Unsymmetrical Bis-Phosphorus Ligands. V. Group VI Metal Carbonyl Derivatives[1]

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Abstract: Coordination compounds of chromium, molybdenum, and tungsten carbonyls with unsymmetrical bis(tertiary phosphine) ligands, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)R$, where R is methyl, ethyl, and isopropyl, and $(C_6H_5)_2PCH_2CH_2PR'_2$, where R' is n-butyl, are described. These are the first coordination compounds reported for these novel ligands. The ligands can behave as bidentate chelates, $LM(CO)_4$, as bidentate bridging ligands, $(OC)_5MLM(CO)_5$, and as monodentate ligands with one phosphorus uncoordinated, $LM(CO)_5$. Phosphorus-31 nmr results are tabulated. The compounds which have the ligands bridging or behaving in a monodentate fashion have the normal downfield ^{31}P coordination shift. The chelate compounds have an extraordinarily large downfield coordination shift. Phosphorus–phosphorus and phosphorus–tungsten coupling constants are discussed.

Extensive studies have been reported on phosphorus-31 nmr studies of coordination compounds.[3,4] Emphasis has been placed mainly on empirical aspects of the chemical shifts[5,6] and on the observation and interpretation of heavy metal–phosphorus coupling constants.[5,7–11] In addition, there has also been active interest in phosphorus–phosphorus coupling constants[3b,12–16] and their variation with stereochemistry. Phosphorus–phosphorus coupling constants can be determined directly and indirectly. They can be obtained indirectly[3b] from, e.g., proton or fluorine nmr spectra of certain compounds with appropriately chosen substituents on phosphorus by line shape analysis and by heteronuclear double resonance methods. Direct determination of $J_{P–P}$ from ^{31}P nmr spectra of

coordination compounds can be made if the phosphorus atoms are chemically and magnetically different as, for example, in the following cases: (a) the compound contains more than one molecule of the same monodentate phosphorus ligand but in different stereochemical positions, e.g., mer-L_3IrX_3;[12] (b) the compound contains a symmetrical chelating diphosphorus ligand but the two ends are in different chemical environments, e.g., trans-$(Ph_2PCH_2CH_2PPh_2)[(EtO)_3P]Mo(CO)_3$;[15] (c) the compound contains two different phosphorus ligands, e.g., $LL'M(CO)_4$;[15] and (d) the compound contains unsymmetrical chelating polyphosphorus ligands.[17] Since types a, b, and c are applicable in only certain instances and not of very general utility, we have developed a synthetic method for preparation of unsymmetrical bis(tertiary phosphines). Although the original impetus for this research was the study of P–P coupling, these compounds are of interest for multiple reasons, which are exemplified later.
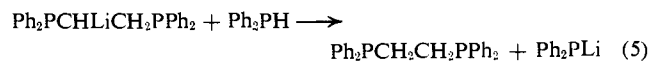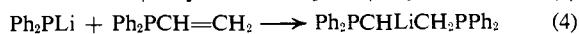
In 1967, Keiter[18] reported that lithium diphenylphosphide adds to the double bond in diphenylvinylphosphine in the following manner

$$Ph_2PLi + Ph_2PCH{=}CH_2 \longrightarrow Ph_2PCHLiCH_2PPh_2 \quad (1)$$
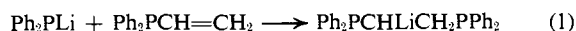
Hydrolysis of the mixture produces the well-known bis-1,2-diphenylphosphinoethane (dppe).

$$Ph_2PCHLiCH_2PPh_2 + H_2O \longrightarrow Ph_2PCH_2CH_2PPh_2 + LiOH \quad (2)$$
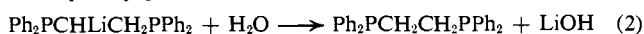
More recently King and Kapoor[19] reported a variation of the same reaction using instead diphenylphosphine (or phenylphosphine) and a strong base (e.g., phenyllithium) in catalytic amounts. Undoubtedly, the reaction proceeds as follows. Phenyllithium reacts with diphenylphosphine to form the lithium phosphide since

$$PhLi + Ph_2PH \longrightarrow Ph_2PLi + C_6H_6 \quad (3)$$
$$Ph_2PLi + Ph_2PCH{=}CH_2 \longrightarrow Ph_2PCHLiCH_2PPh_2 \quad (4)$$
$$Ph_2PCHLiCH_2PPh_2 + Ph_2PH \longrightarrow$$
$$Ph_2PCH_2CH_2PPh_2 + Ph_2PLi \quad (5)$$

(1) (a) Supported in part by the National Science Foundation under Grant No. GP-30703. (b) Taken from the Ph.D. dissertations of R. P. Molenda, University of Maryland, 1970, and J. Del Gaudio, University of Maryland, 1973. (c) Preliminary report given at the Sixth International Conference on Organometallic Chemistry, Abstracts of Papers, p 152, Amherst, Mass., Aug 1973. (d) Part IV: S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 13, 1095 (1974).

(2) (a) University of Maryland. (b) E. I. du Pont de Nemours and Co.

(3) (a) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, 2, 345 (1969); (b) E. G. Finer and R. K. Harris, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 6, J. M. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1961, pp 61–118.

(4) J. G. Verkade, *Coord. Chem. Rev.*, 9, 1 (1972).

(5) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 89, 5573 (1967).

(6) B. E. Mann, C. Masters, B. L. Shaw, and R. M. Slade, *Inorg. Nucl. Chem. Lett.*, 7, 881 (1971).

(7) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 6, 1133 (1967).

(8) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(9) R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, 8, 2115 (1969).

(10) G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).

(11) S. O. Grim, P. J. Lui, and R. L. Keiter, *Inorg. Chem.*, 13, 342 (1974).

(12) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Lett.*, 2, 205 (1966); S. O. Grim and R. A. Ference, *J. Coord. Chem.*, 2, 225 (1973).

(13) R. M. Lynden-Bell, J. F. Nixon, and R. Schmutzler, *J. Chem. Soc. A*, 565 (1970).

(14) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 92, 1908 (1970).

(15) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, 7, 161 (1968).

(16) J. F. Nixon and J. R. Swain, *J. Chem. Soc., Dalton Trans.*, 1038 (1972).

(17) S. O. Grim, R. P. Molenda, and R. L. Keiter, *Chem. Ind. (London)*, 1378 (1970).

(18) R. L. Keiter, Ph.D. Dissertation, University of Maryland, 1967.

(19) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 91, 5191 (1969).

