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Polytertiary Phosphines and Arsines.
19. Some First-row Transition Metal Chloride Complexes of Ditertiary and Tritertiary Phosphines Containing Terminal Methoxy Groups

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The triphosphines $RP[CH_2CH_2P(OCH_3)_2]_2$ (R = CH_3 and C_6H_5) react with the metal(II) chlorides of iron, cobalt, and nickel in methanol solution to form the corresponding $[(triphos)MCl]^+$ cations isolated as the chloride and hexafluorophosphate salts. Magnetic susceptibility data indicate that the yellow diamagnetic nickel complexes are square planar but the blue to green cobalt and brown iron complexes are tetrahedral. Nickel(II) chloride reacts with the diphosphine $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ to give a diamagnetic apparently square planar nickel(II) complex of the stoichiometry $(diphos)_2NiCl_2$ in which each diphosphine unit functions as a monodentate ligand. However, cobalt(II) and iron(II) chlorides react with $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ to give products of stoichiometry $(diphos)MCl_2$ formulated as the dimeric ionic derivatives $[(diphos)_2M_2Cl_2]Cl_2$ on the basis of magnetic measurements, conductivities, and metathesis with NH_4PF_6

Introduction

During the past fifteen years the transition metal coordination chemistry of chelating polytertiary phosphines containing terminal alkyl and aryl groups has received extensive attention [1–3] including papers from this laboratory on metal complexes of chelating polytertiary phosphines containing terminal phenyl [4–6], methyl [7], and neopentyl [8] groups. However, analogous coordination chemistry of chelating polyphosphines containing terminal alkoxy groups has received very little attention even though such polyphosphines would be of interest by exhibiting significantly stronger π-acceptor properties [9] than the polyphosphines with extensive known coordination chemistry. In this connection we investigated several years ago the coordination chemistry of the chelating ditertiary phosphine $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ [10]. We found that this ditertiary phosphine gives a variety of metal carbonyl derivatives but does not form tractable metal chloride complexes with iron, cobalt, and nickel apparently owing to insufficient basicity of the phosphorus atoms.

These previous results make of interest the transition metal coordination chemistry of potentially chelating polyphosphines in which some phosphorus atoms carry terminal alkoxy substituents and the remaining phosphorus atoms carry terminal alkyl or aryl substituents. Several years ago we reported a general method for synthesizing such polyphosphines [11]. This paper presents a survey of the reactions of nickel, cobalt, and iron chlorides with the chelating triphosphines $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$ (abbreviated as Pom-Pf-Pom) and $CH_3P[CH_2CH_2P(OCH_3)_3]_2$ (abbreviated as Pom-Pm-Pom) and the chelating diphosphines $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ (abbreviated as Pom-Pf) and $(CH_3)_2PCH_2CH_2P(OCH_3)_2$ (abbreviated as Pom-Pm).

Experimental

Microanalyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Atlanta, Georgia. Melting and decomposition points (Table I) were taken in capillaries and are uncorrected. Magnetic susceptibilities (Table I) were determined by the Evans method [12] in dichloromethane or methanol solutions using a Varian T-60 spectrometer at 60 MHz for measurement of the frequency shifts. Molar conductance measurements (Table I) were performed in 0.004 *M* and 0.002 *M* nitromethane solutions using a Yellow Springs Instrument Co. model 31 conductivity bridge with platinum electrodes. Electronic spectra in the ultraviolet, visible, and near infrared regions were taken in methanol solutions and recorded on a Cary model 14 spectrometer. Only the near infrared region exhibits maxima and even these maxima (Table I) are poorly defined broad peaks with low extinction coefficients.

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TABLE I. Properties of the Transition Metal Complexes of Polytertiary Phosphines Containing Terminal Methoxy Groups.

