CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Polytertiary Phosphines and Arsines. V. Metal Complexes of a Hexatertiary Phosphine[1]

BY R. B. KING* AND MOHAN SINGH SARAN[2]

Received February 1, 1971

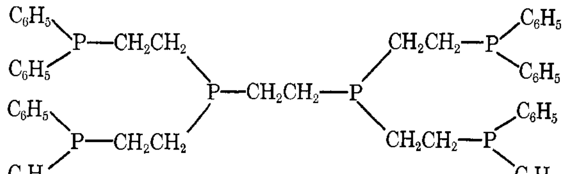
Transition metal complexes of the hexatertiary phosphine 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (abbreviated as $P_2(\text{-}Pf)_4$) are discussed. Reaction of chlorides of nickel, palladium, and platinum with $P_2(\text{-}Pf)_4$ in ethanol solution give the cations $P_2(\text{-}Pf)_4M^{2+}$ (M = Ni (orange), Pd (yellow), and Pt (colorless)) isolated as their hexafluorophosphate salts. Evidence is presented for tetradentate $P_2(\text{-}Pf)_4$ in the cations $P_2(\text{-}Pf)_4M^{2+}$. Reaction of cobalt(II) chloride with $P_2(\text{-}Pf)_4$ in boiling ethanol results in oxidation to the orange cobalt(III) derivative $[P_2(\text{-}Pf)_4CoCl_2]Cl$. The analogous rhodium(III) cation, $P_2(\text{-}Pf)_4RhCl_2^+$, isolable as its hexafluorophosphate salt, may be prepared from hydrated rhodium trichloride and $P_2(\text{-}Pf)_4$ in boiling ethanol. However, the analogous reaction of hydrated iridium trichloride and $P_2(\text{-}Pf)_4$ in boiling ethanol gives the pale gray trinuclear derivative $[P_2(\text{-}Pf)_4]_2Ir_3Cl_9$. Reaction of iron(II) chloride with $P_2(\text{-}Pf)_4$ in boiling ethanol in the presence of hexafluorophosphate gives the brown iron(II) derivative $[P_2(\text{-}Pf)_4FeCl][PF_6]$. A similar treatment of hydrated ruthenium trichloride with $P_2(\text{-}Pf)_4$ in boiling ethanol gives the brown ruthenium(III) cation $P_2(\text{-}Pf)_4RuCl_2^+$ isolable as its hexafluorophosphate salt. Reaction of rhenium trichloride with $P_2(\text{-}Pf)_4$ in boiling 2-methoxyethanol gives the green rhenium(III) cation $P_2(\text{-}Pf)_4ReCl_2^+$ isolable as its hexafluorophosphate salt. Reactions of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with $P_2(\text{-}Pf)_4$ in boiling toluene or xylene give the pale yellow hexaligate bimetallic derivatives $P_2(\text{-}Pf)_4[M(CO)_3]_2$ (M = Cr, Mo, and W). Reactions of the norbornadienemetal tetracarbonyl complexes $C_7H_8M(CO)_4$ (M = Cr and Mo) with $P_2(\text{-}Pf)_4$ in benzene at room temperature give the pale yellow biligate monometallic derivatives $P_2(\text{-}Pf)_4M(CO)_4$ (M = Cr and Mo). Reactions of $CH_3Mn(CO)_5$ with $P_2(\text{-}Pf)_4$ in boiling xylene or mesitylene give the pale yellow hexaligate bimetallic $P_2(\text{-}Pf)_4[Mn(CO)_2CH_3]_2$ and/or the light yellow triligate monometallic $P_2(\text{-}Pf)_4Mn(CO)_2CH_3$. However, reaction of $CH_3Mn(CO)_5$ with $P_2(\text{-}Pf)_4$ in tetrahydrofuran gives the light yellow biligate monometallic acetyl derivative $CH_3COMn(CO)_3P_2(\text{-}Pf)_4$. Reaction of $CH_3Mo(CO)_3C_5H_5$ with $P_2(\text{-}Pf)_4$ in acetonitrile at room temperature gives the pale yellow hexaligate hexametallic derivative $P_2(\text{-}Pf)_4[Mo(CO)_2(COCH_3)(C_5H_5)]_6$. Reactions of the cyclopentadienylmanganese derivatives $C_5H_5Mn(CO)_3$ and $[(C_5H_5Mn(CO)_2NO][PF_6]$ with $P_2(\text{-}Pf)_4$ give the triligate bimetallic derivatives $P_2(\text{-}Pf)_4Mn_2(CO)_3(C_5H_5)_2$ and $[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-}Pf)_4][PF_6]_2$, respectively. The infrared spectra, conductances, and magnetic susceptibilities of some of the new $P_2(\text{-}Pf)_4$ complexes are discussed.

Introduction

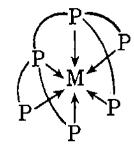
The base-catalyzed addition of the phosphorus–hydrogen bonds in 1,2-diphosphinoethane, $H_2PCH_2CH_2PH_2$, across the vinyl double bonds in 4 equiv of diphenylvinylphosphine provides a reasonably efficient synthesis of the hexatertiary phosphine 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane (alternatively named 1,2-bis[bis(2-diphenylphosphinoethyl)phosphino]ethane), $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (I, abbreviated as $P_2(\text{-}Pf)_4$),[3] apparently the only known hexatertiary phosphine. This hexatertiary phosphine I is of particular interest since the relative locations of its phosphorus atoms resemble the relative locations of the donor atoms in the well-known hexadentate ligand ethylenediaminetetraacetic acid (EDTA)[4] and thus should allow the hexatertiary phosphine I to function as a hexadentate (hexaligate monometallic) ligand as in structure II. This paper presents a survey of the reactions of the hexatertiary phosphine I with various transition metal compounds.

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 General Electric GBL-100C mercury ultraviolet lamp approximately 5 cm from the glass reaction vessel.



I



II

The sources of the transition metal derivatives used in this work are discussed in a previous paper of this series.[5]

Large-Scale Preparation of the Hexatertiary Phosphine 1,1,4,4-Tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane, $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (I, $P_2(\text{-}Pf)_4$).—For the preparation of the large quantities of the hexatertiary phosphine $P_2(\text{-}Pf)_4$ (I) required for this work, the previously reported[3] preparation was modified as described below so that the need for isolating and purifying the pyrophoric $H_2PCH_2CH_2PH_2$ was eliminated.

A suspension of 20 g (527 mmol) of lithium aluminum hydride in 500 ml of anhydrous diethyl ether was treated dropwise at 0° with a solution of 49 g (162 mmol) of $(C_2H_5O)_2P(O)CH_2CH_2P(O)(OC_2H_5)_2$ in 100 ml of diethyl ether over a 3-hr period. The reaction mixture was stirred at room temperature for 36 hr. The reaction mixture was then cooled in a 0° bath and treated dropwise with 400 ml of 6 *N* hydrochloric acid. An exothermic reaction occurred. The ethereal layer was separated, dried over anhydrous sodium sulfate, and then treated with 90 g (424 mmol) of diphenylvinylphosphine, 1.5 g (13.4 mmol) of potassium *tert*-butoxide, and 200 ml of redistilled tetrahydrofuran. The reaction mixture was heated to the boiling point and diethyl ether

---

(1) For Part IV of this series see R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

(2) Postdoctoral research associate, 1969–1971.

(3) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **91**, 5191 (1969); **93**, 4158 (1971).

(4) F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," Van Nostrand, Princeton, N. J., 1958.

(5) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).

was slowly distilled off over an 8–9-hr reaction period. The resulting tetrahydrofuran solution was boiled under reflux for an additional 30-hr period. Tetrahydrofuran was then removed at $\sim$25° (40 mm) to give a thick yellow paste which was dried at 100° (2 mm) for 30 min. The residue was then washed thoroughly with methanol to give 46 g (30% yield based on $(C_2H_5O)_2P(O)CH_2CH_2P(O)(OC_2H_5)_2$) of crude $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$, mp 131–135°. Recrystallization of the crude product from boiling benzene gave the pure hexatertiary phosphine, mp 139–140°.

