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 ($\nu_{C=O}$ 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.

References and Notes

(1) T. B. Rauchfuss and D. M. Roundhill, *J. Organometal. Chem.*, **59**, C30 (1973).
(2) T. B. Rauchfuss and D. M. Roundhill, *J. Amer. Chem. Soc.*, **96**, 3098 (1974).
(3) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627 (1974).
(4) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 632 (1974).
(5) W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organometal. Chem.*, **66**, C11 (1974).
(6) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).
(7) H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi, *J. Chem. Soc. A*, 5210 (1965).
(8) B. Zarli, L. Volponi, and G. De Paoli, *Inorg. Nucl. Chem. Lett.*, **9**, 997 (1973).
(9) Since the completion of this work a report on the synthesis of PO and PtCl$_2$(PO)$_2$ has appeared: C. E. Jones, B. L. Shaw, and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 992 (1974). In an earlier publication this group had considered that electron donation from a methoxyl group strongly influenced the nucleophilicity of iridium(I) toward oxidative addition: E. M. Miller and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 480 (1974).
(10) W. Hieber and R. Kummer, *Chem. Ber.*, **100**, 148 (1967).
(11) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).
(12) J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, **11**, 2714 (1972).
(13) J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, 1749 (1969).
(14) L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J. Chem. Soc., Dalton Trans.*, 1770 (1973).

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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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Table I. Analytical and Physical Data for Diphenylphosphinodiphenylphosphorylalkane Compounds

			% C		% H		% other (element)	
Compd	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
$(C_6H_5)_2P(O)CH_2P(C_6H_5)_2$	White	191-192	75.00	74.52	5.54	5.49	15.47 (P)	15.30 (P)
$(C_6H_5)_2P(O)CH(CH_3)P(C_6H_5)_2$	White	183-184	75.35	75.98	5.84	5.62	14.95 (P)	14.86 (P)
$(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2$	White	165-166	76.00	75.42	6.38	6.40	14.00 (P)	13.70 (P)
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2CH_3]PF_6$	White	101-103	55.72	56.38	4.50	4.46	16.58 (P)	16.71 (P)
$[(C_6H_5)_2P(O)CH(CH_3)P(C_6H_5)_2CH_3]PF_6$	White	104-106	56.45	56.69	4.74	4.61		
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2CH_3]PF_6$	White	105-107	57.81	56.76	5.19	5.01		
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]Cr(CO)_4$	Yellow	161-162 dec	63.37	63.11	4.65	4.78		
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]Mo(CO)_4$	Yellow	175-177 dec	59.09	58.48	4.34	4.44		
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]W(CO)_4$	Orange	150-155 dec	52.05	49.69	3.82	4.00		
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]HgCl_2$	White	217-219	44.69	44.49	3.30	3.32	9.22 (P)	9.11 (P)
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]HgBr_2$	White	130-133	39.46	39.01	2.91	2.70		
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]CdBr_2$	White	238-239	44.64	43.82	3.30	3.25	23.76 (Br)	24.18 (Br)
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]CdBr_2$	White	176-178	47.05	46.67	3.95	4.13	22.36 (Br)	22.38 (Br)
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]HgCl_2$	White	239-241	47.84	47.76	4.30	3.96	8.51 (P)	8.67 (P)
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]HgBr_2$	White	224-226	41.88	41.41	3.51	3.51	7.72 (P)	7.71 (P)
$(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)(C_2H_5)$	White	202-203	68.47	68.38	6.02	6.11	16.82 (P)	16.61 (P)
$(C_6H_5)_2P(O)CH(CH_3)P(O)(C_6H_5)_2$	White	261-262	72.55	72.58	5.62	5.71		

spectrometer and calibrated with polystyrene film for $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]Cr(CO)_4$ and $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]Mo(CO)_4$. Other infrared spectra were recorded of KBr pellets with a Perkin-Elmer 337 infrared spectrophotometer and calibrated with polystyrene film.

Melting points were determined with a Mel-Temp apparatus and are uncorrected.

Microanalyses were performed by Dr. Franz Kasler, University of Maryland. The analytical and physical data appear in Table I.

