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Poly(tertiary phosphines and arsines). XIV. Some Metal Complexes of Neopentyl Poly(tertiary phosphines)[1]

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Metal complexes of the neopentyl di(tertiary phosphine) $(Me_3CCH_2)_2PCH_2CH_2P(CH_2CMe_3)_2$ (abbreviation Pneo-Pneo) of the types $(Pneo\text{-}Pneo)M(CO)_4$ (M = Cr, Mo, W), $(Pneo\text{-}Pneo)M(CO)_3Br_2$ (M = Mo, W), $(Pneo\text{-}Pneo)M(CO)_3Br$ (M = Mn, Re), $(Pneo\text{-}Pneo)MCl_2$ (M = Ni, Pd, Pt), $[(Pneo\text{-}Pneo)_2Rh][PF_6]$, and $[(Pneo\text{-}Pneo)_2MCl_2][PF_6]$ (M = Ru, Rh) have been prepared by standard methods. Metal complexes of the types $[(triphos)MCl][PF_6]$ (M = Ni, Pd, Pt) and $(triphos)RhCl_3$ have been prepared from the neopentyl tri(tertiary phosphine) $Me_3CCH_2P[CH_2CH_2P(CH_2CMe_3)_2]_2$. The neopentyl tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_2CMe_3)_2]_3$ reacts with appropriate metal(II) chloride derivatives and ammonium hexafluorophosphate to form the yellow to white triligate monometallic complexes $[(tetraphos)MCl][PF_6]$ (M = Ni, Pd, Pt) containing one uncomplexed dineopentylphosphino group in contrast to other tripod tetra(tertiary phosphines) which function as tetraligate monometallic ligands in the blue to violet nickel complexes $[(tetraphos)NiCl][PF_6]$.

Introduction

Previous papers of this series have surveyed metal complexes of phenyl[4-6] and methyl[7] poly(tertiary phosphines). This paper describes some metal complexes of the recently reported[1] neopentyl poly(tertiary phosphines) $(Me_3CCH_2)_2PCH_2CH_2P(CH_2CMe_3)_2$, $Me_3CCH_2P[CH_2CH_2P(CH_2CMe_3)_2]_2$, and $P[CH_2CH_2P(CH_2CMe_3)_2]_3$. The phosphorus atoms in the dineopentylphosphino groups in these ligands would be expected to be of basicity similar to that of the phosphorus atoms in dimethylphosphino groups in methyl poly(tertiary phosphines) on the basis of an approximate similarity in the electronic properties of neopentyl and methyl groups. However, the large size of the neopentyl group relative to the methyl group is likely to cause considerable steric hindrance in its interactions with transition metal complexes. Such steric hindrance might reduce considerably the chemical reactivity of neopentylphosphines leading to less highly substituted types of complexes. The effects of the large size of the neopentyl groups in reducing the reactivity of trivalent phosphorus atoms to which they are bonded are illustrated by the contrast between the air-stable trineopentylphosphine[1] and the pyrophoric trimethylphosphine. Furthermore, the large size of the neopentyl group is potentially useful for stabilizing unusual types of polyphosphinemetal complexes by shielding the central metal atom from attack by potentially destructive reagents. In any case comparison of the chemistry of corresponding methyl and neopentyl poly(tertiary phosphines) provides a means for assessing the relative importance of steric and electronic effects of the terminal groups bonded to phosphorus on the complexing properties of trivalent phosphorus atoms with transition metals.

Experimental Section

Materials. The neopentyl poly(tertiary phosphines)[1] $(Me_3CCH_2)_2PCH_2CH_2P(CH_2CMe_3)_2$ (abbreviation Pneo-Pneo), $Me_3CCH_2P[CH_2CH_2P(CH_2CMe_3)_2]_2$ (abbreviation Pneo-Pneo-Pneo), and $P[CH_2CH_2P(CH_2CMe_3)_2]_3$ (abbreviation P(-Pneo)$_3$) as well as the related methyl tripod tetra(tertiary phosphine)[8] $P[CH_2CH_2P(CH_3)_2]_3$ (abbreviation P(-Pm)$_3$) were prepared by methods described elsewhere. The transition metal derivatives were purchased from the indicated commercial sources: $M(CO)_6$ (M = Cr, Mo, W) and $Re_2(CO)_{10}$ (Pressure Chemical Co., Pittsburgh, Pa.), $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corp., New York, N.Y.), platinum metal chlorides (Englehard, Newark, N.J.). The remaining transition metal derivatives $C_7H_8M(CO)_4$ (C_7H_8 = norbornadiene, M = Cr, Mo),[9] $C_7H_8M(CO)_3$ (C_7H_8 = cycloheptatriene, M = Cr, Mo),[9] $Mn_2(CO)_{10}$,[10] $Mn(CO)_5Br$,[9] $Re(CO)_5Br$,[11] $(C_6H_5CN)_2MCl_2$,[12] and $[C_8H_{12}RhCl]_2$[9] were prepared by the cited published procedures.

Preparation of Metal Complexes of the Neopentyl Poly(tertiary phosphines) (Table I). The indicated quantities of transition metal derivative, neopentyl poly(tertiary phosphine), and solvent (Table I) were stirred under the indicated conditions. In cases where the product did not precipitate upon cooling the reaction mixture, solvent was removed under vacuum at ~25°. The products were isolated and purified by column chromatography and/or crystallization under conditions indicated in the appropriate footnotes to Table I. Since the metal complexes of the neopentyl poly(tertiary phosphines) were relatively stable, their crystallization could be carried out relatively slowly without decomposition in order to give well-formed crystals.

Microanalyses of these new neopentyl poly(tertiary phosphine) complexes (Table II) 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 II) were determined in capillaries and are uncorrected. The conductances of the complexes with metal–chlorine bonds (Table II) were determined in 0.0006–0.004 *M* acetone solutions at room temperature using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio, and are quoted in $ohm^{-1}\ cm^2/mol$.

Infrared Spectra (Table II). Infrared spectra of the metal carbonyl derivatives in the 2100–1600-cm^{-1} region were obtained in cyclohexane solution except for the compounds $(Pneo\text{-}Pneo)M(CO)_3Br_2$ (M = Mo, W) where dichloromethane was used for a solvent. All infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film.

