

phosphorus atoms trans to other phosphorus atoms (i.e., the end phosphorus atoms of the tri(tertiary phosphine) ligands) occur in the range 2337–2483 Hz which is within the range found¹¹ for similar phosphorus atoms trans to other phosphorus atoms in monodentate phosphine-square-planar platinum(II) complexes of the types *trans*-L₂PtCl₂ and [L₃PtCl]⁺. However, the $|^1J(\text{Pt-P})|$ values for the phosphorus atoms trans to chlorine (i.e., the center phosphorus atoms of the tri(tertiary phosphine) ligands) occur in the range 3024–3242 Hz, which is appreciably below the 3490–3675-Hz range found¹¹ for similar phosphorus atoms trans to chlorine in monodentate phosphine square-planar platinum(II) complexes of the types *cis*-L₂PtCl₂ and [L₃PtCl]⁺. We suspect that the strain of the two fused five-membered chelate rings weakens the bond from the platinum to the phosphorus common to these chelate rings with resultant lowering of the corresponding $|^1J(\text{Pt-P})|$ coupling constant.

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Registry No. Pm-Pf, 42495-77-2; (Pm-Pf)Cr(CO)₄, 54823-50-6; (Pm-Pf)Mo(CO)₄, 54823-51-7; (Pm-Pf)W(CO)₄, 54823-52-8; (Pm-Pf)NiCl₂, 54823-53-9; (Pm-Pf)PdCl₂, 54823-54-0; (Pm-Pf)PtCl₂, 54823-55-1; [CpFeCO]₂(Pm-Pf), 54823-48-2; Pm-Pm-Pm, 42495-85-2; (Pm-Pm-Pm)Cr(CO)₃, 54823-60-8; (Pm-Pm-Pm)₂[Cr(CO)₄]₃ (IIIa), 54823-49-3; [(Pm-Pm-Pm)NiCl][PF₆], 54823-57-3; [(Pm-Pm-Pm)PdCl]Cl, 54823-58-4; [(Pm-Pm-Pm)-PtCl]Cl, 54823-59-5; Pm-Pf-Pm, 42495-81-8; (Pm-Pf-Pm)Cr(CO)₃,

54823-28-8; (Pm-Pf-Pm)Mo(CO)₃, 54823-29-9; [(Pm-Pf-Pm)-NiCl]Cl, 54823-30-2; [(Pm-Pf-Pm)NiCl][PF₆], 54823-32-4; [(Pm-Pf-Pm)PdCl]Cl, 54823-33-5; [(Pm-Pf-Pm)PtCl]Cl, 54823-34-6; [CpFe(Pm-Pf-Pm)]I, 54823-35-7; (Pm-Pf-Pm)Mn(CO)₂Br, 54823-36-8; Pm-Pm-Pf, 36892-73-6; (Pm-Pm-Pf)NiCl₂, 54823-24-4; Pm-Pf-Pf, 23582-02-7; (Pm-Pf-Pf)Cr(CO)₃, 33847-58-4; (Pm-Pf-Pf)-Mo(CO)₃, 33847-60-8; (Pm-Pf-Pf)W(CO)₃, 33847-61-9; (Pm-Pf-Pf)W(CO)₄, 54823-23-3; [(Pm-Pf-Pf)NiCl][PF₆], 33847-47-1; [(Pm-Pf-Pf)PdCl][PF₆], 33847-48-2; [(Pm-Pf-Pf)PtCl][PF₆], 33847-50-6; CpFe(CO)(Pm-Pf-Pf)C(O)Me (IIa), 54823-37-9; CpFe(CO)(Pm-Pf-Pf)C(O)Me (IIb), 34675-94-0; Pm-Pf-Pf, 54823-20-0; (Pm-Pf-Pf)Cr(CO)₃, 54823-38-0; (Pm-Pf-Pf)Mo(CO)₃, 54823-39-1; [(Pm-Pf-Pf)NiCl][PF₆], 54823-41-5; [(Pm-Pf-Pf)-PdCl]Cl, 54823-42-6; [(Pm-Pf-Pf)PtCl]Cl, 54823-43-7; [CpFe(Pm-Pf-Pf)]I, 54823-44-8; P-(Pm)₃, 42495-87-4; [P-(Pm)₃NiCl][PF₆], 54823-46-0; P-(Pm)₃, 23582-03-8; [P-(Pm)₃NiCl][PF₆], 33881-21-9; P-(Pm)₃Cr(CO)₃, 34652-28-3; P-(Pm)₃Cr(CO)₄, 33864-98-1; MeC(O)Mn(CO)₃P-(Pm)₃, 33849-32-0; [CpMn(NO)P-(Pm)₃][PF₆], 34676-46-5; CpFe(CO)P-(Pm)₃I, 54823-47-1; (Pm-Pm-Pm)₂[Cr(CO)₄]₃ (IIIb), 54868-46-1; ³¹P, 7723-14-0.

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Poly(tertiary phosphines and arsines). XII. Some Metal Complexes of Methylated Di- and Tri(tertiary phosphines)^{1,2}

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Metal complexes of the di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂ of the types (diphos)MCl₂ (M = Ni, Co, Pd, and Pt), (diphos)M(CO)₄ (M = Cr, Mo, and W), [(diphos)₂RhCl₂]⁺, and (diphos)Fe₂(CO)₂(C₅H₅)₂ have been prepared by standard methods. Metal complexes of the tri(tertiary phosphines) R'³P(CH₂CH₂PR₂)₂ (R' = C₆H₅, R = CH₃; R' = CH₃, R = CH₃ and C₆H₅) and (CH₃)₂PCH₂CH₂P(C₆H₅)CH₂CH₂P(C₆H₅)₂ of the types [(triphos)MCl]⁺ (M = Ni, Pd, and Pt), (triphos)M(CO)₃ (M = Cr, Mo, and W), (triphos)Mn(CO)₂Br, (triphos)Mn(CO)₂C(O)CH₃, and [C₅H₅Fe(triphos)]⁺ have been prepared by standard methods. In general, tractable metal complexes of methylated tri(tertiary phosphines) with uncomplexed -CH₂CH₂P(CH₃)₂ groups could not be prepared. The proton NMR spectra of the dimethylphosphino groups in metal complexes of methylated poly(tertiary phosphines) indicate that a single nonplanar five-membered chelate ring, such as that found in metal complexes of the di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂, can undergo rapid inversion on the NMR time scale whereas two fused nonplanar five-membered chelate rings, such as those found in triligate monometallic complexes of tri(tertiary phosphines), remain rigid even on the NMR time scale.