Preparation of $Ph_2P(O)CHRPPh_2$, R = H, CH_3, $n\text{-}C_3H_7$. These compounds were prepared by significantly modifying a procedure, reported by Seyferth[9] for the preparation of $Ph_2P(O)CH_2P(S)Ph_2$. Triphenylphosphine oxide (generally 20–30 g) and 100 ml of anhydrous ether in a nitrogen atmosphere were treated with a stoichiometric amount of the appropriate alkyllithium (MeLi and EtLi were prepared from the alkyl bromides and Li and standardized by the method of Seyferth;[9] *n*-BuLi was purchased from Foote Mineral Co.) added dropwise from an addition funnel to the stirred ether solution cooled with an ice bath. The $Ph_3P{=}O$ dissolved and the solution ranged in color from yellow (MeLi) to red (BuLi). Upon complete addition, the solution was stirred for 20 min at room temperature, transferred under N_2 to a clean funnel, and added dropwise to a stoichiometric amount of Ph_2PCl in 50 ml of deoxygenated anhydrous benzene. The benzene solution was maintained at 15–20° with a cold-water bath and stirred vigorously during the addition. Then the bath was removed and stirring was continued for 1 hr. The solvents were removed by vacuum evaporation and 150 ml of $CHCl_3$ was added to the residue. The mixture was filtered under N_2 through a $CHCl_3$ slurry of diatomaceous earth. Removal of the solvents left a white waxy solid which was redissolved in EtOH. On standing of the mixture for 2 days, $Ph_2P(O)CH_2PPh_2$ (26.0 g, 60% based on 30 g of $Ph_3P{=}O$) and $Ph_2P(O)CHCH_3PPh_2$ (9.4 g, 25% based on 22.5 g of $Ph_3P{=}O$) crystallized. They were recrystallized from absolute EtOH under N_2. The residue containing $Ph_2P(O)CH(n\text{-}C_3H_7)PPh_2$ was redissolved in $CHCl_3$ and passed through a 25-cm column (5-cm diameter) of alumina under N_2. Addition of a small amount of hexane and slow removal of the solvents with a stream of nitrogen yielded crystals of the compound (14.7 g, 48% based on 20.0 g of $Ph_3P{=}O$).

These compounds are air stable when solid but oxidize slowly when in solution. In each case, a phosphorus-31 nmr spectrum of the crude mixture demonstrated that it contained about 80% of the desired product, but further attempts to obtain more of the product inevitably failed. The compounds show a marked tendency to form oils when only minor amounts of phosphorus-containing impurities (even less than 5%) are present.

As reported by Seyferth,[9] *et al.*, and in our early attempts to synthesize these compounds, Ph_2PCl was added to the organolithium phosphine oxide reagent. Yields were poor in both cases. Furthermore, a phosphorus-31 nmr spectrum of the crude reaction mixture demonstrated that it contained only minor amounts of the desired product. Clearly, the inverse addition procedure is superior.

Preparation of $[Ph_2P(O)CHRPPh_2Me]^+[PF_6]^-$. One gram of the appropriate ligand in 50 ml of anhydrous benzene and sufficient THF to ensure solution was placed in a plastic screw cap bottle under N_2. Methyl bromide (5 ml condensed under N_2) was added and the cap was screwed on tightly and allowed to stand overnight. The solution was added to 200 ml of anhydrous ether, stirred several hours, and filtered. The compounds proved too hygroscopic for analysis and were converted to the hexafluorophosphate salts by addition of a water solution of the compound to an excess of an NH_4PF_6 solution.

Preparation of Mercury and Cadmium Complexes. The ligand (0.80 g) was dissolved in 100 ml of ethanol in a nitrogen atmosphere. A stoichiometric amount of the appropriate metal halide dissolved in a minimum amount of ethanol was added to the ligand and the solution was stirred overnight. The volume was reduced to 50 ml; the solid was removed by filtration, washed with ethanol, and dried at room temperature and 0.2 Torr.

Preparation of $[Ph_2P(O)CH(n\text{-}C_3H_7)PPh_2]M(CO)_4$, M = Cr, Mo, W. The ligand (3.0 g, 6.8 mmol) and a 10% molar excess of the appropriate metal hexacarbonyl in 10 ml of anhydrous diethylene glycol dimethyl ether (freshly distilled from sodium–benzophenone) were placed in a 50-ml flask under N_2 and heated to 160°. The course of the reaction was monitored crudely by measuring the volume of CO evolved using a buret inverted in a beaker of oil. The solvents were removed with a rotary evaporator, and the residue was treated with 50 ml of CH_2Cl_2 and filtered. The complex was precipitated rapidly from the filtrate by addition of hexane, collected by filtration, washed with small amounts of MeOH, and finally recrystallized from CH_2Cl_2–MeOH.

