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Unsymmetrical Bis-Phosphorus Ligands. 9. Group 6 Metal Carbonyl Complexes and Other Derivatives of Various (Phosphinomethyl)phosphine Sulfides[1]

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Some chemistry of a new class of compounds, (phosphinomethyl)phosphine sulfides, $Ph_2P(S)CH_2PR^1R^2$, is described. Reaction with sulfur gives disulfides, $Ph_2P(S)CH_2P(S)R^1R^2$, with sodium gives unsymmetrical di(tertiary phosphines), $Ph_2PCH_2PR^1R^2$, with alkyl halides gives phosphonium salts, $[Ph_2P(S)CH_2PR^1R^2R^3]X$, and with group 6 metal carbonyls gives a complex with phosphorus and sulfur bonded to the metal in a five-membered chelate ring, $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$; heating causes the sulfur to transfer to the more basic phosphorus atom, producing $Ph_2PCH_2P(S)R^1R^2$. Extensive phosphorus and proton NMR data are given.

Studies of various unsymmetrical bis-phosphorus ligands have been of considerable interest to us recently,[1c,2-4] since these compounds contain, in the same molecule, two phosphorus atoms which are nonequivalent. These types of molecules allow for the direct measurement of phosphorus–phosphorus coupling, which has received considerable attention[3,5–10] for theoretical and practical bonding investigations.

A relatively new class of compounds, $Ph_2P(S)CH_2PR^1R^2$, called (phosphinomethyl)phosphine sulfides, first reported by Seyferth,[11] provides a novel unsymmetrical system in which the phosphorus nuclei are nonequivalent and P–P coupling is directly measurable from the ^{31}P NMR spectra. In addition, the coordination chemistry of this type of compound with a trivalent phosphorus (phosphine) and a pentavalent phosphorus (phosphine sulfide) in the same molecule had not been explored. In fact, until recently,[12,13] very little work had been done on the coordination aspects of phosphine sulfides. Ainscough and co-workers[14] have prepared group 6 metal carbonyl complexes of various tertiary phosphine sulfides. There have also been several structural studies on tertiary phosphine sulfide coordination compounds.[15,16]

While studies of monodentate phosphine sulfide coordination chemistry are few, even less well studied are the bis(tertiary phosphine) sulfides. Slinkard and Meek[13] have synthesized Co(II), Ni(II), and Pd(II) complexes with $Ph_2P(S)CH_2P(S)Ph_2$. Several workers have studied $R^1R^2P(S)X(S)R^3R^4$ and $R^1{}_2P(S)XP(S)R^2{}_2$ (where X = CH_2, O, S)[17] metal complexes while complexes with anionic ligands such as $[Ph_2P(S)NP(S)R_2]^-$ [18] and $[Ph_2P(S)CHP(S)PH_2]^-$ [19] have also been examined. It became apparent to us, then, that the five-membered ring chelate system provided by the various $Ph_2P(S)CH_2PR^1R^2$ ligands would be a fruitful investigation.

This paper reports the synthesis of numerous (phosphinomethyl)phosphine sulfides and their chemical reactions as well as extensive phosphorus-31 and proton magnetic resonance data.

Experimental Section

Physical Measurements. Phosphorus-31 NMR spectra were recorded on a Varian Associates XL-100-12 spectrometer operating at 40.5 MHz using 10-mm spinning-sample tubes. A 1-mm capillary tube of 85% H_3PO_4 was placed through the center of the cap of the 10-mm tube as an external reference. An ^{19}F external lock was employed; all ^{31}P NMR spectra were obtained in the Fourier transform (FT) mode. All protons were heteronoise decoupled. Methylene chloride was employed as the solvent for the ^{31}P NMR spectra. The chemical shifts are reported as positive if downfield from H_3PO_4. The resolution is at least 1 Hz.

Proton NMR spectra were recorded on a Varian A-60A spectrometer or the XL-100 instrument (in the FT mode) using $CDCl_3$ as the solvent and 1% TMS as the internal reference. The deuterium resonance of $CDCl_3$ served as the field frequency lock signal for the XL-100.

Infrared spectra of saturated solutions of the metal carbonyl complexes were recorded on a Perkin-Elmer Model 225 IR spectrometer using NaCl solution cells with a 0.5-mm sample thickness. The bands are accurate to ± 2 cm^{-1}.

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

Melting points were recorded on a Mel-Temp apparatus and are reported uncorrected.

Preparation of $Ph_2P(S)CH_2PR^1R^2$. The syntheses of the (phosphinomethyl)phosphine sulfide compounds where R^1 = Ph, R^2 = Et, Me, *i*-Pr, NEt_2, Cl, and $R^1 = R^2$ = Ph, *i*-Pr have been described elsewhere.[4]

The compound $Ph_2P(S)CH_2PMe_2$ (previously reported[11] but not fully characterized) has been prepared in 49–53% yield by our method.[4] It melts at 133–136 °C.

Anal. Calcd for $C_{15}H_{18}P_2S$: C, 61.63; H, 6.21; P, 21.19. Found: C, 61.57; H, 6.47; P, 21.42.

Preparation of $Ph_2P(S)CH(Me)PPh_2$. This compound was prepared in a manner similar to that for $Ph_2P(S)CH_2PPh_2$[4] from $Ph_2P(S)CH(CH_3)Li$[20] and Ph_2PCl in 10% yield. It melts at 169–171 °C.

Anal. Calcd for $C_{26}H_{24}P_2S$: C, 72.42; H, 5.78; P, 14.37. Found: C, 72.48; H, 5.84; P, 14.60.

Preparation of $Ph_2PCH_2P(S)R^1R^2$. All of these compounds were prepared by the same procedure. In general, 10.0 g of $Ph_2P(S)CH_2PR^1R^2$ was dissolved in about 20 mL of diethylene glycol dimethyl ether (diglyme). The solution was deoxygenated for 30 min with a water aspirator. After nitrogen was admitted to the evacuated flask, it was heated to ca. 160 °C in an oil bath. The solution was stirred for at least 24 h, when an aliquot of the mixture was checked by ^{31}P NMR. The diglyme was removed under reduced pressure and slight heating to yield a crude oil of the desired compound.

After purification of the crude oil by column chromatography with alumina, the oil $Ph_2PCH_2P(S)PhMe$ was crystallized as a colorless solid, mp 98–101 °C, from absolute EtOH/CH_2Cl_2 in 49% yield.

Anal. Calcd for $C_{20}H_{20}P_2S$: C, 67.78; H, 5.69; P, 17.48. Found: C, 67.78; H, 5.84; P, 17.27.

The colorless compound $Ph_2PCH_2P(S)Me_2$, mp 83–84 °C, was crystallized from absolute EtOH in 50% yield after purification as for the $Ph_2PCH_2P(S)PhMe$ case.

Anal. Calcd for $C_{15}H_{18}P_2S$: C, 61.63; H, 6.21; P, 21.19. Found: C, 61.49; H, 6.40; P, 20.94.

The colorless compound $Ph_2PCH_2P(S)Ph(i\text{-}Pr)$, mp 122–125 °C, was crystallized from absolute EtOH in 78% yield. It was not necessary to purify the crude oil by chromatography.

Anal. Calcd for $C_{22}H_{24}P_2S$: C, 69.09; H, 6.33; P, 16.20. Found: C, 68.82; H, 6.60; P, 16.40.

The colorless compound $Ph_2PCH_2P(S)(i\text{-}Pr)_2$, mp 61–62 °C, was obtained from the crude oil (without chromatography) by crystallization from absolute EtOH in 76% yield.

Anal. Calcd for $C_{19}H_{26}P_2S$: C, 65.49; H, 7.52; P, 17.78. Found: C, 65.22; H, 7.69; P, 17.49.

Preparation of Phosphonium Salts. About 1–4 g (2–10 mmol), generally 2 g, of the appropriate ligand was placed under nitrogen in a pressure bottle which could withstand a pressure of approximately 10 atm along with 25–50 mL of dry benzene and a magnetic stirring pea. While this bottle was cooled in ice, ca. 5 mL (greater than a tenfold stoichiometric excess) of gaseous MeBr (bp 3.59 °C) was condensed in a test tube under N_2 and transferred quickly to the pressure bottle which was immediately capped. The bottle was placed in a water bath maintained at 50–55 °C and stirred from 1 to 2 days; in most cases, a precipitate formed within 1–2 h after heating was begun. Before being opened, the bottle was cooled in an ice bath for 15–20 min. The precipitate that had formed was generally dissolved by the addition of CH_2Cl_2 to the benzene solution. Removal of the solvents by rotary evaporation resulted in colorless solid residues which were recrystallized. These salts were not observed to be hygroscopic. Analytical and preparative data are summarized in Table I.

Preparation of Disulfides. In general, a 2-g sample of the appropriate ligand (ca. 5–7 mmol) was mixed with a stoichiometric amount of elemental sulfur in 50 mL of benzene. The mixture was refluxed under nitrogen with stirring for 30–60 min. The solution was concentrated to an oil which was crystallized as a colorless solid. Analytical and preparative data are summarized in Table II.