Introduction

The discovery of the base-catalyzed addition of phosphorus-hydrogen bonds to vinylphosphorus compounds⁵ has made available numerous poly(tertiary phosphines) with PCH₂CH₂P structural units. Previous papers of this series^{6–8} have surveyed metal complexes of phenylated tri-, tripod tetra-, linear tetra-, and hexa(tertiary phosphines). This paper describes some metal complexes of the partially methylated di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂ and the tri(tertiary

phosphines) (CH₃)₂PCH₂CH₂P(C₆H₅)CH₂CH₂PR₂ (R = CH₃ and C₆H₅) as well as the completely methylated tri(tertiary phosphine) CH₃P[CH₂CH₂P(CH₃)₂]₂. These ligands with -CH₂CH₂P(CH₃)₂ units were of interest in order to determine the effect on metal complex formation of a more basic and less bulky dimethylphosphino group relative to the diphenylphosphino group. An example of a previously reported⁹ drastic effect when dimethylphosphino groups are substituted for diphenylphosphino groups in a di(tertiary

Table I. Preparations of Metal Complexes of the Di(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$

Metal derivative (g, mmol)	Amt of ligand, g (mmol)	Solvent (ml)	Temp, °C	Time, hr	Product	Yield, g (mmol)
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.28, 1.1)	0.31 (1.1)	EtOH (25)	25	2	(Pm-Pf)NiCl ₂	0.30 (0.71) ^a
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24, 1.0)	0.31 (1.1)	EtOH (25)	25	0.5	(Pm-Pf)CoCl ₂	0.29 (0.71) ^b
Na_2PdCl_4 ^c (0.33, 1.1)	0.30 (1.1)	H ₂ O (25), EtOH (50)	25	20	(Pm-Pf)PdCl ₂	0.15 (0.34) ^d
K_2PtCl_4 (0.48, 1.1)	0.31 (1.1)	EtOH (50)	25	16	(Pm-Pf)PtCl ₂	0.32 (0.58) ^e
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.30, 1.1)	0.61 (2.2)	EtOH (50)	25	8	[(Pm-Pf) ₂ RhCl ₂]Cl ₂ ·2H ₂ O	0.34 (0.43) ^f
$\text{C}_7\text{H}_5\text{Cr}(\text{CO})_4$ (0.33, 1.3)	0.36 (1.3)	Hexane (50)	69	8	(Pm-Pf)Cr(CO) ₄	0.17 (0.39) ^g
$\text{Mo}(\text{CO})_6$ (0.31, 1.2)	0.32 (1.2)	Xylene (50)	140	0.75	(Pm-Pf)Mo(CO) ₄	0.31 (0.67) ^g
$\text{W}(\text{CO})_6$ (0.40, 1.1)	0.31 (1.1)	Xylene (50)	140	70	(Pm-Pf)W(CO) ₄	0.25 (0.42) ^h
$[\text{CpFe}(\text{CO})_2]_2$ (0.40, 1.1)	0.30 (1.1)	C_6H_6 (50)	80	7	(Pm-Pf)Fe ₂ (CO) ₂ Cp ₂	0.26 (0.45) ⁱ

^a The crude product was crystallized from a mixture of dichloromethane and 1-butanol. ^b 1-Butanol was added to the reaction mixture and solvent slowly evaporated until the product crystallized. After filtration the product was washed with cold butanol. ^c The Na_2PdCl_4 was obtained by heating stoichiometric quantities of PdCl_2 and NaCl in the water until the PdCl_2 dissolved. ^d The crude product was crystallized from heptane. ^e The crude product was washed with acetone and dried. ^f The crude product was crystallized from a mixture of acetone and hexane. ^g The crude product was crystallized from a mixture of dichloromethane and hexane. ^h Operation in footnote g followed by operation in footnote f. ⁱ Crystallized twice from a mixture of dichloromethane and hexane.

phosphine) is the facile disproportionation of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ at room temperature to give $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2][\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]$ under conditions where $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ does not react with the phenylated analog $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$. Even under more forcing conditions the phenylated di(tertiary phosphine) reacts with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ to give not a disproportionation product but instead the substitution product $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$.

The methyl groups in the methylated poly(tertiary phosphines) also provide useful probes for elucidations of the structures and stereochemistries of metal complexes by proton NMR spectroscopy since each type of methyl group bonded to phosphorus gives in the proton NMR spectrum a sharp doublet (or triplet in cases of virtual coupling). Methyl proton NMR resonances have been used in this manner by Bosnich, Jackson, and Wild¹⁰ to study the stereochemistry of cobalt(III) complexes of the linear tetra(tertiary arsine) $(\text{CH}_3)_2\text{AsCH}_2\text{CH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)_2$.

Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling the methylated poly(tertiary phosphines) and solutions of organometallic compounds except in cases where the latter were known to be air stable, and (c) filling evacuated vessels containing organometallic compounds. All reactions described in this paper were carried out with magnetic stirring.

Materials. The ligands $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (abbreviation Pm-Pf), $\text{CH}_3\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_2$ (abbreviation Pm-Pm-Pm), and $\text{C}_6\text{H}_5\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_2$ (abbreviation Pm-Pf-Pm) were prepared as described elsewhere^{11,12} using base-catalyzed additions of appropriate phosphorus-hydrogen compounds to vinylphosphine sulfides followed by desulfurization with LiAlH_4 in boiling dioxane. The transition metal derivatives were purchased from the indicated commercial sources: $\text{M}(\text{CO})_6$ (M = Cr, Mo, and W), Pressure Chemical Co., Pittsburgh, Pa.; $\text{Fe}(\text{CO})_5$, GAF Corp., New York, N.Y.; $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, Ethyl Corp., New York, N.Y.; platinum metal derivatives, Englehard, Newark, N.J. The remaining transition metal organometallic compounds were prepared by standard published procedures.¹³

Preparation of the Ligand $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (Abbreviation Pm-Pf-Pf). A mixture of 5.46 g (27.6 mmol) of $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{H})\text{C}_6\text{H}_5$,¹⁴ 6.16 g (29 mmol) of diphenylvinylphosphine,¹⁵ and 150 ml of tetrahydrofuran (redistilled over sodium benzophenone ketyl) was treated with sufficient potassium *tert*-butoxide to give a persistent deep orange color (2 spatula tips—~0.2 g). The reaction mixture was boiled under reflux for 24 hr. Tetrahydrofuran was then removed at ~40° (40 mm) to leave a pasty brown residue. Attempts to obtain crystals from this residue by treatment with ethanol and cooling were unsuccessful. The residue was therefore treated with a deaerated mixture of 100 ml of toluene

and 100 ml of water. The toluene layer was separated and the aqueous layer washed with two 20-ml portions of deaerated toluene. After drying over anhydrous sodium sulfate, solvent was removed from the combined toluene solutions at 50° (0.1 mm) to give a very light brown viscous liquid (~10 g).

