A01) and for a grant to purchase NMR equipment (Grant No. GP43155).

Registry No. $L_{I}Cr(CO)_4$, 62264-01-1; $L_{I}Mo(CO)_4$, 54340-52-2; $L_{I}W(CO)_4$, 62264-00-0; $L_{II}Cr(CO)_4$, 62263-99-4; $L_{II}Mo(CO)_4$, 62264-28-2; $L_{II}W(CO)_4$, 62264-27-1; $L_{III}Cr(CO)_4$, 62264-26-0; $L_{III}Mo(CO)_4$, 62264-25-9; $L_{III}W(CO)_4$, 62264-24-8; $L_{IV}Cr(CO)_4$, 62264-23-7; $L_{IV}Mo(CO)_4$, 62264-22-6; $L_{IV}W(CO)_4$, 62264-21-5; $L_{V}Cr(CO)_4$, 62264-20-4; $L_{V}Mo(CO)_4$, 62264-19-1; $L_{V}W(CO)_4$, 62264-18-0; $[Ph_2P(S)CH_2PPh_2Me]^+Br^-$, 62264-60-2; $[Ph_2P(S)CH_2PPhEtMe]^+Br^-$, 62264-59-9; $[Ph_2P(S)CH_2PPh(i\text{-pr})Me]^+Br^-$, 62264-58-8; $[Ph_2P(S)CH_2PPhMe_2]^+Br^-$, 62264-44-2; $[Ph_2P(S)CH_2P(i\text{-pr})_2Me]^+Br^-$, 62264-43-1; $[Ph_2P(S)CH_2PMe_3]^+Br^-$, 62264-42-0; $[Ph_2P(S)CH(CH_3)PPh_2Me]^+Br^-$, 62264-57-7; $[MePh_2PCH_2P(S)PhMe]^+Br^-$, 62264-56-6; $[MePh_2PCH_2P(S)Me_2]^+Br^-$, 62264-55-5; $[MePh_2PCH_2P(S)Ph(i\text{-pr})]^+Br^-$, 62264-54-4; $[MePh_2PCH_2P(S)(i\text{-pr})_2]^+Br^-$, 62264-53-3; $Ph_2P(S)CH_2P(S)Ph_2$, 14633-92-2; $Ph_2P(S)CH_2P(S)PhEt$, 62264-52-2; $Ph_2P(S)CH_2P(S)Ph(i\text{-pr})$, 62264-51-1; $Ph_2P(S)CH_2P(S)PhMe$, 62264-50-0; $Ph_2P(S)CH_2P(S)(i\text{-pr})_2$, 62264-49-7; $Ph_2P(S)CH_2P(S)Me_2$, 38055-42-4; $Ph_2P(S)CH(CH_3)P(S)Ph_2$, 60398-69-8; $Ph_2P(S)CH_2PMe_2$, 23176-51-4; $Ph_2P(S)CH(CH_3)PPh_2$, 62264-48-6; $Ph_2PCH_2P(S)PhMe$, 62264-47-5; $Ph_2PCH_2P(S)Me_2$, 57241-93-7; $Ph_2PCH_2P(S)Ph(i\text{-pr})$, 62264-46-4; $Ph_2PCH_2P(S)(i\text{-pr})_2$, 62264-45-3; $Ph_2PCH_2PMe_2$, 62263-64-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $Ph_2P(S)CH_2PPh(NEt_2)$, 54006-32-5; $Ph_2P(S)CH_2PPhCl$, 54006-33-6; $Ph_2P(S)CH_2PPh_2$, 54006-28-9; $Ph_2P(S)CH_2PPhEt$, 54006-30-3; $Ph_2P(S)CH_2PPh(i\text{-pr})$, 54006-27-8; $Ph_2P(S)CH_2PPhMe$, 54006-29-0; $Ph_2P(S)CH_2P(i\text{-pr})_2$, 54006-31-4.

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Unsymmetrical Bis-Phosphorus Ligands. 10. Synthesis and Group 6 Metal Carbonyl Derivatives of (Diphenylphosphino)(diorganophosphino)methane, $Ph_2PCH_2PR^1R^2$ [1]

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Five new ligands of the type $Ph_2PCH_2PR^1R^2$, with $R^1 = R^2 =$ Me or *i*-Pr and $R^1 =$ Ph, $R^2 =$ Me, Et, or *i*-Pr, have been synthesized by the reduction of $Ph_2P(S)CH_2PR^1R^2$ and by the reaction of Ph_2PCH_2Li with R^1R^2PCl. These ligands react smoothly with $M(CO)_6$, M = Cr, Mo, or W, to form coordination compounds of the type $LM(CO)_4$, which contain four-membered chelate rings. Extensive proton and phosphorus-31 NMR data are reported.

The synthesis of chelating phosphorus ligands with chemically and magnetically different phosphorus atoms has been especially important for investigating coordination compounds of these ligands by phosphorus-31 nuclear magnetic spectroscopy.[1b,2-5] To date, most of the complexes of chelating di(tertiary phosphines), both symmetrical and unsymmetrical, have been of 1,2-bis(diphenylphosphino)ethane or have been similar derivatives, which lead to five-membered chelate rings.[2,5-8] Numerous other chelating ligands containing at least one donor phosphorus atom in a five-member ring have been examined.[1b,4] Currently, without known exception, donor phosphorus atoms in such circumstances have an extraordinarily large and presently unexplained ^{31}P downfield coordination shift.[1b,2-5,9,10] In an attempt to study the ^{31}P NMR spectra of phosphorus-containing chelate rings of other sizes and compare them to the well-examined five-membered rings, we have synthesized the first examples of unsymmetrical (diphenylphosphino)(diorganophosphino)methane, $Ph_2PCH_2PR^1R^2$. These ligands form, of course, four-membered rings when chelated. The following paper[11] reports coordination compounds of unsymmetrical 1,3-bis(diorganophosphino)propanes, which form six-membered chelate rings.

Experimental Section

Physical measurements and analytical data were obtained as described in the previous paper.[1b]

Hexachlorodisilane was used as purchased from PCR, Inc., Gainesville, Fla. (Phosphinomethyl)phosphine sulfides were prepared as described elsewhere.[12] Metal carbonyls were obtained from Climax Molybdenum Corp. and Pressure Chemical Co.

Synthesis of $Ph_2PCH_2PR^1R^2$ by Reduction of $Ph_2P(S)CH_2R^1R^2$ with Si_2Cl_6. $Ph_2PCH_2PPh(i\text{-}Pr)$. Into a 300-mL three-necked flask equipped with a magnetic stirrer, condenser, and a nitrogen inlet was placed 5.00 g (0.013 mol) of $Ph_2P(S)CH_2PPh(i\text{-}Pr)$ along with 20 mL of benzene and a twofold excess of Si_2Cl_6 (0.026 mol, 7.05 g, 4.45 mL). The mixture was refluxed under nitrogen for about 6 h. The yellow solution was carefully hydrolyzed with 30% aqueous NaOH. After hydrolysis, more benzene was added to the reaction mixture, and the solution was filtered to remove the hydrolysis salts. The flask with the benzene solution was placed on a rotary evaporator, and the resulting colorless oil dried for several days under vacuum. The compound $Ph_2PCH_2PPh(i\text{-}Pr)$ was identified by ^{31}P and proton NMR spectra and microanalysis. The yield was 1.80 g (39%).