Preparation of $LCr(CO)_4$ Complexes. The synthesis of $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$ will serve as a representative example. A 3.00-g (7.10-mmol) sample of the ligand was mixed with 1.69 g (7.3 mmol, a slight excess) of $Cr(CO)_6$ and 10 mL of dry diglyme in a 100-mL one-necked round-bottomed flask equipped with a side arm and stopcock. The mixture was deoxygenated for 30 min by means of a water aspirator. Nitrogen was admitted near the middle and at the end of this process. The flask was then attached to an apparatus which allowed the monitoring of the amount of CO evolved during the reaction. With constant stirring, the reaction mixture was heated for ca. 5 h at a bath temperature of 120–140 °C during which time the solution turned a dark orange with approximately the stoichiometric amount of CO being evolved. The apparatus was shaken several times during the course of the reaction to return sublimed $Cr(CO)_6$ to the reaction flask. After completion of the reaction (no more CO evolution), the diglyme was removed under vacuum. The residue was dissolved in hot CH_2Cl_2 with the desired orange-yellow complex being precipitated with hexane. The yield was 3.31 g (79%). Other complexes similarly prepared were $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]Cr(CO)_4$, $[Ph_2P(S)CH_2PPhMe]Cr(CO)_4$, $[PhP(S)CH_2P(i\text{-}Pr)_2]Cr(CO)_4$, and $[Ph_2P(S)CH_2PMe_2]Cr(CO)_4$.

Preparation of $LMo(CO)_4$ Complexes. The complexes $[Ph_2P(S)CH_2PPh_2]Mo(CO)_4$, $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]Mo(CO)_4$, and $[Ph_2P(S)CH_2PMe_2]Mo(CO)_4$ were prepared in a manner similar to that used for the preparation of $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$ with $Mo(CO)_6$ being allowed to react with the various ligands.

Table I. Analytical and Preparative Data of Phosphonium Salts of (Phosphinomethyl)phosphine Sulfides

	% C		% H		% P		% Br			
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C	Yield, %
$[Ph_2P(S)CH_2PPh_2Me]^+Br^-$	61.06	61.09	4.93	5.13	12.11	12.21	15.63	16.00	216-220	46[a]
$[Ph_2P(S)CH_2PPhEtMe]^+Br^-$	57.03	56.75	5.44	5.31	13.37	13.55	17.24	17.10	232-236	52[b]
$[Ph_2P(S)CH_2PPh(i\text{-}Pr)Me]^+Br^-$	57.86	57.63	5.70	5.69	12.98	13.50	16.74	17.02	220-223	78[b]
$[Ph_2P(S)CH_2PPhMe_2]^+Br^-$	56.13	56.02	5.16	5.40	13.79	13.51	17.79	18.20	251	56[b,c]
$[Ph_2P(S)CH_2P(i\text{-}Pr)_2Me]^+Br^-$	54.18	54.06	6.59	6.88	13.97	13.69	18.03	18.40	164-166	72[a]
$[Ph_2P(S)CH_2PMe_3]^+Br^-$	49.62	49.32	5.47	5.60	16.00	15.85	20.64	20.90	217-220	93[a]
$[Ph_2P(S)CH(CH_3)PPh_2Me]^+Br^-$	61.63	60.08	5.31	5.30	11.77	11.37	15.19	15.19	298	20[d]
$[MePh_2PCH_2P(S)PhMe]^+Br^-$	56.13	55.85	5.16	5.40	13.79	13.54	17.79	18.30	192-195	75[a]
$[MePh_2PCH_2P(S)Me_2]^+Br^-$	49.62	49.70	5.47	5.61	16.00	16.30	20.64	20.40	254-256	84[a]
$[MePh_2PCH_2P(S)Ph(i\text{-}Pr)]^+Br^-$	57.86	57.77	5.70	5.77	12.98	12.69	16.74	16.50	197	79[a]
$[MePh_2PCH_2P(S)(i\text{-}Pr)_2]^+Br^-$	54.18	53.91	6.59	6.69	13.97	13.20	18.03	17.75	199-201	85[a]

[a] Crystallization solvent *i*-PrOH/Et_2O. [b] Crystallization solvent $CHCl_3/Et_2O$. [c] Crystallization solvent CH_2Cl_2/hexane. [d] Crystallization solvent CH_2Cl_2/*i*-PrOH/Et_2O.

Table II. Analytical and Preparative Data of (Phosphinomethyl)phosphine Disulfides

	% C		% H		% P				
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C	Yield, %	Crystallizn solvent
$Ph_2P(S)CH_2P(S)Ph_2$[a]	66.94	66.68	4.95	4.76	13.81	13.07	178-180	65	CH_2Cl_2/hexane
$Ph_2P(S)CH_2P(S)PhEt$	62.98	62.66	5.54	5.61	15.47	15.35	129-130	65	CH_2Cl_2/hexane/Et_2O
$Ph_2P(S)CH_2P(S)Ph(i\text{-}Pr)$	63.75	64.04	5.84	5.91	14.95	14.30	116	65	EtOH/pentane
$Ph_2P(S)CH_2P(S)PhMe$	62.16	61.86	5.22	5.16	16.03	15.49	154-156	31	EtOH/pentane
$Ph_2P(S)CH_2P(S)(i\text{-}Pr)_2$	59.97	60.26	6.89	7.10	16.28	15.99	79	36	EtOH/pentane
$Ph_2P(S)CH_2P(S)Me_2$[b]	55.54	55.62	5.59	5.62	19.10	19.38	142-144	87	EtOH
$Ph_2P(S)CH(CH_3)P(S)Ph_2$	67.51	67.48	5.23	5.34	13.39	13.14	221-223	40	CH_2Cl_2/hexane

[a] Previously reported in ref 29 with mp 178 °C. [b] Previously reported in ref 17 with mp 147-148 °C.

Table III. Analytical Data of Metal Carbonyl Derivatives of (Phosphinomethyl)phosphine Sulfide Ligands

	% C		% H		% P			
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C	Yield, %
$Ph_2P(S)CH_2PPh_2$ (L_I)								
$L_ICr(CO)_4$	60.00	59.77	3.82	3.79	10.67	10.63	125-130 dec	79
$L_IMo(CO)_4$	55.78	55.51	3.55	3.57	9.92	9.78	128 dec	90
$L_IW(CO)_4$	48.90	48.56	3.11	3.12	8.70	8.62	146 dec	70
$Ph_2P(S)CH_2PPh(i\text{-}Pr)$ (L_{II})								
$L_{II}Cr(CO)_4$	57.14	56.99	4.43	4.60	11.34	11.10	Dec pt >115	65
$L_{II}Mo(CO)_4$	52.89	53.11	4.10	4.37	10.49	10.46	63 dec	86
$L_{II}W(CO)_4$	46.03	46.04	3.57	3.62	9.13	9.20	Dec pt >148	66
$Ph_2P(S)CH_2PPhMe$ (L_{III})								
$L_{III}Cr(CO)_4$	55.60	55.53	3.89	3.97	11.95	11.69	97-100	66
$L_{III}Mo(CO)_4$	51.26	51.32	3.58	3.71	11.02	11.30	Dec pt >100	81
$L_{III}W(CO)_4$	44.33	44.70	3.10	3.35	9.53	10.06	105-107	73
$Ph_2P(S)CH_2P(i\text{-}Pr)_2$ (L_{IV})								
$L_{IV}Cr(CO)_4$	53.90	53.91	5.11	5.40	12.09	11.81	Dec pt >110	73
$L_{IV}Mo(CO)_4$	49.65	49.51	4.71	4.86	11.13	11.40	Dec pt >120	74
$L_{IV}W(CO)_4$	42.87	42.90	4.07	4.22	9.61	9.90	Dec pt >150	65
$Ph_2P(S)CH_2PMe_2$ (L_V)								
$L_VCr(CO)_4$	50.00	49.74	3.98	4.24	13.58	13.86	Dec pt >155	49
$L_VMo(CO)_4$	45.61	45.64	3.63	3.77	12.38	12.49	Dec pt >155	76
$L_VW(CO)_4$	39.79	38.81	3.08	3.13	10.53	10.23	Dec pt >185	73

Two of the molybdenum complexes, $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]Mo(CO)_4$ and $[Ph_2P(S)CH_2PPhMe]Mo(CO)_4$, were better prepared using an exchange reaction with $C_7H_8Mo(CO)_4$.[21]

In about 50 mL of warm, deoxygenated hexane was dissolved a 2.36-g (7.85-mmol) sample of norbornadienetetracarbonylmolybdenum prepared by published procedures.[22] Under nitrogen, 3.00 g (7.85 mmol) of $Ph_2P(S)CH_2PPh(i\text{-}Pr)$ was added in small amounts with the formation of a gummy precipitate as the exchange proceeded. Methylene chloride was added to make the solution homogeneous, after all of the ligand had been added. The solution was concentrated to an oil which was dissolved in *i*-PrOH/CH_2Cl_2. Pale yellow crystals of $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]Mo(CO)_4$ precipitated; the yield was 3.69 g (86%).

The complex $[Ph_2P(S)CH_2PPhMe]Mo(CO)_4$ was similarly prepared but was crystallized from $MeOH/CH_2Cl_2$.

Preparation of LW(CO)$_4$ Complexes. The complexes $[Ph_2P(S)CH_2PPh_2]W(CO)_4$ and $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]W(CO)_4$ were prepared in a manner similar to that used for the preparation of $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$ with the various ligands being allowed to react with $W(CO)_6$.