Results and Discussion

The diphenylphosphinodiphenylphosphorylalkanes are made by the reaction of triphenylphosphine oxide with an organolithium reagent followed by reaction of the resulting diphenylphosphorylalkyllithium reagent with diphenylphosphinous chloride[9]

$$Ph_3P(O) + RCH_2Li \rightarrow Ph_2P(O)CH(R)Li + C_6H_6$$
$$(R = H, CH_3, n\text{-}C_3H_7)$$

$$Ph_2P(O)CH(R)Li + Ph_2PCl \rightarrow Ph_2P(O)CH(R)PPh_2 + LiCl$$

However, it is important that the phosphorylalkyllithium reagent be added to the phosphinous chloride, which is in excess during the addition; otherwise the yields are low. Presumably, if the phosphorylalkyllithium is in excess, it will metalate the desired product and lead to a complicated reaction mixture

$$Ph_2P(O)CHRLi + Ph_2P(O)CHRPPh_2 \rightarrow Ph_2P(O)CH_2R + Ph_2P(O)C(R)LiPPh_2$$

Side products were indicated by ^{31}P spectra of the crude reaction mixture but were not isolated.

Several attempts to make $Ph_2P(O)CH_2PPhEt$ by using ethylphenylphosphinous chloride instead of diphenylphosphinous chloride resulted in a mixture of products which were not successfully separated. Phosphorus-31 nmr measurements of the product mixture indicated the probable presence of both $Ph_2P(O)CH_2PPhEt$ and $Ph_2PCH_2P(O)PhEt$,

Table II. Phosphorus-31 Nmr and Infrared Data for Diphenylphosphinodiphenylphosphorylalkane Compounds

	Nmr solvent	δ_P[a]	$\delta_{P=O}$[a]	Δ_P[b]	$\Delta_{P=O}$[b]	J_{PP}[c]	$\nu_{P=O}$[d]	$\Delta\nu$[e]
$(C_6H_5)_2P(O)CH_2P(C_6H_5)_2$	CH_2Cl_2	28.4 d	−27.7 d			50 ± 1	1177	
$(C_6H_5)_2P(O)CH(CH_3)P(C_6H_5)_2$	CH_2Cl_2	12.3 d	−33.6 d			62 ± 1	1172	
$(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2$	CH_2Cl_2	9.5 d	−32.7 d			65 ± 1	1170	
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2CH_3]Br$	CH_2Cl_2	−20.8 d	−24.6 d	−49.2	+3.1	12 ± 1	1194	+17
$[(C_6H_5)_2P(O)CH(CH_3)P(C_6H_5)_2CH_3]Br$	CH_2Cl_2	−28.9 d	−31.8 d	−40.3	+1.8	4.2 ± 0.5	1198	+26
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2CH_3]Br$	CH_2Cl_2	−27.9 d	−30.9 d	−37.4	+1.8	3.5 ± 0.5	1194	+24
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]Cr(CO)_4$	CH_2Cl_2	−68.4 d	−58.2 d	−77.9	−25.5	54 ± 2	1135[f]	
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]Mo(CO)_4$	CH_2Cl_2	−48.3 d	−57.1 d	−57.8	−24.4	56 ± 2	1134[g]	−36
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]W(CO)_4$	CH_2Cl_2	−43.6 d, t[h]	−62.6 d	−53.1	−29.9	53 ± 0.5	1128[i]	−42
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]CdBr_2$	Too insoluble to observe a spectrum						1154	−23
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]HgCl_2$	$CHCl_2CN$	−22.8 br	−28.2 br	−51.2	−0.5		1175	−2
$[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2]HgBr_2$	CH_2Cl_2	−18.9 br	−27.5 br	−47.3	+0.2		1166	−11
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]CdBr_2$	CH_2Cl_2	8.9 br	−40.4 d	−0.6	−7.7	23 ± 2	1152	−18
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]HgCl_2$	$CHCl_2CN$	−35.0 d	−36.4 d	−44.5	−2.8	8.5 ± 0.5	1170	0
$[(C_6H_5)_2P(O)CH(n\text{-}C_3H_7)P(C_6H_5)_2]HgBr_2$	$CHCl_2CN$	−31.7 d	−35.8 d	−41.2	−2.2	9 ± 1	1171	+1
$(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)(C_2H_5)$	CH_2Cl_2	−34.7 d[j]	−23.7 d[k]			11 ± 0.5	1185	
$(C_6H_5)_2P(O)CH(CH_3)P(O)(C_6H_5)_2$	CH_2Cl_2		−30.4					