The proton noise-decoupled pulsed Fourier transform phosphorus-31 NMR spectrum of this crude liquid exhibited resonances only at +13.5 ppm (d, $J = 27$ Hz), +17.9 ppm (dd, $J_1 = 27$ Hz, $J_2 = 22$ Hz), and +49.0 ppm (d, $J = 22$ Hz) assigned to the $(\text{C}_6\text{H}_5)_2\text{P}$, $-\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2-$, and $\text{P}(\text{CH}_3)_2$ phosphorus atoms of the expected product $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$. Since the proton NMR spectrum was also consistent with this formulation, this crude product was used without further purification for the syntheses of metal complexes.

Preparation of Metal Complexes of the Methylated Poly(tertiary phosphines) (Tables I and II). The indicated quantities of transition metal derivative, methylated poly(tertiary phosphine), and solvent (Tables I and II) were stirred under the indicated conditions. Solvent was then removed at ~40 mm. The residue was crystallized from the indicated solvent(s) to give the pure products. Since the metal complexes of the methylated poly(tertiary phosphines) were relatively stable, their crystallizations could be carried out relatively slowly without decomposition in order to give well-formed crystals.

Deviations from this general procedure, including additions of ammonium hexafluorophosphate to obtain hexafluorophosphate salts or column chromatography in the cases of $(\text{Pm-Pf-Pm})\text{Mn}(\text{CO})_2\text{Br}$ and $[\text{C}_5\text{H}_5\text{Fe}(\text{Pm-Pf-Pm})]_2$, are indicated as footnotes in Table II.

Microanalyses on these new methylated poly(tertiary phosphine) complexes (Table III) were performed by Atlantic Microlab, Inc. (Atlanta, Ga.), Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.), and the microanalytical laboratory in the Chemistry Department of the University of Georgia. Melting and decomposition points (Table III) were determined in capillaries and are uncorrected. Conductance measurements of selected complexes (Table III) were determined in 0.001 M acetone (A) or nitromethane (N) solutions at room temperature using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co. Inc., Yellow Springs, Ohio.

Infrared Spectra (Table III). Infrared spectra of the metal carbonyl derivatives in the 2200–1500-cm⁻¹ region were obtained using hexane or dichloromethane solutions. Far-infrared spectra of selected metal chloride complexes in the 600–225-cm⁻¹ region were obtained using Nujol mulls pressed between polyethylene plates; for brevity only the bands assigned to $\nu(\text{M}-\text{Cl})$ frequencies are given in Table III. All infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics.

Proton NMR Spectra (Table IV). The proton NMR spectra were recorded at 100 MHz on a Varian HA-100 spectrometer in the indicated solvents.

Ultraviolet and Visible Spectra. The following spectra in the ultraviolet and visible regions were obtained on a Cary Model 15 spectrometer in ethanol solution: (A) $(\text{Pm-Pf})\text{NiCl}_2$, maxima at 445 nm (ϵ 630) and ~303 nm (ϵ 620); (B) $(\text{Pm-Pf})\text{CoCl}_2$, maxima at 656 nm (ϵ 60), 606 nm (ϵ 50), 574 nm (ϵ 30), 398 nm (ϵ 930), 361 nm (ϵ 1300), and 271 nm (ϵ 16,000); (C) $(\text{Pm-Pf})\text{PdCl}_2$, maxima at

Table II. Preparations of Metal Complexes of Various Methylated Tri(tertiary phosphines)

