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REACTIONS OF COORDINATED LIGANDS

VI *. REACTIONS OF *cis*-TETRACARBONYLBIS(CHLORODIPHENYLPHOSPHINE)MOLYBDENUM(0) WITH AMMONIA, METHYLAMINE, *p*-TOLUIDINE, WATER, METHANOL, *p*-CRESOL, AND ETHANETHIOL AND THE SUBSEQUENT REACTIONS OF THE AMMONOLYSIS AND HYDROLYSIS PRODUCTS WITH CHLOROSILANES AND BORON TRIFLUORIDE DIETHYLETHERATE

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Summary

The complex *cis*-$[Mo(CO)_4(PPh_2Cl)_2]$ (I) readily reacts with a variety of nucleophiles, HX where X = NH_2, NHMe, NH-*p*-C_6H_4Me, OCH_3, O-*p*-C_6H_4Me, and SEt, in the presence of a nitrogen base to yield new *cis*-$[Mo(CO)_4(PPh_2X)_2]$ complexes. The reaction of *cis*-$[Mo(CO)_4(PPh_2NH_2)_2]$ (II) first with n-BuLi and then with dichlorosilanes yields unique heterocyclic complexes. The reaction of I with H_2O and Et_3N yields $[Et_3NH]^+$ *cis*-$[Mo(CO)_4((PPh_2O)_2H)]^-$ (VIII) which is postulated to contain a symmetrically-bound hydrogen. The hydrogen may be replaced by a BF_2 group by treatment with $BF_3 \cdot OEt_2$ and with a Na^+ by treatment with NaOH and Et_4NCl. Reaction of VIII with dichlorosilanes yields complexes containing unique heterocyclic rings analogous to those obtained from II. ^1H NMR and infrared spectral properties of the new complexes are given.

Introduction

Although the reactions of coordinated phosphorus donor ligands are receiving increased attention and have been the subject of a review [1], no comprehensive studies of the reactions of phosphorus donor ligands in di- or poly-substituted complexes have been reported. Lovell [2] studied the reactions of several organohalophosphine complexes of nickel(0) with boric acid and phenylboric acids which yield new complexes of chelating diphosphine ligands. Among other

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* For part V see ref. 16.

studies, Austin [3] obtained complexes with chelating diphosphines by treating *cis*-ML_2Cl_2, where M = Pd^{II} or Pt^{II} and L = $PhPCl_2$ or Ph_2PCl, with diols and phenylphosphonic acid. Rattray and Dixon [4,5] extended the work begun by Austin by examining the synthesis of complexes such as $[PtCl(PEt_3)(PPh_2O)_2H]$ and their reactions with boron trifluoride diethyl etherate, $VO(acac)_2$, and chlorosilanes. Johannsen, Stelzer, and Unger [6] prepared *cis*-$[Mo(CO)_4(PR_n(NH_2)_{3-n})_2]$, where R = Ph or Me and n = 1 or 2, and have studied the reactions of the phosphinamide ligand with chlorosilanes. Several of the reactions of coordinated phosphorus donor ligands in the previously cited studies are of interest because they yield unusual heterocyclic ring systems containing chelating diphosphine ligands which had not been previously reported and which are unknown in uncomplexed form.

In this work, a systematic study of the reactions of the coordinated chlorodiphenylphosphine ligands in *cis*-tetracarbonylbis(chlorodiphenylphosphine)molybdenum(0), *cis*-$[Mo(CO)_4(PPh_2Cl)_2]$ (I) with water, alcohols, ammonia, amines, and thiols is presented. Of special interest are the subsequent reactions of the hydrolysis and ammonolysis products with chlorosilanes and boron trifluoride diethyletherate which yield unique inorganic heterocycles. Also of interest is a comparison of the results obtained in this study with those reported by Kraihanzel and Bartish [7,8] of the reactions of $[Mo(CO)_5(PR_2Cl)]$, where R = Ph or Me.

Experimental section

Chlorodiphenylphosphine (Aldrich) was vacuum distilled prior to use. *cis*-Tetracarbonylbis(chlorodiphenylphosphine)molybdenum(0) (I) was synthesized by the method of Ehrl et al. [9]. Tetrahydrofuran (THF) and triethylamine were distilled from calcium hydride. Methanol was distilled from magnesium turnings. Other solvents were used directly from their suppliers. Distillations, reactions and isolation procedures were carried out under dry nitrogen.