[a] Ppm *vs.* 85% H_3PO_4. Key: t, triplet; d, doublet; br, broad. [b] δ(complex) − δ(ligand) in ppm. [c] In Hz. [d] In cm^{-1}. [e] ν(complex) − ν(ligand) in cm^{-1}. [f] ν_{CO} = 2008 (s), 1918 (vs), 1883 (vs), 1864 (vs) cm^{-1}. [g] ν_{CO} = 2010 (s), 1919 (vs), 1896 (vs), 1856 (vs) cm^{-1}. [h] J_{WP} = 233 ± 0.5 Hz. [i] ν_{CO} = 2002 (s), 1884 (vs), 1863 (vs), 1835 (vs) cm^{-1}. [j] $(C_6H_5)(C_2H_5)P(O)$ group. [k] $(C_6H_5)_2P(O)$ group.

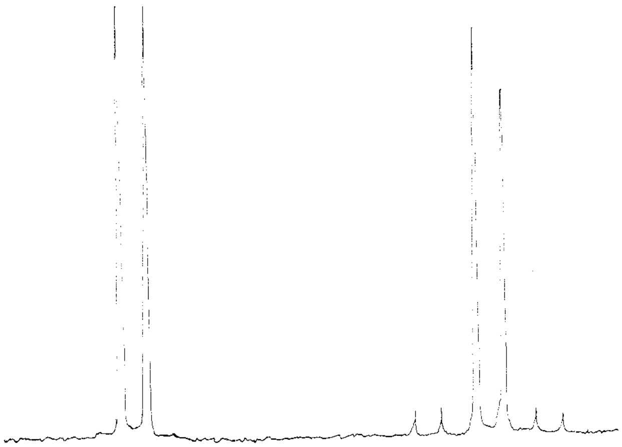

Figure 1. High-resolution ^{31}P nmr spectrum of $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]W(CO)_4$.

the latter possibly resulting from the self-redox of the compound with the more basic ethylphenylphosphino group removing the oxygen from the less basic diphenylphosphino group.[11] Proof that the ethylphenylphosphinous chloride had indeed reacted as expected is given by the isolation of the dioxide, $Ph_2P(O)CH_2P(O)PhEt$, from the reaction mixture upon oxidation. Both of the oxides in the mixture form the same dioxide upon oxidation.

The phosphorus-31 nmr data appear in Table II. The spectra of the ligands exhibit two sharp doublets, one upfield of H_3PO_4 (phosphine end) and one downfield (phosphoryl end).

Assignments for the phosphonium salt–phosphine oxide compounds are not as straightforward; $\Delta_{P=O}$ (δ(complex) − δ(free ligand)) of the $Ph_2P(O)CHR-$ end could be +3.1 or +6.9 for R = H, +1.8 or +4.7 for R = CH_3, and +1.8 or +4.8 for R = *n*-Pr. In an effort to solve this problem $[Ph_2EtPCH(n\text{-}Pr)P(O)Ph_2]^+Br^-$ was synthesized. It shows doublets (J_{PP} = 40 ± 0.5 Hz) at −34.8 and −31.2 ppm, making $\Delta_{P=O}$ either +1.5 or −2.1 ppm. We prefer +1.5 because it seems unlikely that quaternizing the phosphine should give a negative $\Delta_{P=O}$. (Electron-withdrawing groups in phosphine oxides generally cause an upfield shift.[12]) The consistently small upfield shift (+1.8, +1.8, +1.5) of these ligands leads to our tentative assignment. (All Δ values are in ppm.)

