in the case of the molybdenum species, these displacements of the sulfur atoms are all in the same rotational sense with respect to the metal–metal axis, and the fourfold axis of rotation is thus preserved. The C_{4h} symmetry is, however, only approximate and the rigorous, *i.e.*, crystallographically imposed, symmetry is only that due to the presence of an inversion center midway between the rhenium atoms.

The dimensions of the bridging sulfate ions in $Re_2(SO_4)_4(H_2O)_2^{2-}$ are also similar to those found in the molybdenum compounds. In each case the S–O bonds that form part of the bridge system are longer than those which do not. In the present case the relevant average S–O distances and the average difference are 1.54 (1), 1.43 (1), and 0.11 (2) Å. In the case of $Mo_2(SO_4)_4^{4-}$ the corresponding quantities are 1.51 (1), 1.45 (1), and 0.06 (2) Å, while for $Mo_2(SO_4)_4^{3-}$ we found 1.52 (1), 1.44 (1), and 0.08 (2) Å. It appears that the greater the formal charge on the pair of metal atoms, *i.e.*, 6+ for $Re_2(SO_4)_4(H_2O)_2^{2-}$, 5+ for $Mo_2(SO_4)_4^{3-}$, and 4+ for $Mo_2(SO_4)_4^{4-}$, the greater the distortion of the sulfate ions in the sense of having longer S–O bonds inside and shorter ones outside. This is certainly a reasonable observation since the more highly charged metal atoms should form the stronger M–O bonds.

The Re–Re distance here, 2.214 (1) Å, is quite similar to those in other species[19] having quadruple bonds (*i.e.*, Re$\equiv$Re), which have been found to vary from 2.198 (1) to 2.251 (2) Å, with most of them being about 2.23 ± 0.01 Å.

A significant difference between this rhenium species and the two molybdenum ones is in the stronger binding of the coaxial water molecules. Here, the difference between the mean Re–O(S) distance and the Re–O(coax.) distance is only 0.26 Å, whereas in the molybdenum compounds the corresponding differences are 0.45 and 0.48 Å. The ability of the rhenium atoms to bind coaxial ligands more strongly may be at least partly due to the higher formal charge on the metal atoms.

The reactivity of the $Re_2(SO_4)_4^{2-}$ ion is greater than that of the $Re_2Cl_8^{2-}$ ion. It is therefore more difficult to isolate and handle but it may have the advantage of being a superior starting material in the preparation of other species.

Acknowledgment. We thank Dr. Thomas R. Webb for many helpful discussions and the National Science Foundation for financial support under Grant No. 33142X.

Registry No. $Na_2Re_2(SO_4)_4 \cdot 8H_2O$, 53567-40-1; $[(n\text{-}C_4H_3)_4N]_2Re_2Cl_8$, 14023-10-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40616B.

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Platinum Metal Complexes of Amine- and Ether-Substituted Phosphines

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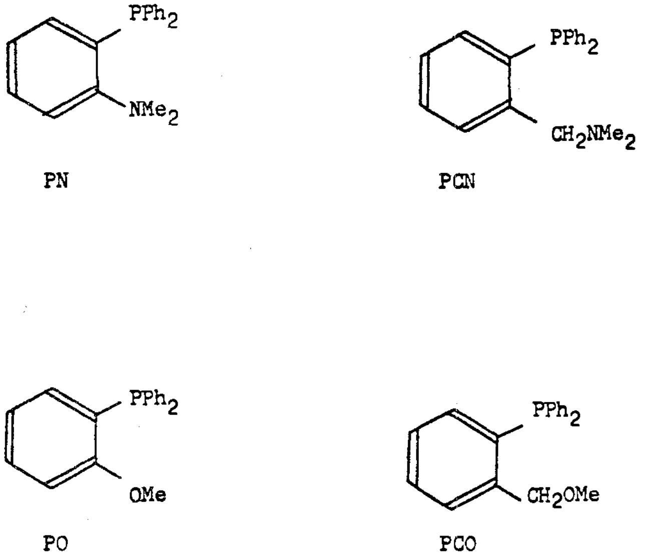
o-Diphenylphosphinoanisole (PO), *o*-diphenylphosphinobenzyl methyl ether (PCO), and *o*-diphenylphosphino-*N*,*N*-dimethylbenzylamine (PCN) have been synthesized. New platinum metal complexes of these ligands and *o*-diphenylphosphino-*N*,*N*-dimethylaniline (PN) have been prepared. Chelate complexes $[Pt(PN)_2](ClO_4)_2$, $PtCl_2(PCN)$, $PdCl_2(PCN)$, $CoCl_2(PCN)$, $RhCl(CO)PCN$, $RuCl_2(PO)_2$, $RuBr_2(PO)_2$, $RuCl_2(PCO)_2$, and $RuCl_2(PN)_2$ have been isolated. ^1H nmr evidence is presented for chelation. The complex $RuCl_2(PO)_2$ will readily undergo carbonylation to give $RuCl_2(CO)(PO)_2$ and $RuCl_2(CO)_2(PO)_2$. The complexes $PtCl_2(PO)_2$, $PtCl_2(PCO)_2$, $PdCl_2(PO)_2$, and $PdCl_2(PCO)_2$ have been prepared, coordination being solely through the phosphines. The position and multiplicity of the metal–chlorine stretching frequencies are used as a guide to stereochemistry. The temperature-dependent ^1H nmr spectrum of $RhCl(CO)PCN$ shows that the two nonequivalent *N*-methyl groups are undergoing fast exchange at room temperature.