The complexes $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]W(CO)_4$, $[Ph_2P(S)CH_2PPhMe]W(CO)$, and $[Ph_2P(S)CH_2PMe_2]W(CO)_4$ were made using the exchange method with $C_7H_8W(CO)_4$

In ca. 10 mL of CH_2Cl_2 under nitrogen were dissolved 2.7 g (7.0 mmol) of $C_7H_8W(CO)_4$[23] and 2.66 g (6.96 mmol) of $Ph_2P(S)CH_2PPh(i\text{-}Pr)$. After 30 min of stirring a ^{31}P NMR spectrum of an aliquot of the solution was taken; it showed only resonances corresponding to the free ligand. After about 6 h of stirring, a ^{31}P NMR spectrum showed almost complete complex formation. After being stirred overnight, the solution was evaporated to an oil. The complex

$[Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)]W(CO)_4$ crystallized from absolute MeOH/hexane in a yield of 3.13 g (66%).

The compound $[Ph_2P(S)CH_2PPhMe]W(CO)_4$ was similarly prepared but was crystallized from absolute $MeOH/CH_2Cl_2$. The compound $[Ph_2P(S)CH_2PMe_2]W(CO)_4$ was prepared using diglyme as the solvent. The complex precipitated almost immediately upon formation and was washed with acetone/hexane. Analytical data for all of the metal carbonyl complexes are contained in Table III.

Proton NMR data for the (phosphinomethyl)phosphine sulfides, the phosphonium salts, the disulfides, and the coordination compounds of the (phosphinomethyl)phosphine sulfides follow. The data are from 60-MHz spectra unless (100) appears after the compound, in which case the data are from 100-MHz spectra. Abbreviations: m, unresolved multiplet; d, doublet; t, triplet; q, quartet. Order of data: proton assignment, italic were necessary; chemical shift (δ) in ppm from tetramethylsilane; multiplicity, in parentheses; coupling constants, in Hz, where known.

$Ph_2P(S)CH_2PPh(NEt_2)$: Ph, 7.1–8.2 (m); PCH_2P and $C\mathit{H}_2CH_3$, 2.5–3.7 (m); $CH_2C\mathit{H}_3$, 0.90 (t), $^3J_{HCCH} = 7.0$. $Ph_2P(S)CH_2PPhCl$: Ph, 7.1–8.0 (m); PCH_2P, 3.51 (d of d), $^2J_{P(S)CH} = 12.0$, $^2J_{PCH} = 3.1$. $Ph_2P(S)CH_2PPh_2$: Ph, 7.0–8.0 (m); PCH_2P, 3.32 (d of d), $^2J_{P(S)CH} = 12.8$, $^2J_{PCH} = 1.0$. $Ph_2P(S)CH(CH_3)PPh_2$: Ph, 7.0–8.2 (m); PCHP, 3.5–3.9 (m); CH_3, 1.18 (d of t), $^3J_{P(S)CCH} = 19.1$, $^3J_{PCCH} \approx {}^3J_{HCCH} = 7.5$. $Ph_2P(S)CH_2PPhEt$ (100): Ph, 7.2–7.9 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 2.9 (m), ABMX; H_A, 2.98; H_B, 2.85, $^2J_{H_ACH_B} = 14.1$; $C\mathit{H}_2CH_3$, centered at 1.8 (m); $CH_2C\mathit{H}_3$, 0.87 (overlapping d of t), $^3J_{PCCH} = 16.7$, $^3J_{HCCH} = 7.6$. $Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)$ (100): Ph, 7.1–7.9 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 3.0 (m), ABMX; H_A, 3.15; H_B, 2.88, $^2J_{H_ACH_B} = 14.4$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.0 (m), $^2J_{PCH} = 2.5$; $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.08 (d of d), $^3J_{PCCH} = 15.9$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 0.80 (d of d), $^3J_{PCCH} = 13.8$, $^3J_{HCCH} = 6.9$. $Ph_2P(S)CH_2PPhMe$ (100): Ph, 7.2–8.0 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 2.9 (m), ABMX; H_A, 2.97; H_B, 2.81, $J_{H_ACH_B} = 14.2$; CH_3, 1.42 (d), $^2J_{PCH} = 4.4$. $Ph_2P(S)CH_2P(\mathit{i}\text{-}Pr)_2$ (100): Ph, 7.4–7.5 and 7.8–8.0 (m); PCH_2P, 2.54 (d of d), $^2J_{P(S)CH} = 13.0$, $^2J_{PCH} = 1.9$; $C\mathit{H}(CH_3)_2$, centered at ca. 1.8 (m); $CH(C\mathit{H}_3)_2$, 0.97 (d of d), $^3J_{PCCH} = 13.1$, $^3J_{HCCH} = 6.9$. $Ph_2P(S)CH_2PMe_2$: Ph, 7.3–8.1 (m); PCH_2P, 2.64 (d), $^2J_{P(S)CH} = 13.0$, $^2J_{PCH} \approx 0$; CH_3, 1.08 (d), $^2J_{PCH} = 3.8$. $Ph_2PCH_2P(S)PhMe$ (100): Ph, 7.2–7.4 and 7.7–7.9 (m); PCH_2P, 2.96 (d), $^2J_{P(S)CH} = 13.2$, $^2J_{PCH} \approx 0$; CH_3, 1.93 (d of d), $^2J_{P(S)CH} = 13.0$, $^4J_{PCPCH} = 0.7\text{–}0.8$. $Ph_2PCH_2P(S)Me_2$: Ph, 7.2–7.8 (m); PCH_2P, 2.84 (d), $^2J_{P(S)CH} = 14.0$, $^2J_{PCH} \approx 0$; CH_3, 1.64 (d of d), $^2J_{P(S)CH} = 13.2$, $^4J_{PCPCH} = 0.9$. $Ph_2PCH_2P(S)Ph(\mathit{i}\text{-}Pr)$ (100): Ph, 7.2–7.4 and 7.7–7.9 (m); PCH_2P, 2.96 (d of d), $^2J_{P(S)CH} = 12.2$, $^2J_{PCH} = 1.2$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.5 (m); $CH(CH_3)_A(CH_3)_B$ (8 lines); $(CH_3)_A$, 1.26 (d of d), $^3J_{PCCH} = 18.3$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 0.95 (d of d), $^3J_{PCCH} = 18.8$, $^3J_{HCCH} = 6.9$. $Ph_2PCH_2P(S)(\mathit{i}\text{-}Pr)_2$ (100): Ph, 7.3–7.6 (m); PCH_2P, 2.67 (d of d), $^2J_{P(S)CH} = 12.0$, $^2J_{PCH} = 1.2$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.3 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.20 (d of d), $^3J_{PCCH} = 17.2$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 1.15 (d of d), $^3J_{PCCH} = 17.0$, $^3J_{HCCH} = 6.9$.

