isomerization of either the thexyl group or the ring moiety was observed except with *B*-thexyl-9-borabicyclononanes. The experimental results were summarized in Table II.

Oxidation of Organoboranes. In most cases oxidation of the reaction mixtures was carried out essentially as described earlier.[16] Oxidation of the distillate was carried out similarly after dissolving the distillate in THF (10 ml per 10 mmol of distillate). *B*-Thexyl-9-borabicyclo[3.3.1]nonane proved to be quite resistant to the usual oxidation conditions. Therefore, 2.06 g (10 mmol) of *B*-thexyl-9-borabicyclo[3.3.1]nonane dissolved in 10 ml of THF was oxidized, after addition of 10 ml of ethanol, with 5 ml each of

30% hydrogen peroxide and 6 N sodium hydroxide at 30–40°. After heating the mixture for 1 hr at 50°, it was worked up as usual. The results were summarized in Table II. Authentic samples of the diols were either commercially available or available in our laboratories.

Reactions of Coordinated Ligands. I. Molybdenum Carbonyl Complexes of Dimethyl- and Diphenylphosphinous Acids and of Several Diphosphoxanes[1]

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Abstract: The compounds [Cl(CH$_3$)$_2$P](CO)$_5$Mo and [Cl(C$_6$H$_5$)$_2$P](CO)$_5$Mo react readily with water in the presence of triethylamine to yield [(CH$_3$)$_2$P(OH)](CO)$_5$Mo and (C$_2$H$_5$)$_3$NH{[(C$_6$H$_5$)$_2$PO](CO)$_5$Mo}, respectively. In the first product, dimethylphosphinous acid is stabilized as the hitherto unknown tautomer of dimethylphosphine oxide. The corresponding complex of diphenylphosphinous acid was obtained upon base hydrolysis of [Cl(C$_6$H$_5$)$_2$-P](CO)$_5$Mo as well as from the thermal reaction of diphenylphosphine oxide with Mo(CO)$_6$. The two phosphinous acid derivatives react smoothly with [Cl(CH$_3$)$_2$P](CO)$_5$Mo in the presence of triethylamine to yield (CO)$_5$MoP-(CH$_3$)$_2$OPR$_2$Mo(CO)$_5$ with R equal to methyl or phenyl. Reaction between [Cl(C$_6$H$_5$)$_2$P](CO)$_5$Mo and (C$_2$H$_5$)$_3$NH{[(C$_6$H$_5$)$_2$PO](CO)$_5$Mo} led to (CO)$_5$MoP(C$_6$H$_5$)$_2$OP(C$_6$H$_5$)$_2$Mo(CO)$_5$. The bridging ligands in the three dimolybdenum complexes contain the very uncommon diphosphoxane linkage.

In general, attempts to synthesize trivalent phosphorus compounds which retain the phosphinous acid structure, R$_2$POH, have been unsuccessful as the thermodynamically more stable phosphine oxide tautomer, R$_2$P(O)H, is obtained.[2] Bis(trifluoromethyl)phosphinous acid, (CF$_3$)$_2$POH, is the only well-documented species in this class.[3] However, the rationalization of considerable kinetic exchange data and the nature of numerous reactions of organophosphorus compounds is possible only if the following equilibria are considered to exist: (RO)$_2$P(O)H $\rightleftharpoons$ (RO)$_2$POH;[4–6] (C$_6$H$_5$)P(O)-H(OH) $\rightleftharpoons$ (C$_6$H$_5$)P(OH)$_2$;[7,8] (C$_6$H$_5$)$_2$P(O)H $\rightleftharpoons$ (C$_6$H$_5$)$_2$-P(OH).[9] Each equilibrium is shifted extensively to the left and attempts to obtain physical evidence for the presence of the trivalent tautomer have been unsuccessful.[10] In this paper, we are concerned with the stabilization of the trivalent form of phosphinous acids upon complexation with molybdenum(0).