Introduction

Recently we have been interested in the synthesis and chemistry of low-valent platinum metal complexes of unsymmetrical chelate ligands.[1,2] The ligands chosen are potentially bidentate, and there is a wide disparity in the coordinating ability of each ligating atom for platinum metals. We have previously shown that a dimethylamino arm of a chelate coordinated to rhodium(I) can readily be displaced by CO, and recent synthetic and kinetic studies by other workers have shown that a similar reaction occurs with other low-valent

Table I. Microanalytical Data

Compd	% C		% H		% N		% Cl		% P	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
PO	78.1	77.9	5.86	6.34						
PCO	78.4	78.1	6.25	6.03						
PCN	79.0	79.0	6.90	6.84	4.39	4.27			9.71	9.75
$PtCl_2(PO)_2$	53.7	53.7	4.03	3.98						
$PtCl_2(PCO)_2$	54.7	55.0	4.36	4.36						
$PdCl_2(PO)_2$	59.9	59.7	4.49	4.37						
$PdCl_2(PCO)_2$	60.8	60.3	4.80	4.74						
$[Pt(PN)_2](ClO_4)_2$	47.8	47.4	3.98	4.02	2.78	2.75	7.06	7.48		
$PtCl_2(PCN)$	43.0	42.7	3.76	3.87	2.39	2.24				
$PdCl_2(PCN)$	50.8	50.2	4.43	4.46	2.82	2.59				
$CoCl_2(PCN)$	56.3	55.6	4.96	4.80	3.13	2.97				
RhCl(CO)PCN	54.4	54.2	4.53	4.51	2.88	2.97				
$RuCl_2(PO)_2$	60.3	60.6	4.53	4.45			9.37	9.66	8.19	8.33
$RuBr_2(PO)_2$	54.0	54.2	4.06	4.13						
$RuCl_2(CO)(PO)_2$	59.7	59.5	4.33	4.57						
$RuCl_2(PCO)_2$	61.2	61.3	4.88	5.10						
$RuCl_2(PN)_2$	60.7	61.4	4.78	5.12	3.52	3.58	9.24	9.07		



PN PCN PO PCO

Figure 1. Structures of the chelate ligands.

metals.[3-5] These complexes are of direct relevance to homogeneous catalysis since the weakly coordinated end of the chelate should undergo ready displacement by incoming π-acceptor ligands. This study discusses our synthetic work leading toward the preparation of low-valent platinum metal chelate complexes of ether-substituted phosphines. We believe that "incipient" coordinately unsaturated complexes can result from this work since the ether function will undergo facile dissociation in the presence of other potential ligands. (Analytical data are given in Table I, and structures of the chelate ligands are given in Figure 1.)

Results and Discussion

Platinum and Palladium. Dihalo complexes of platinum(II) and palladium(II) containing a chelating phosphine ligand have been isolated for a variety of chelates.[6] The five-membered ring chelate complexes $PtCl_2(PN)$ and $PdCl_2(PN)$ have been isolated by Venanzi, *et al.*;[7] however, when later workers attempted to chelate the Sb and N atoms in *o*-dimethylaminophenyldimethylstibine to platinum(II), the products were monodentate complexes of the type PtX_2L_2, where only the antimony was coordinated.[8] A similar result was found with *o*-methoxyphenyldimethylstibine where coordination of the ether function could not be effected.

