Reactions Of Coordinated Phosphine Ligands.

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Reactions of Coordinated Phosphine Ligands

by

Charles M. Bartish

A Dissertation

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

in

Chemistry

Lehigh University

1973

This dissertation is respectfully submitted to the Graduate Committee of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Charles M. Bartish

Charles M. Bartish

Certificate of Approval

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Dedication

To

Joanne

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ABSTRACT

The compounds $(ClR_2P)(CO)_5Mo$, where R is CH_3 or C_6H_5, react readily with a variety of nucleophilic reagents to give new $(R_2PX)(CO)_5Mo$ complexes. Reaction with water in the presence of triethylamine yields $[(CH_3)_2P(OH)](CO)_5Mo$ and $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO](CO)_5Mo\}$. In the first product, dimethylphosphinous acid is stabilized as the hitherto unknown tautomer of diphenylphosphine oxide. The corresponding complex of diphenylphosphinous acid was obtained upon base hydrolysis of $[Cl(C_6H_5)_2P]$-$(CO)_5Mo$ as well as from the thermal reaction $(C_6H_5)_2P(O)H$ with $Mo(CO)_6$. The two phosphinous acid derivatives react smoothly with $[Cl(CH_3)_2P](CO)_5Mo$ in the presence of triethylamine to yield $(CO)_5MoP(CH_3)_2OPR_2Mo(CO)_5$ (R = CH_3 or C_6H_5). Reaction between $[Cl(C_6H_5)_2P](CO)_5Mo$ and $[(C_2H_5)_3NH]$-$\{[(C_6H_5)_2PO]Mo(CO)_5\}$ led to $(CO)_5MoP(C_6H_5)_2OP(C_6H_5)_2Mo(CO)_5$. The bridging ligands in the three dimolybdenum complexes contain the very uncommon diphosphoxane linkage. The complexes $(R_2POR')(CO)_5Mo$, $[R_2P(NR''R''')](CO)_5Mo$, and $(R_2PSC_2H_5)(CO)_5Mo$ are obtained from the reactions with R'OH, R"R'"NH, and C_2H_5SH, respectively. Hydrogen sulfide and $(C_2H_5)_3N$ react with the chlorophosphine complexes to give $[(CH_3)_2PSH]Mo(CO)_5$ and $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO](CO)_5Mo\}$. Also, $(CH_3)_3SiCl$ reacts with $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO](CO)_5Mo\}$ to generate $[(C_6H_5)_2POSi$-$(CH_3)_3](CO)_5Mo$. Grignard reagents react with the chlorophosphine complexes to give the expected $(R_2PR')(CO)_5Mo$ product and $(CO)_5MoPR_2PR_2Mo$-$(CO)_5$. Proton nmr and infrared spectral properties of the new complexes are given.

The synthesis of the metal carbonyl complexes 2-$Mo(CO)_5$-2-X-DMP(DMP = 5,5-dimethyl-1,3,2-dioxaphosphorinane) in which X = Cl, OCH_3,

OC_2H_5, SC_6H_5, CH_3, and $N(CH_3)_2$, and 2-M$(CO)_n$-2-Cl-DMP in which M = Cr, W, Fe, and Ni, and n = 5,5,4,3, respectively, is reported. Analysis of the proton nmr spectra of the new compounds suggests that a common chair structure with the metal carbonyl positioned equatorially is the predominant, if not exclusive, conformer for all of the complexes.
The complexes 2-Mo$(CO)_5$-2-X-MTBP (MTBP = 5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane) in which X = Cl and OCH_3 each exist as mixtures of isomers. The *cis*- and *trans*-isomers of 2-CH_3O-MTBP have been separated. The alcoholysis reaction of 2-Mo$(CO)_5$-2-Cl-MTBP proceeds with inversion of configuration at phosphorus. Mechanistic implications of this result are discussed.

INTRODUCTION

The Alchemists of the Middle Ages were familiar with materials containing phosphorus,[1] but those substances were of little interest, because they were of no use in converting common metals into gold. The element today recognized as white phosphorus was first isolated in 1677 by Hennig Brand of Hamburg.[2] The synthesis of elemental phosphorus by the method of Brand was most demanding and, if necessary today, would dampen the spirits of all but the most dedicated chemists:

> "Take a quantity of urine (not less for one experiment than 50 or 60 pails full); let it lie steeping in one or more tubs...till it putrify and breed worms, as it will do in 14 or 15 days. Then, in a large kettle, set it to boil on a strong fire...till the whole quantity be reduced to a paste...and this may be done in two or three days or more. Then take the said paste, or coal; powder it, and add thereto some fair water, about 15 fingers high...; and boil them together for 1/4 of an hour. Then strain the liquor and all through a woolen cloth...the liquor that passes must be taken and boiled till it come to a salt...Then add... the remainder of Aqua Fortis from Vitriol and Salt of Niter a pound thereof to a half pound of the said salt ...and then for 24 hours steep'd in the most rectify'd Spirit of Wine...Evaporate all in warm sand, and there will remain a reddish salt. Take this salt, put it into a retort, and...fire as high as you can for 24 hours. Sometimes, by the force of the fire, 24 hours proves enough; for when you see the Recipient white, and shining with fire...then the work is finished. And you may scrape it off with a knife, where it sticks."[2]

The chemistry of phosphorus has grown rapidly, and at the present time an extensive inorganic chemistry of this unique element has developed. The diverse nature of phosphorus-containing compounds has been the basis for their wide application in a variety of industries.

The importance of phosphates in biological activity has been recognized, and presently an increasing amount of work is being undertaken to determine further the role of phosphorus in the process of life. The structures of many complex compounds containing phosphorus have been determined by X-ray crystallography, including that of deoxyribonucleic acid, work significant enough to earn its researchers a Nobel Prize.[3]

Kinetic studies of simple hydrolysis or esterification reactions at phosphorus have given chemists insight into the specific mechanisms of reaction at the phosphorus atom. Much information concerning the nature of the bond from phosphorus to other atoms has been collected from spectroscopic investigations, particularly 31-phosphorus nmr.

Many reactions of organophosphorus compounds parallel the behavior of carbon in its chemistry. In this respect the cleavage of a phosphorus-halogen bond has assumed a prominent role in synthetic organophosphorus chemistry. The chemistry of the phosphorus-chlorine bond has been extensively investigated, and some general reactions are outlined in Figure 1. Most of the reactions illustrated in Figure 1 proceed in good yield without difficulty. However, several classes of reaction deserve special comment. The reaction of R_2PCl with ammonia does not give the expected product, R_2PNH_2, but gives the diphosphinoamine, $R_2PN(H)PR_2$, instead.[4] In fact, $R_2PN(H)PR_2$ itself is unstable and upon mild heating equilibrates to a mixture of ammonia and $(R_2P)_3N$.[4] Simple amino derivatives of PCl_3 are also unstable at room temperature. The following sequence of reactions (Eq. 1) illustrates the general instability of primary amino-phosphone derivatives:[5]

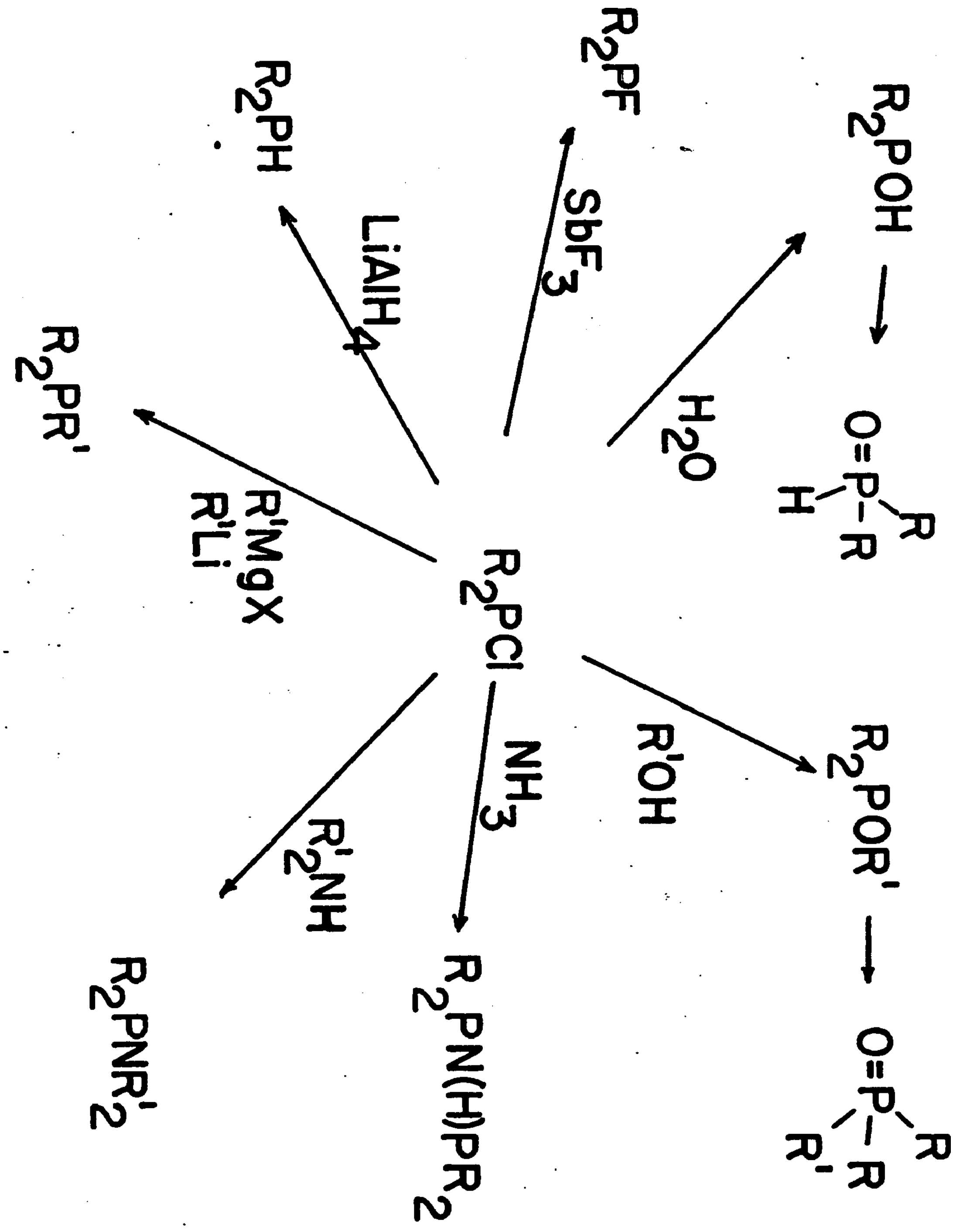


Figure 1. Reactions of trivalent halophosphines.

$$PCl_3 \xrightarrow{NH_3} P(NH_2)_3 \xrightarrow{-NH_3} [P(NH)NH_2)_2]_n \xrightarrow{-NH_3} [P_2(NH)_3]_n \qquad (1)$$

The only stable aminophosphine prepared by ammonolysis is $(CF_3)_2PNH_2$.[6]

Esters of the phosphinous acid show varying degrees of stability. Early work in this area[1] shows the only product from the reaction shown in Eq. 2

$$R_2PCl + R'OH \rightarrow R_2R'PO + HCl \qquad (2)$$

to be a phosphine oxide. When a base was introduced to coordinate the HCl evolved in the reaction, the desired phosphinite ester R_2POR' could be isolated in most instances. Some phosphinites, for example $(CH_3)_2POCH_3$, still rearrange[7] spontaneously to the corresponding phosphine oxide in spite of attempts to preserve the phosphinite structure.

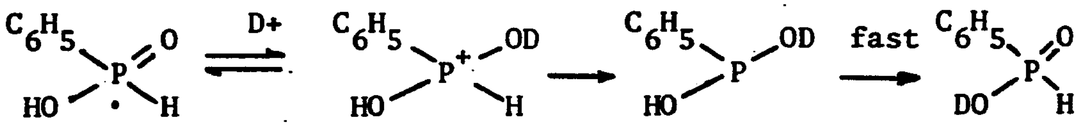
In general, attempts to synthesize trivalent phosphorus compounds which retain the phosphinous acid structure, R_2POH, have been unsuccessful inasmuch as a thermodynamically more stable phosphine oxide structure, $R_2P(O)H$, is obtained.[8] Bis(trifluoromethyl)phosphinous acid, $(CF_3)_2POH$, is the only well-documented species in this class.[9] However, the acid tautomer is thought to play an important role in the activity of many phosphine oxides. For example, rationalization of exchange data for numerous organophosphorus compounds is possible only if the following equilibria (Eq. 3-5) are considered to exist:

$$(RO)_2P(O)H \rightleftharpoons (RO)_2P(OR) \quad ^{10-12} \qquad (3)$$

$$C_6H_5P(O)H(OH) \rightleftharpoons C_6H_5P(OH)_2 \quad ^{13,14} \qquad (4)$$

$$(C_6H_5)_2P(O)H \rightleftharpoons (C_6H_5)_2P(OH) \quad ^{15} \qquad (5)$$

The non-aromatic protons of phenylphosphinic acid, $C_6H_5P(O)H(OH)$, readily exchange with deuterium.[14] The following mechanism is proposed to account for the observed exchange:



Each equilibrium above is shifted extensively to the left, and attempts to obtain physical evidence for the presence of the trivalent tautomer have been unsuccessful.[16]

Phosphorus donor ligands have played a major role in the development of the chemistry of transition metals, particularly metal carbonyls.[17] However, much of the chemistry in this area has dealt with substitution products of simple phosphine ligands, *e.g.*, triphenylphosphine, trimethylphosphite, and tris(dimethylamino)phosphine. At least one reason for this situation may be the difficulties encountered in preparing suitable ligands, inasmuch as many of the potentially most interesting phosphine ligands are prone to rearrange to thermodynamically more stable species which are not capable of behaving as good donors toward a transition metal. One segment of the research to be reported in this thesis has dealt specifically with the problem of preparing complexes of transition metal carbonyls with thermodynamically unstable phosphorus ligands.

The synthetic route used to prepare complexes of unstable ligands of the general formula $(CO)_nMPR_2X$ (where M is the metal, R is any substituent on phosphorus, and X is the substituent which generally rearranges in the trivalent species) was the cleavage of a phosphorus to chlorine bond in a pre-complexed ligand. Conceptually, any of the reactions for the trivalent ligand shown in Figure 1 should be applicable to the coordinated ligands. A second, specific approach to the preparation of complexes of phosphinous acids was the direct reaction of $R_2P(O)H$ with a metal complex in an effort to shift the above-mentioned equilibria to the right by removal of the trivalent tautomer as it is generated.

Over a hundred years ago, Schutzenberger and Fontaine[18] reported what may have been the first examples of reaction of a phosphorus-halogen bond in a coordinated ligand. They found that $[PtCl_2(PCl_3)]_2$ and $Pt(PCl_3)_2Cl_2$ were readily hydrolyzed to complexes characterized as $\{PtCl_2[P(OH)_3]\}_2$ and $PtCl_2[P(OH)_3]_2$ respectively. $\{PtCl_2[P(OH)_3]\}_2$ was reported to react with potassium hydroxide or carbonate to give a complex which they characterized as $Pt_2[P(OK)_3]_2O_2$. The reaction of methanol or ethanol with $[PtCl_2PCl_3]_2$ gave $\{PtCl_2[P(OR)_3]_2\}$, but the reaction with ammonia was more complex. Ammonia also displaced a chloride from platinum, and Eq. 6 was suggested to represent the reaction:

$$[PtCl_2(PCl_3)]_2 + NH_3 \rightarrow \{Pt(NH_3)_2(Cl)[P(NH_2)_3]\}^+ \cdot Cl^- + NH_4Cl \quad (6)$$

Arbuzov and Zoroastrova[19] repeated the earlier work of Schutzenberger, and although they characterized the products obtained from the reactions with water and alcohols, no further information regarding the nature or extent of the reactions of coordinated phosphine ligands was provided. However, they did show that (phosphorus trichloride)gold(I) chloride, $(PCl_3)AuCl$, also reacts with methanol to give a trimethylphosphite gold (I) complex (Eq. 7):[20]

$$(PCl_3)AuCl + 3CH_3OH \rightarrow [P(OCH_3)_3AuCl] + 3HCl \quad (7)$$

Although other metal complexes with phosphorus donor ligands that have phosphorus-halogen bonds have been noted to show differing degrees of reactivity toward water, determination of the nature of the product has not been of interest. Strecker and Schurigin[21] found $Ir(PCl_3)_3Cl_3$ to be inert to cold water. However, a refluxing solution of silver nitrate and $Ir(PCl_3)_3Cl_3$ yielded a precipitate of silver chloride. Davis and Ehrlich[22] reported $(CuCl)_2PCl_3$ to react readily with methanol, but the product is $P(OCH_3)_3CuCl$. The complex $(CuCl)_2PCl_3$ exists only under a significant atmosphere of phosphorus trichloride,[22] hence it is unclear whether the product is obtained from reaction of a coordinated phosphine ligand or arises from trimethylphosphite generated from the excess PCl_3 present.

Wilkinson has noted the lack of reactivity of the phosphorus-fluorine bond in tetrakis(trifluorophosphine)nickel(0).[23] In fact, $Ni(PF_3)_4$ can be steam distilled without decomposition. But more recently Kruck and Höfler[24] have demonstrated that sodium methoxide will displace fluoride from phosphorus in $Ni(PF_3)_4$ to give the well-known tetrakis(trimethylphosphite)nickel(0) complex (Eq. 8):

$$Ni(PF_3)_4 + 12\ NaOCH_3 \rightarrow Ni[P(OCH_3)_3]_4 + 12NaF \tag{8}$$

Bachman *et al.*[25] also obtained $Ni[P(OCH_3)_3]_4$ after treating $Ni(PCl_3)_4$ with sodium methoxide. However, when methanol alone is used as a reactant with $Ni(PCl_3)_4$, oxidation of nickel occurs to give $Ni(CH_3OH)_6^{2+}$ and a variety of other products including chloride, phosphite, methyl chloride, phosphine, and dimethyl phosphonate.[25] These authors suggest that the HCl produced from the methanolysis of phosphorus trichloride reacts with the nickel complex via an oxidative-addition mechanism to finally give nickel(II) and dimethyl phosphonate.

Höfler and Marre[26] found that (phosphorus trichloride)pentacarbonylmolybdenum will react with methanol to give (trimethyl phosphite)pentacarbonylmolybdenum (Eq. 9).

$$Mo(CO)_5PCl_3 + 3CH_3OH \rightarrow Mo(CO)_5P(OCH_3)_3 + 3HCl \qquad (9)$$

The reaction of metal-complexed PCl_3 differs from that of trivalent phosphorus trichloride inasmuch as no rearrangement[1] takes place in the coordinated ligand (Eq. 10).

$$PCl_3 + 3CH_3OH \rightarrow (CH_3O)_2P(O)H + 2HCl + CH_3Cl \qquad (10)$$

They were also able to prepare $Mo(CO)_5PCl_3$ via the reaction of a coordinated aminophosphine (Eq. 11). This particular reaction may become valuable as further applications for this general type of synthesis become apparent.

$$Mo(CO)_5\ P[N(CH_3)_2]_3 + 6HCl \rightarrow Mo(CO)_5PCl_3 + 3(CH_3)_2NH_2Cl \qquad (11)$$

Austin obtained several interesting complexes of palladium and platinum containing acids of phosphorus.[27] The products cis-$PtCl_2[(C_6H_5)_2P(OH)]_2$ and cis-$PtCl_2[(C_6H_5)(Cl)P(OH)]_2$, as well as the palladium derivatives, were formed upon hydrolysis of the metal complexes of chlorodiphenylphosphine and dichlorophenylphosphine, respectively. Of particular interest is the fact that hydrolysis of cis-$PtCl_2(C_6H_5PCl_2)_2$ may be controlled in order to displace only a single chloride per phosphorus. On the other hand, complexes of the type $Pt[P(OR)_2O]_2[P(OR)_2OH]_2$ (where R is CH_3 or C_2H_5) are obtained from the reaction of tetrachloroplatinate(II) ion with a trialkyl phosphite in water or with a dialkyl phosphonate in alcohol[28] as shown in Eq. 12.

$$PtCl_4^{=} + 4(RO)_2P(O)H \rightarrow Pt[P(OR)_2O]_2[P(OR)_2OH]_2 + 2HCl + 2Cl^- \qquad (12)$$

The corresponding complexes where the R groups are phenyl are obtained in poor yield by this synthesis and are more easily prepared by reacting $PtCl_2[CH_3CN]_2$ or $PtCl_2[(C_2H_5)_2S]$ with diphenyl phosphonate.[29]

$$PtCl_2(CH_3CN)_2 + 4(C_6H_5O)_2P(O)H \rightarrow Pt[(C_6H_5O)_2PO]_2[(C_6H_5O)_2POH]_2 + 2HCl + 2CH_3CN \qquad (13)$$

In any case, an equilibrium of the type shown in Eq. 14

$$(RO)_2P(O)H \rightleftharpoons (RO)_2POH \qquad (14)$$

was postulated to account for the hydroxy structure on phosphorus in the resulting complexes.[28,29]

Although several different workers have apparently prepared complexes of thermodynamically unstable ligands as summarized above, each investigator was concerned only with a specific reaction or a particular ligand. Prior to our work, no systematic investigation of the reaction of a single coordinated phosphine ligand with a wide variety of suitable reagents had been reported. In Part I of this thesis, the extent of the reactions of chlorodiphenylphosphine- and chlorodimethylphosphinepentacarbonylmolybdenum, $Mo(CO)_5P(C_6H_5)_2Cl$ and $Mo(CO)_5P(CH_3)_2Cl$ respectively, with selected nucleophiles will be discussed. Particular emphasis will be placed on the synthetic utility of the general reaction scheme and the effects of the molybdenum-phosphorus bond on the reactivity of the complexes as well as their infrared and proton magnetic resonance spectral parameters.

EXPERIMENTAL

MATERIALS:

Solvents

Hexane, benzene, toluene, and chloroform purchased from Lehigh Valley Chemical Company, Easton, Pa., and methylcyclohexane obtained from Matheson, Coleman, and Bell (MCB), East Rutherford, N. J., were distilled from phosphorus pentoxide (MCB) before use. Carbon disulfide, petroleum ether (20-40°), diethyl ether, and chlorobenzene purchased from Baker Chemical Company, Phillipsburg, N. J., and acetonitrile-d_3 obtained from Diaprep, Inc., Atlanta, Ga., were used without further purification.

Reagents

Chlorodiphenylphosphine and dichlorophenylphosphine were purchased from Aldrich Chemical Company, Cedar Knolls, N. J., and vacuum distilled before use. Phosphorus trichloride (Baker Chemical Co.) was used as received. Chlorodimethylphosphine was prepared from tetramethylbiphosphine disulfide[30] by the method of Parshall.[31] Dichloromethylphosphine was a generous gift from the Department of the Army, Edgewood Arsenal, Edgewood, Maryland.

Gaseous ammonia (MCB) was used as received. Triethylamine (Aldrich Chemical Company) was distilled before use. Methylamine was prepared by base hydrolysis of methylammonium chloride (Baker Chemical Co.); dimethylamine was prepared similarly from a 40% aqueous solution obtained from Aldrich Chemical Co. Both amines were dried by passage through tubes filled with potassium hydroxide. Aniline (Baker Chemical Co.) was vacuum distilled before use.

Ethanethiol, thiophenol (Aldrich Chemical Co.), and hydrogen sulfide (Baker Chemical Co.) were used as received.

Methanol, 1-propanol, 2-propanol (Lehigh Valley Chemical Co.), ethanol (U.S. Industrial Chemicals Co.), tert-butanol, and 2,2-dimethyl-1,3-propanediol (Aldrich Chemical Co.) were used without further purification.

Diethylmalonate (Aldrich Chemical Co.), methyl iodide (Columbia Organic Chemicals, Columbia, S.C.), and trimethylchlorosilane (Baker Chemical Co.) were used as received.

Lithium aluminum hydride and methyllithium were purchased from Alfa Inorganics (Beverly, Mass.), and antimony trifluoride was obtained from Ozark-Mahoning Co., Tulsa, Oklahoma. Thallium cyclopentadienide was prepared by the method of Hunt.[32]

Molybdenum and tungsten hexacarbonyls were generous gifts from Climax Molybdenum Co., Greenwich, Conn. Chromium hexacarbonyl was purchased from Pressure Chemical Co., Pittsburgh, Pa. Nickel carbonyl was purchased from Union Carbide Co., Linde Division. Each of the above metal carbonyls was used as received. Triiron dodecacarbonyl was prepared by a literature method.[33]

EXPERIMENTAL TECHNIQUES

Infrared Spectra

Routine scans were performed on a Perkin-Elmer Model 257 spectrometer. More precise spectra were obtained with a Perkin-Elmer Model 21 spectrometer equipped with sodium chloride optics and calibrated with polystyrene as a reference. High resolution spectra in the metal carbonyl stretching region 2100-1800 cm^{-1} were obtained with a Perkin-Elmer Model 621 spectrometer.

Certified n-hexane of 99 mole % purity (Fisher Scientific Co., Fair Lawn, N. J.) was used as solvent in all cases unless noted otherwise. Data were taken in solution using standard 0.05 mm sodium chloride liquid cells. Band positions are ± 1 cm^{-1} for the $A_1^{(1)}$ stretching mode of the (ligand)pentacarbonylmolybdenum complexes. B_1 bands are weak and positioned to ± 2 cm^{-1}. Band positions for overlapping $A_1^{(2)}$ and E modes were estimated by graphical resolution and are accurate to ± 2 cm^{-1} or better. Force constants[34] were calculated using the Fortran IV program CKL written in this laboratory.

Proton Magnetic Resonance

All data were obtained with a Hitachi Perkin-Elmer R20A nuclear magnetic resonance spectrometer employing tetramethylsilane (TMS) as an internal chemical shift standard. Chemical shift values are accurate to ± 1 Hz and coupling constants to ± 0.1 Hz. Frequency measurements were taken with a Takeda Riken TR3824X frequency counter.

Double resonance and nuclear Overhauser effect (NOE) experiments were performed using an R-201 proton spin decoupler.

Variable temperature experiments were performed using an R-202VT variable temperature controller. Samples were allowed to equilibrate for at least 30 minutes at a given temperature before recording spectra. At least two scans at each temperature were recorded in order to reduce error in frequency assignments arising from drift of the magnetic field during a variable temperature experiment.

Complex proton nmr spectra were analyzed with the help of the iterative computer program LAOCN3.[35] Theoretical spectra were drawn on a Cal Comp plotter using the Fortran IV program NMRLOR written in this laboratory making use of data obtained directly from the program LAOCN3. Details of the computer assisted analysis are presented in the Appendix.

Melting Points and Analyses

Melting points were determined in Kimax capillary tubes open to the atmosphere (unless noted otherwise) using a "Mel-Temp" apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. Elemental analyses were performed by Baron Consulting Co., Orange, Conn.

Molecular Weight

Molecular weights were determined cryoscopically in benzene. Volatile compounds were examined by mass spectrometry employing an Hitachi Perkin-Elmer RMU-6E instrument.

PREPARATION OF LIGANDS

Chlorodimethylphosphine

Chlorodimethylphosphine was prepared by the method of Parshall.[31] A mixture of 18.6 g of tetramethylbiphosphine disulfide[30] and 40.6 ml of phenyldichlorophosphine in a 200-ml flask fitted with a Podbielniak distillation head was heated in a nitrogen atmosphere until the mixture became homogeneous at about 200°. The clear, yellow solution was distilled using an oil bath temperature of up to 250° to give a clear colorless liquid, bp 62-109°. Redistillation gave at least 9.4 g (46%) of clear, colorless chlorodimethylphosphine, bp 77°. The product possesses an obnoxious odor and ignites spontaneously upon contact with the atmosphere.

Chloromethylphenylphosphine

Chloromethylphenylphosphine was prepared by either of two syntheses described by Maier. P,P'-dimethyl-P,P'-diphenylbiphosphine disulfide[36] was cleaved with sulfuryl chloride to give chloromethylphenylphosphine sulfide.[37] The sulfide was converted to the free phosphine by abstraction of sulfide with tri-n-butylphosphine.[38] Alternatively, dichlorophenylphosphine can be converted to chloromethylphenylphosphine upon reaction with tetramethyllead.[39]

PREPARATION OF COMPLEXES:

Reactions of (Chlorodiphenylphosphine-) and (Chlorodimethyl-Phosphine)pentacarbonylmolybdenum.

(Chlorodiphenylphosphine)pentacarbonylmolybdenum and trans-bis(Chlorodiphenylphosphine)tetracarbonylmolybdenum.

A mixture of 53 g of $Mo(CO)_6$, 44 g of $(C_6H_5)_2PCl$, and 80 ml of toluene was heated at reflux for one hour. The dark red solution was allowed to cool, after which 200 ml of petroleum ether (bp 20-40°) was added. The mixture was filtered and the volume of the clear red filtrate was reduced under aspirator vacuum to 100 ml. The concentrate was filtered and the tan solid residue was retained. To this filtrate were added 100 ml of petroleum ether and 5 g of anhydrous alumina. The mixture was shaken and then filtered to yield a yellow solution from which all solvent was removed under vacuum. Recrystallization of the solid residue from hexane yielded 64 g (70%) of the pale yellow monosubstituted product, mp 56-58° (lit.[40] 57°). Anal. Calcd for $C_{17}H_{10}O_5ClMoP$: C, 44.90; H, 2.19. Found: C, 45.38; H, 2.37.

The tan solid separated earlier in the work-up was recrystallized several times from hexane-benzene to yield 2 g of bright yellow needles of trans-bis(chlorodiphenylphosphine)tetracarbonylmolybdenum, mp 153-154°; ir (υ_{CO}, hexane) 1898 (w), 1884 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{20}O_4Cl_2MoP_2$: C, 51.77; H, 3.08. Found: C, 51.69; H, 3.28.

(Diphenylphosphinous acid)pentacarbonylmolybdenum.

a. Hydrolysis of (Chlorodiphenylphosphine)pentacarbonylmolybdenum.

To a solution of 1 g of $[Cl(C_6H_5)_2P](CO)_5Mo$ in 15 ml of acetone was added 4 ml of 1 M potassium hydroxide. The mixture was allowed to stir for 1.5 hour at room temperature, then cooled in ice, and acidified with dilute hydrochloric acid to an apparent pH of approximately 2. The hydrolysis product was extracted from the aqueous mixture with hexane. The extract was dried briefly with anhydrous magnesium sulfate and then filtered through a 2-cm layer of alumina on a glass frit. Evaporation of the filtrate under aspirator vacuum left the desired product as a nearly colorless oil admixed with a small quantity of colorless crystals which were identified as μ-tetraphenyldiphosphoxane-decacarbonyldimolybdenum. Inasmuch as $Mo(CO)_5P(C_6H_5)_2OH$ is much more soluble in hexane than is μ-tetraphenyldiphosphoxane-decacarbonyldimolybdenum, it was possible to effect a separation by washing the mixture with a very small amount of hexane. Evaporation of the hexane washings yielded $Mo(CO)_5P(C_6H_5)OH$. Unfortunately, the relative yields of $Mo(CO)_5P(C_6H_5)_2OH$ and μ-tetraphenyldiphosphoxane-decacarbonyldimolybdenum in this preparation are variable. Attempts to purify $Mo(CO)_5P(C_6H_5)_2OH$ by low-temperature recrystallization, sublimation to a cold probe, and high-vacuum distillation were unsuccessful. Further complications include the conversion of $Mo(CO)_5P(C_6H_5)_2OH$ to μ-tetraphenyldiphosphoxane-decacarbonyldimolybdenum under high vacuum over extended periods of time or during column chromatography. Owing to these difficulties no melting or boiling point has been determined for $Mo(CO)_5P(C_6H_5)_2OH$. The oil was further characterized by spectral observations and by derivatization upon reaction with triethylamine to yield a salt and with diazomethane to give the methyl ester, $Mo(CO)_5P(C_6H_5)_2OCH_3$. Anal. Calcd for $C_{17}H_{11}O_6MoP$: C, 46.58; H, 2.51. Found C, 47.27; H, 2.51.

b. Thermal Reaction of Diphenylphosphine Oxide with $Mo(CO)_6$.

A mixture of 1.3 g of $Mo(CO)_6$, 1.0 g of $(C_6H_5)_2P(O)H$,[41] and 15 ml of methylcyclohexane was heated at reflux for 1.5 hr at which time evolution of carbon monoxide had ceased. The cooled solution was filtered, and the filtrate was evaporated to dryness under vacuum to give a waxy residue. This residue was extracted with three 15-ml portions of hexane to yield a solution which was clarified with charcoal, filtered, and evaporated to dryness to yield $[(C_6H_5)_2P(OH)](CO)_5Mo$ as a pale yellow oil. The maximum yield of $Mo(CO)_5P(C_6H_5)_2OH$ by this method of preparation was 50%. The spectral properties of this product were identical with those of the product obtained by method a.

Triethylammonium (Diphenylphosphinito)pentacarbonylmolybdenum.

A mixture of 1 g of $[Cl(C_6H_5)_2P](CO)_5Mo$, 1 ml of water, and 1 ml of triethylamine in 10 ml of acetone was allowed to stir for 0.5 hr. Removal of the acetone under aspirator vacuum left a solid residue which was slurried with 25 ml of water. That part of the residue which was insoluble in water was collected by filtration and recrystallized from hexane-benzene to give a 93% yield of the product as white crystals, mp 130°. Anal. Calcd for $C_{23}H_{26}NO_6MoP$: C, 51.21; H, 4.82. Found: C, 51.66; H, 4.91.

(Methyl Diphenylphosphinite)pentacarbonylmolybdenum.

To a solution of diazomethane in ether prepared from 1.25 g of N,N'-dimethyl-N,N'-dinitrosoterephthalamide[42] was added 1 g of $[(C_6H_5)_2P(OH)](CO)_5Mo$ in 10 ml of ether. The resulting solution was washed with 25 ml of water. The ether layer was dried with magnesium sulfate, filtered, and evaporated to dryness to yield an oily residue. A solution of the oil in 10 ml of hexane was filtered through a short (2 x 5 cm) column of alumina. Removal of hexane from the solution gave the product as an oil which crystallized upon cooling at 0°. Infrared and pmr spectral properties of the product as well as the melting point of 42-43° are in agreement with the same properties of an analytical sample of $Mo(CO)_5P(C_6H_5)_2OCH_3$ prepared by the reaction of $Mo(CO)_5P(C_6H_5)_2Cl$ with methanol as described later.

(Chlorodimethylphosphine)pentacarbonylmolybdenum.

A mixture of 33 g of $Mo(CO)_6$ and 12 g of $(CH_3)_2PCl$ in 40 ml of methylcyclohexane was heated at reflux for five hours. The dark-brown solution was allowed to cool, 100 ml of petroleum ether was added, and the mixture was filtered. Hydrocarbons and unreacted $Mo(CO)_6$ were removed from the filtrate under aspirator vacuum. The resulting red liquid was distilled (93°, 0.30 Torr) to yield a clear yellow liquid which crystallized on standing in the refrigerator.

The solid was recrystallized from hexane to give 22 g (53%) of $Mo(CO)_5P(CH_3)_2Cl$ as white crystals, mp 36-37°. Anal. Calcd for $C_7H_6O_5ClMoP$: C, 25.29; H, 1.81. Found: C, 25.18; H, 1.86.

(Dimethylphosphinous acid)pentacarbonylmolybdenum.

A mixture of 1 g of $[Cl(CH_3)_2P](CO)_5Mo$, 1 ml of water, and 1 ml of triethylamine in 10 ml of acetone was allowed to stir at room temperature for 0.5 hr. The mixture was treated with 25 ml of water and extracted with 10-ml portions of hexane. The hexane extracts were combined, dried with magnesium sulfate, filtered, and evaporated to dryness under aspirator vacuum. Distillation of the liquid residue provided a 65% yield of the product as a clear, colorless liquid, bp 83-84° (0.02 Torr). Anal. Calcd for $C_7H_7O_6MoP$: C, 26.75; H, 2.23. Found: C, 26.61; H, 2.46.

µ-Tetraphenyldiphosphoxane-decacarbonyldimolybdenum.

A mixture of 1 g of $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO](CO)_5Mo\}$ and 1 g of $Mo(CO)_5P(C_6H_5)_2Cl$ in 25 ml of anhydrous ether was allowed to stir for 2 hr at room temperature. A white residue remained upon removal of the solvent under aspirator vacuum. The reaction residue was treated with two separate 15-ml portions of chloroform. Evaporation of the combined chloroform extracts gave a solid which was recrystallized from ethanol-chloroform to yield 60% of pure μ-$[P(C_6H_5)_2OP(C_6H_5)_2](CO)_{10}Mo_2$ as pale yellow crystals, mp 157° dec. Anal. Calcd for $C_{34}H_{20}O_{11}Mo_2P_2$: C, 47.55; H, 2.33. Found: C, 47.57; H, 2.55.

μ-P,P-Dimethyl-P',P'-diphenyldiphosphoxane-decacarbonyldimolybdenum.

A mixture of 1 g of $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO](CO)_5Mo\}$ and 1 g of $Mo(CO)_5P(CH_3)_2Cl$ in 25 ml of anhydrous ether was allowed to stir for 2 hr at room temperature. Solvent was removed under aspirator vacuum to yield a white solid. This residue was extracted with two 15-ml portions of hot hexane and filtered. Concentration of the filtrate under a stream of nitrogen led to precipitation of μ-$[P(CH_3)_2OP(C_6H_5)_2](CO)_{10}Mo_2$. A 27% yield of pure product mp 84-86°, was obtained after several recrystallizations from n-hexane. Anal. Calcd for $C_{24}H_{16}O_{11}Mo_2P_2$: C, 39.24; H, 2.18. Found: C, 38.90; H, 2.34.

μ-Tetramethyldiphosphoxane-decacarbonyldimolybdenum.

A solution consisting of 0.5 g of $[Cl(CH_3)_2P](CO)_5Mo$, 0.5 g of $[(CH_3)_2P(OH)](CO)_5Mo$, and 0.1 g of triethylamine in 25 ml of anhydrous ether was allowed to stir at room temperature for 15 min. Filtration of the solution to remove the precipitate of triethylamonium chloride yielded a clear filtrate from which the crude product was obtained as an oil. Crystallization of the product from petroleum ether following treatment with charcoal was achieved by slow evaporation of the solvent in a stream of dry nitrogen. A 60% yield of μ-$[P(CH_3)_2OP(CH_3)_2](CO)_{10}Mo_2$ as white crystals, mp 66-68°, was obtained. Anal. Calcd for $C_{14}H_{12}O_{11}Mo_2P_2$: C, 27.54; H, 197; mol wt, 610. Found: C, 27.78; H, 2.08; mol wt, 584 (cryoscopic determination in benzene).

(Alkyl diphenylphosphinite)pentacarbonylmolybdenum Complexes.

A mixture of $[(C_6H_5)_2PCl]Mo(CO)_5$ (1 g) and an alcohol (10 ml) was heated at reflux for 1-1.5 hr. The resulting dark solution was added to water (50 ml) and the product was extracted with two 10-ml portions of hexane. The combined hexane extracts were dried over anhydrous magnesium sulfate, decolorized with 2 g of alumina and then filtered. A crude product was obtained by evaporating the hexane from the filtrate under a stream of nitrogen. Crystallization of the (alkyl diphenylphosphinite)pentacarbonylmolybdenum complexes was induced by scratching. These white solids were purified by recrystallization from hexane. Analytical and physical data are summarized in Table 1.

(Alkyl dimethylphosphinite)pentacarbonylmolybdenum Complexes.

Crude (alkyl dimethylphosphinite)pentacarbonylmolybdenum complexes were prepared from $(CH_3)_2PCl\ Mo(CO)_5$ by a procedure completely analogous to that used for the (alkyl diphenylphosphinite)-pentacarbonylmolybdenum complexes. The crude pale yellow to colorless complexes were purified by vacuum distillation in a short path micro distillation apparatus (Kontes K-287100). Analytical and physical data are summarized in Table 2.

(Amino diphenylphosphine)pentacarbonylmolybdenum Complexes.

a. Gaseous amines. Anhydrous ammonia, dry methylamine, or dimethylamine was bubbled through a solution of 1 g of $[(C_6H_5)_2PCl]$-$Mo(CO)_5$ in 25 ml of diethyl ether for about 15 min. The resulting mixture was filtered to remove the precipiated amine hydrochloride. Removal of the ether from the filtrate under aspirator vacuum left a white solid which was recrystallized from ethanol.

b. Aniline. (Anilinodiphenylphosphine)pentacarbonylmolybdenum was prepared directly from $[(C_6H_5)_2PCl]Mo(CO)_5$ and aniline (1:3 mole ratio) in diethyl ether. The white solid product was isolated and purified according to the procedure used for the other solid complexes. Analytical data and physical properties are listed in Table 1.

(Aminodimethylphosphine)pentacarbonylmolybdenum Complexes.

Crude (aminodimethylphosphine)pentacarbonylmolybdenum complexes were prepared from $[(CH_3)_2PCl]Mo(CO)_5$ by a procedure completely analogous to that used for the (aminodiphenylphosphine)pentacarbonylmolybdenum complexes. The crude liquid products were vacuum distilled. Analytical data and physical properties are listed in Table 2.

(Ethyl diphenylthiophosphinite)pentacarbonylmolybdenum.

An excess of ethanethiol (10 ml) was added to 1 g of $[(C_6H_5)_2PCl]Mo(CO)_5$ dissolved in 5 ml of hexane. The solution was stirred well and 1 ml of triethylamine was added slowly. The resultant precipitate of triethylammonium chloride was removed by filtration. Excess ethanethiol and hexane were removed under aspirator vacuum to yield the crude product. Pure (ethyl diphenylthiophosphinite)pentacarbonylmolybdenum was obtained in 85% yield as a white crystalline solid, mp 76-78°, upon recrystallization from hexane. Anal. Calcd for $C_{19}H_{15}MoO_5PS$: C, 47.30; H, 3.12. Found C, 47.25; H, 3.35.

(Ethyl dimethylthiophosphinite)pentacarbonylmolybdenum.

Crude (ethyl dimethylthiophosphinite)pentacarbonylmolybdenum was obtained from $[(CH_3)_2PCl]Mo(CO)_5$ by a procedure completely analogous

TABLE 1

Physical Properties and Analyses for $[(C_6H_5)_2PX]Mo(CO)_5$ Complexes

X	M.p. (°C)	Yield (%)	Analysis found (calcd.)(%)		
			C	H	N
OCH_3	43-44	87	48.06 (47.78)	3.08 (2.87)	
OC_2H_5	47-49	80	48.87 (48.93)	3.31 (3.22)	
$O\text{-}n\text{-}C_3H_7$	47-48	55	49.53 (50.00)	3.36 (3.54)	
$O\text{-}i\text{-}C_3H_7$	47-48	67	50.14 (50.00)	3.32 (3.54)	
NH_2	100-101(dec.)	92	46.88 (46.68)	2.89 (2.75)	3.53 (3.20)
$NH(CH_3)$	88-90(dec.)	87	47.61 (47.89)	3.41 (3.13)	3.09 (3.12)
$N(CH_3)_2$	114-116(dec.)	85	49.26 (49.04)	3.97 (3.44)	3.15 (3.02)
$NH(C_6H_5)$	153-154(dec.)	89	53.79 (53.80)	2.95 (3.12)	2.65 (2.73)
SC_2H_5	76-78	83	47.25 (47.30)	3.35 (3.12)	

TABLE 2

Physical Properties and Analyses for $[(CH_3)_2PX]Mo(CO)_5$ Complexes

X	B.p. (°C/mmHg)	Yield (%)	Analysis found (calcd.)(%)		
			C	H	N
OCH_3	42-42/0.05	89	29.55	2.75	
			(29.27)	(2.74)	
OC_2H_5	40-42/0.03	86	31.51	2.91	
			(31.58)	(3.21)	
$O\text{-}n\text{-}C_3H_7$	62-64/0.03	63	33.32	3.41	
			(33.72)	(3.65)	
$O\text{-}i\text{-}C_3H_7$	66-67/0.03	67	33.06	3.71	
			(33.72)	(3.65)	
NH_2	74-75/0.05[a]	87	26.56	2.11	4.44
			(26.81)	(2.56)	(4.46)
$NH(CH_3)$	70-71/0.03	74	29.61	3.27	4.12
			(29.34)	(3.07)	(4.28)
$N(CH_3)_2$	83-84/0.04	66	31.45	3.81	4.46
			(31.64)	(3.52)	(4.11)
SC_2H_5	[b]	51	30.43	3.19	
			(30.17)	(3.07)	

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[a] M.p. 33-35°.

[b] B.p. uncertain; m.p. 33°.

to that used to prepare (ethyl diphenylphosphinite)pentacarbonylmolybdenum. The pure product was obtained by vacuum distillation in 51% yield as a colorless liquid which solidified on standing, mp 33-35°. Anal. Calcd. for $C_9H_{11}MoO_5PS$: C, 30.17; H, 3.07. Found: C, 30.43; H, 3.19.

Triethylammonium (Diphenylthiophosphinite)pentacarbonylmolybdenum.

Anhydrous hydrogen sulfide was bubbled through a solution of 1 g of $[(C_6H_5)_2PCl]Mo(CO)_5$ and 1 ml of triethylamine in 15 ml of diethyl ether for approximately 15 min. Removal of the solvent under aspirator vacuum left a solid mixture which was slurried with 25 ml of water to dissolve the triethylammonium chloride. The water insoluble product was collected by filtration, dissolved in hot hexane/acetone and treated with charcoal. The mixture was filtered; the filtrate was concentrated in a stream of nitrogen causing precipitation of the white crystalline product, mp 116-117°(dec), in 77% yield. Anal. Calcd. for $C_{23}H_{26}MoNO_5PS$: C, 49.75; H, 4.69; N, 2.52. Found: C, 50.00; H, 4.85; N, 2.66.

(Dimethylthiophosphinous acid)pentacarbonylmolybdenum.

Dry hydrogen sulfide was bubbled through a solution of 1 g of $[(CH_3)_2PCl]Mo(CO)_5$ in 25 ml of diethyl ether. Addition of 1 ml of triethylamine to the solution during passage of the hydrogen sulfide led to formation of a gummy precipitate. After acidification of the mixture with dilute hydrochloric acid, the ether layer was separated and dried with anhydrous magnesium sulfate. Removal of the ether under vacuum left an oil which had spectral properties in agreement with those predicted for the desired product. The compound was not successfully distilled or recrystallized. The acid did not form readily isolable quaternary salts with triethylamine or pyridine.

(Trimethylsilyl diphenylphosphinite)pentacarbonylmolybdenum.

A mixture of 1.4 g (2.6 moles) of $[(C_2H_5)_3NH]\{[(C_6H_5)_2PO]-Mo(CO)_5\}$ and 0.9 g (8.0 moles) of trimethylchlorosilane in 15 ml of anhydrous ether was allowed to stir at room temperature for 0.5 hr. Filtration of the mixture to remove precipitated triethylammonium chloride yielded a yellow filtrate. The residue obtained upon evaporation of the filtrate was recrystallized from hexane to give the product as a waxy, white solid, mp 69-70°. The minimum yield is 65%. The complex was identified by its infrared and proton nmr spectral properties.

