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Unsymmetrical Bis-Phosphorus Ligands. IV. Group VI Metal Carbonyl Derivatives of Diphenylphosphinomethyl and Diphenylphosphinoethyl Phosphinites, $(C_6H_5)_2P(CH_2)_nOP(C_6H_5)_2$, $n = 1$ or 2, and an Unusual Phosphorus Chemical Shift Chelate Effect[1]

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The synthesis of the new ligand $(C_6H_5)_2PCH_2OP(C_6H_5)_2$ is reported. Coordination compounds of this ligand and its analog $(C_6H_5)_2PCH_2CH_2OP(C_6H_5)_2$ with chromium, molybdenum, and tungsten carbonyls and with $PdCl_2$ are reported with ^{31}P and ^1H nmr data, including phosphorus–phosphorus and phosphorus–tungsten coupling constants where appropriate. Phosphorus nmr data are also reported for $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2M(CO)_4$, where M = Cr, Mo, or W and $n = 1, 2,$ or 3. An unusually large downfield phosphorus coordination shift is observed in the case of all five-membered chelate rings, which is not observed in the case of the four- and six-membered chelate rings.

Introduction

We have been interested in the synthesis of chelating bis-phosphorus ligands[1b,2,3] which have chemically different phosphorus atoms in order to study phosphorus–phosphorus spin–spin coupling in coordination compounds by direct observation in the ^{31}P nmr spectra. These compounds are important because the phosphorus atoms of the chelate must necessarily have cis stereochemistry at the metal, whereas, in many cases, this stereochemistry is difficult or impossible to attain with "mixed-ligand" compounds of the bis-monodentate ligand type. We report here the synthesis of a new ligand, diphenylphosphinomethyl diphenylphosphinite, $(C_6H_5)_2PCH_2OP(C_6H_5)_2$, and the preparation and some physical properties of coordination compounds of this ligand and its ethylene analog, $(C_6H_5)_2PCH_2CH_2OP(C_6H_5)_2$, with chromium, molybdenum, and tungsten carbonyls and palladium chloride. In addition, phosphorus nmr data are reported for the series $[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]M(CO)_4$ where M = Cr, Mo, or W and $n = 1, 2,$ or 3.

Experimental Section

Ligands. Bis(diphenylphosphino)methane ($(dpp)_2m$), 1,2-bis(diphenylphosphino)ethane ($(dpp)_2e$), and 1,3-bis(diphenylphosphino)propane ($(dpp)_2p$) were prepared under nitrogen from sodium diphenylphosphide (prepared from triphenylphosphine and sodium and subsequently quenched with the stoichiometric amount of ammonium chloride to destroy the phenylsodium) and the respective dichloroalkane.[4]

Preparation of 1,3-Bis(diphenylphosphino)-1-oxapropane, $(dpp)_2op$. To 200 ml of a filtered (glass wool) and cooled (Dry Ice–acetone) tetrahydrofuran (THF) solution of lithium diphenylphosphide, made from chlorodiphenylphosphine (11 g, 0.05 mol) and excess lithium, was added dropwise while stirring vigorously ethylene oxide (3 ml, 0.06 mol) in 50 ml of THF. The solution was warmed to room temperature for about 15 min and cooled again to −78°. Chlorodiphenylphosphine (9.9 g, 0.045 mol) in 50 ml of THF was then added dropwise with vigorous stirring. The crude product obtained after evaporation of the solvent was separated by chromatography on alumina with benzene to yield a viscous oil (7.6 g, 41%), $(C_6H_5)_2PCH_2CH_2OP(C_6H_5)_2$.

Anal. Calcd for $C_{26}H_{24}OP_2$: C, 75.35; H, 5.8; P, 14.7. Found: C, 75.15; H, 5.9; P, 14.7.

Preparation of Diphenyl(hydroxymethyl)phosphine. Lithium diphenylphosphide was prepared from chlorodiphenylphosphine (11.0 g, 0.05 mol) and finely divided lithium wire (1.4 g, 0.25 g-atom) with vigorous stirring under nitrogen in THF (130 ml). After the reaction mixture, which had refluxed from the heat of reaction, had cooled to room temperature, the deep red solution was transferred by using a siphon with a wisp of glass wool to a pressure-equalizing addition funnel. The $LiP(C_6H_5)_2$ solution was added dropwise to a well-stirred, cooled (0°) suspension of paraformaldehyde (1.8 g, 0.05 mol) in THF (80 ml). The addition required about 90 min, after which the reaction mixture was stirred for an additional 4 hr at 0°. Then 100 ml of 0.5 *M* hydrochloric acid (0.05 mol) in THF (prepared from concentrated aqueous HCl and THF) was added slowly at 0°. After stirring for 1 hr, the solution was allowed to warm to room temperature and the solvent was removed by means of a rotary evaporator to give a viscous oil. Addition of benzene resulted in the precipitation of LiCl which was removed by filtration. Removal of the solvent once more produced a light brown viscous oil, impure $(C_6H_5)_2PCH_2OH$. Attempted purification by vacuum distillation and column chromatography was unsuccessful. The phosphorus nmr spectrum (singlet, δ 13.6 ppm) indicated no phosphorus impurities. Reaction with methyl bromide gave the salt $[(C_6H_5)_2P(CH_3)CH_2OH]Br$, ($\delta_P$ −19.1), which was very hygroscopic and did not crystallize. The phosphine was conclusively identified by conversion to the oxide.[5]

Preparation of Diphenyl(hydroxymethyl)phosphine Oxide. Diphenyl(hydroxymethyl)phosphine (3.0 g, 14 mmol) was stirred in 50 ml of THF in the open air for 5 hr. The white precipitate which had formed was collected by filtration and recrystallized from hot toluene to give pure oxide, mp 140–141° (lit.[5] mp 138–140°), with phosphoryl and hydroxyl infrared stretching frequencies at 1152 and 3220 cm^{-1}, respectively (lit.[6] values 1156 and 3220 cm^{-1}), and a phosphorus chemical shift of −30.0 ppm.