Ph_2PCH_2PPhEt. This compound was prepared as described above by the reaction of 11.8 g (0.032 mol) of $Ph_2P(S)CH_2PPhEt$ with 17.2 g (0.064 mol, 10.9 mL) of Si_2Cl_6 in 100 mL of benzene. After hydrolysis, the oil was passed through a small column of alumina to remove any water and other impurities. The oil was dissolved in absolute EtOH and CH_2Cl_2; and after several months in a freezer (−25 °C), white crystals of the compound formed (mp 49–51 °C) in 1.95-g (18%) yield.

Synthesis of $PH_2PCH_2PR^1R^2$ by Reduction of $Ph_2P(S)CH_2PR^1R^2$ with Na. Ph_2PCH_2PPhMe. This compound was prepared by mixing 8.87 g of $Ph_2P(S)CH_2PPhMe$ (0.025 mol), 2.9 g (0.13 g-atom) of Na (a 2.5-fold excess), and 50 mL of toluene in a 300-mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet. The mixture was heated to reflux for 4 h during which time the solution turned green-brown, with a dark precipitate and finely divided sodium present. A ^{31}P spectrum of an aliquot showed a small amount of Ph_2PMe in addition to the desired compound due to the reduction of $Ph_2P(S)Me$ present as an impurity in the starting material. After the mixture was cooled, it was filtered (with difficulty) through diatomaceous earth to remove the precipitate and sodium. The orange-brown solution contained a small amount of precipitate and was passed through a small column of alumina. Pure Ph_2PCH_2PPhMe in toluene was eluted, and the solution was concentrated to an oil. The yield was 3.4 g (42%). Crystallization of 2.45 g (30%) of solid Ph_2PCH_2PPhMe (mp 54–55 °C) was effected from EtOH–CH_2Cl_2.

$Ph_2PCH_2P(i\text{-}Pr)_2$ and $Ph_2PCH_2PMe_2$. The compound $Ph_2PCH_2P(i\text{-}Pr)_2$ was similarly prepared using 10.0 g (0.029 mol) of $Ph_2P(S)CH_2P(i\text{-}Pr)_2$ and 3.3 g (0.14 g-atom) of Na in 70 mL of toluene. After 19 h of refluxing, 5.1 g (56%) of the oil $Ph_2PCH_2P(i\text{-}Pr)_2$, identified by ^{31}P and proton NMR spectra, was isolated. In another similar run, the compound was produced in 51% yield.

The compound $Ph_2PCH_2PMe_2$ was prepared as above from 10.0 g of $Ph_2P(S)CH_2PMe_2$ in yields of 33% and 63%. In one other run, it was found that the workup of the reaction mixture after refluxing was much easier if the excess sodium was first hydrolyzed with *i*-PrOH. The salts of hydrolysis formed were then treated with MeOH and distilled water, respectively, to dissolve them. Some CH_2Cl_2 was added and the two-layered system was extracted with several 100 mL portions of H_2O. The organic layer was evaporated to an oil and redissolved in CH_2Cl_2; it was dried over Na_2SO_4 and passed through a column of alumina to remove the color from the solution. Upon evaporation, a 55% yield of the Ph_2PCH_2PMe oil was obtained. This compound was identified by ^{31}P and proton NMR spectra.

Synthesis of $Ph_2PCH_2PR^1R^2$ via Ph_2PCH_2Li. $Ph_2PCH_2PPh(i\text{-}Pr)$ and Ph_2PCH_2PPhMe. Ph_2PCH_2Li was prepared as described by Peterson.[13] Into a three-necked flask equipped with a magnetic stirrer and a nitrogen inlet were added successively 41.6 mL of 1.20 M *n*-BuLi (0.0500 mol) in hexane, 5.8 g (0.050 mol) of tetramethylethylenediamine (TMED), and 9.26 mL (10.0 g, 0.050 mol) of Ph_2PMe. Heat was evolved when the *n*-BuLi and TMED were mixed, and the solution turned yellow and became warm again when the Ph_2PMe was added. After about 1 h of stirring, a yellow precipitate formed; and after ca. 2 h of stirring, 25 mL of freshly distilled THF was added to dissolve the precipitate. A ^{31}P spectrum of an aliquot showed two major peaks: at +1 to +2 ppm assigned to Ph_2PCH_2Li and at −28 ppm vs. H_3PO_4 assigned to Ph_2PMe. The ratio was about 1:1. (Longer stirring failed to change the relative amounts.) The red-yellow solution of Ph_2PCH_2Li was transferred under nitrogen to an addition funnel mounted on another three-necked flask equipped with a nitrogen inlet and magnetic stirrer. The Ph_2PCH_2Li was added to 1.35 g (0.0500 mol) of $Ph(i\text{-}Pr)PCl$ in benzene over a 45-min period. After addition was completed, the yellow mixture was stirred overnight. The reaction mixture was reduced to an oil which was dissolved in CH_2Cl_2. The solution was extracted with three 100-mL portions of deoxygenated distilled water to remove the LiCl salts and was dried over Na_2SO_4. Concentration of the solution by evaporation resulted in a light orange oil. A ^{31}P spectrum showed the desired compound $Ph_2PCH_2PPh(i\text{-}Pr)$ plus about 50% Ph_2PMe. Column chromatography with alumina removed only the color, with no separation of Ph_2PMe from the desired compound. The now colorless oil was transferred to a small round-bottomed flask and vacuum-distilled using a short-path distillation head. The bath temperature was taken to about 185 °C to distill the Ph_2PMe (distillate was collected up to 125 °C (0.1 mm); lit.[14] 89–92 °C (0.8 mm)). After cooling, a ^{31}P spectrum showed the residue to be essentially pure $Ph_2PCH_2PPh(i\text{-}Pr)$ although it was yellow due to thermal decomposition. Passing a CH_2Cl_2 solution of the residue again through a short alumina column removed the color. Upon evaporation, 6.0 g (35%) of the oil $Ph_2PCH_2PPh(i\text{-}Pr)$ resulted.

The compound Ph_2PCH_2PPhMe was produced in 16% yield (0.100-mol scale) using the above procedure.

Analytical data for these compounds are given in Table I. Phosphorus-31 NMR data are given in Table II. Proton NMR data are given later in the Experimental Section.

Synthesis of Metal Carbonyl Derivatives $[Ph_2PCH_2PR^1R^2]M(CO)_4$. The metal carbonyl derivatives $[Ph_2PCH_2PR^1R^2]M(CO)_4$, where M = Cr, Mo, or W, were prepared by essentially the same method, which consisted of reaction of about 2 or 3 g of ligand with the stoichiometric (1:1) amount of metal carbonyl in about 10 mL of warm, deoxygenated diethylene glycol dimethyl ether (diglyme) as described earlier[15] until CO evolution ceased. In each case, the amount of CO monitored corresponded approximately to the amount that should have theoretically been displaced in forming an $LM(CO)_4$ complex. After reaction had ceased and the mixtures (yellow solutions of varying intensity) were cooled, the complexes would precipitate from the diglyme in some cases. However, all reaction mixtures were transferred to a small round-bottomed flask and the diglyme was removed under vacuum at a bath temperature of ca. 50 °C and a pressure of ca. 0.1 mm; excess $M(CO)_6$ was also removed by this method.