$[Ph_2P(S)CH_2PPh_2Me]Br$: Ph, 7.1–8.4 (m); PCH_2P, 5.32 (d of d), $^2J_{P(S)CH} = 12.6$, $^2J_{P(+)CH} = 15.6$; CH_3, 2.96 (d), $^2J_{P(+)CH} = 13.9$. $[Ph_2P(S)CH(CH_3)PPh_2Me]Br$ (100): Ph, 7.1–8.0 and 8.2–8.8 (m); PCHP, 6.52 (m, q with ^{31}P double irradiation), $^3J_{HCCH} = 7.0$; PCH_3, 2.80 (d), $^2J_{P(+)CH} = 13.4$; $PCH(C\mathit{H}_3)P$, 1.60 (d of d of d), $^3J_{HCCH} = 7.0$, $^3J_{P(+)CCH}$ or $^3J_{P(S)CCH} = 16.8$, $^3J_{P(+)CCH}$ or $^3J_{P(S)CCH} = 18.2$. $[Ph_2P(S)CH_2PPhEtMe]Br$ (100): Ph, 7.1–8.2 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 5.2 (m), ABMX; H_A, 5.31; H_B, 5.00, $^2J_{H_ACH_B} = 15.1$; $C\mathit{H}_2CH_3$, 3.40 (m, q with ^{31}P irradiation), $^3J_{HCCH} = 7.6$; PCH_3, 2.69 (d), $^2J_{P(+)CH} = 13.6$; $CH_2C\mathit{H}_3$, 1.01 (d of t), $^3J_{PCCH} = 21.1$, $^3J_{HCCH} = 7.6$. $[Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)Me]Br$ (100): Ph, 7.1–8.3 (m); $PC\mathit{H}_A\mathit{H}_MP$, H_A, 5.71 (6 lines, d of d of d), $^2J_{H_ACH_M} = 15.2$, $^2J_{P(S)CH_A} = 12.2$, $^2J_{P(+)CH_A} = 15.2$; H_M, 4.25 (overlaps with $C\mathit{H}(CH_3)_2$ (m)); $C\mathit{H}(CH_3)_2$, centered at ca. 4.3 (m); PCH_3, 2.52 (d), $^2J_{P(+)CH} = 12.7$; $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.53 (d of d), $^3J_{PCCH} = 18.8$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 1.04 (d of d), $^3J_{PCCH} = 19.8$, $^3J_{HCCH} = 7.3$. $[Ph_2P(S)CH_2PPhMe_2]Br$ (100): Ph, 7.1–8.2 (m); PCH_2P, 5.30 (d of d), $^2J_{P(S)CH} = 12.4$, $^2J_{P(+)CH} = 16.3$; PCH_3, 2.71 (d), $^2J_{P(+)CH} = 14.5$. $[Ph_2P(S)CH_2P(\mathit{i}\text{-}Pr)_2Me]Br$ (100): Ph, 7.3–7.6 and 8.3–8.5 (m); PCH_2P, 4.60 (d of d), $^2J_{P(S)CH} = 13.4$, $^2J_{P(+)CH} = 14.8$; $C\mathit{H}(CH_3)_2$, centered at ca. 3.3 (m); $PC\mathit{H}_3$, 1.97 (d), $J_{P(+)CH} = 12.6$; $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (6 lines); $(CH_3)_A$, 1.33 (d of d), $^3J_{PCCH} = 18.0$, $^3J_{HCCH} = 6.9$; $(CH_3)_B$, 1.26 (d of d), $^3J_{PCCH} = 18.0$, $^3J_{HCCH} = 7.1$. $[Ph_2P(S)CH_2PMe_3]Br$ (100): Ph, 7.5–7.6 and 8.2–8.4 (m); PCH_2P, 4.69 (d of d), $^2J_{P(S)CH} = 12.9$, $^2J_{P(+)CH} = 16.4$; CH_3, 2.10 (d), $^2J_{P(+)CH} = 14.1$. $[MePh_2PCH_2P(S)PhMe]Br$ (100): Ph, 7.3–8.3 (m); $PC\mathit{H}_A\mathit{H}_BP$ (m), ABMX; H_A, 5.33 (6 lines, d of d of d), $^2J_{H_ACH_B} = 15.1$, $^2J_{P(S)CH_A} = 13.2$, $^2J_{P(+)CH_A} = 15.4$; H_B, 4.77 (6 lines, d of d of d), $^2J_{H_ACH_B} = 15.1$, $^2J_{P(S)CH_B} = 12.3$, $^3J_{P(+)CH_B} = 15.1$; $P(+)CH_3$, 2.85 (d), $^2J_{P(+)CH} = 13.8$; $P(S)CH_3$, 2.20 (d of d), $^2J_{P(S)CH} = 13.6$, $^4J_{PCPCH} = 1.5$. $[MePh_2PCH_2P(S)Me_2]Br$ (100): Ph, 7.5–7.8 and 8.0–8.2 (m); PCH_2P, 4.99 (d of d), $^2J_{P(S)CH} = 12.8$, $^2J_{P(+)CH} = 15.9$; $P(+)CH_3$, 3.00 (d), $^2J_{P(+)CH} = 13.9$; $P(S)CH_3$, 1.81 (d of d), $^2J_{P(S)CH} = 13.2$, $^4J_{PCPCH} = 1.2$. $[MePh_2PCH_2P(S)Ph(\mathit{i}\text{-}Pr)]Br$ (100): Ph, 7.2–8.1 (m); $PC\mathit{H}_A\mathit{H}_MP$, H_A, 5.95 (6 lines, d of d of d), $^2J_{H_ACH_M} = 15.2$, $^2J_{P(S)CH_A} = 10.5$, $^2J_{P(+)CH_A} = 15.1$; H_M, 3.99 (6 lines, d of d of d), $^2J_{H_ACH_M} = 15.2$, $^2J_{P(S)CH_M} = 13.1$, $^2J_{P(+)CH_M} = 15.8$; $C\mathit{H}(CH_3)_2$, centered at ca. 3.2 (m); $P(+)CH_3$, 2.75 (d), $^2J_{P(+)CH} = 13.9$; $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.45 (d of d), $^3J_{PCCH} = 22.2$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 0.77 (d of d), $^3J_{PCCH} = 21.5$, $^3J_{HCCH} = 6.9$. $[MePh_2PCH_2P(S)(\mathit{i}\text{-}Pr)_2]Br$ (100): Ph, 7.5–7.7 and 8.0–8.2 (m); PCH_2P, 4.50 (d of d), $^2J_{P(S)CH} = 9.9$, $^2J_{P(+)CH} = 16.5$; $P(+)CH_3$, 2.97 (d), $^2J_{P(+)CH} = 13.9$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.4 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.20 (d of d), $^3J_{PCCH} = 18.6$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 1.16 (d of d), $^3J_{PCCH} = 18.8$, $^3J_{HCCH} = 7.0$.

$Ph_2P(S)CH_2P(S)Ph_2$: Ph, 7.1–8.0 (m); PCH_2P, 3.98 (t), $^2J_{P(S)CH} = 13.5$. $Ph_2P(S)CH(CH_3)P(S)Ph_2$: Ph, 7.1–8.3 (m); PCHP, centered at ca. 4.2 (m); $C\mathit{H}_3$, 1.43 (d of t), $^3J_{P(S)CCH} = 17.5$, $^3J_{HCCH} = 7.0$. $Ph_2P(S)CH_2P(S)PhEt$: Ph, 7.0–8.0 (m); PCH_2P, centered at 3.5 (distorted t); $C\mathit{H}_2CH_3$, centered at ca. 2.7 (m); $CH_2C\mathit{H}_3$, 1.13 (d of t), $^3J_{P(S)CCH} = 21.8$, $^3J_{HCCH} = 7.4$. $Ph_2P(S)CH_2P(S)Ph(\mathit{i}\text{-}Pr)$: Ph, 7.0–8.1 (m); PCH_2P and $C\mathit{H}(CH_3)_2$, 3.2–3.8 (overlapping m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.44 (d of d), $^3J_{P(S)CCH} = 19.7$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 0.98, $^3J_{P(S)CCH} = 19.9$, $^3J_{HCCH} = 7.0$. $Ph_2P(S)CH_2P(S)PhMe$ (100): Ph, 7.1–8.0 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 3.5 (distorted t), ABXY; H_A, 3.55, $^2J_{H_ACH_B} = 15.3$; H_B, 3.51; CH_3, 2.38 (d), $^2J_{P(S)CH} = 13.6$. $Ph_2P(S)CH_2P(S)(\mathit{i}\text{-}Pr)_2$ (100): Ph, 7.4–8.0 (m); PCH_2P, 3.31 (d of d), $^2J_{P(Ph)CH} = 12.2$, $^2J_{P(\mathit{i}\text{-}Pr)CH} = 13.8$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.8 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.18 (d of d), $^3J_{P(S)CCH} = 18.2$, $^3J_{HCCH} = 7.1$; $(CH_3)_B$, 1.05 (d of d), $^3J_{P(S)CCH} = 18.2$, $^3J_{HCCH} = 7.1$. $Ph_2P(S)CH_2P(S)Me_2$:[17] Ph, 7.4–8.2 (m); PCH_2P, 3.45 (d of d), $^2J_{P(Ph)CH} = 12.5$, $^2J_{P(Me)CH} = 15.0$; CH_3, 1.87 (d), $^2J_{P(S)CH} = 13.5$.

$[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$: Ph, 7.1–7.8 (m); PCH_2P, 3.63 (d of d), $^2J_{P(S)CH} = 10.0$, $^2J_{PCH} = 7.8$. $[Ph_2P(S)CH_2PPh_2]Mo(CO)_4$: Ph, 7.1–7.8 (m); PCH_2P, 3.62 (d of d), $^2J_{P(S)CH} = 10.0$, $^2J_{PCH} = 7.5$. $[Ph_2P(S)CH_2PPh_2]W(CO)_4$: Ph, 7.1–7.7 (m); PCH_2P, 3.70 (d of d), $^2J_{P(S)CH} = 10.5$, $^2J_{PCH} = 7.6$. $[Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)]Cr(CO)_4$: Ph, 7.2–8.0 (m); PCH_2P, centered at *ca.* 3.4 (distorted d of d), ABMX; $C\mathit{H}(CH_3)_2$, centered at ca. 1.9 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$, $(CH_3)_A$, 1.13, $^3J_{PCCH} = 17.4$, $^3J_{HCCH} = 7.1$; $(CH_3)_B$, 1.02, $^3J_{PCCH} = 13.0$, $^3J_{HCCH} = 6.5$. $[Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)]Mo(CO)_4$ (100): Ph, 7.0–7.9 (m); $PC\mathit{H}_A\mathit{H}_BP$, centered at ca. 3.3 (m), ABMX; H_A, 3.39; H_B, 3.22, $^2J_{H_ACH_B} = 14.5$; $C\mathit{H}(CH_3)_2$, centered at ca. 1.9 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.10 (d of d), $^3J_{PCCH} = 18.8$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 0.96 (d of d), $^3J_{PCCH} = 13.7$, $^3J_{HCCH} = 6.6$. $[Ph_2P(S)CH_2PPh(\mathit{i}\text{-}Pr)]W(CO)_4$: Ph, 7.2–8.0 (m); PCH_2P, centered at ca. 3.5 (m), ABMX; $C\mathit{H}(CH_3)_2$, centered at ca. 1.9 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.12 (d of d), $^3J_{PCCH} = 19.0$, $^3J_{HCCH} = 7.0$; $(CH_3)_B$, 1.00 (d of d), $^3J_{PCCH} = 15.0$, $^3J_{HCCH} = 7.0$. $[Ph_2P(S)CH_2PPhMe]Cr(CO)_4$: Ph, 7.2–8.1 (m); PCH_2P, centered at ca. 3.3 (m), ABMX; $C\mathit{H}_3$, 1.68 (d), $^2J_{PCH} = 5.5$. $[Ph_2P(S)CH_2PPhMe]Mo(CO)_4$: Ph, 7.2–8.0 (m); PCH_2P, centered at ca. 3.3 (m), ABMX; CH_3, 1.62 (d), $^2J_{PCH} = 5.0$. $[Ph_2P(S)CH_2PPhMe]W(CO)_4$: Ph, 7.1–8.0 (m); PCH_2P, centered at ca. 3.4 (m), ABMX; CH_3, 1.75 (d), $^2J_{PCH} = 6.0$. $[Ph_2P(S)CH_2P(\mathit{i}\text{-}Pr)_2]Cr(CO)_4$ (100): Ph, 7.4–7.9 (m); PCH_2P, 2.87 (d of d), $^2J_{P(S)CH} = 10.5$, $^2J_{PCH} = 7.6$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.1 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.25 (d of d), $^3J_{PCCH} = 14.2$, $^3J_{HCCH} = 6.9$; $(CH_3)_B$, 1.23 (d of d), $^3J_{PCCH} = 14.6$, $^3J_{HCCH} = 7.1$. $[Ph_2P(S)CH_2P(\mathit{i}\text{-}Pr)_2]Mo(CO)_4$ (100): Ph, 7.4–8.0 (m); PCH_2P, 2.83 (d of d), $^2J_{P(S)CH}$ 10.6, $^2J_{PCH} = 6.8$; $C\mathit{H}(CH_3)_2$, centered at ca. 1.9 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.22 (d of d), $^3J_{PCCH} = 14.5$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 1.19 (d of d), $^3J_{PCCH} = 15.0$, $^3J_{HCCH} = 7.1$. $[Ph_2P(S)CH_2P(\mathit{i}\text{-}Pr)_2]W(CO)_4$: Ph, 7.6–8.2 (m); PCH_2P, 2.99 (d of d), $^2J_{P(S)CH} = 10.6$, $^2J_{PCH} = 7.0$; $C\mathit{H}(CH_3)_2$, centered at ca. 2.0 (m); $CH(C\mathit{H}_3)_A(C\mathit{H}_3)_B$ (8 lines); $(CH_3)_A$, 1.27 (d of d), $^3J_{PCCH} = 14.8$, $^3J_{HCCH} = 6.8$; $(CH_3)_B$, 1.22 (d of d), $^3J_{PCCH} = 15.6$, $^3J_{HCCH} = 7.2$. $[Ph_2P(S)CH_2PMe_2]Cr(CO)_4$ (100): Ph, 7.4–7.9 (m); PCH_2P, 2.98 (d of d), $^2J_{P(S)CH} = 10.1$, $^2J_{PCH} = 7.7$; CH_3, 1.50 (d), $^2J_{PCH} = 6.2$. $[Ph_2P(S)CH_2PMe_2]Mo(CO)_4$ (100): Ph, 7.5–7.9 (m); PCH_2P, 2.94 (d of d), $^2J_{P(S)CH} = 10.4$, $^2J_{PCH}$

