pf)_3Mn(CO)_2Br$. *Anal.* Calcd for $P(-Pf)_3Mn(CO)_2Br$: C, 61.3; H, 4.9. Found: C, 60.1; H, 4.7.

Reactions of $CH_3Mo(CO)_3C_3H_5$ with the Tetratertiary Phosphines.—A mixture of 0.5 g (1.93 mmol) of $CH_3Mo(CO)_3C_3H_5$, 0.34 g (0.51 mmol) of the linear tetratertiary phosphine $Pf-Pf-Pf-Pf$ (I), and 100 ml of acetonitrile was stirred for 1 hr at room temperature. The resulting precipitate was removed by filtration and dried to give 0.7 g (85% yield) of yellow $(Pf-Pf-Pf-Pf)[Mo(CO)_2(COCH_3)(C_3H_5)]_4$.

A mixture of 0.3 g (1.15 mmol) of $CH_3Mo(CO)_3C_3H_5$, 0.4 g (0.60 mmol) of the tripod tetratertiary phosphine $P(-Pf)_3$ (II), and 50 ml of acetonitrile was stirred for 30 hr at room tempera-

ture. Solvent was then removed from the reaction mixture at $\sim 25^\circ$ (40 mm). The orange-yellow spongy residue was dissolved in a minimum of dichloromethane and chromatographed on alumina. A mixture of dichloromethane and hexane was used to develop the chromatogram and to elute the yellow band of product. Evaporation of this eluate followed by recrystallization of the residue from a mixture of dichloromethane and hexane gave 0.5 g (100% yield based on $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$) of yellow $\text{P}(-\text{Pf})_3[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$.

Reaction of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ with the Linear Tetratertiary Phosphine Pf-Pf-Pf-Pf (I).—A mixture of 0.5 g (1.78 mmol) of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, 1.2 g (1.79 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and ~ 100 ml of benzene was stirred for 64 hr at room temperature. Solvent was removed at $\sim 25^\circ$ (40 mm) to give 1.5 g (91% yield) of yellow-brown $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})]\text{Cl}$. A portion of this sample of chloride was treated in acetone solution with excess aqueous ammonium hexafluorophosphate. The resulting precipitate was removed by filtration and recrystallized twice from mixtures of acetone and benzene to give a yellow-brown solid of approximate composition $(\text{Pf-Pf-Pf-Pf})[\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]_{1.3}[\text{PF}_6]_{1.3}$. *Anal.* Calcd: C, 53.5; H, 4.3; F, 13.0. Found: C, 53.8, 53.8; H, 4.3, 4.3; F, 12.5, 11.8.

Reactions of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ with the Tetratertiary Phosphines.—A mixture of 0.3 g (1.47 mmol) of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, 1.0 g (1.49 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and ~ 350 ml of benzene was exposed to ultraviolet irradiation for 46 hr. Solvent was removed from the filtered red reaction mixture. The resulting residue was crystallized from a mixture of dichloromethane and hexane to give brown $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})$.

In a similar manner ultraviolet irradiation of a mixture of 0.3 g (1.47 mmol) of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and 1.0 g (1.49 mmol) of the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II) gave 0.9 g (75% yield) of orange $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{P}(-\text{Pf})_3)$, mp $44-46^\circ$, after crystallization from a mixture of benzene and heptane.

Reactions of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ with the Tetratertiary Phosphines.—A mixture of 0.4 g (1.14 mmol) of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$, 0.76 g (1.13 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and ~ 50 ml of methanol was boiled under reflux for 24 hr. After cooling to room temperature, a white precipitate of unreacted Pf-Pf-Pf-Pf (I) was removed by filtration. Solvent was removed from the orange filtrate at $\sim 25^\circ$ (40 mm). The residue was recrystallized from a mixture of dichloromethane and ethanol to give 0.61 g (83% yield) of orange $[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})(\text{NO})_2(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]_2$. The analytical sample, mp $193-195^\circ$, was purified by further recrystallization from hot methanol.

A mixture of 0.7 g (2.00 mmol) of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$, 1.31 g (1.95 mmol) of the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II), and ~ 100 ml of methanol containing sufficient benzene to dissolve initially all of the $\text{P}(-\text{Pf})_3$ was boiled under reflux for 24 hr. Solvent was then removed from the reaction mixture at $\sim 25^\circ$ (40 mm). The residue was extracted with 50 ml of methanol in two portions. The filtered methanol extracts were concentrated to ~ 15 ml at $\sim 25^\circ$ (40 mm) and then cooled to -10° for 2 hr. The crystals which separated were removed by filtration and dried to give 0.6 g (32% yield) of orange crystalline $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})\text{P}(-\text{Pf})_3][\text{PF}_6]$, mp $105-107^\circ$. An additional quantity of less pure material (0.8 g, 42% yield) was obtained by evaporation to dryness of the methanol filtrate from the crystallization.

Reactions of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with the Tetratertiary Phosphines.—A mixture of 0.4 g (1.14 mmol) of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, 0.8 g (1.19 mmol) of the tetratertiary phosphine (I or II), and 100 ml of toluene was boiled under reflux for 30 hr. Solvent was removed from the filtered reaction mixture at $\sim 25^\circ$ (0.1 mm) to give ~ 1.0 g of green crystals of the crude (tetraphos) $[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$ derivative containing excess unreacted tetratertiary phosphine. The crude product was chromatographed on alumina in a mixture of dichloromethane and hexane. A small yellow band of ferrocene often preceded the green band of (tetraphos) $[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$. The eluate from the green band was evaporated to dryness at $\sim 25^\circ$ (40 mm). The resulting green crystals were purified further by crystallization from a mixture of dichloromethane and hexane to give ~ 0.7 g (97% yield) of the green (tetraphos) $[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$ derivative.

Reaction of $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ with the Linear Tetratertiary Phosphine Pf-Pf-Pf-Pf (I).—A mixture of 0.3 g (1.56 mmol) of $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, 1.05 g (1.56 mmol) of the linear tetratertiary

phosphine Pf-Pf-Pf-Pf (I), and ~ 50 ml of acetonitrile was boiled under reflux for 20 hr. After cooling to room temperature, the reaction mixture was filtered to remove a white precipitate which appeared to be some unreacted Pf-Pf-Pf-Pf (I). Solvent was removed from the filtrate at $\sim 25^\circ$ (40 mm). The yellow-orange solid residue was recrystallized from a mixture of dichloromethane and hexane to give 0.85 g (63% yield) of orange $\text{CH}_3\text{COFe}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})(\text{C}_5\text{H}_5)$, mp $57-60^\circ$. Because of the relatively high solubility of this compound in the recrystallization solvent mixture, it was necessary to evaporate the solution almost to dryness before crystals were obtained.

Reactions of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ with the Tetratertiary Phosphines.—A mixture of 0.60 g (1.98 mmol) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$, 1.33 g (1.98 mmol) of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), and ~ 350 ml of benzene was exposed to ultraviolet irradiation for 29 hr. At this point the infrared spectrum of the reaction mixture showed no $\nu(\text{CO})$ frequencies. Solvent was removed from the filtered reaction mixture at $\sim 25^\circ$ (40 mm) giving 1.4 g (77% yield) of green crystals of $\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})\text{I}$. An acetone solution of some of this iodide was treated with excess aqueous ammonium hexafluorophosphate. The resulting yellow precipitate was removed by filtration and dried. Further purification of this $[\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]$ was accomplished by chromatography on an alumina column in acetone solution.