Metal derivative (g, mmol)	Ligand (g, mmol)	Solvent ^a (ml)	Temp, °C	Time, ^a hr	Product	Yield, g (mmol)
NiCl ₂ ·6H ₂ O (0.50, 2.1)	Pm-Pm-Pm (0.47, 2.1)	EtOH (50)	79	0.2	[(Pm-Pm-Pm)NiCl]Cl	0.24 (0.68) ^b
NiCl ₂ ·6H ₂ O (0.36, 1.5) + NH ₄ PF ₆ (0.25, 1.5)	Pm-Pm-Pm (0.34, 1.5)	EtOH (100)	79	1	[(Pm-Pm-Pm)NiCl] [PF ₆]	0.54 (1.17) ^c
Na ₂ PdCl ₄ (0.69, 2.4) ^{d,e}	Pm-Pm-Pm (0.53, 2.4)	EtOH (105), H ₂ O (30)	25	~1	[(Pm-Pm-Pm)PdCl]Cl	0.90 (2.24) ^f
K ₂ PtCl ₆ (0.90, 2.2)	Pm-Pm-Pm (0.48, 2.2)	EtOH (50), H ₂ O (50)	25	16	[(Pm-Pm-Pm)PtCl]Cl	0.85 (1.73) ^g
C ₇ H ₈ Cr(CO) ₃ (0.62, 2.7)	Pm-Pm-Pm (0.60, 2.7)	MCH (50)	101	10	(Pm-Pm-Pm)Cr(CO) ₃	0.65 (1.80) ^h
C ₇ H ₈ Cr(CO) ₃ (0.60, 2.3)	Pm-Pm-Pm (0.52, 2.3)	MCH (50)	101	22	(Pm-Pm-Pm) ₂ [Cr(CO) ₄] ₃	0.27 (0.29) ^h
NiCl ₂ ·6H ₂ O (0.26, 1.1)	Pm-Pf-Pm (0.31, 1.1)	EtOH (50)	25	1	[(Pm-Pf-Pm)NiCl] [PF ₆] ⁱ	0.39 (0.75) ^j
Na ₂ PdCl ₄ (0.42, 1.45) ^{d,e}	Pm-Pf-Pm (0.34, 1.2)	EtOH (50)	25	2	[(Pm-Pf-Pm)PdCl]Cl	0.38 (0.84) ^k
K ₂ PtCl ₆ (0.52, 1.2) ^e	Pm-Pf-Pm (0.36, 1.2)	H ₂ O-EtOH	~80	0.5	[(Pm-Pf-Pm)PtCl]Cl	0.25 (0.43) ^k
IrCl ₃ ·3H ₂ O (0.62, 0.87)	Pm-Pf-Pm (0.25, 0.87)	EtOH (50)	25	2	(Pm-Pf-Pm) ₂ (IrCl ₃) ₃	0.41 (0.19) ^l
Cr(CO) ₆ (0.26, 1.2)	Pm-Pf-Pm (0.33, 1.2)	Xyl (50)	140	72	(Pm-Pf-Pm)Cr(CO) ₃	0.38 (1.07) ^m
Mo(CO) ₆ (0.26, 1.0)	Pm-Pf-Pm (0.29, 1.0)	MeCN (75)	82	432	(Pm-Pf-Pm)Mo(CO) ₃	0.38 (0.68) ⁿ
(MeCN) ₃ W(CO) ₃ (0.31, 1.0)	Pm-Pf-Pm (0.29, 1.0)	THF (50)	67	5.5	(Pm-Pf-Pm)W(CO) ₃	0.31 (0.55) ^p
Mn(CO) ₅ Br (0.29, 1.0)	Pm-Pf-Pm (0.29, 1.0)	C ₆ H ₆ (50)	80	33	(Pm-Pf-Pm)Mn(CO) ₅ Br	0.14 (0.28) ^p
MeMn(CO) ₅ (0.21, 1.0)	Pm-Pf-Pm (0.29, 1.0)	Xyl (50)	140	30	(Pm-Pf-Pm)Mn(CO) ₅ C(O)Me	0.30 (0.68) ⁿ
CpFe(CO) ₂ (0.30, 1.0)	Pm-Pf-Pm (0.29, 1.0)	C ₆ H ₆ (150)	25	uv-1	[CpFe(Pm-Pf-Pm)] ^l	0.09 (0.17) ^q
NiCl ₂ ·6H ₂ O (0.26, 1.1) + NH ₄ PF ₆ (0.17, 1.1)	Pm-Pf-Pf (0.34, 1.1)	EtOH (75)	25	~1	[(Pm-Pf-Pf)NiCl] [PF ₆]	0.62 (0.96) ^c
Na ₂ PdCl ₄ (0.38, 1.3) ^e	Pm-Pf-Pf (0.53, 1.3)	FtOH (105), H ₂ O (30)	25	~1	[(Pm-Pf-Pf)PdCl]Cl	0.60 (1.02) ^r
K ₂ PtCl ₆ (0.41, 1.0) ^e	Pm-Pf-Pf (0.41, 1.0)	H ₂ O-EtOH	25	~1	[(Pm-Pf-Pf)PtCl]Cl	0.51 (0.75) ^r
C ₇ H ₈ Cr(CO) ₃ (0.25, 1.1)	Pm-Pf-Pf (0.45, 1.1)	MCH (50)	101	4	(Pm-Pf-Pf)Cr(CO) ₃	0.36 (0.66) ^h
C ₇ H ₈ Mo(CO) ₃ (0.36, 1.3)	Pm-Pf-Pf (0.54, 1.3)	MCH (50)	101	10	(Pm-Pf-Pf)Mo(CO) ₃	0.60 (1.02) ^{h,s}

^a EtOH = ethanol, MCH = methylcyclohexane, Xyl = xylene, MeCN = acetonitrile, THF = tetrahydrofuran, C₆H₆ = benzene, uv = ultraviolet irradiation for the indicated period. ^b Crystallized from a mixture of heptane and dichloromethane. This product was hygroscopic. ^c Crystallized from a mixture of ethanol and dichloromethane. ^d The Na₂PdCl₄ was obtained by heating stoichiometric quantities of PdCl₂ and NaCl in the water until the PdCl₂ dissolved. ^e A solution of the metal complex was added dropwise to a solution of the tri(tertiary phosphine). ^f Crystallized from ethanol. ^g Crystallized from a mixture of ethanol and NaCl in the water until the PdCl₂ dissolved. ^h The product precipitated during the course of the reaction and upon cooling the reaction mixture after the reaction was completed. It was filtered, washed with hexane, and dried. ⁱ A stoichiometric amount of aqueous NH₄PF₆ was added before isolation of the product. ^j Crystallized from a mixture of dichloromethane, ethanol, and butanol. ^k Crystallized from a mixture of dichloromethane and acetone. ^l This product precipitated from the reaction mixture. It was filtered, washed with boiling acetone, and dried. ^m Crystallized from a mixture of acetone and hexane. ⁿ Crystallized from a mixture of dichloromethane and hexane. ^o Crystallized from a mixture of acetone and cyclohexane. ^p Chromatographed on an alumina column with a mixture of dichloromethane and hexane. ^q Chromatographed on an alumina column in dichloromethane solution. Acetone needed to elute the yellow band of product. ^r Crystallized from a mixture of dichloromethane and ethyl acetate. ^s Not obtained analytically pure; the pale yellow solid was identified by its ³¹P NMR spectrum.

Table III. Properties of the New Metal Complexes of the Methylated Di- and Tri(tertiary phosphines)

Compd	Color	Mp, °C	Analyses, %						X or O	Molar conductance ^a	Ir spectrum, $\nu(\text{CO})$ or $\nu(\text{M}-\text{Cl})$
			C		H		N				
			Calcd	Found	Calcd	Found	Calcd	Found			
(Pm-Pf)NiCl ₂	Red	217-219	47.6	47.4	4.9	5.0	17.5 (Cl)	17.4 (Cl)	1.25 Λ	365 m, 325 s	
(Pm-Pf)CoCl ₂	Green	238-241	47.6	47.3	4.9	5.0	17.5 (Cl)	17.3 (Cl)	55.6 Λ	310 s	
(Pm-Pf)PdCl ₂	White	264-268 dec	42.6	42.7	4.4	4.5	15.7 (Cl)	15.8 (Cl)	7.4 Λ	368 m, 300 m	
(Pm-Pf)PtCl ₂	White	258 dec	36.4	36.4	4.3	4.3	12.2 (Cl)	12.5 (Cl)	345 m	345 m	
[(Pm-Pf) ₂ RhCl ₂]Cl·2H ₂ O	Yellow	289-291	48.5	48.3	5.5	5.6	13.4 (Cl)	13.4 (Cl)	75.5 N	365 s	
(Pm-Pf)Cr(CO) ₃	White	178-180 dec	54.9	54.8	4.6	4.7				2017 s, 1922 s, 1899 vs	
(Pm-Pf)Mo(CO) ₄	Cream	173-175 dec	49.8	50.0	4.1	4.3				2029 s, 1931 s, 1908 vs	