The unsymmetrical chelate ligand PCN resembles PN in readily giving the chelate complexes $PtCl_2(PCN)$ and $PdCl_2(PCN)$. The complexes are too insoluble for the ^1H nmr spectrum to be obtained. The ir spectra show two bands at 284 and 338 cm^{-1} for $PtCl_2(PCN)$ and at 280 and 337 cm^{-1} for $PdCl_2(PCN)$. The observation of two separate bands for the metal–chlorine stretching frequency is in agreement with the cis stereochemistry of the chlorines. A further complex which has been isolated containing a chelating phosphorus–nitrogen ligand is $[Pt(PN)_2](ClO_4)_2$ (Λ_m = 46 in nitrobenzene), which was prepared according to eq 1. The ^1H nmr

$$PtCl_2(PN) + PN + 2AgClO_4 \rightarrow [Pt(PN)_2](ClO_4)_2 + 2AgCl \qquad (1)$$

spectrum of this complex shows a doublet separated by 2 Hz and centered at τ 6.64. The ^{195}Pt satellites (J_{PtH} = 18 Hz) show a similar doublet separation. The splitting is due to coupling between the dimethylamino group and a coordinated phosphorus. Since the chemical shift of the dimethylamino group is downfield from that of free PN (τ 7.35), the dimethylamino groups are coordinated to platinum. The value of J_{PtH} is smaller than observed for $PtX_2(PN)$ (X = Br, I); however, these authors reported no coupling of the dimethylamino groups to ^{31}P. The observation of a long-range J_{PH} coupling is suggestive of a cis stereochemistry for $[Pt(PN)_2]^{2+}$. This geometry would place the dimethylamino groups trans to phosphorus, and since a coupling to a trans phosphorus is anticipated to be considerably larger than coupling to a cis phosphorus, the magnitude of J_{PH} in this stereochemistry may be sufficient to be observed.

The ligands PO[9] and PCO react readily with chloroplatinum(II) and chloropalladium(II) salts, but in each case only monodentate complexes of type MCl_2L_2 could be isolated. The complexes $PtCl_2(PO)_2$, $PtCl_2(PCO)_2$, $PdCl_2(PO)_2$, and $PdCl_2(PCO)_2$ are sparingly soluble in organic solvents. The metal–chlorine stretch is a single sharp line which suggests that these new complexes have a trans stereochemistry (Table II). This conclusion is further substantiated by the occurrence of a single band in the Raman spectrum of the complexes $PtCl_2(PCO)_2$, $PdCl_2(PO)_2$, and $PdCl_2(PCO)_2$ at 333, 299, and 302 cm^{-1}, respectively. The uncoordinated ether shows ν_{OAr} and ν_{OMe} coincident with free ligand positions.

Cobalt and Rhodium. The complex $CoCl_2(PN)$ has been reported previously,[7] and the six-membered chelate complex $CoCl_2(PCN)$ can be readily isolated. The magnetic moment in the solution $CHCl_2$–C_6H_{12} (9:1) is 4.10 BM. The visible spectrum as a 10^{-3} *M* solution in acetone shows absorption bands at 5690 Å (ε 360), 6430 Å (ε 330), and 6900 Å (ε 470). These data are consistent with a tetrahedral cobalt(II) complex.

The synthesis and chemistry of RhCl(CO)PN have been recently described,[2] and we have now found that the six-membered ring chelate complex with PCN is readily isolable. The position of $\nu_{C=O}$ in RhCl(CO)PCN (2005 cm^{-1}) suggests that CO lies trans to phosphorus;[10] the same stereochemistry was found in RhCl(CO)PN. The compound RhCl(CO)PCN