A mixture of 0.61 g (2.01 mmol) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$, 1.34 g (2.00 mmol) of the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II), and ~ 50 ml of benzene was boiled under reflux for 48 hr. Upon cooling to room temperature a sticky oil separated from the benzene solution. Sufficient methanol was added to dissolve this oil and the methanol-benzene solution was filtered. Solvent was removed from the filtrate at $\sim 25^\circ$ (40 mm). The resulting residue was recrystallized from methanol at -78° and dried at 25° (0.1 mm) to give 0.76 g (40% yield) of yellow orange $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{P}(-\text{Pf})_3)]\text{I}$, mp $116-118^\circ$. An additional 0.5 g (26% yield) of less pure material was obtained by evaporation of the methanol filtrate. Attempts to purify this compound by chromatography led to almost complete decomposition.

Infrared Spectra.—Far-infrared spectra ($400-100\text{ cm}^{-1}$) of the metal chloride complexes (Table I) were obtained in Nujol

TABLE I
FAR-INFRARED SPECTRA OF SOME OF THE METAL CHLORIDE COMPLEXES OF THE TETRATERTIARY PHOSPHINES^a

Complex ^b	$\nu(\text{M-Cl})$, cm^{-1}	Other bands, cm^{-1}
$\text{P}(-\text{Pf})_3$		400 m, 387 w, 367 w, 357 vw, 316 vw, 299 vw, 294 w, 284 w, 269 w, 225 w
$(\text{Pf-Pf-Pf-Pf})\text{NiCl}_2$	306 vw, 270 m	370 m, ^c 180 w
$[\text{P}(-\text{Pf})_3\text{NiCl}][\text{PF}_6]$	289 vw	369 vw, ^c 183 vw, 155 w, 143 w
$(\text{Pf-Pf-Pf-Pf})(\text{PdCl}_2)_{1.2}$	337 m, 314 vw, 307 vw, 286 vw, 269 w	370 w, ^c 360 w ^c
$\text{P}(-\text{Pf})_3\text{PtCl}_2$	305 w, 280 m	366 m, ^c 173 s, 159 s
$[(\text{Pf-Pf-Pf-Pf})\text{CoCl}][\text{PF}_6]$	303 m	398 vw, 392 w, 325 m, 246 w, 206 vw, 178 w
$[(\text{Pf-Pf-Pf-Pf})\text{CoCl}]_2[\text{CoCl}_4]$	330-275 m, vbr	
$[\text{P}(-\text{Pf})_3\text{CoCl}][\text{PF}_6]$	289 m	
$[\text{P}(-\text{Pf})_3\text{CoCl}]_2[\text{CoCl}_4]$	303 vw, 290 vw	343 vw, 248 vw, 204 w
$[\text{P}(-\text{Pf})_3\text{FeCl}][\text{PF}_6]$	290 m	399 vw, 375 vw, 354 w
$[\text{P}(-\text{Pf})_3\text{FeCl}]_2[\text{FeCl}_4]$	318 w, 288 w	366 m, 228 w, 170 vw, 165 w
$(\text{Pf-Pf-Pf-Pf})\text{RhCl}_3$	309 vw, 285 vw, 269 vw	
$\text{P}(-\text{Pf})_3\text{RhCl}_3$	313 w, 274 m	373 w, 243 vw, 182 vw

^a These spectra ($400-100\text{ cm}^{-1}$) were run in Nujol mulls pressed between polyethylene plates and recorded on a Beckman IR-11 spectrometer. ^b $\text{Pf-Pf-Pf-Pf} = (\text{C}_5\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_5\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_5\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_5\text{H}_5)_2$ (I); $\text{P}(-\text{Pf})_3 = [(\text{C}_5\text{H}_5)_2\text{PCH}_2\text{CH}_2]_3\text{P}$ (II). ^c Probably $\nu(\text{M-P})$.

mulls pressed between polyethylene plates and recorded on a Beckman IR-11 spectrometer. Assignments of the $\nu(\text{M-Cl})$ frequencies were based on comparison with known spectra of related compounds¹²⁻¹⁴ and must be regarded as tentative until

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far-infrared data on corresponding bromides and iodides become available.

Infrared spectra of the metal carbonyl derivatives in the 2100–1600-cm⁻¹ region (Table II) were obtained in the indicated

TABLE II
ν(CO) FREQUENCIES OF SOME METAL CARBONYL
COMPLEXES OF THE TETRATERTIARY PHOSPHINES^a

Compound ^b	ν(CO), cm ⁻¹
(Pf-Pf-Pf-Pf)Cr(CO) ₄	2023 s, 1885 vs, br
(Pf-Pf-Pf-Pf)Mo(CO) ₄	2024 s, 1890 vs, br
P(-Pf) ₃ Cr(CO) ₄	2013 s, 1920 s, 1895 vs, br
P(-Pf) ₃ Mo(CO) ₄	2026 s, 1888 vs, br
(Pf-Pf-Pf-Pf)Cr(CO) ₃	1928 s, 1834 s, br
(Pf-Pf-Pf-Pf)Mo(CO) ₃	1941 s, 1847 s, br
P(-Pf) ₃ Cr(CO) ₃	1940 s, 1845 s, br
P(-Pf) ₃ Mo(CO) ₃	1940 s, 1850 s, br
P(-Pf) ₃ Mo(CO) ₂	1850 s, 1778 s
P(-Pf) ₃ W(CO) ₂	1842 s, 1774 s
CH ₃ Mn(CO) ₃ (Pf-Pf-Pf-Pf)	1991 s, 1904 vs, ~1860 m, sh
CH ₃ COMn(CO) ₂ P(-Pf) ₃	1995 s, 1911 vs, br, 1580 m ^c
CH ₃ Mn(CO) ₂ P(-Pf) ₃	1906 s, 1836 s
(Pf-Pf-Pf-Pf)Mn(CO) ₂ Br	1933 s, 1862 s
P(-Pf) ₃ Mn(CO) ₂ Br ^d	1936 s, 1862 s
(Pf-Pf-Pf-Pf)[Mo(CO) ₂ (COCH ₃)(C ₆ H ₅) ₄]	1931 s, 1847 vs, 1610 m ^e
P(-Pf) ₃ [Mo(CO) ₂ (COCH ₃)(C ₆ H ₅) ₄]	1925 s, 1845 vs, 1600 m ^e
[C ₆ H ₅ Mo(CO) ₂ (Pf-Pf-Pf-Pf)]Cl	1978 s, 1913 s
C ₆ H ₅ Mn(CO)(Pf-Pf-Pf-Pf)	1818 s
C ₆ H ₅ Mn(CO)P(-Pf) ₃ ^g	1838 s
[(C ₆ H ₅) ₂ Mn ₂ (CO)(NO) ₂ (Pf-Pf-Pf-Pf)]PF ₆ ₂	2043 s, 1798 s, ^e 1752 s ^e
[C ₆ H ₅ Mn(NO)P(-Pf) ₃][PF ₆]	1742 s ^e
(Pf-Pf-Pf-Pf)[Fe ₂ (CO) ₂ (C ₆ H ₅) ₂]	1670 s ^f
P(-Pf) ₃ [Fe ₂ (CO) ₂ (C ₆ H ₅) ₂]	1670 s ^f
CH ₃ COFe(CO)(Pf-Pf-Pf-Pf)(C ₆ H ₅)	1913 s, 1585 w ^e
[C ₆ H ₅ Fe(CO)P(-Pf) ₃]I	1970 s

^a These infrared spectra were taken in CH₂Cl₂ solution except where indicated differently and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. The spectra were calibrated against the 1601.4-cm⁻¹ band of polystyrene film.

^b The abbreviations in footnotes *a* of Tables I and II are also used here. ^c Acyl ν(CO) frequency. ^d These spectra were obtained on the purest samples available, but these materials were not completely pure (see Experimental Section). ^e ν(NO) frequency. ^f Bridging ν(CO) frequency. ^g CS₂ solvent.

media and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics.