(Pm-Pf)W(CO) ₄	White	41.1	41.0	3.5	3.6	20.0 (Cl)	19.4 (Cl)	2024 s, 1923 s, 1902 vs 1711 s, 1669 s
(Pm-Pf)Fe ₂ (CO) ₂ Cp ₂	Green	58.6	58.5	5.2	5.3			
[(Pm-Pm-Pm)NiCl]Cl	Yellow-orange	30.5	29.7	6.5	6.4			
[(Pm-Pm-Pm)NiCl][PF ₆]	Orange	23.3	23.2	5.0	5.0	7.7 (Cl)	7.8 (Cl)	1918 s, 1824 vs
[(Pm-Pm-Pm)PdCl]Cl	White	26.9	26.7	5.7	5.8	17.7 (Cl)	17.6 (Cl)	2000 s, 1905 sh, 1880 vs, br
[(Pm-Pm-Pm)PtCl]Cl	White	22.0	21.9	4.7	4.7	14.5 (Cl)	14.6 (Cl)	343 m
(Pm-Pm-Pm)Cr(CO) ₃	Yellow	40.0	40.4	6.4	6.6	14.4 (Cr)	14.7 (Cr)	307 s
(Pm-Pm-Pm) ₂ [Cr(CO) ₃] ₃ ^b	Yellow	38.3	38.4	4.9	5.0	20.4 (O)	20.7 (O)	350 s
[(Pm-Pf-Pm)NiCl][PF ₆]	Yellow	31.9	31.9	4.8	4.8	6.7 (Cl)	6.9 (Cl)	305 s, br
[(Pm-Pf-Pm)PdCl]Cl	White	36.2	35.9	5.4	5.4	15.3 (Cl)	15.5 (Cl)	1940 s, 1860 s
[(Pm-Pf-Pm)PtCl]Cl	White	30.4	30.4	4.5	4.5	12.8 (Cl)	12.6 (Cl)	1926 s, 1831 s
(Pm-Pf-Pm) ₂ (trCl) ₃	Tan	22.9	23.0	3.4	3.5	20.8 (Cl)	20.7 (Cl)	1945 s, 1860 s
(Pm-Pf-Pm)Cr(CO) ₃	Yellow	21.2-21.4 dec	48.0	5.8	6.0			1933 s, 1852 s
(Pm-Pf-Pm)Mo(CO) ₃	Yellow	38.9	38.8	4.9	4.8			1938 s, 1870 s, 1561 m
(Pm-Pf-Pm)W(CO) ₃	Yellow	39.3	39.3	5.1	5.2			
(Pm-Pf-Pm)Mn(CO) ₂ Br	Yellow	40.3	40.2	5.3	5.2	16.7 (Br)	16.5 (Br)	
(Pm-Pf-Pm)Mn(CO) ₂ C(O)Me	Yellow	49.0	48.8	6.4	6.2	10.9 (O)	10.8 (O)	
[CpFe(Pm-Pf-Pm)]	Yellow	42.7	42.6	5.6	5.7	23.8 (I)	23.9 (I)	
[(Pm-Pf-Pf)NiCl][PF ₆]	Yellow-orange	44.4	44.2	4.5	4.6	5.5 (Cl)	5.6 (Cl)	
[(Pm-Pf-Pf)PdCl]Cl	White	49.0	48.9	5.0	5.0	12.1 (Cl)	12.2 (Cl)	
[(Pm-Pf-Pf)PtCl]Cl	White	42.6	42.6	4.3	4.3	10.5 (Cl)	10.5 (Cl)	
(Pm-Pf-Pf)Cr(CO) ₃	Yellow	59.3	60.7	5.3	5.9			1923 s, 1834 s, br

^a The molar conductance values are given in the usual units ohm⁻¹ cm²/mol; A = acetone, N = nitromethane. ^b Anal. Calcd: Cr, 16.6. Found: Cr, 16.6.

287 nm (ϵ 29,000), 260 nm (ϵ 19,000), and 244 nm (ϵ 17,000); (D) [(Pm-Pf-Pm)NiCl][PF₆], maxima at 381 nm (ϵ 2300) and 298 nm (ϵ 4500); (E) [(Pm-Pf-Pm)PdCl]Cl, maximum at 294 nm (ϵ 7800); (F) [(Pm-Pf-Pm)PtCl]Cl, maximum at 246 nm (ϵ 10,000).

Discussion

The new compounds obtained from the methylated poly(tertiary phosphines) and various transition metal derivatives (Table III), except as noted below, were completely analogous to previously reported metal complexes of di-¹⁶ and tri(tertiary phosphines).⁶ They were identified by correct elemental analyses. The expected geometries of the metal carbonyl derivatives were confirmed by their infrared spectra in the $\nu(\text{CO})$ region. The position of the $\nu(\text{CO})$ frequencies in (Pm-Pf)Fe₂(CO)₂(C₅H₅)₂ indicates the presence of bridging carbonyls but the absence of terminal carbonyls similar to the reported¹⁷ green products obtained from [C₅H₅Fe(CO)₂]₂ and other di(tertiary phosphines and arsines). Molar conductance measurements in appropriate solvents showed the compounds (Pm-Pf)MCl₂ (M = Ni and Pd) to be nonionic but (Pm-Pf-Pm)MCl₂ (M = Pd and Pt) to be the 1:1 electrolytes [(Pm-Pf-Pm)MCl]Cl.

Reactions of the phenylated tri(tertiary phosphine) C₆H₅P[CH₂CH₂P(C₆H₅)₂]₂ (abbreviated as Pf-Pf-Pf) with several transition metal derivatives⁶ gave products in which one or both of the terminal P(C₆H₅)₂ groups of the tri(tertiary phosphine) are not bonded to the transition metal. Examples of such compounds are the monoligate monometallic CH₃COFe(CO)(Pf-Pf-Pf)(C₅H₅), the biligate monometallic (Pf-Pf-Pf)M(CO)₄ (M = Cr and Mo), CH₃Mn(CO)₃(Pf-Pf-Pf), and [C₅H₅Mo(CO)₂(Pf-Pf-Pf)]⁺, and the biligate bimetallic (Pf-Pf-Pf)Fe₂(CO)₂(C₅H₅)₂. Attempts to make analogs of some of these compounds with uncomplexed phosphorus atoms using reactions of the methylated tri(tertiary phosphine) C₆H₅P[CH₂CH₂P(CH₃)₂]₂ with CH₃Fe(CO)₂-C₅H₅, [C₅H₅Fe(CO)₂]₂, C₇H₈Cr(CO)₄, and C₅H₅Mo(CO)₃Cl gave intractable products. The reaction of C₆H₅P[CH₂CH₂P(CH₃)₂]₂ with CH₃Mn(CO)₅ in boiling xylene gave a yellow product of stoichiometry CH₃Mn(CO)₃(Pm-Pf-Pm), but the infrared $\nu(\text{CO})$ frequencies of 1938, 1870, and 1561 cm⁻¹ clearly indicate this product to be the triligate monometallic acetyl derivative CH₃COMn(CO)₂(Pm-Pf-Pm) rather than the biligate monometallic methyl derivative CH₃Mn(CO)₃(Pm-Pf-Pm) analogous to the product obtained from the corresponding phenylated tri(tertiary phosphine).