Table II. Spectral Data

Compd	Ir, cm^{-1}	^1H nmr	
		Me	CH_2
PO	1245 (Ar–O) 1018 (Me–O)[a]	6.20	
PCO	1024 (Me–O)	6.68	5.32
PN		7.35	
PCN		7.97	6.79
$PtCl_2(PO)_2$	335 (Pt–Cl), 1255 (Ar–O), 1020 (Me–O)		
$PtCl_2(PCO)_2$	340 (Pt–Cl),[b] 1020 (Me–O)		
$PdCl_2(PO)_2$	350 (Pd–Cl),[c] 1241 (Ar–O), 1018 (Me–O)		
$PdCl_2(PCO)_2$	355 (Pd–Cl),[d] 1026 (Me–O)		
$[Pt(PN)_2](ClO_4)_2$		6.64	
$PtCl_2(PCN)$	284, 338 (Pt–Cl)		
$PdCl_2(PCN)$	280, 337 (Pd–Cl)		
$CoCl_2(PCN)$			
RhCl(CO)(PCN)	290 (Rh–Cl), 2005 (C=O)	7.38	6.67
$RuCl_2(PO)_2$	328 (Ru–Cl), 1220 (Ar–O), 990 (Me–O)	5.37	
$RuBr_2(PO)_2$	1225 (Ar–O), 1005 (Me–O)	5.37	
$RuCl_2(CO)(PO)_2$	1910 (C=O), 1245 (Ar–O)		
$RuCl_2(PCO)_2$	325 (Ru–Cl), 1040 (Me–O)	6.32	4.78
$RuCl_2(PN)_2$	319 (Ru–Cl)	6.73	

[a] These assignments of ν_{Me-O} are tentative since the frequencies are rather lower than anticipated. The assignments in the PCO cases are even less reliable since the presence of an unsymmetrical aliphatic ether may lead to overlapping stretching frequencies. [b] 333 cm^{-1} in the Raman spectrum. [c] 299 cm^{-1} in the Raman spectrum. [d] 302 cm^{-1} in the Raman spectrum.

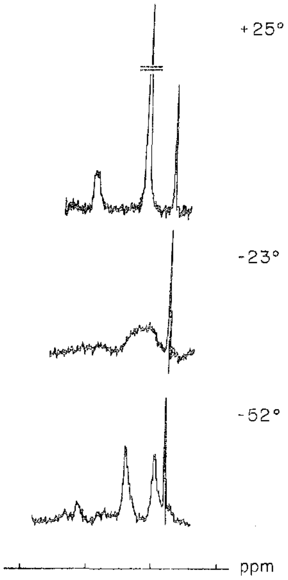


Figure 2. Temperature-dependent methylene and methyl ^1H nmr regions in RhCl(CO)PCN. The sharp single upfield peak is due to acetone.

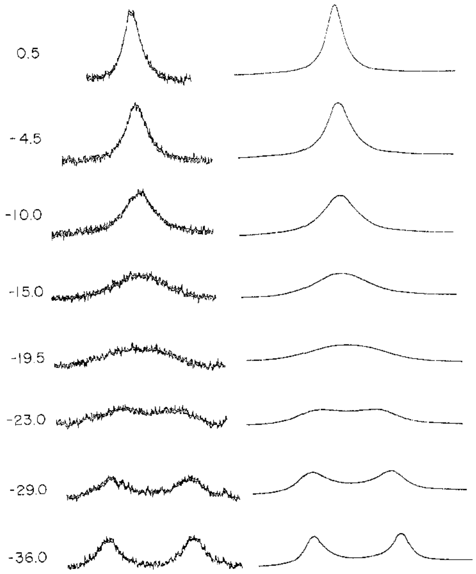


Figure 3. Line shape analysis on the methyl region of the temperature-dependent ^1H nmr spectrum of RhCl(CO)PCN (temperatures in °C).

is less basic than RhCl(CO)PN since the former complex appears to be unaffected by exposure to air either in solution or in the solid state. The lower nucleophilicity of the PCN complex is shown by comparison of the reactivities toward allyl chloride: with RhCl(CO)PN the σ-allyl complex $RhCl_2(C_3H_5)CO(PN)$ is readily obtained but with RhCl(CO)PCN the reaction is reversible. The ^1H nmr of RhCl(CO)PCN shows resonances at τ 7.38 and 6.67 due to NMe_2 and NCH_2, respectively. Models show that the two *N*-methyl resonances should be nonequivalent. On cooling the sample to −52° the resonance broadens and then splits into two lines. The methylene resonance at lower field is also temperature dependent as shown in Figure 2. The ^1H nmr spectrum of the AX system is shown at a 500-Hz width showing the fast (25°), intermediate (−23°), and slow (−52°) exchange rates. The upfield acetone peak remains unchanged showing that there is no crystallization of the complex or increasing of viscosity causing significant line broadening at the lower temperature. A line shape analysis of this nmr spectrum has been carried out (Figure 3) which gives a calculated activation energy of 8.8 kcal/mol for the exchange process. The spectrum shown in Figure 3 is obtained at a width of 100 Hz for the methyl resonance. The temperature range is narrower than that shown in Figure 2 since it is only useful to obtain data in the appropriate rate range for the nmr time scale. The simulated spectra shown alongside were fitted using a DNMR-3 computer program. The spectra were matched and from the temperature–rate correspondence the activation energy was obtained. We believe that the collapse of the separate res-