Ultraviolet and Visible Spectra.—The following ultraviolet and visible spectra were obtained on a Cary Model 14 spectrometer in dichloromethane solution: (A) (Pf-Pf-Pf-Pf)-NiCl₂, maxima at 425 mμ (ε 1800) and 282 mμ (ε 18,500); (B) [(Pf-Pf-Pf-Pf)Ni][PF₆]₂, maximum at 295 mμ (ε 23,000); (C) [P(-Pf)₃NiCl][PF₆], maxima at 545 mμ (ε 1600) and 295 mμ (ε 19,000); (D) (Pf-Pf-Pf-Pf)(PdCl₂)_{1.2}, maximum at 280 mμ (ε 34,000); (E) [(Pf-Pf-Pf-Pf)Pd][PF₆]₂, maximum at 282 mμ (ε 31,000); (F) (Pf-Pf-Pf-Pf)PtCl₂, maximum at 257 mμ (ε 26,000); inflection point at 290 mμ (ε 9000); (G) P(-Pf)₃PtCl₂, maxima at 415 mμ (ε 7000), 370 mμ (ε 7000), and 265 mμ (ε 21,000); (H) [P(-Pf)₃Pt][PF₆]₂, maximum at 255 mμ (ε 38,000); (I) [(Pf-Pf-Pf-Pf)CoCl][PF₆], maxima at 555 mμ (ε 450), 395 mμ (ε 2000), and 267 mμ (ε 16,500); inflection points at 440 mμ (ε 1400), 340 mμ (ε 3900), and 290 mμ (ε 13,500); (J) [(Pf-Pf-Pf-Pf)CoCl]₂[CoCl₄], maxima at 555 mμ (ε 700) and 266 mμ (ε 28,000); inflection points at 433 mμ (ε 2200), 377 mμ (ε 4200), 347 mμ (ε 6200), and 290 mμ (ε 21,000); (K) [P(-Pf)₃CoCl][PF₆], maxima at 470 mμ (ε 2700), 362 mμ (ε 5500), and 265 mμ (ε 24,000); (L) [P(-Pf)₃CoCl]₂[CoCl₄], maxima at 470 mμ (ε 4800), 362 mμ (ε 11,000), and 264 mμ (ε 46,000); (M) (Pf-Pf-Pf-Pf)RhCl₃, maximum at 274 mμ (ε 23,000); (N) P(-Pf)₃RhCl₃, maxima at 324 mμ (ε 12,000) and 247 mμ (ε 35,000); (O) [(Pf-Pf-Pf-Pf)Rh][PF₆], maxima at 486 mμ (ε 100), 418 mμ (ε 2800), and 322 mμ (ε 6600); (P) [P(-Pf)₃FeCl][PF₆], maxima at 521 mμ (ε 2600) and 272 mμ (ε 15,000); inflection points at 367 mμ (ε 2100) and 320 mμ (ε 7500); (Q) [P(-Pf)₃FeCl]₂[FeCl₄], maxima at 520 mμ (ε 2400), 273 mμ (ε 23,000), and 266 mμ (ε 24,000); inflection points at 355 mμ (ε 8900) and

306 mμ (ε 16,000); (R) (Pf-Pf-Pf-Pf)ReCl₃, maximum at 632 mμ (ε 580); (S) P(-Pf)₃ReCl₃, maximum at 623 mμ (ε 470).

Molar Conductance Measurements.—The molar conductances listed in Tables III and IV were determined in 0.00004–0.001 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. Each compound was studied at a minimum of three different concentrations.

Magnetic Susceptibility Measurements.—The following magnetic susceptibilities were measured at room temperature in the solid state on an Alpha Scientific magnetic balance using the Faraday method: (A) (Pf-Pf-Pf-Pf)NiCl₂, χ_{mol}^{27°} = -165 × 10⁻⁶ cm³/mol; (B) [(Pf-Pf-Pf-Pf)Ni][PF₆]₂, χ_{mol}^{27°} = -103 × 10⁻⁶ cm³/mol; (C) [P(-Pf)₃NiCl][PF₆], χ_{mol}^{27°} = +1435 × 10⁻⁶ cm³/mol corresponding to a magnetic moment of 2.23 BM after making a correction of -625 × 10⁻⁶ cm³ mol for the diamagnetism of the ligands; (D) [(Pf-Pf-Pf-Pf)CoCl][PF₆], χ_{mol}^{27°} = +654 × 10⁻⁶ cm³/mol corresponding to a magnetic moment of 1.74 BM after making a correction of -605 × 10⁻⁶ cm³/mol for the diamagnetism of the ligands; (E) [P(-Pf)₃CoCl][PF₆], χ_{mol}^{27°} = +482 × 10⁻⁶ cm³/mol corresponding to a magnetic moment of 1.62 BM after making a correction of -605 × 10⁻⁶ cm³/mol for the diamagnetism of the ligands; (F) [P(-Pf)₃FeCl][PF₆], χ_{mol}^{27°} = +1482 × 10⁻⁶ cm³/mol corresponding to a magnetic moment of 2.24 BM after making a correction of -605 × 10⁻⁶ cm³/mol for the diamagnetism of the ligands; (G) P(-Pf)₃ReCl₃, χ_{mol}^{27°} = +12 × 10⁻⁶ cm³/mol corresponding to a magnetic moment of 1.21 BM after making a relatively large correction of -601 × 10⁻⁶ cm³/mol for the diamagnetism of the ligands.

Discussion

A. Metal Chloride and Metal Hexafluorophosphate Derivatives.—Reaction of nickel chloride with the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) in boiling ethanol gives a solid of composition (Pf-Pf-Pf-Pf)NiCl₂. Reaction of this solid with ammonium hexafluorophosphate in aqueous acetone results in the replacement of both chloride ligands to give the yellow diamagnetic bis-hexafluorophosphate salt [(Pf-Pf-Pf-Pf)Ni][PF₆]₂ containing the (Pf-Pf-Pf-Pf)Ni²⁺ cation with square-planar nickel(II) and tetradentate Pf-Pf-Pf-Pf. The salt [(Pf-Pf-Pf-Pf)Ni][PF₆]₂ exhibits molar conductances in both acetone and nitromethane consistent with formulation as a 1:2 electrolyte.

The reaction between nickel chloride and the tripod tetratertiary phosphine P(-Pf)₃ (II) proceeds entirely differently from the corresponding reaction between nickel chloride and the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) discussed above. The initial product is a deep blue solid which upon treatment with ammonium hexafluorophosphate is converted to the more tractable violet hexafluorophosphate [P(-Pf)₃NiCl][PF₆]. The salt [P(-Pf)₃NiCl][PF₆] is formulated as the pentacoordinate nickel(II) derivative III (M = Ni) on the basis of the following information: (1) the observation of a maximum at 545 mμ (ε 1640) spectrum corresponding to the maximum at 570 mμ (ε ~5000) in the electronic spectrum of the known¹⁵ complex [(QP)-NiCl][ClO₄] (QP = [o-(C₆H₅)₂PC₆H₄]₂P); (2) the molar conductance of [P(-Pf)₃NiCl][PF₆] in both acetone and nitromethane is consistent with formulation as a 1:1 electrolyte. The salt [P(-Pf)₃NiCl][PF₆] is paramagnetic (2.23 BM) in contrast to the diamagnetic reported⁷ derivatives of the (QP)NiCl⁺ cation; the reason for this difference in behavior is not clear. Possibly a high-spin form¹⁶ of the five-coordinate

