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Phosphorus-Nitrogen Donor Ligand Complexes of Chromium, Molybdenum and Tungsten Carbonyls

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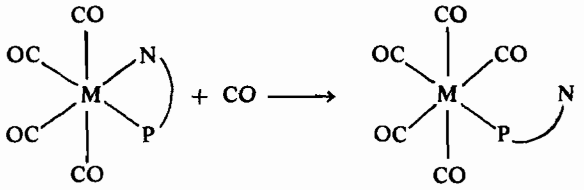
Received February 13, 1973

Metal carbonyl complexes of the general formula $M(CO)_4(P-N)$ containing a phosphorus-nitrogen donor bidentate ligand were prepared and characterized by their proton nmr and infrared spectra. The metals, M, were Cr, Mo, or W, and the ligands contained either (1) alkylamine donor groups as in $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$ and $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$ or (2) pyridine donor groups as in $(C_6H_5)_2PCH_2C_5H_4N$, $(C_6H_5)_2PCH_2CH_2C_5H_4N$, $(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N$ and $(C_6H_5)_2PN(H)C_5H_4N$.

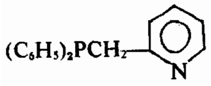
Introduction

Prior to beginning kinetic studies of chelate ring opening reactions of the type,

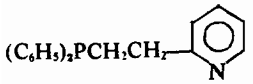


where M = Cr, Mo, or W and P–N = a bidentate phosphorus-nitrogen donor ligand, it was necessary to synthesize a number of P–N ligands and their tetracarbonyl complexes.

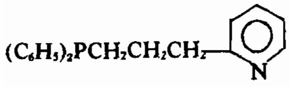
In this paper, we describe the synthesis and characterization of the following ligands and their complexes:



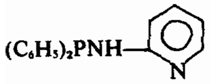
$(C_6H_5)_2PCH_2CH_2N(CH_3)_2$



$(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$



$(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$



The synthesis of some of these has been reported previously by others, as noted in the next section.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 237B spectrophotometer with an auxiliary Beckman Model 1005 linear recorder. The instrument was calibrated in the region above 2000 cm^{-1} with gaseous carbon monoxide and below 2000 cm^{-1} with polystyrene; the resultant frequencies are believed to be accurate within ± 1 cm^{-1}. Proton nmr spectra were obtained on Varian Model A-60 and Hitachi Perkin-Elmer R-20B spectrometers using tetramethylsilane, $\tau = 10.0$, as an internal standard. Melting points were determined on a Kofler hot stage and are uncorrected. Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass., and Chemalytics, Inc., Tempe, Arizona.

Tetrahydrofuran (THF) and *p*-dioxane (D) were dried over $LiAlH_4$ and CaH_2, respectively, and freshly distilled prior to use. All other solvents (reagent grade) were used without further purification. All reactions were conducted in a nitrogen atmosphere and solvents were deoxygenated by purging with N_2 for 10 min before use.

Potassium diphenylphosphide · 2 dioxane, $KP(C_6H_5)_2 \cdot 2D$, was prepared from $ClP(C_6H_5)_2$ by the method of Issleib.[2] Typical yields generally exceeded 60%.

2-(Diphenylphosphinomethyl)pyridine. Although this ligand has not been prepared previously, its synthesis is similar to that outlined by Issleib[3] and Dahlhoff[4] for relate derivatives. The hydrochloride salt of 2-picoly chloride in water was neutralized with Na_2CO_3 to pH 8. The brownish-yellow oil which separated from the aqueous phase was extracted 3 times with diethyl ether. The ether extract was dried for 1 hr over anhydrous Na_2SO_4 and filtered. After removing the ether under water-aspirator vacuum, the unstable[5] 2-picolyl chloride (b.p. 50-52°/2mm Hg) was recovered by vacum distillation and used directly or stored at –80°.