Table I. Preparative and ^{31}P Nmr Data for Ligands and Derivatives

Compound	Yield, %	% C (calcd)	% C (found)	% H (calcd)	% H (found)	δ_P (ppm)^a	J_{PP} (Hz)
		Analysis					
Ph$_2$PCH$_2$CH$_2$PPhMe	50	74.96	75.15	6.60	6.72	13.0, 31.4	26
Ph$_2$PCH$_2$CH$_2$PPhEt	46	75.41	76.19	6.90	6.99	12.9, 15.9	27
Ph$_2$PCH$_2$CH$_2$PPh-i-Pr	55	75.82	76.11	7.18	7.35	12.8, 2.6	30
Ph$_2$PCH$_2$CH$_2$PPhPr	24	75.82	76.22	7.18	7.30	13.2, 21.7	25
Ph$_2$PCH$_2$CH$_2$PP-sec-Bu	30	76.17	76.35	7.46	7.47	12.8, 6.4	30
Ph$_2$PCH$_2$CH$_2$PPh-i-Bu	38	76.17	76.45^b	7.46	7.51	13.5, 25.4	c
Ph$_2$PCH$_2$CH$_2$PPhAm	25	76.51	76.75	7.70	7.50	13.2, 20.9	25
Ph$_2$PCH$_2$CH$_2$P-n-Bu$_2$	15					12.8, 26.1	26
Ph$_2$P(O)CH$_2$CH$_2$P(O)PhMe^d	90	68.47	67.34	6.02	6.00	−31.3, −36.9	51
Ph$_2$P(O)CH$_2$CH$_2$P(O)PhEt^e	90	69.10	68.87^f	6.33	6.39	−30.9, −40.9	50
Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph-i-Pr^g	90	69.69	69.29^h	6.61	6.59	−31.4, −46.0	49

^{a} Chemical shifts vs. H$_3$PO$_4$. The first value is the diphenylphosphorus end; the second is the alkylphenyl or dialkylphosphorus end. ^{b} Mol wt calcd, 378; found (Rast), 360. ^{c} Coupling not resolved. ^{d} Mp 153–156°. ^{e} Mp 170–177°. ^{f} % P calcd, 16.20; found, 15.90. ^{g} Mp 152–158°. ^{h} % P calcd, 15.62; found, 15.50.

phenyl is more basic than diphenylphosphide (3); the lithium phosphide adds to the vinyl group exactly as in our direct reaction (1, 4); the resulting carbon–lithium reagent thus formed reacts with more secondary phosphine to produce the product, dppe, and more lithium phosphide (5); and the cycle continues until the starting materials are exhausted. We have adapted our method to produce unsymmetrical ligands by beginning with alkyldiphenylphosphines or dialkylphenylphosphines.[1b,17] Cleavage of these phosphines with lithium in THF removes a phenyl group with the corresponding alkylphenylphosphide or dialkylphosphide being formed.[20] Reaction in the previous manner produces unsymmetrical bis(tertiary phosphines).

$$Ph_2RP + 2Li \xrightarrow{THF} PhRPLi + PhLi \qquad (6)$$

$$PhRPLi + Ph_2PCH{=}CH_2 \longrightarrow Ph_2PCHLiCH_2PRPh \qquad (7)$$

$$Ph_2PCHLiCH_2PPhR + H_2O \longrightarrow$$
$$Ph_2PCH_2CH_2PPhR + LiOH \qquad (8)$$
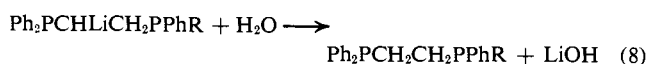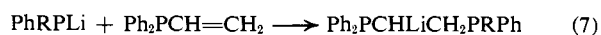
Both methods have some advantages. King's method[19] allows the preparation of poly(tertiary phosphines) with greater than two phosphorus atoms by use of primary phosphines or even phosphine, PH$_3$. Our method eliminates the need for use of the extremely unpleasant secondary and primary phosphines and is much more versatile for introduction of alkyl groups into the polyphosphines. King[21] has also adapted his method to permit use of methyl groups.

This paper reports in detail the synthesis of these ligands, coordination compounds thereof, and ^{31}P nmr data and other physical properties.

Experimental Section

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

Phosphorus-31 nmr spectra were recorded with a Varian Associates DP-60 spectrometer at 24.3 MHz, on solutions in stationary 15-mm tubes or on a Bruker HFX-90 spectrometer at 36.43 MHz, using spinning tubes and a ^{19}F lock on CBrF$_2$CBrF$_2$, with proton noise decoupling.

Proton nmr measurements were recorded on a Varian Associates A60A spectrometer or a Perkin–Elmer Hitachi R20A spectrometer at 60 MHz. Decoupling experiments were performed with the Perkin-Elmer instrument.

Melting points were taken with a Mel-temp apparatus and are reported uncorrected.

(20) S. O. Grim and R. P. Molenda, *Phosphorus*, in press.
(21) R. B. King, J. C. Cloyd, Jr., and P. K. Hendrick, *J. Amer. Chem. Soc.*, **95**, 5083 (1973).

Infrared spectra were recorded with a Perkin-Elmer Model 225 infrared spectrometer. Carbonyl compounds were recorded as cyclohexane solutions, in a NaCl cell of 0.5-mm sample thickness. Ligand oxides were recorded as KBr pellets.

Mass spectra were recorded by Martha Gay, University of Maryland, on a Dupont CEC 21-492 mass spectrometer, with an ionizing voltage of 70 eV and probe temperature of about 200°.

Starting Materials. Tertiary phosphines were prepared by the Grignard method[21] from dichlorophenylphosphine and chlorodiphenylphosphine (Aldrich Chemical Co.). Dibutylphosphine (bp 52–56° (2 Torr)) was prepared in 61% yield by the hydrolysis of lithium dibutylphosphide resulting from the cleavage of dibutylphenylphosphine by lithium in tetrahydrofuran (THF).[20] Metal carbonyls were obtained from Climax Molybdenum Corporation and Pressure Chemical Co.