Compound[a]	Color	M.p., °C		Analyses, %			μ_{eff} (B.M.)	Molar Conductance[b]	Electronic Spectra cm^{-1} (ϵ)[c]
				C	H	Cl			
A) Nickel Derivatives									
(Pom-Pf-Pom)$NiCl_2$	yellow	95	Calcd.	35.0	5.2	14.8	0	52	6900(5.5), 6370(4.9), 5970(7.2)
			Found	35.2	5.1	14.4			
[(Pom-Pf-Pom)NiCl] [PF_6]	yellow	218	Calcd.	28.5	4.2	6.0	0	67	6850(4.3), 6250(4.4), 5880(5.4)
			Found	28.6	4.4	6.4			
(Pom-Pm-Pom)$NiCl_2$	yellow	112 (dec.)	Calcd.	25.9	5.5	17.0	0	59	6890(2.5), 6250(2.2), 5990(3.2)
			Found	25.4	5.5	16.6			
[(Pom-Pm-Pom)NiCl] [PF_6]	yellow	185	Calcd.	20.5	4.4	6.7	0	72	6940(2.3), 6290(2.1), 6020(2.1)
			Found	20.6	4.8	7.1			
$(Pom\text{-}Pf)_2$ $NiCl_2$	red	68	Calcd.	51.8	5.4	9.6	0	55	5980(4.0)
			Found	52.3	5.9	9.2			
[$(Pom\text{-}Pf)_2$NiCl] [PF_6]	orange	210	Calcd.	45.1	4.7	4.2	0	87	5980(2.0)
			Found	45.1	4.7	4.3			
B) Cobalt Derivatives									
(Pom-Pf-Pom)$CoCl_2$	green	135	Calcd.	35.0	5.2	14.8	4.8	74	6920(41), 6370(40), 5960(44)
			Found	34.9	5.1	14.6			
[(Pom-Pf-Pom)CoCl] [PF_6]	green	230	Calcd.	28.5	4.2	6.0	4.7	83	6800(42), 6180(42), 5960(43)
			Found	28.8	4.3	6.4			
(Pom-Pm-Pom)$CoCl_2$	blue	110 (dec.)	Calcd.	25.8	5.5	17.0	4.8	58	6860(35), 5990(40), 5770(44)
			Found	25.7	5.8	16.6			
[(Pom-Pm-Pom)CoCl] [PF_6]	blue	190	Calcd.	20.5	4.4	6.7	4.6	77	6730(30), 5740(42), 5620(40)
			Found	20.7	4.4	7.1			
(Pom-Pf)$CoCl_2$	blue-green	70	Calcd.	44.0	4.6	16.0	4.5	58	6070(40), 5940(40)
			Found	44.1	4.6	16.1			
[(Pom-Pf)CoCl] [PF_6]	blue	115	Calcd.	35.2	3.7	6.9	4.4	75	5920(36), 5750(34)
			Found	35.4	3.8	6.8			
C) Iron Derivatives									
(Pom-Pf-Pom)$FeCl_2$	brown	115	Calcd.	35.2	5.2	14.9	5.2	56	6330(29), 6070(40)
			Found	35.7	5.5	14.4			
[(Pom-Pf-Pom)FeCl] [PF_6]	brown	220	Calcd.	28.6	4.3	6.0	5.1	74	6150(42), 5870(45)
			Found	29.1	4.4	6.4			
(Pom-Pm-Pom)$FeCl_2$	brown	110 (dec.)	Calcd.	26.0	5.5	17.1	5.1	65	6370(20), 5900(20)
			Found	26.1	5.5	16.9			
[(Pom-Pm-Pom)FeCl] [PF_6]	brown	182	Calcd.	20.6	4.4	6.8	4.9	84	6150(25), 5730(30)
			Found	20.5	4.6	7.1			
(Pom-Pf)$FeCl_2$	orange-red	195	Calcd.	44.4	4.6	16.4	5.2	62	6340(37), 6130(29), 5960(31)
			Found	44.1	4.6	16.0			

[(Pom-Pf)FeCl] [PF_6]	red	235	Calcd.	35.4	3.7	6.5	5.1	79	6100(43), 5810(37)
			Found	35.7	3.8	6.3			
(Pom-Pm)$FeCl_2$	brown	107	Calcd.	23.3	5.2	23.0	5.1	69	6075(37), 5950(40), 5830(38)
			Found	23.8	5.3	23.2			

[a] See the text for the ligand abbreviations. [b] These molar conductance data were obtained in 0.002 to 0.004 nitromethane solutions and are reported in ohm^{-1} cm^2 mol^{-1}. [c] These electronic spectra were obtained in methanol solutions. Extinction coefficients are given in parentheses.

TABLE II. Some Reactions of First-row Transition Metal Chlorides with Polytertiary Phosphines Containing Terminal Methoxy Groups.[a]

Metal Chloride (g, mmol)	Ligand[b] (g, mmol)	Product	Yield
A) Nickel Derviatives			
$NiCl_2 \cdot 6H_2O$ (0.68, 2.9)	Pom-Pf-Pom (1.0, 2.9)	(Pom-Pf-Pom)$NiCl_2$	96%
$NiCl_2 \cdot 6H_2O$ (0.83, 3.5)	Pom-Pm-Pom (1.0, 3.5)	(Pom-Pm-Pom)$NiCl_2$	95%
$NiCl_2 \cdot 6H_2O$ (0.78, 3.3)	Pom-Pf (1.0, 3.3)	$(Pom\text{-}Pf)_2NiCl_2$	95%
B) Cobalt Derivatives			
$CoCl_2$ (0.37, 2.9)	Pom-Pf-Pom (1.0, 2.9)	(Pom-Pf-Pom)$CoCl_2$	95%
$CoCl_2$ (0.45, 3.5)	Pom-Pm-Pom (1.0, 3.5)	(Pom-Pm-Pom)$CoCl_2$	96%
$CoCl_2$ (0.42, 3.3)	Pom-Pf (1.0, 3.3)	(Pom-Pf)$CoCl_2$	96%
C) Iron Derivatives			
$FeCl_2 \cdot 4H_2O$ (0.57, 2.9)	Pom-Pf-Pom (1.0, 2.9)	(Pom-Pf-Pom)$FeCl_2$	94%
$FeCl_2 \cdot 4H_2O$ (0.69, 3.5)	Pom-Pm-Pom (1.0, 3.5)	(Pom-Pm-Pom)$FeCl_2$	95%
$FeCl_2 \cdot 4H_2O$ (0.65, 3.3)	Pom-Pf (1.0, 3.3)	(Pom-Pf)$FeCl_2$	96%
$FeCl_2 \cdot 4H_2O$ (1.09, 5.5)	Pom-Pf (1.0, 5.5)	(Pom-Pm)$FeCl_2$	94%