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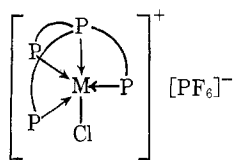
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TABLE III
 METAL COMPLEXES OF HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE

Compound ^a	Color	Mp ^b °C	Analyses, %								Molar conductance ^d
			C		H		X or O		Other		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
(Pf-Pf-Pf-Pf)NiCl ₂	Red-brown	140-142	63.0	62.3	5.6	5.8	8.9 (Cl)	8.6 (Cl)			A, 106; N, 76 ± 13
[(Pf-Pf-Pf-Pf)Ni][PF ₆]	Yellow	210 dec	49.5	48.8	4.2	4.3	22.3 (F)	21.3 (F)			A, 295 ± 15; N, 198 ± 18
[(Pf-Pf-Pf-Pf)Pd][PF ₆] ₂	Yellow	210 dec	47.2	47.6	4.0	4.2	21.3 (F)	19.9 (F)			A, 226 ± 16; N, 178 ± 10
(Pf-Pf-Pf-Pf)PtCl ₂	Pale yellow	198-199	53.9	51.1	4.5	5.5	7.6 (Cl)	7.8 (Cl)			N, 64 ± 8
[(Pf-Pf-Pf-Pf)Pt][PF ₆] ₂	Yellow	175-178	43.6	44.0	3.7	4.2	19.7 (F)	20.2 (F)			A, 255 ± 11; N, 205 ± 15
[(Pf-Pf-Pf-Pf)CoCl] ₂ [CoCl ₄]	Green-gray	190-192	58.3	57.1	4.9	4.8	12.3 (Cl)	11.6 (Cl)			A, insol; N, 98 ± 8
[(Pf-Pf-Pf-Pf)CoCl][PF ₆]	Brown	265-267	55.3	55.3	4.6	4.7	12.5 (F)	11.9 (F)	3.9 (Cl)	4.3 (Cl)	A, 124; N, 83 ± 3
(Pf-Pf-Pf-Pf)RhCl ₃	Yellow	>300	57.3	57.2	4.8	5.1	12.1 (Cl)	12.2 (Cl)	14.1 (P)	13.8 (P)	N, 57 ± 4
[(Pf-Pf-Pf-Pf)Rh][PF ₆]	Yellow	315-318 dec	54.8	51.5	4.6	4.5	12.4 (F)	13.1 (F)			A, 126 ± 7; N, 77 ± 6
(Pf-Pf-Pf-Pf)ReCl ₃	Deep green	169-172	52.3	51.0	4.4	4.4	11.0 (Cl)	11.1 (Cl)			N, 21 ± 1
(Pf-Pf-Pf-Pf)Cr(CO) ₄	Yellow	170-171	66.2	65.8	5.1	5.3	7.7 (O)	8.4 (O)			
(Pf-Pf-Pf-Pf)Mo(CO) ₄	Yellow	114-116	62.9	60.8	4.8	4.6	7.3 (O)	7.6 (O)			
(Pf-Pf-Pf-Pf)Cr(CO) ₃	Yellow	88-90	67.0	65.3	5.2	5.3	6.0 (O)	6.2 (O)			
(Pf-Pf-Pf-Pf)Mo(CO) ₃	Yellow	140-142	63.5	62.8	5.0	5.2	5.6 (O)	6.6 (O)			
CH ₃ M(CO) ₃ (Pf-Pf-Pf-Pf)	Yellow	91-94	66.9	68.0	5.6	5.8	5.8 (O)	6.8 (O)			
(Pf-Pf-Pf-Pf)Mn(CO) ₂ Br	Yellow	122-124	61.3	61.0	4.9	4.7	3.7 (O)	3.9 (O)	6.4 (Mn)	6.7 (Mn)	A, ~0
(Pf-Pf-Pf-Pf)[Mo(CO) ₂ (COCH ₃)-(C ₆ H ₅) ₄]	Yellow	173-174	54.6	54.7	4.4	4.3	11.2 (O)	11.2 (O)			
[C ₆ H ₅ Mo(CO) ₂ (Pf-Pf-Pf-Pf)]Cl	Brown	150-152 dec	63.8	64.0	5.1	5.2	3.5 (O)	4.6 (O)	3.8 (Cl)	3.7 (Cl)	
C ₆ H ₅ Mn(CO)(Pf-Pf-Pf-Pf)	Brown	138-142	70.4	68.7	5.8	5.8	1.9 (O)	1.4 (O)			
[(C ₆ H ₅) ₂ Mn ₂ (CO)(NO) ₂ -(Pf-Pf-Pf-Pf)][PF ₆] ₂	Orange	193-195	49.4	49.4	4.1	4.2	17.7 (F)	17.8 (F)	2.2 (N)	2.3 (N)	A, 253 ± 17; N, 170 ± 4
(Pf-Pf-Pf-Pf)[Fe ₂ (CO) ₂ (C ₆ H ₅) ₂]	Green	193	61.9	61.0	5.0	5.3					
CH ₃ COFe(CO)(Pf-Pf-Pf-Pf)-(C ₆ H ₅)	Orange	57-60	69.6	67.1	5.8	5.6	3.7 (O)	4.9 (O)	6.5 (Fe)	6.3 (Fe)	
[C ₆ H ₅ Fe(Pf-Pf-Pf-Pf)]I	Green	211-214	61.4	61.3	5.1	5.3	13.8 (I)	13.9 (I)			A, insol; N, 75 ± 3
[C ₆ H ₅ Fe(Pf-Pf-Pf-Pf)][PF ₆]	Yellow	169-173	60.3	58.4	5.0	5.0	12.2 (F)	10.6 (F)			A, 135 ± 2; N, 80 ± 6

^a The abbreviation Pf-Pf-Pf-Pf is used for hexaphenyl-1,4,7,10-tetraphosphadecane. ^b Melting points were determined in capillaries and are uncorrected. ^c Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Tungsten(VI) oxide was added prior to the combustions for determinations of carbon and hydrogen. ^d A, acetone solution; N, nitromethane solution; insol, too insoluble for a meaningful measurement to be obtained. Values are given in ohm⁻¹cm²mol⁻¹.

P(-Pf)₃NiCl⁺ (expected¹⁷ $\mu_{\text{eff}} = 3.2$ BM) is in equilibrium with the normal diamagnetic low-spin form.



III

The reaction of sodium tetrachloropalladate(II) with the linear tetra-tertiary phosphine Pf-Pf-Pf-Pf (I) gave a yellow product of stoichiometry (Pf-Pf-Pf-Pf)(PdCl₂)_{1.2}. This is probably a mixture of (Pf-Pf-Pf-Pf)PdCl₂ and (Pf-Pf-Pf-Pf)(PdCl₂)₂; the latter compound would be a nonionic square-planar palladium(II) derivative of tetraligate bimetallic Pf-Pf-Pf-Pf (I). This chloride derivative reacted with ammonium hexafluorophosphate to give yellow [(Pf-Pf-Pf-Pf)Pd][PF₆]₂, a square-planar palladium(II) derivative with tetradentate Pf-Pf-Pf-Pf (I). The molar conductance of [(Pf-Pf-Pf-Pf)Pd][PF₆]₂ was consistent with formulation as a 1:2 electrolyte. The reaction of sodium tetrachloropalladate(II) with the tripod tetra-tertiary phosphine P(-Pf)₃ (II) failed to give pure products.