(Diphenylmethylphosphine)pentacarbonylmolybdenum.

a. A solution of methylmagnesium iodide was prepared from 0.130 g (5.4 mmol) of magnesium, 0.5 ml (5.4 mmol) of methyl iodide, and 50 ml of diethyl ether. A solution of 2.2 g (5 mmol) of $[(C_6H_5)_2PCl]Mo(CO)_5$ in 15 ml of ether was added slowly to the Grignard reagent with good stirring; the mixture was allowed to stir overnight. This mixture was then poured into 75 ml of water and extracted with three 25-ml portions of ether. The ether layer was dried over magnesium sulfate. The mixture was filtered, after which the ether was removed under aspirator vacuum from the filtrate to leave a yellow-brown residue. This residue was dissolved in hexane and chromatographed on an alumina column (2 x 8 cm.). The product was eluted with hexane and preceeded the pale yellow band of unreacted $[(C_6H_5)_2PCl]Mo(CO)_5$. The white solid obtained upon removal of hexane from the eluent was recrystallized from ethanol to give pure (diphenylmethylphosphine)pentacarbonylmolybdenum, mp 84°, in 20% yield. Anal. Calcd. for $C_{18}H_{13}MoO_5P$: C, 49.54; H, 2.98. Found: C, 49.72; H, 3.11.

b. A solution of methylmagnesium iodide (0.05 mole) was prepared from 1.20 g of magnesium, 7.10 g of methyl iodide, and 50 ml of tetrahydrofuran. A solution of 2.2 g (0.005 mol) of $Mo(CO)_5P(C_6H_5)_2Cl$ in 15 ml of THF was added to the Grignard reagent. The mixture was heated at reflux for one hour, after which it was worked-up in a manner identical to that described in a. A yield of 0.5 g (25%) of $Mo(CO)_5[P(C_6H_5)_2CH_3]$ was obtained.

c. Methylmagnesium iodide was prepared as in b. To the cool Grignard reagent 1.0 g (0.01 mol) of CuCl was added. The resulting suspension was stirred vigorously while the $Mo(CO)_5P(C_6H_5)_2Cl$ was added; stirring was continued for an additional hour after which the mixture was worked-up as described in a. A yield of 0.90 g (40%) of $Mo(CO)_5[P(C_6H_5)_2CH_3]$ was obtained.

(Diphenylethylphosphine)pentacarbonylmolybdenum.

A solution of ethylmagnesium bromide (0.05 mol) was prepared from 1.20 g of magnesium, 6.0 g of ethyl bromide, and 50 ml of tetrahydrofuran. A solution of 2.2 g of $Mo(CO)_5P(C_6H_5)_2Cl$ in 15 ml of THF was added slowly to the Grignard reagent, and the resulting mixture was heated at reflux for one hour. The cooled mixture was poured into 200 ml of slightly acidic water and extracted with two 100-ml portions of ether. The ether layer was separated, dried over anhydrous $MgSO_4$, and filtered. Ether was removed under aspirator vacuum leaving a colorless oil which solidified in a refrigerator. The solid was chromatographed on an alumina column (2 x 8 cm) and the product was eluted with hexane. The solid obtained upon removal of hexane was recrystallized from ethanol to give 0.8 g (34%) of pure (diphenylethylphosphine)pentacarbonylmolybdenum, mp 48° (lit.[43], mp 52°). Anal. Calcd. for $C_{19}H_{15}MoO_5P$: C, 50.66; H, 3.34. Found: C, 50.79; H, 3.46.

(Diphenylisopropylphosphine)pentacarbonylmolybdenum.

(Diphenylisopropylphosphine)pentacarbonylmolybdenum was prepared from isopropylmagnesium chloride and $Mo(CO)_5P(C_6H_5)_2Cl$ using a procedure analogous to that for $Mo(CO)_5P(C_6H_5)_2C_2H_5$. The product was obtained only as an oil by this procedure (lit.[43], mp 92°) and was identified by its proton nmr spectrum.

μ-(Tetraphenylphosphine)-decacarbonyldimolybdenum.

A solution of ethylmagnesium bromide (0.01 mol) was prepared from 0.25 g of magnesium, 1 ml of ethyl bromide, and 25 ml of doubly-distilled tetrahydrofuran. The Grignard reagent was cooled in an ice bath and maintained near 5° as 4.56 g (0.01 mol) of $Mo(CO)_5P(C_6H_5)_2Cl$ in 15 ml of THF was added slowly. The mixture was allowed to stir for an additional hour, after which it was poured into 100 ml of cold, distilled water. The orange solution was extracted with two 100-ml portions of ether. The ether layer was separated, dried with $MgSO_4$, and filtered. The ether was removed under aspirator vacuum leaving an oily residue. Hexane (10 ml) was added to the oil, causing precipitation of solid. The solid was recrystallized from ether/ethanol to give 0.2 g (12%) of the lemon-yellow crystalline product, mp 168-169° (dec). Anal. Calcd. for $C_{34}H_{20}Mo_2O_{10}P_2$: C, 48.45; H, 2.38; mol. wt., 842. Found: C, 48.15; H, 2.51; mol. wt., 870.

Reaction of Methylmagnesium Iodide with (Chlorodimethylphosphine)pentacarbonylmolybdenum.

a. A solution of methylmagnesium iodide was prepared from 0.10 g of magnesium, 0.5 g of methyl iodide, and 25 ml of ether. A solution of 1 g of $[(CH_3)_2PCl]Mo(CO)_5$ in 10 ml of ether was added to the Grignard reagent and stirred for 20 hr. The resulting black solution was added to 50 ml of water and extracted with two 15-ml portions of hexane. The hexane extracts were dried with anhydrous magnesium sulfate and filtered. Removal of hexane under aspirator vacuum left a gold solid. Two recrystallizations from hexane/benzene yielded $Mo(CO)_5P(CH_3)_2P(CH_3)_2Mo(CO)_5$ as a white, crystalline solid, mp. 140° (lit.,[44] mp 140-141°). The proton nmr spectrum also agrees with that reported.[44]

b. A solution of methylmagnesium iodide was prepared from 1.2 g of magnesium, 7.1 g of methyl iodide, and 50 ml of tetrahydrofuran. To the cool Grignard reagent 1.0 g of CuCl was added. The resulting suspension was stirred vigorously while 1.7 g of $Mo(CO)_5$-$P(CH_3)_2Cl$ in 10 ml of THF was added. Stirring was continued for 1 hr. The mixture was poured into 100 ml of water and extracted with two 100-ml portions of petroleum ether (20-40°). The extracts were dried over $MgSO_4$ and filtered. The solvent was removed in an aspirator vacuum leaving a dark liquid. The liquid was distilled under high vacuum to give 0.4 g (24%) of colorless $Mo(CO)_5P(CH_3)_3$ which was identified by comparison of its spectral properties to those of a known sample.[45]

(Dimethylphenylphosphine)pentacarbonylmolybdenum.

A solution of phenylmagnesium bromide (0.05 mole) was prepared from 1.2 g of magnesium, 7.8 g of bromobenzene, and 50 ml of tetrahydrofuran. One gram of CuCl was added to the cool Grigard reagent, and the suspension was stirred vigorously as a solution of 1.5 g of $Mo(CO)_5P(CH_3)_2Cl$ in 10 ml of THF was added. The mixture was allowed to stir for an additional hour, after which it was poured into 100 ml of water and extracted with two 100-ml portions of petroleum ether (20-40°). The extracts were dried over $MgSO_4$ and filtered. The solvent was removed in an aspirator vacuum, leaving a yellow oil. The oil was dissolved in hexane and chromatographed on an alumina column (2 x 8 cm). Removal of hexane from the eluent gave a colorless oil which was crystallized from ethanol to give 0.17 g (14%) of white crystals of the pure product, mp 29° (lit.[46], mp 28-29°).

Reactions of Chlorodiphenylphosphine- and (Chlorodimethylphosphine)-pentacarbonylmolybdenum with Methyllithium.

A solution of 5 ml of 2M methyllithium (0.01 mol) in ether was diluted to 50 ml with additional ether. A solution of 5 mmole of $Mo(CO)_5P(CH_3)_2Cl$ or $Mo(CO)_5P(C_6H_5)_2Cl$ and 15 ml of ether was added dropwise to the solution of methyllithium with vigorous stirring. The solution became red in color, and the addition of n-hexane caused precipitation of a yellow solid. The yellow solid was collected by filtration under nitrogen. The yellow solids smoldered spontaneously in air. Infrared spectra of the solids (Nujol) and of the oils obtained upon reaction with methyl iodide indicate the presence of cis-disubstituted metal carbonyls. No further characterization was attempted.

Reaction of (Chlorodiphenylphosphine)pentacarbonylmolybdenum with Sodium Cyclopentadienide.

A solution of NaC_5H_5 in 25 ml of tetrahydrofuran was prepared from 0.30 g of sodium and 1 ml of freshly distilled cyclopentadiene.[47] The solution was transferred to an addition funnel from which it was added dropwise to a solution prepared from 3.3 g of $Mo(CO)_5P(C_6H_5)_2Cl$ and 20 ml of THF. The resulting mixture was allowed to stir for 4 hr, after which the red-orange solution was poured into 100 ml of water and was extracted with three 50-ml portions petroleum ether (20-40°). The extracts were dried over $MgSO_4$ and filtered. Removal of solvents under aspirator vacuum left an orange oil. Addition of 15 ml of hexane to the oil caused precipitation of a tan solid which was collected by filtration and washed with 25 ml of hexane.

Hexane was removed from the filtrate under aspirator vacuum, leaving a colorless oil. The oil was chromatographed on a short (2 x 8 cm) alumina column with hexane as eluent. The hexane was removed under aspirator vacuum, giving a white solid. The solid was recrystallized from ethanol to give 1.26 g (36%) of pure (cyclopentadienyldiphenylphosphine)pentacarbonylmolybdenum, mp 98-99°. Anal. Calcd. for $C_{22}H_{15}MoO_5P$: C, 54.32; H, 3.10. Found: C, 54.18; H, 3.22.

The tan solid isolated earlier in the work-up was recrystallized from ethanol/chloroform to give 1.36 g (42%) of pure μ-cyclopentadienyl-bis(diphenylphosphinopentacarbonylmolybdenum), mp 197°(dec.). Anal. Calcd. for $C_{39}H_{24}Mo_2O_{10}P_2$: C, 51.65; H, 2.65; mol. wt. 906. Found: C, 51.41; H, 2.70; mol. wt., 1000 ±100 (melting point biphenyl).

Reaction of (Chlorodimethylphosphine)pentacarbonylmolybdenum with Sodium Cyclopentadienide.

This reaction was carried out between $Mo(CO)_5P(CH_3)_2Cl$ (3.4 g) and NaC_5H_5 in a manner identical to that described above. Removal of solvent from the reaction extract gave only an oil. The oil was placed on an alumina column (2 x 8 cm) and developed with hexane. Hexane eluent gave a colorless oil identified as (cyclopentadienyldimethylphosphine)pentacarbonylmolybdenum by its nmr spectrum. A 50/50 hexane/benzene mixture gave a yellow band from which a yellow oil, presumably μ-cyclopentadienyl-bis(dimethylphosphinopentacarbonylmolybdenum), was obtained. Pure benzene eluted an orange band from which another yellow oil was obtained whose identity is still uncertain.

Attempt to Prepare (Dichlorophenylphosphine)pentacarbonylmolybdenum.

A mixture of 10.6 g of $Mo(CO)_6$, 7.2 g of dichlorophenylphosphine, and 25 ml of toluene was heated at reflux for about 1 hr at which time the theoretical amount of carbon monoxide had been evolved. The cooled mixture was filtered, diluted with 50 ml of petroleum ether (20-40°0, treated with 3 g of alumina, and filtered again.

This process was repeated twice, at which time the filtrate was a clear yellow solution. Solvents were removed under aspirator vacuum.

Attempts to purify the complex by distillation under high vacuum and by low-temperature recrystallization from petroleum ether were unsuccessful.

An infrared spectrum of the unpurified complex indicated that it was a monosubstituted derivative of molybdenum hexacarbonyl.

Attempt to Prepare (Chloromethylphenylphosphine)pentacarbonylmolybdenum.

A mixture of 5.3 g of $Mo(CO)_6$, 3.0 g chloromethylphenylphosphine, and 25 ml of toluene was heated at reflux for 1 hr. The cooled mixture was filtered, diluted with 50 ml of petroleum ether, treated with 3 g of alumina, and filtered again. This process was repeated twice. Solvent was removed under aspirator vacuum. Attempts to purify the crude product by high vacuum distillation and low temperature recrystallization were unsuccessful.

Infrared and nmr spectra indicated that the unpurified residue was 95% of the desired product.

Attempted Reaction of $[(C_6H_5)_2PCl]Mo(CO)_5$ with Antimony Trifluoride.

A mixture of 2 g of $[(C_6H_5)_2PCl]Mo(CO)_5$, 0.5 g of antimony trifluoride, and 25 ml of hexane was allowed to stir overnight. The solution was filtered and slow removal of hexane under a stream of nitrogen gave a mass of pale yellow crystals, mp 58°. These crystals were further identified as unchanged starting materials by mass spectroscopy.

Attempted Reaction of $[(CH_3)_2PCl]Mo(CO)_5$ with Antimony Trifluoride.

A mixture of 1.5 g of $[(CH_3)_2PCl]Mo(CO)_5$, 0.5 g of SbF_3, and 25 ml of hexane was allowed to stir overnight. The solution was filtered and hexane was removed under aspirator vacuum. The resulting residue was identified as unchanged starting material by its nmr spectrum.

Attempted Reaction of $[(CH_3)_2PCl]Mo(CO)_5$ with Phenol and Sodium Phenoxide.

A mixture of 2 g of $[(CH_3)_2PCl]Mo(CO)_5$, 0.6 g of phenol, and 25 ml of ether was heated at reflux for one hour. Ether was removed at aspirator vacuum, leaving a liquid residue. An nmr spectrum of this crude residue indicated that no reaction had taken place.

A suspension of sodium phenoxide in hexane was prepared from 0.56 g of phenol and 0.14 g of sodium metal. A solution of 1 g of $[(CH_3)_2PCl]Mo(CO)_5$ in 10 ml of hexane was added dropwise to the sodium phenoxide suspension. The resulting mixture was heated at reflux with vigorous stirring for 2 hr. The mixture was filtered and the solvent was removed under aspirator vacuum. Distillation of the remaining liquid under high vacuum gave a mixture of 60% (Phenyl dimethylphosphinite)pentacarbonylmolbydenum and 40% (chlorodimethylphosphine)pentacarbonylmolybdenum as determined by an nmr spectrum of the mixture.

Attempted Reaction of $[(C_6H_5)_2PCl]Mo(CO)_5$ with Diphenylamine.

A mixture of 1 g of $[(C_6H_5)_2PCl]Mo(CO)_5$, 0.8 g of diphenylamine, and 25 ml of tetrahydrofuran was allowed to stir for 1 hr. No diphenylammonium chloride had precipitated; chromatography of the reaction mixture after removal of tetrahydrofuran on an alumina column using hexane as eluent gave unchanged $[(C_6H_5)_2PCl]Mo(CO)_5$.

Attempted Reaction of $[(CH_3)_2PCl]Mo(CO)_5$ with Acetic Acid.

A mixture of 1.1 g of $[(CH_3)_2PCl]Mo(CO)_5$ and 15 ml of glacial acetic acid was heated at reflux for 1 hr. The mixture was added to 50 ml of water and extracted with two 10-ml portions of hexane. Hexane was removed under aspirator vacuum. An nmr spectrum of the remaining liquid was identical to that of $[(CH_3)_2PCl]Mo(CO)_5$.

The unchanged $[(CH_3)_2PCl]Mo(CO)_5$ was then added to a solution of 0.5 g of silver acetate in 15 ml of water and shaken. Heat was evolved. Upon cooling, the solution was filtered and extracted with two 10-ml portions of hexane. The hexane extracts were dried over magnesium sulfate and the hexane was removed under aspirator vacuum. An nmr spectrum of the remaining liquid indicated that it was $[(CH_3)_2P(OH)]Mo(CO)_5$.

Attempted Reaction of $[(C_6H_5)_2PCl]Mo(CO)_5$ with $[(C_6H_5)_2PH]Mo(CO)_5$.

A. (Diphenylphosphine)pentacarbonylmolybdenum.

A mixture of 2.64 g of $Mo(CO)_6$, 1.86 g of diphenylphosphine, and 25 ml of diglyme was heated at reflux until gas evolution ceased. The cooled mixture was added to 100 ml of water and extracted with two 25-ml portions of ether. The ether layer was dried with magnesium sulfate. The ether was removed under aspirator vacuum, leaving a white solid. This solid was recrystallized from ethanol to give white crystals of $[(C_6H_5)_2PH]Mo(CO)_5$, mp 74°, in 80% yield, J(PH) = 331 Hz. (Lit.[48] mp 73-75°; J(PH) = 331 Hz.)

B. A mixture of 1 g of $[(C_6H_5)_2PCl]Mo(CO)_5$, 1 g of $[(C_6H_5)_2PH]$-$Mo(CO)_5$, 1 ml of triethylamine, and 25 ml of hexane was heated at reflux for 2 hr. No precipitate of triethylammonium chloride was observed in this time. An nmr spectrum of the residue remaining after removal of hexane indicated much unreacted (diphenylphosphine)-pentacarbonylmolybdenum.

Attempted Reaction of $[(C_6H_5)_2PCl]Mo(CO)_5$ with Cyclopentadienylthallium.

A mixture of 4.57 g of $[(C_6H_5)_2PCl]Mo(CO)_5$ dissolved in 15 ml of tetrahydrofuran was added to a well-stirred suspension of freshly sublimed TlC_5H_5 in 25 ml of tetrahydrofuran. The mixture was stirred for 2 hr. The resultant mixture was filtered, and THF was removed from the filtrate under aspirator vacuum leaving a white solid. The residue was extracted with several 25-ml portions of 50/50 boiling chloroform/ethanol. Cooling caused precipitation of crystals identified as μ-(tetraphenyldiphosphoxane)-decacarbonyldimolybdenum.

The experiment was repeated several times with the same result. However, none of the bridged complex was formed if the solvent THF was triply distilled from $LiAlH_4$ to insure removal of all water. In this case $[(C_6H_5)_2PCl]Mo(CO)_5$ was recovered unchanged in 95% yield.

Attempted Reaction of $[(CH_3)_2PCl]Mo(CO)_5$ with Cyclopentadienylthallium.

A mixture of 0.5 g of $[(CH_3)_2PCl]Mo(CO)_5$, 0.41 g of TlC_5H_5, and 25 ml of THF was allowed to stir for 4 hr. The mixture was filtered and the precipitate was washed several times with hexane to yield a pale orange filtrate. All solvent was removed under aspirator vacuum leaving a gummy oil. This oil was dissolved in 10 ml of petroleum ether, treated with charcoal, and filtered. Slow removal of solvent under a stream of nitrogen caused precipitation of a white solid, mp 65°, which was later identified as μ-(tetramethyldiphosphoxane)-decacarbonyl-dimolybdenum by comparison of its physical properties with that of an authenic sample.

Attempted Reduction of $[(C_6H_5)_2PCl]Mo(CO)_5$ with Lithium Aluminum Hydride or Calcium Hydride.

A mixture of 2.5 g of $[(C_6H_5)_2PCl]Mo(CO)_5$ in 20 ml of diethyl ether was added dropwise to a well-stirred suspension of 0.06 g of lithium aluminum hydride in 26 ml of ether. The mixture was stirred for an additional hour and then filtered. Ether was removed under aspirator vacuum leaving a yellow material which was identified as unchanged starting material from its melting point and nmr spectrum.

A similar procedure using CaH_2 also failed to give (diphenylphosphine)pentacarbonylmolybdenum.

RESULTS AND DISCUSSION

Synthesis and Characterization of Products

Introduction

Several techniques have been available to synthetic chemists for the preparation of derivatives of transition metal carbonyls.[49] In most cases a direct thermal reaction between a metal carbonyl and a ligand in an appropriate solvent has yielded the desired product as shown in Eq. 15. Generally, the temperatures afforded by refluxing tetrahydrofuran or methylcyclohexane have been sufficient for most reactions, although less reactive metal carbonyls can be forced to undergo substitution reactions at temperatures as high as 250°. The use of solvents such as n-octane, xylene, or diglyme is not uncommon.

$$M(CO)_n + \text{ligand} \xrightarrow{\Delta} [M(CO)_{n-1}(\text{ligand})] + CO \qquad (15)$$

Some metal carbonyls react stubbornly under even extreme thermal conditions but readily entertain substitution reactions in the presence of ultraviolet light (Eq. 16).

$$W(CO)_6 + L \rightarrow W(CO)_5L + CO \qquad (16)$$

The use of ultraviolet irradiation for the preparation of metal carbonyl derivatives is of particular value when a complex of poor thermal stability is to be synthesized. In other cases, the necessary reaction temperature may be lowered drastically by substituting a halopentacarbonylmetallate for the corresponding metal hexacarbonyl (Eq. 17-18).

$$M(CO)_6 + (C_2H_5)_4NI \rightarrow [(C_2H_5)_4N^+][M(CO)_5I]^- + CO \qquad (17)$$

$$[M(CO)_5]^- + L \rightarrow M(CO)_5L + I^- \qquad (18)$$

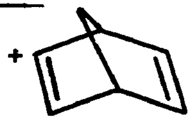
$$M = Cr, Mo, W$$

Still another route to substituted metal carbonyl complexes is available which is useful when ligands having poor donor properties are employed. A labile complex may be prepared using a poor ligand such as tetrahydrofuran or acetonitrile (Eq. 19-20).

$$Mo(CO)_6 + THF \rightarrow [Mo(CO)_5(THF)] \qquad (19)$$

$$[Mo(CO)_5(THF)] + L \rightarrow Mo(CO)_5L + THF \qquad (20)$$

This synthesis is of particular value in preparing substituted octahedral metal carbonyl possessing a specific stereochemistry. For example, bicycloheptadiene displaces two carbonyls from mutually cis positions in molybdenum hexacarbonyl (Eq. 21). The bicycloheptadiene molecule may subsequently be displaced by two other donor atoms to give exclusively cis- substitution (Eq. 22).

$Mo(CO)_6 +$  $\rightarrow [Mo(CO)_4(C_7H_8)]$ (21)

$$[Mo(CO)_4(C_7H_8)] + 2P(C_6H_5)_3 \rightarrow \underline{cis}\text{-}Mo(CO)_4[P(C_6H_5)_3]_2 \qquad (22)$$

In contrast, the direct thermal reaction between molybdenum hexacarbonyl and two moles of triphenylphosphine gives exclusively trans- $Mo(CO)_4[P(C_6H_5)_3]_2$. This general method is also applicable to the preparation of trisubstituted complexes in which, for example, cycloheptatrienetricarbonylmolybdenum is the starting point for cis-trisligandtricarbonylmolybdenum.

In all of the methods described above for the preparation of derivatives of transition metal carbonyls there is one feature shared by each technique. Ultimately, a metal carbonyl and a ligand combine to form a complex. Apparently, complexes prepared by these routes are limited only by the ligands which may be synthesized. Unfortunately, many potentially interesting phosphine ligands cannot be prepared, inasmuch as they rearrange to different thermodynamically preferred structures which are not capable of behaving as ligands. On the other hand, metal carbonyl complexes are known for many transient species which are incapable of independent existence. The unavailability of free cyclobutadiene makes the preparation of cyclobutadiene-metal complexes difficult. However, the dehalogenation of 3,4-dichlorocyclobutene ($C_4H_4Cl_2$) with various metal carbonyl derivatives provides a suitable route to several cyclobutadienemetal complexes such as shown in Eq. 23-25.[50,51]

$$Fe_2(CO)_9 + C_4H_4Cl_2 \rightarrow C_4H_4Fe(CO)_3 + 6CO + FeCl_2 \quad (23)$$

$$Na_2Ru(CO)_4 + C_4H_4Cl_2 \rightarrow C_4H_4Ru(CO)_3 + 2NaCl + CO \quad (24)$$

$$Na_2M(CO)_5 + C_4H_4Cl_2 \rightarrow C_4H_4M(CO)_4 + 2NaCl + CO \quad (25)$$

(M = Cr, Mo, W)

The cyclobutadiene derivatives $C_4H_4Fe(CO)_3$ and $C_5H_5CoC_4H_4$ can also be obtained by ultraviolet irradiation of α-pyrone and an appropriate metal carbonyl as shown in Eq. 26-27.[52]

$$Fe(CO)_5 + \overline{C_4H_4C(O)O} \rightarrow Fe(CO)_3C_4H_4 + 2CO + CO_2 \quad (26)$$

$$C_5H_5Co(CO)_2 + \overline{C_4H_4C(O)O} \rightarrow C_5H_5CoC_4H_4 + 2CO + CO_2 \quad (27)$$

Carbene complexes of transition metals are now well documented[53] (Eq. 28-29), although no free carbenes have been isolated.

$$M(CO)_6 + CH_3Li \rightarrow M(CO)_5[C(CH_3)(OLi)] \quad (28)$$

$$M(CO)_5[C(CH_3)(OLi)] + (CH_3)_3OBF_4 \rightarrow M(CO)_5[C(CH_3)(OCH_3)] + CH_3OCH_3 + LiBF_4 \quad (29)$$

The existence of transition metal complexes of unstable organic species encouraged development of a synthetic procedure capable of producing complexes of thermodynamically unstable phosphorus ligands. Presumably, the availability of the lone electron pair on phosphorus in its trivalent compounds plays a significant role in the behavior of any one particular compound to rearrange. Binding the lone pair of phosphorus to a transition metal carbonyl group appeared to be one reasonable way of eliminating its participation in troublesome rearrangement reactions.

One logical and very exploitable synthetic technique became apparent for the preparation of complexes of unusual phosphine ligands: Instead of preparing a specific ligand for complexation from a reactive phosphine substrate, first bind the reactive ligand to a metal carbonyl and then generate the desired complex using reactions analogous to those for a trivalent phosphine discussed earlier in this thesis. Complexes derived from dialkyl or diarylchlorophosphines were expected to undergo reactions with a variety of nucleophiles to yield complexes of a new phosphine. The scope of this synthetic procedure will be discussed in Part I of this thesis.

(Chlorophosphine)pentacarbonylmolybdenum Complexes.

Most of the reactions of coordinated phosphine ligands in this study were effected on two specific complexes. (Chlorodiphenylphosphine)pentacarbonylmolybdenum, $Mo(CO)_5P(C_6H_5)_2Cl$, and (chlorodimethylphosphine)pentacarbonylmolybdenum, $Mo(CO)_5P(CH_3)_2Cl$, were used as model complexes for several reasons. First, molybdenum hexacarbonyl is commercially available and relatively inexpensive. The ligands chlorodiphenylphosphine and chlorodimethylphosphine are commercially available, although the latter is prepared more economically in the laboratory. The halophosphine complexes are air-stable solids and hence easily handled, weighed, and transferred with minimum difficulty. Further, all the complexes prepared were readily characterized by physical methods. The complexes were particularly well-suited to study by proton magnetic resonance and infrared spectroscopy.

The pentacarbonylmolybdenum complexes of chlorodimethylphosphine and chlorodiphenylphosphine were prepared by classical thermal syntheses. Molybdenum hexacarbonyl and chlorodiphenylphosphine were heated in toluene at reflux for one hour giving the product in 70% yield. Significantly, chlorodiphenylphosphinepentacarbonylmolybdenum had been prepared prior to our work, but in only 21% yield. The synthesis reported in this thesis is a marked improvement in both time and efficiency over the method of Thompson.[40] Chlorodiphenylphosphinepentacarbonylmolybdenum is a low-melting, pale-yellow, crystalline solid. It is very soluble in most organic solvents but may be recrystallized from cold hexane. The complex was not sublimable at pressures as low as 10^{-4} torr, but it did give a mass spectrum.

Chlorodimethylphosphinepentacarbonylmolybdenum was prepared from molybdenum hexacarbonyl and chlorodimethylphosphine in refluxing methylcyclohexane. The product was obtained in 53% yield after a reaction of five hours. The longer time for the chlorodimethylphosphine reaction compared to the analogous chlorodiphenylphosphine reaction may be attributed to the low boiling point of chlorodimethylphosphine, and thus its lower concentration in the reaction vessel.

After a portion of this work had been published, Ehrl and Vahrenkamp[54] reported the synthesis of $Mo(CO)_5P(CH_3)_2Cl$ by the ultraviolet irradiation of a mixture of molybdenum hexacarbonyl and chlorodimethylphosphine. However, they achieved a yield of only 20%. Chlorodimethylphosphinepentacarbonylmolybdenum is a low-melting, white, crystalline solid. It is soluble in most organic solvents, although it may be recrystallized from cold hexane. The complex is volatile enough to be purified by vacuum sublimation.

There is a remarkable difference in the stability of the metal complexes of the halophosphines and the uncomplexed halophosphines. Whereas chlorodimethylphosphine bursts into flame upon contact with air and chlorodiphenylphosphine is oxidized upon standing in air, both complexes have been stored as long as a year in a refrigerator with only slight decomposition. The metal carbonyl complexes oxidize more rapidly in solution, and solutions of these compounds are best handled under a protective nitrogen atmosphere.

Successful reactions upon a coordinated phosphine ligand were also carried out on dichloromethylphosphinepentacarbonylmolybdenum. This complex was prepared by a method analogous to that for $Mo(CO)_5$-$P(CH_3)_2Cl$. Not surprisingly, $Mo(CO)_5PCH_3Cl_2$ is a low-melting, white, crystalline solid and also volatile enough to be purified by vacuum sublimation.

Attempts to prepare and purify dichlorophenylphosphinepentacarbonylmolybdenum were unsuccessful. Although $Mo(CO)_5P(C_6H_5)Cl_2$ was ultimately obtained as an impure yellow liquid, the complex could not be purified further by low-temperature recrystallization or vacuum distillation. Infrared spectroscopy and proton magnetic resonance suggested the compound was at least 95% pure.

Several attempts were made to obtain chloromethylphenylphosphinepentacarbonylmolybdenum, $Mo(CO)_5[P(C_6H_5)CH_3(Cl)]$, in pure form. Unfortunately, this complex presented the same problems as $Mo(CO)_5(PC_6H_5Cl_2)$ in purification, and ultimately only a product judged 95% pure by proton magnetic spectroscopy was obtained. The complex $Mo(CO)_5[P(C_6H_5)CH_3(Cl)]$ was of interest for two specific reasons. First, complexes with physical properties intermediate between $Mo(CO)_5P(C_6H_5)_2Cl$ and $Mo(CO)_5P(CH_3)_2Cl$ would have been available for study. Magnetic resonance is especially sensitive to small changes in the electronic environment of protons and would have been an interesting tool in the study of a series of $Mo(CO)_5[P(C_6H_5)CH_3(X)]$ complexes. Second, the phosphorus atom in $Mo(CO)_5[P(C_6H_5)CH_3(Cl)]$ is asymmetric, and the possibility for optical isomers exists for this complex. Resolution of a single, reactive phosphine complex into its pure optical isomers could lead to a simple way to generate optically pure complexes of many optically active ligands via reaction of the coordinated ligand.

The existence of optical isomers for $Mo(CO)_5[P(C_6H_5)CH_3(Cl)]$ may be one reason for the difficulty in obtaining the complex as a crystalline solid. Presumably, a racemic mixture of $Mo(CO)_5[P(C_6H_5)$-$CH_3(Cl)]$ is generated in the thermal reaction between $Mo(CO)_6$ and $P(C_6H_5)CH_3(Cl)$. Hence, the equal amounts of each complex in the racemic mixture would lower the melting point of each far below its real value. The actual melting point of $Mo(CO)_5[P(C_6H_5)CH_3(Cl)]$ is expected to be low, i.e., less than 40°, inasmuch as the melting points of $Mo(CO)_5P(C_6H_5)_2Cl$ (57°), $Mo(CO)_5P(CH_3)_2Cl$ (37°), and $Mo(CO)_5P(CH_3)_2C_6H_5$ (30°) are all also relatively low. Generally, if the phosphine ligand is a solid, the monosubstituted molybdenum pentacarbonyl complex is also a solid. In this respect, it would seem appropriate to prepare complexes of tert-$C_4H_9PCl_2$ (mp 48°) or ligands derived therefrom, especially tert-$C_4H_9P(CH_3)Cl$, as reasonable compounds from which to extend a study on reactions of coordinated phosphine ligands. Ligands of the type $(RO)PCl_2$, $(RO)_2PCl$, R_2NPCl_2, and $(R_2N)_2PCl$ are also potentially interesting ligands on which a series of complexes might be based.

Complexes of Phosphinous Acids, Thiophosphinous Acids, and Diphosphoxanes

The reaction between a chlorophosphinepentacarbonylmolybdenum complex and water yields a complex of the corresponding phosphinous acid as shown in Eq. 30.

$$Mo(CO)_5PR_2Cl + H_2O \rightarrow Mo(CO)_5PR_2OH + HCl \qquad (30)$$

Since the lone pair on phosphorus is coordinated to the metal, no rearrangement of the type shown in Eq. 31

$$R_2POH \rightarrow R_2P(O)H \qquad (31)$$

occurs.

The reaction of (chlorodimethylphosphine)pentacarbonylmolybdenum with water gives (dimethylphosphinous acid)pentacarbonylmolybdenum in good yield under mild conditions. Triethylamine coordinates the hydrochloric acid generated from the reaction (Eq. 32).

$$Mo(CO)_5P(CH_3)_2Cl + H_2O + N(C_2H_5)_3 \rightarrow Mo(CO)_5P(CH_3)_2OH + (C_2H_5)_3NHCl \qquad (32)$$

(Dimethylphosphinous acid)pentacarbonylmolybdenum is a colorless liquid which may be purified by distillation under high vacuum. The acid complex may also be prepared by the reaction of water alone on the $Mo(CO)_5P(CH_3)_2Cl$, but hydrolysis is considerably faster in the presence of a base.

Several specific observations lead to the assignment of a phosphinous acid structure for the ligand in this complex. First, the positions and intensities of the infrared active bands in the 2100-1900 cm^{-1} region attributed to metal-carbonyl stretching clearly indicate that the phosphorus ligand is coordinated to the molybdenum atom through phosphorus.[34,55,56] Also the infrared spectrum exhibits broad hydroxyl stretching bands centered near 3200 cm^{-1}. In dilute carbon tetrachloride solution, the broad band disappears and a sharp hydroxyl band is noted at 3610 cm^{-1}. This dependence of $\upsilon(OH)$ on concentration is typical of strongly hydrogen bonding molecules.[57] Griffiths and Burg report the appearance of a strong hydroxyl stretching band at 3620 cm^{-1} for $(CF_3)_2POH$.[9] The proton nmr spectrum of $Mo(CO)_5P(CH_3)_2OH$ shown in Figure 2 provides further information to support the structural assignment with the presence of an acidic proton. In particular, the chemical shift for the hydroxyl proton is strongly concentration and temperature dependent, Figure 3, and no splitting of the signal by phosphorus-31 is observed.

The reaction of water with chlorodiphenylphosphinepentacarbonylmolybdenum parallels the chlorodimethylphosphinepentacarbonyl system. However, in the presence of triethylamine, a salt, triethylammonium diphenylphosphinitopentacarbonylmolybdenum, is formed rather

Figure 2. The NMR spectrum of $Mo(CO)_5P(CH_3)_2OH$. Chemical shifts shown in ppm from internal TMS.

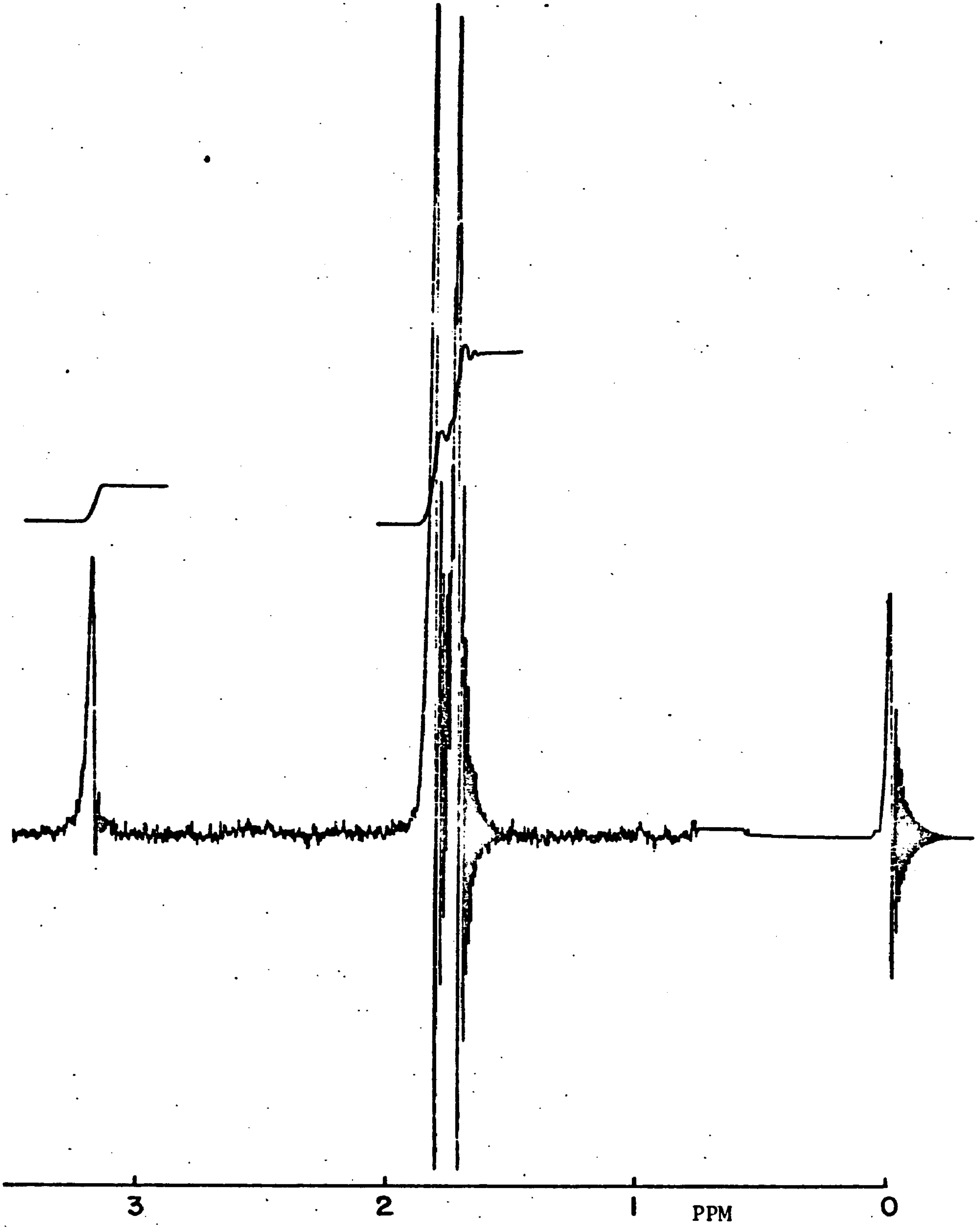
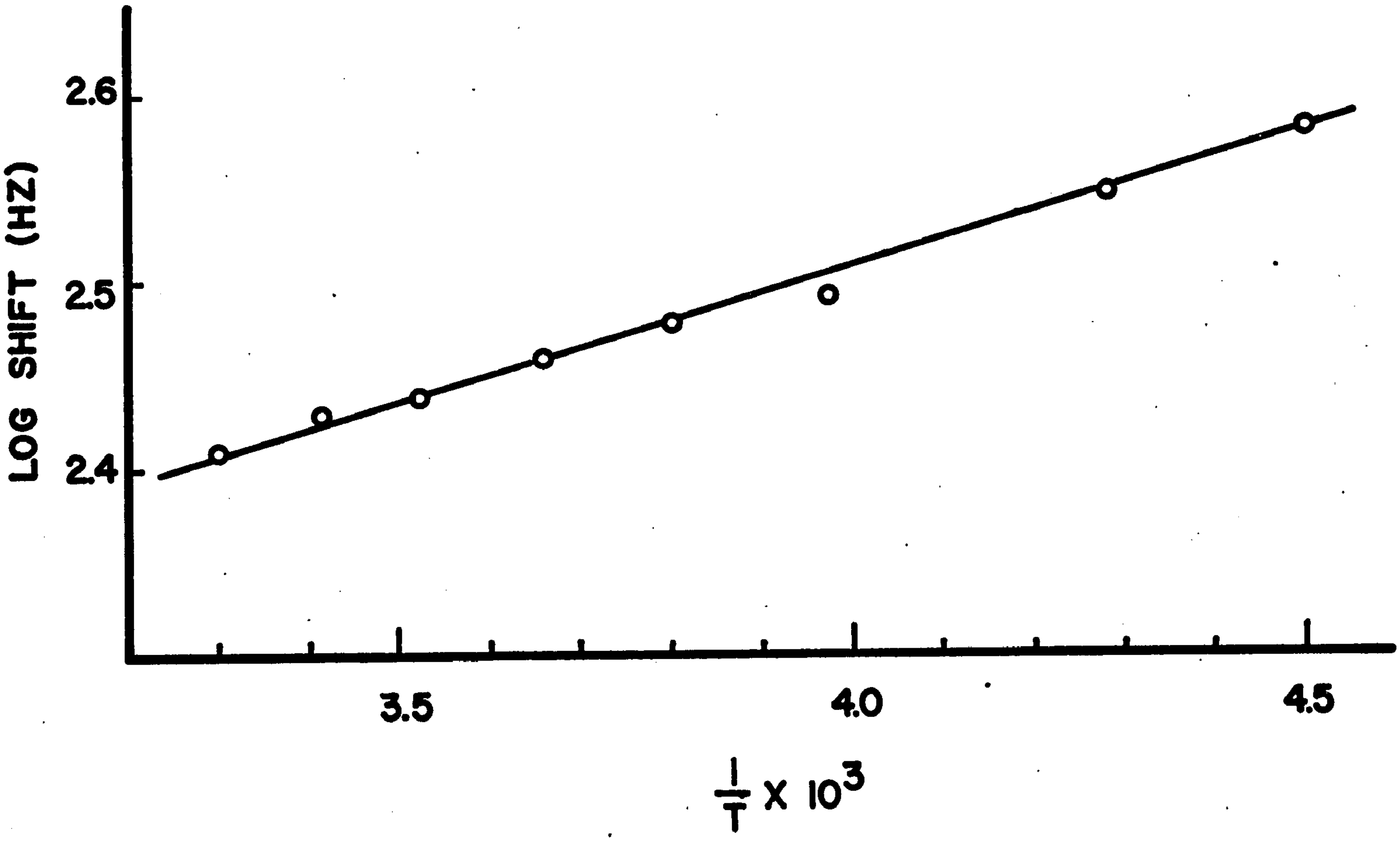


FIGURE 3. TEMPERATURE DEPENDENCE OF THE -OH NMR RESONANCE OF $Mo(CO)_5P(CH_3)_2OH$



than the (diphenylphosphinous acid)pentacarbonylmolybdenum (Eq. 33).

$$Mo(CO)_5P(C_6H_5)Cl + H_2O + 2(C_2H_5)_3N \rightarrow [(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O] + (C_2H_5)_3NHCl \quad (33)$$

Acidification of the salt with dilute hydrochloric acid in acetone gives the diphenylphosphinous acid complex in variable yield (Eq. 34).

$$[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O] + HCl \rightarrow (C_2H_5)_3NHCl + Mo(CO)_5P(C_6H_5)_2OH \quad (34)$$

(Diphenylphosphinous acid)pentacarbonylmolybdenum was characterized by the same methods described for (dimethylphosphinous acid)pentacarbonylmolybdenum. In addition, several other observations confirmed the acidic nature of the diphenylphosphinous acid complex. First, the facile reaction of the acid complex with triethylamine or potassium hydroxide lead to the formation of salts (Eq. 35-36).

$$Mo(CO)_5P(C_6H_5)_2OH + KOH \rightarrow K^+[Mo(CO)_5P(C_6H_5)_2O]^- + H_2O \quad (35)$$

$$Mo(CO)_5P(C_6H_5)_2OH + (C_2H_5)_3N \rightarrow [(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)O] \quad (36)$$

Second, carbene insertion into the -OH bond gave an ester (Eq. 37). The insertion reaction is characteristic of an acidic proton.[58]

$$Mo(CO)_5P(C_6H_5)_2OH + CH_2N_2 \rightarrow Mo(CO)_5[P(C_6H_5)_2OCH_3] + N_2 \quad (37)$$

Several attempts to prepare salts of (dimethylphosphinous acid)pentacarbonylmolybdenum under mild conditions failed. Thus, triethylamine and potassium hydroxide did not give a reaction with $Mo(CO)_5P(C_6H_5)_2OH$. This difference in acidity may be attributed to the greater electron withdrawing capability of phenyl groups compared to methyl groups. A similar argument has been used to explain the strength of inorganic acids.[59] Further, dimethylphosphinic acid, $(CH_3)_2P(O)OH$, has been described as "a very weak acid."[60] The pentacarbonylmolybdenum complex of dimethylphosphinous acid is expected to be a weaker acid than $(CH_3)_2P(O)OH$, since a pentacarbonylmolybdenum group is, on the whole, less electronegative than an oxo group.[59]

Organic chemists have studied the influence of substituents on aromatic rings upon the acidity of organic acids.[56] Generally, small differences in the electronic and steric nature of the substituents have been reflected in the strength of the acid and is the basis for the well-known Hammett relationship. The concept of acid strength might be applied to metal carbonyl complexes of acid derivatives of phosphorus in order to assess the nature of the metal-phosphorus bond. Thus, for a given phosphinous acid, e.g., $(CH_3)_2POH$, a series of complexes $(CO)_nM[P(CH_3)_2OH]$, where M is one of several transition metals, would be synthesized. The value of K_a for the acid complex might reflect subtle differences in the electronic nature of the OH bond. These differences in the observed values of K_a might be directly related to the nature of the transition metal-phosphorus bond. In particular, most electronic effects in transition metal-phosphines are rationalized on the basis of pi bonding between the metal and ligand. In this respect, interesting relationships between K_a and the Cotton-Kraihanzel simplified force constants[34,55,56] might appear. Also of interest in the study of the acidity of metal complexes of phosphorus acids are the nature of substituents on phosphorus and the presence of other ligands on the metal carbonyl. Many biological systems have been shown to involve transition metal ions, and basic studies of the type described above may provide further information on the role of transition metals in body processes.

The (diphenylphosphinous acid)pentacarbonylmolybdenum complex was also prepared by a completely different route taking advantage of the equilibrium (Eq. 38) suggested to exist for diphenylphosphine oxide.[15].

$$(C_6H_5)_2P(O)H \rightleftharpoons (C_6H_5)_2POH \tag{38}$$

Reaction of molybdenum hexacarbonyl with $(C_6H_5)_2P(O)H$ gave $Mo(CO)_5$-$P(C_6H_5)_2OH$ in 50% yield. The success of this reaction has substantiated the existence of the proposed equilibrium. Presumably reaction occurs between the metal carbonyl and the unstable acid tautomer of diphenylphosphine oxide. As the trivalent isomer is trapped by complexation with a metal carbonyl, the equilibrium must shift to the right to maintain the required concentration of the trivalent species. The spectral properties of the product prepared by either route are identical.

A similar reaction was effected between $Mo(CO)_6$ and dimethyl phosphite, $(CH_3O)_2P(O)H$. Although infrared and proton nmr spectroscopy indicated that (dimethylphosphorous acid)pentacarbonylmolybdenum, $[(CH_3O)_2POH]Mo(CO)_5$, had in fact been prepared, a sample of reasonable purity could not be obtained by the usual purification methods.

Of the two procedures developed for the preparation of metal complexes of unstable trivalent acids of phosphorus, the hydrolysis procedure does have some advantages over the thermal method. First, the hydrolysis procedure is fast and can be carried out at ambient temperature or lower. Purification of the complexes is less tedious since there can be no excess ligand precursor as a contaminant. The hydrolysis reaction also gives product in much higher yield, and the problems of multiple substitution and thermal decomposition often encountered in thermal reactions are eliminated. A qualitative comparison of the purity of $Mo(CO)_5P(C_6H_5)_2OH$ prepared by each method showed the hydrolysis product to be more pure than the thermal reaction product.

The reactions of $Mo(CO)_5P(C_6H_5)_2Cl$ and $Mo(CO)_5P(CH_3)_2Cl$ with hydrogen sulfide closely parallel the analogous reaction with water. Thus, $Mo(CO)_5P(CH_3)_2Cl$ and H_2S react in the presence of triethylamine to give (dimethylthiophosphinous acid)pentacarbonylmolybdenum (Eq. 39).

$$Mo(CO)_5P(CH_3)_2Cl + H_2S + (C_2H_5)_3N \rightarrow Mo(CO)_5[P(CH_3)_2SH] + (C_2H_5)_3NHCl \tag{39}$$

Several attempts to obtain a purified product were unsuccessful. The thioacid complex decomposed both on attempts at high vacuum distillation and column chromatography. Like $Mo(CO)_5P(CH_3)_2OH$, $MO(CO_5P(CH_3)_2SH$ does not readily form salts with either triethylamine or pyridine.