= 7.7; CH_3, 1.45 (d), $^2J_{PCH}$ = 6.0. $[Ph_2P(S)CH_2PMe_2]W(CO)_4$ (100): Ph, 7.4–7.9 (m); PCH_2P, 3.01 (d of d), $^2J_{P(S)CH}$ = 10.2, $^2J_{PCH}$ = 8.0; CH_3, 1.58 (d), $^2J_{PCH}$ = 6.8.

Results and Discussion

The following reaction sequence is used to form the (phosphinomethyl)phosphine sulfides

$$Ph_3PS + MeLi \rightarrow Ph_2P(S)CH_2Li + PhH \qquad (I)$$

$$Ph_2P(S)CH_2Li + R^1R^2PCl \rightarrow Ph_2P(S)CH_2PR^1R^2 + LiCl \qquad (II)$$

The mechanism of reaction I has been investigated and discussed elsewhere.[20] It includes an exchange reaction (eq Ia)

$$Ph_3PS + MeLi \rightarrow Ph_2P(S)Me + PhLi \qquad (Ia)$$

and subsequent metalation (eq Ib). We have previously

$$Ph_2P(S)Me + PhLi \rightarrow Ph_2P(S)CH_2Li + PhH \qquad (Ib)$$

reported the details of reaction II.[4] It is important in reaction II to have the phosphinous chloride in excess during the reaction; i.e., $Ph_2P(S)CH_2Li$ should be added slowly to the rapidly stirred solution of phosphinous chloride; otherwise extensive amounts of side products result as shown in reaction III. This series of reactions is similar to those reported for

$$Ph_2P(S)CH_2PR^1R^2 + Ph_2P(S)CH_2Li \rightarrow Ph_2P(S)CHLiPR^1R^2 + Ph_2P(S)Me \qquad (III)$$

Ph_3PO with organolithium reagents.[10,24] However, unlike the reaction of $Ph_2P(O)CH_2Li$ with R^1R^2PCl, which produces a mixture of products,[10] the reactions described here for the sulfur analogue occur in good yield with isolatable products.

The phosphino group of the (phosphinomethyl)phosphine sulfides undergoes the expected reactions of a tertiary phosphine. Specifically, it can be quaternized by reaction with methyl bromide in benzene (eq IV) or oxidized by the direct

$$Ph_2P(S)CH_2PR^1R^2 + MeBr \rightarrow [Ph_2P(S)CH_2P^+R^1R^2Me]Br^- \qquad (IV)$$

reaction of sulfur in benzene (eq V).

$$Ph_2P(S)CH_2PR^1R^2 + S \rightarrow Ph_2P(S)CH_2P(S)R^1R^2 \qquad (V)$$

Likewise, the thiophosphoryl group exhibits normal behavior by being readily reduced with sodium or hexachlorodisilane[25] to produce unsymmetrical di(tertiary phosphines) (eq VI).

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

We found no evidence for salt formation, viz., $[R_3PSMe]^+$, of the tertiary phosphine sulfide during the quaternization of the tertiary phosphine moiety with methyl bromide. More active methylating agents such as trimethyloxonium and dimethyl sulfate have been shown[27] to produce salts with tertiary phosphine sulfides.

The juxtaposition of the phosphino and thiophosphoryl groups in the same molecule provides for an additional unique reaction.[28] It is a well-known synthetic procedure, for example, in which sulfur is transferred to tributylphosphine from sulfides of tertiary phosphines of lesser basicity, especially triarylphosphines.[29] The present system allows for this transfer in the same molecule (reaction VII). When dimethylphos-

$$Ph_2P(S)CH_2PR^1R^2 \rightarrow Ph_2PCH_2P(S)R^1R^2 \qquad (VII)$$

phino(diphenylthiophosphoryl)methane is heated at ca. 160 °C in an inert solvent such as diglyme, the sulfur transfer from the less basic diphenylphosphino group to the more basic dimethylphosphino group occurs readily and the product is formed in good yield (85% estimated from ^1H NMR peak areas; 50% isolated). In a previous study of phosphine–phosphine oxides,[10] pure $Ph_2P(O)CH_2PPhEt$ was not isolated but the "self-redox" reaction of the compound to form $Ph_2PCH_2P(O)PhEt$ was suggested. Unlike the oxide case, however, the $Ph_2P(S)CH_2PR^1R^2$ compounds are easily isolated, are stable at ambient temperatures, and must be heated to effect the sulfur exchange.

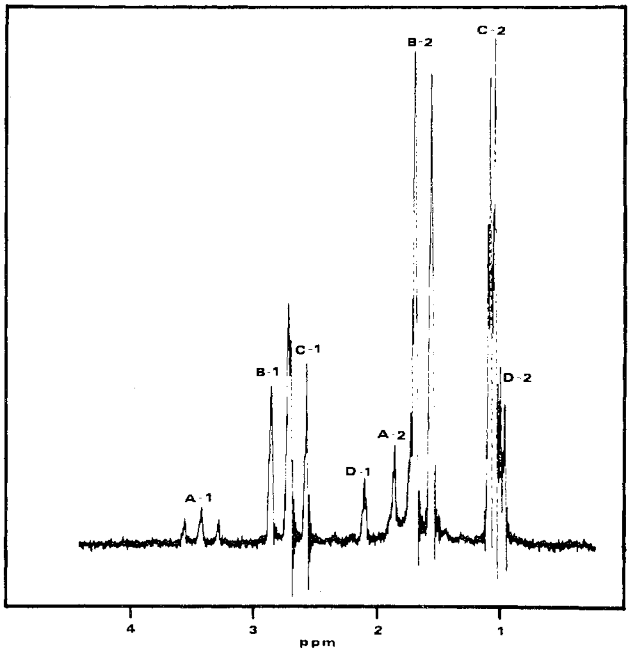


Figure 1. Proton NMR spectrum of the reaction mixture $Ph_2P(S)CH_2PMe_2 \rightarrow Ph_2PCH_2P(S)Me_2$ after 2.5 h at 158 °C. The compounds present are $Ph_2P(S)CH_2P(S)Me_2$ (A), $PH_2PCH_2P(S)Me_2$ (B), $PH_2P(S)CH_2PMe_2$ (C), and $PH_2PCH_2PMe_2$ (D). Label 1 indicates the methylene assignment; 2 indicates the methyl group assignment; the phenyl area is not shown. The chemical shifts and coupling constants are given in Table IV.