A solution of 2-picolyl chloride (4.29g, 33.6 mmole) in 30 ml of THF was slowly added with stirring to a solution of 12.2g (30.5 mmoles) of $KP(C_6H_5)_2 \cdot 2D$ in 80 ml of THF during the course of 1 hr under a

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[1] Fellow of the Alfred P. Sloan Foundation, 1970-1972.

[2] K. Issleib and A. Tzschach, *Chem. Ber.*, *92*, 1118 (1959).

[3] K. Issleib and R. Rieschel, *Chem. Ber.*, *98*, 2086 (1965).

[4] W. Dahlhoff, T. Dick, and S. Nelson, *J. Chem. Soc.* (A), 2919 (1969).

[5] W. Mathes and H. Schüly, *Angew. Chem. Intern. Ed. Engl.*, *2*, 144 (1963).

nitrogen atmosphere at 25°C. The reddish-orange color of the $P(C_6H_5)_2^-$ disappeared, and the resulting pale yellow solution was refluxed for 10 min. After cooling to room temperature, the solution was filtered through Celite Filter-aid and the solvent was removed under water-aspirator vacuum. Unreacted 2-picolyl chloride was removed by vacuum (<0.2mm Hg) distillation, leaving the pale yellow oily product, 2-(diphenylphosphinomethyl)pyridine; 6.20g, 73.4% yield. It was characterized by its proton nmr spectrum (in $CDCl_3$ solvent):[6] τ 1.00-3.20 (m, $-C_5H_4N$, τ 2.00-3.00 (m, $-P(C_6H_5)_2$), and τ 6.05 (d, J(PCH)= 14 Hz, PCH_2–). Attempts to vacuum distill the ligand resulted in decomposition.

2–(β–Diphenylphosphinoethyl)pyridine. The preparation of this ligand was carried out in a similar manner to that described for 2-(diphenylphosphinomethyl)pyridine. The alcohol, 2-(β-hydroxyethyl)pyridine, (58 g, 0.47 moles) was converted to the 2-(β-chloroethyl)pyridine hydrochloride (54g, 65% yield) with thionyl chloride (58g, 35 ml) by an established procedure.[7] The 2-(β-chloroethyl)pyridine was obtained by neutralizing the hydrochloride salt with Na_2CO_3, extracting with ether, drying the extract over Na_2SO_4 and evaporating the ether. Attempted distillation resulted in solidification (probably polymerization). The oil was stored at –80° until used.

A solution of 2-(β-chloroethyl)pyridine (4.96g, 35.0 mmoles) in 30 ml of THF was slowly (over 1 hr period) added to a solution of 13.0g (32.5 mmoles) of $KP(C_6H_5)_2 \cdot 2D$ in 80 ml of THF under an N_2 atmosphere. The solution was then refluxed for 15 min and filtered through Celite. After evaporation of the solvent under a water-aspirator vacuum, hot butanol was added to the residue. On cooling to –20°C, the butanol solution yielded white crystals (3.60g, 38% yield) of 2-(β-diphenylphosphinoethyl) pyridine. It was characterized by its nmr spectrum (in $CDCl_3$ solvent):[6] τ 0.84-2.63 (m, C_5H_4N), τ 1.76-2.34 (m, $P(C_6H_5)_2$), and τ 6.70-7.60 (m, $-CH_2CH_2$–).

2–(γ–Diphenylphosphinopropyl)pyridine. This ligand was prepared by the same method used for 2-(diphenylphosphinomethyl)pyridine. The alcohol, 3-(2-pyridyl)-1-propanol, (64.4g, 0.469 moles) was converted to 2-(γ-chloropropyl)pyridine hydrochloride (65.0g, 72.4% yield) with thionyl chloride.[7] The hydrochloride salt was neutralized with aqueous Na_2CO_3; extraction of the solution with ether was followed by drying over Na_2SO_4 and then evaporation of the ether. Attempted vacuum distillation resulted in solidification; the oil was stored at –80°C.