Synthesis of 1-Isopropylphenylphosphino-2-diphenylphosphinoethane. Into a two-liter three-necked flask fitted with a mechanical stirrer, powder addition funnel, and a water condenser topped with a nitrogen inlet were placed 700 ml of THF (freshly distilled from sodium–benzophenone) and 7.0 g (1 g-atom) of lithium wire which was finely cut with a scissors over the powder funnel so as to drop directly into the flask as it was flushed with N$_2$. Diphenylisopropylphosphine (50 g, 0.22 mol) was added and the powder funnel replaced with a stopper. The mixture was stirred at ambient temperatures for about 5–6 hr. The reaction is only mildly exothermic and the color became deep red as the reaction proceeded. The solution was then filtered through glass wool (to remove the excess lithium) into another three-necked flask which was fitted with a nitrogen inlet and stirrer. The filtering funnel was replaced by an addition funnel. In order to destroy the phenyllithium, 20 g (0.22 mol) of dry t-BuCl in 100 ml of THF was added dropwise with stirring at room temperature over a 1-hr period and then was stirred for an additional hour. The mixture was cooled to −23° with a Dry Ice–CCl$_4$ slush bath and diphenylvinylphosphine (48 g, 0.22 mol) in 150 ml of dry THF was added dropwise with rapid stirring over a period of 4.5 hr. After complete addition, the mixture was stirred for another hour at −23°, then allowed to warm to room temperature and stirred for 2 hr. The red solution was then hydrolyzed by the dropwise addition of deoxygenated saturated NH$_4$Cl solution. Sufficient NH$_4$Cl solution was added to cause the salts to clump and settle out of solution. The clear yellow solution was decanted under N$_2$ into a one-necked round-bottom flask, the residue was washed with THF, and the mixture was decanted again. The solution and washings were concentrated by vacuum evaporation to give a yellow viscous oil. Low boiling fractions were removed by heating the oil at about 80° (0.1 Torr) for 1 hr. A 10-ml aliquot of the crude product was placed in a Hickman still (Fisher, 75 mm diameter × 60 mm height) with a receiving "cow" adapter. The Hickman still was heated with an oil bath. After some lower boiling fractions were removed, the pure compound was collected with the oil bath temperature between 130 and 155° (4 × 10^{-4} Torr). The yield for each aliquot was 3 g of product which corresponds to about a 55% yield overall. The compound, Ph$_2$PCH$_2$CH$_2$PPh-i-Pr, is an air-sensitive oil. Additional experimental data are given in Table I.

1-Diphenylphosphino-2-methylphenylphosphinoethane. This compound was prepared in the same manner as above except that the addition of diphenylvinylphosphine to methylphenyllithium

Table II. Preparative Data for Metal Carbonyl Derivatives

Compound[a]	Yield	Mp, °C	%C (calcd)	%C (found)	%H (calcd)	%H (found)	%P (calcd)	%P (found)
$Cr(CO)_4L_I$	43	167–169	57.77	57.90	4.81	4.63	12.33	13.03
$Mo(CO)_4L_I$	42	92–95	54.26	54.52	3.97	4.10	11.66	11.04
$W(CO)_4L_I$	30	108–112	46.55	47.12	3.42	3.66	10.00	9.16
$[Mo(CO)_5]_2L_I$	60	103–106	46.11	45.99	2.62	2.81	7.67	7.70
$W[CO)_5L_I$	50	Oil	47.37	46.50	3.12	3.27	9.40	9.49
$[W(CO)_5]_2L_I$	80	106–110	37.83	37.15	2.25	2.40	6.29	5.99
$Cr(CO)_4L_{II}$	41	157–159	60.51	60.27	4.96	4.96		
$Mo(CO)_4L_{II}$	42	148–149	55.77	56.00	4.32	4.15		
$W(CO)_4L_{II}$	37	153–154	48.32	47.79	3.74	3.70	9.58	9.73
$Cr(CO)_4L_{III}$	38	208–211	61.37	60.92	4.96	5.02	11.72	11.21
$Mo(CO)_4L_{III}$	37	181–184	56.65	56.46	4.65	4.56	10.82	11.09
$W(CO)_4L_{III}$	37	199–201	49.11	48.81	3.96	4.03	9.37	10.05
$W(CO)_5L_{III}$	70	Oil	48.86	50.39	3.81	4.07		
$W(CO)_4L_{IV}$	42	223–224	49.87	50.15	4.19	4.29	9.19	9.34

a L_I = $Ph_2PCH_2CH_2PPhMe$; L_{II} = $Ph_2PCH_2CH_2PPhEt$; L_{III} = $Ph_2PCH_2CH_2PPh$-i-Pr; L_{IV} = $Ph_2PCH_2CH_2PPh$-sec-Bu.

phosphide was conducted at $-30°$ (bromobenzene–Dry Ice slush bath). The yield was 50%. Other compounds which were prepared in this manner are 1-diphenylphosphino-2-ethylphenylphosphinoethane, 1-sec-butylphenylphosphino-2-diphenylphosphinoethane, 1-isobutylphenylphosphino-2-diphenylphosphinoethane, 1-diphenylphosphino-2-phenylpropylphosphinoethane, and 1-amylphenylphosphino-2-diphenylphosphinoethane. The latter two compounds were purified by column chromatography on alumina (100 g) under nitrogen with benzene–cyclohexane (5:95) as eluent. Fractions of 100 ml were collected with the product appearing in the sixth and seventh fractions.

1-Dibutylphosphino-2-diphenylphosphinoethane. Dibutylphosphine (3.2 g, 0.022 mol) in 50 ml of THF was added slowly to 0.025 mol of phenyllithium (prepared in Et_2O, THF added, and Et_2O removed at reduced pressure) in 100 ml of THF. After stirring for 30 min at room temperature, the reaction vessel was immersed in a Dry Ice–acetone cooling bath. Diphenylvinylphosphine (5.5 g, 0.025 mol) in 50 ml of THF was added slowly with rapid stirring. The solution was stirred overnight and allowed to come to ambient temperature during that time. The solution was hydrolyzed as before, and solvents and low boiling impurities were removed at reduced pressure. Distillation with a Hickman still produced a small yield (15%) of product, $Bu_2PCH_2CH_2PPh_2$, with ^{31}P doublets at 12.8 and 26.1 ppm and $^3J_{PP}$ = 26 Hz. A considerable amount of unidentified polymeric material (^{31}P resonances at 7 and 13 ppm) remained in the distillation pot.

Synthesis of Ligand Dioxides. $Ph_2P(O)CH_2CH_2P(O)PhMe$. A 30% aqueous H_2O_2 solution was added dropwise to a stirred solution of 1.76 g (5.3 mmol) of $Ph_2PCH_2CH_2PPhMe$ in 50 ml of acetone. Addition was continued until further addition failed to produce an exothermic reaction. The solution then was stirred for an hour, the solvent removed by vacuum evaporation, and the residue recrystallized from a CH_2Cl_2–hexane solution, to give white crystals. To remove water of hydration, the crystals were heated to 80° at 0.1 Torr for 10 hr. Additional information is given in Table I. The dioxides, $Ph_2P(O)CH_2CH_2P(O)PhEt$ and $Ph_2P(O)CH_2CH_2P(O)Ph$-i-Pr, were also prepared in the same manner.