Anal. Calcd for $C_{13}H_{13}O_2P$: C, 67.23; H, 5.64; P, 13.34. Found: C, 67.43; H, 5.84; P, 13.55.

Preparation of 1,2-Bis(diphenylphosphino)-1-oxaethane, $(dpp)_2oe$. Into a 500-ml three-necked flask fitted with an N_2 inlet, pressure-equalizing addition funnel (center neck), magnetic stirrer, and exhaust outlet were placed 200 ml of benzene, 7.0 ml (6.5 g, 0.03 mol) of diphenylmethoxyphosphine prepared by the method of McAllister,[7] and 7.0 ml (6.4 g, 0.03 mol) of diphenyl(hydroxymethyl)phosphine. The flask was continuously flushed with N_2 for the duration of the reaction. The mixture was heated by a water bath at 75–80° so that any methanol formed would vaporize and be removed by the passing N_2. As the volume in the flask was reduced due to solvent evaporation, benzene was added periodically from the addition funnel. The course of the reaction was monitored by ^{31}P nmr of aliquots of the solution taken at various times. After 8 hr the reaction was essentially complete. The ^{31}P spectrum showed product peaks (both doublets,[2] $J_{PP} = 16.5$ Hz) at 14.1 and −118.2 ppm (accounting for 85% of the peak areas), no starting materials, and impurity peaks (the remaining

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15%) at −30 ppm (probably oxide) and a sharp doublet ($J = 210$ Hz) at 41 ppm attributable to diphenylphosphine (δ 41.1, $J_{PH} = 214$ Hz).[8] Removal of solvent left a brown viscous oil. Attempted chromatographic purification on alumina and silica gel columns with benzene resulted in partial destruction of the compound. Attempted distillation using a Hickman still at *ca.* 140° and 10^{-4} Torr resulted in partial decomposition of the compound. Evaporation of the middle fraction from the alumina chromatographic experiment and continued pumping (40 hr at 0.03 Torr at room temperature) produced a product, $(C_6H_5)_2PCH_2OP(C_6H_5)_2$, with only a slight impurity of diphenylphosphine.

Anal. Calcd for $C_{25}H_{22}OP_2$: C, 74.99; H, 5.54. Found: C, 75.48; H, 5.94.

The compound was further characterized by its proton nmr spectrum (Table III) and its coordination compounds.

Coordination Compounds. The bis(diphenylphosphinoalkane) derivatives were made by the general method described previously.[9]

Preparation of Bis(1,3-diphenylphosphinopropane)tetracarbonyltungsten(0). A mixture of tungsten hexacarbonyl (10.56 g, 30 mmol), $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (12.36 g, 30 mmol), and 50 ml of diethylene glycol dimethyl ether (diglyme) was heated to 160° under nitrogen for 2 hr. After cooling and addition of methanol (25 ml), the crystals which had formed were removed by filtration. The crude product was recrystallized three times from $CHCl_3$-CH_3OH and resulted in 12.2 g (17 mmol, 58% yield) of pure product, $[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]W(CO)_4$, mp 208°.

Anal. Calcd for $C_{31}H_{26}O_4P_2W$: C, 52.57; H, 3.70; P, 9.03. Found: C, 52.34; H, 3.70; P, 9.03.

Preparation of Other $[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]M(CO)_4$ Compounds. $((ddp)_2p)Cr(CO)_4$ was prepared as in the case of the tungsten analog at 165° for 3 hr. The yield was 13.8 g (80%) of purified crystals, mp 206–207°.

Anal. Calcd for $C_{31}H_{26}O_4P_2Cr$: C, 64.50; H, 4.55; P, 10.74. Found: C, 64.85; H, 4.62; P, 10.45.

$((dpp)_2p)Mo(CO)_4$ was prepared similarly at a reaction temperature of 165° for 2 hr. The yield of product, mp 192–193° (lit.[10] mp 187–191°), was 3.8 g (82%).

$((dpp)_2e)Cr(CO)_4$ was prepared similarly at 135° for 3 hr. The yield of product, mp 211° dec (lit.[11] mp 211–212°), was 6.1 g (35%).

$((dpp)_2e)Mo(CO)_4$ was formed as described at 115° for 25 min. The yield of product, mp 190–191° (lit.[10] mp 191–193°), was 10.4 g (64%).

$((dpp)_2e)W(CO)_4$ was synthesized as described above at 155° for 4 hr. The yield of product, mp 206–207° (lit.[11] mp 208–209°), was 11.2 g (69%).

$((dpp)_2m)Cr(CO)_4$ was prepared similarly at 135° for 3.5 hr. The yield of product, mp 168–170° (lit.[11] mp 170.5–171.5°), was 6.1 g (48%).

$((dpp)_2m)Mo(CO)_4$ was prepared as described at 115° for 10 hr. The yield of crystals, mp 190–191° (lit.[11] mp 195.5–196°), was 11.7 g (75%).

$((dpp)_2m)W(CO)_4$ was prepared as described at 165° for 48 hr. The yield of product, mp 194–195° (lit.[11] mp 200–201.5°), was 10.3 g (51%).