Recrystallizations were carried out with solvent mixtures. In general, the solid was dissolved at room temperature in a minimum amount of the more polar solvent. The solution was heated to boiling under a nitrogen stream and the less polar solvent was added in small increments to maintain the initial volume of solution until the solution was close to saturation. Next, filtration through a 1 cm layer of chromatography grade silica gel on a sintered glass funnel was routinely employed to clarify the solutions. The filtrant was again heated to boiling under a nitrogen stream and additional small increments of the less polar solvent were added to maintain the original volume of the filtrate until the onset of precipitation. The solution was then cooled slowly to —10°C and the precipitate collected by positive pressure nitrogen filtration. Additional crops of product were obtained from the filtrate by repeating the recrystallization procedure.

NMR spectra were obtained with a Hitachi Perkin—Elmer R20A nuclear magnetic resonance spectrometer. Tetramethylsilane (TMS) was used as the internal standard for ^1H NMR measurements.

Frequency measurements were obtained with a Takeda—Riken TR 3824X frequency counter.

Infrared spectra were obtained on a Perkin—Elmer Model 283 instrument. Elemental analyses were performed by Baron Consulting Co., Orange, Conn. Melting points were taken in sealed tubes under nitrogen and are uncorrected.

cis-Tetracarbonylbis(diphenylphosphinamide)molybdenum(0), cis-$[Mo(CO)_4(PPh_2NH_2)_2]$ *(II)*

Dry ammonia was bubbled into a well-stirred solution of 5.00 g (7.7 mmol) of I in 30 ml of THF at room temperature for 1 h. Following filtration to remove the precipitated ammonium chloride the filtrate was evaporated to dryness. The residue was recrystallized from a methylene chloride/hexane mixture to yield 3.59 g (76%) of analytically pure white product, m.p. 135—136°C. (Found: C, 54.95; H, 3.87. $C_{28}H_{24}MoN_2O_4P_2$ calcd.: C, 55.09; H, 3.96%.)

cis-Tetracarbonylbis(N-methyldiphenylphosphinamide)molybdenum(0), cis-$[Mo(CO)_4(PPh_2NHMe)_2]$ *(III)*

The preceding general procedure when followed using dry methylamine in place of ammonia yielded 3.24 g (66%) of analytically pure white product, m.p. 127.5—128.5°C. (Found: C, 56.09; H, 4.66. $C_{30}H_{28}MoN_2O_4P_2$ calcd.: C, 56.43; H, 4.42%.)

cis-Tetracarbonylbis(N-p-tolyldiphenylphosphinamide)molybdenum(0), cis-$[Mo(CO)_4(PPh_2NH\text{-}p\text{-}C_6H_4Me)_2]$ *(IV)*

A solution of 1.96 g (3 mmol) of I and 1.29 g (12 mmol) of *p*-toluidine in 30 ml of THF was stirred at 42°C for 5 h. Following filtration to remove the precipitated *p*-toluidine hydrochloride, the filtrate was evaporated to dryness. The light green residue was recrystallized from a methylene chloride/hexane mixture to yield a first crop of 1.00 g of white product and a second crop of 0.78 g of slightly less pure product for a yield of 72%. A second recrystallization from a methylene chloride/hexane mixture yielded purer product, m.p. 133.5—136°C (dec.). The complex was characterized by IR and ^1H NMR.

cis-Tetracarbonylbis(methyldiphenylphosphinite)molybdenum(0), cis-$[Mo(CO)_4(PPh_2OMe)_2]$ *(V)*

Procedure 1. Triethylamine (2.00 ml) was added dropwise to a well-stirred suspension of 2.00 g (3.1 mmol) of I in 10 ml of methanol at room temperature. This caused the disappearance of the yellow starting material and the formation of the white product. Filtration yielded 1.55 g (79%) of slightly impure product which was recrystallized from a methylene chloride/hexane mixture to yield analytically pure product, m.p. 125—126°C. (Found: C, 55.87; H, 3.92. $C_{30}H_{26}MoO_6P_2$ calcd.: C, 56.26; H, 4.09%.)