NMR Spectra (Table III). The proton NMR spectra were recorded at 100 MHz on a Varian HA-100 spectrometer in the indicated solvents. In addition to the generally sharp and intense methyl resonances listed in Table III, broad unsymmetrical complex ill-defined proton NMR resonances were observed in the τ 7.0–8.6 region arising from the CH_2 resonances of the neopentyl groups and the PCH_2CH_2P bridges.

The phosphorus-31 NMR spectra were taken in dichloromethane solution using a Jeolco PFT-100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in 10-mm NMR tubes containing a concentric 5-mm tube of deuterium oxide used as a lock and a capillary of 85% phosphoric acid used as an external standard. A pulse width of 90° was used with a repetition rate of 2–3 sec. From 200 to 6000 pulses were used to obtain the spectrum depending upon the strength of the sample. The chemical shifts are reported in ppm upfield from the external 85% H_3PO_4 standard.

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) $[(Pneo\text{-}Pneo\text{-}Pneo)NiCl][PF_6]$ maxima at 235 nm (ϵ 19000), 271 nm (ϵ 14000), 406 nm (ϵ 1900); (B) $[P(\text{-}Pneo)_3NiCl][PF_6]$ maxima at 229 nm (ϵ 16000), 267 nm (ϵ 14000), 399 nm (ϵ 2300); (C) $[P(\text{-}Pm)_3NiCl][PF_6]$ maxima at 259 nm (ϵ 8800) and 493 nm (ϵ 2000). For comparative purposes the following reported ultraviolet and visible spectral data on related complexes are summarized: (A)[7] $[(Pm\text{-}Pf\text{-}Pm)NiCl][PF_6]$ maxima at 298 nm (ϵ 4500), 381 nm (ϵ 2300); (B)[4] $[(Pf\text{-}Pf\text{-}Pf)NiCl][PF_6]$ maxima at 289 nm (ϵ 22000) 419 nm (ϵ 3900); (C)[5] [P-

Table I. Some Reactions of Neopentyl Poly(tertiary phosphines) with Transition Metal Derivatives

Metal derivatives (g, mmol)	Ligand (g, mmol)	Solvent (ml)	Temp, °C	Time, hr	Product	Yield, g (mmol)
$C_7H_8Cr(CO)_4$ (0.363, 1.42)	Pneo-Pneo (0.530, 1.42)	Hexane (50)	69	4	*cis*-(Pneo-Pneo)Cr(CO)$_4$[a]	0.48 (0.89)
$C_7H_8Mo(CO)_4$ (0.63, 2.1)	Pneo-Pneo (0.785, 2.1)	Hexane (50)	69	1	*cis*-(Pneo-Pneo)Mo(CO)$_4$[b,c]	0.62 (1.07)
$Mo(CO)_6$ (1.2, 4.6)	Pneo-Pneo (1.72, 4.6)	Xylene (80)	140	62	*cis*-(Pneo-Pneo)Mo(CO)$_4$[o]	2.28 (3.9)
$W(CO)_6$ (0.6, 1.7)	Pneo-Pneo (1.23, 3.3)	Xylene (20)	140	60	*cis*-(Pneo-Pneo)W(CO)$_4$[c,d]	0.9 (1.34)
$Mn(CO)_5Br$ (0.37, 1.34)	Pneo-Pneo (0.5, 1.34)	Benzene (50)	80	7	*fac*-(Pneo-Pneo)Mn(CO)$_3$Br[e,f]	0.47 (0.8)
$Re(CO)_5Br$ (0.87, 2.14)	Pneo-Pneo (0.8, 2.14)	Benzene–heptane (25:25)	~90	1.5	*fac*-(Pneo-Pneo)Re(CO)$_3$Br[e,f]	1.39 (1.93)
$NiCl_2 \cdot 6H_2O$ (0.394, 1.65)	Pneo-Pneo (0.619, 1.65)	EtOH (50)	80	0.2	*cis*-(Pneo-Pneo)NiCl$_2$[e,f]	0.59 (1.09)
Na_2PdCl_4 (0.588, 2.03)[g]	Pneo-Pneo (0.76, 2.0)	H_2O (25), EtOH (25)	25	24	*cis*-(Pneo-Pneo)PdCl$_2$[h]	0.83 (1.50)
K_2PtCl_4 (0.60, 1.44)	Pneo-Pneo (0.54, 1.44)	H_2O (50), EtOH (60)	25	16	*cis*-(Pneo-Pneo)PtCl$_2$[p]	0.71 (1.11)
$(PhCN)_2PtCl_2$ (0.63, 1.34)	Pneo-Pneo (0.5, 1.34)	C_6H_6 (50)	80	24	*cis*-(Pneo-Pneo)PtCl$_2$[i]	0.47 (0.74)
$[C_8H_{12}RhCl]_2$ (0.2, 0.4)	Pneo-Pneo (0.6, 1.6)	EtOH (25)	80	1.5[j]	[(Pneo-Pneo)$_2$Rh][PF$_6$][q]	0.72 (0.72)
$RhCl_3 \cdot 3H_2O$ (0.2, 0.8)	Pneo-Pneo (0.6, 1.6)	EtOH (40)	25	17	[(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$][d,f,j]	0.47 (0.44)
$RuCl_3 \cdot 3H_2O$ (0.24, 0.95)	Pneo-Pneo (0.76, 2.0)	EtOH (40)	25	21[j]	[(Pneo-Pneo)$_2$RuCl$_2$][PF$_6$][e,f]	0.25 (0.24)
$C_7H_8Cr(CO)_3$ (0.22, 1.0)	Pneo-Pneo-Pneo (0.53, 1.05)	MCH[k] (50)	100	4	*fac*-(Pneo-Pneo-Pneo)Cr(CO)$_3$[l,m]	0.12 (0.19)
$C_7H_8Mo(CO)_3$ (0.245, 0.9)	Pneo-Pneo-Pneo (0.50, 1.0)	MCH[k] (50)	100	4	*fac*-(Pneo-Pneo-Pneo)Mo(CO)$_3$[l,m]	0.12 (0.18)
$NiCl_2 \cdot 6H_2O$ (0.127, 0.53)	Pneo-Pneo-Pneo (0.27, 0.53)	EtOH (30)	25	1[j]	[(Pneo-Pneo-Pneo)NiCl][PF$_6$][n]	0.32 (0.42)
Na_2PdCl_4 (0.198, 0.67)[g]	Pneo-Pneo-Pneo (0.34, 0.67)	H_2O (40), EtOH (40)	90	0.75[j]	[(Pneo-Pneo-Pneo)PdCl][PF$_6$][q]	Low
$(PhCN)_2PdCl_2$ (0.53, 1.39)	Pneo-Pneo-Pneo (0.7, 1.39)	Benzene (25)	25	16[j]	[(Pneo-Pneo-Pneo)PdCl][PF$_6$][r]	0.7 (0.88)
$(PhCN)_2PtCl_2$ (0.65, 1.39)	Pneo-Pneo-Pneo (0.7, 1.39)	Benzene (25)	80	0.75[j]	[(Pneo-Pneo-Pneo)PtCl][PF$_6$][a,f]	1.07 (1.22)
$RhCl_3 \cdot 3H_2O$ (1.00, 4.1)	Pneo-Pneo-Pneo (2.05, 4.1)	EtOH (40)	80	18	(Pneo-Pneo-Pneo)RhCl$_3$[a]	0.44 (0.61)
$NiCl_2 \cdot 6H_2O$ (0.1, 0.42)	P(-Pneo)$_3$ (0.3, 0.47)	EtOH (10)	25	0.5[j]	[P(-Pneo)$_3$NiCl][PF$_6$][a,f]	0.25 (0.29)
$(PhCN)_2PdCl_2$ (0.42, 1.1)	P(-Pneo)$_3$ (0.7, 1.1)	C_6H_6 (25)	80	1[j]	[P(-Pneo)$_3$PdCl][PF$_6$][a,f]	0.85 (0.92)
$(PhCN)_2PtCl_2$ (0.52, 1.1)	P(-Pneo)$_3$ (0.7, 1.1)	C_6H_6 (25)	80	1[j]	[P(-Pneo)$_3$PtCl][PF$_6$][a,f]	1.00 (1.0)