Chlorodiphenylphosphinepentacarbonylmolybdenum reacts with H_2S in the presence of $(C_2H_5)_3N$ and gives a salt (Eq. 40), triethylammonium diphenylthiophosphinitopentacarbonylmolybdenum.

$$Mo(CO)_5P(C_6H_5)_2Cl + H_2S + 2N(C_2H_5)_3 \rightarrow [(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2S] + (C_2H_5)_3NHCl \tag{40}$$

This salt was very similar to $[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O]$ in its appearance and in its physical and spectral properties. However, several attempts to prepare (diphenylthiophosphinous acid)pentacarbonylmolybdenum from the salt led to unworkable polymeric residues (Eq. 41).

$$[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2S\ ] + HCl \not\rightarrow Mo(CO)_5[P(C_6H_5)_2SH] \qquad (41)$$

No attempt was made to prepare the thioacid complex using diphenylphosphine sulfide as a source of diphenylthiophosphinous acid by taking advantage of an equilibrium similar to that shown in Eq. 38.

$$(C_6H_5)_2P(S)H \rightleftharpoons (C_6H_5)_2PSH \qquad (42)$$

The pentacarbonylmolybdenum complexes of phosphinous acids are the sources of several other unusual metal complexes. The reaction between a phosphinous acid and a chlorophosphine should give a diphosphoxane -- a binuclear phosphorus compound connected with an oxygen bridge (Eq. 43).

$$R_2POH + R_2PCl + R'_3N \rightarrow R_2P\text{-}O\text{-}PR_2 + R'_3NHCl \qquad (43)$$

Attempts to prepare several alkyl or aryl diphosphoxanes have yielded compounds (Eq. 44) characterized as rearrangement products of the desired species.[61]

$$R_2P\text{-}O\text{-}PR_2 \rightarrow R_2P(O)PR_2 \qquad (44)$$

Prior to the work described in this thesis, only two isolable diphosphoxanes had been reported. Both compounds contained stabilizing fluoro groups. Burg[9] prepared $(CF_3)_2POP(CF_3)_2$ via a unique synthesis (Eq. 45)

$$2(CF_3)_2PCl + Ag_2CO_3 \rightarrow (CF_3)_2POP(CF_3)_2 + 2AgCl \qquad (45)$$

while Rudolph et al.[62] prepared F_2POPF_2. Tetraphenyldiphosphoxane[63] and $(CF_3)_2POP(CH_3)_2$ [9] have been postulated as unstable intermediates, but in general compounds isolated from attempted syntheses of diphosphoxanes are rearrangement and disproportionation products.[61,63]

The reaction between $[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O]$ and $Mo(CO)_5P(C_6H_5)_2Cl$ gave a dinuclear metal complex containing the previously unknown tetraphenyldiphosphoxane linkage (Eq. 46).

$$[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O] + Mo(CO)_5P(C_6H_5)_2Cl \rightarrow$$
$$Mo(CO)_5P(C_6H_5)_2OP(C_6H_5)_2Mo(CO)_5 + (C_2H_5)_3NHCl \qquad (46)$$

The μ-tetramethyldiphosphoxane-decacarbonyldimolybdenum complex was prepared by an analogous procedure (Eq. 47),

$$Mo(CO)_5P(CH_3)_2OH + Mo(CO_5P(CH_3)_2Cl + (C_2H_5)_3N \rightarrow$$
$$Mo(CO)_5P(CH_3)_2OP(CH_3)_2Mo(CO)_5 + (C_2H_5)_3NHCl \qquad (47)$$

and a mixed substituent diphosphoxane was also synthesized (Eq. 48).

$$[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O] + Mo(CO)_5P(CH_3)_2Cl \rightarrow$$
$$Mo(CO)_5P(C_6H_5)_2OP(CH_3)_2Mo(CO)_5 \qquad (48)$$

The diphosphoxane complexes are white or pale-yellow, crystalline solids which are thermodynamically and air-stable. These complexes are not soluble in non-polar organic solvents but exhibit reasonable solubility in polar solvents such as chloroform or ether.

Several observations support the structures assigned to the diphosphoxane metal complexes. The molecular weight of $Mo(CO)_5P(CH_3)_2$-$OP(CH_3)_2Mo(CO)_5$ was determined cryoscopically in benzene. Unfortunately the other complexes exhibit poor solubility in cold benzene and their molecular weights could not be determined with confidence. The mass spectrum of $Mo(CO)_5P(C_6H_5)_2OP(C_6H_5)_2Mo(CO)_5$ does not show a peak corresponding to the molecular ion; the ion with the highest m/e value was

$\{(CO)_4Mo[P(C_6H_5)_2OP(C_6H_5)_2]\}^{\cdot+}$ The ion

$\{(CO)_2Mo[P(C_6H_5)_2OP(C_6H_5)_2]\}^+$ was readily noted, and $\{Mo[P(C_6H_5)_2OP(C_6H_5)_2]\}^+$ was the most abundant ion in the mass spectrum.

The infrared spectra of the complexes in the metal carbonyl stretching region clearly indicate that the phosphorus atoms of the diphosphoxane ligand are bound to the molybdenum carbonyl moieties inasmuch as the positions and intensities of the stretching bands are as expected for a monosubstituted molybdenum carbonyl.[34] The organophosphorus ligand cannot have the isomeric structure $R_2PPR_2(O)$ inasmuch as there is no evidence of a phosphorus-oxygen stretching mode in the 1450-1100 cm^{-1} region. However, strong bands at 860, 895, and 874 cm^{-1} (Nujol) for the complexes in which the diphosphoxane is $[(C_6H_5)_2P]_2O$, $P(C_6H_5)_2OP(CH_3)_2$, and $[(CH_3)_2P]_2O$, respectively, are assignable to the P-O-P asymmetric stretching mode.[64] The phosphine oxide derivatives $(CH_3)_2P(O)OP(O)(CH_3)_2$ and $(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$ are reported to have asymmetric stretching bands at 988 and 962 cm^{-1}, respectively.[64] Bands assignable to the symmetric P-O-P stretch were also present in the spectra, but an unambiguous assignment is not possible.

Finally, apparent triplets for the methyl proton nmr signals $[Mo(CO)_5P(CH_3)_2]_2O$ and $Mo(CO)_5P(C_6H_5)_2OP(CH_3)_2Mo(CO)_5$ must arise from coupling of the methyl protons with both phosphorus nuclei in the $X_6AA'X'_6$ and $AA'X_6$ spin systems respectively.[65] The source of this coupling is discussed in greater detail in the chapter on nmr in this thesis.

In a formal sense the metal diphosphoxane complexes can be considered as anhydrides derived from the corresponding acids (Eq. 49).

$$Mo(CO)_5PR_2OPR_2Mo(CO)_5 + H_2O \rightarrow 2Mo(CO)_5(PR_2OH) \tag{49}$$

Several attempts to prepare the corresponding acid complex from $[Mo(CO)_5P(C_6H_5)_2]_2O$ failed. However, the reverse reaction proceeds readily and varying amounts of $[Mo(CO)_5P(C_6H_5)_2]_2O$ were isolated from all preparations of $Mo(CO)_5P(C_6H_5)_2OH$. Under the dehydrating conditions of heat or high vacuum or both, significant amounts of $Mo(CO)_5P(C_6H_5)_2OH$ were converted to the diphosphoxane complex. This one fact could partially account for the difficulty in obtaining analytically pure samples of $Mo(CO)_5P(C_6H_5)_2OH$.

Qualitatively, the stability of the diphosphoxane complexes $[Mo(CO)_5P(CH_3)_2]_2O$ and $[Mo(CO)_5P(C_6H_5)_2]_2O$ is the same inasmuch as both have been stored in closed vials for over a year with only minimal decomposition. The ease of formation of $[Mo(CO)_5P(C_6H_5)_2]_2O$ directly from (diphenylphosphinous acid)pentacarbonylmolybdenum may reflect the greater acidity of the diphenylphosphinous acid complex.

The thermodynamic stability of $(CF_3)_2POP(CF_3)_2$ has been considered to be a result of strong two way oxygen to phosphorus π bonding and the weakened basicity of phosphorus due to the fluorocarbon substituents which discourages formation of a phosphine oxide structure by way of an Arbusov-type rearrangement.[61] The absence of an infrared band assignable to POP asymmetric stretching in $[(CF_3)_2P]_2O$ confirms its linearity and strengthens the π bonding argument. On the other hand, the thermodynamic instability of $\{Ni_2(CO)_4[(CF_3)_2POP(CF_3)_2]\}$ provides further evidence for the low basicity of phosphorus in the bridging fluorocarbon ligand.[66] In contrast to the nickel complexes, the molybdenum carbonyl complexes prepared in this work exhibit excellent thermal stability. Presumably the basicity of phosphorus in $(C_6H_5)_2POP(C_6H_5)_2$ or $(CH_3)_2POP(CH_3)_2$ is not much different from $(C_6H_5)_3P$ or $P(CH_3)_3$ for which very stable complexes are known. The greater thermodynamic stability of the μ-tetraalkyldiphosphoxanedecacarbonylmolybdenum complexes over the μ-tetrafluoroalkyldiphosphoxane-nickel carbonyl is not surprising. The greatest factor in the stability of these molybdenum-diphosphoxane complexes must be reflected in the strength of the molybdenum-phosphorus bond, and hence the inability of these systems to undergo an Arbuzov rearrangement.

Complexes of Esters of Diphenyl- and Dimethylphosphinous Acid.

Few complexes of alkyl phosphinites and alkyl thiophosphinites, R_2POR' and R_2PSR', have been prepared directly because of the tendency for the free phosphorus ligands to rearrange. Although metal carbonyl complexes of phosphites, $P(OR_3)$, are well known, Jones and Coskran[67] were the first to prepare metal carbonyl complexes of an alkyl phosphonite, $R'P(OR)_2$; no complexes of alkyl phosphinites had been reported prior to this work. Complexes of these ligands may be prepared indirectly by exploiting the chemical reactivity of the P-Cl bond in coordinated halophosphine ligands.

The general reaction used to prepare the alkyl phosphinite is given below in Eq. 50.

$$Mo(CO)_5PR_2Cl + R'OH \rightarrow Mo(CO)_5PR_2OR' + HCl \tag{50}$$

$R = C_6H_5$ or CH_3

$R' = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_3H_7$

Alkyl thiophosphinites are prepared in similar fashion (Eq. 51).

$$\mathrm{Mo(CO)_5PR_2Cl + C_2H_5SH + N(C_2H_5)_3 \rightarrow Mo(CO)_5PR_2SC_2H_5 + (C_2H_5)_3NHCl} \tag{51}$$

$R = CH_3$, C_6H_5

The reactions of the halophosphine complexes with alcohols to give (alkyl diphenylphosphinite)- and (alkyl dimethylphosphinite)-pentacarbonylmolybdenum proceed readily in hot alcohol. The reactions with the less acidic n-propanol and iso-propanol require reflux conditions for one and a half hours. The desired products are obtained in excellent yields. The alkyl diphenylphosphinite complexes are white, low-melting solids which may be purified by recrystallization from a hydrocarbon. The alkyl dimethylphosphinites are clear or pale-yellow liquids which may be purified by distillation under high vacuum.

Both (ethyl diphenylthiophosphinite)- and (ethyl dimethylthiophosphinite)pentacarbonylmolybdenum exhibit physical properties which parallel those of the oxygen esters. However, the thioesters can be prepared only in the presence of triethylamine. This difference in reactivity may reflect a lower nucleophilicity for sulfur at phosphorus or may arise from a lack of sufficient reaction temperature in the thiol reaction medium, inasmuch as ethanethiol boils at only 35° compared to ethanol at 79°.

(Trimethylsilyl diphenylphosphinite)pentacarbonylmolybdenum was prepared by the reaction of triethylammonium diphenylphosphinitopentacarbonylmolybdenum with chlorotrimethylsilane (Eq. 52).

$$\mathrm{[(C_2H_5)_3NH][Mo(CO)_5P(C_6H_5)_2O] + (CH_3)_3SiCl \rightarrow Mo(CO)_5[P(C_6H_5)_2OSi(CH_3)_3] + (C_2H_5)_3NHCl} \tag{52}$$

The trimethylsilyl diphenylphosphinite complex is a white crystalline solid which is stable in air and readily purified by recrystallization.

All of the complexes prepared in this work were characterized by their nmr spectra; the infrared spectra of these compounds in the metal carbonyl stretching region exhibited the pattern predicted for a monosubstituted metal carbonyl.[59-61]

The reaction of $Mo(CO)_5P(CH_3)_2Cl$ with phenol proceeds in poor yield (30%), and attempts to separate $Mo(CO)_5[P(CH_3)_2OC_6H_5]$ from unreacted $Mo(CO)_5P(CH_3)_2Cl$ have been unsuccessful. The use of sodium phenoxide as a nucleophile improves the percentage of $Mo(CO)_5[P(CH_3)_2OC_6H_5]$ obtained to 55%, but complete separation of product and reactant was not possible. Even though phenol is more acidic than alkyl alcohols, phenoxide is a poorer nucleophile than alkoxide, because the negative charge on oxygen may effectively be delocalized onto the aromatic ring system[58] in phenol by any one of the resonance structures shown in Figure 4.

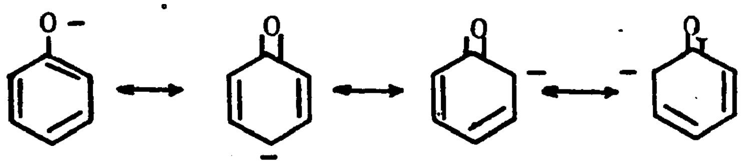


Figure 4. Resonance structures of the phenoxide anion.

Complexes of Amino Phosphines

Metal carbonyl complexes of amino derivatives of phosphorus ligands have been limited to those in which no hydrogen is bonded to nitrogen. King[68] has prepared an extensive series of complexes of $P[N(CH_3)_2]_3$; Jones and Coskran[67] have synthesized complexes of $CH_3P[N(CH_3)_2]_2$. Recently Atkinson and Smith[69] prepared several complexes with the general formula $[R_2NP(C_6H_5)_2]_nMo(CO)_{6-n}$. Significantly, they were unable to prepare $[(CH_3)_2NP(C_6H_5)_2]Mo(CO)_5$ and could prepare $[(C_2H_5)_2NP(C_6H_5)_2]Mo(CO)_5$ only under very severe conditions in a Carius tube.[69]

All attempts to prepare $H_2NP(CH_3)_2$ have led only to $NH[P(CH_3)_2]_2$, which itself easily equilibrates to NH_3 and $N[P(CH_3)_2]_3$ on mild heating.[4] The only aminophosphine obtainable by ammonolysis is $H_2NP(CF_3)_2$.[6] However, complexes of $(CH_3)_2NP(C_6H_5)_2$, $H_2NP(CH_3)_2$, and many other aminophosphine ligands not capable of independent existence have been prepared indirectly by exploiting the reactivity of the P-Cl bond with amines in coordinated halophosphine ligands.

In general, the aminophosphine complexes were prepared by the route shown in Eq. 53.

$$Mo(CO)_5PR_2Cl + 2HNR'R'' \rightarrow Mo(CO)_5PR_2NR'R'' + H_2NR'R''Cl \qquad (53)$$

R	R'	R''
C_6H_5	H	H
	H	CH_3
	CH_3	CH_3
	H	C_6H_5
CH_3	H	H
	H	CH_3
	CH_3	CH_3

The reactions proceed readily at room temperature in a variety of solvents. The aminodiphenylphosphinepentacarbonylmolybdenum complexes are all white solids which may be purified by recrystallization from ethanol. The aminodimethylphosphinepentacarbonylmolybdenum complexes are all colorless liquids, except for $Mo(CO)_5[P(CH_3)_2NH_2]$which has a melting point of 33-35°. The complexes are stable to air. Although $Mo(CO)_5[P(C_6H_5)_2N(CH_3)_2]$ could not be prepared by a direct thermal route,[69] no extraordinary difficulty was encountered in preparing this complex by the reaction of a coordinated ligand.

Special care must be taken to use extremely dry amines in the synthesis of aminophosphine complexes. The presence of water causes a different reaction to take place. For example, the reaction shown in Eq. 54

$$Mo(CO)_5P(C_6H_5)_2Cl + 2HN(CH_3)_2 \overset{H_2O}{\not\rightarrow} Mo(CO)_5[P(C_6H_5)_2N(CH_3)_2] \qquad (54)$$

does not give the desired aminophosphine derivative but instead gives an ammonium salt (Eq. 55).

$$Mo(CO)_5P(C_6H_5)_2Cl + 2HN(CH_3)_2 \overset{H_2O}{\rightarrow}$$
$$(H_2N(CH_3)_2][Mo(CO)_5P(C_6H_5)_2O] + H_2N(CH_3)_2Cl \qquad (55)$$

The reaction proceeds in even a different manner with chlorodimethylphosphinepentacarbonylmolybdenum. A wet amine does not give the desired aminophosphine derivative, nor does it give an ammonium salt of the (dimethylphosphinous acid)pentcarbonylmolybdenum, but it does give a diphosphoxane (Eq. 56).

$$2Mo(CO)_5P(CH_3)_2Cl + 2HN(CH_3)_2 \rightarrow [Mo(CO)_5P(CH_3)_2]_2O +$$
$$2NH_2(CH_3)_2Cl \qquad (56)$$

In fact, this last reaction represents a reasonable synthesis for μ-tetramethyldiphosphoxane-decacarbonyldimolybdenum inasmuch as no $Mo(CO)_5[P(CH_3)_2OH]$ need first be prepared and isolated for reaction with $Mo(CO)_5P(CH_3)_2Cl$.

The aminophosphine complexes prepared in this study are of interest for further reactions. First, the lone electron pair on nitrogen is available for reaction. The acidity of phosphorus acid derivatives of metal complexes has been discussed above; in much the same spirit, the amino derivatives should retain the base properties of the amine. Quaternary ammonium salts should be preparable as in Eq. 57.

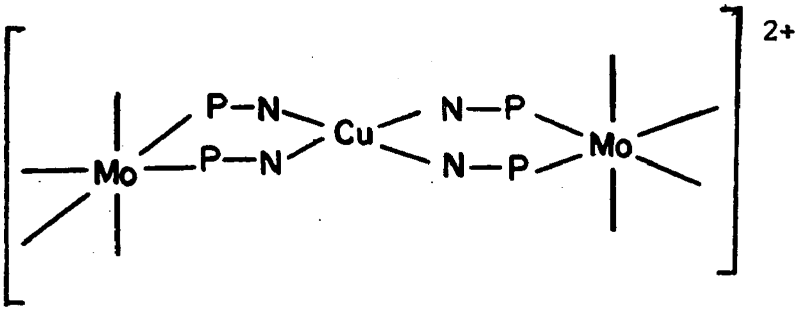
$$Mo(CO)_5[P(C_6H_5)_2N(CH_3)_2] + CH_3I \rightarrow \{Mo(CO)_5[P(C_6H_5)_2N(CH_3)_3]\}^+I^- \quad (57)$$

Ion exchange with $[(C_2H_5)_3NH][OP(C_6H_5)_2Mo(CO)_5]$ would give an unusual salt containing cationic and anionic coordinated ligands (Eq. 58).

$$\{Mo(CO)_5[P(C_6H_5)_2N(CH_3)_3]\}^+I^- + [(C_2H_5)_2NH][OP(C_6H_5)_2Mo(CO)_5] \rightarrow$$
$$\{Mo(CO)_5[P(C_6H_5)_2N(CH_3)_3]\}^{+-}\{[OP(C_6H_5)_2]Mo(CO)_5\} + H(C_2H_5)_3NI \quad (58)$$

Unusual chelating agents could be prepared. This cis-$Mo(CO)_4[PR_2NH_2]$ could coordinate to transition metal ions giving new complexes as shown in Eq. 59.

$$\underline{cis}\text{-}Mo(CO)_4(PR_2NH_2) + Cu(NO_3)_2 \longrightarrow \quad (59)$$



The electronic and steric properties of these new ligands would be investigated by standard techniques.

The complexes $Mo(CO)_5(PR_2NHR')$ could be starting materials for the P-N-P bridged metal complexes similar to the diphosphoxanes (Eq. 60).

$$Mo(CO)_5PR_2NHR' + (ClPR_2)Mo(CO)_5 \xrightarrow{amine} (CO)_5MoPR_2N(R')PR_2Mo(CO)_5 \quad (60)$$

Other reactions typical of secondary amines might also be carried out on the coordinated aminophosphine metal complex (Eq. 61).

$$Mo(CO)_5PR_2NHR' + (CH_3)_3SiCl \rightarrow Mo(CO)_5PR_2N(R')Si(CH_3)_3 \quad (61)$$

Reactions of Coordinated Phosphine Ligands with Grignard Reagents and Organolithium Compounds

Dialkyl and diarylhalophosphines react with Grignard and organolithium reagents to give trisubstituted phosphorus compounds (Eq. 62).

$$R_2PCl + \left\{\begin{matrix} R'MgX \\ R'Li \end{matrix}\right. \longrightarrow R_2PR' + \left\{\begin{matrix} MgXCl \\ LiCl \end{matrix}\right. \quad (62)$$

Conceptually, a vast number of phosphine complexes are preparable by similar reactions (Eq. 63).

$$Mo(CO)_5PR_2Cl + \left\{\begin{matrix} R'MgX \\ R'Li \end{matrix}\right. \longrightarrow Mo(CO)_5PR_2R' \quad (63)$$

However, the results of this investigation have shown that Grignard reagents react reluctantly at best with $Mo(CO)_5PR_2Cl$ to give

$Mo(CO)_5PR_2R'$, and the reaction with R'Li follows a different pathway altogether.

Grignard Reagents

The chlorophosphine metal carbonyl complexes employed in this study show little reactivity toward Grignard reagents under classical reaction conditions. Equimolar quantities of methylmagnesium iodide and $Mo(CO)_5P(C_6H_5)_2Cl$ were allowed to react for 24 hours, but only a 20% yield of $Mo(CO)_5P(C_6H_5)_2CH_3$ was obtained. Under the same conditions, $Mo(CO)_5P(C_6H_5)_2Cl$ did not react with either ethylmagnesium bromide or phenylmagnesium bromide to give the desired products. Further, $Mo(CO)_5P(CH_3)_2Cl$ did not react with any of the reagents named above to give the desired dimethyl-R'-phosphine complex.

However, two ways were found to improve the yields of the desired products in the Grignard reaction. First, a 10:1 molar ratio of Grignard reagent to metal complex was employed. The reaction mixture was heated at reflux for one hour after the addition of the metal complex to the Grignard solution was completed. No significant differences in the yields of products were observed when either diethyl ether or tetrahydrofuran was used as a reaction solvent. Using this method of synthesis the pentacarbonylmolybdenum complexes of diphenylmethylphosphine, diphenylethylphosphine, and diphenylisopropylphosphine were obtained in better than 25% yield after reaction times of about one hour.

A second method which improved the yield of the desired Grignard product was the addition of copper(I) chloride to the organomagnesium halide prior to adding the reactive metal complex. In this way the pentacarbonylmolybdenum complexes of diphenylmethylphosphine, dimethylphenylphosphine, and trimethylphosphine were prepared in 40% yield. Other phosphine derivatives should be readily preparable in reasonable yield by this method.

Organic chemists have used cuprous chloride as a catalyst for the addition of Grignard reagents across double bonds.[70,71] Gilman[72] obtained methylcopper as a yellow, ether-insoluble, apparently polymeric solid $(CH_3Cu)_n$. However, in the presence of methyllithium, a complex is formed (Eq. 64).

$$(CH_3Cu)_n + CH_3Li \xrightarrow{Et_2O} (CH_3)_2Cu(OEt_2)_2Li \qquad (64)$$

On the basis of nmr exchange studied House et al.[71] suggested that the above equilibrium lies far to the right. Presumably, a similar equilibrium exists with CH_3MgI (Eq. 65):

$$(CH_3Cu)_n + CH_3MgI \rightleftharpoons (CH_3)_2Cu(OEt_2)_2MgI \qquad (65)$$

The overall lack of reactivity of coordinated phosphine ligands with Grignard reagents warrants some discussion. First of all, compounds of the type R_2PCl and $R_2P(O)Cl$ both react readily with Grignard reagents to give R_2PR' and $R_2P(O)R'$, respectively. The differences in reactivity between a trivalent halophosphine and its metal carbonyl complex apparently are not related directly to a change in the coordination number of phosphorus from three to four. The lack of reactivity of the phosphorus-chlorine bond with Grignard reagents upon complexation must then reflect some difference in phosphorus due to bonding with a transition metal. The nature of the Grignard reagent must also be considered. One of the most important characteristics of organomagnesium compounds is the polar nature of the carbon-metal bond. Although this does give the alkyl group considerable carbanion character, the bond also has definite covalent character. Further, typical solvents for Grignard reactions are of low ion-solvating power. These facts make Grignard reactions more complicated than a simple combination of carbanions with a suitable reactive site.[73]

A typical Grignard reaction with an organic ketone is shown in Figure 5. The action of magnesium as a Lewis acid by coordinating with the carbonyl oxygen atom is an important factor in the reaction.[73] It has been suggested that one molecule of Grignard reagent coordinates to the ketone while a second donates the alkyl group to the carbonyl carbon. Evidence for this interpretation was presented by Swain[74], who showed that the addition of magnesium bromide, which should coordinate more strongly to a carbonyl group than a Grignard reagent, doubles the yield of addition product in the reaction of n-propylmagnesium bromide with diisopropyl ketone.

Clearly, the lone electron pair on phosphorus in its trivalent compounds may also coordiante to the magnesium atom in a Grignard reagent and reaction can occur. Compounds such as $R_2P(O)Cl$ may coordinate to the Grignard reagent through the phosphoryl oxygen in a fashion similar to that suggested for organic ketones. On the other hand, a phosphine ligand of the type R_2PCl coordinated to a transition metal carbonyl moiety is no longer capable of coordination to the Grignard reagent through phosphorus. The coordinated phosphorus atom probably behaves as a Lewis acid by use of its low-lying 3d orbitals. Reaction

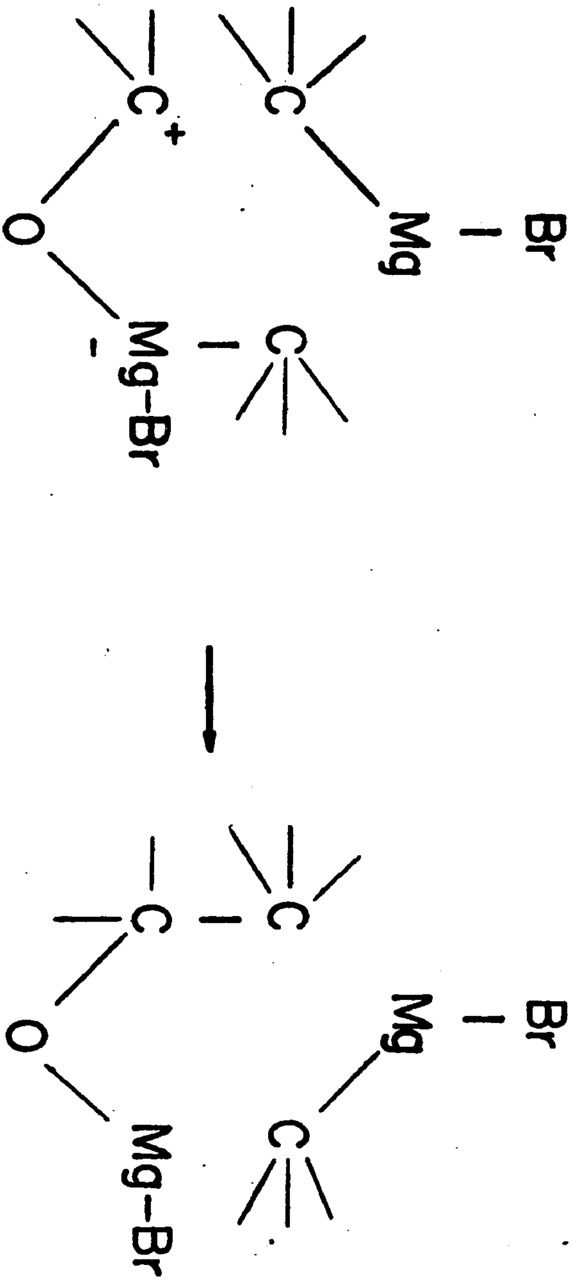


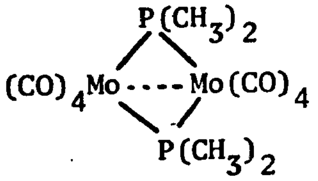
Figure 5. Proposed mechanism of reaction between a Grignard reagent and a ketone.

of the coordinated phosphine ligand with a Grignard reagent must occur through an intermediate coordinated to magnesium via the chloride on phosphorus or even by coordination through a carbonyl group on molybdenum cis to the reacting ligand. The addition of CuCl to the Grignard reagent generates the complex $\{(CH_3)_2Cu(ether)_2\}^-$. The charge on the ion should reside mostly on copper making it a reasonably good nucleophile, and the formation of a phosphorus-copper bonded intermediate which can decompose to the desired product is not unlikely. The low yields obtained in these reactions may also reflect a steric problem encountered at phosphorus. If the mechanism involving two molecules of Grignard reagent for addition at a carbonyl carbon atom may be applied to the reactions at coordinated phosphorus, manifestation of a steric problem is not difficult to envision. The phosphorus atom, coordinated to a large transition metal carbonyl moiety, bonded to two alkyl or aryl groups, and already entertaining a solvent coordinated copper complex, must also be approached by a second Grignard reagent for the transfer of the alkyl group.

Two unexpected products were also obtained from the reaction of $Mo(CO)_5P(CH_3)_2Cl$ and $Mo(CO)_5P(C_6H_5)_2Cl$ with Grignard reagents. When $Mo(CO)_5P(CH_3)_2Cl$ was allowed to react with CH_3MgI under classical conditions, a small yield of $(CO)_5MoP(CH_3)_2P(CH_3)_2Mo(CO)_5$ was obtained. In a similar fashion, $(CO)_5MoP(C_6H_5)_2P(C_6H_5)_2Mo(CO)_5$ was obtained from $Mo(CO)_5P(C_6H_5)_2Cl$ and C_2H_5MgBr.

μ-Tetramethylbiphosphine-decacarbonylmolybdenum has been synthesized by the reaction of $Mo(CO)_6$ with $(CH_3)_4P_2$.[44] However, attempts to synthesize $(CO)_5MoP(C_6H_5)_2P(C_6H_5)_2Mo(CO)_5$ with a bridging

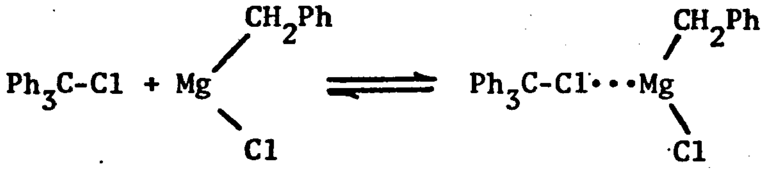
$(C_6H_5)_2PP(C_6H_5)_2$ ligand have lead only to a product with bridging diphenylphosphido-groups.[44,75]



The mechanism by which the bridging phosphine complexes were formed in this study is unclear. The complexes are formed in low yield, and even this yield depends strongly on reaction conditions. The amount of product formed decreases markedly with long reaction times, increased reaction temperature, and acid hydrolysis of the reaction mixture. The effect of light on the reaction has not been considered. A large number of reactions of Grignard reagents with organic halides such as in the equation below, are known to yield products attributable to free readical intermediates, but the mode of formation of the radical intermediates has not yet been explained any more clearly than that suggested by an "oxidation-reduction" process by Kharasch[76] in Eq. 66.

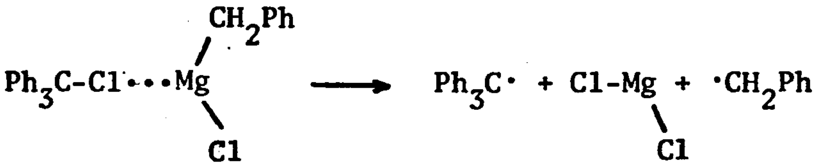
$$C_6H_5CH_2Cl + CH_3MgI \rightarrow C_6H_5CH_2CH_2C_6H_5 + CH_4 + C_2H_6 + C_2H_4 + C_6H_5CH_2CH_3 \quad (66)$$

Recently, the reaction of benzylmagnesium chloride with triphenylmethyl chloride has been examined.[77] Significant quantities of $(C_6H_5)_3CC(C_6H_5)_3$ and 1,2-diphenylethane were found in the reaction mixtures. Also, an esr signal was observed during the reaction of benzylmagnesium chloride with trityl chloride which was not present in the esr spectra of the reagents. The authors[77] suggested a mechanism with a free-radical species present to account for their observations (Eq. 67-71).



$$Ph_3C\text{-}Cl + Mg\overset{CH_2Ph}{\underset{Cl}{}} \rightleftharpoons Ph_3C\text{-}Cl\cdots Mg\overset{CH_2Ph}{\underset{Cl}{}} \qquad (67)$$

(I) (II) (III)



$$Ph_3C\text{-}Cl\cdots Mg\overset{CH_2Ph}{\underset{Cl}{}} \longrightarrow Ph_3C\cdot + Cl\text{-}Mg\underset{Cl}{} + \cdot CH_2Ph \qquad (68)$$

(III)

$$Ph_3C\cdot + \cdot CH_2Ph \rightarrow Ph_3C\text{-}CH_2Ph \qquad (69)$$

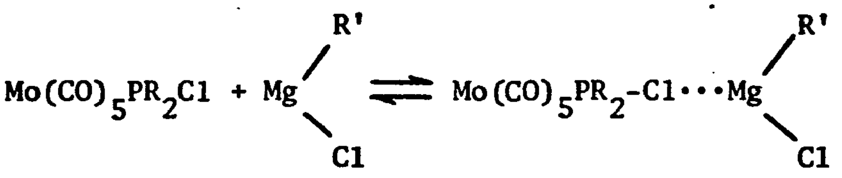
$$Ph_3C\cdot + \cdot CPh_3 \rightarrow Ph_3C\text{-}CPh_3 \qquad (70)$$

$$PhCH_2\cdot + \cdot CH_2Ph \rightarrow PhCH_2\text{-}CH_2Ph \qquad (71)$$

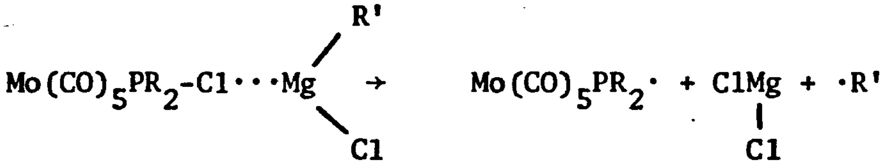
The proposed pathway suggests that on mixing the two reactants the organic halide associates with the Grignard reagent in a fast step through the partially negatively charged chlorine and partially positively charged magnesium atoms. The authors also suggest[77] that this association should polarize the carbon-chlorine and magnesium-carbon bonds further. The complex (III) may break down by the formation of radical species, and the stability of the resultant radicals, which is related to the ease of their formation, controls the rate of the reaction[77].

An analogy between the organic reactions discussed above and the formation of bridged-phosphine metal carbonyls is compelling.

A mechanism for the formation of the complexes is proposed in Eq. 72-76.



$$\mathrm{Mo(CO)_5PR_2Cl} + \underset{\mathrm{Cl}}{\overset{\mathrm{R'}}{\mathrm{Mg}}} \rightleftharpoons \mathrm{Mo(CO)_5PR_2\text{-}Cl\cdots}\underset{\mathrm{Cl}}{\overset{\mathrm{R'}}{\mathrm{Mg}}} \qquad (72)$$



$$\mathrm{Mo(CO)_5PR_2\text{-}Cl\cdots}\underset{\mathrm{Cl}}{\overset{\mathrm{R'}}{\mathrm{Mg}}} \rightarrow \mathrm{Mo(CO)_5PR_2}\cdot + \mathrm{Cl}\underset{\mathrm{Cl}}{\mathrm{Mg}} + \cdot\mathrm{R'} \qquad (73)$$

$$2\ \mathrm{Mo(CO)_5PR_2}\cdot \rightarrow \mathrm{Mo(CO)_5PR_2PR_2Mo(CO)_5} \qquad (74)$$

$$2\mathrm{R'}\cdot \rightarrow \mathrm{R'R'}$$

$$\mathrm{Mo(CO)_5PR_2}\cdot + \mathrm{R'}\cdot \rightarrow \mathrm{Mo(CO)_5PR_2R}\cdot \qquad (76)$$

This mechanism is useful for several reasons. First, it rationalizes the formation of $\mathrm{Mo(CO)_5PR_2PR_2Mo(CO)_5}$. It also accounts for the formation of $\mathrm{Mo(CO)_5PR_2R'}$, of which a small quantity is obtained in this reaction. The low yields of products obtained might reflect a very weak interaction between the Grignard reagent and the chlorophosphine complex in Eq. 72. Subsequently, even the small concentration of activated complex formed in reaction 72 must still give rise to radical species in reaction 73, the presumed slow step of the reaction.

The speculation above has no undisputable experimental support. However, several means are available to the chemist to further investigate the nature of this proposed free-radical reaction. Obviously, esr experiments are in order for this mixture of reactants. Also, an nmr experiment focusing on the phenomenon of chemically induced dynamic nuclear polarization (CIDNP) would help to determine the presence of free radicals.[78] Further, the presence of radical scavengers, such as Ce^{3+}, could lower the yield of bridged product if a free radical mechanism is important.

An attempt to prepare $Mo(CO)_5P(C_6H_5)_2P(C_6H_5)_2Mo(CO)_5$ by the reaction between $Mo(CO)_5P(C_6H_5)_2Cl$ and $Mo(CO)_5P(C_6H_5)_2H$ failed (Eq. 77).

$$Mo(CO)_5P(C_6H_5)_2Cl + Mo(CO)_5P(C_6H_5)_2H + N(C_2H_5)_3 \nrightarrow$$

$$Mo(CO)_5P(C_6H_5)_2P(C_6H_5)_2Mo(CO)_5 + (C_2H_5)_3NHCl \qquad (77)$$

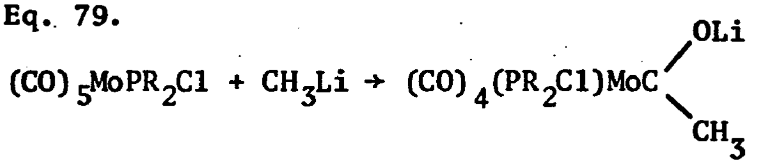
The reasons for the lack of success for this reaction may be extensive, but several points are inviting. First, neither reactant is by itself a nucleophile. Presumably, $Mo(CO)_5P(C_6H_5)_2H$ is acidic enough to react with $N(C_2H_5)_3$ to give a nucleophile (see "General Discussion" below) (Eq. 78),

$$Mo(CO)_5P(C_6H_5)_2H + N(C_2H_5)_3 \quad [Mo(CO)_5P(C_6H_5)_2]^- + NH(C_2H_5)_3^+ \qquad (78)$$

but the nucleophile generated may be too large to attack another coordinated phosphine ligand. The fact that diphenylamine, $(C_6H_5)_2NH$ did not react with $Mo(CO)_5P(C_6H_5)_2Cl$ although aniline $(C_6H_5NH_2)$ readily gave a product, supports a steric argument against reaction. On the other hand, the two radical species, $Mo(CO)_5P(C_6H_5)_2\cdot$, need not form an activated complex but can combine directly to form $[Mo(CO)_5P(C_6H_5)_2]_2$.

Organolithium Compounds

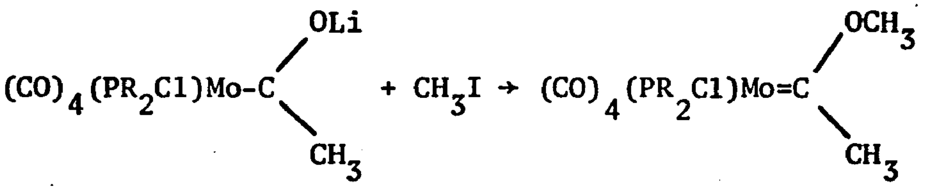
Methyllithium does not seem to react with coordinated phosphine ligands in the classic organic sense. Methyllithium reacts with $Mo(CO)_5PR_2Cl$ apparently to yield a carbene complex as shown in Eq. 79.



$$(CO)_5MoPR_2Cl + CH_3Li \rightarrow (CO)_4(PR_2Cl)Mo\overset{OLi}{\underset{CH_3}{C}} \tag{79}$$

The intermediate lithium salts were obtained as pyrophoric yellow solids. The infrared spectra of these complexes in the metal carbonyl stretching region clearly indicated the presence of cis-disubstituted metal carbonyl complexes.

Attempts to prepare esters of the carbene salts with CH_3I and $CH_3OS(F)O_2$ led to the formation of malodorous red oils



$$(CO)_4(PR_2Cl)Mo\text{-}\overset{OLi}{\underset{CH_3}{C}} + CH_3I \rightarrow (CO)_4(PR_2Cl)Mo{=}\overset{OCH_3}{\underset{CH_3}{C}} \tag{80}$$

The infrared spectra of these oils obtained after chromatography on alumina suggest the products to be cis-disubstituted-tetracarbonylmolybdenum complexes.

Organolithium reagents have been shown to exhibit greater carbanion character in the presence of strong chelating amines. Of great interest is the possibility that coordinated phosphine ligands might react in the classical sense with alkyllithium reagents with such a chelating agent present.

$$\begin{aligned} &Mo(CO)_5PR_2Cl + \{Li[N(CH_3)_2CH_2CH_2N(CH_3)_2]\}^+[CH_3]^- \rightarrow \\ &\qquad Mo(CO)_5PR_2CH_3 \end{aligned} \tag{81}$$

Reactions of Coordinated Phosphine Ligands with Sodium Cyclopentadienide

Sodium cyclopentadienide, NaC_5H_5, is a reagent well-known to organometallic chemists as a precursor to π-cyclopentadienyl-metal complexes. In recent years cyclopentadiene rings sigma-bonded to various metals have been of intense interest to inorganic chemists. Several compounds are known in which the nmr spectrum of the σ-bonded ring suggests that all the cyclopentadiene protons are equivalent.[79] Molecules in which rapid site exchange causes configurations in which the nuclei are magnetically equivalent are said to be fluxional. Also, certain cyclopentadienyl-group IV compounds react with metal carbonyls to give products in which the ring becomes π-bonded to the metal and the group IV moiety becomes sigma bonded to the metal,[80] or in other cases the entire moiety is π-bonded to the metal.[81]

$$Mo(CO)_3(NCCH_3)_3 + (CH_3)_3SnC_5H_5 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3Sn(CH_3)_3 \quad ^{80} \qquad (82)$$

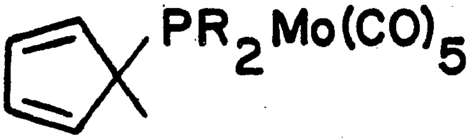
$$Mo(CO)_6 + (CH_3)_3SiC_5H_5 \rightarrow \{\pi\text{-}[(CH_3)_3SiC_5H_4]Mo(CO)_3\}_2 \quad ^{81} \qquad (83)$$

The complexes of the type $Mo(CO)_5(PR_2C_5H_5)$ were of particular interest for two reasons. First, the σ-bonded ring might be expected to react with the metal carbonyl in some way to form a π-C_5H_5 complex. It was also of interest to determine whether a large $Mo(CO)_5PR_2$- group would undergo site exchange on the π-C_5H_5 ring.

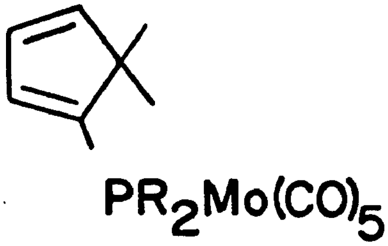
The reaction between $Mo(CO)_5PR_2Cl$ and NaC_5H_5 was carried out by adding the NaC_5H_5 solution to a solution of coordinated phosphine ligand. (Chlorodiphenylphosphine)pentacarbonylmolybdenum gave two products upon reaction with NaC_5H_5. The expected product, $Mo(CO)_5[P(C_6H_5)_2C_5H_5]$, was obtained as a white, crystalline solid. The second complex obtained from the same reaction analyzed for $[Mo(CO)_5P(C_6H_5)_2]_2C_5H_4$. The same reaction with $Mo(CO)_5P(CH_3)_2Cl$ gave at least three products which were separated by column chromatography on alumina. All products were obtained as oils. The first to be eluted from the column was formulated as $Mo(CO)_5[P(CH_3)_2C_5H_5]$ on the basis of its nmr spectrum. The second oil obtained is probably $[Mo(CO)_5P(CH_3)_2]_2C_5H_4$, but a sample sufficiently pure for analysis was not obtained. The nature of the third component is not known at this time.

Structural assignments for the two $Mo(CO)_5(PR_2C_5H_5)$ compounds, where R = CH_3 or C_6H_5, are based on the following information. First, each $Mo(CO)_5P(C_6H_5)_2C_5H_5$ product gave a correct analysis for carbon and hydrogen. Secondly, both $Mo(CO)_5PR_2C_5H_5$ complexes exhibited features in the infrared metal carbonyl stretching region characteristic of $Mo(CO)_5L$ complexes. Finally, the nmr spectrum of $Mo(CO)_5P(CH_3)_2C_5H_5$ gave resonances at expected field strengths and of proper intensity for a $-P(CH_3)_2C_5H_5$ moiety. The $P(CH_3)_2$ resonance appears as a doublet at $\delta 1.68$, J(HP) = 7.0 Hz. A complex multiplet at $\delta 6.58$ (3 protons) is assigned to the vinyl protons, and a broad singlet at $\delta 3.16$ (2 protons) is assigned as the methylene resonance of the cyclopentadiene ring. The nmr spectrum of $Mo(CO)_5P(C_6H_5)_2C_5H_5$ is complicated by overlapping phenyl and vinyl proton regions.

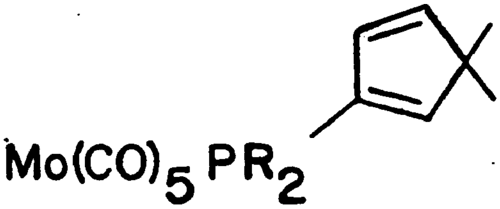
Several structures are possible for the $Mo(CO)_5PR_2C_5H_5$ complexes (Fig. 6). However, assignment of structure <u>C</u> to these complexes



A



B

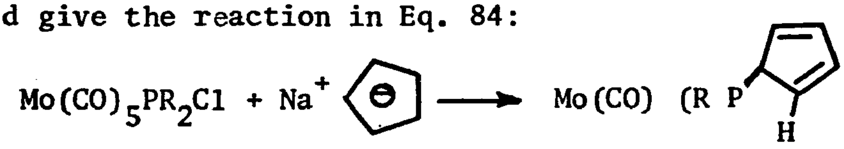


C

Figure 6. Possible isomers of $Mo(CO)_5(PR_2C_5H_5)$, R = CH_3 or C_6H_5.

is favored at the present time. The nmr spectrum of $Mo(CO)_5P(CH_3)_2C_5H_5$ demands a 3:2 ratio for the vinyl: methylene protons of the C_5H_5 ring, hence structure A is ruled out. Both isomers B and C give rise to the 3:2 proton ratio in the nmr spectrum. However, the spectrum of B should be further complicated since phosphorus should split the methylene protons of the ring into a doublet inasmuch as the interacting nuclei are separated by only three bonds. The absence of strong coupling in the methylene resonance is taken as direct evidence for the presence of isomer C.

The nmr spectrum of $Mo(CO)_5[P(C_6H_5)_2C_5H_5]$ shows no changes over a temperature range of -30° to + 100°. Presumably, the cyclopentadienyl ring has no fluxional character in this metal carbonyl complex. However, the metal complex must undergo some rearrangement to arrive at the assigned structure C. Direct reaction between $Mo(CO)_5PR_2Cl$ and NaC_5H_5 would give the reaction in Eq. 84:



(84)

The phosphorus atom initially must share a carbon atom with hydrogen. Subsequent rearrangement to isomer C may occur by a number of processes and will not be discussed in this thesis.