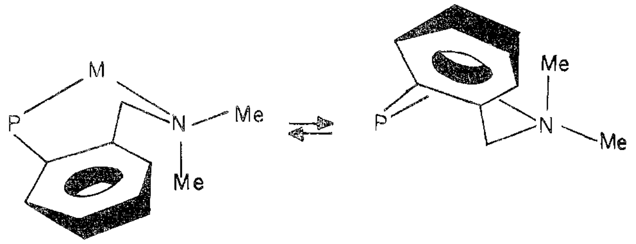


Figure 4. Diagrammatic representation of the proposed conformation interconversion of the PCN chelate ring in RhCl(CO)PCN.

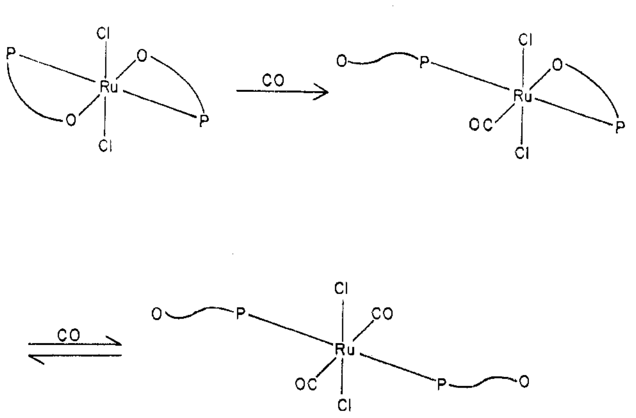


Figure 5. Carbonylation reaction of $RuCl_2(PO)_2$.

onances is a consequence of a conformational interconversion as shown in Figure 4, although we cannot at present rule out a dissociative process.

Ruthenium. Triphenylphosphine will readily stabilize divalent ruthenium as shown by the formation of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$.[11] This led to the preparation of ruthenium(II) complexes containing chelating phosphines[12] or two monodentate phosphines and two other ligands such as amines,[13] nitriles,[13] and sulfur or oxygen ligands.[14] We have found that the compound PN will form the chelate complex $RuCl_2(PN)_2$. The nitrogens are coordinated since the resonance for the dimethylamino group is at τ 6.75, representing a downfield shift of 36 Hz from free PN. The ir spectrum below 400 cm^{-1} shows a single band at 319 cm^{-1} suggesting a mutually trans arrangement for the chlorines. The ligands PO and PCO readily react with hydrated ruthenium trichloride to form the complexes $RuCl_2(PO)_2$ and $RuCl_2(PCO)_2$. The Ru–Cl stretching frequencies are single bands at 328 and 325 cm^{-1} for the PO and PCO complexes, respectively, suggesting trans chlorines. The ^1H nmr spectrum of $RuCl_2(PO)_2$ shows a resonance due to OMe at τ 6.20, which represents a downfield shift of 0.83 ppm from the position of this resonance in free PO. A deshielding of the methoxy resonance corresponds to a similar effect in PN complexes[2,7] and can be taken as indicative of coordination of the ether oxygen. The ^1H nmr spectrum of $RuCl_2(PCO)_2$ shows resonances at τ 6.32 (OMe) and 4.78 (OCH_2). For this PCO complex the OMe and OCH_2 resonance positions are shifted downfield by 21 and 32 Hz, respectively, from their positions in free PCO. The downfield shift of both resonances on coordination of the ether is to be anticipated and correlates with the downfield shift of both NMe_2 and NCH_2 on chelation of PCN in RhCl(CO)PCN. These compounds with an ether group coordinated to ruthenium represent one of the very few examples where an acyclic ether will bond directly to a platinum metal in a lower oxidation state.