In a further attempt to prepare a biligate monometallic derivative of a methylated tri(tertiary phosphine), the reaction of the norbornadiene complex C₇H₈Cr(CO)₄ with CH₃-P[CH₂CH₂P(CH₃)₂]₂ was investigated. The resulting yellow solid had the stoichiometry (Pm-Pm-Pm)₂[Cr(CO)₄]₃ indicating that all of the phosphorus atoms of the tri(tertiary phosphine) were bonded to chromium atoms through formation of a triligate bimetallic complex. The infrared spectrum of this complex in the $\nu(\text{CO})$ region was consistent with the *cis*-L₂Cr(CO)₄ configuration around all three of the chromium atoms.

All of these observations suggest extreme difficulty in preparing metal complexes of methylated poly(tertiary phosphines) with uncomplexed dimethylphosphino groups. This is consistent with the high basicity and low steric requirements of trivalent phosphorus atoms bearing mainly methyl groups which lead to a high reactivity of dimethylphosphino groups toward transition metal systems.

Since all of the methylated di- and tri(tertiary phosphines) have PCH₂CH₂P units, their chelate metal complexes contain five-membered rings consisting of the metal atom, two ligand phosphorus atoms, and the two sp³ carbon atoms of the CH₂CH₂ bridge between the phosphorus atoms. The sp³ hybridization of the ring carbon atoms forces the ring to be

Table IV. Proton NMR Spectra of Metal Complexes of Methylated Poly(tertiary phosphines)

Compd	Solvent	Proton NMR spectrum, ^a τ			
		C ₆ H ₅	CH ₂	(CH ₃) ₂ P	Other
(Pm-Pf)NiCl ₂	CDCl ₃	2.1 b, 2.6 m	7.65 b, 7.9 b	8.32 d (12)	
(Pm-Pf)PdCl ₂	CH ₂ Cl ₂	2.2 b, 2.5 m	~7.5 vb	8.16 d (13)	
(Pm-Pf)Cr(CO) ₄	CH ₂ Cl ₂	2.5 m, 2.65 m	7.4-8.5 m	8.49 d (8)	
(Pm-Pf)Mo(CO) ₄	CH ₂ Cl ₂	2.45 m, 2.65 m	7.4-8.9 m	8.48 d (7)	
(Pm-Pf)W(CO) ₄	CH ₂ Cl ₂	2.5 m, 2.65 m	7.4-8.7 m	8.37 d (8)	
(Pm-Pf)Fe ₂ (CO) ₂ Cp ₂	CH ₂ Cl ₂	2.34 b, 2.68 m	8.26 b	8.80 d (8)	C ₅ H ₅ : ^b 5.59 s, 5.90 s
[(Pm-Pm-Pm)NiCl][PF ₆]	(CD ₃) ₂ CO		7.4-8.6 m	8.35 t (4), 8.36 t (4)	CH ₃ P: 8.20 d (12)
[(Pm-Pm-Pm)PdCl]Cl	D ₂ O		6.9 br, 7.5 m	8.20 t (4), 8.23 t (4)	CH ₃ P: 8.04 d (12)
(Pm-Pm-Pm) ₂ [Cr(CO) ₄] ₃	CH ₂ Cl ₂		~7.9-8.6 b	8.51 d (8)	CH ₃ P: 8.28 d (17)
[(Pm-Pf-Pm)NiCl][PF ₆]	CH ₂ Cl ₂	2.1 b, 2.4 m	7.37 b	8.30 t (5), 8.45 t (4)	
[(Pm-Pf-Pm)PdCl]Cl	CH ₂ Cl ₂	2.15 b, 2.45 m	~6.9-7.4 b	7.99 t (4), 8.37 t (4)	
[(Pm-Pf-Pm)PtCl]Cl	CH ₂ Cl ₂	2.1 b, 2.45 m	~6.8-7.7 b	8.05 t* (4), 8.30 t* (4)	<i>J</i> (Pt-P-CH ₃) = 21, 24 Hz
(Pm-Pf-Pm)Cr(CO) ₃	CH ₂ Cl ₂	2.2 b, 2.6 m	~7.7-8.7 b	8.55 d (6), 8.66 d (6)	
(Pm-Pf-Pm)Mo(CO) ₃	CH ₂ Cl ₂	2.2 m, 2.6 m	~7.6-8.9 b	8.54 d (6), 8.65 d (6)	
(Pm-Pf-Pm)W(CO) ₃	CH ₂ Cl ₂	2.28 b, 2.62 b	~7.7-9.2 b	8.42 d (6), 8.59 d (6)	
(Pm-Pf-Pm)Mn(CO) ₂ Br	CDCl ₃	2.4 b, ~2.6 b	~7.3-8.7 b	8.22 m, 8.49 m	
(Pm-Pf-Pm)Mn(CO) ₂ C(O)Me	CH ₂ Cl ₂	2.3 b, 2.6 b	~8.1-8.9 b	~8.7 m	CH ₃ CO: 7.58 d (17)
[CpFe(Pm-Pf-Pm)]I	CDCl ₃	2.53	~7.3-8.6 b	~8.3 m	C ₅ H ₅ : 5.8 s
[(Pm-Pf-Pf)NiCl][PF ₆]	CH ₂ Cl ₂	~2.1 b, ~2.5 m	~7.3 b	8.24 t (5), 8.38 t (5)	
[(Pm-Pf-Pf)NiCl][PF ₆]	(CD ₃) ₂ CO	~1.8 b, ~2.05, 2.42 d (10), 2.53	~7.0-7.4 b	8.25 t (10)	
[(Pm-Pf-Pf)PdCl]Cl	CDCl ₃	~2.0-2.4 b, ~2.56 s	~6.4-7.1 b	8.00 t (4), 8.25 t (4)	
[(Pm-Pf-Pf)PtCl]Cl	CDCl ₃	~1.9-2.4 b, 2.53 d (2)	~6.6-7.5 b	8.06 d (8), 8.20 d (8)	