Two synthetic routes toward obtaining a general complex L$_x$MPG$_2$(OH) (where L's are ligands on the metal M, and G may be alkyl, aryl, alkoxyl, hydroxyl, etc.) are apparent: (1) hydrolysis of a phosphorus to halogen bond, or other readily cleaved bond to phosphorus, in a precomplexed ligand; (2) direct reaction of G$_2$P(O)H with a metal salt or complex in an effort to shift the above-mentioned equilibria to the right by removal of the trivalent tautomer as it is generated. One century ago Schutzenberger and Fontaine[11] reported what may have been the first example of hydrolysis of a phosphorus–halogen bond in a coordinated ligand. They found PtCl$_2$(PCl$_3$) and PtCl$_2$-(PCl$_3$)$_2$ to be readily hydrolyzed to PtCl$_2$[P(OH)$_3$] (presumably dimeric) and PtCl$_2$[P(OH)$_3$]$_2$ respectively. Although other metal complexes with phosphorus donor ligands that have phosphorus–halogen bonds have been noted to show differing degrees of reactivity toward water, product analysis has not been of interest.[12] More recently, Austin[13] obtained cis-MCl$_2$[(C$_6$H$_5$)$_2$-P(OH)]$_2$ and cis-MCl$_2$[(C$_6$H$_5$)ClP(OH)]$_2$ (where M is Pt or Pd) upon hydrolysis of the metal complexes of chlorodiphenylphosphine and dichlorophenylphosphine.

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In contrast, $Pt[P(OR)_2O]_2[P(OR)_2OH]_2$ complexes (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.[14] The corresponding compound with R as phenyl is most easily prepared by reacting $PtCl_2(CH_3CN)_2$ or $PtCl_2[(C_2H_5)_2S]_2$ with diphenyl phosphonate.[15]

We report here syntheses of the first two metal carbonyl complexes with phosphinous acid ligands and their subsequent utilization in the syntheses of complexes with bridging diphosphoxane ligands.

Experimental Section

Molybdenum hexacarbonyl was a generous gift from Climax Molybdenum Co. Chlorodiphenylphosphine (Aldrich) was vacuum distilled prior to use. Chlorodimethylphosphine was prepared by the method of Parshall.[16] Methylcyclohexane, hexane, and toluene were dried by distillation from phosphorus pentoxide. Reactions and isolation procedures were carried out under dry nitrogen.

Proton nmr spectra were obtained with an Hitachi Perkin-Elmer R20A spectrometer; peak positions are relative to internal tetramethylsilane at τ 10. Infrared spectra in the 2000-cm^{-1} region were observed with a Perkin-Elmer 621 spectrometer; routine scans were obtained with a Perkin-Elmer Model 21 instrument. An Hitachi Perkin-Elmer RMU-6E mass spectrometer was employed. Elemental analyses were performed by Baron Consulting Co., Orange, Conn.

(Chlorodiphenylphosphine)pentacarbonylmolybdenum (1). 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 1 hr. 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.[17] 57°), pmr (CS_2) τ 2.64 (m). 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 $(\nu_{C\equiv O}$, 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 (2). 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 hr 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 2 as a nearly colorless oil admixed with a small quantity of colorless crystals which were identified as the diphosphoxane derivative 5 (see below). Inasmuch as 2 is much more soluble in hexane than is 5, it was possible to effect a separation by washing the mixture with a very small amount of hexane. Evaporation of the hexane washings yielded 2. Unfortunately, the relative yields of 2 and 5 in this preparation are variable. Attempts to purify 2 by low-temperature recrystallization, sublimation to a cold probe, and high-vacuum distillation were unsuccessful. Further complications include the conversion of 2 to 5 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 2. The oil was further characterized by spectral

observations, as discussed in the Results section of this paper, and by derivatization upon reaction with triethylamine to yield the salt 3 and with diazomethane to give the methyl ester 4: pmr (CS_2) τ 2.65 (m, C_6H_5), ~5.0 (s, OH, see Results section). 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 $(C_6H_5)_2P(O)H$,[18] 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 2 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 (3). 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°; pmr (CS_2) τ 2.78 (m, C_6H_5), 7.44 (q, CH_2), 8.95 (t, CH_3). 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 (4). To a solution of diazomethane in ether prepared from 1.25 g of N,N'-dimethyl-N,N'-dinitrosoterephthalamide[19] 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 × 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 4 prepared by an alternative method.[20]

(Chlorodimethylphosphine)pentacarbonylmolybdenum (7). 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 5 hr. 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 7 as white crystals, mp 36–37°, pmr (CS_2) τ 7.98 (d, J_{HP} = 3.8 Hz). Anal. Calcd for $C_7H_6O_5ClMoP$: C, 25.29; H, 1.81. Found: C, 25.18; H, 1.86.

(Dimethylphosphinous acid)pentacarbonylmolybdenum (8). 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 two 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); pmr (CS_2) τ 8.22 (d, CH_3, J_{HP} = 5.5 Hz), 4.5 (s, OH; see Results section). Anal. Calcd for $C_7H_7O_6$-MoP: C, 26.75; H, 2.23. Found: C, 26.61; H, 2.46.