A solution of 5.76 g (37.0 mmoles) of 2-(γ-chloropropyl)pyridine in 30 ml of THF was added to a solution of $KP(C_6H_5)_2 \cdot 2D$ (14.4g, 36.0 mmoles) in 50 ml of THF. After the usual reaction procedure was completed, the solution was filtered and the solvent was removed under a water-aspirator vacuum. The remaining oil was purified by toluene elution from a 60 cm alumina chromatography column. The oily product, 2-(γ-diphenylphosphinopropyl)pyridine, was characterized by its nmr spectrum (in $CDCl_3$ solvent):[6] τ 0.88-2.72 (m, $-C_5H_4N$), τ 1.85-2.53 (m, $-P(C_6H_5)_2$), and τ 8.24-9.35 (m, $CH_2)_3$–).

1–Dimethylamino-2-diphenylphosphinoethane. This ligand was previously prepared by a slightly different method.[8] Commercial N,N-dimethylaminoethylchloride (28.0 g, 0.195 moles) was neutralized with KOH in water; the resulting N,N,-dimethylaminoethyl chloride (13.2g, 63% yield) was purified by vacuum (<0.2 mm Hg) distillation. This somewhat unstable compound[9] was stored at –80°C.

Following the procedure for 2-(diphenylphosphinomethyl)pyridine, 7.05 g (65.6 mmoles) of N,N-dimethylaminoethyl chloride in THF (20 ml) and 21.0 g (52.5 moles) of $KP(C_6H_5)_2 . 2D$ in 80 ml of THF were reacted and worked up in the usual manner to give an oily residue (10.6 g) which was purified by vacuum distillation (b.p. 149-153°/0.1 mm Hg). The product, 1-dimethylamino-2-diphenylphosphinoethane, (8.26 g, 61.2% yield) was characterized by its nmr spectrum (neat):[6] τ 2.35-3.00 (m, $-P(C_6H_5)_2$), τ 7.33-7.88 (m, $-(CH_2)_2$-), and τ 7.96 (s, $N(CH_3)_2$).

1-Diethylamino-2-diphenylphosphinoethane. This ligand has been prepared previously.[3,10] It was prepared by a procedure identical to that described for $(CH_3)_2NCH_2CH_2P(C_6H_5)_2$. The reaction of $(C_2H_5)_2N$-CH_2CH_2Cl (2.46 g, 18.0 mmoles) in 10 ml of THF with $KP(C_6H_5)_2 . 2D$ (6.07 g, 15.1 mmoles) in 50 ml of THF yielded an oily residue which when purified by vacuum distillation (b.p. 173-177°/0.1 mm Hg) gave the desired $(C_2H_5)_2NCH_2CH_2P(C_6H_5)_2$ (2.50 g, 58.2% yield). Its nmr spectrum (neat) showed the following bands:[6] τ 2.38-2.93 (m, $-P(C_6H_5)_2$), τ 7.17-8.00 (m, $-CH_2$-), and τ 9.09 (t, $J(CH_2\text{-}CH_3)$ = 7 Hz, NCH_2CH_3).

1-Dimethylamino-3-diphenylphosphinopropane. This ligand was prepared previously.[8] Following the preparation of $(CH_3)_2NCH_2CH_2P(C_6H_5)_2$, the reaction of $(CH_3)_2NCH_2CH_2CH_2Cl$ (4.82 g, 39.7 mmoles) in THF (10 ml) and 13.2 g (33.1 mmoles) of $KP(C_6H_5)_2 . 2D$ in 80 ml of THF yielded an oily residue which was purified by vacuum distillation (b.p. 162-164°/0.1 mm Hg). The product, $(CH_3)_2NCH_2CH_2CH_2P(C_6H_2)_5$, (5.13 g, 57.2% yield) gave the following proton nmr spectrum (neat): τ 2.35-3.00 (m, $-P(C_6H_5)_2$), τ 7.50-8.80 (m, $-CH_2$-) and τ 7.96 (s, $N(CH_3)_2$).

$Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$. A mixture of 2.00 g (7.78 mmoles) of $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$ and 1.89 g (8.56 mmoles) of $Cr(CO)_6$ in xylene (60 ml) was refluxed for 15 hrs under an N_2 atmosphere. On cooling to room temperature, orange crystals of the product (2.45 g, 75% yield) precipitated. They were purified by dissolving them in acetone and precipitating with water; m.p., 148-150° decomp. *Anal.* Calcd. for $C_{20}H_{20}CrNO_4P$: C, 56.8; H, 4.79; N, 3.32. Found: C, 56.6; H, 4.72; N, 2.98. Its nmr spectrum in $CDCl_3$ solvent follows:[6] τ 2.10-2.80 (m, $-P(C_6H_5)_2$), τ

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[6] $Si(CH_3)_4$ = τ10.00; s = singlet; d = doublet; t = triplet; m = multiplet.

[7] *Org. Syntheses Coll. Vol.*, *4*, 333 (1963).

[8] D.W. Meek, P.E. Nicpon, and V.I. Meek, *J. Amer. Chem. Soc.*, *92*, 5351 (1970).

[9] E. Baer and S. Pavanaram, *J. Biol. Chem.*, *236*, 2410 (1961).

[10] G.R. Dobon, R.C. Taylor, and T.D. Walsh, *Inorg. Chem.*, *6*, 1929 (1967).

7.10-7.90 (m, $-(CH_2)_2-$) and τ 7.37 (s, 7.37 (s, N-$(CH_3)_2$).

$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$. A mixture of 2.00 g (7.78 mmoles) of $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$ and 2.26 g (8.56 mmoles) of $Mo(CO)_6$ in 80 ml of *n*-heptane was refluxed for 4 hrs under N_2. On cooling, yellow crystals of the product (3.36 g, 93% yield) precipitated). They were recrystallized from acetone-water; m.p., 152-158° decomp. *Anal.* Calcd. for $C_{20}H_{20}MoNO_4P$: C, 51.6; H, 4.33; N, 3.01. Found: C, 51.5; H, 4.13; N, 2.97. Nmr spectrum (in $CDCl_3$ solvent):[6] τ 2.10-2.70 (m, $-P(C_6H_5)_2$), τ 7.00-7.70 (m, $-(CH_2)_2-$), and τ 7.27 (s, $-(CH_3)_2$).

$W(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$. A mixture of the ligand (2.00 g, 7.78 mmoles) and $W(CO)_6$ (3.02 g, 8.56 mmoles) in 60 ml of mesitylene was refluxed for 8 hrs. On cooling, yellow crystals of the product (4.17 g, 97% yield) precipitated. They were recrystallized from acetone-water; m.p. 196-199°. *Anal.* Calcd. for $C_{20}H_{20}NO_4PW$: C, 43.4; H, 3.65; N, 2.53. Found: C, 43.2; H, 3.53; N, 2.12. Nmr spectrum (in $CDCl_3$):[6] τ 2.10-2.80 (m, $-(C_6H_5)_2$), τ 6.80-7.60 (m, $-(CH_2)_2-$), and τ 7.03 (s, $-(CH_3)_2$).

$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$. This complex was prepared by the method of Dobson, *et al.*,[10] by refluxing a solution of $(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2$ (0.947 g, 3.33 mmoles), $Mo(CO)_6$ (0.875 g, 3.31 mmoles), and *n*-heptane (30 ml) for 4 hrs. Yellow crystals 1.15 g, 71% yield; m.p., 131-134° decomp.) of the product precipitated on cooling to room temperature. *Anal.* Calcd. for $C_{22}H_{24}MoNO_4P$: C, 53.6; H, 4.90. Found: C, 53.4; H, 4.72. Nmr spectrum (in $CDCl_3$):[6] τ 2.12-2.82 (m, $-P(C_6H_5)_2$, τ 6.55-7.63 (m, $-CH_2-$), and τ 8.86 (t, J$(CH_2CH_3)_2$ = 7 Hz, $N(CH_2CH_3)_2$). The parent ion was observed in the mass spectrum of this compound.