Assignments for the $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]M(CO)_4$ complexes are unambiguous. The proton-decoupled ^{31}P spectrum of $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]W(CO)_4$ (Figure 1) shows a normal $^1J_{WP}$ = 233 Hz for the phosphine end of the ligand, but no $^2J_{WP}$ for the phosphine oxide end. Low-resolution undecoupled spectra (Figure 2) show a sharper doublet (J_{PP}) for the phosphine end; this is because phosphorus–hydrogen coupling constants are smaller in phosphine complexes than in phosphine oxides ($^2J_{PH}$ = 7.1 Hz for $[Ph_2PCH_2CH_2PPhCH_3]Cr(CO)_4$ and 12.4 Hz for $Ph_2P(O)CH_2CH_2P(O)PhCH_3$ and $^3J_{PH}$ = 15.4 Hz for $[Ph_2PCH_2CH_2PPEt]Cr(CO)_4$ and 17.1 Hz for $Ph_2P(O)CH_2CH_2P(O)PhEt$).[2] The assignment gives the rather constant $\Delta_{P=O}$ expected (this phosphorus atom is not directly coordinated but is only part of the chelate backbone) and $|\Delta_P|$ decreases in the order Cr > Mo > W observed earlier[2,3] in diphosphine chelates. Typical coordination shifts in five-membered rings are −92 (Cr), −68 (Mo), and −53 (W) while in *cis*-LL'M(CO)$_4$ with monodentate phosphine ligands they are −59 (Cr), −43 (Mo), and −25 (W). In $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]CdBr_2$ the high-field resonance is clearly due to the phosphine; Δ_P is only −0.6. The only previously reported

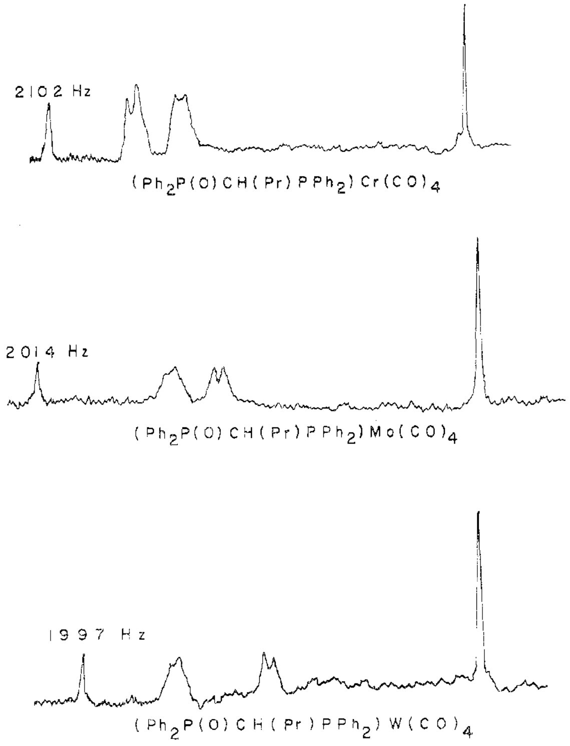

Figure 2. Low-resolution ^{31}P spectra of $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]M(CO)_4$ complexes. The narrow signal at the right is 85% H_3PO_4; a frequency marker is at the left.