Synthesis of Metal Carbonyl Derivatives. $Cr(CO)_4[Ph_2PCH_2CH_2PPhMe]$. Chromium hexacarbonyl (2.1 g, 9.5 mmol, 5% excess), $MePhPCH_2CH_2PPh_2$ (3.0 g, 9 mmol), and 15 ml of dry diglyme were placed in a 50-ml round-bottom flask and carefully deoxygenated by evacuation with a water aspirator. The flask was connected to an apparatus which allowed CO evolution to be monitored and provided a means of returning to the reaction flask any chromium carbonyl which had sublimed out. The reactants were heated to 160° until CO evolution stopped (about 5 hr). The volume of CO given off agreed within 10% of the expected amount for two CO's liberated per mole of $Cr(CO)_6$. After cooling for several hours at room temperature, the precipitate that formed was removed by filtration, the solvent was removed by vacuum evaporation, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 extract was recrystallized from a CH_2Cl_2–hexane solution to yield yellow crystals. Analytical data are given in Table II. Other compounds which were prepared in essentially the same manner are $[Ph_2PCH_2CH_2PPhMe]Mo(CO)_4$, $[Ph_2PCH_2CH_2PPhEt]Cr(CO)_4$, $[Ph_2PCH_2CH_2PPhEt]Mo(CO)_4$, $[Ph_2PCH_2CH_2PPhEt]W(CO)_4$, and $[Ph_2PCH_2CH_2PPh$-sec-Bu]$W(CO)_4$.

$(OC)_5Mo[Ph_2PCH_2CH_2PPhMe]Mo(CO)_5$ was prepared under the same conditions but with a 10 M excess of $Mo(CO)_6$.

$W(CO)_4[Ph_2PCH_2CH_2PPhMe]$. Tungsten hexacarbonyl (6.0 g, 0.017 mol) and $MePhPCH_2CH_2PPh_2$ (5.48 g, 0.016 mol) were allowed to react as described above. The ^{31}P nmr spectra of the reaction mixture showed six peaks. Two peaks, with 60% of the total phosphorus, could be assigned to the bidentate ligand complex and two peaks, with 20% of the total phosphorus, could be assigned to the bridging ligand complex. The remaining two peaks (-16 and $+4$ ppm), 20% of the total phosphorus, and in a 1:1 ratio, could not be assigned. An attempt was made to separate the reaction products chromatographically, using a 24 in. × 1.25 in. aluminum column, with a 15% hexane–85% CH_2Cl_2 eluent. However, only the bidentate ligand complex could be obtained pure. The bridging ligand complex has been prepared by a separate reaction.

$Cr(CO)_4[Ph_2PCH_2CH_2PPh$-i-Pr]$. Chromium hexacarbonyl (2.42 g, 0.011 mol) and (i-Pr)$PhPCH_2CH_2PPh_2$ (4.04 g, 0.011 mol) were allowed to react as described above. However, due to the insolubility of the complex, the workup was somewhat different. On cooling the reaction mixture the complex precipitated. Unreacted metal carbonyl was removed from the reaction mixture by sublimation (50° (25 mm) for 20 min). The remaining mixture was then cooled in an ice bath and filtered. The pure product was obtained by recrystallizing from hot diglyme, then washing the crystals with hexane before drying. Yellow crystals were obtained.

$Mo(CO)_4[Ph_2PCH_2CH_2PPh$-i-Pr]$ and $W(CO)_4[Ph_2PCH_2CH_2PPh$-i-Pr]$ were also synthesized in this manner.

$W(CO)_5[Ph_2PCH_2CH_2PPhMe]$. Anilinetungsten pentacarbonyl (1.38 g, 0.003 mol) and $MePhPCH_2CH_2PPh_2$ (4.0 g, 0.012 mol) were stirred overnight in 100 ml of deoxygenated benzene at ambient temperature. The ^{31}P nmr spectra of the reaction mixture gave the following resonances: -11 and $+4$ ppm (14% of total phosphorus), an unidentified product; $+8$ and $+12$ ppm (26% of total phosphorus), the desired product; and $+12$ and $+31$ ppm (60% of total phosphorus), the unreacted ligand. The reaction mixture was concentrated to a viscous oil by vacuum evaporation and chromatographed on a 18 in. × 1.25 in. deoxygenated alumina column, using a deoxygenated solution of 20% hexane–80% methylene chloride as eluent. The first fraction (100 ml) contained the desired product, a viscous green-yellow oil at room temperature.

$W(CO)_5[Ph_2PCH_2CH_2PPh$-i-Pr]$. The compound was prepared from 3.49 g (0.009 mol) of of ligand and 1.6 g (0.0033 mol) of $PhNH_2W(CO)_5$ using the method described for the previous compound. The reaction is much cleaner than the one above, with only small amounts of side products detected. The compound was purified chromatographically, with a 18 in. × 1.25 in. alumina column and 20% hexane–80% methylene chloride as eluent. Evaporation at reduced pressure yielded a viscous yellow-green oil which did not crystallize on repeated attempts.

$(OC)_5W[Ph_2PCH_2CH_2PPhMe]W(CO)_5$. Anilinetungsten pentacarbonyl (3.0 g, 0.0072 mol) and $MePhPCH_2CH_2PPh_2$ (1.22 g, 0.0036 mol) were dissolved in 75 ml of benzene and stirred overnight. The reaction mixture was vacuum evaporated to dryness, extracted with methylene chloride, and recrystallized from a methylene chloride–hexane solution.