The second product obtained in the reaction of $Mo(CO)_5P(C_6H_5)_2Cl$ with NaC_5H_5 is also of interest. The high-melting complex is formulated as $[Mo(CO)_5P(C_6H_5)_2]_2C_5H_4$ with a bridging cyclopentadienyl group. A bridging cyclopentadienyl group is not unknown in organometallic chemistry. Hoxmeier et al.[82] reported a mixed molybdenum-manganese complex containing a bridging C_5H_4 group:

$$(C_5H_5)_2MoH_2 + CH_3Mn(CO)_5 \rightarrow C_5H_5(CO)Mo\text{-}\mu\text{-}C_5H_4\text{-}Mn(CO)_4 + CH_4 + H_2 \quad (85)$$

The metals were bonded to the C_5H_4 ring as shown in Figure 7.

Fischer et al.[83] synthesized a palladium complex containing a bridging cyclopentadienyl group.

$$PdBr_2 + 4NaC_5H_5 + C_5H_6 \rightarrow Pd_2(C_5H_5)_2C_5H_6 \qquad (86)$$

These authors were unable to unequivocally assign the points of attachment of the cyclopentadienyl ring to the palladium atoms, however.

The nmr spectrum of $[Mo(CO)_5P(CH_3)_2]_2C_5H_4$ shows a triplet for the methyl groups on phosphorus. This triplet structure for the methyl resonance is characteristic of methyl groups in the presence of two phosphorus atoms coupled to each other. No methylene resonances were observed for this compound. On the basis of these observations the best structural assignment for these complexes is shown in Figure 8. This structure has the protons of the C_5H_4 ring in a vinyl environment, and the two phosphorus atoms are close enough to allow virtual coupling.

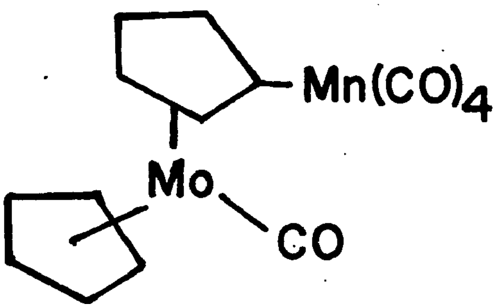


Figure 7. Crystal structure of $C_5H_5(CO)Mo$-μ-C_5H_4-$Mn(CO)_5$.

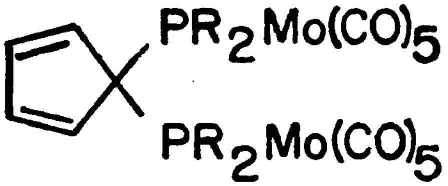


Figure 8. Proposed structure for $Mo(CO)_5PR_2$-μ-C_5H_4-$PR_2Mo(CO)_5$.

GENERAL DISCUSSION

Many of the complexes prepared in this study contain organophosphorus ligands which have not been reported to exist in the free state or are known to be thermodynamically unstable with respect to rearrangement to a four-covalent phosphorus (V) compound. In particular, $(CH_3)_2POCH_3$ has been reported to rearrange to $(CH_3)_3PO$,[7] and all the compounds $(CH_3)_2POH$, $(CH_3)_2PSH$, $(CH_3)_2PNH$, $(CH_3)_2PNH(CH_3)$, $(CH_3)_2POP(CH_3)_2$, $(C_6H_5)_2POH$, $(C_6H_5)_2PSH$, $(C_6H_5)_2PNH_2$, $(C_6H_5)_2POP(C_6H_5)_2$, and $(C_6H_5)_2POP(CH_3)_2$ are previously unknown.

In addition to leading to complexes of thermodynamically unstable ligands, the reactions of coordinated phosphine ligands as employed in this study open a new, useful synthetic pathway to organometallic chemists. Several of the most attractive features of this method of synthesis are listed below:

1. Complexes of thermodynamically unstable phosphine ligands may be readily prepared.
2. A single halophosphine complex can be the starting material for a vast number of phosphorus complexes of a given transition metal. Only the desired halophosphine need be synthesized, and the appropriate complex may be prepared in bulk quantities.
3. Low molecular weight alkyl phosphines are extremely toxic.[84] The use of a precomplexed phosphine ligand minimizes the need for handling toxic material. Further, the preparation of many phosphines often requires utilization of difficult, time-consuming syntheses.

4. Most phosphines are air-sensitive and must be stored individually under a protective atmosphere of dry nitrogen. In contrast, the halophosphine complex needs only to be protected from direct sunlight and atmospheric moisture. The solid complexes are also readily weighed and transferred.

5. Reactions proceed with recovery of product in excellent yield, even when only one- to two-gram quantities of complex are reacted. Hence, the process developed here is relatively inexpensive in terms of the quantities of reagents required to obtain sufficient amounts of complexes for physical measurements.

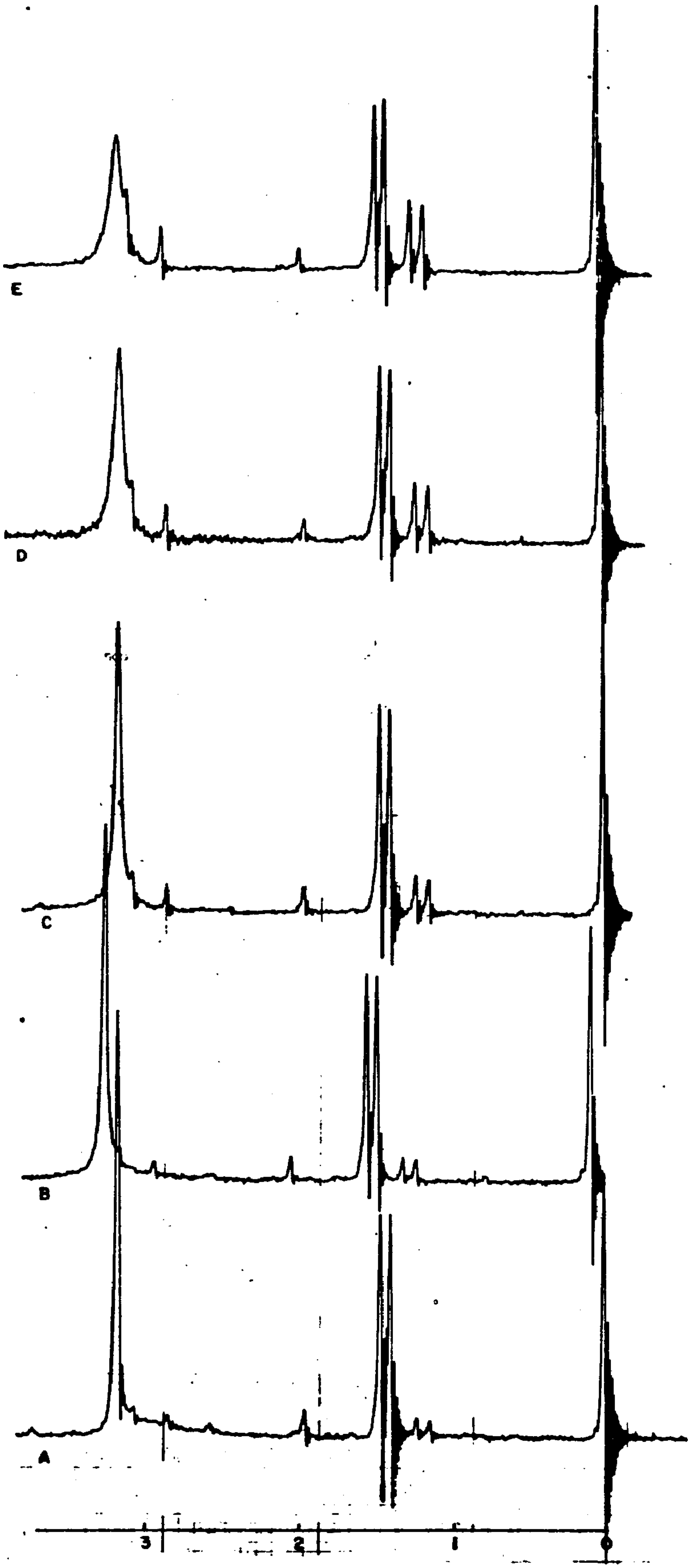
6. Finally, thermal substitution reactions and photochemical syntheses can often lead to mixtures containing more highly substituted products and thermal or photochemical decomposition products as well as the desired product. The reactions of coordinated ligands proceed without any significant side reactions. Product isolation is uncomplicated, and no unseparable mixtures of complex and ligand are obtained as in some classical syntheses.[45]

A decrease in the reactivity of the phosphorus-fluorine bond in transition metal complexes of several fluorophosphines compared to the free phosphine has been noted.[23,24] A lower reactivity for the phosphorus-chlorine bond in the chlorophosphinepentacarbonylmolybdenum complexes prepared here compared to the uncomplexed phosphines has also been observed. To qualitatively illustrate the decreased reactivity of the complexes, the relative rates of cleavage of the phosphorus-chlorine bond in $(C_6H_5)_2PCl$, $Mo(CO)_5P(C_6H_5)_2Cl$, and $Mo(CO)_5P(CH_3)_2Cl$ were examined. Equimolar amounts of the phosphine or halophosphine complex and methanol were dissolved in benzene, and the methanolysis was followed by proton nmr.

Conversion of all the $(C_6H_5)_2PCl$ to $(C_6H_5)_2POCH_3$ was complete within the time required to prepare the sample and record its spectrum, *i.e.* less than five minutes. On the other hand, the rate of reaction of the complexes was very much slower and was followed for a period of several days. The reaction of $Mo(CO)_5P(CH_3)_2Cl$ with methanol was most easy to follow. As $Mo(CO)_5[P(CH_3)_2OCH_3]$ was formed, a doublet upfield from the $P\underline{CH_3}$ resonance of the chloro-complex appeared due to the $P\underline{CH_3}$ resonance of the methyl dimethylphosphinite complex. The doublet due to the $PO\underline{CH_3}$ resonance was partially obscured by the $\underline{CH_3}$ resonance of CH_3OH. A series of spectra showing this reaction is reproduced in Figure 9. Even after 48 hr the reaction is only about half completed. The same reaction using $Mo(CO)_5P(C_6H_5)_2Cl$ and CH_3OH was half complete in about 24 hr. Thus, the relative rates of methanolysis follow the order $(C_6H_5)_2PCl >> Mo(CO)_5P(C_6H_5)_2Cl > Mo(CO)_5$-$P(CH_3)_2Cl$. In general, chlorophosphines and phosphoryl chlorides, R_2PCl and $R_2P(O)Cl$, respectively, react with alcohols at comparable rates. Seemingly then, differences in reactivity of the free ligand and complexed ligand are not related directly to a change in the coordination number of phosphorus from three to four. The significant change in rate upon complexation must reflect a major difference between the phosphorus-oxygen and phosphorus-molybdenum bonds. Removal of electron density on molybdenum by phosphorus through $d\pi$-$d\pi$

Figure 9. Time dependent proton NMR spectra of the reaction between methanol and $Mo(CO)_5P(CH_3)_2Cl$. The doublet arising from the $P(CH_3)_2$-resonance of $Mo(CO)_5P(CH_3)_2Cl$ (ca. 1.5 ppm) decreases with time as the upfield $P(CH_3)_2$-resonance due to $Mo(CO)_5P(CH_3)_2OCH_3$ grows. The doublet due to the $POCH_3$ resonance (near 3 ppm) is partially obscured by the CH_3-resonance of unreacted methanol.

Reaction times: A 3½ hr
B 5½ hr
C 9½ hr
D 21½ hr
E 27 hr

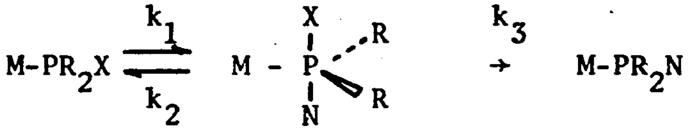

E
D
C
B
A
3
2
1
0

bonding with molybdenum will make the 3d levels less available for forming a five coordinate intermediate in a presumed S_N2 rate determining step at phosphorus. No evidence was obtained for dissociation of the molybdenum-phosphorus bond.

A small degree of oxygen-phosphorus $p\pi$-$d\pi$ bonding has been postulated in order to rationalize the rates of reaction of several phosphoryl fluorides,[85] $R_2P(O)F$. The rate of nucleophilic displacement of fluoride from $(C_2H_5)_2P(O)F$ by hydroxide was observed to be much greater than for $(C_2H_5O)(C_2H_5)P(O)F$ and $(C_2H_5O)_2P(O)F$. When the groups on phosphorus are ethoxy, the empty d orbitals on phosphorus are partially occupied as a result of pi bonding with the filled p orbitals on oxygen. Therefore, less bonding is possible between the incoming nucleophile and the phosphorus atom.[85] Since π bonding in these systems is expected to be much less than in the metal complexes, the marked decrease in reaction rate is not surprising.

Another factor in the rate of hydrolysis or esterification at a coordinated phosphine ligand which must be considered is the steric effect of the large pentacarbonylmolybdenum group. Precise analysis of the mechanism of the reactions of coordinated phosphine ligands must be based upon complete kinetic studies of the metal complexes. However, some speculation is not inappropriate at this time. First, the effect of the size of the metal coordinated to phosphorus upon the rates of reaction might be evaluated. A series of complexes with a particular chlorophosphine ligand could be prepared with a variety of metal carbonyls or transition metals each differing in size or stereochemistry: $Mo(CO)_5$-, $Fe(CO)_4$-, Ir(CO)Cl(L)-, $Ni(CO)_3$-, and CuCl-.

Second, the actual mechanism by which the reactions of coordinated phosphines takes place is of interest. The qualitative rate experiment described above in this thesis is consistent with either an S_N1 or an S_N2 mechanism at phosphorus. Therefore, extensive kinetic studies must be undertaken to discover the actual mechanism. However, most displacement reactions at phosphorus are second order reactions,[85] and the reaction of a coordinated phosphine ligand will most likely be found to proceed <u>via</u> an S_N2 mechanism also. Since displacement on phosphorus does depend on nucleophilic basicity, some interaction between the nucleophile and an open orbital must exist.[85] Interaction of nucleophile and an open d orbital may merely be a stabilization of an S_N2 transition state. This would lower the activation energy for the reaction since bond formation would be well developed before bond breaking became significant. On the other hand, the interaction of nucleophile and orbital could be strong enough to give a definite intermediate with a trigonal-bipyramid structure. Reaction would be of the type shown in Eq. 87.



$$M\text{-}PR_2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M - \overset{X}{\underset{N}{P}}R_2 \xrightarrow{k_3} M\text{-}PR_2N \qquad (87)$$

When $k_3 >> k_2$ the formation of the intermediate is rate-determing and the rate should depend on the strength of the nucleophile.[85] When $k_2 >> k_3$, the breakdown of the intermediate to give product is rate-determining and the nature of the leaving-group becomes important.[85]

Third, the role of acid catalysis must be examined inasmuch as HCl is generated by the methanolysis of the chlorophosphine complexes.

This HCl could force the equilibrium in Eq. 88 to the left.

$$ROH \rightleftharpoons RO^- + H^+ \quad (88)$$

and hence lower the rate of methanolysis. The presence of a base such as pyridine could also affect the rate by shifting the alcohol equilibrium to the right and hence increase the rate, or it could lower the rate by behaving as a competing nucleophile at phosphorus and cause k_2 to assume greater importance.

Although the synthetic utility of reactions of coordinated phosphine ligands enjoys several advantages over more classical synthetic routes, some limitations of this technique have been encountered. In particular, the $Mo(CO)_5PR_2Cl$ compounds employed here show little reactivity toward Grignard reagents under classical reaction conditions as described earlier. Attempts to prepare the complexes $Mo(CO)_5P(C_6H_5)_2H$ and $Mo(CO)_5P(CH_3)_2H$ by reduction of the appropriate $Mo(CO)_5PR_2Cl$ compound failed. Also, several attempts to convert the chlorophosphine complexes into the fluorophosphine complexes (Eq. 89-90) <u>via</u> reaction with antimony trifluoride were unsuccessful

$$4Mo(CO)_5PR_2Cl + LiAlH_4 \rightarrow 4Mo(CO)_5(PR_2H) + LiAlCl_4 \quad (89)$$

$$3Mo(CO)_5PR_2Cl + SbF_3 \rightarrow 3Mo(CO)_5(PR_2F) + SbCl_3 \quad (90)$$

Both R_2PCl and $R_2P(O)Cl$ react readily with $LiAlH_4$ and SbF_3 to form the corresponding phosphines and fluorophosphines, respectively. Thus, as was the case with Grignard reactions, the differences in reactivity between the free ligand and the coordinated ligand with $LiAlH_4$ and SbF_3 are not directly related to a change in the coordination number of phosphorus from three to four. The lack of reactivity of the coordinated phosphine ligand must reflect some significant aspect of the phosphorus-molybdenum bond. The 3d electronic levels of phosphorus are involved in π-bonding with molybdenum making formation of intermediates suitable for decomposition into products difficult. The Li^+ and AlH_4^- ions in $LiAlH_4$ interact with considerable covalent character.[86] Further, AlH_4^- is expected to be a poor nucleophile inasmuch as the charge on the ion may be distributed over four hydrogen atoms. Antimony trifluoride is only weakly basic. The inductive effect of three fluorine atoms greatly reduces the dipole at antimony making the lone pair relatively unavailable for coordination to phosphorus in an activated complex. Presumably, halophosphines react with SbF_3 through the lone pair on phosphorus (or pairs on the phosphoryl oxygen for the corresponding oxides) in the formation of fluorophosphines.

Several halophosphine complexes have been prepared by the reaction of coordinated phosphine ligands, however. The preparation of $Mo(CO)_5PCl_3$ by the reaction of $Mo(CO)_5P[N(CH_3)_2]_3$ with HCl was discussed in the Introduction to this thesis.[26] Bromo- and iodophosphine complexes may be prepared similarly as shown in Eq. 91-93.[26]

$$Mo(CO)_5P[N(CH_3)_2]_3 + 6HCl \rightarrow Mo(CO)_5PCl_3 \tag{91}$$

$$Mo(CO)_5P[N(CH_3)_2]_3 + 6HBr \rightarrow Mo(CO)_5PBr_3 \tag{92}$$

$$Mo(CO)_5P[N(CH_3)_2]_3 + 4HI \rightarrow Mo(CO)_5[N(CH_3)_2PI_2] \tag{93}$$

The same type of procedure[87] has led to the formation of mixed halogen halophosphine complexes as shown in Eq. 94.

$$Mo(CO)_5[PF_2N(C_2H_5)_2] + 2HBr \rightarrow Mo(CO)_5PF_2Br + C_2H_5NH_2Br \tag{94}$$

Recently Höfler[88] reported the formation of fluoro complexes by displacement of diethylamino groups. The degree of substitution can be controlled by choosing appropriate fluorinating agents as illustrated in Eq. 95-96.

$$\pi\text{-}C_5H_5Mn(CO)_2\ C_6H_5P[N(C_2H_5)_2]_2 + 4HF \rightarrow \pi\text{-}C_5H_5Mn(CO)_2(C_6H_5PF_2) \quad (95)$$

$$C_5H_5Mn(CO)_2[PhP(NEt_2)_2] + PhC(O)F \rightarrow C_5H_5Mn(CO)_2[PhP(F)NEt_2] \quad (96)$$

A discussion about the success of the reactions cited above is necessary inasmuch as the complexes under study here failed to undergo similar reactions. The major difference between the P-Cl and P-NR_2 complexes employed by each group of workers is the ready availability of a lone pair on nitrogen. Presumably, this lone pair may interact with a variety of reagents to give activated complexes suitable for collapsing into the desired products. In a formal sense the lone pair on nitrogen may behave in a similar fashion to the lone pairs on oxygen of organic carbonyl groups in their reactions with Grignard reagents. The possibility exists that complexes with nitrogen or oxygen groups on phosphorus may readily undergo reaction with Grignard reagents, SbF_3, and $LiAlH_4$, e.g.

$$Mo(CO)_5(PR_2NR'_2) + R''MgX \rightarrow Mo(CO)_5(PR_2R'') \quad (97)$$

$$Mo(CO)_5[P(OR)_2Cl] + R''MgX \rightarrow Mo(CO)_5[P(OR)_2R''] \quad (98)$$

However, π-$C_5H_5Mn(CO)_2PCl_3$ has been reported[89] to undergo reduction by sodium borohydride to give the phosphine complex, Eq. 99,

$$\pi\text{-}C_5H_5Mn(CO)_2PCl_3 + NaBH_4 \rightarrow \pi\text{-}C_5H_5Mn(CO)_2PH_3 \quad (99)$$

The reasons for the success of this reaction are not entirely clear.

The results of this work regarding the reactivity of coordinated phosphine ligands suggest that reagents which will most efficiently displace chloride from phosphorus will be good nucleophiles. A large number of excellent nucleophiles are available as anions of transition metal complexes. After much of the work discussed in this thesis had been completed, Ehrl and Vahrenkamp[54] reported the reactions of $Mo(CO)_5P(CH_3)_2Cl$ and $Mo(CO)_5As(CH_3)_2Cl$ with sodium pentacarbonylmanganate(-I), $NaMn(CO)_5$. The reactions proceed smoothly and in good yield to give the phosphorus bridged bimetallic complexes $(CO)_5MoE(CH_3)_2$-$Mn(CO)_5$, (E = P,As) as shown in Eq. 100.

$$Mo(CO)_5E(CH_3)_2Cl + NaMn(CO)_5 \rightarrow (CO)_5MoE(CH_3)_2Mn(CO)_5 \quad (100)$$

where E = P,As

The structure of the arsenic compound was determined by X-ray crystallography, and the bridging ligand was confirmed.[90] Presumably, other organometallic anions would also react with $Mo(CO)_5PR_2Cl$, and some possible reactions are suggested in Eq. 101-102.

$$Mo(CO)_5PR_2Cl + NaC_5H_5Mo(CO)_3 \rightarrow (CO)_5MoPR_2Mo(C_5H_5)(CO)_3 \quad (101)$$

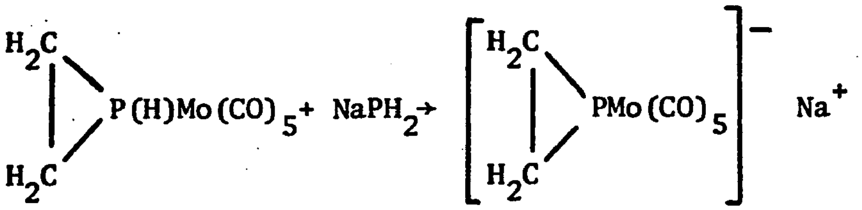
$$2Mo(CO)_5PR_2Cl + Na_2Fe(CO)_4 \rightarrow (CO)_4Fe[PR_2Mo(CO)_5]_2 \quad (102)$$

Recently, Haines *et al.*[91,92] reported a similar reaction (Eq. 103) with a chlorophosphine-iron carbonyl complex

$$Fe(CO)_4P(C_6H_5)_2Cl + NaC_5H_5Fe(CO)_2 \rightarrow Fe(CO)_4P(C_6H_5)_2Fe(C_5H_5)(CO)_2 \quad (103)$$

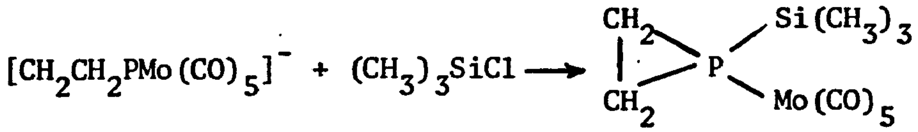
No further reactions of $Fe(CO)_4P(C_6H_5)_2Cl$ were reported, however.

Other examples of reactions of coordinated phosphine ligands have appeared. Most of the reactions cited below exploit the acidity of the P-H bond. (Phosphirane)pentacarbonylmolybdenum reacts with sodium dihydrogenphosphide to give an anion,[93] Eq. 104.



(104)

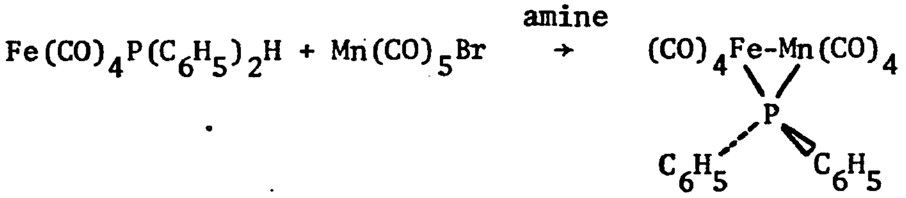
The anion reacts with chlorotrimethylsilane to give (trimethylsilyphosphirane)pentacarbonylmolybdenum, Eq. 105.



(105)

Phosphirane itself is a reactive, low-boiling liquid; the preparation of derivatives of substituted phosphiranes for studies will be made less difficult by the reactions of coordinated ligands.

Yasufuku and Yamazaki have demonstrated the reactivity of coordinated diphenylphosphine under mild conditions.[94] Reaction of $Fe(CO)_4P(C_6H_5)_2H$ or $Ni(CO)_3P(C_6H_5)_2H$ with a transition metal carbonyl bromide gave a phosphine-bridged complex with a metal-metal bond.



(106)

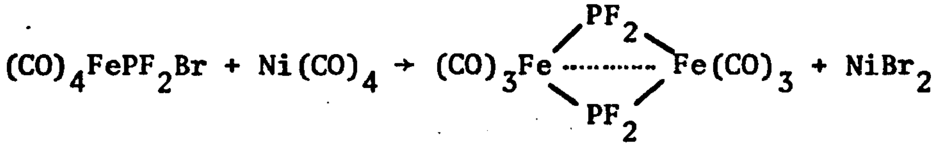
The reactions of several other phosphine complexes of metal carbonyls, *e.g.*, $Fe(CO)_4L$, L = $(C_6H_5)_2PH$, $P(CH_3)_2H$, etc.; $M(CO)_5P(C_6H_5)_2H$, M = Cr,Mo,W, with alkyllithium reagents have been investigated.[95]

$$Fe(CO)_4P(C_6H_5)_2H + n\text{-}C_4H_9Li \rightarrow Fe(CO)_4P(C_6H_5)_2Li + n\text{-}C_4H_{10} \qquad (107)$$

The lithiophosphine metal carbonyl may subsequently be reacted with alkyl halides to give the alkylphosphine complex, Eq. 108.

$$Fe(CO)_4P(C_6H_5)_2Li + CH_3I \rightarrow Fe(CO)_4P(C_6H_5)_2CH_3 + LiI \qquad (108)$$

Other specific reactions of coordinated phosphine ligands have been reported. For example, (Bromodifluorophosphine)tetracarbonyiron reacts with nickel carbonyl according to Eq. 109 to give a binuclear iron complex.[96]



(109)

Schumann[97] has shown that the phosphorus-tin bond may be cleaved (Eq. 110) in coordinated phosphine complexes. The generality of this reaction has not yet been demonstrated, but it may prove useful

$$[(CH_3)_3Sn]_3PMo(CO)_5 + (C_6H_5)_2PCl \rightarrow \{[(C_6H_5)_2P]_3P\}Mo(CO)_5 \qquad (110)$$

The reaction of a coordinated ligand thus has made it possible to prepare the monosubstituted molybdenum complex of the potentially multidentate ligand, $[(C_6H_5)_2P]_3P$.

The synthetic utility of reactions of coordinated phosphine ligands has been recognized only recently. Undoubtedly, new investigators in this young area will contribute many new ideas.

INFRARED SPECTRA

An integral part of most of substituted group VI metal carbonyl complexes has been the interpretation of the carbonyl stretching frequencies and their associated stretching force constants in terms of the metal-ligand bonding.[34,55,56,98-100] Early in the development of the chemistry of the metal carbonyls and their derivatives, it was concluded that the number of infrared active carbonyl stretching vibrations of a complex is determined by the idealized local symmetry of the terminal carbonyl groups. A consequence to this generalization is that the isomeric form of a complex may be determined from the number of bands observed in its infrared spectra in the 2000 cm^{-1} region.

All the monosubstituted pentacarbonylmolybdenum complexes prepared in this study belong to the point group C_{4v} on the basis of their local symmetry at molybdenum. A group theoretical calculation shows the irreducible representation corresponding to the vibrational modes for a molecule of C_{4v} symmetry to be $2A_1 + B_1 + E$.[55] Only the $2A_1$ and E bands are infrared active. However, the actual symmetry of the molecule is always less than C_{4v} because the symmetry of a phosphine ligand can at best be C_{3v}. Thus the Raman active B_1 mode can appear as a weak band in the infrared spectra of $M(CO)_5L$ molecules. It is likely that the extent of divergence from C_{4v} selection rules is determined by the unsymmetrical relationship of the phosphine group with the planar carbonyl groups. It should therefore be particularly sensitive to the size of the metal atom and the substituents on phosphorus.[99] Generally, the monosubstituted metal carbonyl compounds

$M(CO)_5L$ give infrared spectra whose salient features can be predicted. However, when the ligand L becomes more unsymmetrical, a splitting of the E bond is observed. Often for $Mo(CO)_5L$ molecules, accidental degeneracy of an A_1 and the E modes is observed. This lack of resolvability has imposed some limitations on a rigorous comparison of observed and predicted bands.[99] Typical spectra are shown in Figures 10-11.

When correlating the number of infrared-active CO-stretching modes with molecular structure, the phase in which measurements are made has some bearing on the effective molecular symmetry and must therefore be considered. Measurement of the infrared spectra of compounds in the gas phase is ideal because intermolecular interactions can be neglected; the selection rules which determine the number and activity of the CO-stretching modes are those associated with the point group of the isolated molecule. Because of the limited volatility of many carbonyl complexes and their tendency to decompose at higher temperatures, gas phase measurements have been limited. Where possible, most spectra in the CO-stretching region are measured in a nonpolar solvent where solute-solvent interactions are isotropic and it is usually satisfactory to consider the symmetry of the isolated molecule.[99]

In order to rationalize trends in the infrared spectra of substituted metal carbonyls, the nature of bonding between a transition metal and carbon monoxide must be examined. In carbon monoxide both s and p orbitals on the carbon and oxygen atoms combine to form the carbonyl group σ-bonding orbital, leaving an sp hybrid orbital on oxygen and another on carbon. These two orbitals are each occupied

Figure 10. Infrared spectrum of $Mo(CO)_5P(C_6H_5)_2OSi(CH_3)_3$ in the metallocarbonyl stretching region. Note the near degeneracy of the $A_1(2)$ and E bands.

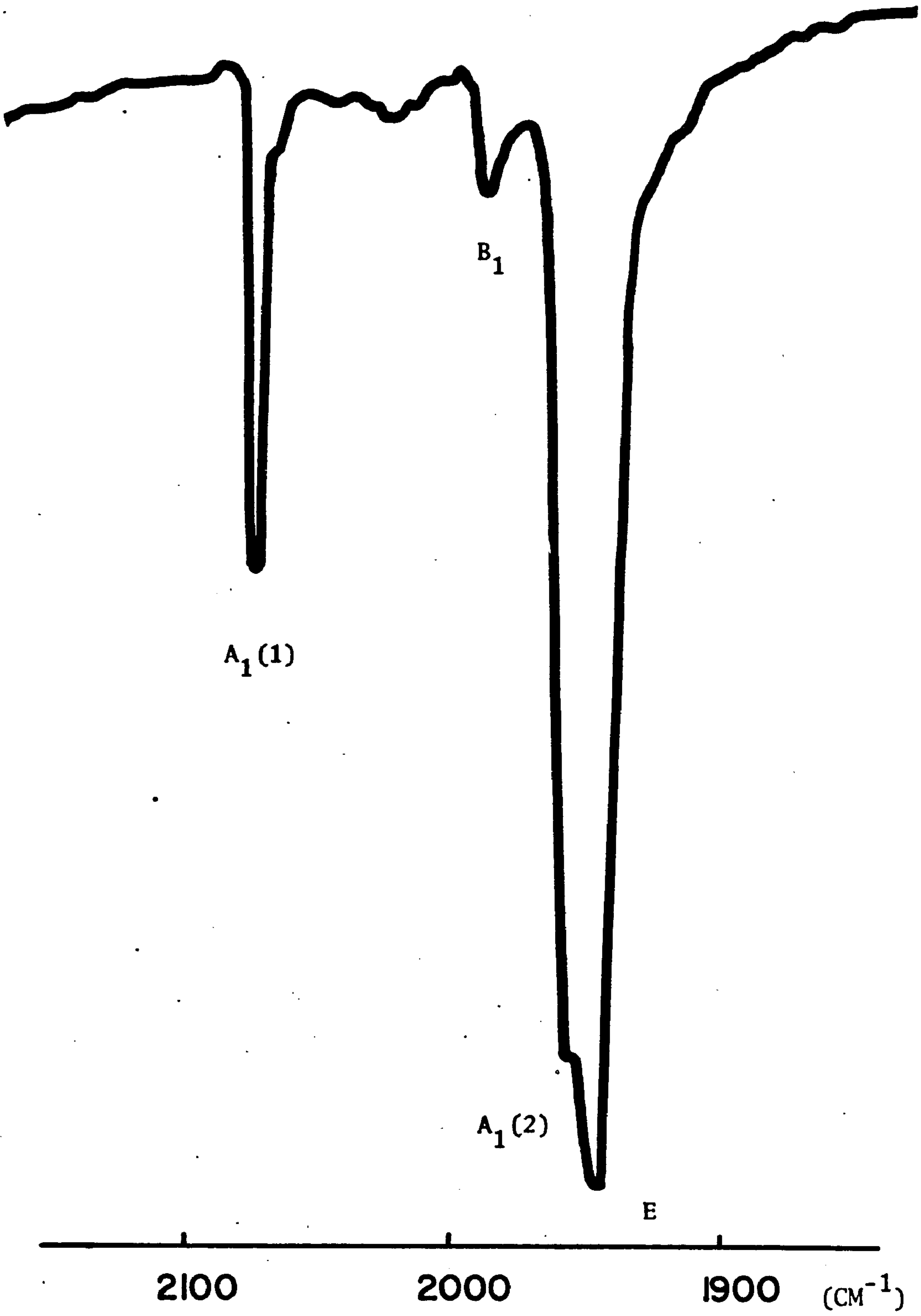
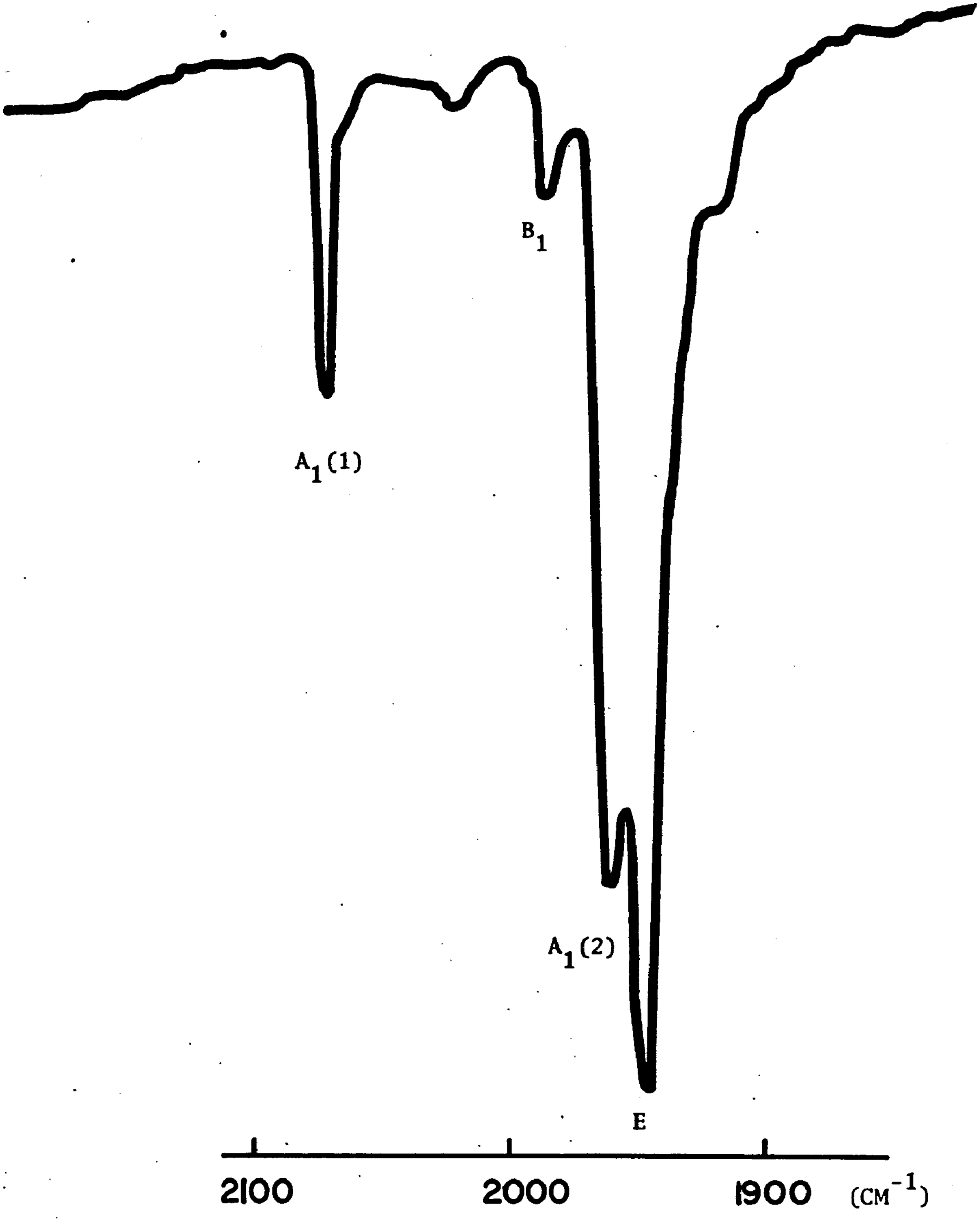


Figure 11. Infrared spectrum of $Mo(CO)_5P(CH_3)_2O$-i-C_3H_7. The $A_1(2)$ and E bands are clearly resolved.



giving lone pairs of electrons that are essentially atomic in character. Two mutually perpendicular, filled π bonding orbitals complete the bonding system of the carbon monoxide molecule. When coordinated to a metal it is the less electronegative atom, carbon, which donates lone-pair electron density to a σ oriented metal orbital. However, the donor properties of carbon monoxide are slight and it does not form adducts with acidic aluminum or boron compounds. A significant amount of stability of the transition metal-carbon monoxide bond must arise from π bonding between filled metal d orbitals and empty antibonding orbitals on carbon monoxide.[100] A schematic representation of this bonding is shown in Figure 12.

Substitution of a CO group by another ligand of different π-acceptor capacity causes a change in the amount of π electron density which must be accepted by the remaining carbonyls. If the ligand is a weaker π acceptor than CO, as is generally the case, a decrease in the frequency of the CO stretching modes will be observed inasmuch as more π electron density is available for donation into the π* orbitals of the remaining carbonyls.

Trends in the CO stretching frequencies for a series of complexes $Mo(CO)_xL_y$ as a function of L have been established. These trends are generally independent of the metal and of the exact nature of the carbonyl complex. Attempts have been made to correlate these trends with the changes in the inductive and mesomeric bonding properties of the ligands. Changes in a ligand which increase its σ donor properties must also in principle affect the tendency of that ligand to form a π bond with the metal. It is difficult to separate these effects, and only the overall σ-π donation of charge will be considered.

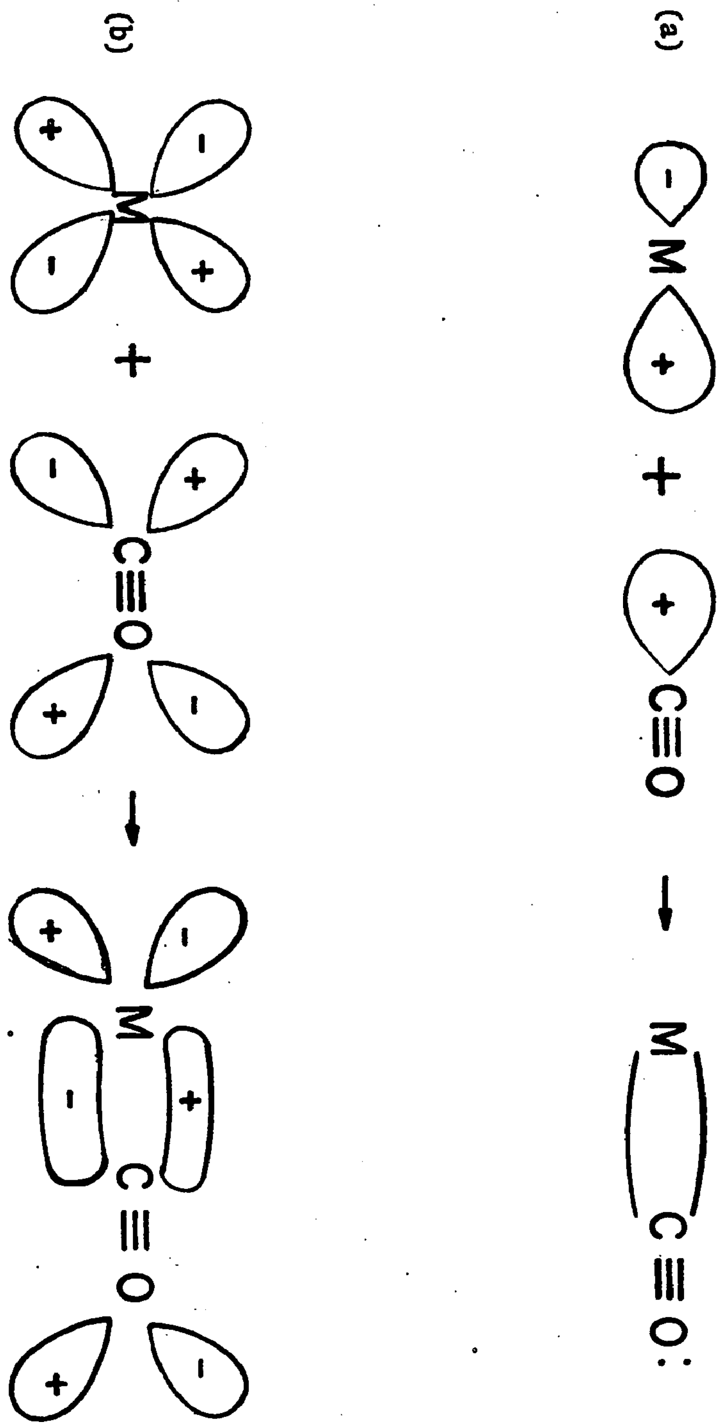


Figure 12. (a) The formation of the carbon-to-metal σ bond using an unshared pair on the C atom. (b) The formation of the metal-to-carbon π bond. The other orbitals on the CO are omitted for clarity. After reference 86.

For a series of substituted carbonyl complexes containing tertiary phosphines, the CO-stretching frequencies decrease according to the ligand order

$$PF_3 > PCl_3 > C_6H_5PCl_2 > P(OC_6H_5)_3 > (C_6H_5)_2PCl > P(OR)_3 > P(C_6H_5)_3 > PR_3$$

(R = alkyl)

This order has been established from measurements of the infrared spectra of compounds of different metals and structure including $C_2H_5V(CO)_3L$, $M(CO)_xL_y$ (M = Cr,Mo,W), $Mn_2(CO)_8L_2$, $Fe(CO)_4L$, $Co(CO)_3L(NO)$, and $Ni(CO)_{4-n}L_n$.[97]

The decrease in the CO stretching frequencies along the series

$PCl_3 > RPCl_2 > PR_2Cl > PR_3$ (R = alkyl); $P(OR)_3 > PR_3$; $P(C_6H_5)_3 > P(CH_3)_3 >$ $P(C_2H_5)_3 > P(C_4H_9)_3 > P(C_3H_7)$; and $P(C_6H_5)_3 > P(C_6H_5)_2(C_2H_5) > P(C_6H_5)(C_2H_5)_2 >$ $P(C_2H_5)_3$

parallels the increase in the electron-withdrawing ability of the groups attached to the phosphorus and can thus be correlated with a decreasing tendency of the ligand to donate charge to the metal.[99,101]

Force constants for the metal-carbonyl stretching frequencies of the complexes prepared in this study have been calculated using the method of Cotton and Kraihanzel.[52] The values of k_1 are for the CO stretching force constants of the CO group trans to the ligand, k_2 for the four CO groups cis to the ligand, and k_1 for the interaction constant between the CO groups. The observed CO stretching frequencies and the calculated force constants for the complexes prepared herein are listed in Table 3.

TABLE 3

CO STRETCHING FREQUENCIES[a] AND FORCE CONSTANTS FOR $(R_2PX)(CO)_5Mo$[b]

X(R = C_6H_5)	Freq. (cm^{-1})				Force constants (mdyn/A)		
	$A_1(1)$	B_1	$A_1(2)$	E	k_1	k_2	K_i
Cl	2079	1989	1965	1957	15.81	16.01	0.30
OCH_3	2074	1991	1961	1951	15.75	15.97	0.30
OC_2H_5	2074	1991	1960	1952	15.73	15.98	0.30
O-n-C_3H_7	2074	1990	1959	1950	15.71	15.96	0.30
O-i-C_3H_7	2073	1990	1958	1949	15.70	15.94	0.30
$OSi(CH_3)_3$	2073	1987	1956	1947	15.67	15.92	0.30
OH	2074	1987	1958	1949	15.70	15.94	0.30
$O^-(C_2H_5)_3NH^+$	2063	1976	- 1932 -		15.29	15.71	0.32
NH_2	2073	1987	1955	1947	15.65	15.92	0.30
$NH(CH_3)$	2073	1988	1954	1946	15.64	15.91	0.31
$N(CH_3)_2$	2073	1988	1950	1941	15.59	15.85	0.32
$NH(C_6H_5)$	2074	1988	1951	1946	15.59	15.91	0.31
SC_2H_5	2075	1990	1958	1950	15.70	15.96	0.30
$S^-(C_2H_5)_3NH^+$	2066		- 1934 -		15.32	15.74	0.32
CH_3	2072	1985	1952	1945	15.61	15.89	0.31
C_2H_5	2072	1985	1952	1946	15.61	15.89	0.31
i-C_3H_7	2072	1984	1952	1945	15.60	15.90	0.31
X(R = CH_3)							
Cl	2080	1989	1971	1956	15.92	16.05	0.30
OCH_3	2077	1990	1962	1948	15.78	15.94	0.31
OC_2H_5	2077	1988	1962	1949	15.78	15.96	0.31
O-n-C_3H_7	2074	1990	1962	1949	15.77	15.94	0.30
O-i-C_3H_7	2074	1988	1957	1942	15.71	15.86	0.32
OH	2074	1988	1966	1949	15.84	15.94	0.30
NH_2	2073	1986	1957	1946	15.69	15.90	0.31
$NH(CH_3)$	2073	1986	1957	1948	15.68	15.93	0.30
$N(CH_3)_2$	2074	1990	1952	1943	15.62	15.88	0.32
SC_2H_5	2074	1987	- 1950 -		15.56	15.96	0.30
SH	2074	1988	- 1945 -		15.61	15.87	0.31
CH_3	2071		1952	1943	15.61	15.87	0.31
C_6H_5	2072	1985	1952	1945	15.61	15.98	0.31
$[((CO)_5Mo)_2$,L	2072	1984	1952	1945	15.60	15.90	0.31
$[P(C_6H_5)_2]_2O$	2074	1993	1952	1949	15.60	15.95	0.30
$[P(CH_3)_2]_2O$	2074	1986	1968	1952	15.87	15.97	0.29
$P(C_6H_5)_2OP(CH_3)_2$	2074	1994	1953	1949	15.61	15.95	0.30

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[a] Hexane employed as solvent. B_1 modes are weak and placed with an uncertainty of several wave numbers. The $A_1(2)$ and E bands overlap to varying extents and the band maxima were determined by graphical resolution. [b] REf. 34. [c] Ref. 45.

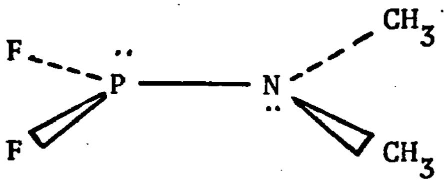
Perhaps the two most striking pieces of data are those for the two complexes assigned the ionic structures

$[(C_2H_5)_3NH]^+[Mo(CO)_5(C_6H_5)_2PO]^-$ and $[(C_2H_5)_3NH]^+[Mo(CO)_5(C_6H_5)_2PS]^-$.