[a] All reactions proceeded instantly in methanol solution as indicated by immediate color changes upon mixing the reactants.
[b] See the text for an explanation of the ligand abbreviations.

Reactions of the Metal Chlorides with the Polyphosphine Ligands

The quantities of metal chloride and polyphosphine ligand indicated in Table II were brought together in anhydrous methanol solution (100 ml) at ambient temperature. An immediate color change indicated a rapid reaction. The cobalt and iron complexes of $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ precipitated spontaneously from the reaction mixture and were purified by crystallization from chloroform. The remaining metal complexes were isolated by evaporation of the methanol solvent followed by addition of diethyl ether in the case of the $CH_3P[CH_2CH_2P(OCH_3)_2]_2$ complexes to facilitate precipitation of the product.

Conversion of the Chloride Complexes to the Corresponding Hexafluorophosphate Salts

Iron Complexes

The hexafluorophosphate salts are relatively sparingly soluble in methanol and thus were precipitated upon treating a saturated methanol solution of the corresponding chloride complex with excess of a concentrated acetone solution of NH_4PF_6.

(Pom-Pf)₂NiCl₂

This chloride complex is not very soluble in methanol but soluble in acetone. The corresponding hexafluorophosphate complex [(Pom-Pf)$_2$NiCl][PF_6] was obtained by mixing stoichiometric amounts of (Pom-Pf)$_2$NiCl$_2$ and NH_4PF_6 in concentrated acetone solutions, filtering off the precipitated NH_4Cl, and then slowly evaporating the filtrate.

Other Cobalt and Nickel Complexes

A saturated methanol solution of the chloride complex was treated with a stoichiometric amount of an acetone solution of NH_4PF_6. Evaporation of solvents to incipient crystallization followed by storage at −10 °C led to precipitation of the hexafluorophosphate salt in crystalline form.

Results and Discussion

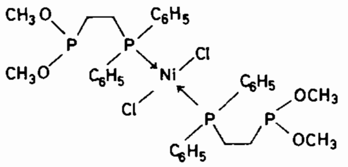
Triphosphine Complexes

The triphosphines $RP[CH_2CH_2P(OCH_3)_2]_2$ (R = CH_3 and C_6H_5) readily form complexes of the stoichiometries (triphos)MCl$_2$ (M = Fe, Co, and Ni) upon reactions with the corresponding metal chlorides in methanol solution. Formulation of these complexes as the ionic tetracoordinate derivatives [(triphos)MCl]Cl is indicated by their conductivities in nitromethane solution and conversion to the corresponding hexafluorophosphate salts [(triphos)MCl][PF_6] by metathesis with ammonium hexafluorophosphate. The hexafluorophosphate salts exhibit similar conductivities, near infrared spectra, colors, and magnetic moments as the corresponding chloride salts suggesting no major change in the metal coordination spheres.

The nickel complexes (triphos)NiCl$_2$ and [(triphos)NiCl][PF_6] are yellow diamagnetic solids indicative of square planar coordination similar to previously reported [(triphos)NiCl]$^+$ derivatives [4, 7]. The blue to green cobalt and brown iron complexes (triphos)MCl$_2$ and [(triphos)MCl][PF_6] exhibit magnetic moments indicative of tetrahedral metal coordination similar to that found for known [2, 3] phosphine metal halide complexes of these metals in the +2 oxidation state.

Diphosphine Complexes

The diphosphines $R_2PCH_2CH_2P(OCH_3)_2$ (R = CH_3 and C_6H_5) form a much more limited range of isolable nickel, cobalt, and iron chloride complexes than the triphosphines. Nickel(II) chloride was found to react with $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ to form a red diamagnetic complex with a 2:1 ligand–metal stoichiometry (Pom-Pf)$_2$NiCl$_2$. This complex is tentatively formulated as the square planar complex I in which the nickel is only bonded to the more basic $(C_6H_5)_2$P-phosphorus atoms. Metathesis of (Pom-Pm)$_2$NiCl$_2$ with ammonium hexafluorophosphate gives orange diamagnetic [(Pom-Pm)$_2$NiCl][PF_6] tentatively formulated as II in which the less basic $(CH_3O)_2$P-phosphorus arm of one of the diphosphines has displaced one of the chloride ligands.