Preparation of $((dpp)_2oe)Cr(CO)_4$. A solution of $Cr(CO)_6$ (2.6 g, 12 mmol) and 4.8 g (12 mmol) of $(dpp)_2oe$ in 50 ml of diglyme under N_2 was heated in an oil bath at 135–140° with stirring. The $Cr(CO)_6$ which sublimed onto cooler portions of the reaction vessel was periodically returned to the solution by shaking the apparatus. The progress of the reaction was monitored by collection of the CO evolved. About 90% of the theoretical volume of CO had been collected in 90 min. The mixture was cooled and the diglyme was removed by distillation at 50° (1 Torr) to leave a yellow solid residue, which was dissolved in 10 ml of CH_2Cl_2 and precipitated with cyclohexane to give 2.5 g (37% yield) of yellow solid. Recrystallization from hot ethanol produced 2.0 g (30% yield) of light yellow crystals, mp 178–179°.

Anal. Calcd for $C_{29}H_{22}O_5P_2Cr$: C, 61.71; H, 3.93; P, 10.98. Found: C, 61.45; H, 4.18; P, 10.70.

$((dpp)_2oe)Mo(CO)_4$ was prepared similarly at 100° for 45 min to give white crystals, mp 176–179°, in 35% yield.

Anal. Calcd for $C_{29}H_{22}O_5P_2Mo$: C, 57.25; H, 3.64; P, 10.18. Found: C, 57.50; H, 3.74; P, 10.37.

$((dpp)_2oe)W(CO)_4$ was prepared by the same method at 135° for 7 hr to give light yellow crystals, mp 180–183° dec, in 30% yield.

Anal. Calcd for $C_{29}H_{22}O_5P_2W$: C, 50.02; H, 3.18; P, 8.90. Found: C, 49.71; H, 3.55; P, 9.00.

$((dpp)_2op)Cr(CO)_4$ was prepared in a similar manner at 135° for 110 min to give a greenish yellow product, mp 170–173°, in 30% yield.

Anal. Calcd for $C_{30}H_{24}O_5P_2Cr$: C, 62.28; H, 4.18; P, 10.71. Found: C, 62.04; H, 4.73; P, 10.81.

$((dpp)_2op)Mo(CO)_4$ was prepared as described above at 100° for 45 min to give a white solid, mp 178–182° dec, in 35% yield.

Anal. Calcd for $C_{30}H_{24}O_5P_2Mo$: C, 57.89; H, 3.89; P, 9.95. Found: C, 57.60; H, 4.10; P, 9.70.

$((dpp)_2op)W(CO)_4$ was synthesized in a similar fashion at 135° for 7 hr to give a light yellow solid, mp 193–194°, in 30% yield.

Anal. Calcd for $C_{30}H_{24}O_5P_2W$: C, 50.71; H, 3.41; P, 8.72. Found: C, 49.50; H, 3.50; P, 8.55.

Preparation of $((dpp)_2oe)PdCl_2$. To $(C_6H_5CN)_2PdCl_2$[12] (1.5 g, 4.2 mmol) in 35 ml of C_6H_6 was added dropwise with stirring under N_2 1.7 g (4.2 mmol) of $(dpp)_2oe$ in 10 ml of C_6H_6. Reaction to form a yellow precipitate was immediate. The product was isolated by filtration, washed with petroleum ether, and dried to give 2.7 g (80% yield) of yellow powder, mp 278–280°.

Anal. Calcd for $C_{25}H_{22}OCl_2P_2Pd$: C, 51.96; H, 3.84; P, 10.72; Cl, 12.27. Found: C, 51.52; H, 3.83; P, 10.21; Cl, 12.01.

Preparation of $((dpp)_2oe)HgBr_2$. To a stirred solution of 4.3 g (12 mmol) of $HgBr_2$ in 70 ml of THF was added dropwise under N_2 4.8 g (12 mmol) of $(dpp)_2oe$ in 10 ml of THF. Within 20–30 min a precipitate began to form. After 12 hr the mixture was filtered and the solid washed with THF to give 3.1 g (35% yield) of white product, mp 119–123°.

Anal. Calcd for $C_{25}H_{22}OBr_2P_2Hg$: C, 39.46; H, 2.91; P, 8.14. Found: C, 39.48; H, 2.94; P, 7.97.

$((dpp)_2oe)HgI_2$ was prepared similarly at 0° to give 3.2 g (30% yield) of white powder, mp 100–104°.

Anal. Calcd for $C_{25}H_{22}OI_2P_2Hg$: C, 35.12; H, 2.59; P, 7.25. Found: C, 34.93; H, 2.54; P, 7.52.

Preparation of $((dpp)_2op)PdCl_2$. A heterogeneous mixture of $(dpp)_2op$ (0.54 g, 1.3 mmol) and K_2PdCl_4 (0.42 g, 1.3 mmol) in 50 ml of CH_2Cl_2 was stirred at room temperature under N_2. A yellow color was detected in solution after 3 hr. After 3 days the K_2PdCl_4 had completely dissolved. The solvent was evaporated and yellow residue was dissolved again in a small amount of CH_2Cl_2. The KCl was removed by filtration and the product was crystallized by the slow addition of cyclohexane. The yield of yellow crystals, mp 267–270°, was 0.6 g (60%).

Anal. Calcd for $C_{26}H_{24}OCl_2P_2Pd$: C, 52.74; H, 4.09; P, 10.46; Cl, 11.98. Found: C, 52.67; H, 4.21; P, 10.66; Cl, 12.24.

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_3PO_4 inserted concentrically by means of a serum stopper. More accurate chemical shifts and coupling constants were obtained with a Bruker HFX-90 at 36.43 MHz operating in the FT mode on about 0.3 g of sample in 1.5 ml of CH_2Cl_2 placed in a 10-mm tube with a concentric 3-mm tube containing $CBrF_2CBrF_2$ to provide ^{19}F lock. Spectra were recorded at 28°, generally employing about 500 pulses per spectrum.

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer in $CDCl_3$ with an internal TMS standard.

Infrared spectra in the carbonyl region were measured on cyclohexane solutions in NaCl cells with a path length of 0.5 mm with a Perkin-Elmer Model 225 spectrometer and were calibrated with polystyrene film.