Table III. Pmr Data of Phosphine–Phosphine Oxide Ligands and Phosphonium Salts

Compd	Group	Integration (theory)	τ, ppm	Assignment	J, Hz
$Ph_2P(O)CH_2PPh_2$	Multiplet	10.0 (10)	2.1–2.8	Phenyl	
	Doublet	1.01 (1)	6.94	CH_2	$^2J_{P(O)CH} = 13$ $^2J_{PCH} \simeq 0$
$[Ph_2P(O)CH_2PPh_2CH_3]^+[PF_6]^-$	Multiplet	20.0 (20)	2.0–2.8	Phenyl	
	Doublets of doublets	1.70 (2)	5.25	CH_2	$^2J_{P(O)CH_2} = 12$; $^2J_{P(+)CH_2} = 17$
	Doublet	2.81 (3)	7.18	CH_3	$^2J_{PCH_3} = 14.6$
$Ph_2P(O)CHCH_3PPh_2$	Multiplet	20.0 (20)	2.0–2.9	Phenyl	
	Multiplet	1.15 (1)	6.5–7.0	$PCHCH_3P$	
	Doublet of triplets	3.10 (3)	8.86	CH_3	$^3J_{HCCH} = {^3J_{PCCH}} = 7.1$; $^3J_{P(O)CCH} = 16.0$
$[Ph_2P(O)CHCH_3PPh_2CH_3]^+[PF_6]^-$	Multiplet	20.0 (20)	1.8–2.9	Phenyl	
	Multiplet	0.92 (1)	4.7–5.3	$PCHCH_3P$	
	Doublet	2.93 (3)	7.10	PCH_3	$^2J_{PCH_3} = 14.2$
	Octet	3.10 (3)	8.63 (3)	$PCHCH_3P$	$^3J_{P(O)CCH}$; $^3J_{P(+)CCH}$; $^3J_{HCCH}$ not assigned
$Ph_2P(O)CHCH_3P(O)Ph_2$	Multiplet	20.0 (20)	1.8–2.8	phenyl	
	Multiplet	0.86 (1)	6.2–7.0	$PCHCH_3P$	$^3J_{HCCH} = 7.6$
	Triplet of doublets	2.91 (3)	8.63	$PCHCH_3P$	$^3J_{PCCH} = 15.6$
$Ph_2P(O)CH(n\text{-}Pr)PPh_2$	Multiplet	20.0 (20)	2.0–3.0	Phenyl	
	Doublet of doublet of triplets	0.91 (1)	6.95	$PCH(Pr)P$	$^2J_{PCH} = 2.0$; $^3J_{HCCH} = 6.8$; $^2J_{P(O)CH} = 12.4$
	Multiplet	4.20 (4)	8.0–9.3	$PCH(CH_2CH_2CH_3)$	
	Triplet	2.72 (3)	9.54	CH_3	$^3J_{HCCH} = 6.8$
$[Ph_2P(O)CH(n\text{-}Pr)PPh_2CH_3]^+[PF_6]^-$	Multiplet	20.0 (20)	1.7–2.9	Phenyl	
	Multiplet	1.10 (1)	3.5–4.2	$PCH(Pr)P$	
	Doublet	2.71 (3)	7.18	PCH_3	$^2J_{PCH} = 12.0$
	Multiplet	4.23 (4)	7.6–9.0	$PCH(CH_2CH_2CH_3)$	
	Triplet	2.91 (3)	9.56	$CH_2CH_2CH_3$	$^3J_{HCCH} = 6.9$
$Ph_2P(O)CH_2P(O)PhEt$	Multiplet	15.0 (15)	2.0–2.9	Phenyl	
	Doublet of doublets	2.04 (2)	6.87	PCH_2P	
	Doublet of quartets	2.13 (2)	7.65	PCH_2CH_3	$^2J_{PCH} = 12.0$
	Doublet of triplets	3.01 (3)	8.92	CH_3	$^3J_{HCCH} = 7.3$; $^3J_{PCCH} = 18.5$

phosphorus nmr data on organophosphine cadmium complexes[16] also reported small phosphorus chemical coordination shifts and rapid ligand exchange at room temperature.

The assignments of the ^{31}P chemical shifts in the mercury complexes are based on the observation that coordination chemical shifts of phosphine oxide complexes of mercury are very small[1a] and that the coordination shifts of mercury(II) monodentate tertiary phosphine complexes and bidentate complexes are similar[17,18] to each other.

The unusual result that $|\Delta_{P=O}| > |\Delta_P|$ in $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]CdBr_2$ suggests that the relatively "hard" cadmium(II) bonds more strongly to the phosphoryl. The softer group VI metal(0) and Hg(II) centers bond more strongly to the phosphine, and give $|\Delta_P| > |\Delta_{P=O}|$.

The phosphorus–phosphorus coupling constants show large variations in Table II. The 15-Hz difference between $Ph_2P(O)CH_2PPh_2$ and $Ph_2P(O)CH(n\text{-}Pr)PPh_2$ cannot be attributed to a simple electronic effect. Models and Newman projections suggest a significant difference in dihedral angles (defined by the planes formed from P–C–P and C–P–lone pair of electrons). Large changes in the magnitudes of J_{PP} (and possibly in the signs) occurred on quaternization and coordination. In the latter case coupling could occur through the metal as well as through the backbone of the chelate. The mercury complexes of $Ph_2P(O)CH_2PPh_2$ show rapid ligand exchange at room temperature and no P–P coupling was observed.

No mercury–phosphorus or cadmium–phosphorus coupling constants were observed. The $^1J_{WP}$ of 233 Hz observed in $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]W(CO)_4$ is of normal magnitude. Only two cases of multibond metal–phosphorus coupling have been reported.[19,20] Both of these represent somewhat unusual cases and both values are small (<4 Hz). Thus the lack of an observable $^2J_{WOP}$ in this complex (Figure 1) is not surprising.