[a] The product crystallized from the reaction mixture upon cooling and slow evaporation of the solvent. [b] The reaction mixture was chromatographed on an alumina column prepared in hexane. The product was eluted with a mixture of hexane and dichloromethane. [c] The product was recrystallized from a mixture of dichloromethane and hexane. [d] The reaction mixture was chromatographed on a Florisil column in dichloromethane solution. The product was eluted with dichloromethane. [e] Solvent was removed under vacuum. [f] The product was recrystallized from a mixture of dichloromethane and ethanol. [g] The Na_2PdCl_4 was obtained by heating stoichiometric quantities of $PdCl_2$ and NaCl until the $PdCl_2$ dissolved. [h] The product precipitated spontaneously from the reaction mixture. It was filtered, washed, and dried. [i] The reaction mixture was concentrated and treated with ethanol to precipitate the product. The product was recrystallized from a mixture of dichloromethane and ethanol. [j] A solution of excess ammonium hexafluorophosphate in methanol or ethanol was added prior to product isolation but after filtering off any insoluble material. [k] MCH = methylcyclohexane. [l] The reaction mixture was evaporated. Oily impurities were washed out with a minimum of pentane at −78°. [m] This product was not obtained analytically pure but identified from its phosphorus-31 NMR spectrum (Table III). [n] The product crystallized from the reaction mixture upon slow cooling to −10°. [o] Operation in footnote *d* followed by operation in footnote *c*. [p] Operation in footnote *h* followed by operation in footnote *f*. [q] Operation in footnote *a*; product then recrystallized twice from a mixture of dichloromethane and ethanol. [r] Operation in footnote *a*; product then recrystallized three times from a mixture of dichloromethane and ethanol.

(-Pf)$_3$NiCl][PF$_6$] maxima at 295 nm (ε 19000), 545 nm (ε 1600).

Bromination of (Pneo-Pneo)Mo(CO)$_4$. A solution of 0.81 g (1.4 mmol) of (Pneo-Pneo)Mo(CO)$_4$ in 30 ml of dichloromethane was treated dropwise with a solution of 0.24 g (1.5 mmol as Br_2) of bromine in 2.3 ml of carbon tetrachloride. After stirring of the mixture at room temperature for 15 min, excess hexane was added. Concentration of the resulting mixture at 25° (25 mm) gave yellow crystals of (Pneo-Pneo)Mo(CO)$_3$Br$_2$ in 75% yield. This compound is stable in the solid state at room temperature. However, the yellow solutions in organic solvents such as dichloromethane rapidly turn red and then purple at room temperature. Reaction of this red solution with carbon monoxide at 25° (1 atm) rapidly causes the solution to revert to its original yellow color. The infrared spectrum of this regenerated yellow solution in the ν(CO) region indicates the regeneration of (Pneo-Pneo)Mo(CO)$_3$Br$_2$. Attempts to isolate a pure product from the red solutions of decomposed (Pneo-Pneo)Mo(CO)$_3$Br$_2$ were unsuccessful.

Bromination of (Pneo-Pneo)W(CO)$_4$. A solution of 0.4 g (0.6 mmol) of (Pneo-Pneo)W(CO)$_4$ in 15 ml of dichloromethane was treated at −78° with a solution of 0.096 g (0.6 mmol as Br_2) of bromine in 1 ml of carbon tetrachloride. After stirring of the mixture at −78° for 15 min, solvent was removed at 0°. The infrared spectrum of the residue in dichloromethane exhibited ν(CO) frequencies at 2092, 2035, 2005, and 1978 cm^{-1} indicating the presence of the cation [(Pneo-Pneo)W(CO)$_4$Br]$^+$ (lit.[13] ν(CO) for [C$_6$H$_4$(AsMe$_2$)$_2$W(CO)$_4$I]$^+$ 2082, 2040, 2005, and 1960 cm^{-1}).