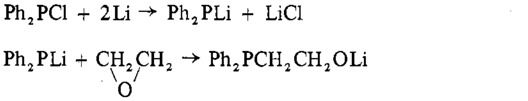
Melting points were determined with a Mel-Temp apparatus and are uncorrected.

Microanalyses were performed by Dr. Franz Kasler, University of Maryland.

Results and Discussion

The reaction sequence to prepare bis(1,3-diphenylphosphino)-1-oxapropane, $(dpp)_2op$, had been previously established,[3] *i.e.*

$$Ph_2PCl + 2Li \rightarrow Ph_2PLi + LiCl \tag{1}$$



$$Ph_2PLi + \underset{\text{O}}{CH_2CH_2} \rightarrow Ph_2PCH_2CH_2OLi \tag{2}$$

$$Ph_2PCH_2CH_2OLi + Ph_2PCl \rightarrow Ph_2PCH_2CH_2OPPh_2 + LiCl \tag{3}$$

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The same sequence was attempted in the preparation of bis-(1,2-diphenylphosphino)-1-oxaethane, $(dpp)_2oe$, with formaldehyde replacing ethylene oxide as the reactant in eq 2. As the polymeric paraformaldehyde solid was added to the deep red lithium phosphide solution, the solution would slowly decolorize to a straw-colored solution of Ph_2PCH_2OLi with a corresponding ^{31}P chemical shift change of 22 ppm for $LiPPh_2$ in THF to a shift of +12.0 ppm.

$$Ph_2PLi + CH_2O \rightarrow Ph_2PCH_2OLi \qquad (4)$$

The fact that the intermediate lithium reagent Ph_2PCH_2OLi had formed was confirmed by hydrolysis and oxidation to the known compound $Ph_2P(O)CH_2OH$.

Further reaction of the intermediate with Ph_2PCl according to reaction 5 was unsuccessful, however, at various temperatures from −76 to +40°, with inverse addition of reactants and with excesses of the different reagents.

$$Ph_2PCH_2OLi + Ph_2PCl \rightarrow Ph_2PCH_2OPPh_2 + LiCl \qquad (5)$$

The major peak (80%) in the ^{31}P spectrum of the reaction mixture was always at 16 ppm which indicates that both phosphorus atoms are equivalent and which corresponds to the compound Ph_2PPPh_2, δ 16.0 ppm.[13] The product can be explained by the reaction

$$Ph_2PCH_2O^- + Ph_2PCl \rightarrow Ph_2PPPh_2 + Cl^- + CH_2O \qquad (6)$$

Another interesting observation was made when excess paraformaldehyde was added to Ph_2PLi. In addition to the chemical shift of 12 ppm expected for Ph_2PCH_2OLi, there was also a peak (whose intensity varied directly with the amount of excess formaldehyde) at 21.5 ppm. This is attributable to longer chain species in equilibrium as shown in reaction 7.

$$Ph_2PLi + CH_2O(\text{excess}) \rightleftarrows Ph_2PCH_2OLi + Ph_2PCH_2OCH_2OLi + \text{higher analogs} \qquad (7)$$

This reaction is reversible since addition of more Ph_2PLi to the solution of excess $(CH_2O)_n$ results in the disappearance of the +21.5-ppm peak and the reappearance of the large peak at +12 ppm.

Another reaction scheme proved satisfactory for the preparation of $(dpp)_2oe$. Reaction 4 was followed by acidification of the lithium reagent, followed by a transesterification reaction

$$Ph_2PCH_2OLi + HCl \rightarrow Ph_2PCH_2OH + LiCl \qquad (8)$$

$$Ph_2PCH_2OH + Ph_2POCH_3 \rightleftarrows Ph_2PCH_2OPPh_2 + CH_3OH \qquad (9)$$

It was found that at 75-80°, in benzene, an equilibrium was established (as determined by ^{31}P spectra of the reaction mixture) at approximately 40-60% completion. In order to drive the reaction to completion, nitrogen was swept over the reaction mixture to remove the volatile methanol. In this way a satisfactory yield of $(dpp)_2oe$ was obtained. Preparation of the metal complexes was straightforward. It should be noted that the use of $(C_6H_5CN)_2PdCl_2$ as a starting material for formation of $((dpp)_2oe)PdCl_2$ was especially advantageous because it reacted rapidly and the product precipitated from an originally homogeneous solution. The use of K_2PdCl_4 in a heterogeneous reaction mixture as illustrated in the preparation of $((dpp)_2op)PdCl_2$ is less satisfactory.

The phosphorus-31 nmr results for the oxygen-containing ligands and complexes are given in Table I. It is seen that the ^{31}P chemical shifts for all the coordination compounds of $(dpp)_2oe$ are considerably downfield from the shifts in the corresponding compounds of $(dpp)_2op$. This extraordinarily large downfield coordination shift has been noted previously in the case of five-membered chelate rings containing phosphorus.[14] The six-membered rings have coordination shifts (Δ_{PC}) for the tertiary phosphine end of the chelate similar to those of the corresponding monodentate ligands.[9,15] Sufficient data are not available for coordination compounds of phosphinites, R_2POR, for comparison of the chemical shifts and coordination shifts with those of the new ligands.