Procedure 2. A solution of 2.00 g (3.1 mmol) of I and 0.78 g (14.4 mmol) of sodium methoxide in 20 ml of THF was stirred at room temperature for 65 h. The mixture was then filtered to remove the precipitated sodium chloride and the excess sodium methoxide. The filtrate was evaporated to dryness and the residue recrystallized from a methylene chloride/hexane mixture to yield 1.17 g (58%) of product, m.p. 124—125°C.

cis-Tetracarbonylbis(p-tolyldiphenylphosphinite)molybdenum(0), cis-[Mo(CO)$_4$-(PPh$_2$O-p-C$_6$H$_4$Me)$_2$] (VI)

A solution of 2.00 g (3.1 mmol) of I in 20 ml of THF was added dropwise to a well-stirred solution of 1.30 g (10 mmol) of sodium *p*-methylphenoxide in 20 ml of THF over a period of 30 minutes at room temperature. After an additional 24 h of stirring the solution was filtered to remove the precipitated sodium chloride and the filtrate evaporated to dryness. The white, oily residue was recrystallized from a methylene chloride/hexane mixture to yield a first crop of 1.34 g of white product and a second crop of 0.15 g of slightly less pure product for a yield of 61%. A second recrystallization from a methylene chloride/hexane mixture yielded analytically pure product, m.p. 166—167°C (dec.). (Found: C, 63.71; H, 4.29. $C_{40}H_{34}MoO_6P_2$ calcd.: C, 63.64; H, 4.07%.)

cis-Tetracarbonylbis(ethyldiphenylthiaphosphinite)molybdenum(0), cis-[Mo-(CO)$_4$(PPh$_2$SEt)$_2$] (VII)

A solution of 2.00 g (3.1 mmol) of I and 10 ml of ethanethiol in 15 ml of THF was stirred at room temperature as a solution of 2.00 ml of triethylamine in 15 ml of THF was slowly added. After stirring for 30 minutes the solution was evaporated to dryness and the red oily residue was transferred to a 2 × 10 cm alumina chromatography column and eluted with benzene. The first fraction which was light yellow was collected and evaporated to dryness. The residue was recrystallized from a methylene chloride/hexane mixture to yield 1.38 g (64%) of yellow product. A second recrystallization with a hot methylene chloride/hexane mixture yielded analytically pure product, m.p. 140.5—143.5°C (dec.). (Found: C, 55.11; H, 4.29. $C_{32}H_{30}MoO_4P_2S_2$ calcd.: C, 54.86; H, 4.31%.)

Triethylammonium cis-tetracarbonyl[bis(diphenylphosphinite)hydrogen(1—)]-molybdenum(0), [Et$_3$NH]$^+$ cis-[Mo(CO)$_4$((PPh$_2$O)$_2$H)]$^-$ (VIII)

A solution of 5.00 g (7.7 mmol) of I, 10 ml of distilled water, and 10 ml of triethylamine in 50 ml of THF was stirred at room temperature for 30 minutes. During this time, the color of the solution faded from bright to pale yellow. The solution was then evaporated to dryness and the white residue washed with three 30 ml portions of distilled water and 10 ml of ethanol. Filtration followed by air drying yielded 4.86 g (88%) of white product. Recrystallization from a methylene chloride/hexane mixture yielded analytically pure product, m.p. 180—182°C (dec.). (Found: C, 56.87; H, 5.16. $C_{34}H_{38}MoNO_6P_2$ calcd.: C, 57.23; H, 5.22%.)

Tetraethylammonium cis-tetracarbonyl[bis(diphenylphosphinito)sodium(1—)]-molybdenum(0), [Et$_4$N]$^+$ cis-[Mo(CO)$_4$((PPh$_2$O)$_2$Na)]$^-$ (IX)

Procedure 1. A solution of 2.00 g (3.1 mmol) of I, 30 ml of distilled water, 0.87 g (3.4 mmol) of tetraethylammonium iodide and 0.37 g (9.24 mmol) of sodium hydroxide in 30 ml of THF was stirred at room temperature for 30 minutes. During this time the color of the solution faded from bright to pale yellow. The solution was then evaporated to dryness and the residue washed with three 30 ml portions of distilled water and 10 ml of ethanol. The residue was filtered and then recrystallized from a methylene chloride/hexane mixture to yield a first crop of 1.44 g of white product and a second crop of 0.45 g of slightly less pure product for a yield of 80%. A second recrystallization from a methylene chloride/hexane mixture yielded analytically pure product which decomposed slowly above 170°C. (Found: C, 56.25; H, 5.51. $C_{36}H_{40}MoNNaO_6P_2$ calcd.: C, 56.63; H, 5.28%.)