Attempts to obtain a pure salt of the [(Pneo-Pneo)W(CO)$_4$Br]$^+$ cation from this residue by crystallization from a mixture of dichloromethane and pentane or hexane or by treatment with ammonium

Table II. Properties of the Metal Complexes of the Neopentyl Poly(tertiary phosphines)

Compd	Color and form	Mp, °C	Analyses, % C Calcd	C Found	H Calcd	H Found	Other Calcd	Other Found	Λ_M (acetone), ohm^{-1} cm^2/mol	Infrared spectra (ν(CO) bands), cm^{-1}
cis-(Pneo-Pneo)Cr(CO)$_4$	Pale yellow needles	146–148 dec	58.0	57.8	9.0	9.0				1999 s, 1908 s, 1883 vs
cis-(Pneo-Pneo)Mo(CO)$_4$	Pale yellow plates	145–150 dec	53.6	53.5	8.3	8.2	11.0 (O)	10.8 (O)		2019 s, 1908 s, 1885 vs
cis-(Pneo-Pneo)W(CO)$_4$	Pale yellow prisms	177–180 dec	46.6	46.9	7.2	7.2				2011 s, 1907 s, 1883 vs
(Pneo-Pneo)Mo(CO)$_3$Br$_2$	Yellow	139–144 dec	42.0	42.1	6.8	7.0	22.4 (Br)	22.1 (Br)	17	2056 s, 1967 vs, 1902 s
(Pneo-Pneo)W(CO)$_3$Br$_2$	Lime yellow	185–187 dec	37.4	37.4	6.1	6.0	19.9 (Br)	19.9 (Br)	13	2042 s, 1950 vs, 1890 s
fac-(Pneo-Pneo)Mn(CO)$_3$Br	Yellow needles	180–182 dec	50.6	50.4	8.1	8.1	13.5 (Br)	13.6 (Br)	1.3	2020 s, 1953 s, 1889 s
fac-(Pneo-Pneo)Re(CO)$_3$Br	Colorless needles	195–196	41.4	41.3	6.7	6.6	11.2 (Br)	11.1 (Br)	0.7	2029 s, 1952 s, 1887 s
cis-(Pneo-Pneo)NiCl$_2$	Copper plates	310–312	52.4	52.3	9.6	9.6	14.2 (Cl)	14.1 (Cl)	0.2	
cis-(Pneo-Pneo)PdCl$_2$	Colorless plates	>360	47.9	48.3	8.8	8.9	12.8 (Cl)	12.9 (Cl)	0.5	
cis-(Pneo-Pneo)PtCl$_2$	Colorless	>360	41.2	41.2	7.6	7.2	11.1 (Cl)	11.1 (Cl)	0.4	
[(Pneo-Pneo)$_2$Rh][PF$_6$]	Yellow needles	221–227	53.0	53.1	9.7	9.7	15.5 (P)	15.5 (P)	142	
[(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$]	Yellow needles	211–213	49.5	49.4	9.1	9.1	6.6 (Cl)	6.7 (Cl)	146	
[(Pneo-Pneo)$_2$RuCl$_2$][PF$_6$]	Green	186–189 dec	49.6	49.9	9.1	9.1	6.6 (Cl)	6.3 (Cl)	144	
[(Pneo-Pneo-Pneo)NiCl][PF$_6$]	Gold needles	294–296	46.8	46.7	8.5	8.6	4.8 (Cl)	4.8 (Cl)	142	
[(Pneo-Pneo-Pneo)PdCl][PF$_6$]	Colorless prisms	318–320 dec	44.0	44.2	8.0	8.0	4.5 (Cl)	4.4 (Cl)	144	
[(Pneo-Pneo-Pneo)PtCl][PF$_6$]	Colorless needles	324–325	39.6	39.5	7.2	7.2	4.0 (Cl)	4.1 (Cl)	140	
(Pneo-Pneo-Pneo)RhCl$_3$	Yellow	267–270 dec	48.8	48.9	8.9	8.9	14.9 (Cl)	14.8 (Cl)	14	
[P(-Pneo)$_3$NiCl][PF$_6$]	Yellow	237–240	49.5	49.2	9.0	9.1	4.1 (Cl)	3.9 (Cl)	137	
[P(-Pneo)$_3$PdCl][PF$_6$]	Colorless needles	247–252	46.9	46.9	8.5	8.4	3.8 (Cl)	3.9 (Cl)	115	
[P(-Pneo)$_3$PtCl][PF$_6$]	Colorless plates	248–253	42.8	41.6	7.8	7.5	3.5 (Cl)	3.4 (Cl)	149	

hexafluorophosphate in ethanol gave only oils. Treatment of this residue with excess methanol resulted in decomposition to give a yellow precipitate of (Pneo-Pneo)W(CO)$_3$Br$_2$.

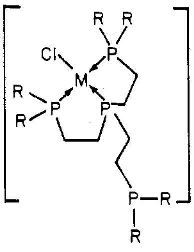
Preparation of [P(-Pm)$_3$NiCl][PF$_6$]. This derivative of the methyl tripod tetra(tertiary phosphine) was prepared in order to compare its properties with those of the corresponding nickel derivative of the neopentyl tripod tetra(tertiary phosphine) [P(-Pneo)$_3$NiCl][PF$_6$] (Table II).

A mixture of 0.367 g (1.23 mmol) of P[CH$_2$CH$_2$P(CH$_3$)$_2$]$_3$, 0.293 g (1.23 mmol) of nickel(II) chloride hexahydrate, and 50 ml of degassed ethanol was stirred at room temperature under nitrogen. The reaction mixture immediately became intense red-purple. Removal of solvent from this mixture gave a red-purple oil which could not be crystallized from ethanol, butanol, or a mixture of dichloromethane and hexane.

A concentrated 1-butanol solution of this red-purple oil was treated with an ethanolic solution containing 0.2 g (1.23 mmol) of ammonium hexafluorophosphate. The solution was heated until formation of the purple precipitate appeared to be complete. This precipitate was filtered and crystallized from a mixture of dichloromethane and ethanol to give 0.34 g (51% yield) of small purple crystals of [P(-Pm)$_3$NiCl][PF$_6$]. Anal. Calcd for C$_{12}$H$_{30}$ClF$_6$NiP$_5$: C, 26.8; H, 5.6; Cl, 6.6. Found: C, 26.8; H, 5.7; Cl, 6.6.

Discussion

The most unexpected aspect of the chemistry of the metal complexes of neopentyl poly(tertiary phosphines) discussed in this paper is the nature of the nickel(II) complex of the neopentyl tripod tetra(tertiary phosphine) [P(-Pneo)$_3$NiCl][PF$_6$] which is a yellow triligate monometallic[14] derivative of structure I (M = Ni, R = CH$_2$C(CH$_3$)$_3$) with



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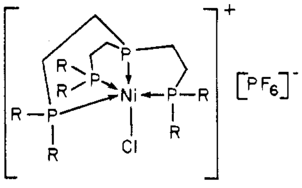


II

four-coordinate square planar nickel(II) rather than a deep purple tetraligate monometallic derivative of structure II (R = CH$_3$ or C$_6$H$_5$) with five-coordinate nickel such as the complexes formed by the related tripod tetra(tertiary phosphines) P(CH$_2$CH$_2$PR$_2$)$_3$ (R = CH$_3$ or C$_6$H$_5$;[5] abbreviated as P(-Pm)$_3$ and P(-Pf)$_3$, respectively). The formulation of [P(-Pneo)$_3$NiCl][PF$_6$] as a triligate monometallic square-planar nickel derivative of structure I (M = Ni, R = CH$_2$C(CH$_3$)$_3$), which is suggested by its yellow color, is further supported by the following observations.