Preparation of the Nickel Derivatives $P_2(\text{-Pf})_4NiCl_2$ and $[P_2(\text{-Pf})_4Ni][PF_6]_2$.—A mixture of 0.2 g (0.84 mmol) of $NiCl_2 \cdot 6H_2O$, 0.79 g (0.84 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of ethanol was boiled under reflux for 24 hr. The original green color of the hydrated nickel chloride became red-brown almost immediately. After the reaction period was over, solvent was removed from the reaction mixture at 25° (40 mm). The residue was crystallized from a mixture of dichloromethane and hexane to give 0.7 g (77% yield) of violet-brown crystalline $P_2(\text{-Pf})_4NiCl_2$, mp 94–95°. The analytical sample was purified by an additional recrystallization from a mixture of dichloromethane and hexane.

The orange hexafluorophosphate salt $[P_2(\text{-Pf})_4Ni][PF_6]_2$ could be prepared either by treatment of the above chloride with excess ammonium hexafluorophosphate in ethanol solution or by repetition of the reaction between $NiCl_2 \cdot 6H_2O$ and the hexatertiary phosphine as described above in the presence of excess ammonium hexafluorophosphate. This hexafluorophosphate salt was purified by recrystallization from a mixture of acetone and ethanol.

Preparation of the Palladium Derivative $[P_2(\text{-Pf})_4Pd][PF_6]_2$.—A mixture of 0.122 g (0.69 mmol) of palladium(II) chloride and 0.08 g (1.37 mmol) of sodium chloride was heated in 15 ml of water until a clear brown solution was obtained. This solution was treated with 0.642 g (0.68 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) and 50 ml of ethanol and the mixture was boiled under reflux for 19 hr. Solvent was removed from the resulting yellow solution at $\sim$25° (40 mm). The residue was extracted with $\sim$20 ml of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at $\sim$25° (40 mm). The residue was then dissolved in $\sim$20 ml of ethanol. Half of this solution was treated with excess warm ethanolic ammonium hexafluorophosphate. The resulting precipitate was removed by filtration and purified by crystallization from a mixture of acetone and ethanol to give 0.18 g (40% yield considering that only half of the reaction mixture was used) of bright yellow crystalline $[P_2(\text{-Pf})_4Pd][PF_6]_2$.

Preparation of the Platinum Derivative $[P_2(\text{-Pf})_4Pt][PF_6]_2$.—A 0.3-g (0.72-mmol) sample of K_2PtCl_4 was dissolved in $\sim$15 ml of water and the resulting orange-red solution was treated with 0.682 g (0.72 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) and 50 ml of ethanol. The resulting mixture was boiled under reflux for 17 hr. During the heating process the color of the reaction mixture changed to light yellow. After the reaction period was over, solvent was removed from the reaction mixture at $\sim$25° (40 mm). The residue was extracted with $\sim$20 ml of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at $\sim$25° (40 mm). The residue was dissolved in $\sim$100 ml of acetone and the solution was concentrated to $\sim$40 ml at $\sim$25° (40 mm). After cooling to -10° for $\sim$12 hr, the resulting precipitate was removed by filtration and dried to give 0.22 g (25% yield) of a light yellow solid, possibly impure $P_2(\text{-Pf})_4PtCl_2$. *Anal.* Calcd for $P_2(\text{-Pf})_4PtCl_2$: C, 57.6; H, 5.0; Cl, 5.9. Found: C, 53.0; H, 5.2; Cl, 5.9. The acetone filtrate was evaporated to dryness at $\sim$25° (40 mm). The residue was dissolved in ethanol and the solution heated with excess ethanolic ammonium hexafluorophosphate. The resulting precipitate was filtered, washed with several portions of water, and recrystallized from a mixture of acetone and ethanol to give 0.44 g (43% yield) of cream-colored crystalline $[P_2(\text{-Pf})_4Pt][PF_6]_2$.

Preparation of the Cobalt Derivative $[P_2(\text{-Pf})_4CoCl_2]Cl$.—A mixture of 0.2 g (0.84 mmol) of $CoCl_2 \cdot 6H_2O$, 0.78 g (0.83 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of ethanol was boiled under reflux for 24 hr. The original blue color soon became brown through an intermediate dirty yellow-green stage. After the reaction period was over, the reaction mixture was concentrated to $\sim$15 ml at $\sim$25° (40 mm). The yellow-orange crystalline precipitate was filtered and recrystallized from ethanol to give 0.4 g (44% yield) of orange fluffy crystalline $[P_2(\text{-Pf})_4CoCl_2]Cl$.

Attempts to obtain a hexafluorophosphate salt of a simple and definite composition from this system by either of the following two methods were unsuccessful: (1) reaction of $CoCl_2 \cdot 6H_2O$ with the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in ethanolic solution in the presence of excess ammonium hexafluorophosphate; (2) treatment of the ethanol filtrate from the isolation of $[P_2(\text{-Pf})_4CoCl_2]Cl$ with excess ammonium hexafluorophosphate. In both cases orange solid hexafluorophosphate salts were obtained, but their analyses suggested nonstoichiometric compositions of the type $P_2(\text{-Pf})_4CoCl_x(OC_2H_5)_y(PF_6)_z$ where $x + y + z = 3$. *Anal.* Calcd for $P_2(\text{-Pf})_4Co(OC_2H_5)_{1.5}(PF_6)_{1.5}$: C, 57.0; H, 5.2; F, 13.3; Cl, 0.0; Co, 4.6. Found on sample I: C, 56.9; H, 5.0; F, 21.4; Cl, 2.3. Found on sample II: C, 59.2; H, 5.1; F, 13.5; Cl, 0.8; Co, 4.9.

Preparations of $P_2(\text{-Pf})_4RhCl_2^+$ Salts.—A mixture of 0.2 g (0.78 mmol) of commercial rhodium trichloride trihydrate (40% rhodium), 0.717 g (0.76 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 60 ml of ethanol was boiled under reflux for 15 hr. The original red color soon became yellow through an intermediate orange stage. After the reaction period was over, the reaction mixture was cooled to room temperature. The precipitate was removed by filtration and dried to give 0.35 g (38% yield) of pale yellow $[P_2(\text{-Pf})_4RhCl_2][HCl_2]$, mp 265–267°. The yellow filtrate after removal of this precipitate was treated with excess ethanolic ammonium hexafluorophosphate. The resulting precipitate was removed by filtration and recrystallized from a mixture of ethanol and acetone to give 0.18 g (19% yield) of yellow crystalline $[P_2(\text{-Pf})_4RhCl_2][PF_6]$.

Preparation of the Iridium Derivative $[P_2(\text{-Pf})_4]_2Ir_3Cl_9$.—A mixture of 0.25 g (0.72 mmol) of commercial hydrated iridium trichloride (55% iridium), 0.668 g (0.71 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of ethanol was boiled under reflux for 24 hr. The original red-brown color of the solution became yellow-brown during the heating period. After cooling to room temperature, the pale gray precipitate was filtered, washed with hexane, and dried to give 0.53 g (80% yield based on iridium) of pale gray $[P_2(\text{-Pf})_4]_2Ir_3Cl_9$.

Preparation of the Iron Derivative $[P_2(\text{-Pf})_4FeCl][PF_6]$.—A mixture of 0.05 g (0.25 mmol) of $FeCl_2 \cdot 6H_2O$, 0.237 g (0.25 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), 0.5 g (3.07 mmol) of ammonium hexafluorophosphate, and 50 ml of ethanol was boiled under reflux for 24 hr. After cooling to room temperature the precipitate was filtered and crystallized from a mixture of acetone and ethanol to give 0.14 g (48% yield) of brown crystalline $[P_2(\text{-Pf})_4FeCl][PF_6]$.