$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$. A mixture of 2.00 g (7.38 mmoles) of $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$ and 1.95 g (7.38 mmoles) of $Mo(CO)_6$ in 80 ml of *n*-heptane was refluxed for 54 hrs under N_2. After cooling, yellow crystals of the desired product (3.22 g, 91% yield) precipitated together with some brown decomposition products. Pure complex was obtained by recrystallization 3 times from acetone-water; m.p., 122-124° decomp. *Anal.* Calcd. for $C_{21}H_{22}MoNO_4P$: C, 52.7; H, 4.64; N, 2.93. Found: C, 52.4; H, 4.41; N, 2.75. Nmr spectrum (in $CDCl_3$):[6] τ 2.10-2.80 (m, $-P(C_6H_5)_2$), τ 7.20-8.40 (m, $-(CH_2)_3-$) and τ 7.40 (s, $-N(CH_3)_2$). The parent ion was observed in the mass spectrum of this compound.

$Mo(CO)_4[(C_6H_5)_2PN(H)C_5H_4N]$. A mixture of 1.50 g (5.40 mmoles) of $(C_6H_5)_2PN(H)C_5H_4N$ (prepared according to the literature[11]) and 1.43 g (5.40 mmoles) of $Mo(CO)_6$ in *n*-heptane (40 ml) was refluxed for 3 hrs under N_2. The solvent was removed under water-aspirator vacuum, and the resulting reddish-brown solid was dissolved in a minimum volume (15 ml) of N_2-saturated CH_2Cl_2. After filtration, the solution was concentrated, treated with excess N_2-saturated hexane and cooled at −20°C for several hrs. The product (2.06 g, 78% yield) crystallized slowly from the solution as pale yellow needles. It was again recrystallized from CH_2Cl_2-hexane; m.p. 146-150° decomp. *Anal.* Calcd. for $C_{21}H_{15}MoN_2O_4P$: C, 51.9; H, 3.12; N, 5.76. Found: C, 51.9; H, 3.53; N, 5.68. Nmr spectrum (in $CDCl_3$):[6] τ 2.30-3.55 (m, $-C_5H_4N$), τ 2.15-2.80 ,m, $-P(C_6H_5)_2$) and τ 4.10 (d, J(PNH) = 7 Hz, $-NH$).

$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$. A mixture of 2-(diphenylphosphinomethyl)pyridine (3.10 g, 11.2 mmoles) and 3.25 g (12.3 mmoles) of $Mo(CO)_6$ in 80 ml of toluene was refluxed for 4.5 hrs under N_2. A bright yellow solution developed initially but on heating changed to an opaque reddish-brown suspension within which an increasing accumulation of dark residue was observed precipitating during the refluxing period. The solution was evaporated to dryness under a water-aspirator vacuum, and the dark residue was dissolved in CH_2Cl_2. After filtering off an appreciable amount of insoluble material, the orange-colored filtrate was concentrated, treated with excess hexane and cooled at −20°C for several hrs. The resulting impure reddish-colored solid was recrystallized 5 times from CH_2Cl_2-hexane to give bright yellow crystals of the product (1.53 g, 28% yield; m.p., 148-150° decomp.). *Anal.* Calcd. for $C_{22}H_{16}MoNO_4P$: C, 54.4; H, 3.32; N, 2.89. Found: C, 54.1; H, 3.36; N, 2.95. Nmr spectrum (in $CDCl_3$):[6] τ 2.10-3.08 (m, $-C_5H_4N$), τ 2.23-2.60 (m, $-P(C_6H_5)_2$), and τ 6.07 (d, J(PCH) = 8 Hz, $-CH_2-$).