In the tungsten compounds the phosphine phosphorus has a smaller J_{WP} than the phosphinite phosphorus: 234 *vs.* 260 Hz for $(dpp)_2oe$ and 222 *vs.* 261 Hz for $(dpp)_2op$. This is expected on the basis of earlier work.[16]

P-P coupling is not observed in free $(dpp)_2op$, in which the phosphorus atoms are four bonds removed. The P-P coupling observed in the chelate complexes is probably transmitted solely through the metal center. In free $(dpp)_2oe$ a $|J_{PP}|$ of 16.5 Hz is observed; the $|J_{PP}|$ in chelate compounds of $(dpp)_2oe$ might be expected to contain contributions of coupling both through the backbone and through the metal center ($|J_{PP}| = J^b{}_{PP} + J^m{}_{PP}$). Values of $|J_{PP}|$ in $((dpp)_2op)M(CO)_4$ complexes of Cr, Mo, and W (46.5, 35, and 31 Hz) are larger than those in the corresponding $(dpp)_2oe$ complexes (31, 18.5, and 11 Hz) by an average of 17.4 ± 1.8 Hz. We attribute this difference to a $J^b{}_{PP}$ in chelate complexes of $(dpp)_2oe$ which is nearly the same as that in the free ligand, but with a sign opposite to that of $J^m{}_{PP}$. This explanation should be considered a tentative empirical postulate until further substantiation is obtained. The decreasing order of $|J_{PP}|$ in the series Cr > Mo > W has been observed earlier with other ligands.[17]

The much larger coordination chemical shifts of diphosphines which form five-membered chelate rings compared to those which form six-membered rings have been explained on the basis of ring strain.[14b] One might then expect that four-membered rings would show the largest shifts. Data in Table II on $[Ph_2P(CH_2)_nPPh_2]M(CO)_4$, where $n = 1, 2,$ or 3 and M = Cr, Mo, or W, clearly show that this is not the case. The large downfield shift on coordination is peculiar to the five-membered rings. Typical coordination shifts for monodentate phosphine complexes *cis*-$LL'Mo(CO)_4$ are about −59, −43, and −25 ppm for Cr, Mo, and W. The six-membered ring values (with $(dpp)_2p$) are somewhat less, −58, −38, and −17 ppm, whereas four-membered ring values (with $(dpp)_2m$) of −49, −24, and 0 ppm are substantially less. The deviations from the monodentate coordination shifts increase in the order Cr << Mo < W, also the order of increasing metal radius.

X-Ray crystal structures are available for $((dpp)_2m)Mo(CO)_4$,[18] $((dpp)_2e)Cr(CO)_4$,[19] $((dpp)_2e)Ir(CH_3)(C_8H_{12})$,[20]

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Table I. Phosphorus Nmr Data for $Ph_2P(CH_2)_nOPPh_2$, $n = 1$ and 2, and Derivatives

Compd	δ_{PC}, ppm	Δ_{PC}, ppm	δ_{PO}, ppm	Δ_{PO}, ppm	J_{PP}, Hz
$(C_6H_5)_2PCH_2OP(C_6H_5)_2$, $(dpp)_2oe$	14.1		−118.2		16.5
$((dpp)_2oe)Cr(CO)_4$	−86.0	−100.1	−196.7	−78.5	31
$((dpp)_2oe)Mo(CO)_4$	−63.4	−77.5	−174.4	−56.2	18.5
$((dpp)_2oe)W(CO)_4$[a]	−49.5	−63.6	−154.9	−36.7	11
$((dpp)_2oe)PdCl_2$	−79.8	−93.9	−159.5	−41.3	17
$(C_6H_5)_2PCH_2CH_2OP(C_6H_5)_2$, $(dpp)_2op$	22.8		−111.6		0
$((dpp)_2op)Cr(CO)_4$	−40.8	−63.6	−161.4	−49.8	46.5
$((dpp)_2op)Mo(CO)_4$	−22.0	−44.8	−141.6	−30.0	35
$((dpp)_2op)W(CO)_4$[b]	−2.2	−25.0	−116.2	−4.6	31
$((dpp)_2op)PdCl_2$	−11.7	−34.5	−107.1	+4.5	9

[a] W–P couplings of 234 and 260 Hz were observed for δ_{PC} and δ_{PO}, respectively. [b] W–P couplings of 222 and 261 Hz were observed for δ_{PC} and δ_{PO}.

Table II. Phosphorus Nmr Data for $[(C_6H_5)_2P(CH_2)_nP(C_6H_5)]M(CO)_4$ ($n = 1, 2, 3$; M = Cr, Mo, W)

Compd	δ, ppm	Δ, ppm	$J_{W\text{-}P}$, Hz
$(C_6H_5)_2PCH_2P(C_6H_5)$, $(dpp)_2m$	23.6[a]		
$((dpp)_2m)Cr(CO)_4$	−25.4	−49.0	
$((dpp)_2m)Mo(CO)_4$	0	−23.6	
$((dpp)_2m)W(CO)_4$	23.6	0	202
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, $(dpp)_2e$	12.5[a]		
$((dpp)_2e)Cr(CO)_4$	−79.4	−91.9	
$((dpp)_2e)Mo(CO)_4$	−54.7	−67.2	
$((dpp)_2e)W(CO)_4$	−40.1 (−35.8)[b]	−52.6 (−48.3)[b]	231 (239)[b]
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_3$, $(dpp)_2p$	17.3[a]		
$((dpp)_2p)Cr(CO)_4$	−41.4	−58.7	
$((dpp)_2p)Mo(CO)_4$	−21.0	−38.3	
$((dpp)_2p)W(CO)_4$	0	−17.3	222

[a] H. G. Horn and K. Sommer, *Spectrochim. Acta, Ser. A*, 27, 1049 (1971). [b] G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).