The oil or powder that remained after diglyme removal was dissolved in CH_2Cl_2, and the desired compound was precipitated with hexane; most of the complexes precipitated immediately. This solvent pair was used for all of the complexes prepared.

After the CH_2Cl_2–hexane solutions (with precipitates) were placed in the freezer for a day or so, the mixtures were filtered; and the complexes were washed with pentane and were dried in vacuo. The melting points, colors, yields, reaction times, and bath temperatures for each complex can be found in Table III. Analytical data are given in Table I; ^{31}P data, in Table II; ^{1}H NMR data, later in the Experimental Section.

The complex $[Ph_2PCH_2PMe_2]Mo(CO)_4$ was prepared using the exchange method with norbornadienetetracarbonylmolybdenum.[16] In

Table I. Analytical Data of (Diphenylphosphino)(diorganophosphino)methane Ligands and Their Metal Carbonyl Derivatives

Species	% C		% H		% P		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	
$Ph_2PCH_2PMe_2$ (L_I)	[a]						Oil
$L_ICr(CO)_4$	53.78	53.13	4.28	4.46	14.60	15.07	160-163
$L_IMo(CO)_4$	48.74	48.90	3.87	3.96	13.23	13.10	Dec pt >135
$L_IW(CO)_4$	41.03	40.53	3.26	3.37	11.14	10.75	170 dec
Ph_2PCH_2PPhMe (L_{II})	74.52	74.50	6.25	6.50	19.22	19.02	54-55
$L_{II}Cr(CO)_4$	59.26	58.45	4.15	4.35	12.74	12.91	156-157
$L_{II}Mo(CO)_4$	54.36	54.36	3.80	3.98	11.68	11.60	144-146 dec
$L_{II}W(CO)_4$	46.63	46.50	3.26	3.38	10.02	9.95	156-157
Ph_2PCH_2PPh(*i*-Pr) (L_{III})	75.41	75.70	6.90	7.07			Oil
$L_{III}Cr(CO)_4$	60.70	59.95	4.70	5.15	12.04	12.37	142-144
$L_{III}Mo(CO)_4$	55.93	54.40	4.33	4.68	11.10	11.84	76-78
$L_{III}W(CO)_4$	48.32	48.60	3.74	4.02	9.59	9.33	85-87
Ph_2PCH_2P(*i*-Pr)$_2$ (L_{IV})	[a]						Oil
$L_{IV}Cr(CO)_4$	57.50	57.21	5.46	5.68	12.90	13.20	192-195
$L_{IV}Mo(CO)_4$	52.68	52.22	5.00	5.00	11.82	11.69	179-186 dec
$L_{IV}W(CO)_4$	45.12	44.99	4.28	4.44	10.12	10.28	207-109
Ph_2PCH_2PPhEt	74.99	74.71	6.59	6.87	18.42	17.82	49-51

[a] Oils were characterized by NMR. Satisfactory elemental analyses were not obtained.

Table II. Phosphorus-31 NMR Data of (Diphenylphosphino)(diorganophosphino)methane Ligands and Metal Carbonyl Complexes

Species	δ_{PPh_2}[a]	Δ_{PPh_2}[b]	$\delta_{PR^1R^2}$[a]	$\Delta_{PR^1R^2}$[b]	$\lvert J_{PP}\rvert$, Hz	$\lvert J_{PW}\rvert$, Hz[c]
$Ph_2PCH_2PMe_2$ (L_I)	−22.8		−52.1		108	
$L_ICr(CO)_4$	+25.8	+48.6	+5.4	+57.5	35	
$L_IMo(CO)_4$	+1.7	+24.5	−24.8	+27.3	8	
$L_IW(CO)_4$	−23.4	−0.6	−53.5	−1.4	13	199 (Ph) 194 (Me)
Ph_2PCH_2PPhMe (L_{II})	−22.5		−39.1		115	
$L_{II}Cr(CO)_4$	+25.9	+48.4	+13.8	+52.9	23	
$L_{II}Mo(CO)_4$	+1.5	+24.0	−13.0	+26.1	17	
$L_{II}W(CO)_4$	−23.5	−1.0	−39.6	−0.5	23	200 (Ph) 199 (Me)
$Ph_2PCH_2PPh_2$ (L)	−23.6[d]					
$LCr(CO)_4$	+25.4[d]	+49.0[d]				
$LMo(CO)_4$	0.0[d]	+23.6[d]				
$LW(CO)_4$	−23.6[d]	0.0[d]				202[d]
Ph_2PCH_2PPh(*i*-Pr) (L_{III})	−22.4		−13.5		114	
$L_{III}Cr(CO)_4$	+26.1	+48.5	+34.8	+48.3	16	
$L_{III}Mo(CO)_4$	+1.6	+24.0	+12.4	+25.9	20	
$L_{III}W(CO)_4$	−23.9	−1.5	−11.5	+2.0	26	200 (Ph) 198 (*i*-Pr)
Ph_2PCH_2P(*i*-Pr)$_2$ (L_{IV})	−19.9		−4.3		119	
$L_{IV}Cr(CO)_4$	+25.7	+45.6	+43.8	+48.1	20	
$L_{IV}Mo(CO)_4$	+1.8	+21.7	+23.7	+28.0	15	
$L_{IV}W(CO)_4$	−23.9	−4.0	+1.1	+5.4	21	203 (Ph) 194 (*i*-Pr)
Ph_2PCH_2PPhEt	−22.7		−25.4		115	

[a] In ppm referenced externally to 85% H_3PO_4; + ppm indicates downfield chemical shift from 85% H_3PO_4. [b] $\Delta \equiv$ coordination chemical shift = $\delta_{\mathrm{complex}} - \delta_{\mathrm{free\ ligand}}$. [c] J_{PPh_2W}(Ph) or $J_{PR^1R^2W}$(R) is indicated. [d] Data for comparison purposes from ref 3.

a small flask were mixed 1.00 g (3.84 mmol) of $Ph_2PCH_2PMe_2$, 1.15 g (3.84 mmol) of $C_7H_8Mo(CO)_4$, and about 10–20 mL of CH_2Cl_2. After stirring of the mixture under nitrogen for several minutes, the CH_2Cl_2 was removed by evaporation. The resulting residue was recrystallized from a CH_2Cl_2–hexane mixture. The yellow-brown complex $[Ph_2PCH_2PMe_2]Mo(CO)_4$ was collected in a yield of 0.96 g (53%); it decomposes at temperatures greater than 135 °C.