The low values of 15.3 and 15.7 mdyn/Å for k_1 and k_2, respectively, support the ionic formulation of the complexes. Apparently the negative charge on oxygen or sulfur of the phosphinite or thiophosphinite ligands lowers the π-acceptor capacity of the phosphorus atom and demands a greater amount of charge delocalization into the π* orbitals of the carbonyl groups than is possible with neutral phosphine ligands.

Overall, the observed range in the stretching frequencies and the force constants calculated therefrom is not large, and extensive speculation concerning the relative π acceptor capabilities for the various ligands is probably not warranted. However, a general order of apparent electron withdrawing ability for the R_2PX ligands is possible. The order is based mainly on trends in the value of k_1. Since k_1 is the force constant of the CO group trans to the ligand in an $Mo(CO)_5L$ complex, k_1 is expected to be more sensitive to the electronic nature of the phosphine ligand than k_2, inasmuch as the phosphine ligand and the CO molecule are sharing the same metal orbital.

The general order of apparent electron withdrawing ability for the R_2PX ligands is $X = Cl > OR' > NR'_2 \geq CH_3$ or C_6H_5. Surprisingly, there are little differences in acceptor capacity between the series $(C_6H_5)_2PX$ and $(CH_3)_2PX$ although $(C_6H_5)_3P$ was found to be a better acceptor than $(CH_3)_3P$[101]. Attempts to order extensive lists of ligands with respect to their π acceptor ability have been made.[67] The gross trend in the acceptor capacity of the R_2PX ligands is best rationalized in terms of the electronegativity of the atom X. At first glance the observed π acceptor capacity does in fact follow the known electronegativity of the atom X. As the electronegativity of X increases, the pi-acceptor ability of the phosphine ligand also increases. However, the pi-acceptor capacities of $R_2PNR'_2$ and R_2PCH_3 are very similar. Further, the acceptor ability of $R_2PNR'_2$ shows a marked dependence on the nature of R'. The "best" pi-acid of the series is R_2PNH_2 and the "poorest" is $R_2PN(CH_3)_2$. Although the phosphorus atom is bonded to nitrogen in each case, the electronegativity of nitrogen is affected by its substituents. This result is best explained by suggesting that a certain amount of pπ-dπ nitrogen to phosphorus bonding is possible. Other workers have also suggested the need to postulate pπ-dπ bonding of the type mentioned above. Morris and Nordman[102] found that the phosphorus, nitrogen and carbon atoms of $F_2PN(CH_3)_2$ were almost planar and suggested the hybridization about nitrogen to be nearly pure sp^2.



In addition, the P-N bond length was shorter than the sum of the covalent radii for phosphorus and nitrogen.

Cowly and Schweiger[103] presented evidence for strong pπ-dπ bonding in the compounds $(CF_3)_2PNH_2$, $(CF_3S)_2NH$, and $PF_3(NH_2)_2$ based on the magnitude of the $^{31}P-^{15}N$ coupling constant. Jones and

Coskran[67] also have postulated pπ-dπ bonding in order to rationalize spectral observations. The most compelling evidence for the pi-bonding theory has been reported by Barlow <u>et al</u>.[104] A series of molybdenum carbonyl complexes containing fluorophosphine ligands were synthesized. The following decreasing order of pi-acceptor capacity was found:

$CF_3PF_2 \sim (CF_3)_2PF > PF_3 > CCl_3PF_2 > ClCH_2PF_2 \sim C_6H_5PF_2 > ROPF_2 > R_2NPF_2 > RPF(NR_2) \sim (R_2N)_2PF >> R_3P$.

The greater ability for CF_3PF_2 and $(CF_3)_2PF$ to accept pi-electron density compared to PF_3 must arise from the fact that a CF_3 group cannot pi-bond to phosphorus. Even though fluoride is more electronegative than CF_3, fluoride-phosphorus pπ-dπ bonding reduces the "effective electronegativity" of a fluoride group compared to a trifluoromethyl group in this situation.

Thus, pπ-dπ bonding from nitrogen to phosphorus in the ligands $R_2PNR'_2$ effectively lowers the ability of phosphorus to accept electron density from a transition metal and $R_2PNR'_2$ and R_2PR' become nearly equivalent in their pi-acceptor capacity. Some evidence exists for pi-bonding between phosphorus and oxygen in R_2POR' ligands. Presumably, the pi interaction between phosphorus and oxygen is weaker than pi interaction between phosphorus and nitrogen for two reasons. First, the greater electronegativity of oxygen works in a direction opposite to oxygen to phosphorus pi-bonding. And, secondly, the inductive effect of a single substituent on oxygen is expected to be less favorable than that of two groups on a trivalent nitrogen atom.[67] Further, little change in the pi-acceptor capacity of R_2POR' is observed as R' is varied, a fact which may reflect the smaller -- even unimportant

-- degree of oxygen-to-phosphorus pi-bonding in phosphinite ligands.

Much evidence has been accumulated to support oxygen to silicon pπ-dπ bonding in organosilicon compounds.[84] This type of multiple bond character is supported by the rather large bond angles in siloxanes and by the much stronger acidity and hydrogen bonding of silanols such as $(CH_3)_3SiOH$ compared to $(CH_3)_3COH$. The fact that one lone pair remains on the oxygen is consistent with the fact that base character of the silanol is not much lowered in spite of its stronger acidity compared to the alcohol. A similar type of delocalization from oxygen to silicon in $Mo(CO)_5[(C_6H_5)_2POSi(CH_3)_3]$ would be expected to diminish oxygen to phosphorus pπ-dπ bonding in the silicon derivative and thereby enhance its pi acceptor capability as a ligand relative to the alkoxy derivative. However, the differences in k_1 and k_2 for (alkyl diphenylphosphinite)- and (trimethylsilyl diphenylphosphinite)-pentacarbonylmolybdenum are very small. Conceivably, oxygen to phosphorus pπ-dπ bonding is minimal, if important at all, as was suggested above in less quantitative terms.

Correlations of CO-stretching frequency data with certain physical properties of the ligands L have been made for a series of related derivatives $M(CO_xL_y$. Bigorgne[105] correlated changes in the group R for a series of ligands PR_3 in the compounds $Ni(CO)_{4-n}L_n$ with the Taft polarity constant σ^* of the group R which directly reflects the inductive effect of R. A linear dependence was found between the CO-stretching frequencies and σ^* for the ligands PR_3, where R = CH_3, C_2H_5, C_6H_5, $C{\equiv}CC_6H_5$, or CF_3. Other dependencies have been noted between the CO-stretching frequency and the sum of electronegativities of substituents,[106] dipole moments of substituents,[99] and the sum of σ^* for the substituents on a ligand.[99] It must be emphasized that the success of these correlations is based on changes in the σ-donor ability of a ligand while the pi-acceptor capacity apparently has remained constant.[99]

Several attempts to correlate the infrared data obtained in this study to physical parameters have been made. No correlation which includes all the data obtained has been successful, a fact which must indicate the importance of pi-bonding in at least some of the complexes prepared in this study.

Proton Magnetic Resonance

Nuclear magnetic resonance studies are of particular value as an aid in interpreting the nature of the molybdenum-phosphorus bond in complexes of the type $Mo(CO)_5PR_3$. Considerable attention has been given to ^{31}P nmr studies of phosphorus ligands coordinated to metal carbonyls. Meriwether and Leto[107] noted the large ^{31}P chemical shift differences between uncoordinated and complexed phosphine ligands. They examined changes in this difference caused by changes in the substituents on the phosphine, the number of phosphine ligands, and chelation. Grim _et al_.[43] have examined complexes of the group VI metal carbonyls in order to allow comparisons of variation of the ^{31}P chemical shift with changing atomic weight of the metal while valency and stereochemistry remain constant as well as to measure ^{183}W-^{31}P spin-spin coupling constants. Inasmuch as facilities for extensive ^{31}P studies were not available at the time this work was underway, no such data will be presented in this thesis.

However, valuable information about a metal-phosphorus bond may be obtained from proton nmr studies of specific complexes. Compounds which contain a methyl group bonded to phosphorus are particularly well-suited for study by ^{1}H nmr. Unlike ^{31}P nmr, chemical shift differences encountered in ^{1}H nmr for a series of compounds are generally insensitive to minor changes at the phosphorus atom. For this reason, most of the information obtained about the nature of the phosphorus-metal bond is derived from phosphorus-hydrogen coupling constants.

The methyl resonance of the $Mo(CO)_5[P(CH_3)_2X]$ complexes appears as a simple doublet near 2 ppm downfield of internal tetramethylsilane (TMS). The resonance of the methyl protons in the complexes is downfield of the corresponding resonance in the free ligand. This observation is expected since the electronegativity of phosphorus in the coordination complex is greater than that in the free ligand.[43] Grim also has noted the downfield shift of a methyl group in a quarternary phosphonium salt relative to the corresponding free phosphine and suggests the following general decreasing order of chemical shift for the ^{1}H resonance of methyl groups bonded to phosphorus.[43]

$$R_3PCH_3 > MPR_2CH_3 > R_2PCH_3$$

M = transition metal

The degree of coupling of the methyl protons with the ^{31}P nucleus in the complexes $Mo(CO)_5[P(CH_3)_2X]$ varies with the nature of the substituent X and will be discussed in detail below. Nmr data for the

$Mo(CO)_5P(CH_3)_2X$ and $Mo(CO)_5P(C_6H_5)_2X$ complexes are listed in Tables 4 and 5, respectively.

The chemical shift of the methyl protons in $Mo(CO)_5[P(CH_3)_2X]$ depends on the nature of the substituent X. The ability of the substituent X to shield the methyl protons closely parallels the order observed in organic molecules. The following decreasing order for the chemical shifts of the methyl protons was observed in the $Mo(CO)_5[P(CH_3)_2X]$ complexes:

$$X = Cl > SR > OR > NR_2 \sim R$$

Clearly, the observed differences in chemical shift for the methyl groups are small and any physical significance attached to these changes is difficult to assess. As was the case with the infrared spectra of these complexes, subtle changes in the nature of the phosphine ligand have provided only slight variations in a given spectral parameter. Attempts to correlate the observed chemical shifts with Hammett and Taft parameters for the substituent X were unsuccessful. Also, no direct relationship was observed between the chemical shift and ν_{CO}, Cotton-Kraihanzel force constants, or coupling constants for the complexes.

The values of $^2J(PH)$ for the $Mo(CO)_5P(CH_3)_2X$ complexes are quite different from the values of $^2J(PH)$ for the free ligands. Values of $^2J(PH)$ for several methylphosphine compounds are listed in Table 6 for comparison. The differences in $^2J(PH)$ between free phosphines and their complexes are of particular interest. Manatt *et al.*[108] have suggested that the sign of the geminal coupling P-C-H ($^2J(PH)$) in a

TABLE 4

^{1}H NMR DATA FOR Mo(CO)$_5$P(CH$_3$)$_2$X COMPLEXES[a]

X	τCH_3-P[b] (ppm)	$\lvert ^2J(HP) \rvert$ (Hz)	τCH_n-E[b] (E=O,N,S)	$\lvert ^3J(HP) \rvert$ (Hz)	Other[b]
OCH_3	8.23d	5.0	6.49d	13.6	
OC_2H_5	8.28d	5.0	6.28[c]	7.9[c]	$C\underline{H}_3C$:τ8.73t[^3J(HH)=7.0 Hz]
O-n-C_3H_7	8.25d	4.9	6.40[d]	7.7[d]	$C\underline{H}_3$:τ9.07tC$C\underline{H}_2$C:τ8.35m
O-i-C_3H_7	8.32d	4.7	5.87[e]	12.4[e]	$C\underline{H}_3C$:τ8.77d[^3J(HH) = 5.9 Hz]
NH_2	8.38d	6.4			$N\underline{H}_2$:τ8.0br
$NH(CH_3)$	8.43d	5.7	7.41d	10.8	
$N(CH_3)_2$	8.42d	5.4	7.45d	12.3	
SC_2H_5	8.18d	4.3	7.26[c]	7.8[c]	$C\underline{H}_3C$:τ8.65t[^3J(HH) = 7.5 Hz]
SH	8.08d	4.8			S$\underline{H}$:τ7.84
OH	8.22	5.5			O$\underline{H}$:τ4.5
$\underline{C}H_3$	8.50	7.1			
C_6H_5	8.19	7.0			

[a] CS_2 solutions, τ values relative to internal TMS at τ10 ppm.

[b] Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

[c] Apparent quintet; coupling constant measured from doublet obtained upon spin decoupling from the $C\underline{H}_3C$ group.

[d] Apparent quarter; coupling constant measured from doublet obtained upon spin decoupling from the $C\underline{H}_2$ protons.

[e] Apparent septet; coupling constant measured from doublet obtained upon spin decoupling from the $C\underline{H}_3C$ groups.

TABLE 5

^{2}H NMR DATA FOR $Mo(CO)_5\ P(C_6H_5)_2X$ COMPLEXES[a]

X	τCH_3P[b] (ppm)	$\lvert ^2J(HP)\rvert$ (Hz)	τCH_n-E[b] (E=O,N,S)	$\lvert ^3J(HP)\rvert$ (Hz)	Other[b]
OCH_3			6.56d	13.2	
OC_2H_5			6.36[c]	6.5[c]	$C\underline{H}_3C:\tau 8.75t\ [^3J(HH) = 6.9\ Hz]$
O-n-C_3H_7			6.50[d]	6.4[d]	$C\underline{H}_3C:\tau 9.09t\ CC\underline{H}_2C:\tau 8.40m$
O-i-C_3H_7			5.56[e]	10.8[e]	$C\underline{H}_3C:\tau 8.92d\ [^3J(HH) = 6.2\ Hz]$
$OSi(CH_3)$					$C\underline{H}_3Si:\tau 9.95s$
NH_2					$N\underline{H}_2:\tau 7.54br$
$NH(CH_3)$			7.68d	10.1	
$N(CH_3)_2$			7.40d	11.7	
SC_2H_5			7.74[c]	6.4[c]	$C\underline{H}_3C:\tau 8.99\ [^3J(HH) = 7.5\ Hz]$
CH_3	7.97	5.8			
C_2H_5				7.4	$C\underline{H}_3C:\tau 9.01\ [^2J(HP) = 17.8\ Hz;\ ^3J(HH) = 7.4\ Hz]$
C H					$CH_2C:\tau 7.65$
i-C_3H_7				15.5	$C\underline{H}_3C:\tau 8.98\ [^3J(HH) = 6.8]$ $C\underline{H}:\ \tau 7.66$

[a] CS_2 solutions. τ values relative to internal TMS at τ 10 ppm.

[b] Abbreviations: s,singlet; d,doublet; t,triplet; m,multiplet; br,broad

[c] Apparent quintet; coupling constant measured from doublet obtained upon spin decoupling from the $C\underline{H}_3C$ group.

[d] Apparent quartet; coupling constant measured from doublet obtained upon spin decoupling from the $CC\underline{H}_2$ protons.

[e] Apparent septet; coupling constant measured from doublet obtained upon decoupling from the $C\underline{H}_3C$ groups.

TABLE 6

VALUES OF $^2J(PH)$ FOR SEVERAL METHYLPHOSPHINES

PHOSPHINE	$^2J(PH)$	REFERENCE
$(CH_3)_3P$	+2.7	a.
$(CH_3)_2PCl$	+8.7	Ref. 7
	+8.3	a.
CH_3PCl_2	+17.6	b.
$(CH_3)_2PN(CH_3)_2$	+5.7	c.
$CH_3P[N(CH_3)_2]_2$	+8.0	Ref. 67
$(CH_3)_2POCH_3$	+5.5	
$CH_3P(OCH_3)_2$	+8.5	Ref. 67
$(CH_3)_2PSCH_3$	+6.5	Ref. 7
$(CH_3)_2PC_6H_5$	+3.4	d.
$CH_3P(C_6H_5)_2$	+4.2	d.
$(CH_3)_2PCN$	+4.5	e.
$CH_3P(CN)_2$	+7.5	e.

a. R. K. Harris and R. G. Hayter, Can. J. Chem., 42, 2282 (1964).

b. J. F. Nixon and R. Schmutzler, Spectrochim. Acta., 22, 565 (1966).

c. A. Clemens and H. Sisler, Inorg. Chem., 4, 1222 (1965).

d. P. K. Maples, Ph.D. Thesis, Lehigh University, 1968.

e. C. E. Jones and K. J. Coskran, Inorg. Chem., 10, 1536 (1971).

variety of trivalent phosphorus compounds is positive and that the value of $^2J(PH)$ becomes more negative as the s character of the phosphorus bonding orbitals to carbon increases. The sign of $^2J(PH)$ apparently becomes negative in all recorded instances when three-covalent phosphorus is converted into a four-covalent species such as an oxide, sulfide, or quarternary salt.[109-111] For example, $^2J(PH)$ in $P(CH_3)_3$ is +2.7 Hz, but $^2J(HP)$ in $(CH_3)_4P^+$ and $(CH_3)_3PO$ are -14.4 and -13.3 Hz, respectively. The hybridization about phosphorus in $(CH_3)_4P^+$ is nearly pure sp^3 and more s character is expected in that P-C bond than in $P(CH_3)_3$.

Presumably, the sign of $^2J(PH)$ in the dimethylphosphine complexes prepared in this study is also negative. Upon complexation to a metal carbonyl, the phosphorus atom is partially oxidized because of donation of its lone pair to the metal. This results in an increase in the s character of the PC bond, and the value of $^2J(PH)$ for the complexed ligand should be more negative than for the free ligand. Jones and Coskran[67] have suggested that $^2J(PH)$ is negative in the complexes $[(CH_3O)_2PCH_3]_nMo(CO)_{6-n}$. They argue that in going from the mono- to di- to trisubstituted compounds, the phosphorus atom is oxidized to a lesser extent, because increased negative charge is placed on the metal as a result of the increased substitution of the weakly basic carbon monoxide groups by the more basic phosphine ligands. Consequently, there should be less s character in the PC bonds and $^2J(PH)$ should become more positive with increased substitution. They observed values for $|^2J(PH)|$ of 3.0, 2.5, and 1.0 Hz for the mono-, di-, and trisubstituted complexes, respectively. These values of $^2J(PH)$ were suggested to be negative in order to show the required increase in $^2J(PH)$ with increased substitution.[67] The difficulty in choosing a correct sign for $^2J(PH)$ was compounded by the fact that the absolute value of the coupling constants was so close to zero.

As a result of part of the work completed for this thesis, compelling evidence is available for assigning negative values to $^2J(PH)$ in coordinated methylphosphine ligands. The trend in σ-donor strength of a series of ligands, e.g., $(CH_3)_2PCl$, $(CH_3)_2POCH_3$, and $(CH_3)_3P$ is predictable based on the electron-withdrawing capability of the X substituents. Qualitatively the order of increasing σ-donor strength for these ligands should be

$$(CH_3)_2PCl < (CH_3)_2POCH_3 < (CH_3)_3P$$

The more basic $(CH_3)_3P$ should oxidize molybdenum to a greater extent than $(CH_3)_2PCl$, and thus $^2J(PH)$ for $Mo(CO)_5P(CH_3)_3$ should be more negative than $^2J(PH)$ for $Mo(CO)_5P(CH_3)_2Cl$. Since the absolute values of $^2J(PH)$ for the complexes $Mo(CO)_5P(CH_3)_2Cl$ and $Mo(CO)_5P(CH_3)_3$ are 3.8 and 7.1 Hz, respectively, and since the coupling constant for $Mo(CO)_5P(CH_3)_3$ must be the more negative of the pair, the coupling constants must be negative.

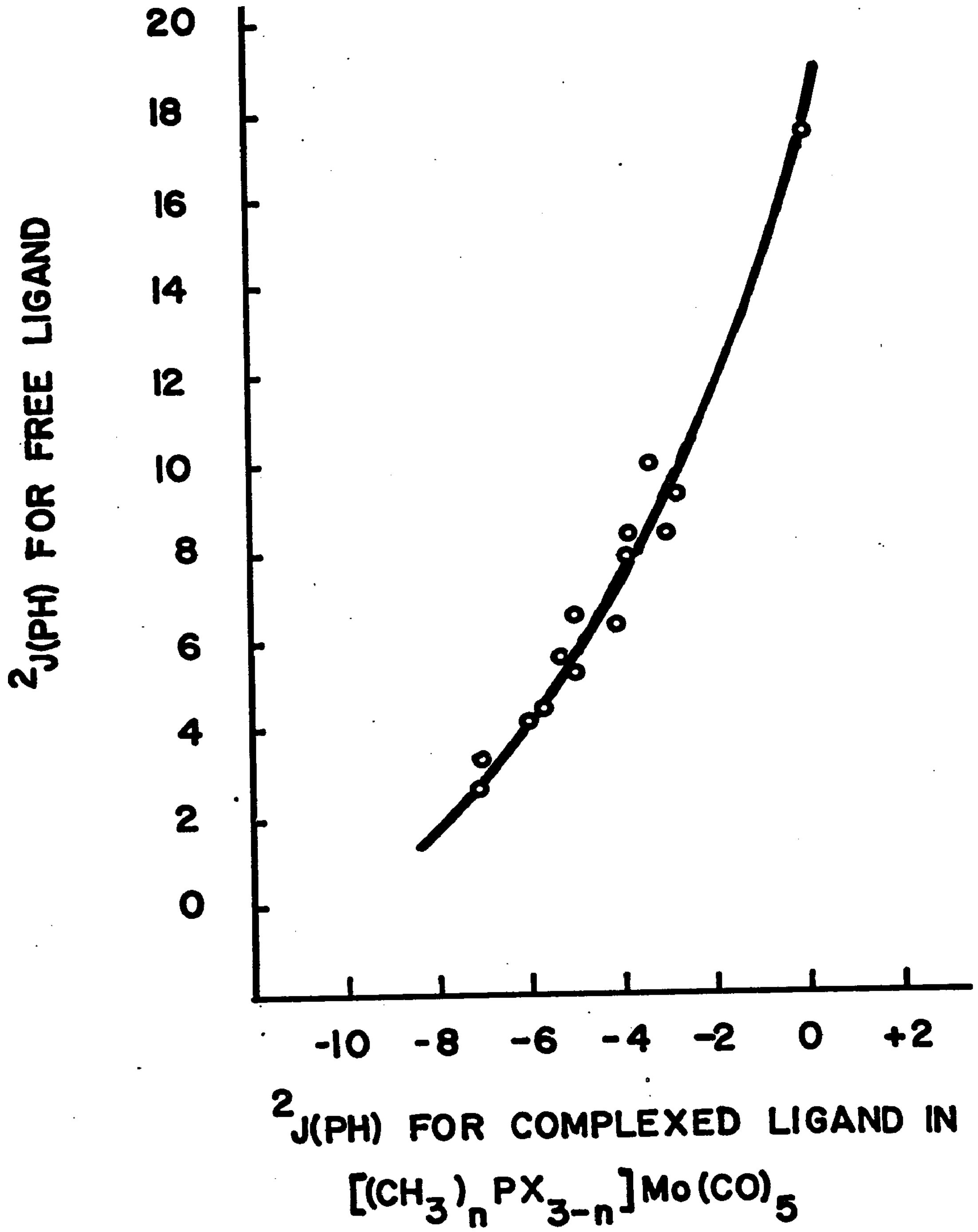
In general, as the substituents of the phosphorus ligand become more electron-withdrawing, the value of $^2J(PH)$ increases. Significantly in $Mo(CO)_5(CH_3PCl_2)$ the s character in the PC bond decreases enough so that $^2J(PH)$ becomes zero and the nmr spectrum of $Mo(CO)_5(CH_3PCl_2)$ appears as a sharp singlet. Greater electron-withdrawing substituents on phosphorus should give rise to further increases in $^2J(PH)$ for the complexed ligands. With ligands such as CH_3PF_2 and $(CF_3)_2PCH_3$ the coupling constant should become non-zero again, but the values of $^2J(PH)$ for $Mo(CO)_5(PCH_3F_2)$ and $Mo(CO)_5[CH_3P(CF_3)_2]$ would have positive signs.

An empirical relationship between $^2J(PH)$ in the free ligand and in the complex is shown in Figure 13. The s character in the phosphorus-carbon bonds should vary uniformly between the complexes and the free ligand if the pentacarbonylmolybdenum group oxidizes each phosphorus ligand to its maximum possible extent.

Although a linear relationship might be anticipated, Manatt *et al.* have pointed out that a good linear relationship between s character and the phosphorus-hydrogen coupling constant probably does not exist.[108] The graph shown in Figure 13 effectively measures the difference in s character in the PC bonds between a phosphine ligand and its monosubstituted molybdenum carbonyl complex and probably is not linear. Attempts to correlate $^2J(PH)$ with various classical sets of resonance and inductive parameters of substituents were unsuccessful.

Jones and Coskran have suggested that the methyl coupling constant gives an indication of the strength of the metal-phosphorus σ bond, if $^2J(PH)$ in these complexes is a reflection of the extent of phosphorus to metal σ-donation.[67] Attempts to separate the σ and pi components of a metal-phosphorus bond using infrared spectral data have met with only limited success.[112] Some qualitative idea of the relative amounts of sigma and pi bonding in a transition metal-phosphine complex might be obtained from $^2J(PH)$ and the CO-stretching force constant k_1. A large negative value for $^2J(PH)$ suggests strong sigma bonding for a phosphine ligand whereas a large value for k_1 reflects effective metal-

Figure 13. Plot of $^2J(PH)$ in several trivalent methylphosphines *vs.* $^2J(PH)$ in their analogous $Mo(CO)_5$- complexes. Coupling constants in Hz.



phosphorus pi bonding. For example, $^2J(PH)$ for $Mo(CO)_5P(C_6H_5)_2CH_3$ is -6.0 Hz suggesting good metal-phosphorus sigma interaction, and the value of 15.6 for k_1 suggests good pi bonding also. However, the same values for $Mo(CO)_5(CH_3PCl_2)$ are 0.0 and 16.2, respectively. The weaker sigma bonding in $Mo(CO)_5(CH_3PCl_2)$ is compensated for by increased pi bonding.

This particular method for qualitatively assessing the relative sigma and pi contribution to a metal-phosphorus bond is obviously limited to complexes of methylphosphine derivatives. Perhaps its greatest value is derived from the fact that numbers are being used to reinforce long-standing qualitative concepts of organometallic chemistry.

The chemical shift and coupling constants of protons three or more bonds away from phosphorus are relatively insensitive to change upon complexation. Resonances due to OCH_3 or $N(CH_3)$ groups bonded to a metal-complexed phosphorus atom appear as doublets at somewhat lower field than the $P(CH_3)_2$ resonance. The values of $^3J(PH)$ in the metal complexes remain essentially unchanged from their free-ligand values.

Spectroscopists have recognized that $^3J(PH)$ depends on several factors.[108] Clearly the nature of the atoms and their substituents between the phosphorus atom and the proton of interest is important (Table 7). The dihedral angle from phosphorus to the proton is also significant. Thus, $^3J(PH)$ is 13.6 Hz in $Mo(CO)_5P(CH_3)_2OCH_3$ but only 7.9 Hz in $Mo(CO)_5P(CH_3)_2OCH_2CH_3$. (The value of $^3J(PH)$ in the latter complex was obtained after the methyl protons of the ethyl group were decoupled.) Rapid rotation about the P-O-C bonds in $Mo(CO)_5PR_2OCH_3$

TABLE 7

SEVERAL VALUES OF $^3J(PH)$ FOR COMPOUNDS OF THE TYPE $R_2PECH_{3-n}R'_n$

COMPOUND	E	$^3J(PH)$	REFERENCE
$Mo(CO)_5P(CH_3)_2OCH_3$	O	13.6	a.
$Mo(CO)_5P(CH_3)_2N(CH_3)_2$	N	12.3	a.
$(CH_3O)_3PO$	O	11.0	b.
$Mo(CO)_5P(C_6H_5)_2i\text{-}C_3H_7$	C	15.5	a.
$Mo(CO)_5P(C_6H_5)_2C_2H_5$	C	7.4	a.
$Mo(CO)_5P(C_6H_5)_2OC_2H_5$	O	6.5	a.
$Mo(CO)_5P(C_6H_5)_2SC_2H_5$	S	6.4	a.

a. This work

b. J. F. Nixon and R. Schmutzler, Spectrochim. Acta., 22, 565 (1966).

and $Mo(CO)_5PR_2OCH_2CH_3$ allows each set of protons to experience the same environment on a time averaged basis. However, consideration of specific static conformation for each of the complexes as shown in Figure 14 suggests an explanation for the differences in the magnitude of $^3J(PH)$ for the two complexes. The value of $^3J(PH)$ for $Mo(CO)_5PR_2OCH_3$ is given by the expression

$$^3J(PH) = \frac{2(^3J(PH_a)) + {}^3J(PH_b)}{3} \qquad (1)$$

whereas $^3J(PH)$ for $Mo(CO)_5PR_2OCH_2CH_3$ would be either

$$^3J(PH) = {}^3J(PH_c) \qquad \text{or} \qquad (2)$$

$$^3J(PH) = \frac{^3J(PH_d) + {}^3J(PHe)}{2} \qquad (3)$$

Using expression (1) a value of 10 Hz is obtained for $^3J(PH)$ for $Mo(CO)_5P(CH_3)_2OCH_3$. The disagreement with the experimentally observed value of 13.6 Hz is not severe inasmuch as the approximate values for $^3J(PH_b)$ and $^3J(PH_a)$ assumed from $^3J(PH)$ for $Mo(CO)_5P(CH_3)_2OCH(CH_3)_2$ and $Mo(CO)_5P(CH_3)_2OC_2H_5$, respectively, are certainly subject to error arising from substituent effects. Recently, Thomson et al.[113] were able to show clearly by variable temperature nmr spectroscopy that there are two different values for $^3J(PNiCH)$ that must be considered in $\pi\text{-}C_5H_5NiP(C_6H_5)_3CH_2Si(CH_3)_3$.

The nmr spectra of the compounds $Mo(CO)_5P(CH_3)_2OP(CH_3)_2Mo(CO)_5$ and $Mo(CO)_5P(CH_3)_2OP(C_6H_5)_2Mo(CO)_5$ appear as "triplets" rather than simple doublets. This apparent "triplet" is a result of both phosphorus-hydrogen and phosphorus-phorphorus coupling and has previously been

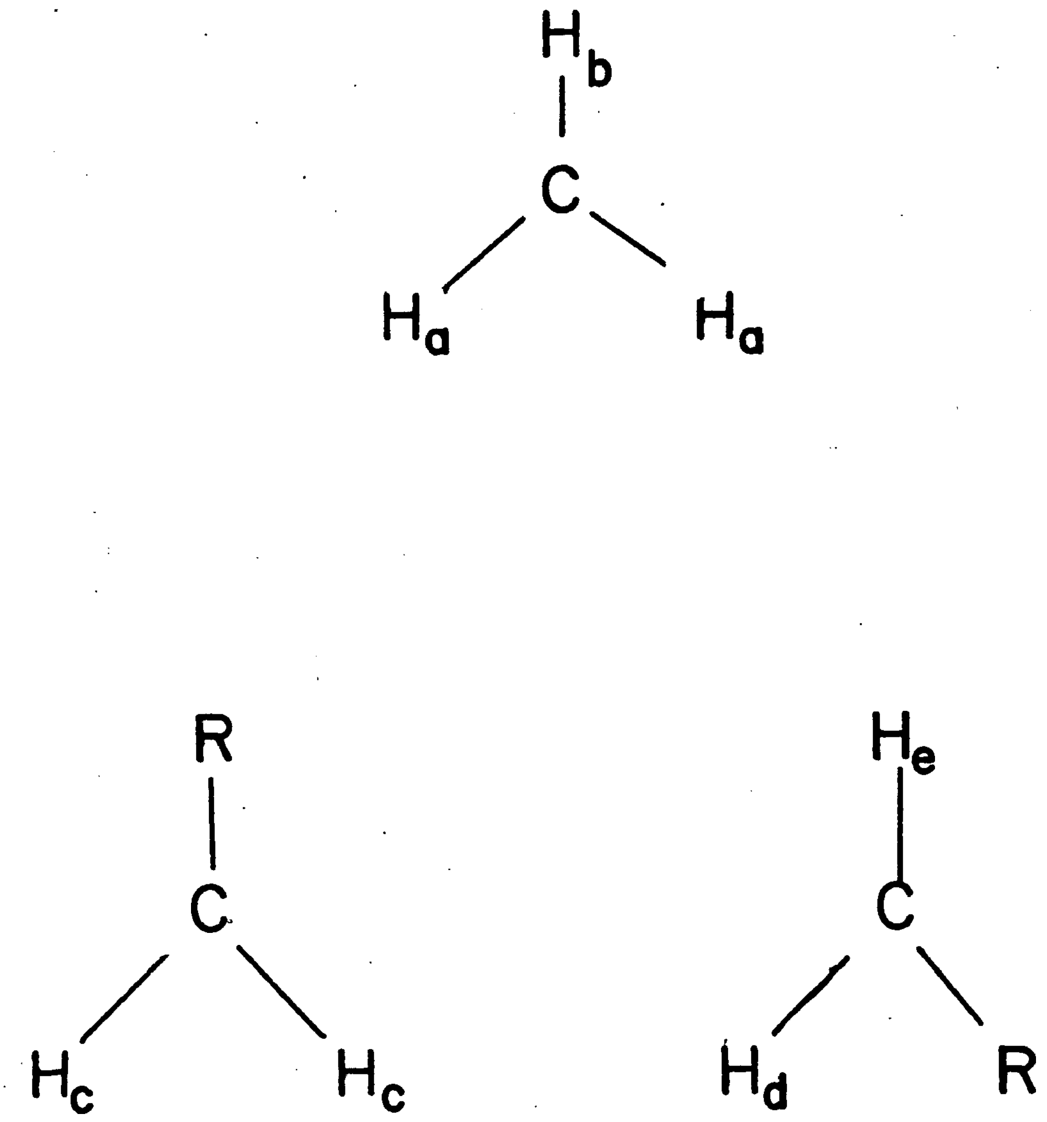


FIGURE 14. RIGID CONFORMATIONS OF E-CH_n-R VIEWED ALONG THE E-C AXIS.

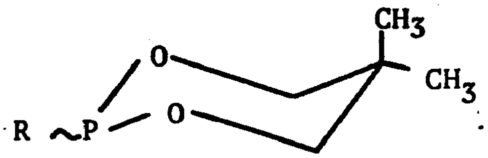
observed in a variety of compounds.[46] The complexes mentioned above give rise to spectra characteristic of $X_6AA'X_6$ and X_6AA' systems, respectively. The separation of the outermost peaks of the triplet is discribed by $|J_{AX} + J_{AX'}|$.[65] Since $J_{AX'}$ takes place through four bonds, it is probably very small and $|J_{AX} + J_{AX'}|$ becomes a good approximation for $^2J(PH)$. The values of 4.0 and 4.1 Hz measured for $Mo(CO)_5P(C_6H_5)_2OP(CH_3)_2Mo(CO)_5$ and $\{[Mo(CO)_5P(CH_3)_2]_2O\}$, respectively, are presumed to be negative.

PART II

INTRODUCTION

The conformation of the 1,3,2-dioxaphosphorinane ring and the conformational preference of substituents on such a ring have received considerable attention in recent years. Although studies on the cyclic organophosphorus compounds were preceeded by investigations on other six-membered heterocycles such as cyclohexanes, dioxanes, and sulfites, no direct comparisons could be made regarding the stereochemical requirements between any two families of compounds. Therefore, particular interest has been focused in three main areas in the study of 1,3,2-dioxaphosphorinanes. First, whether the preferred conformation of the phosphorus heterocycle is a chair or a boat must be determined. Secondly, the presence or absence of conformational equilibria must be established. Most 1,3,2-dioxaphosphorinanes have been found to exist in a rigid chair conformation in solution, but several cases are well documented in which mixtures of rapidly interconverting conformers are present in solution. Thirdly, the configuration of substituents on phosphorus and on the ring carbon atoms must be determined. In this respect the spatial requirements of the lone electron pair on trivalent phosphorus must be considered.

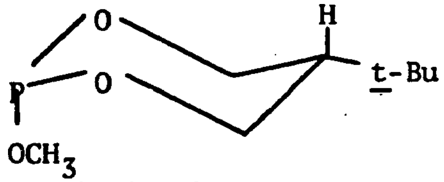
Gagnaire _et_ _al_.[114] were among the first investigators to speculate extensively about the stereochemical requirements of 1,3,2-dioxaphosphorinanes. They concluded that derivatives of 2-R-5,5-dimethyl-1,3,2-dioxaphosphorinane (hereafter referred to as 2-R-DMP) exist in a rigid chair conformation with the substituent R oriented in the equatorial position



(1)

Also, White et al.[115-117] were able to conclude that a rigid chair was the preferred conformation for the 2-R-DMP derivatives, but they argued for an axial R substituent. Gagnaire's arguments for an equatorial substituent were based largely on the presumed steric needs of a typical substituent. On the other hand, the results of crystal structure determinations of several 2-oxo-1,3,2-dioxaphosphorinanes showed a flattening of the OPO end of the phosphorus ring. Thus, White et al. reasoned that a similar flattening should occur in the 1,3,2-dioxaphosphorinanes. The flattening of the ring should serve to relieve steric interaction between the axial substituent at phosphorus and the ring, but electronic interaction between an axial lone pair on phosphorus and the lone electron pairs of the oxa-group would still be severe.

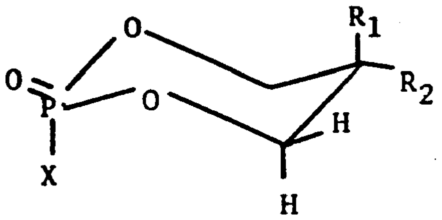
Further support that the assignment of an axial R group in 1,3,2-dioxaphosphorinanes was correct came from Bentrude et al.[118-119] X-ray analysis of the stereospecific oxidation products of 2-methoxy-5-t-butyl-1,3,2-dioxaphosphorinane suggested an axial methoxy group and



(2)

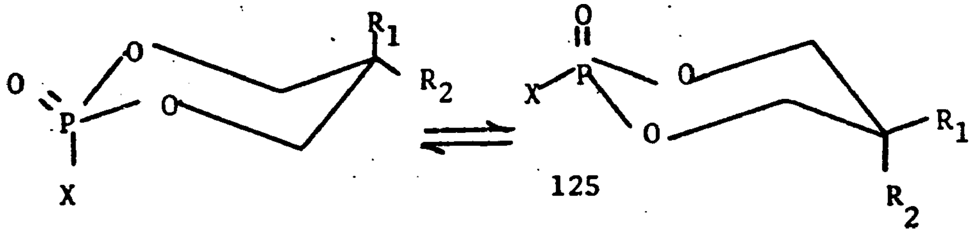
an equatorial lone pair in the thermodynamically more stable trivalent 1,3,2-dioxaphosphorinane (2). Recently, however, two independent studies have shown that the thermodynamically preferred configuration for a 2-dimethylamino-1,3,2-dioxaphosphorinane is one in which the 2-dimethylamino group is oriented equatorially and the lone pair on phosphorus axially.[120,121] These findings further support the idea that electronic interactions at the phosphorus end of the ring are probably the dominant force in determining the configuration at phosphorus. The dimethylamino group has nearly the same steric requirements as an isopropyl group[120], but its electronic effects with a lone pair on nitrogen are clearly different.

Structural studies, both X-ray determinations and nmr analyses, have been carried out on a number of 2-oxo-2-R-DMP derivatives as well as on other 2-oxo-1,3,2-dioxaphosphorinanes (3)[115,122-129] Most of the 2-oxo derivatives exist in solution in chair conformations,



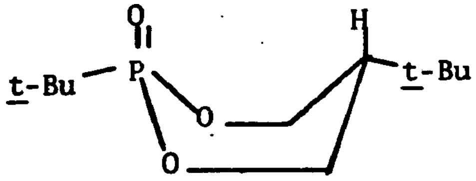
(3)

but the mobility of the heterocyclic ring is very dependent on the R group at phosphorus. Generally, when X is chloride or alkoxide, a single rigid conformer exists in solution with the X group oriented axially. However, when X is methyl, phenyl, trityl, or dimethylamino, a mixture of rapidly interconverting conformers exists in solution. Furthermore, Majoral et al.[122-128] have shown that the ratio of conformers in Equation 111 X = phenyl, depends both on temperature and on the nature of the solvent employed



(111)

Not all 2-oxo-1,3,2-dioxaphosphorinanes exist in chair conformations. The compound cis-2,5-di-t-butyl-2-oxo-1,3,2-dioxaphosphorinane (4) assumes a boat conformation with both t-butyl groups oriented in equatorial positions.[130] Presumably the steric requirements



(4)

of the two bulky organic groups are dominant in determining the stereochemistry of this specific compound.

The variety of results obtained in studies of 1,3,2-dioxaphosphorinanes appears to be dependent to a large extent on the nature of the group coordinated to phosphorus. This fact suggested that transition metal carbonyl derivatives of 1,3,2-dioxaphosphorinanes might also display properties directly attributable to the presence of a metal carbonyl. Parrot[131] has reported the preparation of several metal complexes of 2-CH_3O-DMP and 2-C_6H_5O-DMP. Although he suggested that the metal carbonyl group occupies an equatorial position at phosphorus in a chair conformer,[131] an exhaustive study of the chemistry of metal carbonyl complexes of 1,3,2-dioxaphosphorinanes was not undertaken.

Specifically, the work described herein was undertaken in order to ascertain how a large metal carbonyl moiety coordinated to a 1,3,2-dioxaphosphorinane ring through phosphorus would influence the ring conformation, conformational equilibria, the stereochemistry of substituents at phosphorus, the chemical reactivity at phosphorus, and the phosphorus-hydrogen coupling constants.

EXPERIMENTAL

Sources of materials and physical techniques have been described in the Experimental Section of Part I.

2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane.

An adaptation of the procedure of Lucas[132] was used to prepare 2-Cl-DMP. A solution of 1 mole (104 g) of 2,2-dimethyl-1,3-propanediol in 200 ml of diethyl ether was added dropwise to a vigorously stirred solution of 1 mole (137 g) of PCl_3 in 150 ml of dichloromethane. Solvents were removed under aspirator vacuum leaving a pale yellow liquid. This liquid was distilled to give 120 g (71%) of clear, colorless 2-Cl-DMP, bp 78°/22 torr (lit.,[116] 70°/12 torr).

2-Phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane.

A literature method[117] was used to prepare 2-C_6H_5-DMP. A solution of 11.6 g of 2,2-dimethyl-1,3-propanediol in 150 ml of ether was added slowly to a well-stirred mixture of 20 g of $C_6H_5PCl_2$ and 23 g of triethylamine in 200 ml of ether cooled in an ice bath. The precipitate of triethylammonium chloride was removed by filtration and washed several times with ether. The ether from the combined filtrates was removed under aspirator vacuum leaving a thick oil. The oil was distilled under high vacuum to give 12 g (61%) of 2-C_6H_5-DMP as a viscuous liquid, bp 96°/0.5 Torr (lit[117] 100°/1.5 torr), which solidified on standing, mp 82-83°.

2,5,5-Trimethyl-1,3,2-dioxaphosphorinane.

A procedure identical to that used for 2-C_6H_5-DMP was used to prepare 2-CH_3-DMP from 24 g of CH_3PCl_2, 20.8 g of 2,2-dimethyl-1,3-propanediol, and 40.4 g of triethylamine. Distillation of the crude liquid gave 15 g (51%) of clear, colorless, air-sensitive 2-CH_3-DMP, bp 60-61°/1 torr.

2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane.

A solution of 10 ml of methanol in 50 ml of ether was added to a well-stirred solution of 16.8 g of 2-Cl-DMP and 10.1 g of triethylamine in 150 ml of ether. The mixture was filtered and the precipitate of triethylammonium chloride was washed with 50-ml portions of hexane. Solvent was removed from the filtrate under aspirator vacuum leaving a clear liquid. The pure product was obtained in 95% yield after distillation as a clear, colorless liquid, bp 66°/21 torr (lit.[116] 65-66°/23 torr).

2-Thiophenoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane.

A solution of 11 g of thiophenol in 50 ml of ether was added to a solution of 16.8 g of 2-Cl-DMP and 10 g of triethylamine in 150 ml of ether. The triethylammonium chloride was removed by filtration and washed with ether. Ether was removed from the filtrate under aspirator vacuum, leaving a white solid. The solid was recrystallized from pet ether to give pure 2-C_6H_5S-DMP as a white solid, mp 72-74° (lit.[116] 70-75°) in 94% yield.

2-Dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane.

A three-necked 500-ml flask was fitted with a stirrer, condenser, and a gas inlet tube. A solution of 16.8 g of 2-Cl-DMP in 250 ml of ether was stirred vigorously as dimethylamine was passed rapidly into the flask. The flow of gas was continued for 15 min after which the reaction mixture was filtered to remove the dimethylammonium chloride. The precipitate was washed with two 50-ml portions of hexane. Solvent was removed from the filtrate, leaving a colorless liquid. Pure $2\text{-N(CH}_3)_2\text{-DMP}$ was obtained upon distillation as a colorless liquid, bp 81°/21 torr, in 76% yield.

2-Hydroxy-2-oxo-1,3,2-dioxaphosphorinane monohydrate.

The method of McConnell and Coover[133] was used for the preparation of $2\text{-OH-2-oxo-DMP}\cdot\text{H}_2\text{O}$. Anal. for $C_5H_{11}O_4P\cdot H_2O$: Calcd. C, 32.60; H, 7.06. Found: C, 32.68; H, 7.06; mp 174°.

2,2,5,5-Tetramethyl-1,3,2-dioxaphosphorinanium Iodide.

A solution of 3.0 g of $2\text{-CH}_3\text{-DMP}$ and 25 ml of diethyl ether was stirred vigorously as 4.0 g of methyl iodide was added dropwise. The resulting precipitate was filtered under nitrogen, washed with two 25-ml portions of hexane and dried in a stream of purified nitrogen. The yield of white solid, mp 134° (dec) was nearly quantitative. The complex is stable under a nitrogen atmosphere but slowly decomposes in a vacuum. Anal. Calcd. for $C_{17}H_{16}IO_2P$: C, 28.93; H, 5.54. Found: C, 28.96; H, 5.69.

Diethyl tert-butyl(methyl)malonate.

A three-necked 3-l flask was fitted with a condenser, a mechanical stirrer, and a pressure equalizing dropping funnel. The flask was charged with 1500 ml of tert-butanol. Slowly, 82 g of potassium metal was added to the tert-butanol in small pieces. After all the potassium had reacted, 432 g (2 moles) of diethyl tert-butylmalonate[134] was added rapidly through the dropping funnel. The solution darkened to a deep red color at this point. The flask was arranged for distillation and the tert-butanol was removed by distillation at atmospheric pressure. As the volume of the solution decreased, toluene was added. This process was continued until the boiling point of the distilling vapor reached that of toluene, 110°. The volume of the solution was adjusted to about 800 ml with additonal toluene.

After the deeply colored solution had cooled, 310 g (2.18 mol) of methyl iodide was added dropwise to the solution of diethyl tert-butyl(potassio)malonate. The mixture was stirred for an additional hour after the addition of methyl iodide was complete. The solution was allowed to cool and 800 ml of water was added to dissolve the precipitated sodium iodide. The organic layer was separated and the remaining aqueous layer was extracted with two 100-ml portions of ether. The organic phases were combined and then shaken with 100 ml of a 10% aqueous solution of sodium thiosulfate to reduce any free iodine in the organic layer. The solvents were removed under aspirator vacuum and the remaining liquid was distilled from 1 g of zinc metal. Pure diethyl tert-butyl(methyl)malonate was obtained upon distillation as a clear, colorless liquid, bp 116-119°/13 torr (lit[135] bp 100°/5 torr) in 61% yield. The nmr spectrum of the product (CCl_4 solution) has peaks at δ 1.09 (singlet, tert-butyl), δ 1.24 (triplet, $OCH_2C\underline{H}_3$), δ 1.43 (singlet, $C\text{-}C\underline{H}_3$), and 4.10 (quartet, $OC\underline{H}_2CH_3$).