Table III. Pmr Data[a] for Chelating Ligands and Complexes

Compd	$\tau_{a,d}$, ppm	τ_b, ppm	τ_c, ppm	$J_{P_aH_b}$, Hz	$J_{P_dH_b}$, Hz	$J_{P_dH_c}$, Hz	$J_{H_bH_c}$, Hz
$(C_6H_5)_2POCH_2P(C_6H_5)$ (a) (b) (d)	2.79	5.43		8.20	6.10		
$((dpp)_2oe)Cr(CO)_4$	2.58	5.45		19.3	~0		
$((dpp)_2oe)Mo(CO)_4$	2.58	5.55		19.7	0.9		
$((dpp)_2oe)W(CO)_4$	2.59	5.54		19.4	~0		
$(C_6H_5)_2POCH_2CH_2P(C_6H_5)$[b] (a) (b) (c) (d)	2.63	5.97	7.50	8.4	8.4	~0	7.8
$((dpp)_2op)Cr(CO)_4$	2.68	5.69	7.42	20.5	15.5	3.7	4.8
$((dpp)_2op)Mo(CO)_4$	2.63	5.68	7.41	22.0	17.3	3.2	5.0
$((dpp)_2op)W(CO)_4$	2.63	5.68	7.40	22.2	16.8	3.7	5.0
$((dpp)_2op)PdCl_2$	2.45	5.92	7.50	19	14	~2-3	5
$(C_6H_5)_2PCH_2P(C_6H_5)_2$ (a) (b) (a)	2.72	7.26		1.2 (1.5)[c]			
$((dpp)_2m)Cr(CO)_4$	2.53	5.52		9.5			
$((dpp)_2m)Mo(CO)_4$	2.57	5.52		9.0			
$((dpp)_2m)W(CO)_4$	2.58	5.10		8.5			
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (a) (b) (c) (d)	2.65	7.90			8.5[d] (8.5)[c]		
$((dpp)_2e)Cr(CO)_4$	2.59	7.42			17.0[d]		
$((dpp)_2e)Mo(CO)_4$	2.56	7.47			18.0[d]		
$((dpp)_2e)W(CO)_4$	2.57	7.43			17.0[d]		
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (a) (b) (a)	2.60	7.75					
$((dpp)_2p)Cr(CO)_4$	2.55	7.58					
$((dpp)_2p)Mo(CO)_4$	2.61	7.53					
$((dpp)_2p)W(CO)_4$	2.63	7.44					

[a] Measured in $CDCl_3$ solution. [b] Data from ref 3. [c] A. J. Carty and R. K. Harris, *Chem. Commun.*, 234 (1967). [d] Peak separations represent $N = |{}^3J_{P_dH_b} + {}^2J_{P_dH_c}|$; see also footnote *c*.

and $((dpp)_2p)Ir(CH_3)(C_8H_{12})$.[21] The similarity in $(dpp)_2e$ geometries in the Cr and Ir complexes suggests that coordinated ligand geometries may be rather similar in different compounds. From the known studies the angles about phosphorus can be used to calculate[22] the percentage of s character in the phosphorus-centered orbitals forming the M–P bonds: $(dpp)_2m$, 23%; $(dpp)_2e$, 42%; $(dpp)_2p$, 51.5%. Values of J_{WP} in the $LL'W(CO)_4$ complexes of 202, 231, and 222 Hz do not simply reflect the percentage s character.

Proton data are given in Table III. The methylene protons of free $(dpp)_2oe$ are coupled with both phosphorus atoms resulting in a doublet of doublets, with coupling constants of 6.1 and 8.2 Hz. J_{POCH} is taken as 8.2 Hz. This is consistent with J_{POCH} values of 9.7 Hz[23] for $(C_6H_5)_2POCH_2$-

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Table IV. Infrared Stretching Frequencies in Metal Carbonyl Region[a]

Compd	ν_{CO}, cm^{-1}
$((dpp)_2oe)Cr(CO)_4$	2022 s, 1937 s, 1917 vs, 1910 s
$((dpp)_2oe)Mo(CO)_4$	2036 s, 1944 m, 1925 vs, 1918 s
$((dpp)_2oe)W(CO)_4$	2026 s, 1933 m, 1914 s, 1909 m
$((dpp)_2op)Cr(CO)_4$	2022 s, 1927 m, 1916 vs, 1900 vs
$((dpp)_2op)Mo(CO)_4$	2028 s, 1933 m, 1921 vs, 1907 vs
$((dpp)_2op)W(CO)_4$	2027 s, 1928 s, 1915 vs, 1903 vs
$((dpp)_2m)Cr(CO)_4$	2020, 1931, 1913, 1898 (2006, 1915, 1897, 1875)[b]
$((dpp)_2m)Mo(CO)_4$	2020, 1925, 1919, 1900 (2020, 1920, 1907, 1879)[b]
$((dpp)_2m)W(CO)_4$	2022, 1927, 1913, 1896 (2013, 1909, 1902, 1871)[b]
$((dpp)_2e)Cr(CO)_4$	2011, 1924, 1911, 1896 (2009, 1914, 1899, 1877)[b]
$((dpp)_2e)Mo(CO)_4$	2021, 1929, 1919, 1903 (2020, 1919, 1907, 1881)[b]
$((dpp)_2e)W(CO)_4$	2019, 1922, 1909, 1897 (2016, 1912, 1901, 1876)[b]
$((dpp)_2p)Cr(CO)_4$	2012, 1928, 1908, 1890 (2010, 1929, 1908, 1890)[c]
$((dpp)_2p)Mo(CO)_4$	2019, 1932, 1908, 1901 (2020, 1920, 1903, 1885)[d]
$((dpp)_2p)W(CO)_4$	2022, 1930, 1910, 1898

[a] Taken in cyclohexane solution with polystyrene calibration. [b] Taken in $ClCH_2CH_2Cl$ solution.[11] [c] Taken in *n*-octane solution.[14b] [d] Taken in $CHCl_3$ solution, J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometal. Chem.*, 29, 105 (1971).