^a The following abbreviations are used: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet; t*, triplet with additional metal satellites. Separations in Hz are given in parentheses. ^b These chemical shifts were determined in CDCl₃ solution.

nonplanar, which makes nonequivalent the two methyl groups attached to the same ring phosphorus atom. However, the proton NMR spectra of all of the metal complexes of the di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂ exhibit only a single doublet resonance for the geminal methyls of the ligand dimethylphosphino group. This indicates that the five-membered chelate ring in the metal complexes of the di(tertiary phosphine) is undergoing rapid inversion on the NMR time scale. A similar effect is also observed in the chromium carbonyl complex (Pm-Pm-Pm)₂[Cr(CO)₄]₃, which, although it contains a tri- rather than a di(tertiary phosphine), can have no more than one five-membered chelate ring for each chromium atom.

The square-planar metal complexes of the type [(triphos)MCl]⁺ (M = Ni, Pd, and Pt) exhibit two methyl resonances of equal relative intensities arising from the geminal methyls of the ligand dimethylphosphino units. That this effect arises from nonequivalence of the two geminal methyl groups attached to a given phosphorus atom rather than nonequivalence of different dimethylphosphino groups is shown by the observation of two similar methyl resonances in the complexes [(Pm-Pf-Pf)MCl]⁺ (M = Ni, Pd, and Pt) which contain only one dimethylphosphino group. These methyl resonances in the [(triphos)MCl]⁺ complexes are triplets rather than simple doublets because of the large trans *J*(P-P) which results in virtual coupling.¹⁸ The observations of nonequivalent dimethylphosphino geminal methyl groups in the complexes [(triphos)MCl]⁺ in which the three phosphorus donor atoms and the metal atom are all in the same plane indicate that the two fused nonplanar chelate rings are rigid on the NMR time scale.

The positions and intensities of the ν (CO) frequencies of the complexes (Pm-Pf-Pm)M(CO)₃ (M = Cr, Mo, and W) indicate them to be the facial isomers rather than the corresponding meridional isomers¹⁹ in accord with expectations. In *fac*-(Pm-Pf-Pm)M(CO)₃ the three phosphorus atoms and the metal atom are not in the same plane. The geminal methyl groups on each dimethylphosphino unit of the complexed tri(tertiary phosphine) thus must be nonequivalent regardless of the inversion rate of the two fused five-membered chelate rings. The proton NMR spectra of all of the (Pm-Pf-Pm)-M(CO)₃ derivatives exhibit two doublets in the dimethyl-

phosphino region in accord with this prediction of non-equivalence of the geminal methyl groups on each dimethylphosphino unit. Virtual coupling¹⁸ is absent in these NMR spectra.

These proton NMR results on metal complexes of poly(tertiary phosphines) with terminal dimethylphosphino units indicate that a single nonplanar five-membered chelate ring can undergo rapid inversion on the NMR time scale whereas two fused nonplanar five-membered chelate rings remain rigid even on the NMR time scale.

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Registry No. (Pm-Pf)NiCl₂, 54823-53-9; (Pm-Pf)CoCl₂, 54823-63-1; (Pm-Pf)PdCl₂, 54823-54-0; (Pm-Pf)PtCl₂, 54823-55-1; [(Pm-Pf)₂RhCl₂]Cl, 54823-62-0; (Pm-Pf)Cr(CO)₄, 54823-50-6; (Pm-Pf)Mo(CO)₄, 54823-51-7; (Pm-Pf)W(CO)₄, 54823-52-8; (Pm-Pf)Fe₂(CO)₂Cp₂, 54823-48-2; [(Pm-Pm-Pm)NiCl]Cl, 54823-61-9; [(Pm-Pm-Pm)NiCl][PF₆], 54823-57-3; [(Pm-Pm-Pm)PdCl]Cl, 54823-58-4; [(Pm-Pm-Pm)PtCl]Cl, 54823-59-5; (Pm-Pm-Pm)Cr(CO)₃, 54823-60-8; (Pm-Pm-Pm)₂[Cr(CO)₄]₃, 54823-49-3; [(Pm-Pf-Pm)NiCl][PF₆], 54823-32-4; [(Pm-Pf-Pm)PdCl]Cl, 54823-33-5; [(Pm-Pf-Pm)PtCl]Cl, 54823-34-6; (Pm-Pf-Pm)₂(IrCl₃)₃, 54931-36-1; (Pm-Pf-Pm)Cr(CO)₃, 54823-28-8; (Pm-Pf-Pm)Mo(CO)₃, 54823-29-9; (Pm-Pf-Pm)W(CO)₃, 54823-65-3; (Pm-Pf-Pm)Mn(CO)₂Br, 54823-36-8; (Pm-Pf-Pm)Mn(CO)₂C(O)Me, 54823-64-2; [CpFe(Pm-Pf-Pm)]I, 54823-35-7; [(Pm-Pf-Pf)NiCl][PF₆], 54823-41-5; [(Pm-Pf-Pf)PdCl]Cl, 54823-42-6; [(Pm-Pf-Pf)PtCl]Cl, 54823-43-7; (Pm-Pf-Pf)Cr(CO)₃, 54823-38-0; (Pm-Pf-Pf)Mo(CO)₃, 54823-39-1; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; [CpFe(CO)₂]₂, 12154-95-9; Cr(CO)₆, 13007-92-6; (MeCN)₃W(CO)₃, 16800-47-8; Mn(CO)₅Br, 14516-54-2; MeMn(CO)₅, 13601-24-6; CpFe(CO)₂I, 12078-28-3.