Table III. Phosphorus Nmr Data for the Group VI Metal Carbonyls

Compound	δ (ppm)ᵃ	Δ (ppm)ᵇ	δ' (ppm)ᶜ	Δ' (ppm)	$^2J_{PP}{}^{cis}$ (Hz)	$^1J_{WP}$ (Hz)	$^1J_{WP'}$ (Hz)ᶜ
L₁Cr(CO)₄ᵈ	−80.0	−93.0	−65.0	−96.4	12 ± 1		
L₁Mo(CO)₄	−55.7	−68.7	−39.0	−70.4	4.8 ± 3		
L₁W(CO)₄	−41.0	−54.0	−22.6	−54.0	4.0 ± 0.5	232 ± 2	226 ± 2
L₁[Mo(CO)₅]₂	−30.7	−43.7	−11.3	−42.7	31 ± 1		
L₁[W(CO)₅]₂	−11.9	−24.9	+9.4	−22.0	32 ± 1		239 ± 3
L₁W(CO)₅	+13.0	0.0	+9.0	−22.4	32 ± 1		239 ± 3
L₁₁Cr(CO)₄	−78.5	−91.4	−76.8	−92.7	12.5 ± 0.5		
L₁₁Mo(CO)₄	−54.8	−67.7	−53.7	−69.6	4.5 ± 0.5		
L₁₁W(CO)₄	−39.5	−52.4	−38.2	−54.1	4.0 ± 0.5	228 ± 1	225 ± 1
L₁₁[Mo(CO)₅]₂	−31.2	−44.1	−25.3	−41.2	30 ± 1		
L₁₁₁Cr(CO)₄	−77.4	−90.2	−84.6	−87.4	13.5 ± 0.5		
L₁₁₁Mo(CO)₄	−53.9	−66.7	−63.6	−66.2	6 ± 1		
L₁₁₁W(CO)₄	−38.9	−51.7	−49.1	−51.7	4.0 ± 5	229 ± 2	225 ± 2
L₁₁₁W(CO)₅ᵉ	−12.7	−25.5	+2.7	+0.1	33	244 ± 4	
L₁₁₁W(CO)₅ᶠ	+12.4	−0.4	−25.8	−28.4			
L₁ᵥW(CO)₄	−38.6	−51.4	−49.1	−55.5	4.0 ± 0.5	293 ± 3	283 ± 3
LᵥW(CO)₄	−40.7	−53.5	−29.0	−55.1			

ᵃ Relative to 85% phosphoric acid. ᵇ Δ = coordination chemical shift = δ_complex − δ_ligand. ᶜ Primed symbol indicates –PPhR end of ligand. ᵈ L₁, Ph₂PCH₂CH₂PPhMe; L₁₁, Ph₂PCH₂CH₂PPhEt; L₁₁₁, Ph₂PCH₂CH₂PPh(i-Pr); L₁ᵥ, Ph₂PCH₂CH₂PPh(sec-Bu); Lᵥ, Ph₂PCH₂CH₂P(Bu)₂. ᵉ PPh₂ end coordinated. ᶠ –PPh(i-Pr) end coordinated.

Results and Discussion

We have prepared seven unsymmetrical bis(tertiary phosphine) ligands, Ph₂PCH₂CH₂PRPh, where R = methyl, ethyl, n-propyl, isopropyl, sec-butyl, isobutyl, and n-amyl, by the reaction of diphenylvinylphosphine with lithium alkylphenylphosphide. In addition, Ph₂-PCH₂CH₂PBu₂ has been prepared by the addition of dibutyllithium phosphide to diphenylvinylphosphine followed by hydrolysis. The ³¹P chemical shifts of the two phosphorus atoms in each compound are very close to those expected from the known group contributions[22,23] of the organic groups attached to phosphorus, with the diphenylphosphino end always occurring at about 13 ppm. The alkylphenylphosphorus has its chemical shift at roughly δ (ppm) = (13 − phenyl group contribution + alkyl group contribution) or 13 − 3 + 21 = 31, for Me (exptl, 31.4); 13 − 3 + 7 = 17, for Et (15.9); 13 − 3 + 11 = 21, for Pr (21.7); 13 − 3 − 6 = 4, for i-Pr (2.6); 13 − 3 + 15 = 25, for i-Bu (25.4); 13 − 3 − 3 = 7, for sec-Bu (6.4); and 13 − 3 + 11 = 21, for Am (20.9). Likewise, Ph₂PCH₂CH₂PBu₂ has predictable chemical shifts of 12.8 and 26.1 ppm. ³J_PP's for the free ligands are in the range of 25–30 Hz.

The phosphines are straightforwardly oxidized by 30% aqueous hydrogen peroxide to the dioxides with a corresponding downfield shift in the ³¹P resonances to about −31 ppm for the diphenylphosphoryl group with the alkylphenylphosphoryl group being downfield slightly further depending on the particular alkyl group. ³J_PP increases to about 50 Hz in the dioxides, reflecting the change in oxidation state from +3 to +5 and the correspondingly larger s character in the phosphorus bonds (from less than 25% to approximately 25%).

A series of group VI metal carbonyl derivatives was made with Ph₂PCH₂CH₂PRPh, where R = Me, Et, and i-Pr. The ligands and M(CO)₆ in a 1:1 molar ratio react in hot (150–160°) diethylene glycol dimethyl ether to give a recrystallized yield of about 40% of the ex-pected chelate complex

$$(P^\frown P')M(CO)_4$$
I
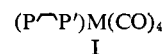
The ³¹P nmr data are given in Table III, infrared frequencies in the CO stretching region are given in Table IV, and pmr data in the methyl region are given in Table V.

Reaction in a similar manner but with a 10 M excess of molybdenum carbonyl produced the compound with the bridging structure

$$(OC)_5MoP \frown P'Mo(CO)_5$$
II
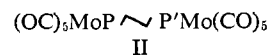
in 60% yield where R = Me. The analogous reaction in the case of W(CO)₆ was not as clean (as determined by the ³¹P nmr spectrum of the crude reaction mixture); however, the bridging ligand compound in the case of tungsten was obtained by the reaction of (C₆H₅NH₂)W-(CO)₅ and MePhPCH₂CH₂PPh₂ in 2:1 molar ratio.

A third type of complex, viz., one in which the potentially bidentate ligand behaves as a monodentate ligand,[24] was prepared with (C₆H₅NH₂)W(CO)₅ and MePhPCH₂CH₂PPh₂ or i-PrPhPCH₂CH₂PPh₂ in a 1:1 molar ratio. In this case the interesting possibility of linkage isomerism arises since the two phosphorus atoms are chemically different. A previous case of linkage isomerism involving different phosphorus atoms in the same molecule, P(OCH₂)₃P, has been elegantly investigated by Verkade and coworkers.[25,26] The results for each of these three types of compounds are discussed in turn.