When CO is bubbled through a solution of $RuCl_2(PO)_2$ carbonylation readily occurs to give $RuCl_2(CO)(PO)_2$ and then $RuCl_2(CO)_2(PO)_2$ (Figure 5). The latter compound undergoes facile decarbonylation but the monocarbonyl complex can be characterized. When CO is bubbled through a solution of $RuCl_2(PN)_2$ under identical conditions, no reaction occurs. This reaction is significant in that it verifies that with Ru(II) a coordinated methyl ether will undergo more facile dissociation than a coordinated dimethylamino group.

Experimental Section

Melting points were obtained on a hot-stage microscope and are uncorrected. ^1H nmr spectra were obtained on Varian A-60, T-60, or EM 360 spectrometers, and ir spectra on Perkin-Elmer 700 or 457 spectrometers. Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz., by Galbraith Inc., Knoxville, Tenn., or by us on a Perkin-Elmer Model 240 elemental analyzer. All preparations were carried out in an inert atmosphere. Raman spectra were obtained on solid samples using a Cary Model 81 spectrometer with a laser exciting line at 5682 Å.

o-Diphenylphosphinoanisole, o-$MeOC_6H_4PPh_2$ (PO). To the Grignard reagent prepared from *o*-bromoanisole (24.7 g) and magnesium (3.2 g) was slowly added chlorodiphenylphosphine (17.2 g). The product was recrystallized from ethanol; yield 10.0 g (44%), mp 120–121°.

o-Diphenylphosphinobenzyl Methyl Ether, o-$MeOCH_2C_6H_4PPh_2$ (PCO). *o*-Bromotoluene (41.9 g) was treated with bromine under the influence of light to give *o*-bromobenzyl bromide. This compound was converted into *o*-bromobenzyl methyl ether (9.86 g; bp 107° (16 mm)) with sodium methoxide. Conversion to the Grignard reagent followed by slow addition of chlorodiphenylphosphine (12.1 g) gave the product; yield 5.98 g (40%); mp 91°.

o-Diphenylphosphino-*N*,*N*-dimethylbenzylamine (PCN). $C_6H_5CH_2NMe_2$ (17.7 g, 0.14 mol) was added to ether (100 ml) containing butyllithium (110 ml of 1.66 *M*; 0.18 mol). After standing of the mixture overnight at room temperature, orange crystals are deposited. After 18 hr this mixture was cooled to −78° and chlorodiphenylphosphine (26 g; 0.12 mol) in ether (100 ml) was added. The mixture was allowed to warm to room temperature and stirred for 1 hr. Ethanol (5 ml) was added and then water (100 ml). The product was ether extracted and dried with sodium sulfate. Purification by distillation gave an oil, bp 202–204° (0.5 mm); yield *ca.* 16 g (40%). The compound slowly gave colorless crystals, mp 54–56°.

Dichlorobis(o-diphenylphosphinoanisole)platinum, $PtCl_2(PO)_2$. To an aqueous solution of K_2PtCl_4 (200 mg) was added PO (312 mg) in warm ethanol. The colorless precipitate was filtered, washed with ethanol and ether, and dried *in vacuo*; yield 352 mg (86%); mp >300°.

Dichlorobis(o-diphenylphosphinobenzyl methyl ether)platinum, $PtCl_2(PCO)_2$. To a solution of K_2PtCl_4 (50 mg) in water (1.5 ml) was added a suspension of PCO (88 mg) in ethanol (18 ml). The reaction was stirred for 3 hr. The complex was filtered, washed consecutively with water, ethanol, and ether, and dried *in vacuo*; yield 74 mg (70%); mp 267°.

Dichlorobis(o-diphenylphosphinoanisole)palladium, $PdCl_2(PO)_2$. To an ethanolic solution of Na_2PdCl_4 (100 mg) was added PO (221 mg) in warm ethanol. The yellow precipitate was filtered, washed consecutively with water, ethanol, and ether, and dried *in vacuo*; yield 197 mg (76%); mp 208–210°.

Dichlorobis(o-diphenylphosphinobenzyl methyl ether)palladium, $PdCl_2(PCO)$. A mixture of $PdCl_2$(1,5-COD) (43 mg) and PCO (101 mg) in methanol (15 ml) was refluxed for 10 min. The mixture was cooled slowly, and the yellow precipitate was filtered. After being washed with methanol and ether, the complex was dried *in vacuo*; yield 116 mg (98%); mp 275°.