Procedure 2. A solution of 1.00 g (1.4 mmol) of VIII, 0.10 g (2.5 mmol) of sodium hydroxide, 0.25 g (1.6 mmol) of tetraethylammonium chloride and 2.00 ml of distilled water in 20 ml of THF was stirred at room temperature for 30 minutes. Then the solution was evaporated to dryness and the residue recrystallized from a methylene chloride/diethyl ether mixture to yield 0.86 g (80%) of white product.

Triethylammonium cis-tetracarbonyl[bis(diphenylphosphinito)difluoroboron-(1—)]molybdenum(0), $[Et_3N]^+$ *cis*-$[Mo(CO)_4((PPh_2O)_2BF_2)]^-$ (X)

A solution of 1.43 g (2.0 mmol) of VIII and 0.30 ml of triethylamine in 15 ml of THF was stirred at room temperature as a solution of 0.27 ml (2.1 mmol) of boron trifluoride diethyl etherate in 15 ml of THF was added dropwise over a 30 minute period. Then after the addition of 20 ml of cyclohexane the solution was filtered through 1 cm of chromatography grade silica gel on a sintered glass funnel. The filtrate was heated to boiling and then concentrated under a stream of nitrogen until the cloud point was reached. After cooling at —10°C for several hours, filtration yielded 1.33 g (85%) of white product. Three recrystallizations from a methylene chloride/diethyl ether mixture yielded analytically pure product; m.p. 157—158°C (dec.). (Found: C, 53.62; H, 5.01. $C_{36}BH_{40}F_2MoNO_6P_2$ calcd.: C, 53.50; H, 4.75%.)

cis-Tetracarbonylbis(trimethylsilyldiphenylphosphinite)molybdenum(0), cis-$[Mo(CO)_4(PPh_2OSiMe_3)_2]$ (XI)

A solution of 1.00 g (1.4 mmol) of VIII, 0.42 ml (3.2 mmol) of chlorotrimethylsilane and 0.17 ml (1.6 mmol) of triethylamine in 20 ml of THF was stirred at room temperature for 30 minutes. Then, after filtration to remove the precipitated triethylammonium chloride, the solution was evaporated to dryness and the residue was recrystallized from a methylene chloride/hexane mixture to yield a first crop of 0.65 g of analytically pure, white product and a second crop of 0.20 g of slightly less pure product, m.p. 144—146°C, for a yield of 81%. (Found: C, 53.79; H, 5.02. $C_{34}H_{38}MoO_6P_2Si_2$ calcd.: C, 53.96; H, 5.06%.)

cis-Tetracarbonyl[bis(diphenylphosphinito)dimethylsilane-P,P′]-molybdenum(0), cis-$[Mo(CO)_4((PPh_2O)_2SiMe_2)]$ (XII)

The general procedure used to synthesize XI was repeated using 1.50 g (2.1 mmol) of VIII, 0.311 g (2.4 mmol) of dichlorodimethylsilane and 0.335 ml (2.4 mmol) of triethylamine to yield a first crop of 1.25 g of white, analytically pure product, m.p. 171.5—172.5° C, and a second crop of 0.10 g of slightly less pure product for a yield of 96%. (Found: C, 53.70; H, 3.93. $C_{30}H_{26}MoO_6P_2Si$ calcd.: C, 53.90; H, 3.93%.)

cis-Tetracarbonyl[bis(diphenylphosphinito)methylphenylsilane-P,P′]molybdenum-(0), cis-$[Mo(CO)_4((PPh_2O)_2SiMePh)]$ (XIII)

The general procedure used to synthesize XI was repeated using 1.43 g (2 mmol) of VIII, 0.33 ml (2 mmol) of dichloromethylphenylsilane and 0.28 ml (2 mmol) of triethylamine to yield 1.33 g (91%) of white, analytically pure product, m.p. 156°C. (Found: C, 57.10; H, 4.05. $C_{35}H_{28}MoO_6P_2Si$ calcd.: C, 57.38; H, 3.85%.)