The ³¹P chemical shift assignments are straightforward for the methyl and isopropyl ligand chelate complexes, since these groups have group contributions sufficiently different from phenyl. It was previously shown[5,6] that on complex formation the coordination shifts are linearly related to the ligand chemical shifts; hence the methylphenyl end of Ph₂PCH₂CH₂PPhMe

(22) S. O. Grim, E. F. Davidoff, and W. McFarlane, J. Org. Chem., 32, 781 (1967).
(23) S. O. Grim, E. F. Davidoff, and T. J. Marks, Z. Naturforsch. B, 26, 184 (1971).

(24) R. L. Keiter and D. P. Shah, Inorg. Chem., 11, 191 (1972).
(25) R. D. Bertrand, D. A. Allison, and J. G. Verkade, J. Amer. Chem. Soc., 92, 71 (1970).
(26) D. A. Allison, J. Clardy, and J. G. Verkade, Inorg. Chem., 11, 2804 (1972).

Table IV. Infrared Data in the Carbonyl Region for the Group VI Compounds[a,b]

	Tetracarbonyls			
	CO stretching frequencies (cm⁻¹)			
Compound	$A_1{}^2$	$A_1{}^1$	B_1	B_2
Cr(CO)₄(MePhPCH₂CH₂PPh₂)	2011 m	1922 m	1898 s	(Unresolved doublet)
Mo(CO)₄(MePhPCH₂CH₂PPh₂)	2025 m	1930 m	1904 s	1901 s
W(CO)₄(MePhPCH₂CH₂PPh₂)	2018 m	1920 m	1900 s	(Unresolved doublet)
Cr(CO)₄(EtPhPCH₂CH₂PPh₂)	2011 m	1921 m	1896 s	(Unresolved doublet)
Mo(CO)₄(EtPhPCH₂CH₂PPh₂)	2020 m	1927 m	1908 s	1901 s
W(CO)₄(EtPhPCH₂CH₂PPh₂)	2022 m	1922 m	1900 s	(Unresolved doublet)
Cr(CO)₄[(i-Pr)PhPCH₂CH₂PPh₂]	2012 m	1920 m	1901 s	1890 s
Mo(CO)₄[(i-Pr)PhPCH₂CH₂PPh₂]	2023 m	1927 m	1911 s	1900 s
W(CO)₄[(i-Pr)PhPCH₂CH₁PPh₂]	2025 m	1921 m	1902 s	1895 s
W(CO)₄Ph₂PCH₂CH₂PPh(sec-Bu)	2020 m	1920 m	1900 s	2891 s

	Pentacarbonyls			
	Frequencies (cm⁻¹)			
Compound	$A_1{}^2$	E	$A_1{}^1$	B_1
W(CO)₅(MePhPCH₂CH₂PPh₂)[c]	2073 m	1937 s	1946 s	1976 vw
W(CO)₅[(i-Pr)PhPCH₂CH₂PPh₂][d]	2073 w	1938 m	1946 s	1978 vw
[Mo(CO)₅]₂(MePhPCH₂CH₂PPh₂)	2070 m	1942 s	1957 s	1988 w
[W(CO)₅]₂(MePhPCH₂CH₂PPh₂)	2075 w	1938 s	1949 s	1980 vw

[a] Accurate to ±1 cm⁻¹. [b] Obtained on cyclohexane solutions. [c] About 90% –PMePh bound isomer. [d] About 85% –PPh₂ bound isomer. [e] Key: vw, very weak; w, weak; m, medium; s, strong.

Table V. Proton Nmr Data for Group VI Metal Carbonyls[a]

Compound	δ_{CH_3} (ppm)[b]	δ_{CH_3} (ppm)[c]	$^2J_{PH}$ (Hz)	$^3J_{PH}$ (Hz)	$^3J_{PH}$ (Hz)[c]	$^3J_{HH}$ (±0.1 Hz)	$^3J_{HH}{}^c$ (±0.1 Hz)
L₁Cr(CO)₄[d]	1.72		7.1				
L₁Mo(CO)₄	1.73		6.5				
L₁W(CO)₄	1.93		7.3				
L₁[Mo(CO)₅]₂	1.75		6.2				
L₁[W(CO)₅]₂	1.95		6.7				
L₁W(CO)₅	1.92		6.7				
L₁₁Cr(CO)₄	0.99			15.4		7.4	
L₁₁Mo(CO)₄	0.99			17.2		7.2	
L₁₁W(CO)₄	0.97			17.2		7.3	
L₁₁₁Cr(CO)₄	1.21	1.00		16.5	13.5	7.0	7.0
L₁₁₁Mo(CO)₄	1.14	0.99		17.1	13.8	7.1	6.8
L₁₁₁W(CO)₄	1.15	0.98		16.5	14.0	6.8	6.5
L₁₁₁W(CO)₅	1.07	0.75		14.9	14.7	6.5	6.5

[a] Obtained in CDCl₃ solutions. [b] Relative to TMS. [c] Upfield Me group from i-Pr ligand. [d] L₁ = Ph₂PCH₂CH₂PPhMe; L₁₁ = Ph₂PCH₂CH₂PPhEt; L₁₁₁ = Ph₂PCH₂CH₂PPh(i-Pr).

should always be upfield from the diphenyl end, whereas, in Ph₂PCH₂CH₂PPh-i-Pr, the isopropylphenyl end will be downfield from the diphenyl end. On first inspection the assignment of the ³¹P resonances for the ethyl compound is somewhat ambiguous because the group contributions for phenyl (3 ppm) and ethyl (7 ppm) are similar and the chemical shifts in the coordination compounds are usually within a few parts per million of each other. Selective double irradiation was used to aid assignment of these peaks. The ³¹P nmr spectrum was first recorded without simultaneous proton irradiation. Then it was recorded again with double irradiation in the alkyl proton region. The phosphorus signal which sharpened the most was therefore assigned as due to the ethylphenyl phosphorus. Wide band noise proton irradiation sharpened both phosphorus signals further.

The ³¹P chemical shifts for the chelate complexes, I, occur at unusually low field compared to monodentate tertiary phosphine complexes of the same metal carbonyls. For Cr, Mo, and W the ³¹P coordination shifts[7] are about −91, −67, and −52 ppm, respectively, compared to about −60, −40, and −20 ppm for LCr(CO)₅, LMo(CO)₅, and LW(CO)₅ or cis-L₂Cr(CO)₄,

cis-L₂Mo(CO)₄, and cis-L₂W(CO)₄, respectively, where L is a monodentate tertiary phosphine.[15,27] This large chelate effect has been noted previously for five-membered chelate rings[28-31] and has been ascribed to ring strain.[29] Ring strain alone is inadequate to explain the coordination chemical shift of five-membered rings since the more highly strained four-membered rings show a much smaller chemical shift effect.[1d] It is a very useful property since inspection of the ³¹P spectrum of crude reaction mixtures allows determination of the relative amounts of chelate product vs. other products.