The complex $[Ph_2PCH_2PPh$(*i*-Pr)$]Mo(CO)_4$ was initially prepared using toluene instead of diglyme. In 20 mL of toluene were placed 1.80 g (5.15 mmol) of ligand and 1.4 g (5.3 mmol) of $Mo(CO)_6$. The mixture was heated over a 5-h period at ca. 110 °C. After the evolution of CO had ceased, the toluene was removed by evaporation; and CH_2Cl_2 was added to dissolve the darkened residue. After column chromatography using alumina, the resulting light yellow solution was concentrated to an oil which was dissolved in a $CHCl_3$–hexane mixture. Light yellow crystals of the complex formed in the freezer after about 2 days. The yield was 1.85 g (64%); the complex melted at 76–78 °C after several recrystallizations.

Proton NMR data for each compound are listed below in the following order: compounds, assignment, chemical shift (ppm) downfield from tetramethylsilane, multiplicity, and coupling constant in Hz. Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet. Spectra are from the 100-MHz instrument unless (60) appears after the compound, in which case the spectra are from a 60-MHz instrument.

Ph_2PCH_2PPh(*i*-Pr): Ph, 7.0–7.8 (m); PCH_2P, 2.50 (distorted d), $^2J_{P(i\text{-}Pr)CH}$ or $^2J_{P(Ph)CH} = 1.5$; $CH(CH_3)_2$, centered at ca. 2.0 (m); $CH(CH_3)_A(CH_3)_B$ (8 lines); $(CH_3)_A$, 1.13 (d of d), $^3J_{PCCH} = 14.4$, $^3J_{HCCH} = 6.9$; $(CH_3)_B$, 0.86 (d of d), $^3J_{PCCH} = 13.2$, $^3J_{HCCH} = 6.8$. Ph_2PCH_2PPhEt: Ph, 7.2–7.5 (m); PCH_2P, 2.46 (s); CH_2CH_3, centered at 1.79 (broadened q); CH_2CH_3, 0.96 (m), $^3J_{HCCH} = 7.6$. Ph_2PCH_2PPhMe: Ph, 7.2–7.6 (m); PCH_AH_BP, centered at ca. 2.4 (m), ABMX; H_A, 2.52, $^2J_{H_ACH_B} = 13.2$; H_B, 2.38, $^2J_{P(Me)CH}$ or $^2J_{P(Ph)CH} = 1.3$; CH_3, 1.36 (d), $^2J_{PCH} = 3.6$. Ph_2PCH_2P(*i*-Pr)$_2$: Ph, 7.2–7.6 (m); PCH_2P, 2.07 (d), $^2J_{P(i\text{-}Pr)CH}$ or $^2J_{P(Ph)CH} = 2.1$; $CH(CH_3)_2$, centered at ca. 1.8 (m); $CH(CH_3)_A(CH_3)_B$ (6 lines); $(CH_3)_A$, 1.09

Table III. Preparative Data of Metal Carbonyl Derivatives of (Diphenylphosphino)(diorganophosphino)methane Ligands

Compd	Color	Reacn time, h	Bath temp, °C	Yield, %
$Ph_2PCH_2PMe_2$ (L_I)				
$L_ICr(CO)_4$	Bright yellow	2	130-145	27
$L_IMo(CO)_4$	Yellow-brown	*a*		53
$L_IW(CO)_4$	Light yellow	3	140-155	46
Ph_2PCH_2PPhMe (L_{II})				
$L_{II}Cr(CO)_4$	Yellow	5	135	39
$L_{II}Mo(CO)_4$	Light yellow	2.5	90-100	79
$L_{II}W(CO)_4$	Yellow	2.5	140-160	80
$Ph_2PCH_2PPh(i\text{-}Pr)$ (L_{III})				
$L_{III}Cr(CO)_4$	Yellow	2.75	120-140	67
$L_{III}Mo(CO)_4$	Off-white	2	90-120	44
$L_{III}W(CO)_4$	Light yellow	3.5	140-155	61
$Ph_2PCH_2P(i\text{-}Pr)_2$ (L_{IV})				
$L_{IV}Cr(CO)_4$	Yellow	3.5	130-145	56
$L_{IV}Mo(CO)_4$	Yellow	1.25	100-110	46
$L_{IV}W(CO)_4$	Yellow	3	145-155	63

[a] Prepared by exchange with $(C_7H_8)Mo(CO)_4$; see Experimental Section.

(d of d), $^3J_{PCCH} = 11.0$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 1.04 (d of d), $^3J_{PCCH} = 13.6$, $^3J_{HCCH} = 6.9$. $Ph_2PCH_2PMe_2$: Ph, 7.1–7.5 (m); PCH_2P, 2.12 (s); CH_3, 1.06 (d), $^2J_{PCH} = 2.6$.