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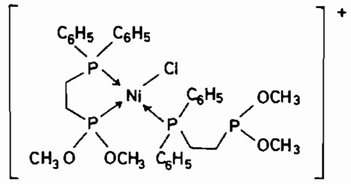
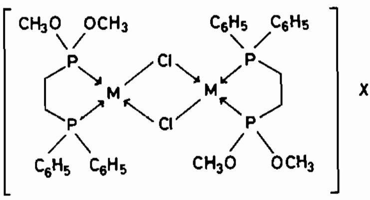


II

Cobalt(II) and iron(II) chlorides react with $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ to form products of stoichiometry (Pom-Pf)MCl$_2$. Formulation of these complexes as the dimeric ionic derivatives [(Pf-Pom)$_2$M$_2$Cl$_2$]Cl$_2$ (III: X = Cl) rather than the simple non-ionic monomeric derivatives (Pf-Pom)MCl$_2$ is suggested for the following reasons:

(1) The molar conductance in nitromethane is consistent with a 1:1 electrolyte based on a monomeric formulation (Pom-Pf)MCl$_2$ or a 1:2 electrolyte based on a dimeric formulation (Pom-Pf)$_2$M$_2$Cl$_4$; (2)

Metathesis with ammonium hexafluorophosphate gives products of stoichiometry (Pom-Pf)$MClPF_6$ which must be formulated as the dimers [(Pom-Pf)$_2$-M_2Cl_2][PF_6]$_2$ (III: X = PF_6) to avoid the unlikely possibilities of three-coordinate metal (see item 3 below) or coordinated hexafluorophosphate; (3) The magnetic moments and colors (except for minor variations in hue) of the (Pom-Pf)MCl_2 are very similar to those of the triphosphine complexes [(triphos)MCl]X (triphos = $RP[CH_2CH_2P(OCH_3)_2]_2$; R = CH_3 or C_6H_5; M = Co or Fe; X = Cl or PF_6) suggesting analogous tetrahedral metal coordination; (4) The compounds (Pom-Pf)MCl_2 (Co and Fe) are less soluble in methanol than the [(triphos)MCl]Cl derivatives suggesting a higher molecular complexity.



III

The ligand $(CH_3)_2PCH_2CH_2P(OCH_3)_2$ reacts with all three metal chlorides in methanol solution. However, only in the case of iron could a tractable product be isolated. The brown iron complex (Pom-Pm)$FeCl_2$ exhibits a magnetic moment suggestive of tetrahedral iron(II) and conductance corresponding to a 1:1 electrolyte for a monomeric formulation. A formulation analogous to III is tentatively suggested, but attempted metathesis with NH_4PF_6 failed to give a crystalline hexafluorophosphate salt. Also the reaction of neither diphosphine $R_2PCH_2CH_2P(OCH_3)_2$ (R = CH_3 or C_6H_5) with iron(II) chloride gave any evidence for the formation of an octahedral iron(II)(diphos)$_2FeCl_2$ derivative, which would have the favored rare gas electronic configuration.

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References

1 For Part 18 of this series, see G. M. Brown, J. E. Finholt, R. B. King and J. W. Bibber, *Inorg. Chem.*, in press.
2 C. A. McAuliffe, ed., 'Transition Metal Complexes Containing Phosphorus, Arsenic, and Antimony Ligands', Macmillan Press, London, 1973.
3 C. A. McAuliffe and W. Levason, 'Phosphine, Arsine, and Stibine Complexes of the Transition Elements', Elsevier, Amsterdam, 1979.
4 R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem., 10,* 1841 (1971).
5 R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem., 10,* 1851 (1971).
6 R. B. King and M. S. Saran, *Inorg. Chem., 10,* 1861 (1971).
7 R. B. King, J. A. Zinich and J. C. Cloyd, Jr., *Inorg. Chem., 14,* 1554 (1975).
8 R. B. King, J. C. Cloyd, Jr., and R. H. Reimann, *Inorg. Chem., 15,* 449 (1976).
9 G. R. Dobson, I. W. Stolz and R. K. Sheline, *Adv. Inorg. Chem. Radiochem., 8,* 1 (1966).
10 R. B. King and W. M. Rhee, *Inorg. Chem., 17,* 2961 (1978).
11 R. B. King and W. F. Masler, *J. Am. Chem. Soc., 99,* 4001 (1977).
12 D. F. Evans, *J. Chem. Soc.*, 2003 (1959).