$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$. A mixture of 2 (β-diphenylphosphinoethyl)pyridine (2.00 g, 6.87 m moles) and 2.00 g (7.58 mmoles) of $Mo(CO)_6$ in 80 ml of toluene was refluxed for 3 hrs under N_2. After cooling, 200 ml of *n*-heptane was added and the solution was cooled in an ice-water bath for 1 hr. Bright yellow crystals (3.10 g, 90% yield) of the product separated from solution. They were purified by recrystallization 3 times from CH_2Cl_2-hexane; m.p., 145-148° decomp. *Anal.* Calcd. for $C_{23}H_{18}MoNO_4P$: C, 55.3; H, 3.63; N, 2.81. Found: C, 55.1; H, 3.72; N, 2.80. Nmr spectrum (in $CDCl_3$):[6] τ 1.42-3.18 (m, $-C_5H_4N$), τ 2.20-2.85 (m, $-P(C_6H_5)_2$), and τ 6.47-7.80 (m, $-(CH_2)_2-$).

$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$. Following the procedure for the preparation of $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$, 3.00 g (9.83 mmoles) of 2-(γ-diphenylphosphinopropyl)pyridine and 3.00 g (11.4 mmoles) of $Mo(CO)_6$ in 80 ml of toluene gave yellow crystals of the product (2.80 g, 56% yield). They were purified by recrystallization 5 times from CH_2Cl_2-hexane; m.p., 133-136° decomp. *Anal.* Calcd. for $C_{24}H_{20}MoNO_4P$: C, 56.1; H, 3.94; N, 2.73. Found: C, 55.4; H, 4.05; N, 2.56. Nmr spectrum (in $CDCl_3$):[6] τ 1.54-3.17 (m, $-C_5H_4N$), τ 2.40-2.90 (m, $-P(C_6H_5)_2$), and τ 8.16-9.20 (m, $-(CH_2)_3-$).

Results and Discussion

Metal carbonyl complexes of the general formula $M(CO)_4(P\text{-}N)$, where M = Cr, Mo, or W, and the P-N bidentate ligand was one of those listed in the Introduction, were prepared by the reaction of $M(CO)_6$ with the desired ligands. They were characte-

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(11) E.W. Ainscough and L.K. Peterson, *Inorg. Chem.*, 9, 2699 (1970).

Table I. Infrared Spectra of $M(CO)_4(P—N)$ Complexes.[a]

	ν(C—O), cm^{-1}			
Compound	*m*[c]	*s*[d]	*s*[d]	*s*[d]
$Cr(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$[b]	2009	1898	1886	1844
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$	2015	1906	1893	1849
$W(CO)_4[(C_6H_5)_2PCH_2CH_2N(CH_3)_2]$[b]	2013	1899	1885	1844
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2N(C_2H_5)_2]$	2014	1906	1891	1849
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2]$	2015	1906	1891	1849
$Mo(CO)_4[(C_6H_5)_2PN(H)C_5H_4N]$	2021	1914	1908	1858
$Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$	2018	1911	1897	1850
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$	2018	1909	1898	1850
$Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$	2018	1909	1898	1850

[a] In $CHCl_3$ solvent except where indicated otherwise. [b] In CH_2Cl_2 solvent. [c] Medium intensity. [d] Strong intensity.

rized by analysis and their proton nmr and infrared spectra (Table I). The four observed ν(C-O) frequencies are consistent with their C_s local symmetry. The frequencies are very similar for all of the complexes, with the pyridine-donor ligands giving complexes with slightly higher ν(C-O) values than those of the alkylamine ligand complexes. In the nmr, the N-methyl protons of $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$ and $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$, τ 7.96, shift to lower field on complexation, τ 7.03 to τ 7.40, as expected for a strong electron-donor group such as the alkyl amines.

Acknowledgment. We are grateful to the National Science Foundation (GP-28480) for support of this research.