(1) The electronic spectrum of the tripod tetra(tertiary phosphine) complex [P(-Pneo)$_3$NiCl][PF$_6$] is similar to that of the neopentyl tri(tertiary phosphine) complex [(Pneo-Pneo-Pneo)NiCl][PF$_6$]. Furthermore, the position of the 399-nm maximum in [P(-Pneo)$_3$NiCl][PF$_6$] is close to that of corresponding maxima in several related triligate monometallic four-coordinate tri(tertiary phosphine)nickel(II) complexes [(Pneo-Pneo-Pneo)NiCl][PF$_6$] (406 nm), [(Pm-Pf-Pm)NiCl][PF$_6$] (381 nm), and [(Pf-Pf-Pf)NiCl][PF$_6$] (419 nm) but very different from the position of the maxima in the purple tetraligate monometallic five-coordinate tripod tetra(tertiary phosphine) complexes [P(-Pf)$_3$NiCl][PF$_6$] (II, R = C$_6$H$_5$) and [P(-Pm)$_3$NiCl][PF$_6$] (II, R = CH$_3$) at 545 and 493 nm, respectively.

(2) The coordination chemical shifts in the phosphorus-31 NMR spectrum of [P(-Pneo)$_3$NiCl][PF$_6$] (Table III) are similar to those in various complexes of the type [(triphos)NiCl][PF$_6$][15] including [(Pneo-Pneo-Pneo)NiCl][PF$_6$]. In addition the phosphorus-31 NMR spectrum of [P-

Table III. Proton and Phosphorus-31 NMR Spectra of Metal Complexes of Neopentyl Poly(tertiary phosphines)

	Proton NMR spectrum		Phosphorus-31 NMR spectrum						
				Chem shifts, δ		Coord chem shifts, δ[b]		Coupling constants, Hz	
Compd	Solvent	τ(CH_3)[a]	Solvent	(Me_3CCH_2)$_2$P	Other P	(Me_3CCH_2)$_2$P	Other P	*J*(PP)	*J*(MP)
cis-(Pneo-Pneo)Cr(CO)$_4$	$CDCl_3$	8.83	CH_2Cl_2	−61.6		−104.2			
cis-(Pneo-Pneo)Mo(CO)$_4$	$CDCl_3$	8.83	CH_2Cl_2	−31.3		−73.9			
cis-(Pneo-Pneo)W(CO)$_4$	$CDCl_3$	8.82	CH_2Cl_2	−17.4		−60.0			215
(Pneo-Pneo)Mo(CO)$_3$Br$_2$	$CDCl_3$	8.80							
(Pneo-Pneo)W(CO)$_3$Br$_2$	$CDCl_3$	8.82							
fac-(Pneo-Pneo)Mn(CO)$_3$Br	(CD_3)$_2$CO	8.74, 8.82	CH_2Cl_2	−57.1		−99.7			
fac-(Pneo-Pneo)Re(CO)$_3$Br	$CDCl_3$	8.78, 8.84	CH_2Cl_2	−11.5		−54.1			
cis-(Pneo-Pneo)NiCl$_2$	$CDCl_3$	8.70	CH_2Cl_2	−58.0		−100.6			
cis-(Pneo-Pneo)PdCl$_2$	$CDCl_3$	8.76	CH_2Cl_2	−65.6		−108.2			
cis-(Pneo-Pneo)PtCl$_2$	$CDCl_3$	8.77	CH_2Cl_2	−37.1		−79.7			3496
[(Pneo-Pneo)$_2$Rh][PF$_6$]	$CDCl_3$	8.84	CH_2Cl_2	−46.3		−88.9			129
[(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$]	$CDCl_3$	8.81	CH_2Cl_2	−40.0		−82.6			80
(Pneo-Pneo-Pneo)Cr(CO)$_3$			CH_2Cl_2	−62.3	−100.0	−105.3	−130.6	19	
(Pneo-Pneo-Pneo)Mo(CO)$_3$			CH_2Cl_2	−37.5	−63.6	−80.5	−94.2	8	
[(Pneo-Pneo-Pneo)NiCl][PF$_6$]	$CDCl_3$	8.77, 8.80	CH_2Cl_2	−44.1	−102.7	−87.1	−133.3	41	
[(Pneo-Pneo-Pneo)PdCl][PF$_6$]	(CD_3)$_2$CO	8.74, 8.75, 8.81	CH_2Cl_2	−43.1	−104.8	−86.1	−135.4	<2	
[(Pneo-Pneo-Pneo)PtCl][PF$_6$]	(CD_3)$_2$CO	8.76, 8.78, 8.82	CH_2Cl_2	−37.4	−77.5	−80.4	−108.1	<2	2309,[c] 3125[d]
(Pneo-Pneo-Pneo)RhCl$_3$	$CDCl_3$	8.76, 8.85 br	CH_2Cl_2	−56.5	−95.3	−99.5	−125.9	<2	117,[c] 112[d]
[P(-Pneo)$_3$NiCl][PF$_6$]	$CDCl_3$	8.76, 8.79, 9.00	CH_2Cl_2	−45.7, −45.2, +38.4	−107.5	−88.5, −88.0, −4.4	−126.3	41	
[P(-Pneo)$_3$PdCl][PF$_6$]	(CD_3)$_2$CO	8.80, 8.83, 8.85	CH_2Cl_2	−44.1, +38.5	−107.8	−86.9, −4.3	−126.6	26[e]	
[P(-Pneo)$_3$PtCl][PF$_6$]	$CDCl_3$	8.81, 8.86, 8.98	CH_2Cl_2	−38.5, +39.3	−81.6	−81.3, −3.5	−100.4	27[e]	2289,[c] 3108[d]

[a] In addition to the listed sharp singlet CH_3 resonance, broad resonances and/or unsymmetrical multiplets were observed in the τ 7.0–8.6 region. These may be assigned to the CH_2 resonances of both the neopentyl groups and the PCH_2CH_2 bridges. However, the complexity of these resonances prevented precise assignments. [b] The following values were used for the free ligands: Pneo-Pneo, +42.6 ppm: Pneo-Pneo-Pneo, +43.0 and +30.6 ppm for the two outer and one center phosphorus atoms, respectively; P(-Pneo)$_3$, +42.8 and +18.8 ppm for the three outer and one center phosphorus atoms, respectively. [c] Coupling of the metal to the outer phosphorus atoms. [d] Coupling of the metal to the center phosphorus atom. [e] Coupling of the center phosphorus atom to the uncomplexed end phosphorus atom.