μ-[Tetrakis(diphenylphosphinito)silane-P,P′:P″,P‴]-cis-bis(tetracarbonylmolybdenum(0)), cis-[Mo(CO)$_4$(PPh$_2$O)$_2$]$_2$Si (XIV)

The general procedure used to synthesize XI was repeated using 1.43 g (2 mmol) of VIII, 0.115 ml (1 mmol) of silicon tetrachloride and 0.30 ml (2.2 mmol) of dry triethylamine to yield 1.19 g (95%) of white, analytically pure product, m.p. 257—260°C. (Found: C, 53.49; H, 2.98. $C_{56}H_{40}Mo_2O_{12}P_4Si_2$ calcd.: C, 53.69; H, 3.22%.)

cis-Tetracarbonylbis(N-trimethylsilyldiphenylphosphinamide)molybdenum(0), cis-[Mo(CO)$_4$(PPh$_2$NHSiMe$_3$)$_2$] (XV)

A solution of 1.22 g (2 mmol) of II in 20 ml of THF was stirred at 5°C as a solution of 1.10 ml (4 mmol) of 3.8 *M* n-butyllithium in hexane in 10 ml of THF was added dropwise over a 10 minute period. The addition first caused the clear solution to become bright yellow and then the precipitation of a yellow solid. When the addition was completed, the solution was stirred for 10 minutes and then a second solution of 0.51 ml (4 mmol) of chlorotrimethylsilane in 10 ml of THF was added dropwise over a 20 minute period. Next the solution was stirred for 30 minutes while warmed to room temperature and then was evaporated to dryness. The yellow oily residue was recrystallized from a diethyl ether/hexane mixture to yield 1.01 g (70%) of white, analytically pure product, m.p. 168—170.5°C (dec.). (Found: C, 53.79; H, 5.02. $C_{34}H_{40}MoN_2O_4P_2Si_2$ calcd.: C, 53.96; H, 5.06%.)

cis-Tetracarbonyl[bis(diphenylphosphinamido)dimethylsilane-P,P′]molybdenum(0), cis-[Mo(CO)$_4$((PPh$_2$NH)$_2$SiMe$_2$)] (XVI)

The general procedure used to synthesize XV was repeated using 1.60 g (2.62 mmol) of II, 3.00 ml (6.3 mmol) of 2.1 *M* n-butyllithium in hexane and 0.41 ml (3.2 mmol) of dichlorodimethylsilane to yield a first crop of 1.03 g of white, analytically pure product, which decomposes slowly above 230°C, and a second crop of 0.25 g of slightly less pure product for a yield of 70%. (Found: C, 54.27; H, 4.35. $C_{30}H_{32}MoN_2O_4P_2Si$ calcd.: C, 54.06; H, 4.23%.)

cis-Tetracarbonyl[bis(diphenylphosphinamido)methylphenylsilane-P,P′]molybdenum(0), cis-[Mo(CO)$_4$((PPh$_2$NH)$_2$Si(Me)Ph)] (XVII)

The general procedure used to synthesize XV was repeated using 1.22 g (2 mmol) of II, 1.10 ml (4.2 mmol) of 3.8 *M* n-butyllithium in hexanes and 0.33 ml (2 mmol) of dichloromethylphenylsilane to yield a first crop of 0.84 g of white, analytically pure product, which decomposes slowly above 197°C, and a second crop of 0.25 g of slightly less pure product for a yield of 88%. (Found: C, 57.59; H, 4.31. $C_{35}H_{34}MoN_2O_4P_2Si$ calcd.: C, 57.70; H, 4.15%.)

Triethylammonium pentacarbonyl(hydrogenphenylphosphinate)molybdenum(0), $[Et_3NH]^+$ $[Mo(CO)_5(PPh(OH)(O))]^-$ (XVIII)

A solution of 3.00 g (7.2 mmol) of $[Mo(CO)_5(PPhCl_2)]$, 3.00 ml of distilled water and 3.00 ml of triethylamine in 30 ml of acetone was stirred at room temperature for 30 minutes and then evaporated to dryness. The yellow-white residue was washed with 20 ml of distilled water and 20 ml of benzene and then recrystallized from methylene chloride to yield 1.76 g (51%) of white, analytically pure product, m.p. 119—119.5°C. (Found: C, 42.27; H, 4.52. $C_{17}H_{17}MoNO_7P$ calcd.: C, 42.27; H, 4.62%.)