Preparation of the Ruthenium Derivative $[P_2(\text{-Pf})_4RuCl_2][PF_6]$.—A mixture of 0.2 g (0.77 mmol) of commercial hydrated ruthenium trichloride (39% ruthenium), 0.721 g (0.76 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 60 ml of ethanol was boiled under reflux for 15 hr. The original red-brown color became yellow-brown during the heating period with an intermediate orange-brown stage. After cooling the reaction mixture to room temperature the precipitate which had separated was removed by filtration and dried to give 0.27 g of a light yellow-brown solid, mp 230–233°, possibly crude $P_2(\text{-Pf})_4RuCl_3$. *Anal.* Calcd for $P_2(\text{-Pf})_4RuCl_3$: C, 60.6; H, 5.3; Cl, 9.3. Found: C, 57.9; H, 5.2; Cl, 8.1. Treatment of some of the filtrate with excess ethanolic ammonium hexafluorophosphate gave a precipitate which was crystallized from a mixture of ethanol and acetone to give brown $[P_2(\text{-Pf})_4RuCl_2][PF_6]$.

Preparation of the Rhenium Derivative $[P_2(\text{-Pf})_4ReCl_2][PF_6]$.—A mixture of 0.3 g (1.03 mmol as $ReCl_3$) of commercial rhenium trichloride, 0.816 g (0.87 mmoles) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of 2-methoxyethanol was boiled under reflux for 44 hr. The original red color became a deep green through an intermediate purple stage. Solvent was removed from the filtered reaction mixture at $\sim$25° (0.1 mm). The green residue was dissolved in $\sim$20 ml of acetone and the filtered acetone solution was treated with $\sim$100 ml of diethyl ether. The green precipitate was removed by filtration, washed with diethyl ether, and dried to give 0.56 g of green crystals, mp 214–215°, possibly impure $P_2(\text{-Pf})_4ReCl_3$. *Anal.* Calcd for $P_2(\text{-Pf})_4ReCl_3$: C, 56.4; H, 4.9; Cl, 8.6. Found: C, 52.4; H, 4.9; Cl, 7.7. Solvent was removed from the green filtrate at $\sim$25° (40 mm). The residue was dissolved in $\sim$25 ml of ethanol and the filtered solution was treated with excess ethanolic ammonium hexafluorophosphate. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from a mixture of acetone and ethanol to give 0.23 g (20% yield) of green $[P_2(\text{-Pf})_4ReCl_2][PF_6]$, mp 217–218° dec.

Reactions of the Metal Hexacarbonyls $M(CO)_6$ (M = Cr,

TABLE I

METAL COMPLEXES OF 1,1,4,4-TETRAKIS(2-DIPHENYLPHOSPHINOETHYL)-1,4-DIPHOSPHABUTANE

Compound[a]	Color	Mp,[b] °C	Analyses,[c] %								Molar conductance[d]
			C		H		X or O		Other		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$P_2(\text{-Pf})_4\text{NiCl}_2$	Brown	94–95	64.8	62.8	5.6	5.5	6.6 (Cl)	7.0 (Cl)			A, insol; N, 77 ± 3
$[P_2(\text{-Pf})_4\text{Ni}][\text{PF}_6]_2$	Orange	233 dec	53.8	53.9	4.7	4.8	17.6 (F)	17.7 (F)	0.0 (Cl)	0.6 (Cl)	A, 350 ± 30; N, 170 ± 10
$[P_2(\text{-Pf})_4\text{Pd}][\text{PF}_6]_2$	Yellow	263–264	52.0	51.7	4.5	4.7	17.0 (F)	16.3 (F)	0.0 (Cl)	0.5 (Cl)	A, 330 ± 30; N, 185 ± 20
$[P_2(\text{-Pf})_4\text{Pt}][\text{PF}_6]_2$	Cream	296–297	48.7	48.7	4.2	4.0	16.0 (F)	18.5 (F)			A, 240 ± 20;[e] N, 178 ± 8
$[P_2(\text{-Pf})_4\text{CoCl}_2]\text{Cl}$	Orange	221 dec	62.9	61.3	5.4	5.5	9.6 (Cl)	9.5 (Cl)	5.3 (Co)	5.7 (Co)	A, ~100;[e] N, 69 ± 3
$[P_2(\text{-Pf})_4\text{RhCl}_2][\text{HCl}_2]$	Pale yellow	265–267	58.6	57.0	5.1	5.1	12.0 (Cl)	11.2 (Cl)			A, insol
$[P_2(\text{-Pf})_4\text{RhCl}_2][\text{PF}_6]$	Yellow	185–187	55.2	56.9	4.8	4.9	9.0 (F)	11.3 (F)	5.5 (Cl)	4.9 (Cl)	A, 148 ± 8; N, 75 ± 5
$[P_2(\text{-Pf})_4]_2\text{Ir}_3\text{Cl}_9$	Pale gray	272–274 dec	50.1	49.7	4.3	4.4	11.5 (Cl)	11.5 (Cl)			
$[P_2(\text{-PF})_4\text{FeCl}][\text{PF}_6]$	Brown	170 dec	59.2	57.4	5.1	5.1	9.7 (F)	10.3 (F)	3.0 (Cl)	1.9 (Cl)	A, 155 ± 20; N, 75 ± 9
$[P_2(\text{-Pf})_4\text{RuCl}_2][\text{PF}_6]$	Brown	216–218	55.3	56.9	4.8	5.0	9.1 (F)	9.6 (F)	5.6 (Cl)	3.7 (Cl)	A, 123 ± 7; N, 73 ± 7
$[P_2(\text{-Pf})_4\text{ReCl}_2][\text{PF}_6]$	Green	217–218	51.7	49.3	4.5	4.4	8.5 (F)	9.8 (F)	5.3 (Cl)	5.2 (Cl)	A, 134 ± 6; N, 82 ± 7
$P_2(\text{-Pf})_4[\text{Cr(CO)}_3]_2$	Light yellow	>310	63.3	63.1	5.0	4.9	7.9 (O)	8.1 (O)			
$P_2(\text{-Pf})_4[\text{Mo(CO)}_3]_2$	Pale yellow	>310	59.0	58.6	4.6	4.7	7.4 (O)	7.6 (O)			
$P_2(\text{-Pf})_4[\text{W(CO)}_3]_2$	Pale yellow-brown	>340	52.1	52.2	4.2	4.3	6.5 (O)	7.5 (O)			
$P_2(\text{-Pf})_4\text{Mo(CO)}_4$	Pale yellow	126–128	62.9	63.2	4.8	5.0	7.3 (O)	7.1 (O)			
$P_2(\text{-Pf})_4\text{Mn(CO)}_2\text{CH}_3$	Light yellow	64–66	68.6	68.1	5.9	5.9	3.0 (O)	2.8 (O)			
$P_2(\text{-Pf})_4[\text{Mn(CO)}_2\text{CH}_3]_2$	Pale yellow	320 dec	64.3	63.2	5.6	5.4	5.4 (O)	5.7 (O)			
$P_2(\text{-Pf})_4\text{Mn(CO)}_3\text{COCH}_3$	Light yellow	55–56	67.2	68.0	5.6	5.6	5.7 (O)	4.8 (O)			
$P_2(\text{-Pf})_4[\text{Mo(CO)}_2(\text{COCH}_3)\text{-}(\text{C}_5\text{H}_5)]_6$	Pale yellow	150–152	53.7	51.2	4.3	4.5	11.5 (O)	13.7 (O)			
$P_2(\text{-Pf})_4\text{Mn}_2(\text{CO})_3(\text{C}_5\text{H}_5)_2$	Brown	63–65	67.4	65.3	5.5	5.8	3.8 (O)	4.2 (O)			
$[(\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})(\text{NO})_2P_2\text{-}(\text{-Pf})_4][\text{PF}_6]_2$	Light orange	171–173	53.1	52.8	4.5	4.7	14.6 (F)	15.8 (F)	1.8 (N)	1.7 (N)	

[a] $P_2(\text{-Pf})_4$ refers to 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane. [b] These melting and decomposition 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. Even so the carbon values for many compounds, particularly the halides, tended to be low. [d] A, acetone solution; N, nitromethane solution; insol, too insoluble for a meaningful measurement to be obtained. Molar conductance values are given in the usual ohm^{-1} cm^2/mol. [e] This conductance value is probably slightly too low because of difficulty in dissolving the compound completely in acetone.