The ³¹P coordination shifts for the compounds which exhibit bridging ligand behavior, II, are normal compared to monodentate ligand behavior. Infrared spectra, elemental analyses, and molecular weight measurements confirm the structure. The relative inten-

(27) R. Mathieu, M. Lenzi, and R. Poilblanc, Inorg. Chem., 9, 2030 (1970).

(28) L. S. Meriwether and J. R. Leto, J. Amer. Chem. Soc., 83, 3192 (1961).

(29) J. A. Connor, J. J. Day, E. M. Jones, and G. K. McEwen, J. Chem. Soc., Dalton Trans., 347 (1973).

(30) S. O. Grim, J. Del Gaudio, C. A. Tolman, and J. P. Jesson, Inorg. Nucl. Chem. Lett., 9, 1083 (1973).

(31) W. L. Briggs, M. S. Thesis, University of Maryland, 1972.

Table VI. Relative Intensities of Some Ions in the Mass Spectra of Metal Carbonyl Compounds

	[Mo(CO)₅]₂L L = Ph₂PCH₂- CH₂PPhMe	Cr(CO)₄L L = Ph₂PCH₂- CH₂PPh₂Me	W(CO)₄L L = [Ph₂PCH₂CH₂- PPh(i-Pr)]
$LM_2(CO)_{10}^+$	100[a]		
$LM_2(CO)_9^+$	133		
$LM_2(CO)_8^+$	66		
$LM_2(CO)_7^+$	200		
$LM_2(CO)_6^+$	400		
$LM_2(CO)_5^+$	16		
$LM_2(CO)_4^+$	33		
$LM_2(CO)_3^+$	33		
$LM_2(CO)_2^+$	33		
$LM_2(CO)^+$	66		
LM_2^+	33		
$LM(CO)_4^+$	1900	100[a]	100[a]
$LM(CO)_3^+$	332	b	57
$LM(CO)_2^+$	430	63	43
$LM(CO)^+$	2400	170	57
LM^+	1900	154	25

[a] Molecular ion. [b] The absence of this species in the mass spectra has been noticed by other workers and is attributed to the formation of π-arene complexes (see ref 29).

sities of the mass spectra peaks of [Mo(CO)₅]₂(Ph₂-PCH₂CH₂PPhMe) are given in Table VI. Prominent peaks indicate a stepwise removal of CO's from the molecular ion $LMo_2(CO)_{10}^+$ (molecular weight due molybdenum isotope pattern clustered about 812) as well as very large peaks due to $LMo(CO)_4^+$ and the species resulting from stepwise removal of CO's from it. These observations are quite normal for binuclear metal carbonyl derivatives,[32,33] although the present work does illustrate parent ions with unusually large molecular weights.

A particularly interesting situation is the linkage isomerism observed when the potentially bidentate unsymmetrical ligands behave as a monodentate ligands, *i.e.*

$$(P\!\!\sim\!\!P')M(CO)_5 \text{ and } (P'\!\!\sim\!\!P)M(CO)_5$$
$$\text{III} \qquad\qquad \text{IV}$$
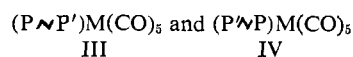
Many of the usual techniques for structural determination are not applicable in this case but ³¹P nmr spectroscopy is ideal since the coordinated phosphorus will be shifted downfield in the expected manner whereas the uncoordinated phosphorus will retain approximately the same value as in the free ligand. This is demonstrated by the results in Table I. In the case of Me-PhPCH₂CH₂PPh₂, the methylphenyl phosphorus is coordinated and has the normal coordination shift of −22.4 ppm. The diphenyl phosphorus is unshifted from the free ligand. Further, only the coordinated phosphorus shows coupling with tungsten −183 ($J_{W-P} = 239$ Hz). The data for *i*-PrPhPCH₂CH₂-PPh₂W(CO)₅ indicate a mixture of isomers. The principal isomer (85%) has the diphenyl phosphorus coordinated with a coordination shift of −25.1, whereas the isopropylphenyl phosphorus is essentially unshifted from the free ligand. The coordinated phosphorus is split by ¹⁸³W ($J_{W-P} = 244$ Hz). In the minor isomer (15%), the isopropylphenyl phosphorus is shifted downfield by −25.8 ppm and the diphenyl phosphorus is

essentially unshifted. Tungsten–phosphorus coupling was not observed because of the small amount of the compound present and the low intensity of the tungsten satellites. The factors which might determine which phosphorus is coordinated include steric and electronic (basicity and π-acceptor ability) effects. On the basis of previous work including carbonyl stretching frequencies and phosphorus–tungsten coupling constants,[5,9] it was expected that the phosphine with the most phenyl groups would form the strongest bond to tungsten. However, the present results indicate that the favored order for bond formation is PhMeP– > Ph₂P– > Ph-*i*-PrP–, which is the steric order. Effective ligand cone angles for the ends of these chelates are 122, 130, and 132°, respectively,[30,34] which agree with the experimentally found order.

Phosphorus–tungsten coupling constants in the chelate compounds were also observed. In each case, the value for the diphenyl phosphorus was only slightly larger than that for the alkylphenyl phosphorus when chelated. This is in agreement with previous results for $(Ph_nBu_{3-n}P)W(CO)_5$, $n = 0, 1, 2$, or 3, in which larger values of n (*i.e.*, more phenyl groups) resulted in larger magnitudes of J_{W-P}.[5] The magnitude of J_{W-P} in a chelate is less than J_{W-P} for the same phosphorus of the same ligand when it bonds as a bridging or monodentate ligand. This again could reflect some ring strain in the chelate ring which results in a slight weakening of the tungsten–phosphorus bond due to the smaller orbital overlap.