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- (1) Part XI: R. B. King and J. C. Cloyd, Jr., preceding paper.
- (2) Portions of this work were presented at the 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974; see Abstracts, No. INOR 6.
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Pyrothiophosphatometal and (Alkyl pyrothiophosphato)metal Complexes¹

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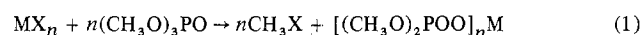
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Alkali metal iodides ($M = \text{Li, Na, K, Rb, Cs}$) react with triethyl (TETP) and tri-*n*-butyl thiophosphate (TBTP) at elevated temperatures (180–270°), to yield the corresponding (alkyl pyrothiophosphato)metal(I) complexes $\text{M}_2(\text{PETP})(\text{OH}_2)_2$ and $\text{M}_2(\text{PBTP})(\text{OH}_2)_n$, respectively; $n = 2$ or 0). Under the same conditions, MCl_2 ($M = \text{Mn, Co, Zn}$) compounds react with TETP to produce $\text{M}(\text{PETP})(\text{OH}_2)$ complexes, while the corresponding reactions with TBTP ($M = \text{Mn, Co, Ni, Zn}$) lead to the formation of inorganic metal(II) pyrothiophosphates $\text{M}_2(\text{PTP})(\text{OH}_2)_6$. AlCl_3 reacts with TBTP to yield a complex of the type $\text{Al}_2(\text{PBTP})_3 \cdot 3\text{H}_2\text{O}$. The above reactions proceed via formation of a metal halide–TETP or –TBTP adduct, which subsequently decomposes to the corresponding metal dialkyl thiophosphate, with simultaneous formation of alkyl halide, alkene, and hydrogen halide. The last product reacts with the metal dialkyl thiophosphate complex, to yield either an (alkyl hydrogen thiophosphato)- or a (dihydrogen thiophosphato)metal complex, which undergoes a condensation reaction at the reaction temperature, forming H_2S and the corresponding (alkyl pyrothiophosphato)metal or pyrothiophosphatometal complex, respectively. Ir evidence suggests that the PETP, PBTP, and PTP ligands are characterized by the presence of P–S–P rather than P–O–P linkages in the new metal complexes. These compounds were characterized by means of spectral and magnetic studies. Possible structures of the new complexes are discussed. Thus, the $\text{M}_2(\text{L})(\text{OH}_2)_x$ ($M = \text{Li, Na, K, Rb, Cs}$; $L = \text{PETP, PBTP}$; $x = 2$ or 0) and $\text{M}_2(\text{PTP})(\text{OH}_2)_6$ ($M = \text{Mn, Co, Ni, Zn}$) complexes appear to be monomeric, bimetallic compounds, while $\text{M}(\text{PETP})(\text{OH}_2)$ ($M = \text{Mn, Co, Zn}$) and $\text{Al}_2(\text{PBTP})_3 \cdot 3\text{H}_2\text{O}$ are apparently polynuclear.

Introduction

Neutral phosphate and phosphonate methyl esters react with metal halides at elevated temperatures to form metal complexes of the corresponding dimethyl phosphato and methyl alkyl phosphonato ligands, respectively,^{2–4} viz.



Under similar conditions, the corresponding neutral higher alkyl esters (ethyl, propyl, etc.) may lose more than one alkoxy alkyl group per neutral ester molecule, and produce metal complexes of the corresponding phosphate and phosphonate monoalkyl esters or their condensation products (pyrophosphates and pyrophosphonates).^{2,5–9} Studies of analogous reactions between metal halides and neutral thiophosphate esters ($(\text{RO}_3)\text{PS}$; $R = \text{C}_2\text{H}_5$ or $n\text{-C}_4\text{H}_9$) were recently undertaken by this laboratory.^{1,10} As already reported, chlorides of $\text{M}(\text{III})$ ($M = \text{Ti, V, Cr, Fe, Sc, Y, Ln}$), $\text{M}(\text{IV})$ ($M = \text{Th, U}$), $\text{Fe}(\text{II})$, and VO^{2+} react with these neutral esters to yield (dialkyl thiophosphato)metal complexes ($[(\text{RO})_2\text{POS}]_n\text{M}$).^{1,10} The present communication deals with metal halide–neutral thiophosphate ester reactions, involving elimination of more than one alkyl group per neutral ester molecule.

Experimental Section

Reactions. Reagent grade alkali metal iodides, $\text{Al}(\text{III})$ and 3d metal chlorides, and triethyl and tri-*n*-butyl thiophosphates (Matheson products) were utilized as received. The reactions, which were carried out in the drybox (N_2 atmosphere), involved suspension of the anhydrous or hydrated^{4–6,9,10} metal halide in an excess of the neutral thiophosphate ester at room temperature and subsequent dissolution

of the salt at ca. 100°. The resulting solutions were then heated to 180–270° for several minutes. Under these conditions, metal ethyl pyrothiophosphates are precipitated when halides of alkali metals, $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Zn}(\text{II})$ react with $(\text{C}_2\text{H}_5\text{O})_3\text{PS}$, and metal *n*-butyl pyrothiophosphates are formed during reactions of $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$ with alkali metal and aluminum(III) halides. These complexes were filtered, washed with acetone and anhydrous diethyl ether, and stored in an evacuated desiccator over calcium chloride. During reaction of $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$ with chlorides of $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Zn}(\text{II})$, the corresponding inorganic metal pyrothiophosphates are formed; their precipitation from the reaction mixture is effected by addition of an excess of ligroin (boiling range 63–75°), after cooling to room temperature. These compounds were filtered, washed with ether, and stored as above. Reactions of $(\text{C}_2\text{H}_5\text{O})_3\text{PS}$ with chlorides of $\text{Al}(\text{III})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$ or $(n\text{-C}_4\text{H}_9\text{O})_3\text{PS}$ with CuCl_2 led to solid products of uncertain nature, as shown by analyses. These products were not studied any further.

It should be noted that it was established that, for a given metal ion, the same complex is formed, regardless of whether the anhydrous or hydrated metal chloride, bromide, or iodide is used during the synthesis. With the exception of the potassium and cesium *n*-butyl pyrothiophosphates, the new complexes are obtained in the form of hydrates, which are not dehydrated, even after prolonged desiccation over a number of effective drying agents (e.g., CaCl_2 , $\text{Mg}(\text{ClO}_4)_2$, P_2O_5). The new compounds reported are insoluble in most common organic solvents (hydrocarbons, halocarbons, acetone, acetonitrile, nitrobenzene, nitromethane, *N,N*-dimethylformamide, etc.), and very sparingly soluble in methanol. The alkali metal complexes are water soluble, while the rest of the complexes show limited solubility in water. During the synthetic reactions, evolution of alkyl halide, alkene (C_2 or C_4), hydrogen halide,^{2,4–6,8–11} and H_2S was observed. These products were collected and identified by methods previously described.^{12a} For analytical (Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany), ir and electronic spectral, and magnetic data (obtained by methods described elsewhere^{12b,c})

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