The sulfur-exchange reaction is general for all $Ph_2P(S)CH_2PR^1R^2$ complexes examined, viz., $R^1 = R^2$ = Me, *i*-Pr (gross yield by ^1H NMR >95%; isolated yield 76%), R^1 = Ph, R^2 = Me (gross yield 67%; isolated 49%), and R^2 = *i*-Pr (gross yield >95%; isolated 78%). The bulkier isopropyl groups do not seem to deter the rate nor lower the extent of reaction. These four compounds were selected for study because the progress of the reaction can be easily monitored by observation of the ^1H NMR spectra of the methyl and methylene regions. It was also noted in the ^1H NMR of aliquots of the reaction mixture that two intermediates, viz., the disulfides and the reduced di(tertiary phosphines), appeared early in the progress of the reaction in small, approximately equivalent amounts and then remained essentially constant throughout the remainder of the reaction. Although the methyl region of the ^1H NMR spectra is rather complex (see Figure 1), the assignments can be made unequivocally because the two intermediate compounds have also been independently synthesized, isolated, and characterized (see Experimental Section and Table IV). Additionally, the bridging methylene group aids in the assignments. For example, in the case of $R^1 = R^2$ = Me, the four compounds involved are the reactant $Ph_2P(S)CH_2PMe_2$ (C), the intermediates $Ph_2P(S)CH_2P(S)Me_2$ (A) and $Ph_2PCH_2PMe_2$ (D),[26] and the product $Ph_2PCH_2P(S)Me_2$ (B). The methylene protons of A are adjacent to two relatively electronegative thiophosphoryl groups and thus their signal appears furthest downfield (δ 3.45) and is coupled to each of the pentavalent phosphorus atoms by a relatively large amount (12.5 and 15.0 Hz) appearing as an overlapping doublet of doublets (almost a triplet). The methylenes of B and C lie between one relatively electronegative thiophosphoryl with large coupling to it (14.0 and 13.0 Hz, respectively) and a phosphino phosphorus with little coupling to it (ca. 0 Hz). The CH_2 signals for B and C are thus doublets (unfortunately

Table IV. Summary of Proton NMR Data for P-CH_3

	$R^1 = Ph, R^2 = Me$		$R^1 = R^2 = Me$	
Compd	δ_{Me},[a] ppm	$\lvert J_{PCH}\rvert$, Hz	δ_{Me},[a] ppm	$\lvert J_{PCH}\rvert$, Hz
$Ph_2P(S)CH_2PR^1R^2$	1.42	4.4	1.08 (C)[b]	3.8 (C)[b]
$[Ph_2P(S)CH_2PR^1R^2]$-$M(CO)_4$				
M = Cr	1.68	5.5	1.50	6.2
M = Mo	1.62	5.0	1.45	6.0
M = W	1.75	6.0	1.58	6.8
$Ph_2PCH_2P(S)R^1R^2$	1.93	13.0	1.64 (B)[b]	13.2 (B)[b]
$Ph_2P(S)CH_2P(S)R^1R^2$	2.38	13.6	1.87 (A)[b]	13.5 (A)[b]
$[MePh_2PCH_2P(S)$-$R^1R^2]^+Br^-$	2.20	13.6	1.81	13.2
$[Ph_2P(S)CH_2PR^1R^2$-$Me]^+Br^-$	2.71	14.5	2.10	14.1
$Ph_2PCH_2PR^1R^2$ [c]	1.36	3.6	1.06 (D)[b]	2.6 (D)[b]

[a] Refers to CH_3 on the R^1-R^2 end of the compound. [b] Letter refers to compound discussed in text under the sulfur-transfer reaction. [c] Reference 26.

overlapping) of intermediate chemical shift (2.84 and 2.64 ppm, respectively). The methylene of D lies between two trivalent phosphorus atoms, is coupled to them by an insignificant magnitude, and appears as a singlet relatively upfield, δ 2.12. A similar analysis can be given for the methyl region of the four compounds A–D (Figure 1 and Table IV).

Although the mechanism has not yet been established, preliminary kinetic measurements and the observation of $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$ indicate that the reaction is not a simple intramolecular sulfur-transfer process. A separate reaction between pure starting materials, $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$, does produce $Ph_2PCH_2P(S)Me_2$ in good yield. These processes are being investigated further.

The (phosphinomethyl)phosphine sulfides react with $Cr(CO)_6$ and $Mo(CO)_6$ in diglyme at about 120–140 °C to produce chelate complexes in which the phosphino phosphorus and the sulfur are the donor atoms, thus producing a five-membered chelate ring. Although the chelate behavior of di(tertiary phosphines)[3,30] has been investigated extensively and that of di(tertiary phosphine) sulfides[12,13,16] somewhat, the ligands here represent a new type of chelate ring. Recently, some bidentate phosphorus–sulfur ligands have been prepared,[31] but their coordination chemistry has not been reported.

The reaction of $Ph_2P(S)CH_2PR^1R^2$ with $W(CO)_6$ in diglyme normally requires higher temperatures than for $Mo(CO)_6$ and $Cr(CO)_6$, and the sulfur-transfer reaction becomes competitive with the carbonyl substitution reaction so that a mixture can result. Thus, the tungsten derivatives were better prepared by the displacement of norbornadiene from $C_7H_8W(CO)_4$ in dichloromethane solution at room temperature. Some of the molybdenum complexes were also prepared in this manner.

Phosphorus-31 NMR data are given in Table V for the (phosphinomethyl)phosphine sulfides and the phosphonium salts and disulfide derivatives. The $Ph_2P(S)CH_2PR^1R^2$ compounds are characterized by two sets of doublets, one set to the high-field side of H_3PO_4, assigned to the phosphino group, and the other set downfield from H_3PO_4, assigned to the phosphine sulfide. The chemical shifts for the $-PR^1R^2$ group correlate with the published group contributions[32] of R^1 and R^2 and can be predicted by using $Ph_2P(S)CH_2PPh_2$ ($-CH_2PPh_2$, −28 ppm) as the model compound.

Phosphorus–phosphorus coupling (56–77 Hz) is directly observable in the ^{31}P spectra since the phosphorus atoms are nonequivalent. An increase in the magnitude of $^2J_{PP}$ is observed as the bulkiness of the R^1 and R^2 groups increases. A bulkier group results in larger bond angles around the phosphino phosphorus with a concomitant increase in the s character of the bonds (the lone pair gets more p character), which, as noted by others,[33,34] contributes to increasing J_{PP}. Introduction of a methyl group for one of the bridging methylene protons results in the expected[32] downfield chemical shift for both phosphorus atoms in $Ph_2P(S)CH(CH_3)PPh_2$. However, $^2J_{PP}$ is unusually large (95 Hz) in this compound. The negligible $^2J_{PP}$ in $[Ph_2P(S)CH(CH_3)PPh_2Me]Br$ is also anomalous compared to the other phosphonium salts in the series with a bridging methylene group.

Table V. Phosphorus-31 NMR Data for (Phosphinomethyl)phosphine Sulfides and Derivatives

Compd	δ_{PPh_2},[a] ppm	$\delta_{PR^1R^2}$,[a] ppm	$\lvert J_{PP}\rvert$, Hz
$Ph_2P(S)CH_2PMe_2$	39.0	−53.8	56
$Ph_2P(S)CH_2PPhMe$	39.1	−43.3	66
	(39.7)	(−42.8)	(67)[b]
$Ph_2P(S)CH_2PPhEt$	39.6	−30.9	68
	(39.9)	(−30.6)	(68)[b]
$Ph_2P(S)CH_2PPh(i\text{-}Pr)$	40.5	−19.3	71
	(40.9)	(−19.0)	(72)[b]
$Ph_2P(S)CH_2PPh_2$	40.1	−28.0	76
	(40.5)	(−28.1)	(79)[b]
$Ph_2P(S)CH_2P(i\text{-}Pr)_2$	41.6	−9.3	77
	(41.9)	(−9.4)	(77)[b]
$Ph_2P(S)CH(CH_3)PPh_2$	51.8	−13.0	95
$Ph_2PCH_2P(S)Me_2$	−26.2	35.4	62
$Ph_2PCH_2P(S)PhMe$	−27.1	36.9	68
$Ph_2PCH_2P(S)Ph(i\text{-}Pr)$	−27.7	55.1	65
$Ph_2PCH_2P(S)(i\text{-}Pr)_2$	−27.8	65.6	52
$Ph_2P(S)CH_2P(S)Me_2$	32.4	35.3	17
	(32.8)	(35.9)[c]	
$Ph_2P(S)CH_2P(S)PhMe$	33.3	34.6	16
$Ph_2P(S)CH_2P(S)PhEt$	33.3	44.4	15
$Ph_2P(S)CH_2P(S)Ph_2$	34.6		
	(36.8)[d]		
$Ph_2P(S)CH_2P(S)Ph(i\text{-}Pr)$	33.1	53.3	18
$Ph_2P(S)CH_2P(S)(i\text{-}Pr)_2$	31.9	69.5	16
$Ph_2P(S)CH(CH_3)P(S)Ph_2$	46.5		
$[Ph_2P(S)CH_2PMe_3]^+Br^-$	33.3	27.4	12
$[Ph_2P(S)CH_2PPhMe_2]^+Br^-$	33.7	22.9	12
$[Ph_2P(S)CH_2PPhEtMe]^+Br^-$	33.7	28.3	12
$[Ph_2P(S)CH_2PPh_2Me]^+Br^-$	33.7	21.2	9
$[Ph_2P(S)CH_2PPh(i\text{-}Pr)Me]^+Br^-$	33.7	32.1	13
$[Ph_2P(S)CH_2P(i\text{-}Pr)_2Me]^+Br^-$	33.4	44.2	14
$[Ph_2P(S)CH(CH_3)PPh_2Me]^+Br^-$	46.9	27.8	0
$[MePh_2PCH_2P(S)Me_2]^+Br^-$	20.4	34.5	12
$[MePh_2PCH_2P(S)PhMe]^+Br^-$	20.2	33.5	12
$[MePh_2PCH_2P(S)Ph(i\text{-}Pr)]^+Br^-$	20.7	50.7	15
$[MePh_2PCH_2P(S)(i\text{-}Pr)_2]^+Br^-$	22.9	64.4	14

[a] Positive values are ppm downfield from 85% H_3PO_4. [b] Reference 4. [c] Reference 17. [d] Reference 29.