Mo, and W) with the Hexatertiary Phosphine $P_2(\text{-Pf})_4$ (I).—A mixture of 0.3 g of the metal hexacarbonyl $M(CO)_6$ (M = Cr: 1.37 mmol; M = Mo: 1.14 mmol), 0.5 equiv of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I: 0.643 g, 0.68 mmol for M = Cr; 0.536 g, 0.57 mmol for M = Mo), and 50 ml of toluene was boiled under reflux for 48 hr (M = Cr) or 12 hr (M = Mo). The crystals which separated upon cooling to room temperature were filtered, washed with hexane, and dried to give ~0.6 g (73–81% yield) of the light yellow crystalline $P_2(\text{-Pf})_4[\text{M(CO)}_3]_2$ (M = Cr or Mo) derivative.

Because of the lower reactivity of hexacarbonyltungsten, its reaction with the hexatertiary phosphine I was carried out under more vigorous conditions. Thus xylene rather than toluene was used as the solvent and the reaction time was increased to 10 days; otherwise the procedure was the same. From 0.4 g (1.13 mmol) of hexacarbonyltungsten and 0.536 g (0.57 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in 50 ml of xylene, 0.4 g (47% yield) of light brown-yellow $P_2(\text{-Pf})_4[\text{W(CO)}_3]_2$ was obtained.

Reaction of the Cycloheptatriene Complex $C_7H_8Mo(CO)_3$ with the Hexatertiary Phosphine.—A mixture of 0.2 g (0.74 mmol) of cycloheptatrienetricarbonylmolybdenum, 0.693 g (0.74 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of benzene was stirred for 18 hr at room temperature. The precipitate which separated was removed by filtration and dried to give 0.2 g (21% yield based on $C_7H_8Mo(CO)_3$) of $P_2(\text{-Pf})_4[\text{Mo(CO)}_3]_2$ identified by its ν(CO) frequencies and elemental analysis. *Anal.* Calcd for $P_2(\text{-Pf})_4[\text{Mo(CO)}_3]_2$: see Table I. Found: C, 56.7; H, 4.5; O, 8.5. Evaporation of the yellow filtrate at ~25° (40 mm) gave a yellow solid which was purified further by dissolving in dichloromethane and precipitating with diethyl ether. The infrared spectrum of this yellow solid in the ν(CO) region corresponded to that expected for a *cis*-$(R_3P)_2Mo(CO)_3$ derivative, but the analytical data did not agree with any obvious formula of this type.

Reactions of the Norbornadiene Complexes $C_7H_8Mo(CO)_4$ (M = Cr or Mo) with the Hexatertiary Phosphine.—A mixture of 0.2 g (0.67 mmol) of norbornadienetetracarbonylmolybdenum, 0.629 g (0.67 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of hexane was boiled under reflux for 15 hr. After cooling to room temperature, the dirty yellow-brown precipitate was removed by filtration and purified by crystallization from a mixture of dichloromethane and diethyl ether at −78° to give 0.42 g (55% yield) of yellow-brown crystalline $P_2(\text{-Pf})_4\text{Mo(CO)}_4$, mp 125–127°.

A similar reaction of the norbornadienechromium complex $C_7H_8Cr(CO)_4$ with the hexatertiary phosphine in boiling hexane for 48 hr gave a light yellow crystalline solid, mp 136–138°, with an infrared spectrum in the ν(CO) region (Table II) similar to that of the molybdenum derivative $P_2(\text{-Pf})_4\text{Mo(CO)}_4$ described above. However, elemental analyses indicated that the chromium compound was not completely pure. *Anal.* Calcd for $P_2(\text{-Pf})_4\text{Cr(CO)}_4$: C, 67.3; H, 5.5; O, 5.8. Found: C, 62.4; H, 5.4; O, 6.4.

Reaction of $CH_3Mn(CO)_5$ with the Hexatertiary Phosphine.—A mixture of 0.2 g (0.95 mmol) of $CH_3Mn(CO)_5$, 0.898 g (0.95 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of xylene was boiled under reflux for 24 hr. After cooling to room temperature, the resulting precipitate was removed by filtration, washed with xylene, and dried to give 0.1 g (18% yield) of light yellow $P_2(\text{-Pf})_4[\text{Mn(CO)}_2\text{CH}_3]_2$, mp 320° dec. Solvent was removed from the yellow xylene filtrate at 25° (0.1 mm). The remaining solid was washed with hexane and dried to give 0.7 g of a yellow solid. This yellow solid was chromatographed on a 2.5 × 30 cm alumina column in a mixture of dichloromethane and hex-

TABLE II

ν(CO) FREQUENCIES OF SOME METAL CARBONYL COMPLEXES OF THE HEXATERTIARY PHOSPHINE 1,1,4,4-TETRAKIS(2-DIPHENYLPHOSPHINOETHYL)-1,4-DIPHOSPHABUTANE[a,b]

Compound	Medium[c]	ν(CO), cm^{-1}
$P_2(\text{-Pf})_4[Cr(CO)_3]_2$	KBr	1932 s, 1830 vs, br
$P_2(\text{-Pf})_4[Mo(CO)_3]_2$	KBr	1932 s, 1833 vs, br
$P_2(\text{-Pf})_4[W(CO)_3]_2$	KBr	1930 s, 1827 vs, br
$P_2(\text{-Pf})_4Cr(CO)_4$[d]	CH_2Cl_2	2011 m, 1914 s, sh, 1883 vs, br
$P_2(\text{-Pf})_4Mo(CO)_4$	CH_2Cl_2	2026 m, 1923 s, sh, 1888 vs, br
$P_2(\text{-Pf})_4Mn(CO)_2CH_3$	CH	1915 s, 1841 s
$P_2(\text{-Pf})_4[(Mn(CO)_2CH_3]_2$	KBr	1897 sh, 1888 s, 1822 sh, 1816 s
$P_2(\text{-Pf})_4Mn(CO)_3COCH_3$	CH_2Cl_2	1995 s, 1911 vs, 1580 m[e]
$P_2(\text{-Pf})_4[Mo(CO)_2(COCH_3)(C_5H_5)]_6$	CH_2Cl_2	1932 s, 1846 vs, 1601 m[e]
$P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$	CH_2Cl_2	1960 m, 1890 m, 1818 vs
$C_5H_5Mn(CO)_2PCH_3(C_6H_5)_2$[f]	CS_2	1935 s, 1872 s
$C_5H_5Mn(CO)(PCH_3(C_6H_5)_2)_2$[f]	CS_2	1835 s
$[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-Pf})_4][PF_6]_2$	CH_2Cl_2	2040 m, 1794 m,[g] 1741 s[g]
$P_2(\text{-Pf})_4[FeI(CO)(C_5H_5)]_{1.5}$	CH_2Cl_2	1961 s

[a] These spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. [b] The spectra were calibrated with the 1601.4-cm^{-1} band of polystyrene film. [c] CH = cyclohexane solution. [d] These ν(CO) frequencies were obtained from an incompletely purified sample. [e] Acyl ν(CO) frequency. [f] Data of R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964). [g] Nitrosyl ν(NO) frequency.

ane. The eluate from the yellow bands was evaporated at ~25° (40 mm) to give 0.31 g (31% yield) of light yellow crystalline $P_2(\text{-Pf})_4Mn(CO)_2CH_3$, mp 64–66°.

In an experiment designed to maximize the yield of the binuclear derivative $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$ relative to the mononuclear derivative $P_2(\text{-Pf})_4Mn(CO)_2CH_3$, a mixture of 0.2 g (0.95 mmol) of $CH_3Mn(CO)_5$, 0.45 g (0.48 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of mesitylene was boiled under reflux for 48 hr. After cooling to room temperature, the yellow precipitate was removed by filtration and dried to give 0.4 g (70% yield) of dirty yellow $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$ identified by comparison of its melting point and infrared ν(CO) frequencies with those of material prepared in xylene solution.