(-Pneo)$_3$NiCl][PF$_6$] contains a resonance at +38 ppm which may be assigned to the uncomplexed phosphorus atom of the triligate monometallic tripod tetraphosphine ligand.

(3) The proton NMR spectrum of [P(-Pneo)$_3$NiCl][PF$_6$] (Table III) contains a resonance at τ 9.00 which can be assigned to the methyl groups of the $-CH_2CH_2P(CH_2CMe_3)_2$ arm of the tripod tetra(tertiary phosphine) not bonded to the nickel atom in addition to resonances at τ 8.76 and 8.79 which can be assigned to the methyl groups of the two $CH_2CH_2P(CH_2CMe_3)_2$ arms of the tripod tetra(tertiary phosphine) bonded to the nickel atom. The tendency for the neopentyl tripod tetra(tertiary phosphine) to function as a triligate monometallic ligand in [P(-Pneo)$_3$NiCl][PF$_6$] in contrast to the tendency for other tripod tetra(tertiary phosphines) to function as tetraligate monometallic ligands in [(tetraphos)NiCl]$^+$ derivatives[5,7,16] may mean that the steric requirements of neopentyl groups are so large that after two dineopentylphosphino units are coordinated to a metal atom, there is insufficient space for a third dineopentylphosphino unit to coordinate to the same metal atom while maintaining reasonable bond angles in the two fused five-membered chelate rings in contrast to dialkylphosphino groups with smaller alkyl substituents.

In our previous work[17] with the tripod tetra(tertiary phosphines) $P(CH_2CH_2PR_2)_3$ (R = CH_3 and C_6H_5) we were unable to obtain pure palladium and platinum derivatives by reactions of the ligands with the tetrachlorometalates(II), MCl_4^{2-} (M = Pd, Pt). In this work we obtained pure complexes of the type [P(-Pneo)$_3$MCl][PF$_6$] (M = Pd, Pt) by using the benzonitrile complexes $(C_6H_5CN)_2MCl_2$ (M = Pd, Pt) as sources of the metal. These tripod tetra(tertiary phosphine) complexes appear to be triligate monometallic metal(II) derivatives (I, M = Pd, Pt, R = $CH_2C(CH_3)_3$) similar to the analogous nickel complex discussed above on the basis of similarities in their proton and phosphorus-31 NMR spectra.

Most of the remaining reactions of the neopentyl tri(tertiary phosphine) $Me_3CCH_2P[CH_2CH_2P(CH_2CMe_3)_2]_2$ and the neopentyl tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_2CMe_3)_2]_3$ with transition metal derivatives including $[C_8H_{12}RhCl]_2$ in ethanol and $M(CO)_5Br$ (M = Mn, Re) in boiling benzene or xylene gave oily or tarry products which could not be crystallized or otherwise purified. Reaction of the neopentyl tri(tertiary phosphine) $Me_3CCH_2P[CH_2CH_2P(CH_2CMe_3)_2]_2$ with the cycloheptatriene complexes $C_7H_8M(CO)_3$ (M = Cr, Mo) gave noncrystalline products which likewise could not be purified. However, the infrared ν(CO) frequencies (strong bands at 1934, 1852, and 1835 cm^{-1} for the chromium derivative and at 1949, 1861, and 1851 cm^{-1} for the molybdenum derivative) as well as the phosphorus-31 NMR spectra of these products indicated them to contain mainly the corresponding (Pneo-Pneo-Pneo)M(CO)$_3$ (M = Cr, Mo) derivative.

The complexes (Pneo-Pneo)M(CO)$_4$ (M = Cr, Mo, W), *fac*-(Pneo-Pneo)M(CO)$_3$Br (M = Mn, Re), [(Pneo-Pneo)$_2$MCl$_2$][PF$_6$] (M = Ru, Rh), [(Pneo-Pneo)$_2$Rh][PF$_6$], and (Pneo-Pneo)MCl$_2$ (M = Ni, Pd, Pt) were prepared from the di(tertiary phosphine) $(Me_3CCH_2)_2PCH_2CH_2P(CH_2CMe_3)_2$ by normal methods.[18] These complexes were identified by correct analyses for three elements as well as appropriate infrared ν(CO) frequencies for the metal carbonyl derivatives and appropriate conductance values for the metal chloride derivatives.

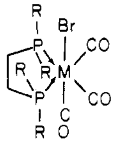
Several reports have appeared on the halogenation of (diphos)M(CO)$_4$[19] and (diars)M(CO)$_4$[13,20] (M = Mo, W) derivatives to give seven-coordinate metal(II) complexes. We found that the reaction of (Pneo-Pneo)Mo(CO)$_4$ with bromine at room temperature gave the expected (Pneo-Pneo)Mo(CO)$_3$Br$_2$ with loss of one carbonyl group. This yellow product was stable in the solid state but became dark red in solution upon mild warming. The dark red solutions reverted to the yellow (Pneo-Pneo)Mo(CO)$_3$Br$_2$ upon treatment with carbon monoxide at room temperature and atmospheric pressure suggesting that the dark red material, which could not be isolated in the pure state, was a decarbonylation product of (Pneo-Pneo)Mo(CO)$_3$Br$_2$. The related derivatives (R$_3$P)$_2$Mo(CO)$_3$Br$_2$ (R = C$_2$H$_5$[21] and C$_6$H$_5$[22,23]) have been reported to lose carbon monoxide reversibly to give blue products of the type (R$_3$P)$_2$Mo(CO)$_2$Br$_2$ but a similar reversible carbon monoxide loss has not been previously observed for di(tertiary phosphine)molybdenum(II) carbonyl complexes.