2-tert-butyl-2-methyl-1,3-propanediol.

A procedure outlined by Lampman[136] was adapted for the reduction of diethyl tert-butyl(methyl)malonate to the corresponding diol. A mixture of 61 g (1.6 mol) of $LiAlH_4$ in 1200 ml of ether was stirred vigorously as 230 g (1 mol) of diethyl tert-butyl(methyl)malonate was added dropwise. The reaction vessel was cooled by an external ice bath during the addition. The ice bath was removed and stirring was continued for another hour. The resulting dark gray slurry was transferred to a 4000-ml beaker. A 30% solution of sodium tartrate was added very carefully and with vigorous stirring to the reaction mixture to complex aluminum salts and release the diol. No further tartrate solution was added when the precipitate appeared white throughout. The tartrate complex was removed by filtration. Ether was removed from the filtrate, leaving a white solid which was distilled to give the product as a clear, colorless liquid, bp 134-136°/13 torr, which solidified on standing, mp 122-124°. The solid tartrate was extracted with ether in a Soxhlet apparatus for 3-4 days to yield more diol. The overall yield was 108 g (74%).

An integrated nmr spectrum in $CHCl_3$ gave the correct ratios for the tert-butyl protons at δ 0.87, the methyl protons at δ 0.96, and the methylene protons as a complex multiplet at δ 3.8. Anal. Calcd. for $C_8H_{18}O_2$: C, 65.75; H, 12.31. Found: C, 65.48; H, 12.11.

2-Chloro-5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane.

A solution of 73 g (0.5 mol) of 2-*tert*-butyl-2-methyl-1,3-propanediol in 200 ml of ether was added dropwise to a solution of 70 g (0.51 mol) of PCl_3 and 101 g (1 mol) of triethylamine in 400 ml of ether cooled in an ice bath. The triethylammonium chloride was removed by filtration and washed with two 100-ml portions of ether. Ether was removed from the filtrate under aspirator vacuum, leaving a pale yellow oil. The oil was distilled to give 61 g (58%) of 2-Cl-MTBP, bp 84°/2 torr, as a colorless liquid which solidifed on standing. Anal. Calcd. for $C_8H_{16}ClO_2P$: C, 45.71; H, 7.63; Found: C, 45.83; H, 7.81.

2-Methoxy-5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane.

A solution of 5 ml of methanol and 5 ml of triethylamine in 10 ml of ether was added dropwise to 6.1 g of 2-Cl-TBMP in 100 ml of ether cooled in an ice bath. The triethylammonium chloride was removed by filtration and washed with two 50-ml portions of ether. Ether was removed from the filtrate under aspirator vacuum. The remaining liquid was distilled to yield 5.3 g (90%) of clear, colorless 2-CH_3O-MTBP, bp 64°/0.1 torr. Anal. Calcd. for $C_9H_{19}O_3P$: C, 52.42; H, 9.23. Found: C, 52.40; H, 9.10.

Metal Carbonyl Complexes of 1,3,2-Dioxaphosphorinanes.

(2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

A mixture of 6.6 g (25 mmol) of Mo(CO)$_6$ and 4.2 g (25 mmol) of 2-Cl-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed under aspirator vacuum, and unreacted Mo(CO)$_6$ was removed by sublimation at 40°/0.1 torr. Pure (2-Cl-DMP)Mo(CO)$_5$ was obtained in 90% yield as white crystals, mp 92-93°, after two recrystallizations from n-hexane. Anal. Calcd. for $C_{10}H_{10}ClMoO_7P$: C, 29.64; H, 2.47. Found: C, 29.93; H, 2.61.

(2-Phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

A mixture of 2.6 g (10 mmol) of Mo(CO)$_6$ and 2 g (10 mmol) of 2-C_6H_5-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed under aspirator vacuum and unreacted Mo(CO)$_6$ at 40°/0.1 torr. Pure (2-C_6H_5-DMP)Mo(CO)$_5$ was obtained in 70% yield as white crystals, mp 91-92°, after recrystallization from ethanol/water. Anal. Calcd. for $C_{16}H_{15}MoO_7P$: C, 43.05; H, 3.36. Found: C, 42.83; H, 3.56.

(2,5,5-Trimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

a. Thermal reaction. A mixture of 2.6 g of Mo(CO)$_6$ and 1.5 g of 2-CH_3-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed at aspirator vacuum and unreacted Mo(CO)$_6$ at 40°/0.1 torr. The remaining solid was sublimed at 70°/0.05 torr to yield pure (2-CH_3-DMP)Mo(CO)$_5$, mp 97-98°, as white crystals in 54% yield. Anal. Calcd. for $C_{11}H_{13}MoO_7P$: C, 34.37; H, 3.38. Found: C, 35.00; H. 3.78.

b. Reaction of a coordinated ligand. A mixture of 2 g of $(CH_3PCl_2)Mo(CO)_5$, 4 g of 2,2-dimethyl-1,3-propanediol, and 15 ml of benzene was heated at reflux for 1.5 hr. The cooled mixture was shaken with 50 ml of water and extracted with two separate 25-ml portions of ether. The ether extracts were dried over magnesium sulfate, filtered and concentrated to dryness under aspirator vacuum to leave a residue from which pure $(2\text{-}CH_3\text{-DMP})Mo(CO)_5$ was sublimed at 70°/0.05 torr in 41% yield.

(2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

a. Thermal reaction. A mixture of 2.6 g of $Mo(CO)_6$ and 1.7 g of $2\text{-}CH_3O\text{-DMP}$ in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed under aspirator vacuum and unreacted $Mo(CO)_6$ at 40°/0.1 torr. Pure $(2\text{-}CH_3O\text{-DMP})Mo(CO)_5$ was obtained in 76% yield upon further sublimation at 80°/0.05 torr as white crystals, mp 93°. Anal. Calcd. for $C_{11}H_{13}MoO_8P$: C, 33.00; H, 3.28. Found: C, 33.25; H, 3.24.

b. Reaction of a coordinated ligand. A mixture of 1 g of $(2\text{-Cl-DMP})Mo(CO)_5$ and 20 ml of methanol was heated at reflux for 3 hr. The alcohol was removed under aspirator vacuum leaving a gummy residue. Fractional sublimation at 0.05 torr yielded unreacted starting material at 50° and pure $(2\text{-}CH_3O\text{-DMP})Mo(CO)_5$ at 80° in 60% yield.

(2-Ethoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

$(2\text{-}C_2H_5O\text{-DMP})Mo(CO)_5$ was prepared in a manner identical to that described for $(2\text{-}CH_3O\text{-DMP})Mo(CO)_5$ in b above. The pure product was obtained in 60% yield as white crystals, mp 60-62°.

(2-Thiophenoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

A mixture of 2.6 g of Mo(CO)$_6$ and 2.4 g of 2-C$_6$H$_5$S-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed under aspirator vacuum and unreacted Mo(CO)$_6$ at 40°/0.1 torr. Pure (2-C$_6$H$_5$S-DMP)Mo(CO)$_5$ was obtained in 74% yield upon recrystallization from hexane as buff-colored crystals, mp 111-112°. Anal. Calcd. for $C_{16}H_{15}MoO_7PS$: C, 40.17; H, 3.14. Found: C, 40.27; H, 3.39.

(2-Dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

A mixture of 2.6 g of Mo(CO)$_6$ and 1.8 g of 2-(CH$_3$)$_2$N-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed at aspirator vacuum and unreacted Mo(CO)$_6$ at 40°/0.1 torr. Pure [2-(CH$_3$)$_2$N-DMP]Mo(CO)$_5$ was obtained in 78% yield upon sublimation at 80°/0.05 torr, mp 81-81°. Anal. Calcd. for $C_{12}H_{16}MoNO_7P$: C, 34.86; H, 3.86; N, 3.39. Found: C, 34.72; H, 3.99; N, 3.61.

(2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylchromium.

A mixture of 2.2 g of Cr(CO)$_6$, 1.7 g of 2-Cl-DMP, and 20 ml of methylcyclohexane was heated at reflux for 10 hr. The reaction mixture was concentrated to dryness under aspirator vacuum. Fractional sublimation of the residue yielded unreacted Cr(CO)$_6$ at 40°/0.05 torr and pure (2-Cl-DMP)Cr(CO)$_5$ at 65°/0.05 torr as white crystals, mp 88-89°, in 50% yield. Anal. Calcd. for $C_{10}H_{10}ClCrO_7P$: C, 33.30; H, 2.77. Found: C, 33.25; H, 2.95.

(2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonyltungsten.

A mixture of 3.52 g of $W(CO)_6$ and 10 ml of 2-Cl-DMP was heated at 150° for 7 hr. Excess 2-Cl-DMP was removed by distillation at 75°/10 torr. Addition of hexane to the residual oil gave a crude solid product. Pure (2-Cl-DMP)$W(CO)_5$, mp 97-99°, was obtained as white crystals in 63% yield by subsequent recrystallization of the crude solid from hexane containing a small amount of activated charcoal. Anal. Calcd. for $C_{10}H_{10}ClO_7PW$: C, 24.48; H, 2.04. Found: C, 24.74; H, 2.10.

(2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)tricarbonylnickel.

A solution of 13 g of 2-Cl-DMP in 10 ml of hexane was added to a well-stirred solution of 15 g of nickel tetracarbonyl in 40 ml of hexane at such a rate that the carbon monoxide evolution could be controlled. The total reaction time was 4 hr. Concentration of the reaction mixture to dryness left a solid residue from which pure (2-Cl-DMP)$Ni(CO)_3$, mp 103-104°, was obtained in 79% yield upon recrystallization from hexane. Anal. Calcd. for $C_8H_{10}ClNiO_5$: C, 30.87; H, 3.22. Found: C, 31.18; H, 3.47.

(2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)tetracarbonyliron.

A mixture of 7.9 g of triiron dodecacarbonyl, 7.9 g of 2-Cl-DMP and 50 ml of dry benzene was heated at reflux for 45 min. The solution was allowed to cool to room temperature whereupon a yellow solid precipitated. The solid was collected by filtration and washed with two 25-ml portions of pet ether. Addition of the pet ether washings to the oil obtained upon concentration of the benzene filtrate caused precipitation of additional yellow solid. The filtrate obtained after removal of this second crop of yellow solid was concentrated to yield a red liquid. The liquid was distilled at 91-92°/0.04 torr to give (2-Cl-DMP)Fe(CO)$_4$ in 52% yield as a yellow liquid which solidified on standing, mp 56°. Anal. Calcd. for $C_9H_{10}ClFeO_6P$: C, 32.14; H, 297. Found: C, 32.29; H, 2.98.

The yellow solid isolated earlier in the workup was recrystallized from hexane to give bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)diiron hexacarbonyl as a yellow, microcrystalline powder, mp 182-184° (dec). Anal. for $C_8H_{10}FeO_5P$: C, 35.26; H, 3.66. Found: C, 36.01; H, 3.86.

(2-Chloro-5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum.

A mixture of 14 g of Mo(CO)$_6$, 10.5 g of 2-Cl-MTBP, and 50 ml of methylcyclohexane was heated at reflux for 2.5 hr. Solvent was removed under aspirator vacuum and unreacted Mo(CO)$_6$ was sublimed at 40°/0.1 torr. The remaining solid was recrystallized twice from hexane with activated charcoal. The product was obtained in 78% yield as white crystals, mp 94-95°. Anal. Calcd. for $C_{13}H_{16}ClMoO_7P$: C, 34.92; H, 3.58. Found: C, 34.84; H, 3.61.

The product was shown to consist of 90% chair conformer via proton nmr.

trans-(2-Methoxy-5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane)-pentacarbonylmolybdenum (Chair isomer)

A mixture of 2.65 g of Mo(CO)$_6$, 2.1 g of 2-CH_3O-MTBP, and 25 ml of methylcyclohexane was heated at reflux for 2 hr. Solvent was removed under aspirator vacuum and unreacted Mo(CO)$_6$ at 40°/0.1 torr.

The pure product was obtained in 75% yield upon recrystallization from hexane as white crystals, mp 91-92°. Anal. Calcd. for $C_{14}H_{19}MoO_8P$: C, 38.01; H, 4.30. Found: C, 37.99; H, 4.29.

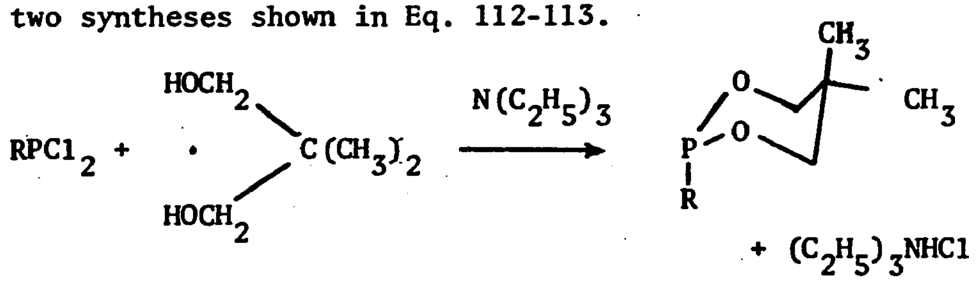
cis-(2-Methoxy-5-methyl-5-tert-butyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum. (Boat isomer)

A mixture of 3 g of (2-Cl-MTBP)Mo$(CO)_5$ and 25 ml of methanol was heated at reflux for 4-5 hr. The cooled mixture was mixed with 75 ml of water from which the product was extracted with three 25-ml portions of ether. The ether layer was dried with anhydrous magnesium sulfate. The ether was removed under aspirator vacuum, leaving a white solid containing both isomers of (2-CH_3O-MTBP)Mo$(CO)_5$. The solid was dissolved in a minimum amount of pet ether. Slow removal of the pet ether in a stream of nitrogen caused preferential precipitation of the cis isomer. These crystals were further recrystallized from pet ether to give the pure cis product as white crystals, mp 87-88°, in 30% yield. Anal. Calcd. for $C_{14}H_{19}MoO_8P$: C, 38.01; H, 4.30. Found: C, 38.08; H, 4.23.

The melting point of a 50/50 (weight/weight) mixture of the two isomers was 63-65°.

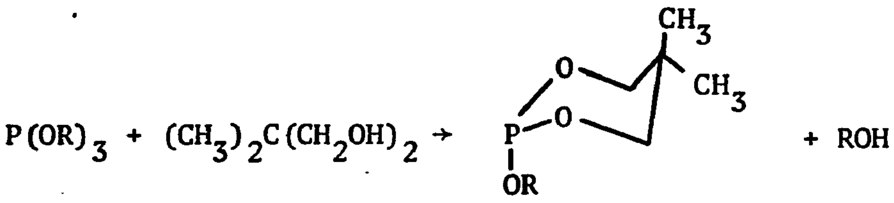
SYNTHETIC RESULTS

The 1,3,2-dioxaphosphorinane ring is best prepared by either of the two syntheses shown in Eq. 112-113.



(112)

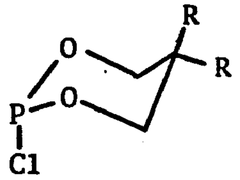
where R = Cl, C_6H_5, CH_3; or



(113)

R = CH_3

The 2-chloro-1,3,2-dioxaphosphorinanes are reactive and may be used to prepare other 1,3,2-dioxaphosphorinanes with a variety of substituents at the 2-position (Eq. 114-116).



\+ $(CH_3)_2NH \longrightarrow$ 2-N$(CH_3)_2$-DMP (114)

$CH_3OH \longrightarrow$ 2-CH_3O-DMP (115)

$C_6H_5SH \longrightarrow$ 2-C_6H_5S-DMP (116)

R = CH_3

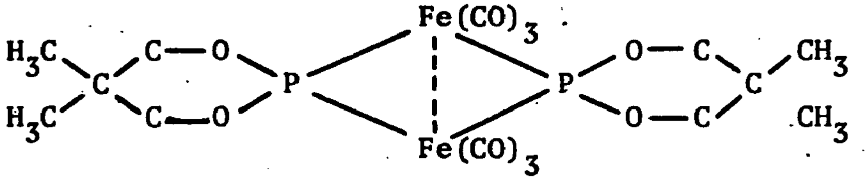
Generally, the 2-X-DMP derivaties are colorless liquids which are easily purified by vacuum distillation. The 2-X-MTBP, 2-X-5-methyl-5-*tert*-butyl-1,3,2-dioxphosphorinane, products are also colorless liquids and distillable under high vacuum, but 2-Cl-MTBP solidifies on standing to a low-melting solid. The 1,3,2-dioxaphosphorinanes are oxidized by atmospheric oxygen and hydrolyzed by moisture, but they may be stored for long periods under nitrogen with no apparent change.

The metal carbonyl complexes of 1,3,2-dioxaphosphorinanes studied in this investigation were synthesized by two different procedures. Except for (2-C_2H_5O-DMP)Mo$(CO)_5$ and cis-(2-CH_3O-MTBP)Mo$(CO)_5$, all of the complexes were prepared by a direct reaction between the free ligand and a metal carbonyl. Nickel carbonyl reacts with 2-Cl-DMP at room temperature in an inert solvent to give Ni$(CO)_3$(2-Cl-DMP). Molybdenum hexacarbonyl reacts with a variety of 2-X-DMP's in refluxing methylcyclohexane (bp 101°) to give the monosubstituted products in excellent yield. The physical properties of Mo$(CO)_5$(2-Cl-DMP), Cr$(CO)_5$-(2-Cl-DMP), and W$(CO)_5$(2-Cl-DMP) are very similar. However, the conditions for preparing the chromium and tungsten complexes are much more severe than for the molybdenum complex. This differing degree of reactivity has been observed in most reactions of the group VI metal carbonyls[49] and is not unique to the ligand system employed here. In general, the order of decreasing reactivity of the group VI hexacarbonyls,

$$Mo(CO)_6 >> Cr(CO)_6 > W(CO)_6$$

has been attributed to stronger pi-bonding in $W(CO)_6$ and $Cr(CO)_6$ than in $Mo(CO)_6$.[137]

Triiron dodecacarbonyl gives two products upon reaction with 2-Cl-DMP. The simple coordination complex, Fe$(CO)_4$(2-Cl-DMP), is an orange solid which may be distilled or sublimed under high vacuum. A lemon-yellow product, 5, which was identified as a dimer containing bridging 5,5-dimethyl-1,3,2-dioxaphosphorinane groups was obtained also and will be discussed in detail in a later chapter in this thesis.



(5)

A second procedure employed to prepare complexes of 1,3,2-dioxaphosphorinanes involved the reactions of coordinated chlorophosphine ligands. Both $Mo(CO)_5(2\text{-}CH_3O\text{-}DMP)$ and $Mo(CO)_5(2\text{-}C_2H_5O\text{-}DMP)$ were prepared by heating $Mo(CO)_5(2\text{-}Cl\text{-}DMP)$ in methanol and ethanol, respectively, as shown in Eq. 117.

$$Mo(CO)_5(2\text{-}Cl\text{-}DMP) + ROH \rightarrow Mo(CO)_5(2\text{-}RO\text{-}DMP) + HCl \qquad (117)$$

The 1,3,2-dioxaphosphorinane ring was formed directly by the reaction between 2,2-dimethyl-1,3-propanediol and (dichloromethylphosphine)-pentacarbonylmolybdenum in refluxing benzene. No differences in the physical or spectral properties of the two samples of $(2\text{-}CH_3O\text{-}DMP)Mo(CO)_5$ or the two samples of $(2\text{-}CH_3\text{-}DMP)Mo(CO)_5$ prepared by the two different procedures were observed.

In contrast to the complexes studied in Part I of this thesis which react readily at room temperature with ammonia and dimethylamine to give complexes of aminophosphine ligands, (2-Cl-DMP)pentacarbonylmolybdenum dissolved in ether does not react at all with either ammonia or dimethylamine at room temperature. Further, conditions for the formation of $(2\text{-}CH_3O\text{-}DMP)Mo(CO)_5$ from $(2\text{-}Cl\text{-}DMP)Mo(CO)_5$ are much more severe compared to those required for reaction of the acyclic complexes discussed in Part I. For example, $Mo(CO)_5P(C_6H_5)_2Cl$ reacts with an excess of warm methanol in less than ten minutes, but Mo(CO)$_5$(2-Cl-DMP) may be recrystallized from a methanol/water mixture with essentially no change. This greater lack of reactivity of (2-Cl-DMP)Mo(CO)$_5$ probably arises from steric crowding about phosphorus caused by both the Mo(CO)$_5$ moiety and the heterocyclic ring itself.

The metal carbonyl complexes of 2-X-DMP were identified by elemental analysis, infrared spectroscopy, and proton nmr spectroscopy. All the complexes gave correct analyses for carbon and hydrogen. The nmr spectra of the complexes show essentially the same features as the trivalent 1,3,2-dioxaphosphorinanes, and it was concluded that the 1,3,2-dioxaphosphorinanes formed complexes without disruption of the heterocyclic ring.

The 2000 cm^{-1} region in the infrared spectra of the metal complexes of 1,3,2-dioxaphosphorinanes clearly indicates that complex formation is between the metal and the phosphorus atom of the heterocyclic ring.[56] Infrared data for the complexes prepared in this study are listed in Table 8.

The net electron withdrawing effect of the phosphorinane ligands is as expected based upon previous observations of complexes of phosphite esters. Several direct comparisons of force constants between (2-X-DMP)Mo(CO)$_5$ complexes and their isostructural acyclic cogeners are possible and are listed in Table 9.

TABLE 8

METAL CARBONYL STRETCHING FREQUENCIES (cm^{-1}) AND SIMPLIFIED FORCE CONSTANTS (mdyn/Å) FOR M(CO)$_n$(2-R-DMP) and Mo(CO)$_5$(2-X-MTBP)[a]

Compound	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E	k_1	k_2	k_i
Mo(CO)$_5$(2-Cl-DMP)	2088	2004	1980	1973	16.03	16.28	0.28
Mo(CO)$_5$(2-CH$_3$-DMP)	2081	1993	1965	1952	15.83	16.01	0.31
Mo(CO)$_5$(2-C$_6$H$_5$-DMP)	2081	1996	1969	1962	15.86	16.12	0.29
Mo(CO)$_5$(2-CH$_3$O-DMP)	2083	1999	1970	1959	15.90	16.10	0.30
Mo(CO)$_5$(2-C$_2$H$_5$O-DMP)	2082	1999	1970	1957	15.90	16.07	0.30
Mo(CO)$_5$(2-C$_6$H$_5$S-DMP)	2082	1999	1971	1957	15.92	16.07	0.30
Mo(CO)$_5$[2-(CH$_3$)$_2$N-DMP]	2078	1992	1958	1948	15.71	15.95	0.31
Cr(CO)$_5$(2-Cl-DMP)	2082	2001	1978	1967	16.01	16.18	0.28
W(CO)$_5$(2-Cl-DMP)	2089	2003	1977	1967	16.00	16.22	0.30
trans-Mo(CO)$_5$(2-Cl-MTBP)	2087	2003	1978	1968	16.01	16.24	0.29
trans-Mo(CO)$_5$(2-CH$_3$O-MTBP)	2083	1999	1970	1958	15.90	16.10	0.30
cis-Mo(CO)$_5$(2-CH$_3$O-MTBP)	2082	1999	1971	1958	15.90	16.09	0.30
Fe(CO)$_4$(2-Cl-DMP)	2073	2004	1975br				
Ni(CO)$_3$(2-Cl-DMP)	2061	2012					
(Fe(CO)$_3$-μ-DMP)$_2$	2066m	2026vs	2005s	1978m	1954m		

a. Hexane solvent. Abbreviations: s = strong; v = very; m = medium; br = broad.

TABLE 9

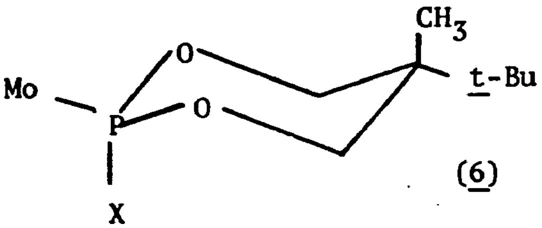
COMPARATIVE INFRARED DATA FOR SEVERAL ISOSTRUCTURAL PHOSPHITE COMPLEXES[a]

Complexes	k_1	k_2	Ref.
$Mo(CO)_5CH_3P(OCH_3)_2$	15.85	16.01	67
$Mo(CO)_5(2\text{-}CH_3\text{-}DMP)$	15.83	16.01	this work
$Mo(CO)_5P(OCH_3)_3$	15.90	16.06	138
$Mo(CO)_5(2\text{-}CH_3O\text{-}DMP)$	15.90	16.10	this work

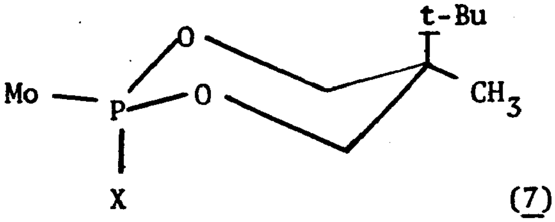
[a] Hexane solvent.

Clearly, only the electronic nature of the substituents on phosphorus is of major importance in determining the capability of the ligand to accept pi-electron density.

The pentacarbonylmolybdenum complexes of 2-X-TBMP are of special interest. The presence of two different substituents at the 5-carbon of the phosphorinane ring makes possible the existence of isomers, since the $Mo(CO)_5$ group can be either trans (6) or cis (7) to the t-butyl group.



(6)



(7)

The direct reaction between $Mo(CO)_6$ and either 2-Cl-MTBP or $2\text{-}CH_3O\text{-}MTBP$ gave the analytically pure complexes $Mo(CO)_5(2\text{-}Cl\text{-}MTBP)$ and $Mo(CO)_5$-$(2\text{-}CH_3O\text{-}MTBP)$, respectively. However, each of the complexes was obtained as a mixture of isomers in a 90:10 ratio with the trans product being the greater fraction in each case. The trans isomer was obtained almost free of the cis isomer after repeated recrystallization from petroleum ether. The cis isomers could not be obtained pure via fractional recrystallization of these mixtures.

An alternative route to the cis isomer of $Mo(CO)_5(2\text{-}CH_3O\text{-}MTBP)$ became available. The reaction of trans-$Mo(CO)_5(2\text{-}Cl\text{-}MTBP)$ with methanol gave cis-$Mo(CO)_5(2\text{-}CH_3O\text{-}MTBP)$ in sufficient yield to obtain pure gram quantities of sample by fractional recrystallization of the reaction mixture. The physical appearance, melting point, and infrared spectra of the cis and trans isomers of $(2\text{-}CH_3O\text{-}MTBP)Mo(CO)_5$ are very similar. However, a mixed melting point determination upon a 50:50 mixture of the two isomers showed a decrease of nearly 30° from the melting point of each pure isomer. Also, the nmr spectrum of each is markedly different and provides an excellent way to determine the relative concentration of each in a mixture.

The compound 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinanium iodide was prepared by the reaction of methyl iodide with $2\text{-}CH_3\text{-}DMP$. The resulting quasi-phosphonium salt is a white crystalline solid which decomposes at its melting point. The salt is also decomposed by water and must be stored under a protective nitrogen atmosphere. The salt is insoluble in most organic solvents but shows limited solubility in acetonitrile.

CONFORMATION OF THE HETEROCYCLIC RING IN THE 1,3,2-DIOXAPHOSPHORINANE COMPLEXES

Although the structures of a few 1,3,2-dioxaphosphorinanes have been determined by X-ray crystallography,[139-141] accurate conclusions regarding the conformation of the heterocyclic ring can be drawn from analysis of the nmr spectra of the 1,3,2-dioxaphosphorinanes. Generally, the pmr spectra of the 2-X-DMP complexes prepared in this study exhibit several features common to each other; a typical ^1H nmr spectrum is shown in Figure 15. The methyl groups for each complex give rise to a pair of apparent singlets separated by 25-45 Hz depending upon the substituents on phosphorus. The methyl resonance at lower field, corresponding to the axial methyl group, is broader than the higher field methyl signal. For all of the complexes, except the molybdenum carbonyl complexes of 2-methyl and 2-phenyl-DMP, which will be discussed in more detail below, the methylene protons give rise to two distinct quartets. The higher field equatorial proton resonance signals exhibit fine structure. The lower field methylene resonance signals are broadened with no apparent fine structure. When the lower field methyl protons are decoupled, the lower field methylene resonance assumes the fine structure apparent in the higher field methylene resonance (Figures 16-17). The pmr spectral parameters of the 2-X-DMP complexes were refined with the use of the iterative program LAOCN3 and are listed in Tables 10 and 11. Details concerning analysis of the nmr spectra of the compounds prepared in this study are discussed in the Appendix. Finally, no appreciable changes in the various calculated spectral

TABLE 10

^1H CHEMICAL SHIFTS[a] OF THE METHYL GROUPS IN 2-R-DMP-M(CO)$_n$

Metal	R	δ equatorial	δ axial	Difference
Ni	Cl	0.84	1.28	0.44
Fe	Cl	0.88	1.33	0.45
Cr	Cl	0.88	1.33	0.45
W	Cl	0.88	1.33	0.45
Mo	Cl	0.88	1.32	0.44
Mo	OCH_3	0.80	1.30	0.50
Mo	OC_2H_5	0.80	1.31	0.51
Mo	$N(CH_3)_2$	0.77	1.31	0.54
Mo	SC_6H_5	0.85	1.34	0.49
Mo	C_6H_5	0.64	1.40	0.76
Mo	CH_3	0.83	1.29	0.46

a. Chloroform solvent at 34°. Shifts are downfield in ppm from internal tetramethylsilane.

TABLE 11. PMR SPECTRAL PARAMETERS OF 2-R-DMP METAL CARBONYL COMPLEXES[a]

COMPD	TEMP	SOLVENT	δCH_2 eq	δCH_2 ax	$J^b_{Heq\ Hax}$	J_{PHeq}	J_{PHax}	$J^c_{Heq\ Heq}$
$Mo(CO)_5(2\text{-}Cl\text{-}DMP)$	-35	$CHCl_3$	223.9 (0.06)	262.4 (0.06)	-10.9 (0.05)	19.6 (0.07)	6.20 (0.06)	2.60 (0.06)
	34	$CHCl_3$	222.4 (0.03)	259.1 (0.03)	-10.9 (0.03)	19.7 (0.06)	6.03 (0.95)	2.60 (0.06)
	50	$CHCl_3$	220.4 (0.09)	261.4 (0.10)	-10.9 (0.10)	19.3 (0.16)	6.06 (0.16)	2.60 (0.20)
	60	$CHCl_3$	220.6 (0.10)	260.9 (0.10)	-10.9 (0.10)	19.3 (0.16)	6.01 (0.19)	2.60 (0.20)
$Mo(CO)_5(2\text{-}CH_3\text{-}DMP)$	34	$CHCl_3$	222.4 (0.12)	238.3 (0.15)	-10.8 (0.11)	16.9 (0.19)	4.20 (0.12)	2.73 (0.20)
	34	CD_3CN	219.7 (0.04)	245.2 (0.14)	-10.8 (0.06)	17.0 (0.08)	3.73 (0.07)	2.63 (0.07)
	34	CS_2	219.9 (0.11)	235.2 (0.12)	-11.1 (0.10)	16.6 (0.19)	4.40 (0.11)	2.75 (0.13)
	34	C_6H_5Cl	201.0 (0.10)	215.1 (0.15)	-11.1 (0.10)	17.3 (0.16)	4.16 (0.12)	2.61 (0.21)
	80	C_6H_5Cl	205.5 (0.10)	217.8 (0.12)	-11.1 (0.07)	16.3 (0.17)	3.82 (0.09)	2.70 (0.17)
$Mo(CO)_5(2\text{-}C_6H_5\text{-}DMP)$	-50	$CHCl_3$	219.2 (0.14)	228.1 (0.14)	-10.4 (0.05)	17.2 (0.27)	3.51 (0.27)	2.62 (0.04)
	34	$CHCl_3$	220.3 (0.14)	227.4 (0.14)	-10.2 (0.05)	17.5 (0.27)	3.35 (0.27)	2.60 (0.04)
	50	$CHCl_3$	218.0 (0.11)	227.0 (0.11)	-10.3 (0.06)	17.3 (0.18)	3.39 (0.18)	2.61 (0.05)
	34	C_5H_5N	218.5 (0.13)	227.9 (0.13)	-10.4 (0.07)	17.1 (0.19)	3.46 (0.19)	2.66 (0.04)
	34	CS_2	216.1 (0.14)	227.6 (0.14)	-10.5 (0.06)	17.6 (0.20)	3.51 (0.20)	2.71 (0.20)
$Mo(CO)_5(2\text{-}Ch_3O\text{-}DMP)$	-35	$CHCl_3$	211.1 (0.03)	248.7 (0.03)	-10.7 (0.04)	16.6 (0.06)	3.41 (0.04)	2.66 (0.05)
	34	$CHCl_3$	211.6 (0.03)	248.5 (0.03)	-10.6 (0.04)	16.5 (0.06)	3.38 (0.05)	2.65 (0.05)
	60	$CHCl_3$	212.1 (0.04)	249.1 (0.04)	-10.5 (0.04)	16.6 (0.06)	3.42 (0.05)	2.71 (0.05)

TABLE 11 - CONTINUED

COMPD	TEMP	SOLVENT	δCH_2 eq	δCH_2 ax	$J^b_{Heq\ Hax}$	J_{PHeq}	J_{PHax}	$J^c_{Heq\ Heq}$
Mo(CO)$_5$(2-C$_2$H$_5$O-DMP)	34	CHCl$_3$	211.4 (0.02)	249.8 (0.02)	-10.6 (0.03)	16.9 (0.04)	3.43 (0.04)	2.54 (0.04)
	60	CHCl$_3$	211.6 (0.02)	249.9 (0.02)	-10.5 (0.02)	16.7 (0.03)	3.40 (0.03)	2.61 (0.04)
Mo(CO)$_5$(2-C$_6$H$_5$S-DMP)	34	CHCl$_3$	224.7 (0.02)	269.2 (0.02)	-11.0 (0.02)	18.3 (0.03)	5.15 (0.03)	2.60 (0.03)
	60	CHCl$_3$	223.2 (0.01)	268.4 (0.01)	-10.8 (0.02)	18.02 (0.02)	5.12 (0.02)	2.65 (0.02)
Mo(CO)$_5$[2-(CH$_3$)$_2$-N-DMP]	34	CHCl$_3$	205.4 (0.02)	244.3 (0.02)	-10.4 (0.02)	16.8 (0.03)	3.09 (0.03)	2.50 (0.03)
	60	CHCl$_3$	205.9 (0.02)	244.9 (0.02)	-10.6 (0.02)	16.9 (0.02)	3.17 (0.02)	2.61 (0.03)
Cr(CO)$_5$(2-Cl-DMP)	34	CHCl$_3$	225.6 (0.05)	263.4 (0.05)	-11.2 (0.07)	20.3 (0.09)	5.75 (0.08)	2.40 (0.09)
	60	CHCl$_3$	226.3 (0.05)	263.7 (0.05)	-11.1 (0.06)	20.3 (0.08)	5.78 (0.08)	2.45 (0.08)
W(CO)$_5$(2-Cl-DMP)	34	CHCl$_3$	221.9 (0.01)	260.7 (0.01)	-11.2 (0.02)	20.2 (0.03)	6.43 (0.03)	2.67 (0.03)
	60	CHCl$_3$	222.4 (0.02)	261.3 (0.02)	-11.1 (0.05)	20.2 (0.04)	6.41 (0.04)	2.64 (0.03)
Fe(CO)$_4$(2-Cl-DMP)	34	CHCl$_3$	229.9 (0.02)	262.8 (0.02)	-11.1 (0.03)	22.5 (0.04)	5.68 (0.04)	2.78 (0.04)
	60	CHCl$_3$	230.1 (0.01)	263.4 (0.02)	-10.9 (0.02)	22.4 (0.02)	5.64 (0.04)	2.69 (0.04)
Ni(CO)$_3$(2-Cl-DMP)	34	CHCl$_3$	219.0 (0.01)	259.3 (0.02)	-11.0 (0.02)	18.2 (0.02)	3.53 (0.02)	2.84 (0.03)
	60	CHCl$_3$	219.4 (0.02)	259.3 (0.02)	-11.0 (0.02)	18.2 (0.03)	3.53 (0.02)	2.70 (0.03)

---

a. Chemical shift values (Hz) are relative to internal TMS at $\delta = 0$. Values in parentheses are the probable errors generated by LAOCN3. Experimental error is at least ±0.2 Hz.

b. Sign of $J_{Heq\ Hax}$ assigned as suggested by Gagnaire *et al*.

c. $J_{Hax\ Hax}$ assumed to be zero.

Figure 15. The proton NMR spectrum of $Mo(CO)_5$(2-Cl-DMP).

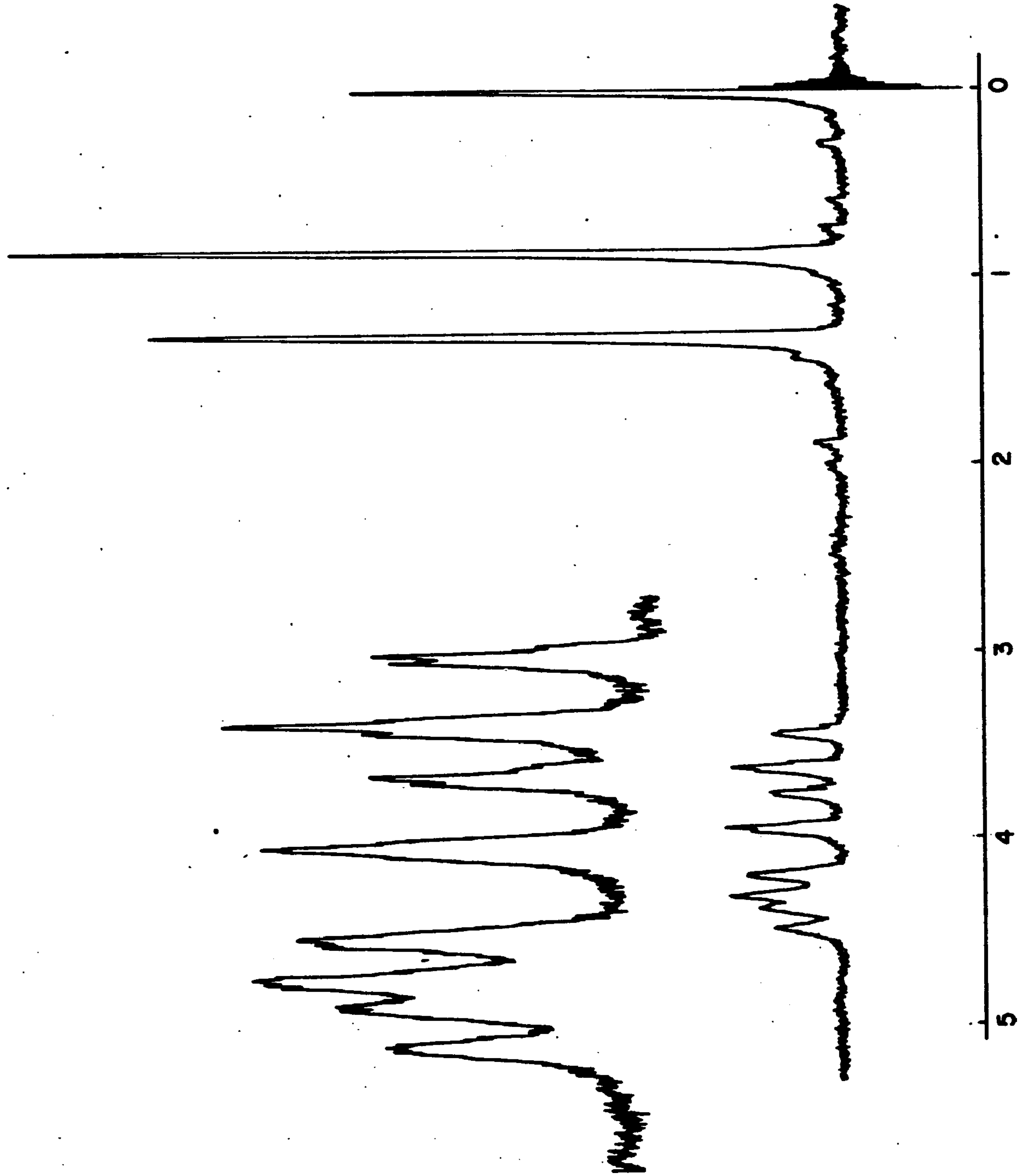


Figure 16. Axial methylene proton NMR spectrum of $(2\text{-Cl-DMP})Mo(CO)_5$. (A) Same spectrum with axial methyl protons decoupled. (B)

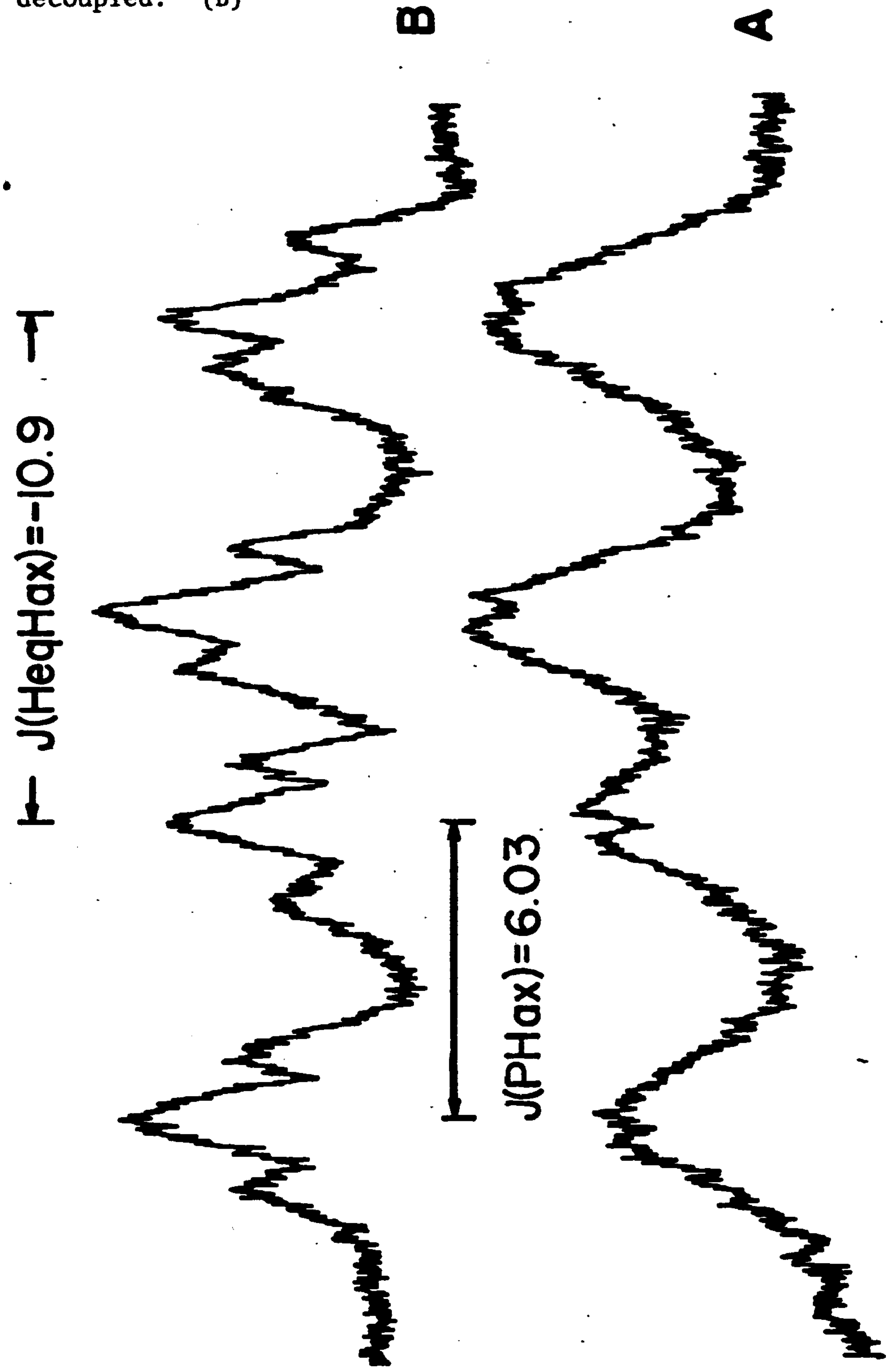
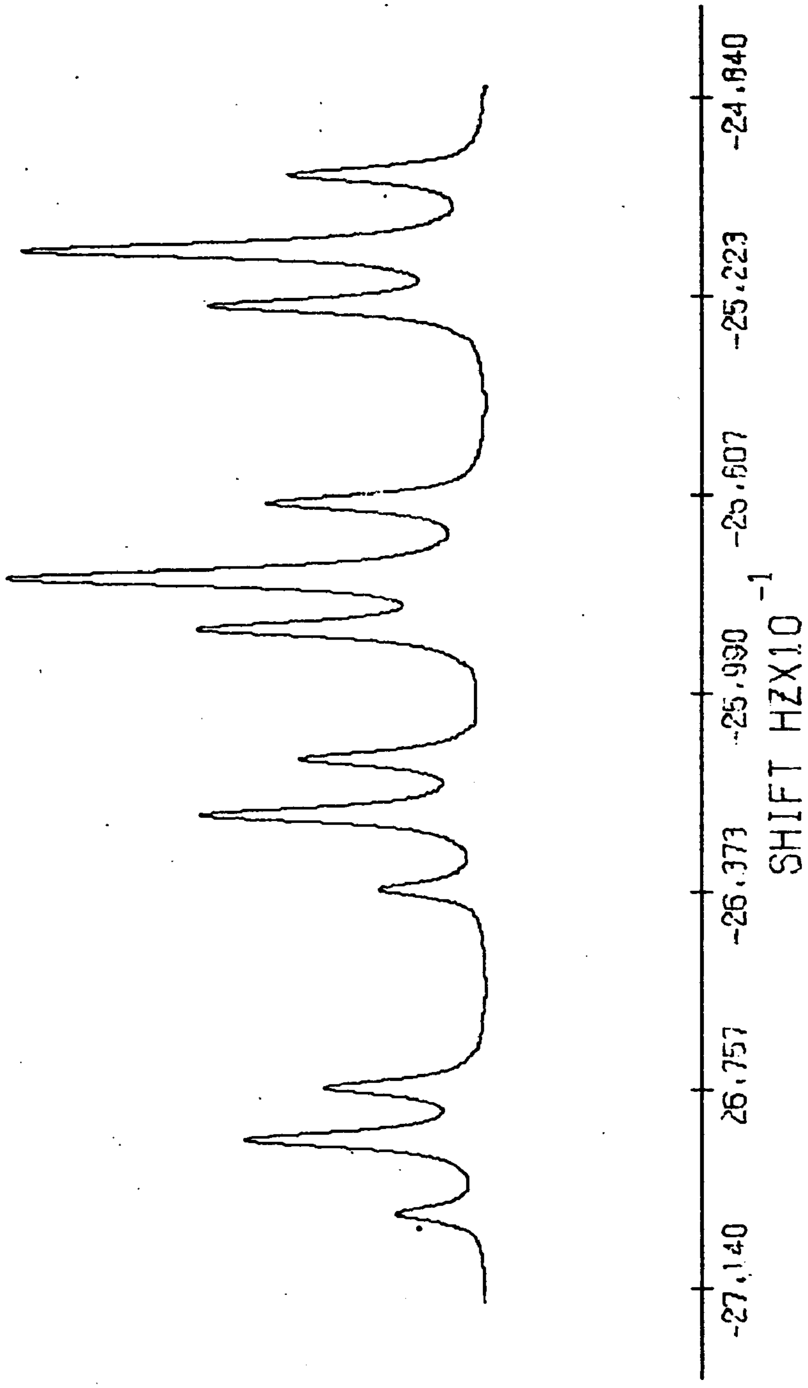


Figure 17. Computer synthesized spectrum of the axial methylene protons of (2-Cl-DMP)Mo$(CO)_5$.