In order to prepare an acetyl derivative the reaction between $CH_3Mn(CO)_5$ and the hexatertiary phosphine I was also carried out in tetrahydrofuran solution. A mixture of 0.15 g (0.71 mmol) of $CH_3Mn(CO)_5$, 0.673 g (0.71 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of redistilled tetrahydrofuran was heated in a sealed tube at 42° for 40 hr. Tetrahydrofuran was then removed at ~25° (40 mm). The residue was extracted with ~25 ml of acetone and solvent was removed from the filtered acetone extract at ~25° (40 mm). Attempts to obtain a crystalline product by crystallization from a mixture of dichloromethane and hexane were unsuccessful apparently owing to the high solubility of the compound. Extraction of the residue with dichloromethane followed by evaporation of the filtered dichloromethane extracts gave 0.7 g (88% yield) of light yellow $CH_3COMn(CO)_3P_2(\text{-Pf})_4$.

Reaction of $CH_3Mo(CO)_3C_5H_5$ with the Hexatertiary Phosphine.—A mixture of 0.827 g (3.18 mmol) of $CH_3Mo(CO)_3C_5H_5$, 0.5 g (0.53 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of acetonitrile was stirred for 48 hr at room temperature. The yellow precipitate was removed by filtration, washed with several portions of acetonitrile, and dried to give 1.2 g (91% yield) of pale yellow $P_2(\text{-Pf})_4[Mo(CO)_2(COCH_3)C_5H_5)]_6$.

Reaction of $C_5H_5Mn(CO)_3$ with the Hexatertiary Phosphine.—A mixture of 0.102 g (0.50 mmol) of $C_5H_5Mn(CO)_3$, 0.472 g (0.50 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of benzene was exposed to ultraviolet irradiation for 15 hr. Solvent was removed from the filtered orange solution at ~25° (40 mm). Attempts to obtain a crystalline product from the residue by crystallization from a mixture of dichloromethane and hexane were unsuccessful. The residue was therefore extracted with 25 ml of benzene and solvent was removed from the filtered benzene solution at ~25° (40 mm) to give 0.32 g (100% yield) of brown $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$.

Reaction of $[C_5H_5Mn(CO)_2NO][PF_6]$ with the Hexatertiary Phosphine.—A mixture of 0.2 g (0.57 mmol) of $[C_5H_5Mn(CO)_2NO][PF_6]$, 0.537 g (0.57 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 60 ml of methanol was boiled under reflux for 24 hr. After cooling to room temperature, the white precipitate was removed by filtration and dried to give 0.35 g (65% recovery) of unreacted hexatertiary phosphine I, mp 141°. Solvent was removed from the orange filtrate at ~25° (40 mm). The residue was recrystallized from a mixture of acetone and methanol to give 0.21 g (68% yield based on unrecovered hexatertiary phosphine I) of light orange $[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-Pf})_4][PF_6]_2$, mp 171–173°.

Reaction of $C_5H_5Fe(CO)_2I$ with the Hexatertiary Phosphine.—A mixture of 0.152 g (0.5 mmol) of $C_5H_5Fe(CO)_2I$, 0.472 g (0.5 mmol) of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I), and 50 ml of xylene was boiled under reflux for 48 hr. Solvent was removed from the filtered reaction mixture at ~25° (0.1 mm). The residue was extracted with ~10 ml of dichloromethane. The filtered extracts were treated with 25 ml of methanol and the resulting white precipitate, apparently some unreacted hexatertiary phosphine, was removed by filtration. Solvent was removed from the filtrate at ~25° (40 mm). The residue was washed with hexane to give 0.34 g (76% yield) of yellow-brown crystals, mp 126–127°, of composition $P_2(\text{-Pf})_4[FeI(CO)(C_5H_5)]_{1.5}$. *Anal.* Calcd for $P_2(\text{-Pf})_4[FeI(CO)(C_5H_5)]_{1.5}$: C, 58.8; H, 5.0; O, 1.8; I, 14.3. Found: C, 59.3; H, 5.2; O, 2.9; I, 14.4.

Infrared Spectra.—Far-infrared spectra (400–100 cm^{-1}) of the metal chloride complexes (Table III) 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[6–8] and must be regarded as tentative until far-infrared data on corresponding bromides and iodides become available.

TABLE III

FAR-INFRARED SPECTRA OF SOME OF THE METAL CHLORIDE COMPLEXES OF 1,1,4,4-TETRAKIS(2-DIPHENYLPHOSPHINOETHYL)-1,4-DIPHOSPHABUTANE[a]

Complex	ν(M–Cl), cm^{-1}	Other bands, cm^{-1}
$P_2(\text{-Pf})_4$	. . .	373 s, 334 w, 309 w, 292 w, 268 w, 229 vw, 210 w, 154 w,
$P_2(\text{-Pf})_4NiCl_2$	305 w, 293 w, 284 w, 273 vw	256 vw, 229 w, 216 w, 180 w
$[P_2(\text{-Pf})_4CoCl_2]Cl$	377 w	339 vw, 318 w, 308 vw, 289 sh, 274 w
$[P_2(\text{-Pf})_4RhCl_2][HCl_2]$	346 m	268 m
$[P_2(\text{-Pf})_4RhCl_2][PF_6]$	~351 vvw	
$[P_2(\text{-Pf})_4]_2Ir_3Cl_9$	313 m, 270 w	
$[P_2(\text{-Pf})_4ReCl_2][PF_6]$	337 w	310 w, 293 w, 267 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.

Infrared spectra of the metal carbonyl derivatives in the 2100–1600-cm^{-1} region (Table II) were obtained in the indicated media and recorded on a Perkin-Elmer Model 621 spectrometer.

Ultraviolet and Visible Spectra.—The following ultraviolet and visible spectra were obtained on a Cary Model 14 spectrometer in dichloromethane solution: (A) $P_2(\text{-Pf})_4NiCl_2$, maximum at 422 mμ (ϵ 3000); inflection point at 273 mμ (ϵ 25,000); (B) $[P_2(\text{-Pf})_4Ni][PF_6]_2$, maxima at 417 m$\mu$ (ϵ 4000) and 273 mμ (ϵ 40,000); (C) $[P_2(\text{-Pf})_4CoCl_2]Cl$, maximum at 365 m$\mu$ (ϵ 14,000); (D) $[P_2(\text{-Pf})_4FeCl][PF_6]$, maxima at 465 m$\mu$ (ϵ 700) and 372 mμ (ϵ 3000); (E) $[P_2(\text{-Pf})_4ReCl_2][PF_6]$, maximum at 643 m$\mu$ (ϵ 580).

Molar Conductance Measurements.—The molar conductances listed in Table I were determined in ~0.0001–0.003 *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

---

(6) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's, New York, N. Y., 1968.

(7) J. Lewis, R. S. Nyholm, and G. A. Rodley, *J. Chem. Soc.*, 1483 (1965).

(8) J. Chatt, G. J. Leigh, and D. M. P. Mingos, *ibid.*, *A*, 1674 (1969).