$[Ph_2PCH_2PPh(i\text{-}Pr)]Cr(CO)_4$: Ph, 7.2–7.8 (m); PCH_2P, 4.07 (t), $^2J_{P(i\text{-}Pr)CH} \simeq {}^2J_{P(Ph)CH} = 9.2$; $CH(CH_3)_2$, centered at ca. 2.1 (m); $CH(CH_3)_A(CH_3)_B$ (6 lines); $(CH_3)_A$, 1.06 (d of d), $^3J_{PCCH} = 19.2$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 0.96 (d of d), $^3J_{PCCH} = 13.4$, $^3J_{HCCH} = 6.8$. $[Ph_2PCH_2PPh(i\text{-}Pr)]Mo(CO)_4$: Ph, 7.2–7.8 (m); PCH_2P, 4.10 (t), $^2J_{P(i\text{-}Pr)CH} \simeq {}^2J_{P(Ph)CH} = 8.6$; $CH(CH_3)_2$, centered at ca. 2.0 (m); $CH(CH_3)_A(CH_3)_B$ (6 lines); $(CH_3)_A$, 1.02 (d of d), $^3J_{PCCH} = 19.4$, $^3J_{HCCH} = 7.1$; $(CH_3)_B$, 0.92 (d of d), $^3J_{PCCH} = 14.5$, $^3J_{HCCH} = 6.9$. $[Ph_2PCH_2PPh(i\text{-}Pr)]W(CO)_4$: Ph, 7.2–7.8 (m); PCH_AH_BP, centered at 4.5 (distorted t), ABMX; H_A, 4.55; H_B, 4.50, $^2J_{H_ACH_B} = 15.0$; $CH(CH_3)_2$, centered at ca. 2.0 (m); $CH(CH_3)_A(CH_3)_B$ (6 lines); $(CH_3)_A$, 1.01 (d of d), $^3J_{PCCH} = 19.2$, $^3J_{HCCH} = 7.1$; $(CH_3)_B$, 0.92 (d of d), $^3J_{PCCH} = 14.6$, $^3J_{HCCH} = 6.8$. $[Ph_2PCH_2PPhMe]Cr(CO)_4$: Ph, 7.3–7.8 (m); PCH_AH_BP, centered at ca. 4.1, ABMX; H_A, 4.12; H_B, 4.00, $^2J_{H_ACH_B} = 15.0$; CH_3, 1.74 (d of d), $^2J_{PCH} = 7.2$, $^4J_{PCPCH} = 0.8$. $[Ph_2PCH_2PPhMe]Mo(CO)_4$: Ph, 7.2–7.8 (m); PCH_AH_BP, centered at ca. 4.1 (m), ABMX; H_A, 4.19; H_B, 3.92, $^2J_{H_ACH_B} = 14.9$; CH_3, 1.72 (d), $^2J_{PCH} = 6.3$. $[Ph_2PCH_2PPhMe]W(CO)_4$ (60): Ph, 7.1–7.9 (m); PCH_2P, centered at ca. 4.5 (m); CH_3, 1.88 (d), $^2J_{PCH} = 7.3$. $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$: Ph, 7.3–7.7 (m); PCH_2P, 3.64 (d of d), $^2J_{P(i\text{-}Pr)CH} = 8.3$, $^2J_{P(PH)CH} = 9.6$; $CH(CH_3)_2$, centered at ca. 2.1 (m); $CH(CH_3)_A(CH_3)_B$ (8 lines); $(CH_3)_A$, 1.21 (d of d), $^3J_{PCCH} = 14.7$, $^3J_{HCCH} = 6.9$; $(CH_3)_B$, 1.19 (d of d), $^3J_{PCCH} = 16.0$, $^3J_{HCCH} = 7.1$. $[Ph_2PCH_2P(i\text{-}Pr)_2]Mo(CO)_4$ (60): Ph, 7.2–7.8 (m); PCH_2P, 3.69 (d of d), $^2J_{P(i\text{-}Pr)CH} = 7.8$, $^2J_{P(Ph)CH} = 9.0$; $CH(CH_3)_2$, centered at ca. 1.9 (m); $CH(CH_3)_A(CH_3)_B$ (6 lines); $(CH_3)_A$, 1.14 (d of d), $^3J_{PCCH} = 15.0$, $J_{HCCH} = 6.9$; $(CH_3)_B$, 1.13 (d of d), $^3J_{PCCH} = 16.8$, $^3J_{HCCH} = 7.2$. $[Ph_2PCH_2P(i\text{-}Pr)_2]W(CO)_4$ (60): Ph, 7.3–7.8 (m); PCH_2P, 4.13 (d of d), $^2J_{P(i\text{-}Pr)CH} = 8.0$, $^2J_{P(Ph)CH} = 9.0$; $CH(CH_3)_2$, centered at ca. 2.0 (m); $CH(CH_3)_A(CH_3)_B$ (8 lines); $(CH_3)_A$, 1.16 (d of d), $^3J_{PCCH} = 15.9$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 1.12 (d of d), $^3J_{PCCH} = 16.2$, $^3J_{HCCH} = 7.1$. $[Ph_2PCH_2PMe_2]Cr(CO)_4$: Ph, 7.3–7.7 (m); PCH_2P, 3.76 (t), $^2J_{P(Me)CH} \simeq {}^2J_{P(Ph)CH} = 9.5$; CH_3, 1.57 (d of d), $^2J_{PCH} = 7.8$, $^4J_{PCPCH} = 0.6$. $[Ph_2PCH_2PMe_2]Mo(CO)_4$ (60): Ph, 7.2–7.8 (m); PCH_2P, 3.77 (t), $^2J_{P(Me)CH} \simeq {}^2J_{P(Ph)CH} = 8.8$; CH_3, 1.53 (d), $^2J_{PCH} = 7.2$. $[Ph_2PCH_2PMe_2]W(CO)_4$ (60): Ph, 7.2–7.8 (m); PCH_2P, 4.24 (t), $^2J_{P(Me)CH} \simeq {}^2J_{P(Ph)CH} = 9.1$; CH_3, 1.66 (d), $^2J_{PCH} = 7.8$.

Results and Discussion

(Diphenylphosphino)(diorganophosphino)methanes, $Ph_2PCH_2PR^1R^2$, where $R^1 = R^2$ = Me or *i*-Pr and R^1 = Ph, R^2 = Me, Et, or *i*-Pr, were prepared by two methods: reduction of (phosphinomethyl)phosphine sulfides with sodium (eq I) or hexachlorodisilane and reaction of (lithiomethyl)diphenylphosphine[13] with a diorganophosphinous chloride (eq II).

$$Ph_2P(S)CH_2PR^1R^2 + 2Na \rightarrow Ph_2PCH_2PR^1R^2 + Na_2S \qquad (I)$$

$$Ph_2PCH_2Li + R^1R^2PCl \rightarrow Ph_2PCH_2PR^1R^2 + LiCl \qquad (II)$$

The reduction reaction of the tertiary phosphine sulfide was carried out with equal convenience with sodium[17] in toluene or with Si_2Cl_6[18] although, considering the relative costs of the reagents, the sodium reduction is favored. We found no evidence of phenyl cleavage from phosphorus in this reaction by Na although such cleavage by alkali metals in tetrahydrofuran is a well-known high-yield reaction.[19]

The use of Ph_2PCHLi seems to be an appealing method to form $Ph_2PCH_2PR^1R^2$ compounds since it is the most direct and the most amenable to large-scale reactions. One problem, however, is that the metalation reaction of Ph_2PMe with *n*-butyllithium in tetramethylethylenediamine (TMED) occurs to an approximately 70% completion.[13] Actually, in our laboratory, an aliquot of the *n*-BuLi/TMED–Ph_2PMe reaction mixture after 2 h showed two ^{31}P NMR peaks of equal intensity: one at −28 ppm vs. H_3PO_4 assigned to the starting material Ph_2PMe and one at about +1 or +2 ppm assigned to the lithio reagent Ph_2PCH_2Li. Longer reaction time failed to change the relative amounts. Thus, the maximum expected yield based on the starting tertiary phosphine is about 50%. In addition, the removal of the unreacted Ph_2PMe from the product presents a purification problem for the noncrystalline products, viz., $Ph_2PCH_2PPh(i\text{-}Pr)$, $Ph_2PCH_2PMe_2$, and $Ph_2PCH_2P(i\text{-}Pr)_2$.

Phosphorus-31 NMR data for the ligands are given in Table II. The chemical shift of the diphenylphosphino group shows reasonable constancy at about −22 ppm throughout the series. The chemical shifts of the R_1R_2P– groups are reasonably predictable (except that for Me_2P– which is somewhat lower than expected) from the group contributions (GC)[20] of the organic groups by using δ (ppm) = $-22 + 3n + nGC_{alkyl}$, where n is the number of the alkyl groups and the group contributions[21] are as follows: Ph, −3; Me, −21; Et, −7; *i*-Pr, +6. The resulting estimated (found) chemical shifts are as follows: Me_2P–, −58 (−52.1); MePhP–, −40 (−39.1); EtPhP–, −26 (−25.4); *i*-PrPhP–, −13 (−13.5); *i*-Pr_2P–, −4 (−4.3). The coupling constants range from 108 Hz (Me_2P– compound) to 119 Hz (*i*-Pr_2P– compound). The ligands, except for Ph_2PCH_2PPhEt, have essentially first-order ^{31}P spectra. There is a slight beginning of second-order perturbation, e.g., in Ph_2PCH_2PPhMe (supplementary Figure 1) which has δ/J of about 5.8. However, for Ph_2PCH_2PPhEt, the ethyl and phenyl groups have similar group contribution values and thus δ/J is 0.95 and the resultant spectrum (supplementary Figure 2) is a classic case of an AB spectrum. Because of the closeness of the two ^{31}P resonances, which would make the assignments