μ-Tetraphenyldiphosphoxane-decacarbonyldimolybdenum (5), and μ-P,P-Dimethyl-P',P'-diphenyldiphosphoxane-decacarbonyldimolybdenum (6). A mixture of 1 g of $(C_2H_5)_3NH\{[C_6H_5]_2PO]$-$(CO)_5Mo\}$ and 1 g of $(ClR_2P)(CO)_5Mo$, where R is CH_3 or C_6H_5, in 25 ml of anhydrous ether was allowed to stir for 2 hr at room temperature. A white residue remained in each case upon removal of the solvent under aspirator vacuum.

For R equal to CH_3, the residue was extracted with two 15-ml portions of hot hexane and filtered. Concentration of the filtrate to a few milliliters 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,

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mp 84–86°, was obtained after several recrystallizations from *n*-hexane; pmr (CS$_2$) τ 8.36 ("apparent triplet," CH$_3$, separation of outer lines = 4.0 Hz). *Anal.* Calcd for C$_{24}$H$_{16}$O$_{11}$Mo$_2$P$_2$: C, 39.24; H, 2.18. Found: C, 38.90; H, 2.34.
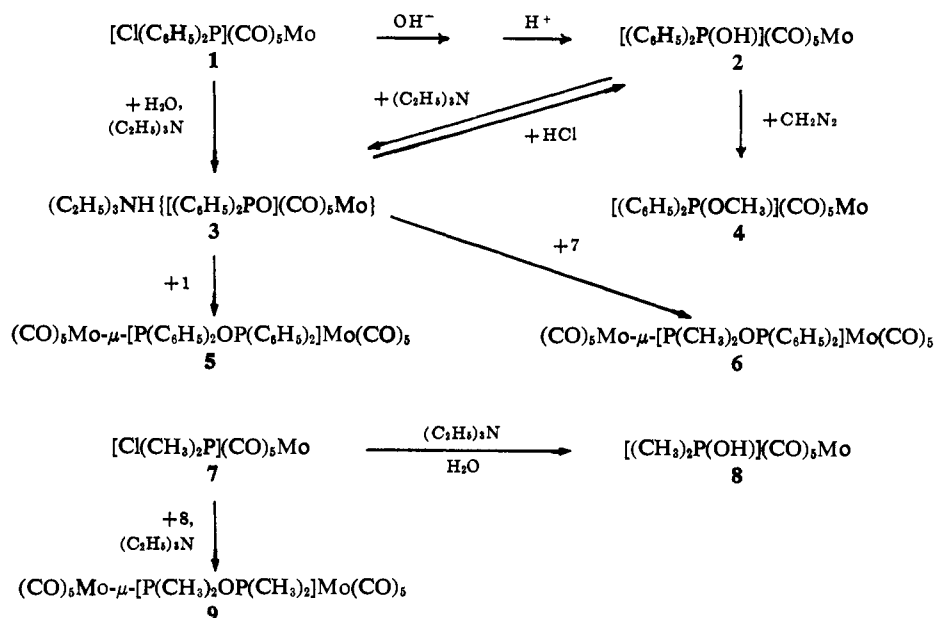
Where R is C$_6$H$_5$, the reaction residue was treated with two 15-ml portions of chloroform. Evaporation of the combined chloroform extracts gave a solid which was recrystallized from ethanol–chloroform to yield 60% of pure μ-[P(C$_6$H$_5$)$_2$OP(C$_6$H$_5$)$_2$](CO)$_{10}$Mo$_2$ as pale yellow crystals, mp 157° dec, pmr (CS$_2$) τ 2.56 (m, C$_6$H$_5$). *Anal.* Calcd for C$_{34}$H$_{20}$O$_{11}$Mo$_2$P$_2$: C, 47.55; H, 2.33. Found: C, 47.57; H, 2.55.

μ-**Tetramethyldiphosphoxane-decacarbonyldimolybdenum (9).** A solution consisting of 0.5 g of [Cl(CH$_3$)$_2$P](CO)$_5$Mo, 0.5 g of [(CH$_3$)$_2$P(OH)](CO)$_5$Mo, 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 triethylamine hydrochloride 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$_3$)$_2$OP(CH$_3$)$_2$](CO)$_{10}$Mo$_2$ as white crystals, mp 66–68°, was obtained; pmr (CS$_2$) τ 8.00 ("apparent triplet," CH$_3$, separation of outer lines = 4.1 Hz). *Anal.* Calcd for C$_{14}$H$_{12}$O$_{11}$Mo$_2$P$_2$: C, 27.54; H, 1.97; mol wt, 610. Found: C, 27.78; H, 2.08; mol wt, 584 (cryoscopic determination in benzene).