Springs, Ohio. Each compound was studied at a minimum of three different concentrations in each solvent used.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured at room temperature in the solid state on an Alpha Scientific magnetic balance using the Faraday method. Because of the high formula weights of the P_2(-Pf)$_4$ (I) complexes, the values of $\chi_g^{27^\circ}$ were low relative to $\chi_{mol}^{27^\circ}$ and μ_{eff} values, and hence the usual degree of precision for diamagnetic and weakly paramagnetic compounds could not be obtained. Nevertheless, the following P_2(-Pf)$_4$ complexes were clearly demonstrated to be diamagnetic: P_2(-Pf)$_4$NiCl$_2$, [P_2(-Pf)$_4$Ni][PF$_6$]$_2$, [P_2(-Pf)$_4$Pd][PF$_6$]$_2$, [P_2(-Pf)$_4$Pt][PF$_6$]$_2$, [P_2(-Pf)$_4$CoCl$_2$]Cl, [P_2(-Pf)$_4$RhCl$_2$][HCl$_2$], [P_2(-Pf)$_4$RhCl$_2$][PF$_6$], and [P_2(-Pf)$_4$]$_2$-Ir$_3$Cl$_9$. The following compounds were paramagnetic: (A) [P_2(-Pf)$_4$FeCl][PF$_6$], $\chi_{mol}^{27^\circ} = +1930 \times 10^{-6}$ cm^3/mol corresponding to a magnetic moment of 2.5 BM after making a correction of -826×10^{-6} cm^3/mol for the diamagnetism of the ligands; (B) [P_2(-Pf)$_4$RuCl$_2$][PF$_6$], $\chi_{mol}^{27^\circ} = +256 \times 10^{-6}$ cm^3/mol corresponding to a magnetic moment of 1.7 BM after making a relatively large correction of -846×10^{-6} cm^3/mol for the diamagnetism of the ligands; (C) [P_2(-Pf)$_4$ReCl$_2$][PF$_6$], $\chi_{mol}^{27^\circ} = -130 \times 10^{-6}$ cm^3/mol corresponding to a magnetic moment of 1.3 BM because of the relatively large correction of -803×10^{-6} cm^3/mol for the diamagnetism of the ligands.

Discussion

A. Metal Halide and Metal Hexafluorophosphate Derivatives.—Reactions of appropriate metal(II) chlorides of nickel, palladium, and platinum with the hexatertiary phosphine P_2(-Pf)$_4$ (I) in ethanol gave solutions from which ammonium hexafluorophosphate precipitated diamagnetic chloride-free derivatives of the general type [P_2(-Pf)$_4$M][PF$_6$]$_2$ (M = Ni (orange), Pd (yellow), and Pt (cream)). The molar conductances of all three salts in nitromethane solution (Table I) were around 180 ohm^{-1} cm^2/mol indicative of 1:2 electrolytes. Cations of the type P_2(-Pf)$_4$M^{2+} can contain tetradentate, pentadentate, or hexadentate hexatertiary phosphine P_2(-Pf)$_4$ (I) with coordination numbers 4, 5, or 6, respectively, for the central metal atom. The cations P_2(-Pf)$_4$M^{2+} (M = Ni, Pd, or Pt) are probably square-planar metal derivatives with tetradentate hexatertiary phosphine I for the following reasons: (1) their diamagnetism, which excludes formulation of the nickel complex as a six-coordinate octahedral derivative; (2) the relatively weak colors of the P_2(-Pf)$_4$M^{2+} cations (orange to white) as contrasted with the more intense colors for species such as the five-coordinate (QP)MX$^+$ (X = halogen, etc., QP = [o-(C$_6$H$_5$)$_2$PC$_6$H$_4$]$_3$P, M = Ni (blue to violet)[9] or Pd (red-violet))[10] and tetrahedral (R$_3$P)$_2$NiX$_2$ (green);[11] also the ultraviolet and visible spectra of [P_2(-Pf)$_4$Ni][PF$_6$]$_2$ resemble those of the tetratertiary phosphine derivative [(Pf-Pf-Pf-Pf)Ni][PF$_6$]$_2$ where the nickel atom must be four-coordinate.[1]

The reaction between nickel(II) chloride and the hexatertiary phosphine P_2(-Pf)$_4$ (I) in the absence of any hexafluorophosphate gave a violet-brown diamagnetic product P_2(-Pf)$_4$NiCl$_2$. This nickel compound was an electrolyte in nitromethane solution exhibiting a molar conductance of 77 ± 3 ohm^{-1} cm^2/mol. The problem of the formulation of P_2(-Pf)$_4$NiCl$_2$ is complicated by the possibility of equilibria involving the isomeric 2:1 electrolyte [P_2(-Pf)$_4$Ni]Cl$_2$, 1:1 electrolyte [P_2(-Pf)$_4$NiCl]Cl, and nonelectrolyte P_2(-Pf)$_4$NiCl$_2$. The far-infrared spectrum of this nickel complex P_2(-Pf)$_4$NiCl$_2$ (Table III) exhibits several apparent ν(Ni–Cl) frequencies around 300 cm^{-1} indicating the presence of nickel–chlorine bonds.

Reactions of cobalt(II) chloride with chelating tritertiary[5] and tetratertiary[1] phosphines in boiling ethanol give paramagnetic cobalt(II) derivatives. However, the corresponding reaction of cobalt(II) chloride with the hexatertiary phosphine P_2(-Pf)$_4$ (I) in boiling ethanol gave a diamagnetic orange solid of composition P_2(-Pf)$_4$CoCl$_3$. The composition and diamagnetism of this orange solid indicate it to be an octahedral cobalt(III) derivative. The molar conductance of P_2(-Pf)$_4$CoCl$_3$ in nitromethane solution (Table I) was close to 70 ohm^{-1} cm^2/mol indicative of a 1:1 electrolyte. The cobalt derivative P_2(-Pf)$_4$CoCl$_3$ is therefore formulated as [P_2(-Pf)$_4$CoCl$_2$]Cl with tetradentate P_2(-Pf)$_4$ (I). The formulation [P_2(-Pf)$_4$CoCl$_2$]Cl is also supported by the observed ν(Co–Cl) frequency at 377 cm^{-1} which is close to the 384-cm^{-1} ν(Co–Cl) infrared frequency found in [(diars)$_2$CoCl$_2$]Cl.[7] Addition of ammonium hexafluorophosphate to the filtrate from the preparation of [P_2(-Pf)$_4$CoCl$_2$]Cl gave an orange hexafluorophosphate salt of variable composition; apparently more than one cation which forms sparingly soluble hexafluorophosphate salts is present in the reaction solution.

Reaction of hydrated rhodium trichloride with the hexatertiary phosphine P_2(-Pf)$_4$ (I) in boiling ethanol gave a pale yellow solid of stoichiometry P_2(-Pf)$_4$RhCl$_4$. The diamagnetism of this compound excludes its formulation as a rhodium(IV) derivative. This compound exhibits a far-infrared ν(Rh–Cl) frequency at 346 cm^{-1} close to the 349-cm^{-1} infrared ν(Rh–Cl) frequency found in [(diars)$_2$RhCl$_2$]Cl; for this reason "P_2(-Pf)$_4$RhCl$_4$" is formulated as [P_2(-Pf)$_4$RhCl$_2$]Cl · HCl with octahedral rhodium(III) and tetradentate hexatertiary phosphine P_2(-Pf)$_4$ (I). The "extra" hydrogen chloride molecule either can add to the chloride anion to form the HCl$_2^-$ anion[12] or can protonate one of the uncomplexed phosphorus atoms in the hexatertiary phosphine P_2(-Pf)$_4$ (I). The latter possibility appears to be excluded by the absence of any ν(PH) frequencies around 2400–2200 cm^{-1} in the infrared spectrum of [P_2(-Pf)$_4$RhCl$_2$]Cl · HCl taken in a KBr pellet concentrated enough for the strongest bands to absorb full scale. As a further confirmation of the existence of the P_2(-Pf$_4$)RhCl$_2^+$ cation, its hexafluorophosphate salt was also prepared. This hexafluorophosphate salt gave somewhat high fluorine analyses and low chlorine analyses for [P_2(-Pf)$_4$RhCl$_2$][PF$_6$]; this suggests the possibility of some contamination with [P_2(-Pf)$_4$RhCl][PF$_6$]$_2$ which would be an octahedral rhodium(III) derivative with pentadentate P_2(-Pf)$_4$ (I).

The reaction between hydrated iridium trichloride and the hexatertiary phosphine P_2(-Pf)$_4$ (I) appeared to proceed in an entirely different manner from that of the corresponding reaction with rhodium trichloride. A gray diamagnetic product of stoichiometry [P_2(-Pf)$_4$]$_2$-Ir$_3$Cl$_9$ precipitated from the reaction mixture. The far-infrared spectrum of this trinuclear complex exhibited ν(Ir–Cl) frequencies at 313 (m) and 270 cm^{-1} (w) suggesting that the three chlorine atoms of each IrCl$_3$

---

(9) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem., Soc.*, 1293 (1965); G. Dyer and L. M. Venanzi, *ibid.*, 2771 (1965).