Table II also gives infrared data for $\nu_{P=O}$, usually the strongest band between 1100 and 1300 cm^{-1}.[21] The 7-cm^{-1} decrease in $\nu_{P=O}$ in going from $Ph_2P(O)CH_2PPh_2$ to $Ph_2P(O)CH(n\text{-}Pr)Ph_2$ is attributable to the electron-donating action of the alkyl. The increase of ~20 cm^{-1} on quaternization is due to the formal positive charge two atoms away from the phosphoryl; electron withdrawal gives a stronger and shorter P═O bond. This effect has been noted on substitution of electronegative groups in aldehydes, ketones, phosphates, and OPX_3.[21]

A decrease in $\nu_{P=O}$ on coordination of monodentate phosphine oxides has been attributed to a weakening of the double bond.[22,23] The usual decrease is 25–40 cm^{-1} [21-28] in complexes of metal cations. Our Cd(II) and Hg(II) complexes show much smaller decreases and even a small increase in one case. The observed $\Delta\nu_{P=O}$ must be a combination of the normal drop in $\nu_{P=O}$ on phosphoryl coordination and an increase caused by a positive charge on the coordinated phosphine (pseudoquaternization).

The normal decrease in $\nu_{P=O}$ in metal carbonyl complexes is −10 to −28 cm^{-1} for $Ph_3P(O)$ and −7 to −15 cm^{-1} for $Ph_2P(O)CH_2P(O)Ph_2$.[27,28] Our Cr, Mo, and W complexes show larger shifts (−33 to −43 cm^{-1}) which might suggest a net transfer of electronic charge from the metal(0) to the phosphine.

Proton nmr data for the phosphine–phosphine oxides, dioxides, and phosphine oxide–methylphosphonium salts are given in Table III. Most of the coupling constant assignments are readily made. However, in the case of the $[Ph_2P(O)CH_2PPh_2Me]PF_6$ methylene, which appears as a doublet of doublets, it is not obvious which phosphorus couples by 17 Hz and which by 12. The signal of the bridging methine proton in $[Ph_2P(O)CHRPPh_2Me]PF_6$ is weak and the complex signal was not analyzed.

Registry No. $Ph_2P(O)CH_2Li$, 23182-99-2; $Ph_2P(O)CH(CH_3)Li$, 25082-62-6; $Ph_2P(O)CH(n\text{-}Pr)Li$, 53849-91-5; Ph_2PCl, 1079-66-9; PhEtPCl, 15849-83-9; $Ph_2P(O)CH_2PPh_2$, 23176-18-3; $Ph_2P(O)CH(CH_3)PPh_2$, 53849-92-6; $Ph_2P(O)CH(n\text{-}Pr)PPh_2$, 53849-93-7; $[Ph_2P(O)CH_2PPh_2CH_3]PF_6$, 53849-73-3; $[Ph_2P(O)CH(CH_3)PPh_2CH_3]PF_6$, 53849-41-5; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2CH_3]PF_6$, 53849-43-7; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]Cr(CO)_4$, 53849-44-8; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]Mo(CO)_4$, 53849-45-9; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]W(CO)_4$, 53849-46-0; $[Ph_2P(O)CH_2PPh_2]HgCl_2$, 53849-47-1; $[Ph_2P(O)CH_2PPh_2]HgBr_2$, 53849-48-2; $[Ph_2P(O)CH_2PPh_2]CdBr_2$, 53849-49-3; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]CdBr_2$, 53849-50-6; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]HgCl_2$, 53849-51-7; $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]HgBr_2$, 53849-52-8; $Ph_2P(O)CH_2P(O)PhEt$, 17045-59-9; $Ph_2P(O)CH(CH_3)P(O)Ph_2$, 53849-94-8.