Results and Characterization of Products

The reaction outline shown in Scheme I summarizes the syntheses reported in this paper. All of the compounds except **1** are new. Although **1** and **7** may be hydrolyzed by water alone to yield **2** and **8**, respectively, the rates of hydrolysis are considerably faster in the presence of hydroxide or triethylamine. Several specific spectral observations lead to the structural assignments given above. To begin, the positions and intensities of the infrared active bands in the 2100–1900 cm^{-1} region for **2** and **8** indicate clearly that the organophosphorus ligand is coordinated through phosphorus to the molybdenum atom in each instance.[21] Further, the infrared spectra of pure **2** and **8** exhibit broad hydroxyl stretching bands centered near 3200 cm^{-1}. In very dilute carbon tetrachloride solution, the broad bands disappear and sharp hydroxyl stretching bands are noted at 3610 cm^{-1}. This dependence of ν_{OH} on

concentration is typical of strongly hydrogen bonding molecules.[22] Griffiths and Burg report the appearance of a strong hydroxyl stretching band at 3620 cm^{-1} for (CF$_3$)$_2$POH.[3] The pmr spectra of **2** and **8** provide further information to support the structural assignment. In particular, a slightly broadened hydroxyl proton resonance signal is noted and the chemical shift value for the signal is strongly temperature and concentration dependent. No splitting of the signal by phosphorus-31 is seen. Additional evidence for the acidic nature of **2** is provided by the facile reactions with diazomethane and triethylamine to yield **4** and **3**, respectively.

An ionic formulation for **3** is indicated by the low values of 15.3 and 15.7 mdyn/Å for the carbonyl ligand stretching force constants k_1 and k_2, respectively. Apparently, the negative charge of the diphenylphosphinito ligand leads to greater charge delocalization from filled metal d orbitals into the π antibonding levels of the carbonyl ligands than is possible with uncharged phosphorus donor ligands. Amine salts were not readily obtained from **8** and may indicate, as would be predicted, that the diphenylphosphinous acid complex is more acidic than the dimethylphosphinous acid complex.

Scheme I

Complexes **5**, **6**, and **9** are of special interest because they contain bridging tetraorganodiphosphoxane ligands. Evidence in support of the assigned structures comes from several sources in addition to the elemental analyses. The molecular weight of **9** was determined cryoscopically. Owing to the low solubilities of **5** and **6** in cold benzene, the molecular weights of these compounds could not be determined with confidence by cryoscopic means. The mass spectrum of **5** showed {(CO)$_4$Mo[P(C$_6$H$_5$)$_2$OP(C$_6$H$_5$)$_2$]}$^+$ as the ion with the highest m/e value. The ion {(CO)$_2$Mo[P(C$_6$H$_5$)$_2$OP-(C$_6$H$_5$)$_2$]}$^+$ was readily noted and {Mo[P(C$_6$H$_5$)$_2$OP-(C$_6$H$_5$)$_2$]}$^+$ was the most abundant ion in the mass spectrum. Infrared spectra of **5**, **6**, and **9** indicated the following: (1) coordination exclusively through

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Table I. Metal Carbonyl Stretching Frequencies (cm^{-1}) and Simplified Stretching Force Constants[21] (mdyn/Å) for [(CO)$_5$MoL] and [((CO)$_5$Mo)$_2$L]^a

Compd	Ligand	A$_1$(1)	B$_1$	A$_1$(2)	E	k_1	k_2	k_i
1	P(C$_6$H$_5$)$_2$Cl	2079	1989	1965	1957	15.81	16.06	0.30
7	P(CH$_3$)$_2$Cl	2080	1989	1971	1956	15.92	16.05	0.30
2	P(C$_6$H$_5$)$_2$OH	2074	1987	1958	1949	15.70	15.94	0.30
8	P(CH$_3$)$_2$OH	2074	1988	1966	1949	15.84	15.94	0.30
6	P(C$_6$H$_5$)$_2$OP(CH$_3$)$_2$	2074	1994	1953	1949	15.61	15.95	0.30
5	P(C$_6$H$_5$)$_2$OP(C$_6$H$_5$)$_2$	2074	1993	1952	1949	15.60	15.95	0.30
9	P(CH$_3$)$_2$OP(CH$_3$)$_2$	2074	1986	1968	1952	15.87	15.97	0.29
3	P(C$_6$H$_5$)$_2$O$^-$ (C$_2$H$_5$)$_3$NH$^+$	2063	1976	1932		15.29	15.71	0.32
4	P(C$_6$H$_5$)$_2$(OCH$_3$)	2074	1985	1965	1957	15.81	16.06	0.30