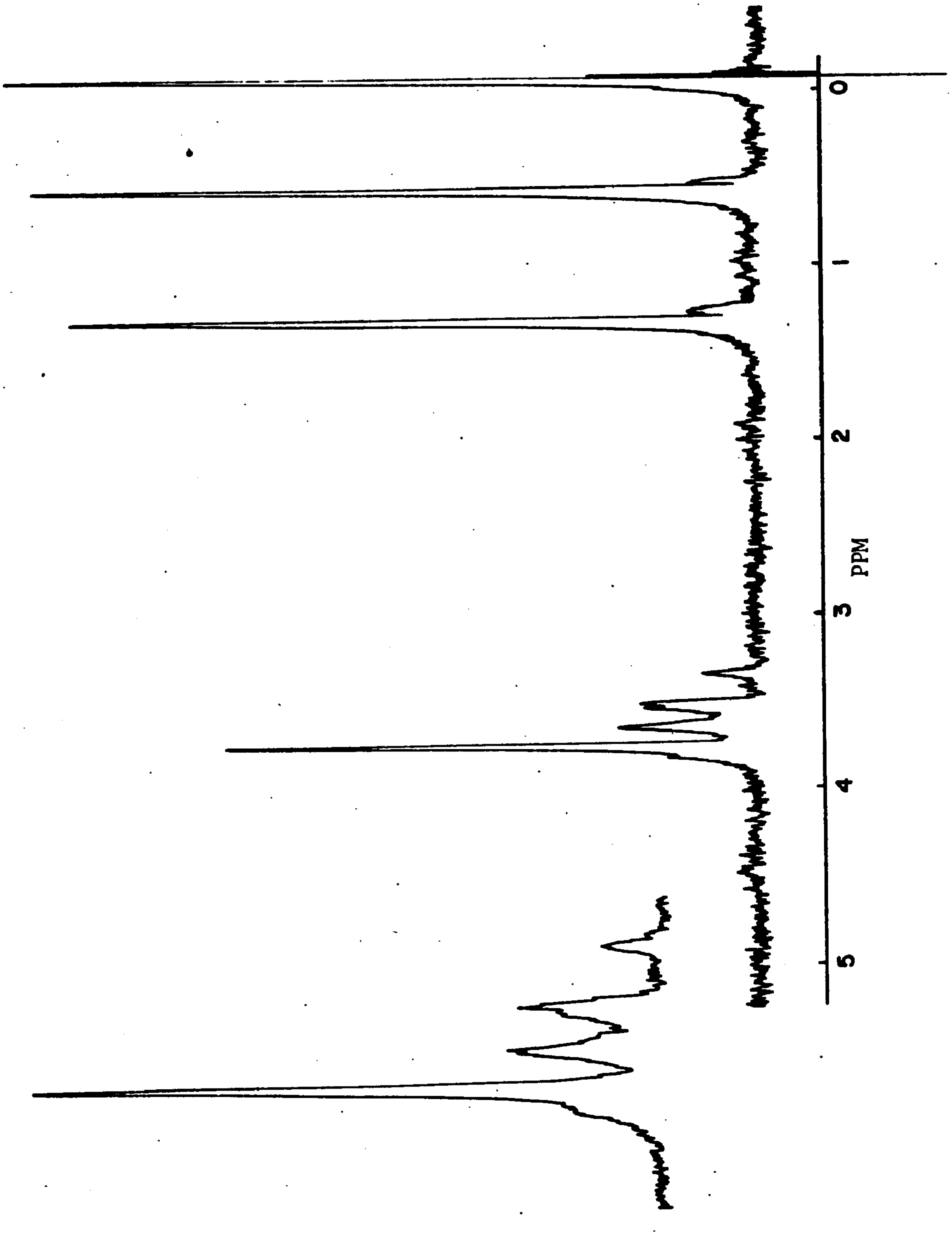
parameters were noted over the temperature ranges indicated in Table 11.

Although the pertinent coupling constants for (2-CH_3-DMP)Mo$(CO)_5$ were found to be invariant within calculational errors over the range of solvents indicated in Table 11, the difference between the chemical shifts for the axial and equatorial methylene protons was noted to be very solvent dependent. In the lower dielectric constant solvents chloroform, carbon disulfide, and chlorobenzene this difference in chemical shift is on the order of 12-16 Hz. As a result of these small differences, simple first order spectra are not observed for the methylene protons in the above-mentioned solvents. However, the chemical shift difference between the axial and equatorial methylene proton resonance signals for the same complex is 25 Hz in deuterioacetonitrile at 34°. This larger separation causes the spectrum to have the same appearance as the spectra of the other complexes in chloroform.

Analysis of the spectra of (2-C_6H_5-DMP)Mo$(CO)_5$ reveals the coupling constants for the ring system to be effectively independent of changes in both temperature and solvent. However, owing to the consistently small difference between the chemical shifts of the methylene protons, the spectrum maintains a deceptively simple appearance under all of the conditions employed here. The nmr spectrum of (2-C_6H_5-DMP)-Mo$(CO)_5$ is shown in Figure 18.

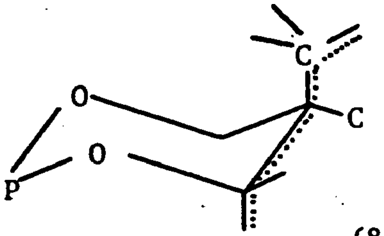
The results of the nmr spectral analysis of the 2-X-DMP complexes can be used in establishing the conformation of the heterocyclic ring. First, the relatively small range of values observed for each coupling constant is quite noticeable. This fact, as well as the observation of invariance of the phosphorus-methylene proton coupling

Figure 18. The proton NMR spectrum of $Mo(CO)_5(2\text{-}C_6H_5\text{-DMP})$.



constants with temperature changes, leads to the natural conclusion[114,117] that a single, common conformation is the predominate form of the 1,3,2-dioxaphosphorinane ring in each compound.

Arguments leading to the assignment of a particular conformation for the 1,3,2-dioxaphosphorinane system have been published[114,117] and similar reasoning may be applied to the metal complexes prepared in this study. First, one set of methyl protons couples slightly (<1.0 Hz) to one group of methylene protons as demonstrated by the decoupling experiment described above (Figure 16). Also, there is appreciable coupling (2.6 Hz) between one set of methylene protons (BB'), but negligible coupling between the AA' methylene protons. These enhanced four-bond HCCCH couplings are usually found when the bonds linking the coupled nuclei form a planar W.[142] This arrangement allows interaction between the antibonding lobes of the sp^3 orbitals on the appropriate carbon atoms leading to a pathway for the coupling to occur.[142] This type of pathway exists between the equatorial methylene protons as well as between the axial methylene protons and the protons of an axial methyl group as shown below.



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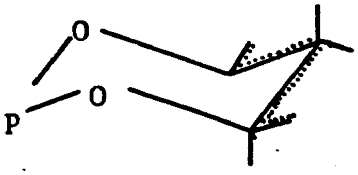
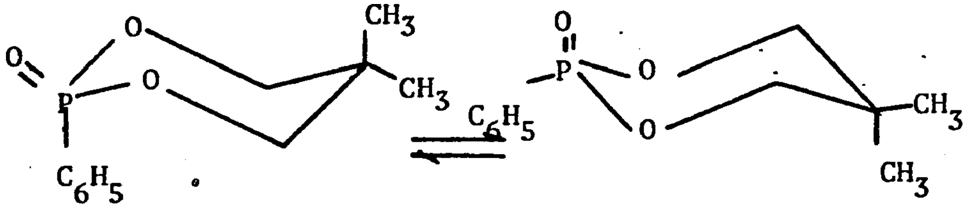


(9)

On the basis of these considerations, it was concluded that the equatorial methylene protons are more shielded than the axial methylene protons in all the metal carbonyl-2-X-DMP complexes prepared in this study, and the phosphorus-equatorial methylene proton coupling is always greater than the corresponding axial methylene proton coupling to phosphorus. Also, the axial 5-methyl protons resonate at lower field than the equatorial 5-methyl protons. In particular, the presence of the observed four-bond proton-proton coupling rules out consideration of unsymmetrical boat or twist-boat conformations, inasmuch as they would not possess all of the protons in appropriate positions. Comparable quantities of rapidly interconverting chair or boat conformers can also be ruled out because the enhanced long-range coupling would then be averaged among all of the methylene and methyl protons according to the ratio of conformers.[117]

The ring POCH coupling constants of the 2-X-DMP-metal complexes (Table 11) may be taken as evidence against the presence of a boat conformer. Several workers have suggested that a dihedral angle dependence exists for J(POCH) similar to that for J(HCCH).[143-145] A boat conformation, with both POCH dihedral angles approximately 120°, should give rise to two nearly equal values of ^{3}J(POCH) for any one complex. But a chair conformation, with dihedral angles of nearly 180° and 60°, should yield two different values of J(POCH). Clearly, all of the 2-X-DMP-metal complexes prepared in this study exhibit two different values of J(POCH). It must be concluded that a rigid chair structure is the predominate, if not exclusive, conformer for all of the complexes.

The compounds $(2\text{-}CH_3\text{-DMP})Mo(CO)_5$ and $(2\text{-}C_6H_5\text{-DMP})Mo(CO)_5$ show different behavior with respect to conformational mobility when compared to the corresponding compounds with the pentacarbonylmolybdenum group replaced by a 2-oxo group. Both 2-methyl- and 2-phenyl-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane have been shown to be conformationally mobile (Eq. 117),[115,127] but the same 2-oxo derivatives with chloro- or alkoxy- are locked in a single conformation.

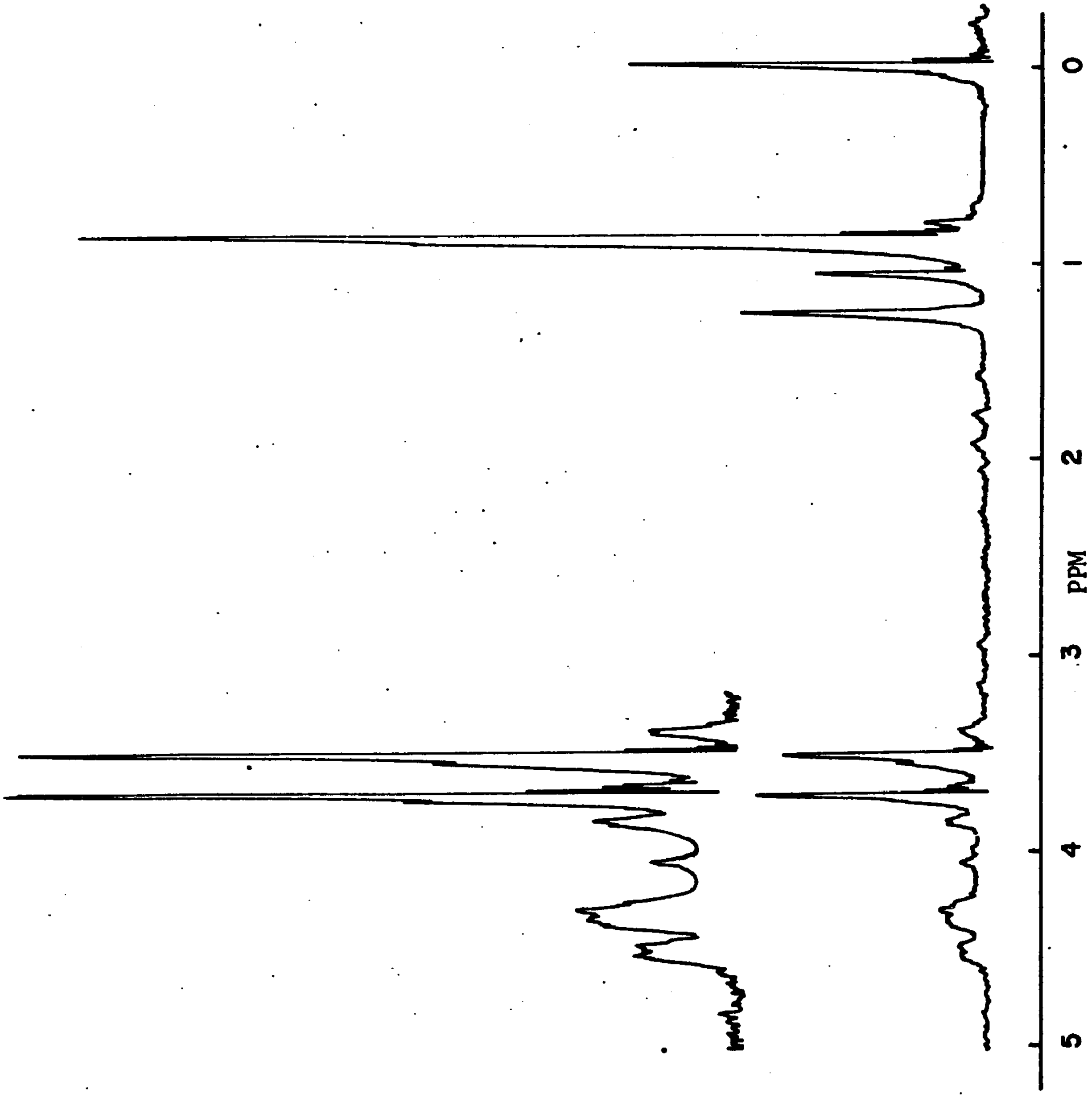


(117)

Unfortunately, the differences in conformational flexibility in the above-mentioned compounds are not all readily rationalized. However, the large metal carbonyl moiety in the complexes of the 1,3,2-dioxaphosphorinanes may act as a holding group. Apparently, the decided preference of a metal carbonyl group for a particular stereochemical orientation is sufficient to control the flexibility of the 1,3,2-dioxaphosphorinane ring.

Conclusions similar to those drawn for the 2-X-DMP-metal complexes have been reached for the trans-$Mo(CO)_5$(2-X-MTBP) complexes (X = Cl, OCH_3). The nmr spectra for these complexes closely resemble those of the analogous 2-X-DMP complexes; however, a sharp tert-butyl resonance appears in place of the high-field 5-methyl absorption. The methylene protons give two quartets from which the various J(POCH) coupling constants may be obtained. Significantly, the lower-field methylene quartet is broadened relative to the higher field quartet which exhibits fine structure. When the 5-methyl resonance is decoupled, fine structure appears in the previously broad lower field resonance. Using the same arguments developed for the 2-X-DMP complexes, the 5-methyl group and the lower field methylene protons both must occupy axial positions on the 1,3,2-dioxaphosphorinane ring. The values of ^3J(POCH) for the trans-$Mo(CO)_5$-2-X-MTBP complex are nearly the same as those for the corresponding $Mo(CO)_5$-2-X-DMP complexes, and it naturally follows

Figure 19. The proton NMR spectrum of trans-(2-CH_3O-MTBP)Mo(CO)$_5$



that a rigid chair structure is the predominate conformer for the trans complexes. Proton nmr data are listed in Tables 12 and 13.

The nmr spectrum of cis-Mo(CO)$_5$-2-CH$_3$O-MTBP (Figure 20) is quite different from that of the trans isomer. First, the positions of the tert-butyl and methyl resonances are inverted. Also the chemical shift difference between the axial and equatorial methylene proton resonances is small and an AA'BB'X pattern is observed instead of simple first order spectrum (Figure 21). Analysis of the spectra (Appendix) gave the LAOCN3-refined spectral parameters listed in Table 14. Quite noticeable are the differences in the values of ^3J(POCH) from the analogous trans-CH$_3$O-MTBP complex and the 2-X-DMP complexes described previously. Whereas trans-(CH$_3$O-MTBP)Mo(CO)$_5$ exhibits values of J(POCH) differing by nearly 14 Hz, the same values in the cis complex differ by only 6-7 Hz. These facts lead to the conclusion that the conformation of the heterocyclic ring in the cis complex is significantly different from that in all the other complexes investigated.

Karplus[146] has suggested that the dihedral angular dependence of a coupling constant can be expressed as shown in Eq. 118:

$$J = A \cos^2\theta + C \qquad (\theta<90°) \tag{118}$$

For calculational purposes, the cis isomer was assumed to exist in nearly a boat conformation. Further, available data[143] on several 1,3,2-dioxaphosphorinanes which exist in chair conformations indicate that the phosphorus-axial methylene proton dihedral angle is consistently 67°. Therefore, an angle of 67° was associated with the coupling constant of 3.6 Hz in trans-2-CH$_3$O-MTBP-Mo(CO)$_5$ in order to estimate the dihedral angles in the cis isomer. The equations 119-121 were solved simultaneously

TABLE 12. NMR DATA FOR SEVERAL 2-X-MTBP DERIVATIVES.[a]

COMPOUND	δT-Bu	δCH_3	$\delta POCH_3$	$J(POCH_3)$
2-Cl-MTBP	0.94	1.23	--	--
$2\text{-}CH_3O\text{-}MTBP$	0.88	1.23	3.53	12.0
<u>trans</u>-$(2\text{-}Cl\text{-}MTBP)Mo(CO)_5$	0.94	1.28	--	--
<u>trans</u>-$(2\text{-}CH_3O\text{-}MTBP)Mo(CO)_5$	0.91	1.29	3.66	12.3
<u>cis</u>-$(2\text{-}CH_3O\text{-}MTBP)Mo(CO)_5$	1.08	0.81	3.69	12.3

a. Chloroform solvent at 34°. Chemical shifts in ppm from internal TMS. Coupling constants in hertz.

TABLE 13. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF *trans*-2-R-MTBP derivatives.[a]

COMPOUND	TEMP	δCH_2 eq	δCH_2 ax	$J_{Hax\ Heq}$	J_{PHeq}	J_{PHax}	$J_{Heq\ Heq}$	RMS[b]
2-Cl-MTBP	34	221.1 (.015)	279.2 (.015)	-10.9 (.022)	11.2 (.026)	5.77 (.030)	2.54 (.030)	0.10
2-CH_3O-MTBP	34	204.2 (.015)	265.4 (.015)	-10.7 (.020)	10.8 (.026)	3.26 (.031)	2.61 (.030)	0.10
(2-Cl-MTBP)Mo(CO)$_5$	34	231.5 (0.013)	281.4 (0.013)	-11.0 (0.019)	20.1 (.026)	6.15 (.023)	2.85 (0.026)	0.087
	60	231.7 (0.020)	281.8 (0.020)	-10.9 (0.019)	20.1 (0.027)	6.12 (0.027)	2.69 (0.031)	0.110
(2-CH_3O-MTBP)Mo-(CO)$_5$	34	219.9 (0.026)	267.1 (0.935)	-10.4 (0.043)	17.4 (0.055)	3.59 (0.052)	2.71 (0.069)	0.170
	60	220.4 (0.031)	266.9 (0.031)	-10.5 (0.045)	17.6 (0.050)	3.43 (0.055)	2.59 (0.071)	0.200

a. Chloroform solvent. Numbers in parentheses are probable errors (Hz) generated by LAOCN3.

b. RMS = root mean square error between calculated and experimental transition frequencies.

TABLE 14. PROTON NMR DATA[a] FOR cis-Mo(CO)$_5$-(2-CH$_3$O-MTBP)

TEMP	SOLVENT	CH_2^A	CH_2^B	J_{PH_A}	J_{PH_B}	$J_{H_AH_B}$	RMS[b]
34	$CHCl_3$	247.0 (.22)	238.1 (.22)	14.8 (.43)	7.85 (.43)	-11.7 (.11)	0.16
34	CD_3CN	250.1 (.26)	242.1 (.26)	13.8 (.52)	8.46 (.52)	-11.8 (.12)	0.19
34	CS_2	244.7 (.23)	236.1 (.23)	14.4 (.46)	8.05 (.46)	-11.5 (.11)	0.17
34	C_6H_5Cl	234.5 (.24)	225.9 (.24)	14.4 (.48)	8.08 (.48)	-11.6 (.12)	0.18
70	C_6H_5Cl	237.8 (.12)	226.5 (.10)	14.1 (.23)	8.67 (.17)	-11.6 (.11)	0.22
110	C_6H_5Cl	240.7 (.09)	227.5 (.09)	13.1 (.19)	9.50 (.19)	-11.4 (.12)	0.18
130	C_6H_5Cl	242.0 (.07)	227.4 (.07)	13.1 (.16)	9.57 (.16)	-11.7 (.10)	0.18

a. The methylene protons are labelled A and B for an AA'BB'X analysis. Numbers in parentheses are probable errors in Hz generated by LAOCN3.

b. RMS = root mean square error between calculated and experimental transition frequencies. A value of $J_{H_AH_A} = 2.6$ Hz was employed throughout.

Figure 20. The proton NMR spectrum of cis-(2-CH_3O-MTBP)Mo$(CO)_5$.

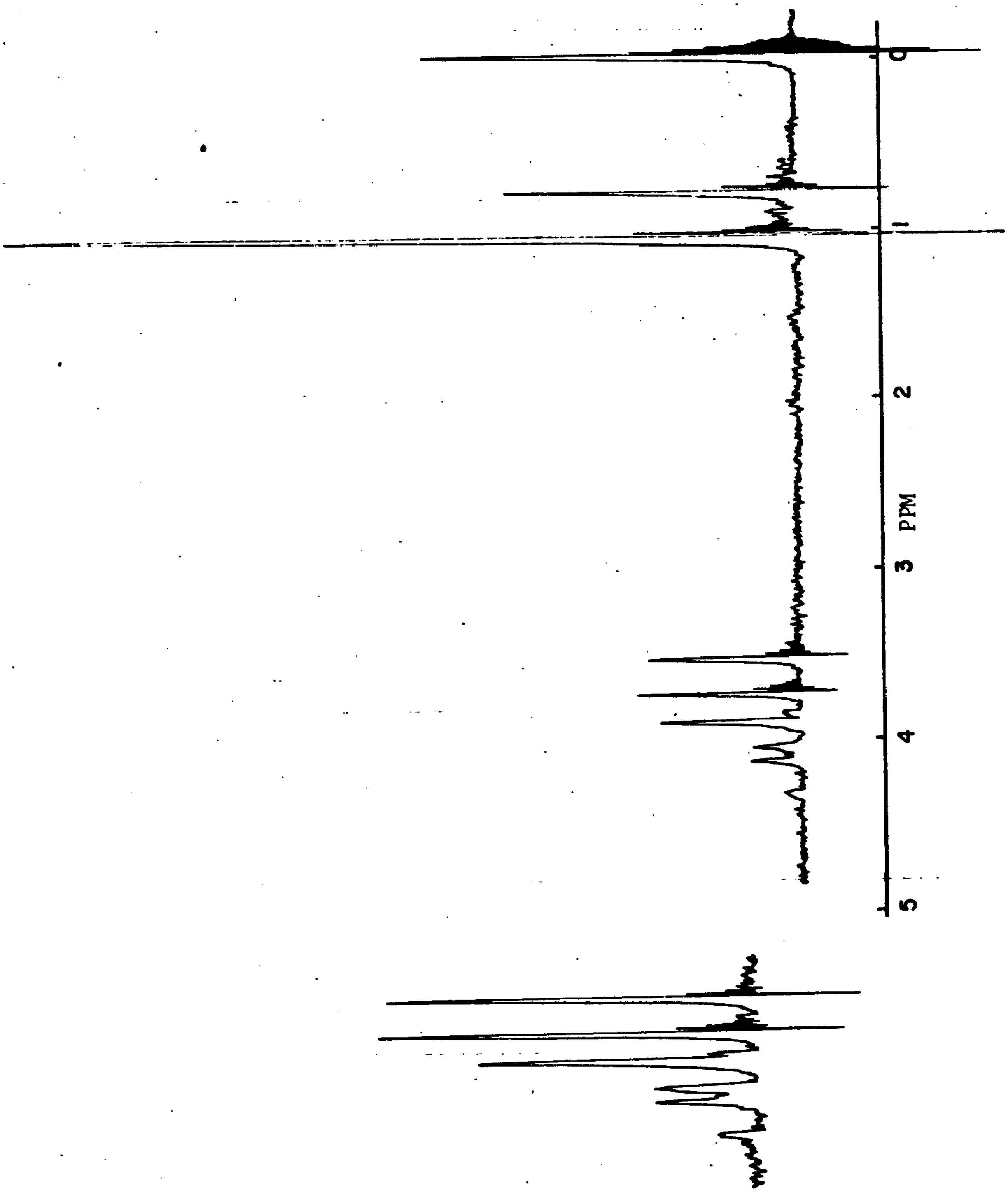
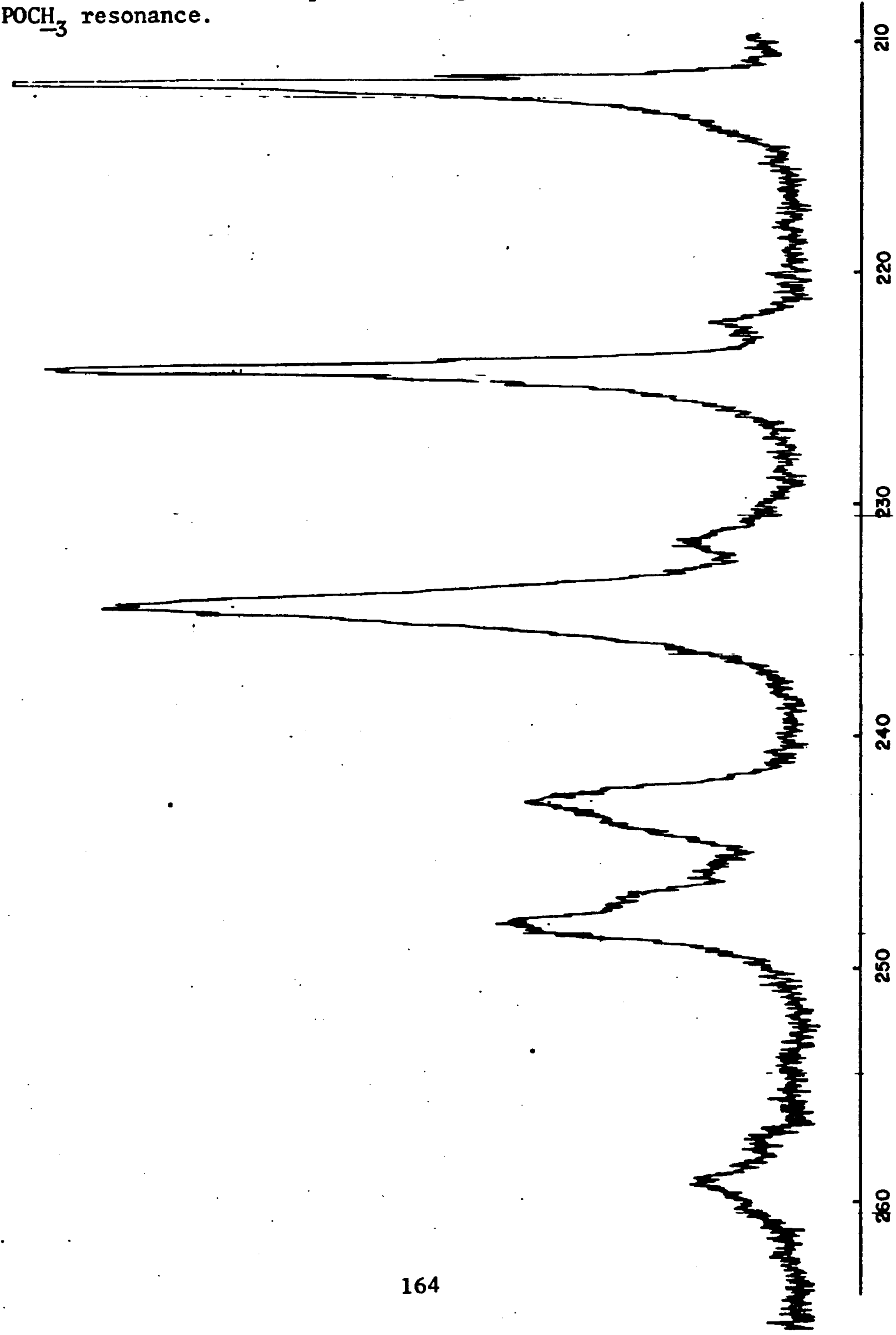


Figure 21. Expanded scale NMR spectrum of the methylene protons of <u>cis</u>-(2-CH_3O-MTBP)Mo$(CO)_5$. Chemical shift in Hz downfield from internal TMS. The two peaks at highest field are due to the PO$C\underline{H}_3$ resonance.



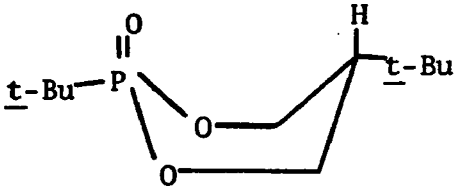
assuming that A and C were the same for both isomers.

$$14.0 = A \cos^2(60 + x) + C \quad \text{(cis)} \qquad (119)$$

$$8.0 = A \cos^2(60 - x) + C \quad \text{(cis)} \qquad (120)$$

$$3.6 = A \cos^2(67) + C \quad \text{(trans)} \qquad (121)$$

Values for the dihedral angles in the cis conformation were obtained as nearly 50 and 70° which are consistent with a boat conformation. Bentrude[130] has determined that cis-2,5-di-t- butyl-2-oxo-1,3,2-dioxaphosphorinane (10) exists in a boat conformation and both values for ^3J(POCH) were observed to be equal, suggesting identical dihedral angles.



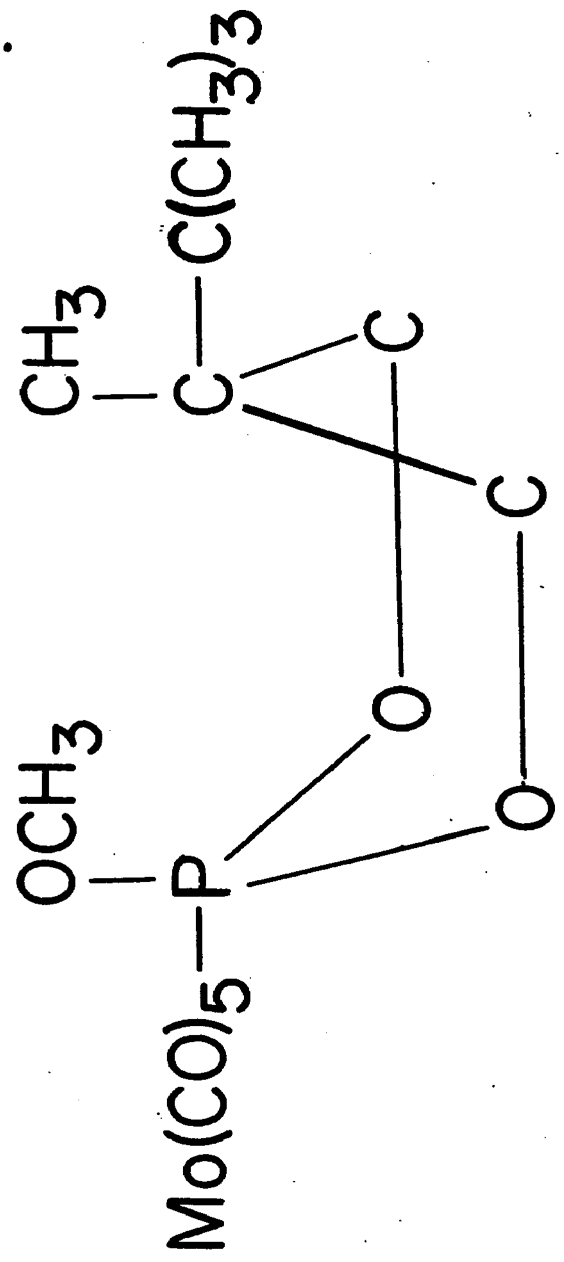
(10)

However, the metal complex studied here (Figure 22) is subject to several internal steric interactions and it is not unreasonable to assume that deviations from the ideal angles are necessary. A flattening of the phosphorus end of the ring could alleviate some of the steric interactions between the axial methoxy and methyl groups. As a result the dihedral angles must be distorted from their ideal values of 60°.

Configuration at Phosphorus

Many groups of workers have attempted to deduce the stereochemistry at phosphorus in 2-R-1,3,2-dioxaphosphorinanes. The conclusions reached by these authors have been arrived at using a variety of experimental techniques: (1) dipole moment measurement; (2) X-ray structural investigations on reaction products of the phosphites which form in a stereospecific manner by an assumed retention or inversion mechanism;

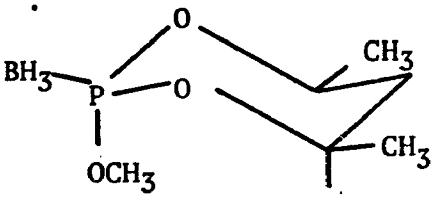
Figure 22. Proposed chair structure for *cis*-(2-CH$_3$O-MTBP)Mo(CO)$_5$.



(3) evaluation of nmr data; (4) stereochemical arguments based on molecular models; and (5) interpretation of phosphoryl (P = O) stretching bands in the infrared spectra.

Gagnaire et al.[114] concluded from nmr studies that the R group in 2-R-DMP occupies the equatorial position at phosphorus in a chair conformer. Their argument was based on steric grounds and on the dependence of the magnitude of J(POCH) on the POCH dihedral angle and the disposition of the phosphorus lone pair relative to the coupled nuclei. On the other hand, White et al.,[117] Bodkin and Simpson,[147] and Bentrude and Hargis[118] concluded that the R group occupies the axial position of a chair conformer in at least the more stable isomer of three different pairs of geometrically isomeric phosphites. The steric argument of Gagnaire was attacked when the structures of several cyclic phosphorus compounds were shown to exhibit ring flattening at the phosphorus end of the ring.[140,148]

The latter view, i.e. an axial R group, has received more general support. An X-ray diffraction study of 11



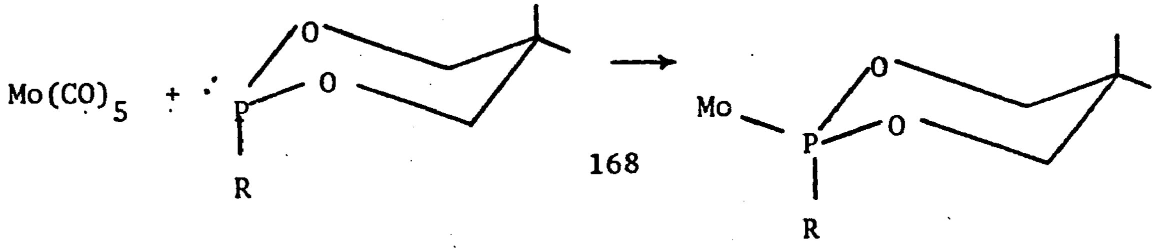
(11)

formed with retention of configuration via the reaction between B_2H_6 and the phosphorinane[141], shows the BH_3 group to occupy the equatorial position, as would be expected if the parent phosphite possessed an axial methoxy group.

Four independent arguments lead to the conclusion that the metal carbonyl moiety occupies the equatorial position at phosphorus in the complexes prepared in this study. First, an examination of models of the two conceivable chair conformers reveals that the conformer with an equatorial metal carbonyl is the more favorable as the steric crowding is less severe than in the structure with the metal carbonyl group situated axially. Although the steric argument has lost some favor in view of the discussion above, an equatorially oriented metal carbonyl group is far less sterically hindered than an axial metal group even if the phosphorus end of the ring flattens somewhat.

A second argument which leads to the assignment of an equatorial metal group is based on the expected mode of reactions of 2-R-DMP. Sufficient evidence has been presented to show that 2-R-DMP exists in a chair conformation with the R group oriented axially. In this configuration, the phosphorus lone pair is directed equatorially and can react with electrophilic reagents with retention of configuration at phosphorus. The formation of 2-oxo derivatives from 1,3,2-dioxaphosphorinanes upon reaction with t-butylhydroperoxides,[118] 2-thio derivatives from elemental sulfur,[147] and the borane derivative cited above have been shown to be formed with retention of configuration at phosphorus. Inasmuch as substitution of carbonyl groups in metal carbonyls by Lewis base ligands usually involves predissociation of a carbonyl ligand from the metal to form a coordinately unsaturated intermediate,[149,150] this intermediate should react with 2-R-DMP or 2-R-MTBP to produce complexes with retention of configuration at phosphorus as shown in Eq. 122-123.

$$\mathrm{Mo(CO)_6} \rightarrow \mathrm{Mo(CO)_5} + \mathrm{CO} \qquad (122)$$



(123)

It is important to note that the temperature at which the syntheses described in this thesis were carried out were low enough to preclude thermal inversion of the phosphorus center prior to complexation and variable temperature nmr studies of the free ligands have shown the predominance of a single chair conformer even at 160°.[117]

A third fact which may indicate axiality of the covalently bonded 2-phenyl group in $Mo(CO)_5(2\text{-}C_6H_5\text{-DMP})$ is the very small difference of 7-9 Hz in the chemical shifts of the axial and equatorial methylene protons. As can be noted from Table 11, the chemical shift value of 200 Hz for the equatorial methylene protons in chloroform at 34° is very close to the average of 219 Hz noted for all of the compounds examined. This indicates that the equatorial methylene protons are essentially unaffected by the changes in the substituents on phosphorus. On the other hand, the chemical shift of 227 Hz noted for the axial methylene protons seems abnormally low when compared to the average of 256 Hz calculated from the other ten compounds. This extraordinary shielding of the axial protons may be caused by the ring current of an axially oriented phenyl ring. If the metal carbonyl group were the cause of this abnormal shift, then shifts of a similar nature should have been noted for all of the compounds inasmuch as the spectral data support a common conformation for all of the compounds. A similar conclusion can be reached from the data summarized in Table 15. Clearly, for the group R = Cl with a variety of metals, little change is noted in the chemical shifts of the methylene protons.

TABLE 15

SELECTED NMR PARAMETERS FOR SEVERAL METAL 2-R-DMP COMPLEXES

Metal	R	CH_2eq	CH_2ax
$(CO)_5Mo$	OCH_3	211.6	248.5
$(CO)_5$	$N(CH_3)_2$	205.4	244.3
$(CO)_5Mo$	SC_6H_5	224.7	269.2
$(CO)_5Mo$	Cl	222.4	259.1
$(CO)_5Cr$	Cl	225.6	263.4
$(CO)_4Fe$	Cl	222.9	262.8
$(CO)_3Ni$	Cl	219.0	259.3

However, when the metal group is kept the same and the group R is varied, the chemical shifts of both the axial and equatorial methylene protons are affected. The results are best explained on the basis of the different anisotropies of the group nearest the environment of the methylene protons, i.e., the axial position at phosphorus. Thus, it must be concluded that the R group is axial and the metal group is equatorial.

Fourth, interpretation of the results of a nuclear Overhauser effect (NOE) experiment suggests an axial R group in trans-(2-CH_3O-MTBP)-$Mo(CO)_5$. Attempts to demonstrate an NOE on (2-CH_3-DMP)$Mo(CO)_5$ were inconclusive inasmuch as the high spectral amplification needed to obtain the spectra led to unreliable spectral integration.

The experimental technique involved in the observation of intramolecular NOE's is similar to that used in other double resonance studies.[151] One of the protons or groups of protons is irradiated at its resonance frequency while the spectrum is observed by means of a frequency sweep. Intensity changes in the peaks of a high-resolution nmr spectrum are caused by changes in the populations of the eigenstates of the spin Hamiltonian. Thus, one saturates a given proton or group of protons and observes the nmr spectra of the molecule. An increase in the integrated area of some other peak(s) in the spectrum indicates the presence of an NOE. The nuclear Overhauser effect makes it possible to determine which protons are in close molecular proximity but which need not be spin-spin coupled.[151]

The results of the NOE experiment on trans-(2-CH_3O-MTBP)$Mo(CO)_5$ are listed in Table 16. The *t*-butyl group occupies the equatorial position at the 5-carbon and the methyl group is axial.

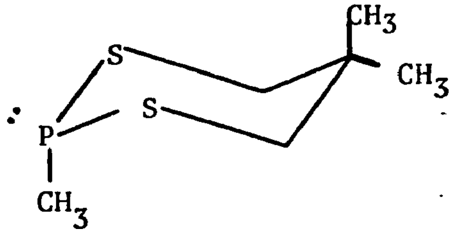
TABLE 16

NUCLEAR OVERHAUSER EFFECT DATA FOR TRANS-(2-CH_3O-MTBP)$Mo(CO)_5$

Irradiation at	% Enhancement	
	CH_2(ax)	CH_2(eq) + $POCH_3$[a]
5-*t*-Bu	+26	+17
5-CH_3	+4	-3

[a] Overlap of the CH_2(eq) and $POCH_3$ resonances prevented clear assessment of the NOE on each resonance separately. The enhancement for both resonances is reported.

Irradiation of the *t*-butyl group gives a significant increase in the intensity of the axial and equatorial methylene protons and the $POCH_3$ protons, whereas irradiation at the methyl group has little effect on the spectral amplitude of those same resonances. These facts are consistent with the presence of an axial methoxy group and an equatorial pentacarbonylmolybdenum moiety. A model clearly shows that the t-butyl group confronts both sets of methylene protons and that there is overlap between the van der Waal radii of the methoxy and t-butyl protons. The 5-methyl group is oriented away from spatial interaction with the methoxy and axial methylene protons and so no NOE is predicted. The use of NOE is an exceptionally powerful tool in aiding the assignment of configuration at phosphorus and in confirming the configuration at ring carbon atoms. Recently, Hutchins[152] used NOE to demonstrate the axiality of the methyl group on phosphorus in 2,5,5-trimethyl-1,3,2-dithiaphosphorinane (12).



(12)

The technique should find important application to other 1,3,2-dioxaphosphorinane systems.

The nuclear Overhauser effect has provided considerable information about the structure of cis-(2-CH_3O-MTBP)Mo$(CO)_5$. The results of the NOE experiment on cis-(2-CH_3O-MTBP)Mo$(CO)_5$ are listed in Table 17.

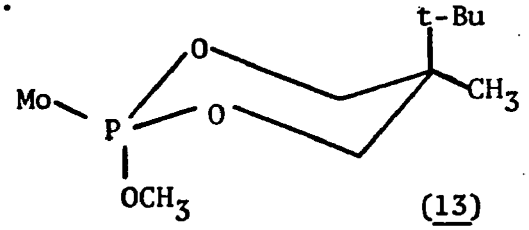
TABLE 17

NUCLEAR OVERHAUSER EFFECT DATA FOR cis-(2-CH_3O-MTBP)Mo$(CO)_5$

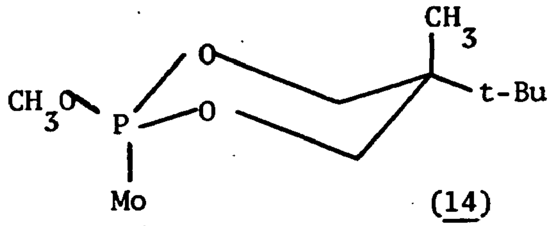
Irradiation at	% Enhancement			
	$POCH_3$	CH_3	t-Bu	methylene
t-Bu	+15	-	-	+14
CH_3	+19	-	-	+1
$POCH_3$	-	+9	+11	-

The effects of irradiation upon the individual methylene protons are difficult to evaluate since the axial and equatorial resonances overlap considerably. The data, however, are consistent with a boat structure in which the *t*-butyl and pentacarbonylmolybdenum groups are oriented equatorially and the methyl and methoxy groups are oriented axially, as shown in Figure 22. First, enhancement of the methoxy proton resonance is observed upon irradiation of both the methyl and *t*-butyl proton resonances suggesting proximity of all three groups. Irradiation of the methyl resonance has little effect on the methylene proton intensity and suggests little spatial interaction between these sets of protons. On the other hand, the equatorial position at the 5-carbon of the ring should allow interaction of this type. It follows that the 5-methyl group is oriented axially. The methoxy group must also be oriented axially in order for it to be positioned appropriately for interaction with the methyl and *t*-butyl groups.

A chair structure for *cis*-(2CH$_3$O-MTBP)Mo(CO)$_5$ can be ruled out on the basis of this NOE data. Possible *cis*-chair structures are shown below.



(13)



(14)

The first structure (13) should allow enhanced methylene proton intensity upon irradiation of the methyl group (not observed) and no methoxy-*t*-butyl interaction would be expected (observed). The second chair conformer (14) places the methoxy group far from both the methyl and *t*-butyl groups, leaving no expected interaction at all between these sets of protons, a fact in considerable disagreement with the observed data.

Conformationally Mobile 1,3,2-Dioxaphosphorinanes

One significant conclusion arising from this work is that a metal carbonyl group plays a dominant role in controlling the stereochemistry of complexed heterocyclic phosphites. The metal carbonyl group occupies an equatorial position at phosphorus in all of the complexes prepared in this study and acts as an effective locking group in maintaining a rigid conformation in the 1,3,2-dioxaphosphorinane ring. However, the heterocyclic ring in one complex prepared in this work, bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)diiron hexacarbonyl, is conformationally mobile. The complex is formulated as shown in Figure 23.

Each 1,3,2-dioxaphosphorinane ring in [μ-DMP-Fe(CO)$_3$]$_2$ is bonded through phosphorus to two equivalent Fe(CO)$_3$ groups. Inasmuch as neither Fe(CO)$_3$ group can exclusively occupy the equatorial position as phosphorus, competition for the thermodynamically preferred site causes the heterocyclic ring to undergo conformational motion. This conclusion is based on the appearance of the proton nmr spectrum of the complex. First, only a single 5-methyl resonance is observed rather than the pair of single lines observed for the methyl resonances of other 2-R-DMP complexes. Secondly, the methylene region of the pmr spectrum of [μ-DMP-Fe(CO)$_3$]$_2$ appears relatively simple. The methylene protons appear as a quartet (two overlapping triplets) in both chloroform and acetonitrile-d$_3$ and as a single broadened triplet in chlorobenzene (Figures 24-26). Nmr data for [μ-DMP-Fe(CO)$_3$]$_2$ are summarized in Table 18.