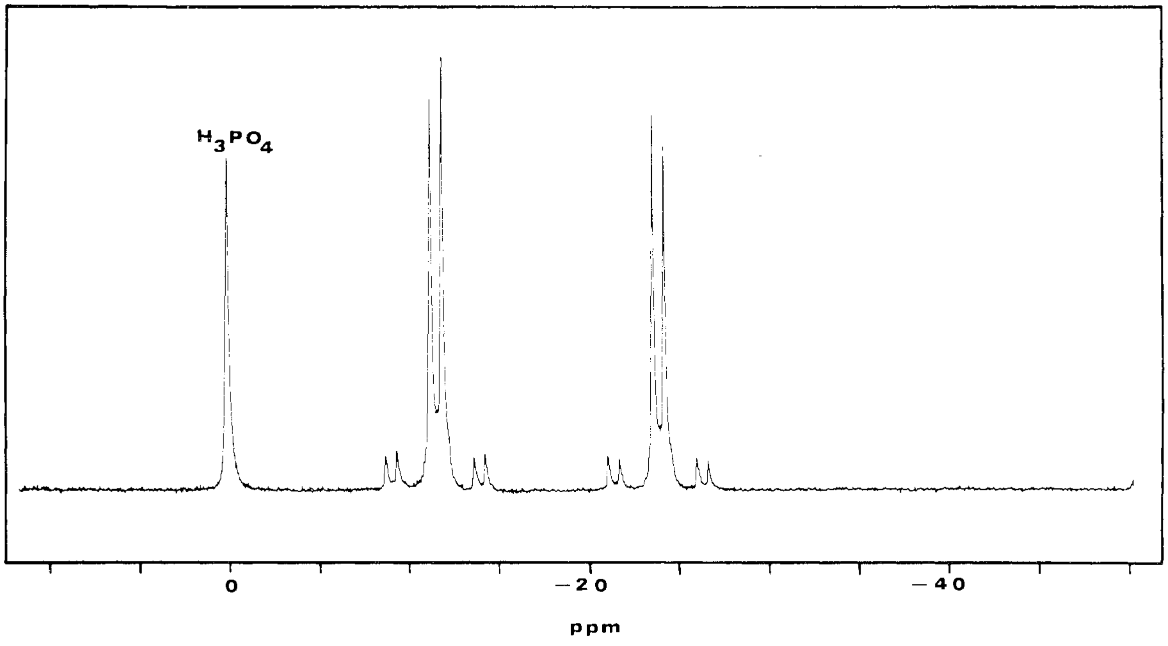

Figure 3. ^{31}P NMR spectrum (40.5 MHz) of $[Ph_2PCH_2PPh(i\text{-}Pr)]W(CO)_4$.

difficult in complexes of this ligand, it was not used in the subsequent coordination studies.

The ligands react readily with equimolar amounts (or a slight excess of the metal carbonyl) of $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ in hot diglyme to produce the expected products $LM(CO)_4$, where L = $Ph_2PCH_2PMe_2$, Ph_2PCH_2PPhMe, $Ph_2PCH_2PPh(i\text{-}Pr)$, or $Ph_2PCH_2P(i\text{-}Pr)_2$ and M = Cr, Mo, or W, in which the ligands show bidentate behavior and in which there is a four-membered chelate ring. Phosphorus-31 NMR data are summarized in Table II. Unlike the very large coordination shifts[2,9] for donor phosphorus atoms in five-membered rings, the coordination shifts in the four-membered rings are smaller, averaging (including both ends of the chelate) about 50 for the Cr complexes, 25 for Mo, and 0 for W. These are about the same values as found before[3] for the symmetrical bis(diphenylphosphino)methane complexes of the group 6 metal carbonyls. Also, similar behavior, viz., very large coordination shifts for five-membered chelate rings and small coordination shifts for four-membered rings, has been found with bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane in platinum complexes.[10] No satisfactory explanation has been promulgated for these observations.

Table IV. Ligand Size vs. Coordination Shift for $[Ph_2PCH_2PR^1R^2]M(CO)_4$ Complexes

Ligand			Coordn chem shift (Δ),[b] ppm		
R^1	R^2	θ,[a] deg	Cr	Mo	W
Me	Me	101	+57.5	+27.3	−1.4
Ph	Me	110	+52.9	+26.1	−0.5
Ph	Ph[c]	119	+49.0[c]	+23.6[c]	0.0[c]
Ph	*i*-Pr	124	+48.3	+25.9	+2.0
i-Pr	*i*-Pr	129	+48.1	+28.0	+5.4

[a] Ligand cone angle; see text. [b] R^1R^2P– end only. [c] Reference 3.

It is interesting to note the change in coordination shift with bulkiness of the ligands in Table IV. The bulkiness is estimated by the ligand cone angle,[22] θ, calculated from $\theta = {}^2/_3\sum_{i=1}^{3}\theta_i/2$, where θ_i is the estimated ligand cone angle for symmetrical R_3P species and the PMP angle (about 67°[23]) is used as one of the θ_i's in chelate rings.[24] The coordination shifts decrease in magnitude as the ligand sizes increase for the chromium complexes. This is the expected behavior based on other observations[15,25] and is possibly due in part to a smaller change of hybridization at phosphorus during coordination of the ligands with bulky groups. Although the trend is not clear for the molybdenum complexes, the tungsten compounds actually show a slight trend in the opposite direction from the chromium complexes, i.e., a larger coordination shift for the phosphorus in the bulky ligands. This may be due to the larger Mo and W atoms being more capable of accommodating the bulky ligands in a strained four-membered ring. However, there is no evidence for a marked increase in bonding of the bulky ligands to tungsten as reflected in the tungsten–phosphorus coupling constants or in the C═O stretching frequencies (vide infra). In fact, both the largest ($(i\text{-}Pr)_2P$–) and the smallest (Me_2P–) groups have the smallest ${}^1J_{WP}$ (194 Hz). This is probably more an indication of electronic effects since it has generally been found[2,15,26] that the tertiary phosphines with more aryl groups have larger phosphorus–tungsten coupling constants. The range of values of ${}^1J_{WP}$ for these compounds is 194–203 Hz. The assignment of coupling constants to the particular phosphino group is straightforward. Figure 3 shows a typical ^{31}P NMR spectrum of a tungsten complex of an unsymmetrical ligand with the tungsten-183 (14.3% abundance) satellites easily discernible. The phosphorus–phosphorus coupling constants range from 8 to 35 Hz with no apparent trends except that the molybdenum compounds show a minimum (smaller than the Cr and W cases) for three of the four ligands. It has been found that ${}^2J_{PMP}$ values in cis–disubstituted metal carbonyls (Cr, Mo, W) are generally negative and increase algebraically in the order Cr < Mo < W.[27,28] For $EtN(PF_2)_2M(CO)_4$ compounds, which are four-membered ring complexes, J_{PP} values are positive and follow the above trend.[29] Our J_{PP} values are discussed further in the following paper.[11]