The proton nmr data (Table V) are given only for the methyl groups. The phenyl resonances are relatively uninteresting at 60 MHz, and the ethylene region is extremely complex. Due to the nonequivalent phosphorus atoms and the asymmetry at one phosphorus, all four ethylene bridge protons are unique and split by the other three and the two phosphorus atoms. There are two points of interest. In the case of the methyl ligand, the methyl group is shifted downfield further in the tungsten compound than in the molybdenum and chromium compounds. Secondly, the methyl groups of the isopropyl ligand are interesting since they are nonequivalent and each is split by phosphorus and the methine proton. The assignments can be made in several ways on the basis of the 60-MHz proton spectra. The 220-MHz spectrum is unambiguous: τ_a 8.86, τ_b 9.02, $^3J_{PH}{}^a = 17.1$, $^3J_{PH}{}^b = 13.8$, $^3J_{HH}{}^a = 7.1$, and $^3J_{HH}{}^b = 6.8$ Hz. $^3J_{PH}$ values of 17.1 and 13.8 Hz are comparable to values of 14.0–14.5 Hz for $^3J_{PH}$ in (Ph₂-*t*-BuP)M(CO)₅ compounds,[5] 17.5–18.0 Hz in (Ph₂EtP)-M(CO)₅,[5] and 14.8 Hz in *mer*-(Et₂PhP)₃IrCl₃.[35]

Likewise, the methyl protons in Ph₂P(O)CH₂CH₂P-(O)Ph-*i*-Pr provide an interesting pattern that appears as a 1:2:2:2:1 quintet in the normal 500-Hz sweep width of the 60-MHz instrument. When the spectrum is spread out (50-Hz sweep width), peaks 2 and 4 appear as doublets with the middle peak retaining its relative intensity of 2, so that the spectrum is an eight-line pattern with two peaks overlapping. This arises from magnetically nonequivalent methyl groups (τ 8.49, 8.99) because of the asymmetry about the one phosphorus atom. The upfield methyl group is split by phosphorus ($^3J_{PH} = 16.5$ Hz) and the methine

(32) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **49**, 1447 (1966).
(33) J. Mueller and K. Fenderl, *Chem. Ber.*, **103**, 3141 (1970).

(34) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
(35) E. W. Randall and D. Shaw, *Mol. Phys.*, **10**, 41 (1965).

proton ($^3J_{HH}$ = 7.3 Hz). The lower field methyl is split by phosphorus ($^3J_{PH}$ = 15.9 Hz) and by the methine proton ($^3J_{HH}$ = 7.3 Hz). These are in reasonable agreement with the coordination compounds of the isopropyl-containing ligands discussed above.

In general, most of the proton data other than for the methyl groups are rather uninformative. The ethylene bridge region is too complex (presumably ABCDXY or A_2BCXY patterns) for resolution and is often superimposed on the methylene region of the alkyl groups. However, correct integration ratios of aryl:alkyl protons were obtained for all compounds. The methyl group in $Ph_2PCH_2CH_2PPhMe$ appears as a doublet ($^2J_{PH}$ = 3.2 Hz) at τ 8.77 ppm and in the dioxide of the same ligand as a doublet ($^2J_{PH}$ = 12.4 Hz) at τ 8.30

ppm. The methyl group in $Ph_2PCH_2CH_2PPhEt$ appears as a doublet ($^3J_{PH}$ = 15.2 Hz) of triplets ($^3J_{HH}$ = 6.0 Hz) at τ 9.12. In the dioxide the corresponding values are $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.3 Hz, and τ 8.93.

The infrared spectra of the coordination compounds in the carbonyl stretching are helpful in confirming the structural assignments. For example, the bridging ligand complexes

$$(OC)_5MP{\sim}P'M(CO)_5$$

and the monodentate ligand complexes, IV, both have the absorptions expected for local symmetry C_{4v} at the metal.[36] Likewise the chelate complexes have the absorptions expected for C_{2v} local symmetry.

(36) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, 12, 53 (1969).

# A Nuclear Magnetic Resonance Study of Some Five-Membered Rings in Chelate Complexes of the Group VI Metal Carbonyls

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Contribution from the Department of Chemistry, The University of British Columbia, Vancouver 8, British Columbia, Canada. Received October 9, 1973

Abstract: The synthesis of some new di(tertiary arsine) and di(tertiary phosphine) chelate derivatives of group VI hexacarbonyls is described. Parameters determined from analysis of the nmr spectra of the ligands and complexes are interpreted in terms of ligand rotamer populations and of conformational preferences of the chelate rings. The effects of systematic variations of solvent, donor atoms, and metal atoms are discussed. Changes in the puckering of the chelate rings induced by metal atom variations are predicted. Calculations of the dihedral angles and coefficients in the Karplus relationships pertaining to these complexes are also described.

In a recent report[2] we described the synthesis of a number of chromium carbonyl complexes of substituted ditertiary arsines A (M = Cr; 3 = Si(CH₃)₃, SiCl₃, F, Cl, CN; 3′, 4, and 4′ = H; and 3 = H; 3′, 4, and 4′ = F). The ligands were deliberately chosen so that the nmr spectra of their chelate complexes would be suitable for complete analysis. As anticipated, we found that a "bulky" substituent such as a trimethylsilyl group adopted an "equatorial" orientation on the five-membered chelate ring, but unexpectedly, a fluorine substituent showed a strong "axial" preference.[2,3] Other substituents such as chlorine and a cyano group did not seem to strongly favor particular orientations.

The object of the present investigation was to *systematically* examine the effects of varying the transition metal atom, donor atom, and solvent on the conformations of a number of related chelate complexes. Thus complexes of type A (M = Mo and W) were prepared using many of the same ditertiary arsine ligands used to synthesize the analogous chromium
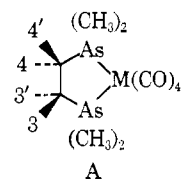
chelate complexes.[2] In addition, we also describe five-membered ring chelate complexes obtained from four ligands not considered in our earlier work. Future work will be concerned with variations in ring size and the effect of cis and trans substituents on the conformations of the chelate ring.

Experimental Section

Dimethylarsinic acid, the group VI hexacarbonyls, and the various olefins were purchased commercially and were used without further purification. Tetramethyldiarsine was obtained by the reduction of dimethylarsinic acid in 2 M hydrochloric acid with hypophosphorous acid;[4] the diarsine was used without further purification. 1,2-Bis(dimethylphosphino)-1,1,2-trifluoroethane (1) was prepared by the photolytic addition of tetramethyldiphosphine to trifluoroethylene as described by Haszeldine and coworkers.[5] 2,3-Dimethylarsino-1,1,1,2,3,3-hexafluoropropane was synthesized by a previously published method,[6] but the yield of this compound

(2) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **94**, 5702 (1972).
(3) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Commun.*, 625 (1970).
(4) V. Auger, *C. R. Acad. Sci.*, 142, 1151 (1906).
(5) R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc. C*, 744 (1970).
(6) W. R. Cullen and N. K. Hota, *Can. J. Chem.*, 42, 1123 (1964).