The tungsten derivative (Pneo-Pneo)W(CO)$_4$ was allowed to react with bromine at low temperatures in an attempt to obtain the cation [(Pneo-Pneo)W(CO)$_4$Br]$^+$, hoping that the greater stability of tungsten–carbonyl bonds relative to molybdenum–carbonyl bonds[24] would allow the isolation of a product of this type. The initial product from the reaction of equimolar quantities of (Pneo-Pneo)W(CO)$_4$ and Br$_2$ was a solid indicated to be mainly [(Pneo-Pneo)W(CO)$_4$Br]Br by the similarity of its ν(CO) frequencies to those of reported [(diars)W(CO)$_4$I]$^+$ salts which have been isolated in the pure state.[14] However, this product could not be recrystallized and decomposed rapidly in methanol or ethanol with carbon monoxide evolution to give (Pneo-Pneo)W(CO)$_3$Br$_2$ with properties completely analogous to those of the corresponding molybdenum compound. This instability of the initially formed [(Pneo-Pneo)W(CO)$_4$Br]Br in alcohols is probably a consequence of the tendency of the bromide anion to displace one of the carbonyl groups in polar solvents to form a second tungsten–bromine bond. Furthermore, the instability of [(Pneo-Pneo)W(CO)$_4$Br]Br in polar solvents prevented its metathesis with salts of large anions like hexafluorophosphate and tetraphenylborate in efforts to obtain a more crystalline [(Pneo-Pneo)W(CO)$_4$Br]$^+$ salt with a nonreactive anion.

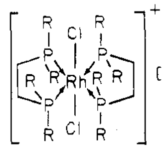
The relative oxidative stability of neopentyl phosphines apparently because of the protection of the trivalent phosphorus by the bulky neopentyl groups suggested that metal alkyls and hydrides as well as low oxidation state metal derivatives of unusual oxidative stability might be obtained by using neopentylphosphines as ligands rather than phosphines with less bulky alkyl groups. In attempts to test this idea, the nickel complex (Pneo-Pneo)NiCl$_2$ was allowed to react at room temperature with phenyllithium in a mixture of benzene and diethyl ether, with LiAlH$_4$ in tetrahydrofuran, and with sodium borohydride in methanol. These reactions resulted either in the recovery of starting material or in apparent decomposition with no evidence for products like (Pneo-Pneo)NiRCl (R = H, C$_6$H$_5$), (Pneo-Pneo)NiR$_2$ (R = H, C$_6$H$_5$), or (Pneo-Pneo)$_2$Ni. The question of the ability of the neopentyl phosphines to stabilize metal alkyls and hydrides through steric inhibition of metal oxidation thus remains unresolved, although our results suggest that the large size of the neopentyl groups in (Pneo-Pneo)NiCl$_2$ interferes with the reactions necessary to form hydrides and alkyls.

The methyl groups of methyl poly(tertiary phosphines) were found to be useful proton NMR probes[7] for elucidating some of the structural features of their metal complexes as well as for estimating the relative inversion rate of the five-membered chelate rings.[25] We were interested in determining whether methyl groups in neopentyl poly(tertiary phosphines) would still be useful as proton NMR probes in view of the greater distance and number of chemical bonds between neopentyl methyl groups and both the phosphorus and metal atoms. The four bonds between the neopentyl methyl protons and the phosphorus atom in neopentylphosphorus derivatives makes the ^4J(PH) phosphorus–proton coupling negligible. This means that any multiplicity of neopentyl methyl resonances must arise from nonequivalence of the neopentyl groups.

The proton NMR spectra of the neopentyl di(tertiary phosphine) complexes (Pneo-Pneo)M(CO)$_3$Br (M = Mn, Re) (Table III) exhibit two neopentyl methyl resonances consistent with the facial isomer III (M = Mn, Re; R = CH$_2$C(CH$_3$)$_3$)



III



IV

with rapid inversion of the chelate ring but nonequivalence of both sides of the chelate ring thereby leading to equivalent phosphorus atoms with nonequivalent neopentyl groups on each phosphorus atom. The proton NMR spectra of the remaining neopentyl di(tertiary phosphine) complexes (Pneo-Pneo)M(CO)$_4$ (M = Cr, Mo, W), (Pneo-Pneo)M(CO)$_3$Br$_2$ (M = Mo, W), (Pneo-Pneo)MCl$_2$ (M = Ni, Pd, Pt), [(Pneo-Pneo)$_2$Rh][PF$_6$], and [(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$] exhibit only a sharp singlet neopentyl methyl resonance consistent with rapid inversion of the chelate rings and equivalence of both sides of the chelate rings with the additional possibility of stereochemical nonrigidity for the seven-coordinate derivatives (Pneo-Pneo)M(CO)$_3$Br$_2$. The single neopentyl methyl resonance in [(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$] indicates formulation as the trans isomer IV rather than the corresponding cis isomer.

The sensitivity of the neopentyl methyl proton resonances (Table III) is barely sufficient to detect some of the nonequivalent neopentyl groups in the metal complexes of the neopentyl tri(tertiary phosphines) and tripod tetra(tertiary phosphines). In complexes of the type [(triphos)MCl][PF$_6$] (M = Ni, Pd, Pt) containing ligands with donor CH$_2$CH$_2$P(CH$_3$)$_2$ units the geminal methyl groups are nonequivalent in the proton NMR spectrum because of the rigidity and nonplanarity of the two fused five-membered chelate rings.[7] The neopentyl tri(tertiary phosphine) complexes [(Pneo-Pneo-Pneo)MCl][PF$_6$] (M = Ni, Pd, Pt) should exhibit a 1:2:2 pattern of neopentyl methyl resonances if the fused chelate rings are similarly nonplanar and rigid. This pattern is observed in the palladium and platinum derivatives, but the chemical shift difference between the methyls of the unique neopentyl group on the center phosphorus atom and the methyls of the pair of neopentyl groups on terminal phosphorus atoms appearing at lower chemical shifts is so small that these two resonances are barely resolved. The tripod tetra(tertiary phosphine) complexes [P(-Pneo)$_3$MCl][PF$_6$] (M = Ni, Pd, Pt) exhibit three neopentyl methyl resonances consistent with the triligate monometallic structure I (R = CH$_2$C(CH$_3$)$_3$) discussed above with equivalence of the two coordinating dineopentylphosphino units but nonequivalence of their geminal neopentyl groups and with a unique noncoordinating dineopentylphosphino unit with equivalent geminal neopentyl groups. The separation between the resonance around τ 9.00 tentatively assigned to the neopentyl methyls of the noncoordinating dineopentylphosphino group and the resonances of the neopentyl methyls of the two coordinating dineopentylphosphine groups in the [P(-Pneo)$_3$MCl][PF$_6$] (M = Ni, Pd, Pt) complexes appears to be much better in spectra taken in CDCl$_3$ than in spectra taken in (CD$_3$)$_2$CO for reasons that are not clear.