Results and discussion

Reactions of cis-[Mo(CO)$_4$(PPh$_2$Cl)$_2$] (I)

The reactions (Scheme 1) observed between the coordinated chlorodiphenylphosphine ligands in I and alcohols, amines, and thiols are similar to those observed for the corresponding monophosphine complexes [8] in that the products contain only simple monodentate P-donor ligands.

SCHEME 1

$$cis\text{-}[Mo(CO)_4(PPh_2Cl)_2] + 2REH_n + 2Et_3N \text{ (or } 2REH_n) \xrightarrow{THF}$$

$$cis\text{-}[Mo(CO)_4(PPh_2EH_{n-1}R)_2] + 2Et_3NHCl \text{ (or } + 2REH_{n+1}Cl)$$

(II—VII)

(II: R = H, E = N, n = 2;
III: R = Me, E = N, n = 2;
IV: R = p-tolyl, E = N, n = 2;
V: R = Me, E = O, n = 1;
VI: R = p-tolyl, E = O, n = 1;
VII: R = Et, E = S, n = 1)

These reactions all proceed rapidly at room temperature in the presence of an amine. The products II—VI are colorless crystalline solids, while VII is a yellow crystalline solid. All are readily soluble in benzene, chloroform, methylene chloride, THF, and acetone and, in the solid state, all are air stable although some darken when exposed to light over a period of several days. Although ammonia and primary amines contain more than one reactive proton and could possibly lead to disubstituted aminodiphosphine ligands, only one proton per molecule was observed to react under the conditions used. Johannsen, Stelzer, and Unger [6] observed similar results in their work. The diminished reactivity of the coordinated aminophosphine ligands is probably due to steric effects in the *cis*-disubstituted configuration. Attempts to isolate stable complexes from reactions of I with dimethyl- and diethylamine were unsuccessful, a fact which may also be related to a steric effect between two large Ph_2PNR_2 ligands. It should be noted, however, that *sym-N,N'*-dimethylethylenediamine does react to yield complexes of chelating diphosphine ligands of the type $R_2PNMe(CH_2)_2NMePR_2$ (R = Me [6] and R = Ph [10]), which are isolable due to greater thermodynamic and hydrolytic stability relative to the complexes of monodentate ligands.

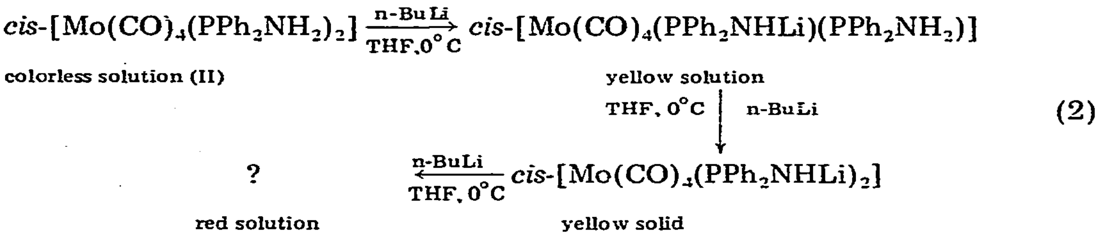
Reactions of cis-[Mo(CO)$_4$(PPh$_2$NH$_2$)$_2$] (II) with n-butyllithium and chlorosilanes

Johanssen, Stelzer, und Unger [6] found *cis*-[Mo(CO)$_4$(PMe$_2$NH$_2$)$_2$] to react with chlorosilanes in the presence of triethylamine to give complexes containing the P—N—Si linkage. However, when an attempt was made to have II react with chlorosilanes in the presence of triethylamine, II was recovered quantitatively. If the rate-determining step of the reaction is a nucleophilic attack of the nitrogen on silicon, this lack of reactivity might be expected for either or both of the following reasons. Replacement of the phosphorus-methyl groups by the more strongly electron-withdrawing phenyl groups would reduce the nucleophilicity of the nitrogen as well as considerably increase the steric bulk of the phosphine ligand. Thus, the absence of reaction might be ascribed to electronic and/or steric effects.