References and Notes

(1) (a) Taken in part from the Ph.D. dissertation of L. C. Satek, University of Maryland, 1972. (b) Preliminary report: Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., 1973, No. INOR 158. (c) Part VI: S. O. Grim and J. D. Mitchell, *Syn. Reactiv. Inorg. Metal-Org. Chem.*, **4**, 221 (1974). (d) Partially supported by the National Science Foundation under Grant No. GP 30703.
(2) S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman, and J. P. Jesson, *J. Amer. Chem. Soc.*, **96**, 3416 (1974).
(3) S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974).
(4) E. G. Finer and R. K. Harris, *Progr. Nucl. Magn. Resonance Spectrosc.*, **6**, 61 (1970).
(5) (a) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Lett.*, **2**, 205 (1966); (b) R. M. Lynden-Bell, J. F. Nixon, and R. Schmutzler, *J. Chem. Soc. A*, 565 (1970).
(6) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970).
(7) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, **7**, 161 (1968).
(8) J. F. Nixon and J. R. Swain, *J. Chem. Soc., Dalton Trans.*, 1038 (1972).
(9) D. Seyferth, D. E. Welch, and J. K. Herren, *J. Amer. Chem. Soc.*, **86**, 1100 (1964).
(10) W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971).
(11) Independent evidence for this type of reaction has been found in the case of analogous sulfur compounds, which undergo the self-redox reaction: S. O. Grim and J. D. Mitchell, unpublished results.
(12) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, (1967).
(13) J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).
(14) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).
(15) R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, **9**, 2030 (1970).
(16) B. E. Mann, *Inorg. Nucl. Chem. Lett.*, **7**, 696 (1971).
(17) S. O. Grim, P. J. Lui, and R. L. Keiter, *Inorg. Chem.*, **13**, 342 (1974).
(18) S. O. Grim and J. Del Gaudio, unpublished results.
(19) R. L. Keiter and L. W. Cary, *J. Amer. Chem. Soc.*, **94**, 9232 (1972).
(20) W. McFarlane, A. M. Noble, and J. M. Winfield, *J. Chem. Soc. A*, 948 (1971).
(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1960.
(22) J. C. Sheldon and S. Y. Tyree, *J. Amer. Chem. Soc.*, **80**, 4775 (1958).
(23) F. A. Cotton and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, **82**, 5772 (1960).
(24) S. H. Hunter, V. M. Langford, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc. A*, 305 (1968).
(25) M. J. Froyer, W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963).
(26) C. Owens, N. Karayannis, L. Pytlewski, and M. Labes, *J. Phys. Chem.*, **75**, 637 (1971).
(27) V. Sartorelli, F. Canyiani, and F. Zingales, *Inorg. Chem.*, **5**, 2233 (1966).
(28) F. Canyiani, F. Zingales, and V. Sartorelli, *Gazz. Chim. Ital.*, **94**, 841 (1964).

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Cyanide, Isocyanide, and Nitrile Derivatives of Cyclopentadienyliron. Interaction of Chiral Metal Complexes with an Optically Active Shift Reagent

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The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ with excess cyanide yields $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$. Ethylation with Et_3OPF_6 yields $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNEt)(PPh_3)]PF_6$. This isocyanide compound does not react with a variety of nucleophiles to yield addition products but was clearly shown to be an isocyanide compound by comparison with $[(\eta^5\text{-}C_5H_5)Fe(CO)(NCMe)(PPh_3)]BF_4$. The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ with KCN yields $K[(\eta^5\text{-}C_5H_5)Fe(CN)_2(PPh_3)]$. This reaction is contrasted by the reaction of excess KCN with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ in ethanol to yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ and in ethanol–water to yield $K[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]$. The conversion of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ to $K[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]$ in ethanol–water with KCN showed that the latter reaction takes place in two steps. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}(CH_2)_nCN)$ ($n = 1, 2$) were prepared respectively by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ with $LiCH_2CN$ ($n = 1$) and the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}C_2H_4)]BF_4$ with KCN ($n = 2$). The ^1H and ^{13}C nmr of these two new complexes and $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$, complexes containing a chiral metal center, in the presence of various concentrations of Yb-Optishift I[1] was measured. Resolution of the enantiotopic protons of the $\eta^5\text{-}C_5H_5$ was observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(CN)(PPh_3)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CN)$ whereas none was observed for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$. Very little resolution was observed for any resonances in the ^{13}C spectra.

Introduction

The chemistry of cyanide and isocyanide ligands, formally isoelectronic to carbon monoxide, has not been explored in as great detail as the chemistry of the carbonyl ligand. Because these ligands offer considerable potential synthetic utility, recent interest in the synthesis and reactivity of transition metal organometallic cyanide and isocyanide compounds has been quite high. The main emphasis of this work, especially with isocyanides, has been on nickel, palladium, and platinum compounds[2,3] although research on other transition metals has been carried out.[4] Of particular interest has been the reactivity of the isocyanide ligand toward nucleophilic reagents.[2b,3b,4b] Reactions with hydroxide, sulfides, and amides yield carboxamido, thiocarboxamido, and amidinium metal complexes, respectively.[2b] Reactions with amines and alcohols yield carbene complexes.[3b,4b] This reactivity is analogous to nucleophilic reactions of the carbon of a metal carbonyl.[5,6]

This report describes the reaction of cyanide with $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]I$ and compares it to the reaction of cyanide with $(\eta^5\text{-}C_5H_5)Fe$-