(10) C. A. Savage and L. M. Venanzi, *ibid.*, 1548 (1962).

(11) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton, and L. M. Venanzi, *ibid.*, 4816 (1961).

(12) R. E. Vallee and D. H. McDaniel, *J. Amer. Chem. Soc.*, **84**, 3412 (1962); K. M. Harman and S. Davis, *ibid.*, **84**, 4359 (1962).

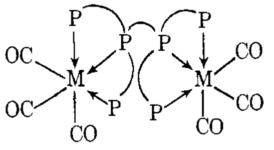
group occupy meridional positions in an octahedron (ν(Ir–Cl) reported[7] for *mer*-$[(C_2H_5)_3P]_3IrCl_3$: 313 and 267 cm^{-1}). In $[P_2(\text{-Pf})_4]_2Ir_3Cl_9$ the hexatertiary phosphines $P_2(\text{-Pf})_4$ (I) probably bridge the three $IrCl_3$ groups; bridging chlorine atoms may also be present.

The reaction between hydrated ferrous chloride and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in boiling ethanol in the presence of ammonium hexafluorophosphate gave a brown hexafluorophosphate salt $[P_2(\text{-Pf})_4FeCl][PF_6]$. This hexafluorophosphate salt exhibited a paramagnetism of 2.5 BM close to the values of 3.0–3.2 BM reported[13] for pentacoordinate iron(II) derivatives of the type (tetraphos)FeCl$^+$ and to the value of 2.8 BM found[1] for the likewise pentacoordinate iron(II) derivative $[P(\text{-Pf})_3FeCl][PF_6]$. Accordingly the compound $[P_2(\text{-Pf})_4FeCl][PF_6]$ may be an analogous pentacoordinate iron(II) derivative with the hexatertiary phosphine I acting as a tetradentate ligand. The electronic spectrum of $[P_2(\text{-Pf})_4FeCl][PF_6]$ exhibited maxima at 465 and 372 mμ which may correspond to the maxima at 540 and 332 mμ reported[13] for [FeCl(QP)]Cl and to the maxima at 521 and 320 mμ found[1] for $[P(\text{-Pf})_3FeCl][PF_6]$; however, the extinction coefficients of the maxima in $[P_2(\text{-Pf})_4FeCl][PF_6]$ are much less than those of the corresponding maxima in the tetratertiary phosphine complexes and the light brown color of $[P_2(\text{-Pf})_4FeCl][PF_6]$ is much lighter than the deep purple colors of the five-coordinate (tetraphos)FeCl$^+$ derivatives. The reasons for the shifts in the positions of the maxima, the reduction of the extinction coefficients, and the lighter color in $[P_2(\text{-Pf})_4FeCl][PF_6]$ relative to the tetratertiary phosphine complexes [FeCl(QP)]Cl and $[P(\text{-Pf})_3FeCl][PF_6]$ are not clear but might be linked in some obscure manner to the presence of two uncomplexed phosphorus atoms in $[P_2(\text{-Pf})_4FeCl][PF_6]$ if so formulated as a five-coordinate iron(II) derivative with tetradentate $P_2(\text{-Pf})_4$. Another entirely different possibility is that $[P_2(\text{-Pf})_4FeCl][PF_6]$ is a six-coordinate iron(II) complex in an anomalous spin state.[14]

The reaction between hydrated ruthenium trichloride and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in boiling ethanol gave the $P_2(\text{-Pf})_4RuCl_2^+$ cation, isolated as its hexafluorophosphate salt. This salt exhibited the required conductance properties for a 1:1 electrolyte and paramagnetism corresponding to 1.7 BM, the value expected for a ruthenium(III) complex which has one unpaired electron. The cation $P_2(\text{-Pf})_4RuCl_2^+$ is apparently an octahedral ruthenium(III) derivative with tetradentate $P_2(\text{-Pf})_4$ (I).

The reaction between rhenium trichloride and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in boiling 2-methoxyethanol gave a green product suggested by analysis to be a crude sample of $P_2(\text{-Pf})_4ReCl_3$. Addition of ammonium hexafluorophosphate to the filtrate from the isolation of this green solid gave eventually a green slightly paramagnetic hexafluorophosphate salt $[P_2(\text{-Pf})_4ReCl_2][PF_6]$. The magnetic susceptibility and electronic spectrum of the cation $P_2(\text{-Pf})_4ReCl_2^+$ resemble those of the tritertiary phosphine derivative[5] (Pf-Pf-Pf)$ReCl_3$ and the tetratertiary phosphine derivatives[1] (tetraphos)$ReCl_3$, all of which have been tentatively formulated as octahedral rhenium(III) derivatives with tridentate polytertiary phosphine ligands. Accordingly the cation $P_2(\text{-Pf})_4ReCl_2^+$ is likewise tentatively formulated as an octahedral rhenium(III) derivative, this time with a tetradentate polytertiary phosphine ligand.

B. Metal Carbonyl and Metal Cyclopentadienyl Derivatives.—The three metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) all reacted with the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) in a boiling aromatic hydrocarbon solvent (toluene or xylene) to give the light yellow compounds $P_2(\text{-Pf})_4[M(CO)_3]_2$ (M = Cr, Mo, and W). These compounds all exhibited two ν(CO) frequencies (Table II) in the expected positions and of the expected relative intensities for *cis*-$(R_3P)_3M(CO)_3$ derivatives.[15] The $P_2(\text{-Pf})_4[M(CO)_3]_2$ derivatives thus have hexaligate bimetallic $P_2(\text{-Pf})_4$ bonded to the metal atoms as in structure III. The reaction between the cycloheptatrienemolybdenum complex $C_7H_8Mo(CO)_3$ and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) at room temperature also gave $P_2(\text{-Pf})_4[Mo(CO)_3]_2$ as the only identifiable product isolated in the pure state. The reaction between the norbornadienemolybdenum complex $C_7H_8Mo(CO)_4$ and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) gave a mononuclear complex $P_2(\text{-Pf})_4Mo(CO)_4$ which had infrared ν(CO) frequencies in the expected positions and of the expected relative intensities for a *cis*-$(R_3P)_2M(CO)_4$ derivative.[15] An analogous chromium compound $P_2(\text{-Pf})_4Cr(CO)_4$ was obtained from the reaction between the norbornadienechromium complex $C_7H_8Cr(CO)_4$ and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I); it was identified by its ν(CO) frequencies but was not obtained analytically pure. The $P_2(\text{-Pf})_4M(CO)_4$ (M = Cr and Mo) complexes have biligate monometallic $P_2(\text{-Pf})_4$.



III

The reaction between the methylmanganese derivative $CH_3Mn(CO)_5$ and the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) gave three different characterizable products depending upon the reaction conditions. Reaction of $CH_3Mn(CO)_5$ with $P_2(\text{-Pf})_4$ in boiling xylene in a 1:1 mole ratio gave the yellow xylene-insoluble hexaligate bimetallic derivative $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$ and the yellow xylene-soluble triligate monometallic derivative $P_2(\text{-Pf})_4Mn(CO)_2CH_3$. The yield of the hexaligate bimetallic derivative $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$ was increased by using a 2:1 mole ratio of $CH_3Mn(CO)_5$ to $P_2(\text{-Pf})_4$ and boiling mesitylene rather than boiling xylene for the solvent. Reaction of $CH_3Mn(CO)_5$ with $P_2(\text{-Pf})_4$ in tetrahydrofuran under relatively mild conditions gave the light yellow biligate monometallic acyl derivative $CH_3COMn(CO)_3P_2(\text{-Pf})_4$. The bonding of an acetyl group rather than a methyl group to the manganese atom in $CH_3COMn(CO)_3P_2(\text{-Pf})_4$ is indicated by the acyl ν(CO) frequency at 1580 cm^{-1} in this compound. Comparable infrared frequencies are absent in $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$ and $P_2(\text{-Pf})_4Mn(CO)_2CH_3$.