The reaction of potassium tetrachloroplatinate(II)

with either tetra-tertiary phosphine I or II first gave a yellow product of composition (tetraphos)PtCl₂. The compound P(-Pf)₃PtCl₂ exhibited two infrared ν (Pt-Cl) frequencies at 305 and 280 cm⁻¹ (Table I) indicating formulation in the solid state as a square-planar non-ionic *cis*-L₂PtCl₂ derivative with bidentate P(-Pf)₂. However, the molar conductance of P(-Pf)₃PtCl₂ in nitromethane indicated this compound to be a 1:1 electrolyte presumably [P(-Pf)₃PtCl]Cl with tridentate P(-Pf)₃. This suggests that upon dissolving the bidentate P(-Pf)₂PtCl₂ in nitromethane one of the uncoordinated phosphorus atoms in P(-Pf)₃ displaces one of the chloride ligands to form the tridentate P(-Pf)₃PtCl⁺ cation.

Treatment of the platinum derivatives (tetraphos)-PtCl₂ (or the reaction mixtures from their preparation) with ammonium hexafluorophosphate gave the corresponding hexafluorophosphate salts [(tetraphos)Pt][PF₆]₂. The derivative [(Pf-Pf-Pf-Pf)Pt][PF₆]₂ was soluble in acetone and nitromethane and exhibited molar conductances in both of those solvents consistent with formulation as a 1:2 electrolyte. However, the derivative [P(-Pf)₃Pt][PF₆]₂, unlike the other hexafluorophosphates studied in this work, was very sparingly soluble in both acetone and nitromethane. These anomalous properties of [P(-Pf)₃Pt][PF₆]₂ may relate to the steric difficulty for the tripod tetra-tertiary phosphine P(-Pf)₃ (II) to act as a tetradentate ligand to-

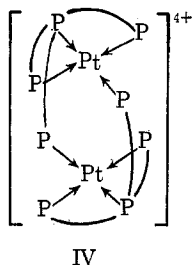
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TABLE IV
 METAL COMPLEXES OF TRIS(2-DIPHENYLPHOSPHINOETHYL)PHOSPHINE

Compound ^a	Color	Mp ^b °C	C		H		Analyses, % ^c		Other		Molar conductance ^f
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
[P(-Pf) ₃ NiCl][PF ₆] ^d	Violet	295-298	55.4	55.2	4.6	4.6	3.9 (Cl)	3.8 (Cl)	12.5 (F)	12.7 (F)	A, 98; N, 75 ± 6
P(-Pf) ₃ PtCl ₂	Yellow	271-272	53.9	52.0	4.5	4.8	7.6 (Cl)	7.9 (Cl)			A, insol; N, 69 ± 6
[P(-Pf) ₃ Pt][PF ₆] ₂	White	268-274 dec	43.6	42.8	3.7	3.8	19.7 (F)	19.8 (F)			A, insol; N, insol
[P(-Pf) ₃ CoCl] ₂ [CoCl ₄]	Gray- green	288-291 dec	58.3	57.9	4.9	5.2	12.3 (Cl)	12.0 (Cl)			A, insol; N, 175 ± 8
[P(-Pf) ₃ CoCl][PF ₆] ^e	Brown	274-277	55.3	54.9	4.6	4.4	3.9 (Cl)	4.2 (Cl)	12.5 (F)	12.9 (F)	A, 119 ± 10; N, 82 ± 5
P(-Pf) ₃ RhCl ₃	Yellow	220-224	57.3	57.2	4.8	5.1	12.1 (Cl)	12.2 (Cl)			N, ~0
[P(-Pf) ₃ Rh][PF ₆]	Yellow	205 dec	54.8	52.9	4.6	4.5	12.4 (F)	11.2 (F)			
[P(-Pf) ₃ FeCl] ₂ [FeCl ₄]	Violet	106-107	58.8	56.8	4.9	4.7	12.4 (Cl)	12.2 (Cl)			A, insol; N, 107 ± 10
[P(-Pf) ₃ FeCl][PF ₆]	Violet	278-280	55.6	55.6	4.7	4.5	3.9 (Cl)	5.0 (Cl)	12.6 (F)	13.0 (F)	A, 132 ± 2; N, 80 ± 5
[P(-Pf) ₃] ₂ Re ₂ Cl ₉	Green	241-242	45.4	45.9	3.8	3.9	14.4 (Cl)	12.2 (Cl)	11.1 (P)	10.0 (P)	A, > ~100; N, > ~70 ^g
P(-Pf) ₃ ReCl ₃	Green	119-121	52.3	51.6	4.4	4.7	11.0 (Cl)	9.5 (Cl)			A, insol; N, 39 ± 10
P(-Pf) ₃ Cr(CO) ₄	Yellow	86-88 dec	66.2	67.6	5.7	5.4	7.7 (O)	7.0 (O)			
P(-Pf) ₃ Mo(CO) ₄	Pale yellow	126-128	62.9	63.2	4.8	5.0	7.3 (O)	7.1 (O)			
P(-Pf) ₃ Cr(CO) ₃	Yellow	78	67.0	66.7	5.2	5.4	5.9 (O)	6.4 (O)	15.3 (P)	14.8 (P)	
P(-Pf) ₃ Mo(CO) ₃	Yellow	260 dec	63.5	62.2	5.0	4.8	5.6 (O)	6.1 (O)	14.1 (P)	14.2 (P)	
P(-Pf) ₃ W(CO) ₂	Yellow	169-172 dec	58.1	56.4	4.7	4.9	3.5 (O)	3.6 (O)			
CH ₃ COMn(CO) ₂ P(-Pf) ₃	Light yellow	60	66.3	66.4	5.3	5.5	7.5 (O)	7.6 (O)			
CH ₃ Mn(CO) ₂ P(-Pf) ₃	Light brown	131	67.8	65.4	5.8	6.0	4.0 (O)	5.0 (O)			
P(-Pf) ₃ [Mo(CO) ₂ (COCH ₃)(C ₆ H ₅) ₄]	Yellow	98-102	54.6	54.7	4.4	4.6	11.2 (O)	11.1 (O)	7.2 (P)	7.2 (P)	
C ₆ H ₅ Mn(CO)P(-Pf) ₃	Orange	44-46	70.4	70.5	5.8	6.0	1.9 (O)	1.9 (O)			
[C ₆ H ₅ Mn(NO)P(-Pf) ₃][PF ₆]	Orange	105-107	58.4	57.1	4.9	4.8	11.8 (F)	11.5 (F)	1.4 (N)	1.5 (N)	
P(-Pf) ₃ [Fe ₂ (CO) ₂ (C ₆ H ₅) ₂]	Green	85	61.9	62.1	5.0	5.3	5.0 (O)	5.5 (O)	9.8 (P)	10.6 (P)	
[C ₆ H ₅ Fe(CO)P(-Pf) ₃]I	Yellow	116-118	60.9	60.2	5.0	5.0	1.7 (O)	1.6 (O)	13.4 (I)	13.5 (I)	

^a The abbreviation P(-Pf)₃ is used for tris(2-diphenylphosphinoethyl)phosphine. ^b Melting points were determined in capillaries and are uncorrected. ^c Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Tungsten(VI) oxide was used as a catalyst for the combustions to determine carbon and hydrogen. ^d Calcd: Ni, 6.5; P, 17.0. Found: Ni, 6.6; P, 16.8. ^e Calcd: Co, 6.5; P, 17.0. Found: Co, 6.4; P, 17.2. ^f A, acetone solution; N, nitromethane solution; insol, too insoluble for a meaningful measurement to be obtained. Values are given in ohm⁻¹ cm² mol⁻¹. ^g This compound was not completely soluble in the solvents tried.

ward a square-planar metal atom because of the need for one of the PCH₂CH₂P units to bridge the diagonal of the square. For this reason the cation may be the dimeric [P(-Pf)₃]₂Pt₂⁴⁺ with tetraligate bimetallic P(-Pf)₃ (II) and with a structure such as IV. Unfortunately, the low solubility of [P(-Pf)₃Pt][PF₆]₂ prevented measurement of its molar conductance.