Upon sulfurization or quaternization, the chemical shift of the phosphino group moves downfield, as expected, consistent with a change from P(III) to P(V) or P^+. The chemical shifts for the diphenylthiophosphoryl group remain fairly constant for $Ph_2P(S)CH_2PR^1R^2$, ca. 40 ppm, for $Ph_2P(S)CH_2P(S)R^1R^2$, ca. 33 ppm, and for $[Ph_2P(S)CH_2PR^1R^2Me]^+Br^-$, ca. 34 ppm. Likewise the diphenylphosphino group in $Ph_2PCH_2P(S)R^1R^2$ has a ^{31}P shift of about −27 ppm and the diphenylmethylphosphonium group has a shift of about 21 ppm in $[MePh_2PCH_2P(S)R^1R^2]^+Br^-$. These constant values for a particular type of phosphorus functional group were very useful in making the chemical shift assignments for the compounds. Also, the phosphonium group shifts correlate with earlier group contributions in phosphonium salts.[35]

The $\lvert ^2J_{PP}\rvert$ values for the disulfides and phosphonium salts are small and relatively constant at 16 and 12 Hz, respectively, with the exception of that for $[Ph_2P(S)CH(CH_3)PPh_2Me]^+Br^-$ as noted above. With both sulfurization and quaternization, the s character of the phosphorus bonds should increase as the quadruply connected phosphorus approaches sp^3 hybridization. In addition, the effective nuclear charge increases upon

Table VI. Phosphorus-31 NMR Data of (Phosphinomethyl)phosphine Sulfide-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	$\lvert J_{PPh_2W}\rvert$, Hz
$Ph_2P(S)CH_2PMe_2$ (L_V)	+39.0		−53.8		56	
$L_VCr(CO)_4$	+57.3	+18.3	+42.5	+96.3	78	
$L_VMo(CO)_4$	+54.9	+15.9	+13.2	+67.0	71	
$L_VW(CO)_4$	+59.1	+20.1	−4.2	+49.6	71	232
$Ph_2P(S)CH_2PPhMe$ (L_{III})[c]	+39.1		−43.3		66	
$L_{III}Cr(CO)_4$	+56.8	+17.7	+50.2	+93.5	79	
$L_{III}Mo(CO)_4$	+54.6	+15.5	+23.7	+67.0	73	
$L_{III}W(CO)_4$	+58.9	+19.8	+8.8	+52.1	73	241
$Ph_2P(S)CH_2PPh_2$ (L_I)[c]	+40.1		−28.0		76	
$L_ICr(CO)_4$	+57.5	+17.4	+63.9	+91.9	83	
$L_IMo(CO)_4$	+55.5	+15.1	+37.9	+65.9	78	
$L_IW(CO)_4$	+59.6	+19.5	+25.2	+53.2	76	240
$Ph_2P(S)CH_2PPh(i\text{-}Pr)$ (L_{II})[c]	+40.5		−19.3		71	
$L_{II}Cr(CO)_4$	+57.2	+16.7	+68.7	+88.0	77	
$L_{II}Mo(CO)_4$	+55.3	+14.8	+45.7	+65.0	70	
$L_{II}W(CO)_4$	+59.7	+19.2	+33.0	+52.3	68	238
$Ph_2P(S)CH_2P(i\text{-}Pr)_2$ (L_{IV})[c]	+41.6		−9.3		77	
$L_{IV}Cr(CO)_4$	+57.9	+16.3	+82.3	+91.6	70	
$L_{IV}Mo(CO)_4$	+55.5	+13.9	+60.5	+69.8	64	
$L_{IV}W(CO)_4$	+60.2	+18.6	+49.0	+58.3	62	227

[a] In ppm referenced externally to 85% H_3PO_4; + ppm indicates downfield chemical shift from 85% H_3PO_4. [b] Δ = coordination chemical shift $\equiv \delta_{complex} - \delta_{free\ ligand}$. [c] These data are more accurate than those reported in ref 4.

sulfurization or quaternization. It has been proposed[5] that the change in $^2J_{PP}$ in $(OC)_5WPh_2PCH_2PPh_2$ upon quaternization of the free phosphine end is due to changes in s character and effective nuclear charge at this phosphorus atom. Our findings seem to support this observation: if the $^2J_{PP}$ values in the $Ph_2P(S)CH_2PR^1R^2$ and $Ph_2PCH_2P(S)R^1R^2$ compounds are initially negative, increasing the s character and the effective nuclear charge (which contribute to a positive increase in J_{PP})[33] by sulfurization and quaternization causes $^2J_{PP}$ to increase to ±16 and ±12 Hz for the disulfides and phosphonium salts, respectively.

The coordination shifts ($\Delta = \delta_{complex} - \delta_{free\ ligand}$) of the coordinated phosphino group in the group 6 metal carbonyl complexes are the typically large values observed in five-membered chelate ring systems[3,36,37] (see Table VI), with the Δ values being about 92 ppm for the Cr series, 67 ppm for the Mo series, and 53 ppm for the W complexes. These data are good proof for the formation of the chelate ring. Additionally, the thiophosphoryl groups have coordination shifts of about 17 ppm for Cr, 15 ppm for Mo, and 19 ppm for W complexes. Coordination (pseudoquaternization) of the phosphine group without simultaneous coordination of the phosphine sulfide group would tend to decrease the phosphine sulfide chemical shift a small amount, e.g., from 39.1 ppm in $Ph_2P(S)CH_2PPhMe$ to 33.3 ppm in $Ph_2P(S)CH_2P(S)PhMe$ and 33.7 ppm in $[Ph_2P(S)CH_2PPhMe_2]^+Br^-$. Indeed, the shift of the uncoordinated thiophosphoryl phosphorus in $(OC)_5Mo[PhMePCH_2P(S)Ph_2]$ is 33.8 ppm.[38] Thus, the observed increase in shift upon coordination corroborates the fact that the thiophosphoryl is coordinated. The relative magnitudes of Δ_{PS} (ppm) for Cr (17), Mo (15), and W (19) is not understood. On first inspection, one might expect the trend to reflect the varying size of the metal and resulting differences in ring strain on the one hand and the varying strength of the soft–soft sulfur–metal interaction on the other. However, a similar unexplained trend is observed for Δ_{PO} of the tertiary phosphine–phosphine oxide complexes.[10]

Within each series, Δ_{PS} decreases with increasing bulkiness of the R^1 and R^2 groups. For example, the Δ_{PS} values for $[Ph_2P(S)CH_2PR^1R^2]Cr(CO)_4$ are as follows for R^1R^2: Me_2, 18.3 ppm; MePh, 17.7 ppm; Ph_2, 17.4 ppm; Ph(*i*-Pr), 16.7 ppm; $(i\text{-}Pr)_2$, 16.3 ppm. The same trend holds for the Mo and W compounds. Thus, the bulky ligands on the phosphino group cause more shielding in the thiophosphoryl group across the ring (1,3 interaction), possibly by weakening the thiophosphoryl–metal bond.

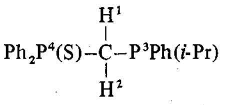
The $|J_{PP}|$ values for the $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$ complexes vary from slightly larger than the values in the free ligand (most of the compounds) to slightly less than that in the free ligand $Ph_2P(S)CH_2P(i\text{-}Pr)_2$. $|J_{PP}|$ can be represented as the sum of the contributions of phosphorus–phosphorus coupling through the P–C–P backbone, $^2J^B_{PP}$, and through the metal center, $^2J^M_{PP}$. It is not possible at this time to separate these terms. However, other results indicate that this model has validity.[2,39] $|J_{PP}|$ is consistently 5–7 Hz larger for the chromium complexes than for the respective molybdenum and tungsten complexes, in which $|J_{PP}|$ is nearly identical. $|J_{PP}|$ in *cis*-$L_2M(CO)_4$, where L is a phosphorus ligand, has been found to be larger when M = Cr than when M = Mo and W.[3,40] Also, $|J_{PP}|$ is largest for the diphenyl complexes, i.e., $[Ph_2P(S)CH_2PPh_2]M(CO)_4$, and smallest for the dialkyl complexes, $[Ph_2P(S)CH_2PR_2]M(CO)_4$.