---

(13) M. T. Halfpenny, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 627 (1967).

(14) E. König and K. Madeja, *Inorg. Chem.*, **7**, 1848 (1968), and references cited therein.

(15) F. A. Cotton, *ibid.*, **3**, 702 (1964).

The methylmolybdenum derivative $CH_3Mo(CO)_3C_5H_5$ has been shown[1,5,16] to react with most polytertiary phosphines in acetonitrile without carbon monoxide evolution to bond all phosphorus atoms to different molybdenum atoms forming polynuclear species containing $R_3PMo(CO)_2(COCH_3)(C_5H_5)$ units linked together by the bridges of the polytertiary phosphine. Thus the tritertiary phosphine[5] $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$(Pf-Pf-Pf) forms the triligate trimetallic (Pf-Pf-Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$ with $CH_3Mo(CO)_3C_5H_5$ and the tetratertiary phosphines[1] such as $[(C_6H_5)_2PCH_2CH_2]_3P$ form the tetraligate tetrametallic (tetraphos)$[Mo(CO)_2(COCH_3)(C_5H_5)]_4$ with $CH_3Mo(CO)_3C_5H_5$. The hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) reacted similarly with $CH_3Mo(CO)_3C_5H_5$ in acetonitrile solution at room temperature to give a precipitate of the yellow hexaligate hexametallic derivative $P_2(\text{-Pf})_4[Mo(CO)_2(COCH_3)(C_5H_5)]_6$.

Reactions of cyclopentadienylmanganese carbonyl derivatives with the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) gave the triligate bimetallic derivatives $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$ and $[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-Pf})_4][PF_6]_2$. The infrared spectrum of $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$ exhibited two ν(CO) frequencies at 1960 and 1890 cm^{-1} arising from the $C_5H_5Mn(CO)_2$ group and a third ν(CO) frequency at 1818 cm^{-1} arising from the C_5H_5MnCO group. These assignments of the infrared ν(CO) frequencies in $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$ were based on their comparison with those of known[17] $C_5H_5Mn(CO)_2PR_3$ and $C_5H_5MnCO(PR_3)_2$ derivatives. The analytical data obtained on $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$ actually were closer to the required values for the pentaligate trimetallic derivative $P_2(\text{-Pf})_4Mn_3(CO)_4(C_5H_5)_3$, but this latter formula can be excluded on the basis that its yield from $C_5H_5Mn(CO)_3$ and $P_2(\text{-Pf})_4$ (I) would be an impossible $\sim$135%. The infrared spectrum of the triligate bimetallic cyclopentadienylmanganese nitrosyl derivative $[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-Pf})_4][PF_6]_2$ in the ν(CO) and ν(NO) regions resemble closely the reported spectra of known[5,18] $[(C_5H_5)_2Mn(CO)(NO)_2$(triphos)$][PF_6]_2$ derivatives.

Reaction of $C_5H_5Fe(CO)_2I$ with the hexatertiary phosphine $P_2(\text{-Pf})_4$ in boiling xylene gave a yellow-brown material of composition $P_2(\text{-Pf})_4[FeI(CO)(C_5H_5)]_{1.5}$, probably an inseparable mixture of approximately equimolar quantities of the biligate monometallic salt $[C_5H_5Fe(CO)P_2(\text{-Pf})_4]I$ and the tetraligate bimetallic salt $[(C_5H_5)_2Fe_2(CO)_2P_2(\text{-Pf})_4]I_2$. The infrared spectrum of $P_2(\text{-Pf})_4[FeI(CO)(C_5H_5)]_{1.5}$ exhibited a single ν(CO) frequency at 1961 cm^{-1} which is close to the 1970-cm^{-1} ν(CO) frequency found[19] in the cation $C_5H_5Fe(CO)(CH_3)_2PCH_2CH_2P(CH_3)_2^+$.

C. Conclusion.—Despite the wide variety of transition metal systems investigated no complexes of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) were obtained in this work in which the hexatertiary phosphine unambiguously acted as a hexadentate (hexaligate monometallic) ligand as in structure II. This contrasts with the behavior of ethylenediaminetetraacetic acid (EDTA) which forms hexadentate complexes very easily.[4] Most often the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) acted as a tetradentate ligand in products obtained by reactions with metal halide derivatives where the chances for observing hexaligate monometallic $P_2(\text{-Pf})_4$ might have been the greatest. Apparently it is difficult to bend the five CH_2CH_2 bridges in $P_2(\text{-Pf})_4$ around so that all six phosphorus atoms in $P_2(\text{-Pf})_4$ (I) can bond to a single metal atom as in structure II. On the other hand, there is no particular difficulty in bonding all six phosphorus atoms in $P_2(\text{-Pf})_4$ (I) to a pair of metal atoms as in the hexaligate bimetallic complexes $P_2(\text{-Pf})_4[M(CO)_3]_2$ (M = Cr, Mo, and W) and $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$.

A hexatertiary phosphine such as $P_2(\text{-Pf})_4$ (I) can coordinate to one or more metal atoms in $(1/2)(6)(6 + 1) = 21$ different ways if differences arising from the nonequivalence of phosphorus atoms in the hexatertiary phosphine are ignored.[20] Of these 21 possible ways of coordinating the phosphorus atoms in $P_2(\text{-Pf})_4$ (I) to metal atoms, the following have been identified in the indicated complexes described in this paper: (1) biligate monometallic: $P_2(\text{-Pf})_4M(CO)_4$ (M = Mo and probably Cr) and $CH_3COMn(CO)_3P_2(\text{-Pf})_4$; (2) triligate monometallic: $P_2(\text{-Pf})_4Mn(CO)_2CH_3$; (3) tetraligate monometallic: the cations $P_2(\text{-Pf})_4M^{2+}$ (M = Ni, Pd, and Pt) and $P_2(\text{-Pf})_4MCl_2^+$ (M = Co, Rh, Ru, and Re); (4) triligate bimetallic: $P_2(\text{-Pf})_4Mn_2(CO)_3(C_5H_5)_2$ and $[(C_5H_5)_2Mn_2(CO)(NO)_2P_2(\text{-Pf})_4][PF_6]_2$; (5) hexaligate bimetallic: $P_2(\text{-Pf})_4[M(CO)_3]_2$ (M = Cr, Mo, and W) and $P_2(\text{-Pf})_4[Mn(CO)_2CH_3]_2$; (6) hexaligate hexametallic: $P_2(\text{-Pf})_4[Mo(CO)_2(COCH_3)(C_5H_5)]_6$. Unfortunately, the relatively low solubilities of most of the metal complexes of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) complicate their purification by recrystallization and prevent the use of chromatography to separate two different complexes or a complex produced from unreacted $P_2(\text{-Pf})_4$ (I). This limits the number of $P_2(\text{-Pf})_4$ complexes that could be isolated in a state sufficiently pure for characterization. The low solubility of $P_2(\text{-Pf})_4$ (I) complexes also limits the application of physical techniques such as nmr that require relatively concentrated solutions. Finally some difficulty was experienced in obtaining reliable combustion analyses for carbon on certain metal complexes of the hexatertiary phosphine $P_2(\text{-Pf})_4$ (I). All of these difficulties associated with the study of metal complexes of the phenylated hexatertiary phosphine $P_2(\text{-Pf})_4$ (I) are largely a consequence of the presence of eight phenyl rings in $P_2(\text{-Pf})_4$. These considerations suggest the use of completely aliphatic hexatertiary phosphines for further studies on the complexing properties of this type of polytertiary phosphine ligand. Such completely aliphatic hexatertiary phosphines are not presently known but presumably should be preparable by the base-catalyzed addition[3] of the four phosphorus–hydrogen bonds in $H_2PCH_2CH_2PH_2$ across the carbon–carbon double bonds in 4 equiv of an appropriate aliphatic dialkylvinylphosphine.

Acknowledgment.—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68.

---

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

(17) R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

(18) R. B. King and A. Efraty, *Inorg. Chem.*, **8**, 2374 (1969).

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

(20) R. B. King, *J. Coord. Chem.*, in press.