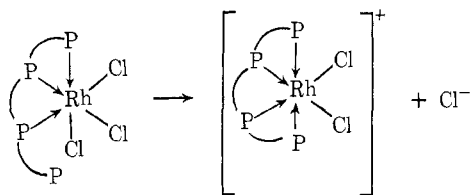


The reaction of hydrated cobalt(II) chloride with either tetratertiary phosphine I or II in boiling ethanol gave a gray-green precipitate of composition (tetraphos)₂Co₂Cl₆, probably [(tetraphos)CoCl]₂[CoCl₄]. Addition of ammonium hexafluorophosphate to the filtrate from the isolation of (tetraphos)₂Co₂Cl₆ gave the brown [(tetraphos)CoCl][PF₆] derivatives. Both [(tetraphos)CoCl][PF₆] derivatives exhibited magnetic moments around 1.7 BM corresponding to the expected one unpaired electron for a low-spin cobalt(II) complex. Furthermore, both [(tetraphos)CoCl][PF₆] de-

rivatives exhibited molar conductance values consistent with formulations as 1:1 electrolytes thereby suggesting that the chlorine is covalently bonded to the cobalt atom. This suggests formulation of the [(tetraphos)CoCl][PF₆] derivatives as pentacoordinate cobalt(II) derivatives with tetradentate tetratertiary phosphine ligands. The electronic spectrum of [P(-Pf)₃CoCl][PF₆] derivatives exhibited maxima around 470 and 360 mμ analogous to maxima around 500 and 400 mμ reported¹⁵ for (QP)CoNO₃⁺ with likewise five-coordinate cobalt(II) but with the weaker field nitrate as the fifth ligand.

The reactions of hydrated rhodium trichloride with either tetratertiary phosphine in boiling ethanol gave yellow rhodium (III) derivatives of the type (tetraphos)RhCl₃. Both of these rhodium(III) derivatives exhibited far-infrared ν(Rh-Cl) frequencies (Table I) close to the values reported previously¹⁴ for facial isomers of the type fac-(R₃P)₃RhCl₃ (i.e., ν(Rh-Cl) reported for fac-[C₆H₅P(CH₃)₂]₃RhCl₃: 297 and 281 cm⁻¹). Accordingly, the compounds (tetraphos)RhCl₃ are formulated as octahedral nonionic rhodium(III) derivatives with tridentate tetratertiary phosphine ligands. In accord with this formulation, the tripod tetratertiary phosphine derivative P(-Pf)₃RhCl₃ was a nonelectrolyte in nitromethane solution. However, the linear tetratertiary phosphine derivative (Pf-Pf-Pf)RhCl₃ acted as a 1:1 electrolyte in nitromethane

solution. This suggests that upon dissolving (Pf-Pf-Pf-Pf)RhCl₃ in a polar solvent the uncoordinated phosphorus atom in the tridentate Pf-Pf-Pf-Pf displaces one of the chloride ligands to form the cation (Pf-Pf-Pf-Pf)RhCl₂⁺ with tetradentate Pf-Pf-Pf-Pf (I) according to the scheme



The different behavior of the uncoordinated phosphorus atom of the two isomeric tetra-tertiary phosphines I and II in their (tetraphos)RhCl₃ complexes when dissolved in nitromethane is an interesting consequence of the different stereochemistry of the two tetradentate ligands.

In order to prepare rhodium(I) derivatives of the tetra-tertiary phosphines I and II, their reactions with the rhodium(I) derivative [(C₆H₅)₃P]₃RhCl in boiling toluene were investigated. In both cases addition of ammonium hexafluorophosphate dissolved in aqueous acetone to the reaction mixture gave the yellow salts [(tetraphos)Rh][PF₆]. These are presumably square-planar rhodium(I) derivatives, but the mode of bonding the tetraligate tripod tetra-tertiary phosphine P(-Pf)₃ (II) to a square-planar metal atom without steric interference involving the PCH₂CH₂P group that must bridge the diagonal of the square is not clear.

The two tetra-tertiary phosphines I and II differed in their behavior upon reaction with hydrated ferrous chloride. The linear tetra-tertiary phosphine Pf-Pf-Pf-Pf (I) and ferrous chloride failed to react even upon prolonged heating in boiling ethanol. No color change was observed. On the other hand, the tripod tetra-tertiary phosphine P(-Pf)₃ reacted rapidly with hydrated ferrous chloride in boiling ethanol to give a deep violet solution which deposited upon cooling violet crystals of composition [P(-Pf)₃]₂Fe₂Cl₆, probably [P(-Pf)₃FeCl]₂[FeCl₄]. The filtrate gave violet [P(-Pf)₃FeCl][PF₆] upon treatment with ammonium hexafluorophosphate. The salt [P(-Pf)₃FeCl][PF₆] is formulated as a five-coordinate iron(II) derivative similar to (QP)FeCl⁺ on the basis of the following information: (1) maxima in its electronic spectrum at 521 and 320 mμ analogous to the maxima at 540 and 332 mμ reported¹⁸ for the five-coordinate iron(II) derivative [(QP)FeCl]Cl; (2) a molar conductance in both acetone and nitromethane corresponding to a 1:1 electrolyte. The magnetic susceptibility of [P(-Pf)₃FeCl][PF₆] was only 2.24 BM which is much less than the 3.0–3.2-BM values found¹⁸ for five-coordinate (QP)FeX⁺ derivatives; the reasons for this difference are not clear.

The reaction of rhenium trichloride with either tetra-tertiary phosphine I or II in boiling 2-methoxyethanol gave green solids of the stoichiometry (tetraphos)ReCl₃. Each of these compounds exhibited an electronic spectrum similar to that of the green tritertiary phosphine derivative¹ (Pf-Pf-Pf)ReCl₃ suggesting that only three of the four phosphorus atoms of either tetra-tertiary

phosphine are involved in the bonding to the rhenium atom. The electronic spectrum of either (tetraphos)-ReCl₃ derivative did not resemble the electronic spectra of binuclear rhenium (III) derivatives¹⁹ such as Re₂Cl₈²⁻ or [R₃PReCl₃]₂ although binuclear derivatives of the latter type are sometimes green. Furthermore, the infrared spectrum of neither (tetraphos)ReCl₃ derivative contained a band around 980 cm⁻¹ which could be attributed to a ν(Re-O) frequency.²⁰ Both (tetraphos)ReCl₃ derivatives exhibited molar conductances in nitromethane one-third to one-half the expected values for 1:1 electrolytes. This suggests nonionic formulations for the (tetraphos)ReCl₃ derivatives but with some tendency for the uncoordinated phosphorus atom of the apparently tridentate tetra-tertiary phosphine to displace a chloride ligand giving some of the corresponding (tetraphos)ReCl₂⁺ cation. All of these observations on the (tetraphos)ReCl₃ derivatives support their formulations as octahedral rhenium(III) derivatives with a tridentate tetra-tertiary phosphine ligand. The magnetic moment of P(-Pf)₃ReCl₃ was found to be ~1.2 BM. This low magnetic moment of P(-Pf)₃ReCl₃ and the green color of the (tetraphos)ReCl₃ complexes differ appreciably from the higher magnetic moments (2.0–2.4 BM) and yellow to orange colors of known²⁰ (R₃P)₃ReCl₃ derivatives. The reasons for this discrepancy are not clear, but further complexities in the already complicated coordination chemistry of rhenium(III)^{21,22} are suggested.