Bis(o-diphenylphosphino-*N*,*N*-dimethylaniline)platinum Bis(perchlorate), $[Pt(PN)_2](ClO_4)_2$. $PtCl_2(PN)$ (140 mg) in CH_3CN was treated with PN (150 mg) and silver perchlorate (140 mg) in CH_3CN (4 ml). After being stirred for 10 min, the reaction was filtered. After removal of the solvent on a rotary evaporator, the residue was dissolved in the minimum volume of CH_3CN. A mixed solvent containing ethanol and ether was added to the solution until it became cloudy. After crystallization the complex was filtered and dried *in vacuo*; yield 150 mg (61%); mp 200° dec.

Dichloro(o-diphenylphosphino-*N*,*N*-dimethylbenzylamine)palladium, $PdCl_2(PCN)$. Na_2PdCl_4 (200 mg) in methanol (10 ml) was filtered and treated with excess PCN in methanol. The product was recrystallized from dichloromethane and methanol; yield 245 mg (49%); mp 175° (darkens).

Dichloro(o-diphenylphosphino-*N*,*N*-dimethylbenzylamine)cobalt, $CoCl_2(PCN)$. PCN (550 mg) in ethanol (2 ml) was added to hydrated cobalt chloride (200 mg) in ethanol (20 ml). The mixture was stirred for 1 hr. The blue crystals were filtered and dried *in vacuo* at 78° for 24 hr; yield 344 mg (90%); mp 243–244°. Recrystallization can be carried out from acetone and ethanol.

Chlorocarbonyl(o-diphenylphosphino-*N*,*N*-dimethylbenzylamine)rhodium, RhCl(CO)PCN. To a solution of excess PCN in acetone (7 ml) was added $Rh_2Cl_2(CO)_4$ (128 mg). A vigorous effervescence occurred. After stirring of the mixture for 30 min the yellow compound was filtered and washed with ether; yield 280 mg (87%); mp 287°.

Dichlorobis(o-diphenylphosphinoanisole)ruthenium, $RuCl_2(PO)_2$. A mixture of hydrated ruthenium trichloride (1.02 g) and PO (4.56 g) was refluxed in ethanol for 5 hr. The burgundy-colored crystals were filtered and dried *in vacuo*; yield 228 mg (77%); mp 263° dec.

Dibromobis(*o*-diphenylphosphinoanisole)ruthenium, RuBr$_2$(PO)$_2$. RuCl$_2$(PO)$_2$ (200 mg) was refluxed with LiBr (460 mg) for 2 hr in acetone (25 ml). The complex was obtained as a violet powder; yield 186 mg (83%).

Dichlorocarbonylbis(*o*-diphenylphosphinoanisole)ruthenium, RuCl$_2$(CO)(PO)$_2$. Through a purple solution of RuCl$_2$(PO)$_2$ (200 mg) in CH$_2$Cl$_2$ (10 ml) was bubbled CO until the solution became yellow. The solution was filtered through Celite and diluted with methanol. Removal of CH$_2$Cl$_2$ gave yellow crystals which were a mixture of monocarbonyl and dicarbonyl ($\nu_{\mathrm{C{=}O}}$ at 1910 and 2000 cm^{-1}, respectively). The mixture was dissolved in CH$_2$Cl$_2$ and nitrogen was bubbled through the solution until the monocarbonyl was obtained pure. Recrystallization gave the yellow complex, mp 204° dec.

Dichlorobis(*o*-diphenylphosphinobenzyl methyl ether)ruthenium, RuCl$_2$(PCO)$_2$. By use of the procedure for RuCl$_2$(PO)$_2$ with hydrated ruthenium trichloride (82 mg) and PCO (383 mg) the complex was obtained as burgundy-colored crystals; yield 221 mg (90%); mp 239° dec.

Dichlorobis(*o*-diphenylphosphino-*N*,*N*-dimethylaniline)ruthenium, RuCl$_2$(PN)$_2$. Hydrated ruthenium trichloride (100 mg) in water (3 ml) was added to refluxing ethanol followed by PN (370 mg). After 5 min a red precipitate formed. The solution was cooled. The complex was filtered, washed with ethanol and ether, and dried *in vacuo*; yield 160 mg (53%). The complex can be recrystallized from dichloromethane and methanol.