Proton NMR data are given in the Experimental Section for the ligands $Ph_2PCH_2PR^1R^2$ and their complexes. The methylene region is inherently quite interesting because of the ABMX situation when $R^1 \neq R^2$ and the A_2MX group when $R^1 = R^2$. In the free ligands, however, ${}^2J_{PCH}$ and δ_{AB} are apparently quite small or zero. Consequently, the bridging methylene protons appear as a singlet in Ph_2PCH_2PPhEt (100 MHz) and $Ph_2PCH_2Me_2$ (100 MHz), as a doublet in $Ph_2PCH_2P(i\text{-}Pr)_2$ (${}^2J_{P(PH)CH}$ or ${}^2J_{P(i\text{-}Pr)CH}$ = 2.1 Hz), and as a distorted doublet in $Ph_2PCH_2PPh(i\text{-}Pr)$ (${}^2J_{P(Ph)CH}$ or

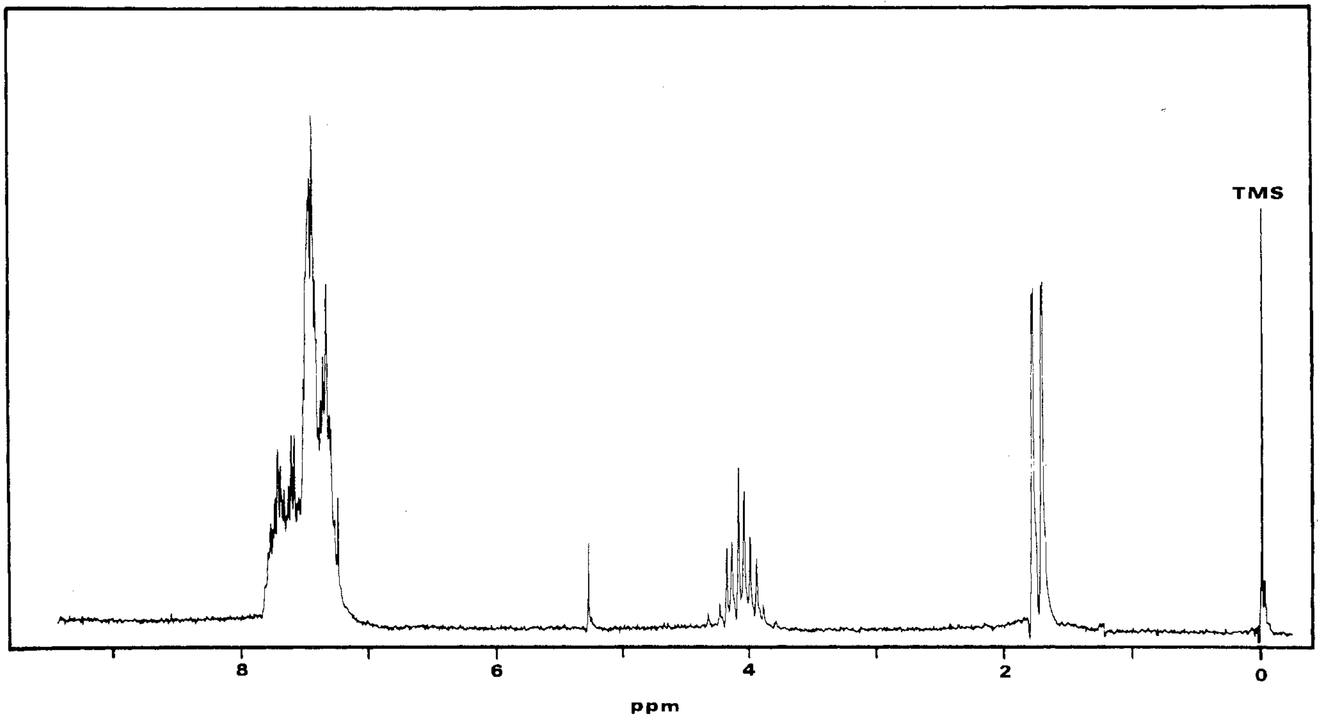

Figure 5. ^{1}H NMR spectrum (100 MHz) of $[Ph_2PCH_2PPhMe]Cr(CO)_4$.

$^2J_{P(i\text{-}Pr)CH}$ = 1.5 Hz). Ph_2PCH_2PPhMe (supplementary Figure 4) shows the expected AB pattern for the methylene region with slight additional coupling to the phosphorus atom(s).

The methylene regions of the coordination compounds show different behaviors depending mainly on the R^1 and R^2 groups but sometimes also on the metal. $|^2J_{PCH}|$ is larger in these complexes than in the uncomplexed ligand, which is usually the case.[30,31] $[Ph_2PCH_2PPh(i\text{-}Pr)]M(CO)_4$ has a simple triplet for the methylene region when M = Cr and Mo. The W complex has a distorted triplet which gives an AB pattern upon double irradiation at the phosphorus frequency. The AB protons, however, have very close chemical shifts, different by about 0.05 ppm. When R^1 = Ph and R^2 = Me, the complex splitting pattern reappears (Figure 5) for the Cr, Mo, and W series. When $R^1 = R^2 = i$-Pr, a doublet of doublet pattern appears for the methylene region of the Cr, Mo, and W complexes. $^2J_{P(i\text{-}Pr)CH}$ and $^2J_{P(Ph)CH}$ have nearly the same magnitudes, but the slightly larger coupling is assigned to the phenyl end since the values observed here are similar to the couplings observed in the $[Ph_2PCH_2PPh_2]M(CO)_4$ complexes.[3] Again, when $R^1 = R^2$ = Me, $^2J_{P(Me)CH}$ and $^2J_{P(PH)CH}$ are virtually indentical, since the spectra have a sharp triplet in the methylene region (e.g., see supplementary Figure 6).

In all cases, the methylene region is shifted downfield in the complexes when compared to the free ligand, with the W complexes showing the greatest downfield shift.

The methyl groups attached to phosphorus show expected behavior, i.e., doublets with $^2J_{PCH}$ ranging from 6.3 to 7.8 Hz, with the values about the same for Cr and W and smaller with Mo for a particular ligand. Again, as with the methylene shifts upon coordination, the largest shifts of the methyl groups occurred in the W compounds.[30,31] In two Cr compounds, where R^1 = Ph, R^2 = Me and $R^1 = R^2$ = Me, a small additional coupling, 0.8 and 0.6 Hz, respectively (see Figure 5 and supplementary Figure 6), is observed due to the distant phosphorus, four bonds removed, $J = {}^4J_{PCPCH} + {}^4J_{PMPCH}$.

The isopropyl groups, which contain diastereotopic methyl groups,[32] have similar characteristics to those discussed earlier.[1b,2] The expected eight-line pattern is occasionally six lines due to the accidental overlapping of two pairs. The methine proton of the isopropyl group is generally too complex to decipher.