CH_3, and 8.4 Hz for $(dpp)_2op$. A value of 6.1 Hz for J_{PCH} is consistent with values of 5 Hz[24] for $(dpp)_2op$ and 6 Hz[25] for $(C_6H_5)_2PCH_3$. Also consistent with these assignments is the trend that $^3J_{PH}$ values are generally larger (in absolute magnitude) than $^2J_{PH}$ values.[26] The chemical shift of τ 5.43 for the methylene protons of $(dpp)_2oe$ compares with the value of τ 5.68[24] for the methylene protons of $(C_6H_5)_2PCH_2OCH_2P(C_6H_5)_2$.

The coupling in free $(dpp)_2op$ has been described previously.[3]

In complexes of $(dpp)_2oe$ the methylene protons are coupled with both phosphorus atoms although the coupling constants change quite drastically compared to the free ligand. The two couplings are generally about 20 and 0-1 Hz. The value for J_{POCH} is considered to be the larger value. The phosphorus-hydrogen coupling constants are generally higher for hydrogen on β carbon than on α carbon.[26] Other bases for these assignments are discussed below.

In complexes of $(dpp)_2op$, the protons on the methylene attached to phosphorus occur as a quartet. This results from coupling with phosphorus (3-4 Hz) and the other methylene protons (4-5 Hz) giving a doublet of partially overlapping triplets. The (latter) methylene protons appear as a symmetrical arrangment of a quartet and two triplets. These protons couple with both phosphorus atoms (15 and 20 Hz) and the (former) methylene protons (4-5 Hz). The observed arrangement arises from four triplets situated such that the central triplets overlap to give a quartet. It is suggested that J_{POCH} is the larger value of about 20 Hz and J_{PCCH} is about 15 Hz. The following points support the given assignments. (1) J_{POCH} could be expected to have similar values in complexes of both $(dpp)_2oe$ (19 Hz) and $(dpp)_2op$ (20 Hz). (2) Values of J_{PCCH} of 14.5-16.6 Hz[27,28] observed in diethylphenylphosphine complexes of rhodium and iridium compare to a J_{PCCH} of 15 Hz for complexes of $(dpp)_2op$. (3) Verkade[29] has found that the two ligands of $[P(CH_2O)_3P]_2Fe(CO)_3$ are coordinated through different phosphorus atoms. Coordination of the phosphite phosphorus causes J_{POCH} to increase from 2.8 to 6.2 Hz while coordination of the phosphine phosphorus decreases J_{PCH} from 6.1 to ~0 Hz. Coordination of $(C_6H_5)_2POCH_2P(C_6H_5)$ in $((dpp)_2oe)Cr(CO)_4$ increases J_{POCH} from 8.2 to 19.3 Hz and decreases J_{PCH} from 6.1 to ~0 Hz. (4) It has been observed in other four-coordinate phosphorus compounds[25] (*e.g.*, phosphonium salts) that the magnitude of J_{PCH} increases as the electronegativity of the substituent decreases. The increase in J_{PCH} from ~0 to 3-4 Hz in going from $(dpp)_2oe$ to $(dpp)_2op$ complexes is understandable since $-OP(C_6H_5)_2$ is being replaced by $-CH_2OP(C_6H_5)_2$.

The pmr spectra of the ligands $(dpp)_2m$ and $(dpp)_2e$ have been thoroughly analyzed.[30] The simple 1:2:1 triplet of the free ligand $(dpp)_2m$ (τ 2.72, $J_{PCH} = 1.2$ Hz) moves downfield considerably (*ca.* 1.5-2.0 ppm) and the coupling increases substantially upon complex formation. The "deceptively simple" triplet[30] of the methylene protons of the free ligand $(dpp)_2e$ changes substantially upon complex formation to give a fairly sharp doublet (peak separation *ca.* 17-18 Hz which corresponds to $|J_{PCH} + J_{PCCH}|$) superimposed on a broad symmetrical base of low intensity lying mainly to the outside of the doublet. The spectra were not analyzed further. The methylene region of the $(dpp)_2p$ complexes was a broad unresolved band.

Carbonyl stretching frequencies from the infrared spectra of cyclohexane solutions are tabulated in Table IV. They all have the usual appearance characteristic of *cis*-$L_2M(CO)_4$ structures. Some of the literature values[11,14b] for the $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ compounds are at considerably lower frequency than the values reported here. The literature spectra were obtained in polar solvents, which often result in lower observed frequencies.[31] In the one case, $((dpp)_2p)Cr(CO)_4$, in which the literature value[14b] was obtained from a nonpolar solvent, *n*-octane, our agreement is excellent.

In summary, 13 new compounds are reported along with preparative data and infrared, ^{31}P, and proton nmr spectra. Currently unexplained phosphorus chemical shifts occur for chelates with five-membered rings (considerably downfield from the usual coordination shift) and four-membered rings (considerably upfield from the usual coordination shift). Chelates with six-membered rings show almost normal coordination shift behavior. Phosphorus-tungsten coupling is abnormally small in the four-membered chelate ring.