^{a} Hexane employed as solvent except for **3, 5,** and **6,** where CS$_2$ was used. Band positions are ± 1 cm^{-1} for A$_1$(1). B$_1$ bands are very weak and are positioned to ± 2 cm^{-1}. The A$_1$(2) and E-mode bands are resolved only for the (CH$_3$)$_2$P complexes and are estimated valid to ± 2 cm^{-1} or better. The values listed for the A$_1$(2) and E bands of the (C$_6$H$_5$)$_2$P derivatives were estimated by graphical resolution of the overlapping bands.

phosphorus to the two required Mo(CO)$_5$ moieties per molecule as shown by the positions and intensities of the metal carbonyl stretching bands; (2) the organophosphorus ligand cannot have the isomeric structure R$_2$PPR$_2$(O) inasmuch as there is no evidence of a phosphorus–oxygen stretching mode in the 1450–1080-cm^{-1} region; (3) the organophosphorus ligand must have a phosphorus–oxygen–phosphorus backbone inasmuch as strong bands at 860, 895, and 874 cm^{-1} (Nujol) for **5, 6,** and **9,** respectively, are assignable to a P–O–P asymmetric stretching mode.[23] The phosphine oxide derivatives (CH$_3$)$_2$P(O)OP(O)(CH$_3$)$_2$ and (C$_6$H$_5$)$_2$P(O)OP(O)(C$_6$H$_5$)$_2$ are reported to have asymmetric P–O–P stretching bands at 988 and 962 cm^{-1}, respectively.[23]

The apparent triplets for the methyl pmr signals of **6** and **9** must arise from coupling of the protons with both phosphorus nuclei in the respective AA'X$_6$ and X$_6$AA'X$_6$' spin systems.[24]

Discussion

This study has shown the feasibility of preparing simple complexes of diphenylphosphinous and dimethylphosphinous acids by hydrolysis of a phosphorus–chlorine bond in a precomplexed ligand. In addition, the existence of a tautomeric equilibrium between diphenylphosphine oxide and diphenylphosphinous acid[9] has been further substantiated by our success in trapping the unstable tricovalent isomer in a molybdenum carbonyl complex. Although the latter procedure will undoubtedly be exploited further in the preparations of other metal complexes of the thermodynamically unstable form of phosphorus acids, the hydrolysis procedures developed here have some inherent advantages over the thermal method. To begin, the hydrolysis procedure is fast and can be carried out at ambient temperatures or lower. Furthermore, direct thermal reactions often lead to multiply substituted products in addition to thermal decomposition. A qualitative comparison of the purities of the products **2** obtained by both procedures showed the

hydrolysis product to be significantly purer than the thermal reaction product.

Most unique in this investigation has been the development of procedures involving the reactions of coordinated ligands on two separate molecules with each other which have led to complexes of three previously unknown diphosphoxanes. Subsequent to the present study only two isolable phosphoxanes, (CF$_3$)$_2$POP(CF$_3$)$_2$[3] and F$_2$POPF$_2$,[25] had been reported. Tetraphenyldiphosphoxane[26] and (CF$_3$)$_2$POP(CH$_3$)$_2$[3] have been postulated as unstable intermediates. Burg has noted that numerous attempts to prepare other alkyl- and aryldiphosphoxanes, even those containing the stabilizing (CF$_3$)$_2$PO group, have failed. In general, compounds isolated from the attempted syntheses are rearrangement and disproportionation products.[3,26] The stability of (CF$_3$)$_2$POP(CF$_3$)$_2$ has been considered to be a result of strong two-way O→P π bonding and the weak basicity of phosphorus which discourages formation of a phosphine oxide structure by way of an Arbusov-type rearrangement.[27] The thermodynamic instability of the nickel sesquicarbonyl complex, Ni$_2$(CO)$_4$[(CF$_3$)$_2$POP(CF$_3$)$_2$], provides further evidence of the low nucleophilicity of phosphorus in the bridging ligand. By comparison, the complexes of (C$_6$H$_5$)$_2$POP(C$_6$H$_5$)$_2$, (C$_6$H$_5$)$_2$POP(CH$_3$)$_2$, and (CH$_3$)$_2$POP(CH$_3$)$_2$ obtained in the present work have good thermodynamic stability and have been stored in closed vials at room temperature for nearly a year with only minimal decomposition. The stability of nickel complexes with the diphosphoxanes obtained in this work will have to await further synthetic work.

Finally, in the absence of isolable diphosphoxanes, the synthetic route employed here appears to be the only straightforward way that diphosphoxanes may be routinely prepared, albeit in complexed form.

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