B. Metal Carbonyl Derivatives.—The tetra-tertiary phosphines Pf-Pf-Pf-Pf (I) and P(-Pf)₃ (II) can act as bidentate, tridentate, or tetradentate ligands in substitution products of the octahedral metal carbonyls. Especially striking is the series P(-Pf)₃Mo(CO)₄, P(-Pf)₃Mo(CO)₃, and P(-Pf)₃Mo(CO)₂ where the tripod tetra-tertiary phosphine P(-Pf)₃ (II) acts as a bidentate, tridentate, and tetradentate ligand, respectively. The bidentate derivatives (tetraphos)M(CO)₄ were prepared by displacement of the norbornadiene ligand in the norbornadienemetal tetracarbonyls with the tetra-tertiary phosphine. Similarly the tridentate derivatives (tetraphos)M(CO)₃ could be prepared by displacement of the cycloheptatriene ligand in the cycloheptatrienemetal tricarbonyls with the tetra-tertiary phosphine. However, the reactions between the free metal hexacarbonyls and the tetra-tertiary phosphines in boiling toluene (M = Cr or Mo) provided more convenient preparations of the tridentate derivatives (tetraphos)-M(CO)₃. The tetradentate derivatives (tetraphos)-M(CO)₂ were obtained by displacement of the two 1,3-cyclohexadiene ligands in the (C₆H₅)₂M(CO)₂ derivatives with the tetra-tertiary phosphine. All of the tetra-tertiary phosphine substitution products of the octahedral metal carbonyls were identified by their characteristic ν(CO) frequencies which resembled those well-established for other similarly substituted octahedral metal carbonyls.^{23,24}

Several reactions of the methylmanganese derivative CH₃Mn(CO)₅ with both tetra-tertiary phosphines were

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investigated. The linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ in boiling benzene to give the bidentate methylmanganese derivative $\text{CH}_3\text{Mn}(\text{CO})_3(\text{Pf-Pf-Pf-Pf})$ which is completely analogous to the bidentate methylmanganese $\text{CH}_3\text{Mn}(\text{CO})_3(\text{Pf-Pf-Pf})$ derivative prepared similarly from $\text{CH}_3\text{Mn}(\text{CO})_5$ and the tritertiary phosphine Pf-Pf-Pf.¹ The tripod tetratertiary phosphine P(-Pf)₃ reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ in boiling xylene to give the tridentate methylmanganese derivative $\text{CH}_3\text{Mn}(\text{CO})_2\text{-P(-Pf)}_3$. The infrared spectrum of the dicarbonyl $\text{CH}_3\text{Mn}(\text{CO})_2\text{P(-Pf)}_3$ exhibited the expected two $\nu(\text{CO})$ frequencies (1906 and 1836 cm^{-1}) which occur at somewhat lower values than the $\nu(\text{CO})$ frequencies in the tricarbonyl $\text{CH}_3\text{Mn}(\text{CO})_3(\text{Pf-Pf-Pf-Pf})$. This is consistent with the increased retrodonative bonding of the manganese atom to the remaining two carbonyl groups when one of the original three carbonyl groups is replaced by a weaker π acceptor such as a trivalent phosphorus atom. The tripod tetratertiary phosphine P(-Pf)₃ (II) reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ in tetrahydrofuran to give the bidentate acetylmanganese derivative $\text{CH}_3\text{COMn}(\text{CO})_3\text{P(-Pf)}_3$ with carbon monoxide insertion into the methylmanganese bond. The presence of the acyl carbonyl group in $\text{CH}_3\text{COMn}(\text{CO})_3\text{P(-Pf)}_3$ was shown by the 1580- cm^{-1} $\nu(\text{CO})$ frequency in its infrared spectrum. The use of tetrahydrofuran as a solvent to promote carbonyl insertion in reactions of tertiary phosphines with $\text{CH}_3\text{Mn}(\text{CO})_5$ is now well established.²⁵

The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with either tetratertiary phosphine I or II in boiling benzene gave tridentate derivatives of the type (tetraphos) $\text{Mn}(\text{CO})_2\text{Br}$. Compounds of this type exhibited the expected two strong $\nu(\text{CO})$ frequencies at about 1930 and 1860 cm^{-1} .

C. Cyclopentadienylmetal Derivatives.—The methylmolybdenum derivative $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ has been shown to react with various types of tertiary phosphines in acetonitrile solution at room temperature without carbon monoxide evolution. Most ditertiary phosphines give the biligate bimetallic derivatives²⁶ (diphos) $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_2$ and the tritertiary phosphine Pf-Pf-Pf gives the triligate trimetallic derivative¹ (Pf-Pf-Pf) $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_3$. The reactions of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with either tetratertiary phosphine I or II in acetonitrile solution at room temperature give yellow precipitates of the corresponding tetraligate tetrametallic (tetraphos)- $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$ derivatives. The infrared spectra of the (tetraphos) $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$ derivatives in the $\nu(\text{CO})$ region resemble those of the (diphos) $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_2$ and (Pf-Pf-Pf)- $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_3$ derivatives indicating similar arrangements of the ligands around the molybdenum atom.

Reaction of the molybdenum derivative $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ with the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) gives the yellow-brown derivative $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})]\text{Cl}$, apparently a salt of the cation $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})^+$, in which the linear tetratertiary phosphine I acts as a bidentate ligand. This formulation is supported by

the $\nu(\text{CO})$ frequencies for $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})]\text{Cl}$ (1978 and 1913 cm^{-1}) which are close to those reported for known cations of the type $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-(diphos)}^+$ (e.g., $\nu(\text{CO})$ for $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf})][\text{PF}_6]$:²⁷ 1991 and 1927 cm^{-1}). Attempts to convert $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})]\text{Cl}$ to the corresponding hexafluorophosphate salt led instead to partial decomposition giving a product with the reproducible composition $(\text{Pf-Pf-Pf-Pf})[\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]_{1.3}[\text{PF}_6]_{1.3}$, apparently a mixture of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]$ with biligate monometallic Pf-Pf-Pf-Pf (I) and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2(\text{Pf-Pf-Pf-Pf})[\text{PF}_6]_2$ with tetraligate bimetallic Pf-Pf-Pf-Pf.

Some reactions of cyclopentadienylmanganese carbonyl derivatives with the tetratertiary phosphines I and II were investigated. Ultraviolet irradiation of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ with either tetratertiary phosphine I or II in benzene solution gave monocarbonyls of the type $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{tetraphos})$ with bidentate tetratertiary phosphine ligands; these compounds were identified not only by elemental analyses but also by the single $\nu(\text{CO})$ frequency around 1830 cm^{-1} in each compound characteristic of a $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{PR}_3)_2$ derivative.²⁸ In a similar manner the tripod tetratertiary phosphine P(-Pf)₃ (II) reacted with the salt $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ in boiling methanol in a 1:1 mole ratio to give the orange carbonyl-free salt $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})\text{P(-Pf)}_3][\text{PF}_6]$ with bidentate (biligate monometallic) P(-Pf)₃ (II). However, the analogous reaction between the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) and $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ in boiling methanol in the same 1:1 mole ratio gave the triligate bimetallic derivative $[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})(\text{NO})_2(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]_2$ similar to the triligate bimetallic derivatives of the type $[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})(\text{NO})_2(\text{triphos})][\text{PF}_6]_2$ analogously obtained from $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{NO})][\text{PF}_6]$ and the tritertiary phosphines $\text{CH}_3\text{C}[\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_3$ ²⁹ and $[(\text{C}_6\text{H}_5)_2\text{-PCH}_2\text{CH}_2]_2\text{PC}_6\text{H}_5$.¹

The tetraligate tetrametallic derivatives (tetraphos)- $[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$ are described above. Another series of tetraligate tetrametallic derivatives of the tetratertiary phosphines are the green iron complexes (tetraphos) $[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$, which were obtained by reactions of the tetratertiary phosphines I and II with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ in boiling toluene. The presence of a bridging $\nu(\text{CO})$ frequency at 1670 cm^{-1} and the absence of all terminal $\nu(\text{CO})$ frequencies in the (tetraphos) $[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$ complexes indicates that the trivalent phosphorus atoms have replaced terminal rather than bridging carbonyl groups in the reactions of the tetratertiary phosphines with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. This is consistent with previous studies on the reactions of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with ditertiary³⁰ and tritertiary¹ phosphines.