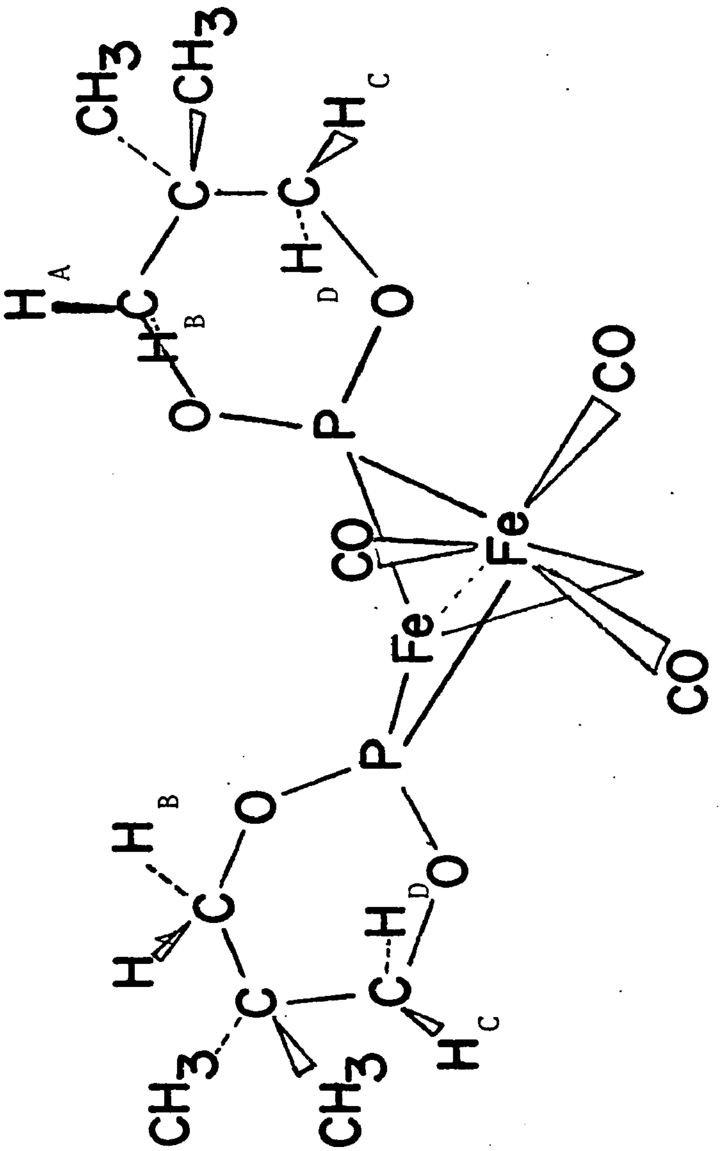
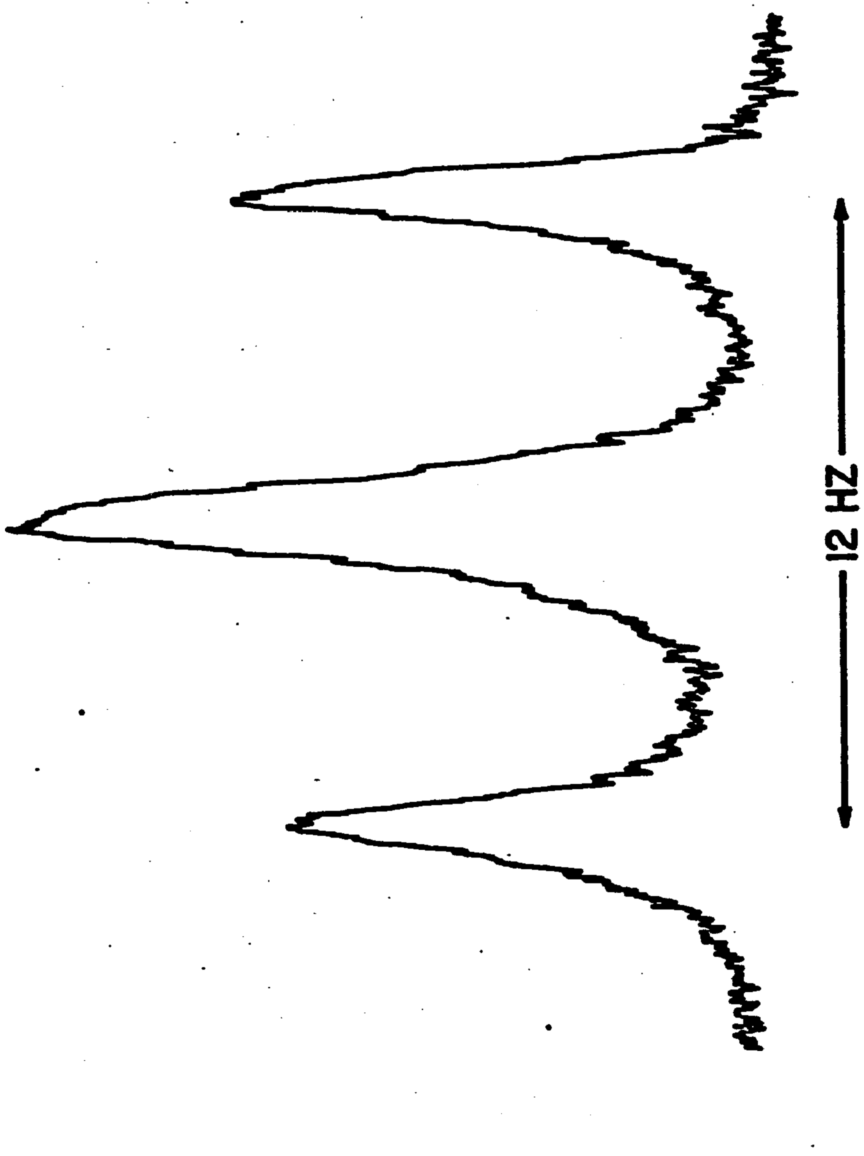


Figure 23. Proposed structure for bis-μ-(5,5-dimethyl-1,3,2-dioxaphosphorinano)diiron hexacarbonyl.

Figure 24. Proton NMR spectrum of the methylene protons of $\{\mu\text{-DMP-Fe(CO)}_3\}_2$ in chlorobenzene solution.



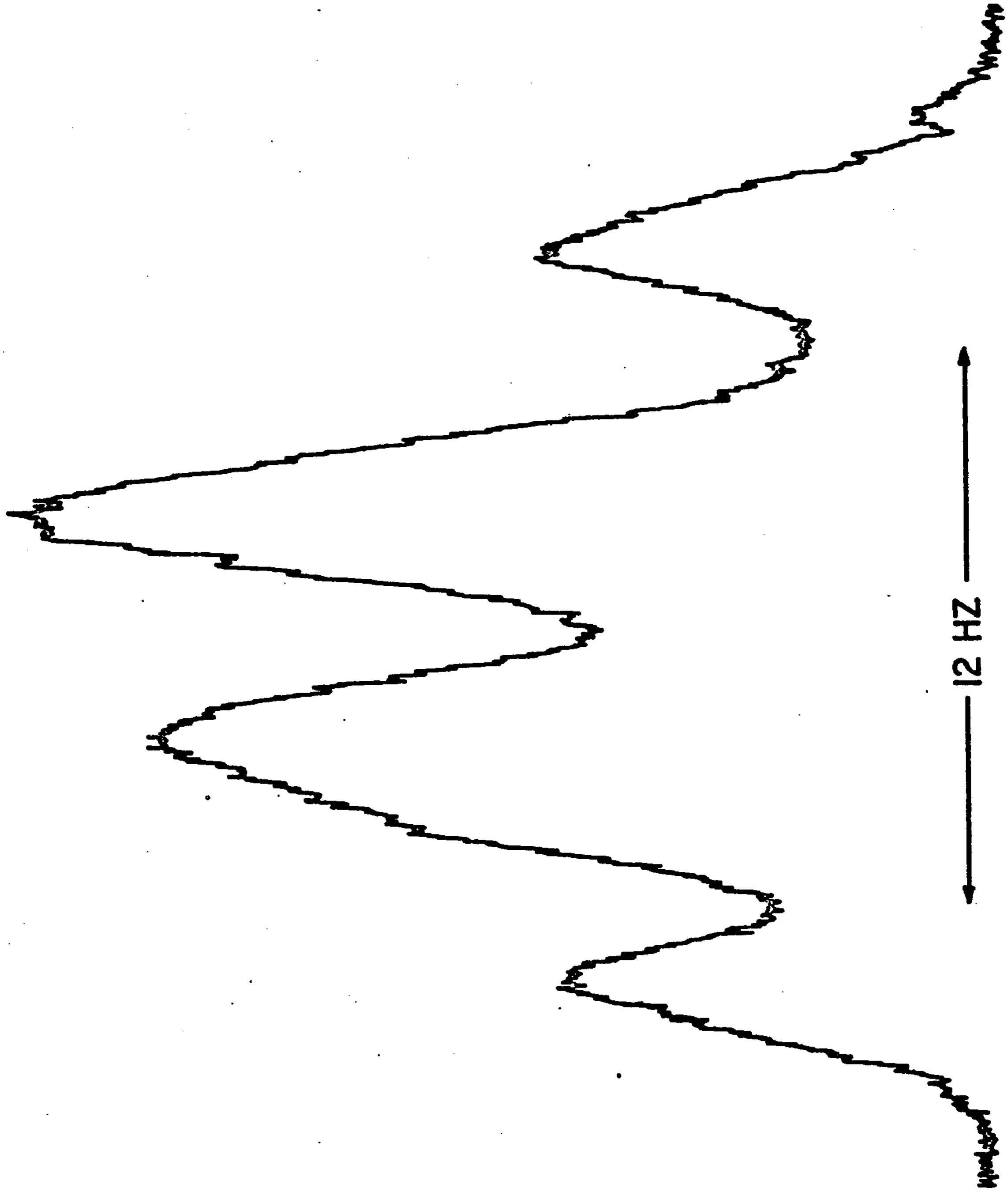


Figure 25. Proton NMR spectrum of the methylene protons of $\{\mu\text{-DMP-Fe(CO)}_3\}_2$ in chloroform solution.

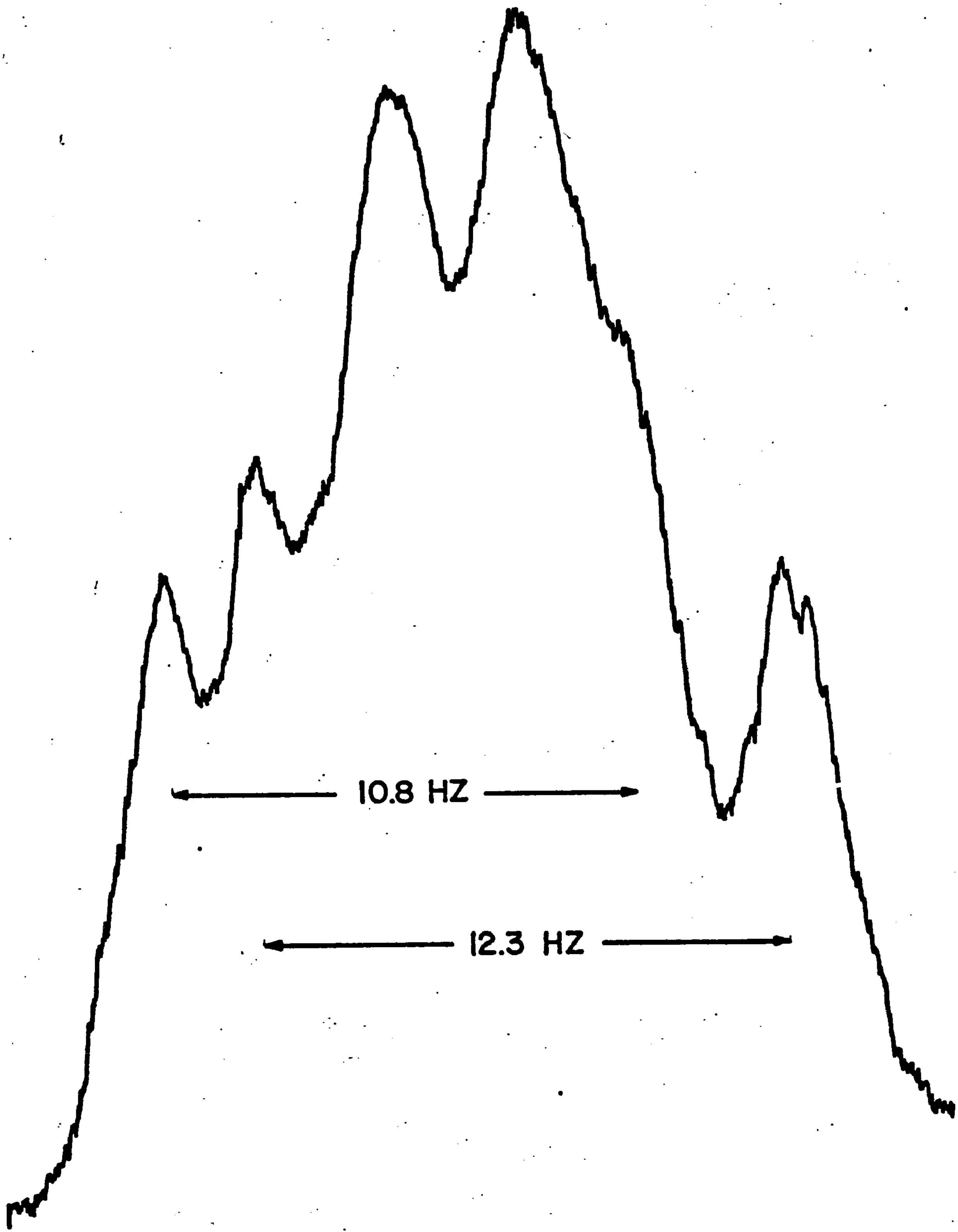


Figure 26. Proton NMR spectrum of the methylene protons of $\{\mu\text{-DMP-Fe(CO)}_3\}_2$ in the presence of the lanthanide shift reagent $Eu(fod)_3$.

TABLE 18

PROTON NMR DATA FOR $[\mu\text{-DMP-Fe(CO)}_3]_2$[a]

Solvent	δCH_3	δ methylene		J_{HP}[b]	
		A	B	A	B
CD_3CN[c]	62.0	243.4	237.0	11.0	12.2
$CHCl_3$[c]	64.9	241.9	237.1	10.6	11.4
$CDCl_3$[d]	64.2	241.0	238.0	10.8	12.3
C_6H_5Cl[e]	44.4	--225.6--		12.0	

[a] Shifts and coupling constants in Hz. Measurement at 34°.

[b] "Apparent" coupling constant. Separation of outermost peaks of triplets.

[c] Broad quartet

[d] Equimolar $Eu(fod)_3$ added (see text). Two clearly resolved triplets.

[e] Triplet.

If the heterocyclic ring in $[\mu\text{-DMP-Fe(CO)}_3]_2$ exists in a rigid conformation, two separate methyl resonances are expected in its nmr spectrum. There is no plane of symmetry by which the two sets of methyl resonances can become equivalent in a non-mobile conformation. However, in a system enjoying rapid interconversion of the phosphite ring, the two sets of methyl groups experience the same chemical environment on a time-averaged basis and are magnetically equivalent. Thus, the observation of the single methyl resonance is consistent with the presence of a mobile heterocyclic ring.

A rigid 1,3,2-dioxaphosphorinane ring in $[\mu\text{-DMP-Fe(CO)}_3]_2$ gives rise to four sets of non-equivalent methylene protons. With the two phosphorus atoms, the rigid system would be expected to generate a complex AA'BB'CC'DD'XX' spin pattern for the methylene region of the nmr spectrum of [μ-DMP-Fe(CO)$_3$]$_2$. On the other hand, a mobile ring would yield a much simpler pattern for the methylene resonance of the complex since protons A and B and C and D are equivalent on a time-averaged basis. In fact, the resulting spin system can be analyzed as an ACXX' system. A further simplification of even this result is apparent when it is recognized that $J(H_AH_C) = 0$, since H_A and H_C are separated by four bonds. The simple spectra observed for the methylene region of [μ-DMP-Fe(CO)$_3$]$_2$ are consistent with a mobile heterocyclic ring.

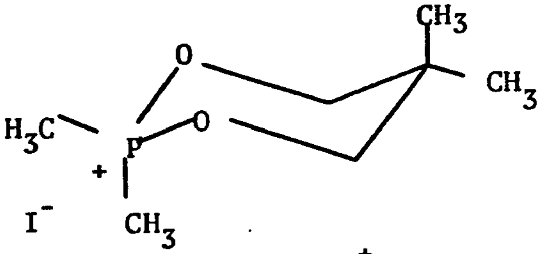
The triplet structure itself must arise from virtual coupling of the two phosphorus atoms in [μ-DMP-Fe(CO)$_3$]$_2$. The condition $J(PP') > |J(PH) - J(P'H)|$ must be fulfilled in order for the triplet to appear.[65] Since J(P'H) is probably very small, the width of the outermost lines of the triplet can be used to approximate $^3J(PH)$. The "values" of $^3J(PH)$ observed for [μ-DMP-Fe(CO)$_3$]$_2$ (Table 18) compare favorably with the average of $^3J(PH)$ observed for other 1,3,2-dioxaphosphorinanes. Strong phosphorus-phosphorus coupling, and thus a subsequent triplet structure, has been observed in several other compounds containing bridging phosphine ligands. Hayter[44] observed that each of the methyl resonances of μ-bis(dimethylphosphido)diiron hexacarbonyl, $[Fe(CO)_3P(CH_3)_2]_2$, is a distinct triplet. Treichel, et al.,[95] also observed a similar result in the spectra of both sym- and antisym-$\{Fe(CO)_3[P(CH_3)(C_6H_5)]\}_2$.

Because the triplets comprising the methylene portion of the nmr spectrum of [μ-DMP-Fe(CO)$_3$]$_2$ overlap severely, precise determination of the separation of the outermost lines of the triplets is not possible. However, the addition of the lanthanide shift reagent tris(1,1,1,2,2,-3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III), Eu(fod)$_3$, to a sample of [μ-DMP-Fe(CO)$_3$]$_2$ in chloroform caused the methylene portion of the nmr spectrum to appear as two clearly resolved triplets. The magnitude of the induced chemical shifts are not great, suggesting that the site of coordination of the europium reagent is far from the methylene protons. In several reported examples of the use of shift reagents in the study of 2-oxo-1,3,2-dioxaphosphorinanes, the site of coordination of the heterocycle to the shift reagent has been the phosphoryl oxygen,[153-155] and relatively large chemical shifts have been observed for the methylene protons. Three reasonable sites are available for coordination to $Eu(fod)_3$ in $[\mu\text{-DMP-Fe(CO)}_3]_2$. First, the 1,3-dioxa oxygens are ruled out because of the small shifts observed. A second possible site, which cannot be completely dismissed, is the electron density of the iron-iron bond in the complex. The most likely site of attachment, however, is a carbonyl oxygen atom. Several recent reports[156] have confirmed the ability of suitable reagents to form complexes through coordination to the carbonyl oxygen atoms in a metal complex. Further, the distance between this site and the methylene protons could account for the slight chemical shifts observed.

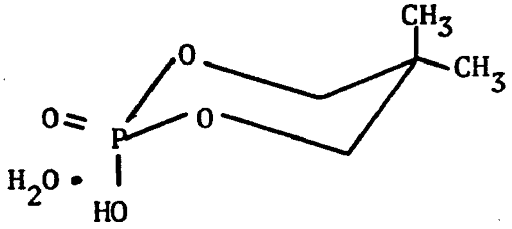
The nmr spectrum of $[\mu\text{-DMP-Fe(CO)}_3]_2$ was also studied over the temperature range -40° to +160° in order to determine whether the ring motion could be controlled or even stopped. However, no changes in the nmr spectra were observed over this temperature range. Poor solubility of $[\mu\text{-DMP-Fe(CO)}_3]_2$ at low temperature prevented further work in this area.

The non-rigid behavior of the heterocyclic ring in $[\mu\text{-DMP-Fe(CO)}_3]_2$ is a property more closely related to behavior of the 1,3,2-dioxaphosphorinane ring rather than to a μ-phosphido-iron system. Hayter reported that the methyl groups of bis(μ-dimethylphosphido)diiron hexacarbonyl do not exchange even at high temperature.[44] However, the methyl groups of the isoelectronic complex bis - dimethylgermyl-dicobalt hexacarbonyl do appear equivalent at room temperature.[157] This fact probably reflects significant differences in iron-carbon monoxide and cobalt-carbon monoxide bonds, since the fluxional behavior in the latter complex is thought to involve cleavage of the metal-carbonyl bond.

Two other 1,3,2-dioxaphosphorinanes are known whose behavior in solution suggests that they exist as equimolar pairs of rapidly interconverting conformers. The two compounds are shown below.



[2,2-(CH)$_3$)$_2$-DMP]$^+$ 15



2-oxo-2-OH-DMP·H_2O 16

These two compounds share several features of their nmr spectra, summarized in Table 19, with [μ-DMP-Fe(CO)$_3$]$_2$. First, the spectrum of 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinanium iodide appears as a singlet for the 5-methyl resonance, a doublet for the P-methyl resonance, and a simple doublet for the methylene protons. Similarly, the spectrum of 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane shows only a single methyl resonance and a simple methylene doublet. These observations are consistent with the conclusion that both compounds exist in solution in very mobile equilibria. White has also examined the nmr spectrum of the 2,2-(CH$_3$)$_2$-DMP cation.[158] He also concluded that ring inversion in [2,2-(CH$_3$)$_2$-DMP]$^+$ is rapid on the nmr time scale even at temperatures as low as -81°.

TABLE 19

PMR DATA[a] FOR $[2,2\text{-}(CH_3)_2\text{-DMP}]^+$ AND 2-oxo-2-OH-DMP

Compound	5-CH_3	CH_2	$^3J(PH)$	PCH_3	$^2J(PH)$	Ref (solvent)
$[2,2\text{-}(CH_3)_2\text{-DMP}]^+I^-$	1.05	4.43	11.0	2.24	14.7	b,e
$[2,2\text{-}(CH_3)_2\text{-DMP}]^+BF_4^-$	1.12	4.34	11	2.17	14.5	c,f
$[2,2\text{-}(CH_3)_2\text{-DMP}]^+BF_4^-$	1.20	4.51	11.3	2.24	15.0	c,g
2-oxo-2-OH-DMP·H_2O	1.07	4.03	12.0	--	--	b,h
2-oxo-2-OH-DMP·H_2O	1.06	4.00	12.0	--	--	d,i

a. Chemical shifts in ppm downfield from internal TMS. Coupling constants in Hz.

b. This work.

c. Ref. 158

d. Ref. 160

e. CD_3CN

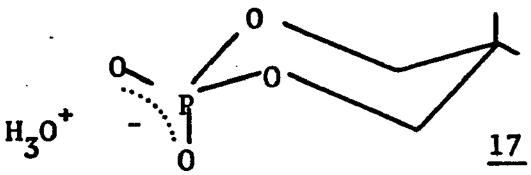
f. CH_3CN

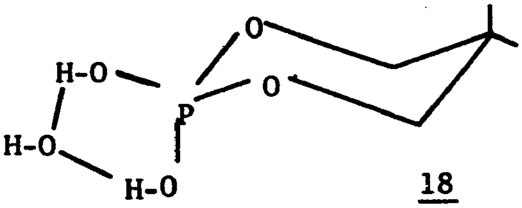
g. SO_2, spectra recorded at -80°

h. $CHCl_3$

i. $CDCl_3$

The compound 2-oxo-2-hydroxy-DMP is of particular interest. In the solid state a molecule of water of crystallization is present for each molecule of the 1,3,2-dioxaphosphorinane in the lattice.[159] Further, it is surprising to find that the phosphorus-oxygen bond lengths in the P = O and P-O-H linkages are different: 1.465 Å and 1.546 Å, respectively.[159] These observations suggest that the water of crystallization plays an important role in making the subsituents on phosphorus stereochemically equivalent in solution. It is possible that either of the following solution structures contributes to the equivalence at phosphorus.


17

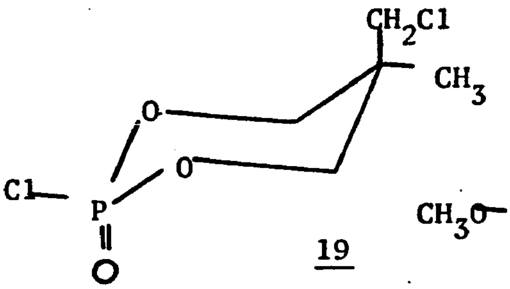

18

The ionic formulation 17 is not unreasonable inasmuch as many inorganic acids are known to form hydroxonium salts.[86] Structure 18 also demands consideration; hydrogen bonding in the manner shown allows phosphorus to be in the center of two classically stable six-membered rings. Hall and Malcolm[160] also have recognized the mobile nature of the ring in 2-oxo-2-hydroxy-DMP. However, they did not comment on the presence of the water of crystallization in their sample nor speculate on the possible role played by it in the mobility of the 1,3,2-dioxaphosphorinane ring.

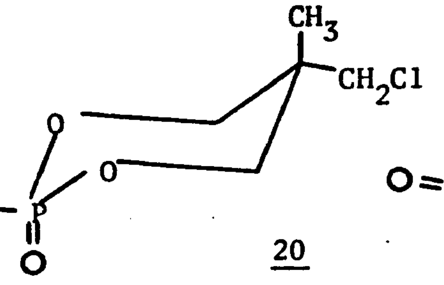
Nucleophilic Displacement at Phosphorus

Considerable information is available concerning substitution reactions at phosphorus. The results of kinetic and stereochemical studies have led to the suggestion that both monomolecular, S_N1, and bimolecular, S_N2, mechanisms are possible for displacement reactions at phosphorus.[161] Further, the S_N2 pathway may proceed either with inversion or without inversion *via* a pseudorotation mechanism. Although no kinetic studies involving 1,3,2-dioxaphosphorinanes have been reported, some speculation concerning the mode of reaction at phosphorus has been presented.[161-163] This speculation has been based on knowledge of the stereochemistry of both the starting materials and the products.

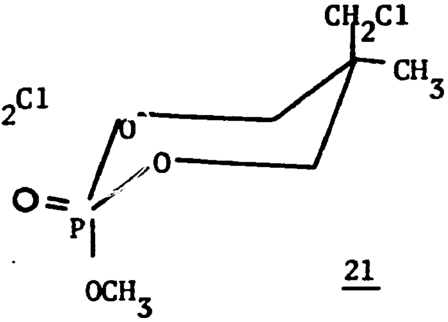
Wadsworth reported that the methanolysis of 19 gave the two products, 20 and 21.[162] The ester 21 must result from direct S_N2 (P) substitution with inversion at phosphorus. The suggestion that 20 was formed *via* an S_N1 (P) mechanism was strengthened by the discovery that the methanolysis when carried out in the presence of silver ions yields only that ester with a changed conformation, 20, and none of 21. The isomeric esters 20 and 21 are not interconvertible thermally.



19

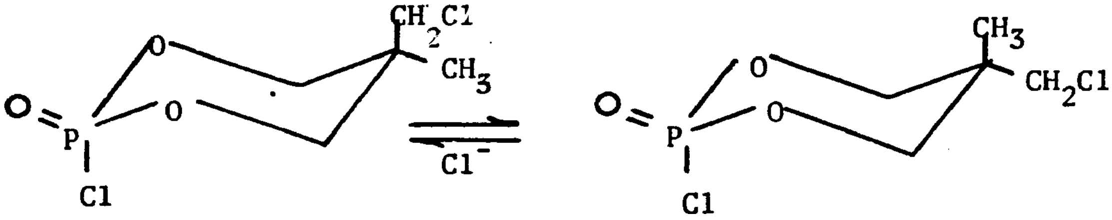


20



21

In a later paper Wadsworth, *et al.*,[161] presented evidence that the reaction of 19 with amines proceeds exclusively *via* inversion of configuration at phosphorus. Further, the addition of chloride to 19 caused the equilibrium shown in Eq. 124 to take place.

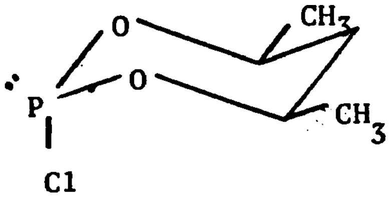


(124)

These results strengthen the idea that a simple S_N2 (P) mechanism accompanied with inversion of configuration at phosphorus is of significant importance in the displacement of halide from phosphorus in 1,3,2-dioxaphosphorinanes. The possibility that silver ion might be coordinated to the phosphoryl oxygen atom and subsequently effect an equilibrium similar to that in Eq. 124 has not been explored and suggests that the

S_N1 (P) mechanism be seriously questioned.

Mosbo and Verkade[162] examined the displacement of chloride from 22 and interpreted their results in terms of an S_N2 (P) mechanism.



22

These workers also suggested that acid catalysis could play a role in causing rearrangement of the desired product.

The pentacarbonylmolybdenum complex of 2-Cl-MTBP is particularly suitable for use in obtaining mechanistic information about the displacement of chloride by methanol from a coordinated 1,3,2-dioxaphosphorinane. The nmr resonances of both isomers of $(2\text{-}CH_3O\text{-MTBP})\text{-}Mo(CO)_5$ are easily assigned to a particular isomer. Also, rearrangement products arising according to the scheme of Mosbo and Verkade are unlikely, since a pentacarbonylmolybdenum group is not as good a base site as the phosphoryl oxygen.

2-X-DMP Complexes

The complex $Mo(CO)_5(2\text{-}CH_3O\text{-DMP})$ was prepared by two different procedures as described earlier, and the products obtained by each method were identical. Both $Mo(CO)_5(2\text{-Cl-DMP})$ and $Mo(CO)_5(2\text{-}CH_3O\text{-DMP})$ exist with the 1,3,2-dioxaphosphorinane ring in a chair conformation with the $Mo(CO)_5$- group oriented equatorially at phosphorus. Thus, this observation alone could lead to the conclusion that the methanolysis of $(2\text{-Cl-DMP})Mo(CO)_5$ (Eq. 125) proceeds without inversion of configuration

$$Mo(CO)_5(2\text{-Cl-DMP}) + CH_3OH \rightarrow Mo(CO)_5(2\text{-}CH_3O\text{-DMP}) + HCl \qquad (125)$$

at phosphorus.

Three different pathways can account for the stereochemistry of the product. First, an S_N1 (P) mechanism cannot be ruled out solely on the information provided by the reaction shown in Eq. 125. A first-order displacement reaction would provide a trigonal intermediate at the phosphorus atom. Subsequent attack at phosphorus by methanol could produce, theoretically at least, a product in which the methoxy group assumed either an axial or equatorial orientation. However, the preference of the large pentacarbonylmolybdenum group to occupy the equatorial position at phosphorus is dominant and would lead to formation of only that product in which its steric demand is met.

Secondly, reaction 125 could proceed <u>via</u> an S_N2 (P) mechanism with retention of configuration if a pseudorotation mechanism is important.[164] However, six-membered phosphorus ring compounds generally prefer the diequatorial orientation in a 5-coordinate phosphorane intermediate,[164] and thus, the importance of a pseudorotation mechanism is probably minimal.

And thirdly, the observed product could arise <u>via</u> an S_N2 (P) mechanism as shown in Figure 27. If the methanolysis of (2-Cl-DMP)Mo—$(CO)_5$ proceeds with inversion of configuration at phosphorus, as is expected in a classical S_N2 mechanism, the resulting species would be the boat conformer 27-<u>A</u> with an axial $Mo(CO)_5$- group. However, since this configuration is probably thermodynamically unfavorable with the bulky $Mo(CO)_5$- group oriented axially, the "phosphorus end" of the molecule could undergo a conformational flip into a chair conformation yielding the more stable structure 27-<u>B</u> with an equatorially oriented penta-

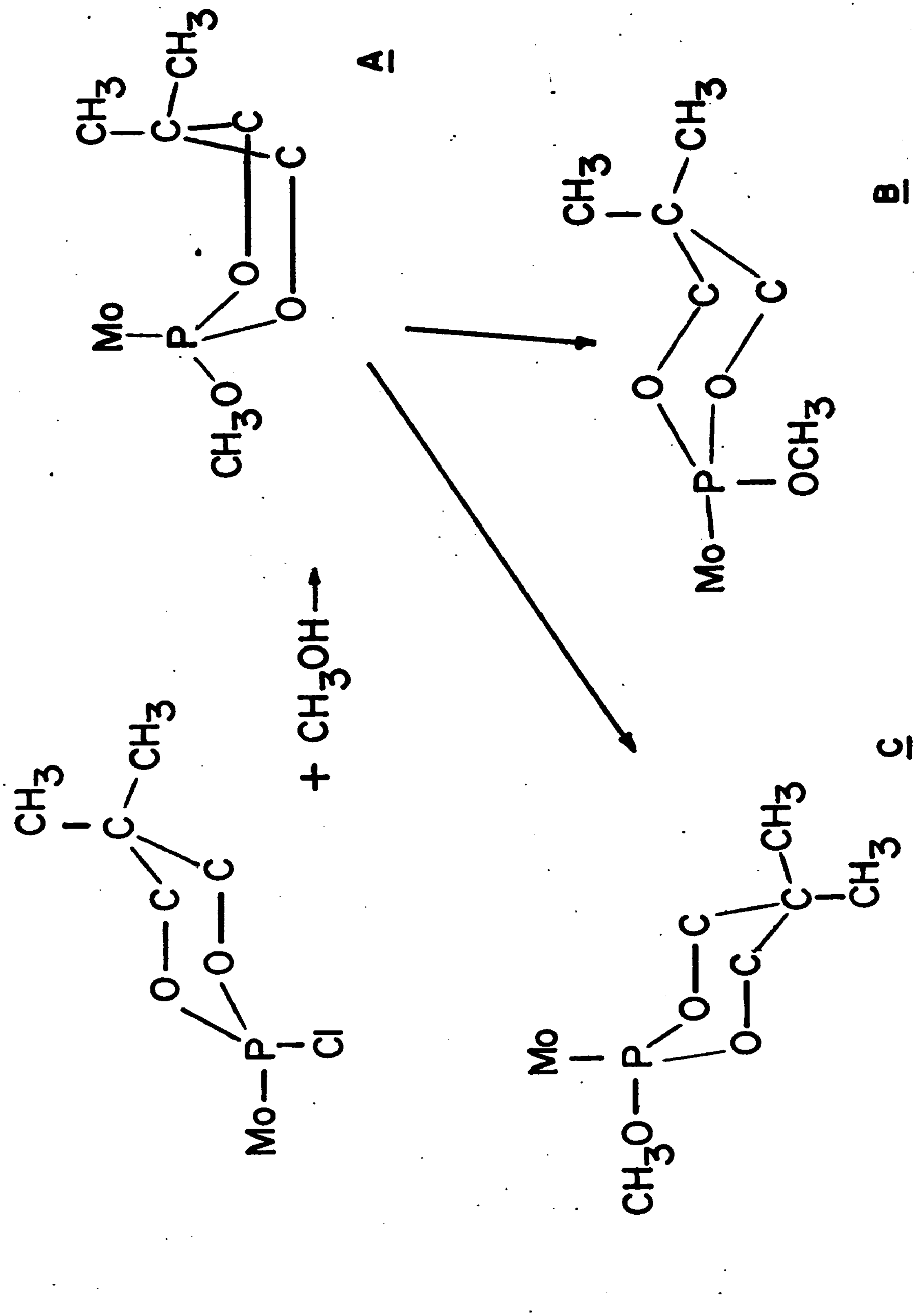


Figure 27. The reaction of $Mo(CO)_5$(2-Cl-DMP) with methanol.

carbonylmolybdenum group. Although the "carbon end" of the phosphite ring in 27-A might also undergo a conformational flip, the resulting structure 27-C would still contain an axial metal carbonyl group and is predicted to be less thermodynamically stable than 27-B. Unfortunately, the exact mechanism of the reaction at phosphorus in $Mo(CO)_5$(2-Cl-DMP) cannot be stated with certainty owing to the identical substituents at the 5-carbon.

2-X-MTBP Complexes

More meaningful mechanistic information about the reactions of coordinated phosphorus ligands can be obtained from the methanolysis of $Mo(CO)_5$(2-Cl-MTBP). The reaction shown in Eq. 126 may be followed as a function of time by nuclear magnetic resonance spectroscopy. The

$$\underline{\text{trans}}\text{-Mo(CO)}_5\text{(2-Cl-MTBP)} + \text{CH}_3\text{OH} \rightarrow$$
$$\underline{\text{cis}}\text{- and }\underline{\text{trans}}\text{-Mo(CO)}_5\text{(2-CH}_3\text{O-MTBP)} + \text{HCl} \qquad (126)$$

distribution of isomers formed in reaction 126 is shown in Table 20.

TABLE 20

DISTRIBUTION OF ISOMERS OF $Mo(CO)_5$(2-CH_3O-MTBP) OBTAINED FROM METHANOLYSIS OF $Mo(CO)_5$(2-Cl-MTBP)

	(2-CH_3O-MTBP)$Mo(CO)_5$	
Time	% Trans	% Cis
4 hr	40	60
6 hr	44	56
17 hr	59	41
48 hr	86	14

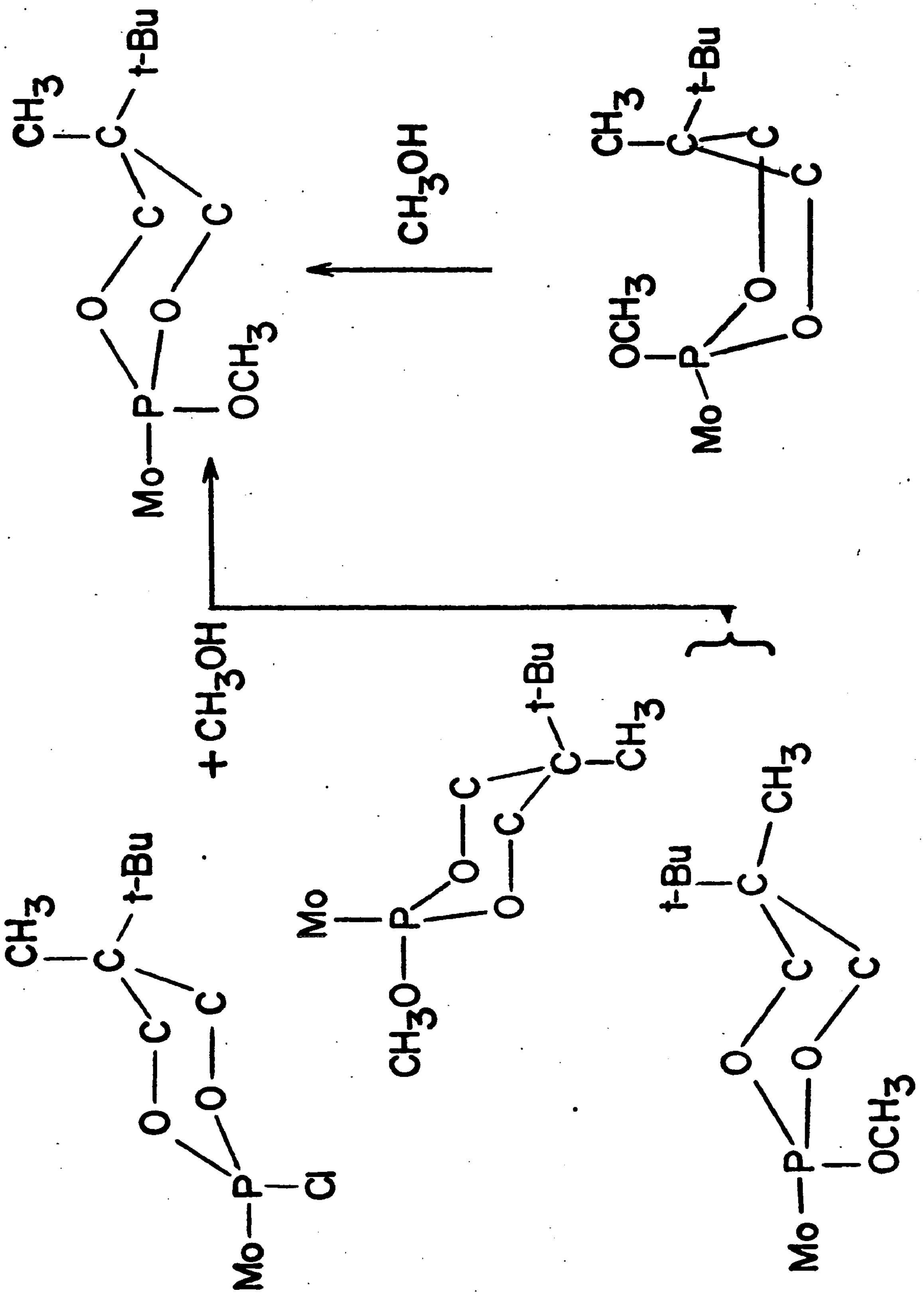
The three mechanistic considerations developed for the methanolysis of (2-Cl-DMP)Mo$(CO)_5$ also apply to the methanolysis of (2-Cl-MTBP)-Mo$(CO)_5$. First, a pseudorotation mechanism will not be considered for the same reasons as discussed above. Secondly, the data in Table 20 suggest that an S_N1 (P) mechanism is not of considerable importance. In an S_N1 (P) mechanism an unsymmetrical transition state is developed. Subsequent attack by methanol should occur in such a way as to form the thermodynamically more stable trans- product. However, the data in Table 20 show that a greater percentage of cis- isomer is formed first, and this observation is taken as direct evidence against an S_N1 (P) mechanism.

The information listed in Table 20 does support an S_N2 (P) mechanism. Initially, the cis isomer is formed accompanied by inversion of configuration at phosphorus (Figure 28). Isolation and characterization of cis-(2-CH_3O-MTBP)Mo$(CO)_5$ from reaction mixtures indicates that the boat conformer is formed rather than either of the other two alternate cis products. Increased reaction time leads to the conversion of the cis-complex to the thermodynamically preferred trans-complex. Presumably, this reaction occurs via Eq. 127

$$\text{cis-(2-CH}_3\text{O-MTBP)Mo(CO)}_5 \xrightarrow{CH_3OH} \text{trans-(2-CH}_3\text{O-MTBP)Mo(CO)}_5 \qquad (127)$$

and is analogous to the chloride induced equilibrium discussed in equation 124. The methanolysis of cis-(2-CH_3O-MTBP)Mo$(CO)_5$ to the trans isomer also probably proceeds via an S_N2 (P) mechanism accompanied by inversion of configuration at phosphorus, since the interconversion of cis-(2-CH_3O-MTBP)Mo$(CO)_5$ and trans-(2-CH_3O-MTBP)Mo$(CO)_5$ was not observed

Figure 28. The reaction of trans-(2-Cl-MTBP)Mo(CO)$_5$ with methanol.



at temperatures as high as 130° unless methanol was present. After a reaction time of 48 hr the isomer ratio of cis- and trans-(2-CH_3O-MTBP)-$Mo(CO)_5$ is very nearly that obtained when the complex was prepared directly from $Mo(CO)_6$ and the ligand. This observation emphasizes the preference for the 1,3,2-dioxaphosphorinane ring to assume a chair conformation whenever it is thermodynamically possible.

It is clear that no first-hand proof of an S_N2 (P) mechanism at phosphorus in the displacement of chloride from a coordinated phosphorus ligand is available. It seems imperative that further endeavor in the area of 1,3,2-dioxaphosphorinane chemistry include effort to determine accurately the mechanism of reaction at phosphorus and to ascertain the effect of a transition metal and other substituents on phosphorus upon the rate of displacement of varied leaving groups.

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APPENDIX

Nmr spectral parameters were obtained for most of the complexes prepared in this study using first-order analysis. The parameters thus obtained were further refined <u>via</u> least-squares analysis using the iterative computer program LAOCN3. Generally, the root-mean-square error was reduced below 0.2 Hz and often below 0.1 Hz. The detailed analysis of the spectrum of $Mo(CO)_5(2\text{-}Cl\text{-}TBMP)$ is presented as an illustrative example:

The following parameters for the 1,3,2-dioxaphosphorinane ring were obtained directly from the recorded spectrum and were used to calculate a trial theoretical spectrum by LAoCN3.

Chemical Shift: Axial methylene	282.0 Hz
Chemical Shift: Equatorial methylene	230.9 Hz
$J(H_{eq}H_{ax})$	- 11.2 Hz
$J(PH_{eq})$	20.0 Hz
$J(PH_{ax})$	6.2 Hz
$J(H_{eq}H_{eq})$	2.65 Hz

The trial spectrum is shown below:

LINE	CALC. FREQ.	INTEN
204	213.291	.599
178	213.308	.597
52	214.764	1.621
123	214.787	1.623
141	215.893	1.028
134	215.909	1.033
198	224.817	1.403
184	224.835	1.398
187	225.939	2.375
207	225.964	2.379
130	227.419	967
145	227.437	.976
57	233.133	.553
108	233.160	.550
4	234.602	1.509
39	234.640	1.513
27	235.702	.962
20	235.729	.969
98	244.670	1.450
67	244.701	1.442
76	245.759	2.480
156	245.802	2.491
21	247.238	1.031
26	247.270	1.049
202	272.363	.976
154	272.381	.967
54	273.836	2.379
142	273.861	2.375
121	274.965	1.398
180	274.983	1.403
56	278.730	1.049
10	278.762	1.031
3	280.198	2.491
28	280.241	2.480
37	281.299	1.442
109	281.330	1.450
150	283.891	1.033
182	283.907	1.028
194	285.013	1.623
209	285.036	1.621
200	286.492	.597
125	286.509	.599
11	290.271	.969
66	290.298	.962
87	291.360	1.513
161	291.398	1.509
99	292.840	.550
36	292.867	.553

From a comparison of the trial and observed spectra, each theoretical transition was matched to an observed peak. The oomputer applied a least-squares adjustment between the theoretical and experimental spectra to yield a new "best spectrum." This spectrum is shown below.

LINE	EXP. FREQ.	CALC. FREQ.	INTEN	ERROR (Hz)
204	213,800	213,768	.581	.032
178	213.800	213.785	.578	.015
52	215.300	215.370	1.621	-.070
123	215.300	215.395	1.623	-.095
141	216.700	216.571	1.049	.129
134	216.700	216.588	1.053	.112
198	225.000	225.144	1.422	-.144
184	225.000	225.164	1.417	-.164
187	226.500	226.337	2.374	.163
207	226.500	226.365	2.379	.135
130	227.900	227.947	..947	-.047
145	227.900	227.966	.957	-.066
57	233.700	233.742	.534	-.042
108	233.700	233.770	.530	-.070
4	235.300	235.337	1.504	-.037
39	235.300	235.379	1.509	-.079
27	236.500	236.507	.978	-.007
20	236.500	236.535	.986	-.035
98	245.200	245.129	1.470	.071
67	245.200	245.163	1.461	.037
76	246.400	246.285	2.484	.115
156	246.400	246.332	2.496	.068
21	247.900	247.894	1.014	.006
26	247.900	247.928	1.034	-.028
202	271.800	271.734	.957	.066
154	271.800	271.753	.947	.047
54	273.300	273.335	2.379	-.035
142	273.300	273.363	2.374	-.063
121	274.400	274.536	1.417	-.136
180	274.400	274.556	1.422	-.156
56	278.200	278.056	1.034	.144
10	278.200	278.090	1.014	.110
3	279.700	279.651	2.496	.049
28	279.700	279.699	2.484	.001
37	280.900	280.821	1.461	.079
109	280.900	280.854	1.470	.046
150	283.100	283.112	1.053	-.012
182	283.100	283.129	1.049	-.029
194	284.400	284.305	1.623	.095
209	284.400	284.330	1.621	.070
200	286.000	285.915	.578	.085
125	286.000	285.932	.581	.068
11	289.300	289.477	.978	-.177

LINE	EXP. FREQ.	CALC. FREQ.	INTEN	ERROR (Hz)
66	289.300	289.477	.978	-.177
87	290.600	290.604	1.509	-.004
161	290.600	290.646	1.504	-.046
99	292.200	292.213	.530	-.013
36	292.200	292.242	.534	-.042

Associated with this "best spectrum" are new values for the chemical shift of the methylene protons and the various coupling constants. This information is summarized below:

	"Trial"	"Best"
Chemical Shift - axial	282.0	281.381
Chemical Shift - equatorial	230.9	231.460
$J(H_{eq}H_{ax})$	-11.2	-10.995
$J(PH_{eq})$	20.0	20.134
$J(PH_{ax})$	6.2	6.149
$J(H_{eq}H_{eq})$	2.65	2.854

Clearly, the first order analysis of $Mo(CO)_5$(2-Cl-TBMP) gave reasonable values for the various nmr parameters.

Analysis of the nmr spectrum of cis-$Mo(CO)_5$(2-CH_3O-TBMP) presented a greater problem. The difference of $|\delta_{eq}-\delta_{ax}|$ was nearly the same value as the various coupling constants, and a non-first-order spectrum was obtained. Trial parameters for this system were obtained upon actual mathematical analysis of the nmr spectrum. The AA'BB'X system was treated as an ABX spectrum in order to obtain the trial parameters; details of analysis of an ABX spectrum are presented in reference 146. After the theoretical spectrum was obtained, the same iterative procedure as outlined above was following using LAOCN3.

VITA

Charles M. Bartish was born in Easton, Pennsylvania, on June 4, 1947, the son of A. Charles and Justina Y. Bartish. He received his primary and secondary education in the Easton Area School District and was graduated from Easton Area High School in 1965.

Mr. Bartish entered Villanova University in September, 1965, and received the degree of Bachelor of Science in Chemistry in May, 1969.

In June, 1969, Mr. Bartish married the former Joanne A. Campbell of Easton, Pennsylvania, a graduate of Sacred Heart Hospital School of Nursing, Allentown, Pennsylvania.

Mr. Bartish entered Lehigh University in September, 1969, and in February, 1970, was awarded an NDEA Fellowship.

In June, 1970, the Bartish's first child, a daughter, Jennifer Lynn was born.

Mr. Bartish is a member of the American Chemical Society and Sigma Xi. He has co-authored the following papers with Dr. Charles S. Kraihanzel:

"Reactions of Coordinated Ligands:"

I. "Molybdenum Carbonyl Complexes of Dimethyl- and Diphenylphosphinous Acids and of Several Diphosphoxanes," J. Amer. Chem. Soc., 94, 3572 (1972).

II. "Reactions of Chlorodimethylphosphine- and Chlorodiphenylphosphinepentacarbonylmolybdenum with Selected Alcohols, Ethanethiol, Hydrogen Sulfide, Ammonia, and Several Amines," J. Organometal. Chem., 43, 343 (1972).

III. "Conformational Analysis of Metal Carbonyl Complexes of 2-Substituted 5,5-dimethyl-1,3,2-dioxaphosphorinanes," Inorg. Chem., 12, 391 (1973).