Registry No. $((dpp)_2p)Cr(CO)_4$, 40545-09-3; $((dpp)_2p)Mo(CO)_4$, 15553-68-1; $((dpp)_2p)W(CO)_4$, 50860-43-0; $((dpp)_2e)Cr$-

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$(CO)_4$, 29890-04-8; $((dpp)_2e)Mo(CO)_4$, 15444-66-3; $((dpp)_2e)W(CO)_4$, 29890-05-9; $((dpp)_2m)Cr(CO)_4$, 16743-46-7; $((dpp)_2m)Mo(CO)_4$, 26743-81-7; $((dpp)_2m)W(CO)_4$, 41830-14-2; $((dpp)_2oe)Cr(CO)_4$, 50860-44-1; $((dpp)_2oe)Mo(CO)_4$, 50860-45-2; $((dpp)_2oe)W(CO)_4$, 50860-46-3; $((dpp)op)Cr(CO)_4$, 50860-47-4; $((dpp)op)Mo(CO)_4$, 50860-48-5; $((dpp)op)W(CO)_4$, 50860-49-6; $((dpp)_2oe)PdCl_2$, 50860-50-9; $((dpp)_2op)PdCl_2$, 50860-51-0; $((dpp)_2oe)HgBr_2$, 50860-52-1; $((dpp)_2oe)HgI_2$, 50860-53-2; $(dpp)_2oe$, 50860-54-3; $(dpp)_2op$, 32309-62-9; $(dpp)_2m$, 2071-20-7; $(dpp)_2e$, 1663-45-2; $(dpp)_2p$, 6737-42-4; Ph_2PLi, 15968-89-5; C_2H_4O, 75-21-8; Ph_2PCl, 1079-66-9; Ph_2POCH_3, 4020-99-9; Ph_2PCH_2OH, 5958-44-1; $W(CO)_6$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $(C_6H_5CN)_2PdCl_2$, 14220-64-5; ^{31}P, 7723-14-0.

Contribution No. 507 from Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387

Preparation and Characterization of Two Series of Dimeric Molybdenum(V) *N,N*-Dialkyldithiocarbamates. Their Interrelationship and Chemistry as a Model for the Active Site of Nitrogenase

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Refluxing aqueous solutions containing molybdenum(V) react with sodium *N,N*-dialkyldithiocarbamates (Na(dtc); 1 mol) to yield a series of new complexes, $Mo_2O_4(dtc)_2$, while at 0° with Na(dtc) (>4 mol), $Mo_2O_3(dtc)_4$ is produced. The former complexes may be converted to the latter by further reaction with Na(dtc). Assignments of the molybdenum–oxygen stretching frequencies in the infrared spectra have been made and the visible spectra have been investigated. The interrelationship and chemistry of these two types of complex are suggested as a possible model for the interaction of two molybdenum atoms at an enzymic active site.

There is at present a growing interest in the chemistry of coordination compounds of molybdenum, particularly because of their possible relationship to redox-active molybdoenzymes.[1] The most recent reports suggest that the iron-molybdenum protein component[2] of nitrogenase (component I) (from *Azotobacter vinelandii*[2] or *Clostridium pasteurianum*,[3] but not from *Klebsiella pneumoniae*[4]) and xanthine oxidase (from all known sources[5]) both contain two molybdenum atoms per mole of enzyme. There is a distinct possibility in these cases that the two molybdenum atoms are at the active site, working in conjunction during catalysis. As part of our studies[6] of models for such enzymes, we sought to investigate this possibility and chose the supposedly well-established dimeric molybdenum(V) dithiocarbamates, *i.e.*, $Mo_2O_3(dtc)_4$, as our initial subject. This choice was dictated primarily by our recent successful reduction of diethyl azodicarboxylate (a useful two-electron acceptor model) by some *N,N*-dialkyldithiocarbamate complexes of molybdenum(IV). This reduction was accomplished by an initial oxidative addition of the azo double bond thus forming a 1:1 adduct, followed by hydrolysis to give the substituted hydrazine and the appropriate *cis*-dioxomolybdenum(VI) complex.[6] One to one adducts were also prepared with some related acetylenic and olefinic compounds.[6]

In this paper, we describe the synthesis and characterization of a new type of molybdenum(V) dithiocarbamate complex, μ-dioxo-bis[oxo-*N,N*-dialkyldithiocarbamatomolybdenum(V)], $Mo_2O_4(dtc)_2$, and an improved method for the preparation of μ-oxo-bis[oxobis(*N,N*-dialkyldithiocarbamato)molybdenum(V)], $Mo_2O_3(dtc)_4$. Assignments of the various molybdenum–oxygen vibrations in the infrared spectra have been made and the visible spectra have been reinvestigated and interpreted. The interrelationship of these two types of complex and some of their relevant chemistry are described and used as a basis for a possible mechanism of interaction for two molybdenum atoms at enzymic active sites.

Experimental Section

Materials and Physical Measurements. The known sodium salts of the dithiocarbamic acids were prepared in the customary manner[7] by dropwise addition of the appropriate dialkylamine (1.0 mol) to carbon disulfide (1.1 mol) in aqueous ethanol at room temperature, followed by dropwise addition of 10 *N* sodium hydroxide (1.0 mol). After the mixture had stood for several hours, the salt could usually be crystallized by the addition of acetone and then chilling to 0°. In the case of the diisopropyl compound a reaction temperature of 40° was used and the solvent was ether–acetone. All gave satisfactory C, H, and N analyses which indicated varying degrees of hydration.

All reactions and physical measurements were carried out under an atmosphere of purified argon using degassed analytical reagent grade solvents.

Infrared spectra were recorded as KBr disks with a Beckman IR-20A spectrophotometer, visible spectra were measured with a Cary Model 14 recording spectrophotometer, and microanalyses were obtained with a Hewlett-Packard 185 CHN Analyzer.

All analytical data are collected in Table I.

Preparation of $Mo_2O_3(dtc)_4$ Complexes. A solution of molybdenum pentachloride (0.50 g, 1.8 mmol) in water (50 ml) was slowly added to an ice-cold solution of the dithiocarbamate salt (*ca.* 18 mmol) in water (50 ml). The dark purple precipitate of $Mo_2O_3(dtc)_4$ (*ca.* 70% yield), which formed immediately, was collected by filtration, washed thoroughly with water, and dried *in vacuo*.

Preparation of $Mo_2O_4(dtc)_2$ Complexes. In a typical preparation, a solution containing molybdenum pentachloride (2.0 g, 7.3 mmol) and the dithiocarbamate salt (7.3 mmol) in water (50 ml) was

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