The proton-decoupled phosphorus-31 NMR spectra of all of the neopentyl di(tertiary phosphine) derivatives (Table III) exhibit the expected singlet with coordination chemical shifts similar to those of the related di(tertiary phosphine) complexes.[15] The proton-decoupled phosphorus-31 NMR spectra of the neopentyl tri(tertiary phosphine) complexes (Pneo-Pneo-Pneo)M(CO)$_3$ (M = Cr, Mo) and [(Pneo-Pneo-Pneo)NiCl][PF$_6$] exhibit the expected low-field triplet from the ligand center phosphorus atoms and the expected higher field doublet from the two ligand outer phosphorus atoms with coordination chemical shifts and phosphorus–phosphorus coupling constants similar to those of the related tri(tertiary phosphine) complexes.[15] The proton-decoupled phosphorus-31 NMR spectra of the remaining neopentyl tri(tertiary phosphine) complexes (Pneo-Pneo-Pneo)RhCl$_3$ and [(Pneo-Pneo-Pneo)MCl][PF$_6$] (M = Pd, Pt) exhibit two singlets since the phosphorus–phosphorus coupling is below the resolution limits of the spectrometer. The decrease in phosphorus–phosphorus coupling constants between two phosphorus atoms in a five-membered chelate ring formed by a poly(tertiary phosphine) upon descending a column of the periodic table from nickel through palladium to platinum was observed in the previous phosphorus-31 NMR study.[15]

The platinum–phosphorus coupling constants $|^1J(\text{Pt–P})|$ in the complexes [(Pneo-Pneo-Pneo)PtCl][PF$_6$] and [P(-Pneo)$_3$PtCl][PF$_6$] are readily determined from the satellites in their proton-decoupled phosphorus-31 NMR spectra. The $|^1J(\text{Pt–P})|$ coupling constants for the center phosphorus atoms appear around 3115 ± 10 Hz which is within the 3024–3242-Hz range found for similar phosphorus atoms in the previous work.[15] The $|^1J(\text{Pt–P})|$ coupling constants for the end phosphorus atoms in coordinating P(CH$_2$CMe$_3$)$_2$ groups appear around 2300 Hz which is slightly below the 2340-Hz values found for the $|^1J(\text{Pt–P})|$ coupling constants of the end phosphorus atoms in coordinating P(CH$_3$)$_2$ groups.[15]

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Registry No. *cis*-(Pneo-Pneo)Cr(CO)$_4$, 57396-30-2; *cis*-(Pneo-Pneo)Mo(CO)$_4$, 57396-31-3; *cis*-(Pneo-Pneo)W(CO)$_4$, 57396-32-4; *fac*-(Pneo-Pneo)Mn(CO)$_3$Br, 57396-33-5; *fac*-(Pneo-Pneo)Re(CO)$_3$Br, 57396-34-6; *cis*-(Pneo-Pneo)NiCl$_2$, 57396-35-7; *cis*-(Pneo-Pneo)PdCl$_2$, 57396-36-8; *cis*-(Pneo-Pneo)PtCl$_2$, 57396-37-9; [(Pneo-Pneo)$_2$Rh][PF$_6$], 57396-39-1; [(Pneo-Pneo)$_2$RhCl$_2$][PF$_6$], 57396-41-5; [(Pneo-Pneo)$_2$RuCl$_2$][PF$_6$], 57396-43-7; *fac*-(Pneo-Pneo-Pneo)Cr(CO)$_3$, 57396-44-8; *fac*-(Pneo-Pneo-Pneo)Mo(CO)$_3$, 57396-45-9; [(Pneo-Pneo-Pneo)NiCl][PF$_6$], 57396-47-1; [(Pneo-Pneo-Pneo)PdCl][PF$_6$], 57396-49-3; [(Pneo-Pneo-Pneo)PtCl][PF$_6$], 57396-51-7; (Pneo-Pneo-Pneo)RhCl$_3$, 57396-52-8; [P(-Pneo)$_3$NiCl][PF$_6$], 57396-54-0; [P(-Pneo)$_3$PdCl][PF$_6$], 57396-56-2; [P(-Pneo)$_3$PtCl][PF$_6$], 57396-58-4; (Pneo-Pneo)Mo(CO)$_3$Br$_2$, 57396-59-5; [(Pneo-Pneo)W(CO)$_4$Br]$^+$, 57396-60-8; [P(-Pm)$_3$NiCl][PF$_6$], 54823-46-0; (Pneo-Pneo)W(CO)$_3$Br$_2$, 57396-61-9; C$_7$H$_8$Cr(CO)$_4$, 12146-36-0; C$_7$H$_8$Mo(CO)$_4$, 12146-37-1; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; Mn(CO)$_5$Br, 14516-54-2; Re(CO)$_5$Br, 14220-21-4; (PhCN)$_2$PtCl$_2$, 14873-63-3; [C$_8$H$_{12}$RhCl]$_2$, 12092-47-6; C$_7$H$_8$Cr(CO)$_3$, 12125-72-3; C$_7$H$_8$Mo(CO)$_3$, 12125-77-8; (PhCN)$_2$PdCl$_2$, 14220-64-5.

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Charge-Transfer Spectra of Tetrahedral Transition Metal Complexes

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A simple model is proposed for the description of charge-transfer states in transition metal complexes. The electron repulsion effects in the LMCT excited states are evaluated by using ligand field data. Indeed, the relative energies of certain excited CT states in a d^n system can be related to the ligand field levels of the corresponding d^{n+1} central ion complexes. The applicability of the proposed scheme is tested and demonstrated by studying the charge-transfer absorption spectra of a number of tetrahedral compounds, leading to a coherent interpretation of the spectral data.

I. Introduction

It is the purpose of this paper to make a few general remarks on the study of charge-transfer states in transition metal complexes. Important progress in this field has been made by Jorgensen,[1,2,19,24] Day, DiSipio, Oleari,[3-5] Gray,[6] and many others. Most of the work of these authors centers on a one-electron description, either in terms of optical electronegativities or in terms of a simplified molecular orbital theory. Only in a limited number of cases has the attention been focused on electron repulsion effects. Apparently, the theory