Phosphorus–tungsten coupling is observed for the $[Ph_2P(S)CH_2PR^1R^2]W(CO)_4$ complexes, with only one pair of satellites, which arises from coupling of the directly bonded tertiary phosphine, being observed. No $^2J_{WSP}$ is seen. Similarly, no $^2J_{WOP}$ was observed in the similar complex $[Ph_2P(O)CH(n\text{-}Pr)PPh_2]W(CO)_4$.[10] The $^1J_{WP}$ values range from a lows of 227 $(i\text{-}Pr)_2$ and 232 Hz (Me_2) to highs of 238 (Ph(*i*-Pr)), 241 (PhMe), and 240 Hz (Ph_2). This is consistent with previous observations that the tertiary phosphines with the more phenyl groups generally have higher J_{WP}'s than the tertiary phosphines with more alkyl groups, which has been attributed to the greater π-acceptor ability of the arylphosphines.[41]

These compounds furnish a very fecund area for proton NMR investigations. The proton data are given in the Experimental Section. The methylene bridge protons of the $Ph_2P(S)CH_2PR^1R^2$ ligands and derivatives are especially interesting. When R^1 and R^2 are different, the phosphorus (PR^1R^2) is asymmetric which makes the methylene protons nonequivalent and in most cases results in formation of an AB pair (with simultaneous phosphorus double irradiation) or a complex ABMX or ABXY system without phosphorus decoupling. When $R^1 = R^2$, the spin system is simplified to an A_2MX or A_2XY.

In most cases, decoupling of the phosphorus nuclei was used to simplify the methylene bridge resonances. In one case, the

LAOCOON III[42] computer NMR simulation program was used to elucidate the methylene region in the compound $Ph_2P(S)CH_2PPh(i\text{-}Pr)$. The following simulation for this ABMX system was calculated and fitted to 60-MHz NMR spectrum of the methylene region expanded to 50 Hz. The values follow for



$$\begin{array}{c} H^1 \\ | \\ Ph_2P^4(S)\text{–}C\text{–}P^3Ph(i\text{-}Pr) \\ | \\ H^2 \end{array}$$

$\delta(H^1) = 172.723 \pm 0.029$ Hz, δ 2.88 (actual δ 2.88); $\delta(H^2) = 187.393 \pm 0.027$ Hz, δ 3.12 (actual δ 3.15); $^2J_{1,2} = -14.487 \pm 0.033$ Hz (actual $|14.4|$ Hz). For the P–H couplings, $^2J_{1,3} = -0.165 \pm 0.052$ Hz, $^2J_{1,4} = -15.249 \pm 0.059$ Hz, $^2J_{2,3} = +1.879 \pm 0.051$ Hz, and $^2J_{2,4} = -11.956 \pm 0.051$ Hz. The relative intensities for the computed spectrum correspond to those of the actual spectrum. The root-mean-square error for the iteration is 0.053. The computed values for the various P–H coupling constants are in good agreement with others found in the literature.[43,44] In the compounds where $R^1 = R^2$, $^2J_{PCH}$ values for the methylene region are 0–2 Hz while $^2J_{P(S)CH}$ values are usually around 13 Hz. It can be seen that the data from the computer fit are quite reasonable.

In all of the compounds where R^1 and/or R^2 is an isopropyl group, an eight-line (or overlapping six-line) pattern is found for the methyl region of the isopropyl protons. This nonequivalency is due to the diastereotopic nature of the protons involved. McFarlane[45] and others[3] have noted this nonequivalency of methyl groups in compounds with isopropyl groups. The main cause for this nonequivalence has been ascribed to intrinsic asymmetry (not temperature dependent) rather than to unequally populated conformers (temperature dependent) for the $PPh(i\text{-}Pr)_2$ system when this case was studied over the range 40–150 °C.[45] When the phosphorus nuclei are decoupled, the multiline patterns collapse to more simplified ones (e.g., an eight-line pattern collapses to a four-line pattern—actually, two sets of doublets). It is then possible to unequivocally assign lines belonging to the individual methyl groups and assign the various chemical shifts and coupling constants. These assignments are given in the Experimental Section for all of the isopropyl cases.

In several cases where $R^1 = R^2 =$ alkyl, the splitting pattern for the bridging methylene region is a doublet of doublets. It was not possible to unambiguously assign coupling constants without selective phosphorus-31 irradiation since the coupling from the alkylphosphorus group in the compound is of similar magnitude to that of the diphenylphosphorus group. We applied this technique to several cases where it was necessary to elucidate the various couplings. For example, the couplings in the methylene bridge of the compound $Ph_2P(S)CH_2P(S)(i\text{-}Pr)_2$ were found to be $|^2J_{P(Ph)CH}| = 12.2$ Hz and $|^2J_{P(i\text{-}Pr)CH}| = 13.8$ Hz, by irradiating first the $-P(S)(i\text{-}Pr)_2$ region and then the $Ph_2P(S)-$ region at the appropriate phosphorus-31 frequencies. In each case, the methylene region collapses to a simple doublet upon selective irradiation and the appropriate coupling can be measured.

Table IV contains a summary of the proton NMR data for the methyl groups where $R^1 = Ph$, $R^2 = Me$ and $R^1 = R^2 = Me$ for the ligands and various derivatives. In general, it can be seen that the chemical shifts of the protons in the methyl groups follow the trend $Ph_2P(S)CH_2PR^1R^2 < [Ph_2P(S)CH_2PR^1R^2]M(CO)_4 < Ph_2PCH_2P(S)R^1R^2 < Ph_2P(S)CH_2P(S)R^1R^2 \simeq [MePh_2PCH_2P(S)R^1R^2]^+Br^- < [Ph_2P(S)CH_2PR^1R^2Me]^+Br^-$. On the basis of inductive factors the amount of deshielding of the protons nearby the R^1–R^2 phosphorus should follow this approximate trend[46] since the "effective" electronegativity of the phosphorus atom increases in this order. It can also be seen from our table that $|^2J_{PCH}|$ values for the methyl group increase in the order $Ph_2P(S)CH_2PR^1R^2 < [Ph_2P(S)CH_2PR^1R^2]M(CO)_4 < Ph_2PCH_2P(S)R^1R^2 \simeq [MePh_2PCH_2P(S)R^1R^2]^+Br^- \simeq Ph_2P(S)CH_2P(S)R^1R^2 < [Ph_2P(S)CH_2PR^1R^2Me]^+Br^-$. Again, this is approximately the order of (increasing) electronegativity of the "groups" on phosphorus[33] and the order of increasing s character in the phosphorus bonding orbitals. It has been observed that $^2J_{PCH}$ becomes less positive with an increase in s character of the phosphorus bonding orbitals to carbon;[47] thus, if $^2J_{PCH}$ is positive (and small) in the free phosphine and decreases to a larger negative value for the quaternized phosphorus,[48] then our observations are consistent with the increasing electronegativity trend.

Table VII. IR Data of $Ph_2P(S)CH_2PR^1R^2$-Metal Carbonyl Complexes (CO Region)[a]

Compd	Freq, cm^{-1}			
	ν_1	ν_2	ν_3	ν_4
	$Ph_2P(S)CH_2PPh_2$ (L_I)			
$L_ICr(CO)_4$	2012 (2014)[b]	1921 (1924)[b]	1897 (1903)[b]	1861 (1869)[b]
$L_IMo(CO)_4$	2022	1927	1907	1867
$L_IW(CO)_4$	2018	1921	1897	1862
	$Ph_2P(S)CR_2PPh(i\text{-}Pr)$ (L_{II})			
$L_{II}Cr(CO)_4$	2011	1919	1893	1854
$L_{II}Mo(CO)_4$	2020	1925	1906	1859
$L_{II}W(CO)_4$	2016	1918	1894	1857
	$Ph_2P(S)CH_2PPhMe$ (L_{III})			
$L_{III}Cr(CO)_4$	2012	1925	1895	1862
$L_{III}Mo(CO)_4$	2020	1925	1902	1862
$L_{III}W(CO)_4$	2016	1918	1892	1860
	$Ph_2P(S)CH_2P(i\text{-}Pr)_2$ (L_{IV})			
$L_{IV}Cr(CO)_4$	2006	1912	1887	1856
$L_{IV}Mo(CO)_4$	2016	1918	1896	1858
$L_{IV}W(CO)_4$	2013	1914	1887	1857
	$Ph_2P(S)CH_2PMe_2$ (L_V)			
$L_VCr(CO)_4$[c]	2009	1889[d]		1842
$L_VMo(CO)_4$[c]	2019	1903[d]		1848
$L_VW(CO)_4$[c]	2013	1892[d]		1840

[a] Saturated CCl_4 solutions unless otherwise noted; resolution ±2 cm^{-1}. [b] Saturated cyclohexane solution. [c] Saturated CH_2Cl_2 solution. [d] Unresolved doublet.

Infrared stretching frequency data are given in Table VII. It is expected that these cis-disubstituted octahedral metal carbonyl complexes would show four infrared-active CO stretching modes[49] consistent with their C_s symmetry. These are observed. It was necessary to obtain the solution spectra of most of the complexes in CCl_4 due to their limited solubility in cyclohexane; however, the dimethyl compounds $[Ph_2P(S)CH_2PMe_2]M(CO)_4$ also had low solubility in CCl_4 and were run in CH_2Cl_2. A comparison of the frequencies for $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$ in CCl_4 and cyclohexane shows only very small solvent shifts.

In summary, the synthesis and some reactions of (diphenylphosphinomethyl)phosphine sulfides are described. The functional groups of these compounds behave normally: the tertiary phosphino group can be quaternized, oxidized by the direct addition of sulfur, self-oxidized by the tertiary phosphine sulfide inter- or intramolecularly, or coordinated to metals; the tertiary phosphine sulfide can be reduced with sodium or hexachlorodisilane or by the neighboring tertiary phosphino group and can be coordinated to metals. A new chelate ring system is formed by these ligands. Extensive proton and phosphorus-31 NMR data are given for the approximately 40 new compounds described here.

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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,