Table V. IR Data for $Ph_2PCH_2PR^1R^2$ Metal Carbonyl Complexes (CO Region)[a]

Compd	Freq, cm^{-1}			
	$A_1{}^2$	$A_1{}^1$	B_1	B_2
$Ph_2PCH_2PMe_2$ (L_I)				
$L_ICr(CO)_4$	2007	1923	1895[c]	
$L_IMo(CO)_4$	2021	1929	1909	1901
$L_IW(CO)_4$	2016	1922	1902	1895
Ph_2PCH_2PPhMe (L_{II})				
$L_{II}Cr(CO)_4$	2009	1924	1902	1894
$L_{II}Mo(CO)_4$	2021	1929	1914	1901
$L_{II}W(CO)_4$	2018	1924	1908	1895
$Ph_2PCH_2PPh_2$ (L)				
$LCr(CO)_4$[b]	2020	1931	1913	1898
$LMo(CO)_4$[b]	2020	1925	1919	1900
$LW(CO)_4$[b]	2022	1927	1913	1896
$Ph_2PCH_2PPh(i\text{-}Pr)$ (L_{III})				
$L_{III}Cr(CO)_4$	2017	1928	1908	1897
$L_{III}Mo(CO)_4$	2021	1929	1915	1899
$L_{III}W(CO)_4$	2017	1922	1907	1891
$Ph_2PCH_2P(i\text{-}Pr)_2$ (L_{IV})				
$L_{IV}Cr(CO)_4$	2006	1920	1896	1890
$L_{IV}Mo(CO)_4$	2017	1925	1908	1897
$L_{IV}W(CO)_4$	2014	1919	1900	1891

[a] Saturated cyclohexane solutions; resolution ±2 cm^{-1}. [b] Reference 3. [c] Unresolved doublet.

The carbonyl infrared stretching frequencies of the metal complexes in cyclohexane solution are given in Table V and are of the expected numbers and frequencies for this class of compounds with the Mo–CO stretching frequencies slightly higher than for the Cr and W complexes.[33] No other obvious trends are apparent by a compound to compound comparison. However, if the 12 CO frequencies for the three metal carbonyls of each ligand are averaged, the order of the ligands with increasing CO frequencies is $R^1 = R^2 = i$-Pr (1931.9 cm^{-1}) < Me_2 (1934.6 cm^{-1}) < PhMe (1936.6 cm^{-1}) < Ph(i-Pr)

(1937.6 cm^{-1}) < Ph_2 (1940.3 cm^{-1}). This agrees with predictions of the increased π-acceptor ability[34,35] of tertiary phosphines containing a larger number of phenyl groups in place of alkyl groups[2,15,35] and does not seem consistent with steric factors in this series of ligands although steric factors might be expected to be more prominent in a four-membered ring.

In summary, the syntheses of a new series of five ligands of the type $Ph_2PCH_2PR^1R^2$ (where $R^1 = R^2$ = Me or *i*-Pr and R^1 = Ph, R^2 = Me, Et, or *i*-Pr) and of 12 group 6 metal carbonyl derivatives of the type $[Ph_2PCH_2PR^1R^2]M(CO)_4$ (where $R^1 = R^2$ = Me or *i*-Pr; R^1 = Ph, R^2 = Me or *i*-Pr, and M = Cr, Mo, or W) are reported. These compounds are an important component in a larger study of unsymmetrical bis-phosphorus chelating ligands and their coordination compounds which contain various-sized chelate rings. Extensive ^{31}P and ^1H NMR results are reported.

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Registry No. $L_ICr(CO)_4$, 62264-03-3; $L_IMo(CO)_4$, 62264-04-4; $L_IW(CO)_4$, 62264-05-5; $L_{II}Cr(CO)_4$, 62264-06-6; $L_{II}Mo(CO)_4$, 62264-07-7; $L_{II}W(CO)_4$, 62264-08-8; $L_{III}Cr(CO)_4$, 62264-09-9; $L_{III}Mo(CO)_4$, 62264-10-2; $L_{III}W(CO)_4$, 62264-11-3; $L_{IV}Cr(CO)_4$, 62264-12-4; $L_{IV}Mo(CO)_4$, 62264-13-5; $L_{IV}W(CO)_4$, 62264-14-6; L_I, 62263-64-3; L_{II}, 62263-65-4; L_{III}, 62263-66-5; L_{IV}, 62263-67-6; Ph_2PCH_2PPhEt, 62263-68-7; $Ph_2P(S)CH_2PPh(i\text{-}Pr)$, 54006-27-8; $Ph_2P(S)CH_2PPhEt$, 54006-30-3; $Ph_2P(S)CH_2PPhMe$, 54006-29-0; $Ph_2P(S)CH_2P(i\text{-}Pr)_2$, 54006-31-4; $Ph_2P(S)CH_2PMe_2$, 23176-51-4; Ph_2PMe, 1486-28-8; Ph_2PCH_2Li, 62263-69-8; $Ph(i\text{-}Pr)PCl$, 54006-34-7; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $C_7H_8Mo(CO)_4$, 12146-37-1.

Supplementary Material Available: Figures 1, 2, 4, and 6 showing NMR spectra (4 pages). Ordering information is given on any current masthead page.

References and Notes

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Unsymmetrical Bis-Phosphorus Ligands. 11. Group 6 Metal Carbonyl Derivatives of 1-(Diphenylphosphino)-3-(alkylphenylphosphino)propane[1,2]

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Nine new compounds of the type $[Ph_2P(CH_2)_3PPhR]M(CO)_4$, where R = Me, Et, or *i*-Pr and M = Cr, Mo, or W, have been synthesized and characterized by proton and phosphorus nuclear magnetic resonance and infrared spectroscopy. The disulfide derivatives, $Ph_2P(S)(CH_2)_3P(S)PhR$, of the ligands are also reported. It is demonstrated that J_{PP} in these six-membered chelate rings and in the corresponding analogues containing five- and four-membered chelate rings, $[Ph_2P(CH_2)_2PR^1R^2]M(CO)_4$ and $[Ph_2PCH_2PR^1R^2]M(CO)_4$, is a sum of two identifiable components: a contribution via the ligand backbone and a contribution via the metal center, such that $J_{PP} = J^B{}_{PP} + J^M{}_{PP}$.

Previous studies of group 6 metal carbonyl complexes with unsymmetrical di(tertiary phosphine) ligands, $Ph_2P(CH_2)_nPR^1R^2$, with $n = 1$[2] or 2,[3,4] have been reported. These ligands form four- and five-membered chelate rings, respectively. This paper reports similar complexes with $Ph_2P(CH_2)_3PPhR$,[5] with R = Me, Et, or *i*-Pr, which form six-membered chelate rings, and compares the phosphorus-31 NMR results for each series and the variation of chemical shifts and coupling constants with ring size.

Experimental Section

The physical measurements were carried out as described in the preceding paper.[2] The ligands were synthesized as previously reported.[5] Disulfides of the ligands were prepared by the reaction of a slight