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Registry No. PO, 53111-20-9; PCO, 13175-76-3; PCN, 53881-33-7; PtCl$_2$(PO)$_2$, 53043-32-6; PtCl$_2$(PCO)$_2$, 53897-05-5; PdCl$_2$(PO)$_2$, 53897-06-6; PdCl$_2$(PCO)$_2$, 53897-07-7; [Pt(PN)$_2$](ClO$_4$)$_2$, 53896-98-3; PtCl$_2$(PCN), 53897-09-9; PdCl$_2$(PCN), 53897-10-2; CoCl$_2$(PCN), 53897-11-3; RhCl(CO)PCN, 53897-08-8; RuCl$_2$(PO)$_2$, 53897-21-5; RuBr$_2$(PO)$_2$, 53897-13-5; RuCl$_2$(CO)(PO)$_2$, 53897-22-6; RuCl$_2$(PCO)$_2$, 53897-23-7; RuCl$_2$(PN)$_2$, 53897-24-8; *o*-bromoanisole, 578-57-4; chlorodiphenylphosphine, 1079-66-9; *o*-bromobenzyl methyl ether, 52711-30-5; *N*,*N*-dimethylbenzylamine, 103-83-3; Rh$_2$Cl$_2$(CO)$_4$, 14523-22-9.

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Unsymmetrical Bis-Phosphorus Ligands. VII. Metal Complexes with Diphenylphosphinodiphenylphosphorylalkanes[1]

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The syntheses of some mixed phosphine–phosphine oxide ligands, Ph$_2$P(O)CHRPPh$_2$ (R = H, CH$_3$, *n*-Pr), are described. Some phosphonium salts and chelate coordination compounds with mercury and cadmium halides and chromium, molybdenum, and tungsten carbonyls are reported with ^{31}P nmr, pmr, and phosphoryl stretching frequency data. Large variations in ^{31}P chemical shifts and J_{PP} and unusual changes in the phosphoryl stretching frequencies on coordination are observed.

Introduction

Previously we have reported the synthesis and phosphorus-31 nmr spectra of coordination compounds containing chelating bidentate phosphorus ligands with chemically different phosphorus atoms.[2,3] Such ligands must necessarily have a cis stereochemistry, resulting usually in simple phosphorus-31 nmr spectra with directly observable phosphorus–phosphorus coupling. There is currently much interest in determining the variation of P–P coupling constants with stereochemistry.[4-8] To date, all of the complexes reported were of the P(III)–P(III) type. Here we report a modification of an earlier synthesis[9] for Ph$_2$P(S)CH$_2$P(O)Ph$_2$ to yield the new ligands Ph$_2$P(O)CHRPPh$_2$ (where R is H, CH$_3$, *n*-C$_3$H$_7$), as well as their methylphosphonium salts, [Ph$_2$P(O)CHRPPh$_2$Me]$^+$[PF$_6$]$^-$, and some metal complexes. These represent the first reported complexes with ligands containing both a phosphine and a phosphine oxide involved in the coordination sphere, although a complex has been reported of a phosphine–phosphine oxide in which the phosphoryl group is not coordinated.[10]

Experimental Section

Physical Measurements. Routine ^{31}P nmr spectra were recorded with a Varian DP60 spectrometer at 24.3 MHz in 13-mm stationary tubes with a 2-mm reference tube of 85% H$_3$PO$_4$ inserted concentrically by means of a serum stopper. More accurate chemical shifts and coupling constants were obtained at 36.43 MHz with a Bruker HFX-90, Diglab FTS-3 system on about 0.3 g of sample in 1.5 ml of CH$_2$Cl$_2$ or CHCl$_2$CN placed in a 10-mm tube with a concentric 3-mm tube containing CBrF$_2$CBrF$_2$ to provide a ^{19}F lock. Spectra were recorded at 28°, generally employing about 500 pulses per spectrum. Chemical shifts were measured with respect to external 85% H$_3$PO$_4$ and are accurate to 0.1 ppm.

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer with TMS as an internal standard.

Infrared spectra were recorded on cyclohexane solutions with a cyclohexane blank in NaCl cells with a Perkin-Elmer Model 225

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