Other cyclopentadienyliron dicarbonyl derivatives also gave products of interest upon reaction with the tetratertiary phosphines I or II. Reaction of $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ with the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) in boiling acetonitrile (to promote the

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carbon monoxide insertion reaction) gave the monoligate monometallic derivative $\text{CH}_3\text{COFe}(\text{CO})(\text{Pf-Pf-Pf-Pf})(\text{C}_5\text{H}_5)$ without evolution of carbon monoxide. This is the only monoligate monometallic derivative of either tetratertiary phosphine (I or II) prepared during the course of this work. The formulation $\text{CH}_3\text{COFe}(\text{CO})(\text{Pf-Pf-Pf-Pf})(\text{C}_5\text{H}_5)$ is supported by the presence of a single terminal metal $\nu(\text{CO})$ frequency at 1913 cm^{-1} and a single acyl $\nu(\text{CO})$ frequency at 1585 cm^{-1} . Ultraviolet irradiation of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ with the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) in benzene solution gave green crystalline $\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})\text{I}$. This iodide exhibited the expected molar conductance for a 1:1 electrolyte in nitromethane and thus, at least in solution, appears to be the iodide salt of the cation $\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})^+$ with tridentate Pf-Pf-Pf-Pf (I). Furthermore, this iodide can be converted into the corresponding hexafluorophosphate salt $[\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]$ by treatment with ammonium hexafluorophosphate. Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ with the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II) in boiling benzene gave the yellow-orange bidentate derivative $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(-\text{Pf})_3]\text{I}$. The formulation of this compound as the iodide salt of the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(-\text{Pf})_3^+$ cation is supported by the presence of a single $\nu(\text{CO})$ frequency at 1970 cm^{-1} which is close to the $\nu(\text{CO})$ frequencies found for known cations of the type $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{diphos})^+$ (e.g., $\nu(\text{CO})$ for $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CH}_3)_2\text{-PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2^+$; 1970 cm^{-1}).

D. Conclusions.—A tetratertiary phosphine such as the linear Pf-Pf-Pf-Pf (I) or the tripod $\text{P}(-\text{Pf})_3$ (II) can coordinate to one or more metal atoms in $(1/2)(4 \cdot (4 + 1)) = 10$ different ways if differences arising from the nonequivalence of the phosphorus atoms in the tetratertiary phosphine are ignored.³¹ Of these 10 possible ways of coordinating the phosphorus atoms in the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I), the following six have been identified in the indicated complexes described in this paper: (1) monoligate monometallic: $\text{CH}_3\text{COFe}(\text{CO})(\text{Pf-Pf-Pf-Pf})(\text{C}_5\text{H}_5)$; (2) biligate monometallic: $(\text{Pf-Pf-Pf-Pf})\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}$ and Mo), $\text{CH}_3\text{Mn}(\text{CO})_3(\text{Pf-Pf-Pf-Pf})$, $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{Pf-Pf-Pf-Pf})]\text{Cl}$, and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{Pf-Pf-Pf-Pf})$; (3) triligate monometallic: $(\text{Pf-Pf-Pf-Pf})\text{MCl}_3$ ($\text{M} = \text{Rh}$ and Re), $(\text{Pf-Pf-Pf-Pf})\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$ and Mo), $(\text{Pf-Pf-Pf-Pf})\text{Mn}(\text{CO})_2\text{Br}$, and $\text{C}_5\text{H}_5\text{Fe}(\text{Pf-Pf-Pf-Pf})^+$; (4) tetraligate monometallic: $(\text{Pf-Pf-Pf-Pf})\text{M}^{2+}$ ($\text{M} = \text{Ni}$, Pd , and Pt), $(\text{Pf-Pf-Pf-Pf})\text{CoCl}^+$, and $(\text{Pf-Pf-Pf-Pf})\text{Rh}^+$; (5) triligate bimetallic: $[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})-$

$(\text{NO})_2(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]_2$; (6) tetraligate tetrametallic: $(\text{Pf-Pf-Pf-Pf})[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$ and $(\text{Pf-Pf-Pf-Pf})[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$. Of these 10 possible ways of coordinating the phosphorus atoms in the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II), the following four have been identified in the indicated complexes described in this paper: (1) biligate monometallic: $\text{P}(-\text{Pf})_3\text{PtCl}_2$, $\text{P}(-\text{Pf})_3\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}$ or Mo), $\text{CH}_3\text{-COMn}(\text{CO})_3\text{P}(-\text{Pf})_3$, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})\text{P}(-\text{Pf})_3$, $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})\text{P}(-\text{Pf})_3][\text{PF}_6]$, and $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{P}(-\text{Pf})_3]\text{I}$; (2) triligate monometallic: $\text{P}(-\text{Pf})_3\text{MCl}_3$ ($\text{M} = \text{Rh}$ and Re), $\text{P}(-\text{Pf})_3\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$ and Mo), $\text{CH}_3\text{Mn}(\text{CO})_2\text{-P}(-\text{Pf})_3$, and $\text{P}(-\text{Pf})_3\text{Mn}(\text{CO})_2\text{Br}$; (3) tetraligate monometallic: $\text{P}(-\text{Pf})_3\text{MCl}^+$ ($\text{M} = \text{Ni}$, Co , and Fe) and $\text{P}(-\text{Pf})_3\text{M}(\text{CO})_2$ ($\text{M} = \text{Mo}$ and W); (4) tetraligate tetrametallic: $\text{P}(-\text{Pf})_3[\text{Mo}(\text{CO})_2(\text{COCH}_3)(\text{C}_5\text{H}_5)]_4$ and $\text{P}(-\text{Pf})_3[\text{Fe}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]_2$.

The following were the major differences between the coordination chemistry of the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) and the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II) observed in this work: (1) the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) reacts with nickel(II) chloride to form brown to yellow square-planar nickel(II) derivatives whereas the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ (II) reacts with nickel(II) chloride under similar conditions to give blue to violet five-coordinate nickel(II) derivatives; (2) the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ reacts with ferrous chloride to give the violet five-coordinate derivative $\text{P}(-\text{Pf})_3\text{FeCl}^+$ whereas the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) does not react at all with ferrous chloride under the same conditions; (3) the linear tetratertiary phosphine Pf-Pf-Pf-Pf (I) reacts with $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{-NO}][\text{PF}_6]$ to form the triligate bimetallic derivative $[(\text{C}_5\text{H}_5)_2\text{Mn}(\text{CO})(\text{NO})_2(\text{Pf-Pf-Pf-Pf})][\text{PF}_6]_2$ whereas the tripod tetratertiary phosphine $\text{P}(-\text{Pf})_3$ reacts with $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$ under the same conditions including mole ratios of reactants to give the biligate monometallic derivative $[\text{C}_5\text{H}_5\text{Mn}(\text{NO})\text{P}(-\text{Pf})_3][\text{PF}_6]$. These observations demonstrate that the relative arrangements of the phosphorus atoms in otherwise identical and isomeric polytertiary phosphines can affect the types of complexes formed with transition metal derivatives.

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