The nitrogen protons of the diphenylphosphinamide ligands of II may be removed by n-butyllithium. Slow addition of n-butyllithium to a THF solution of II at 0°C first results in a change in the color of the solution from colorless to bright yellow. When the mol ratio of n-butyllithium to II becomes greater than 1/1, a yellow solid, which appears to be *cis*-[$Mo(CO)_4(PPh_2NHLi)_2$], begins to precipitate. If the mol ratio becomes greater than 2/1, the solution turns a deep red and the yields of products from subsequent reactions are decreased. The cause of the deep red color is not known for certain but could arise either from the removal of a third nitrogen proton or from attack of the n-butyllithium on one of the carbonyl ligands.

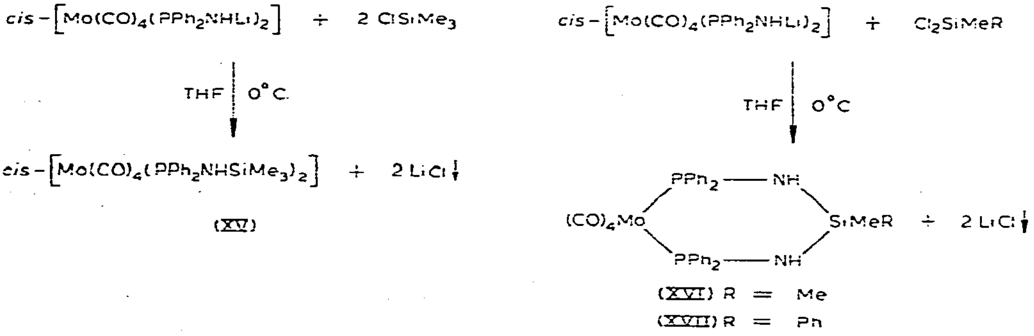
The reactions of n-butyllithium with II are summarized in Scheme 2.

SCHEME 2



The major evidence that the yellow solid formed from the reaction of n-butyllithium with II is indeed *cis*-[$Mo(CO)_4(PPh_2NHLi)_2$] is chemical in nature. The results of the subsequent reactions of this lithio intermediate with chlorosilanes are given in Scheme 3.

SCHEME 3

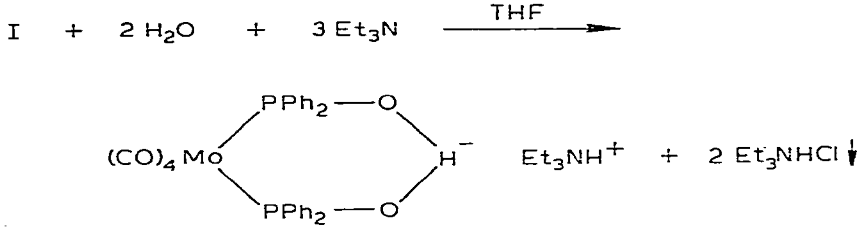


The products are all air stable, white crystalline solids.

Synthesis and reactions of $[Et_3NH]$-cis-$[Mo(CO)_4((PPh_2O)_2H)]$ (III)

When I was dissolved in a mixture of THF and distilled water, no reaction occurred at room temperature until triethylamine was added. The reaction is believed to occur as is shown in Scheme 4 and the product (VIII) is believed to have a symmetrical hydrogen bridge as pictured. The ^1H NMR spectrum of VIII contained only phenyl and ethyl resonances in a ratio of 4 to 3. The infrared spectrum of VIII showed carbonyl stretching absorptions corresponding to a *cis*-geometry about the molybdenum and also contained absorptions arising from the (P)—O—H and N—H stretching modes. Since the infrared spectrum clearly indicated the presence of protons on both the oxygen and nitrogen, the absence of a resonance(s) for these protons may be attributed to both rapid exchange of the OH and NH protons on the time scale of the NMR measurement and to the interaction of the protons with the nitrogen quadrupole moment. This interpretation is given credence by the NMR spectrum observed for $[Et_3NH]^+$ $[Mo(CO)_5(PPh(OH)O)]^-$ (XVIII) in which a broad resonance with an integration corresponding to two protons is observed at τ 1.30 ppm. The exchange of the protons in XVIII probably occurs more rapidly than in VIII, giving rise to an observable resonance for the two protons. The ionic nature of VIII is further confirmed by a comparison of the carbonyl stretching frequencies of VIII with those of II—VII. The observed shift to lower frequencies is indicative of a negatively charged ligand whose charge has been delocalized onto the metal thereby increasing the M_d—CO_{π^*} backbonding [7].

SCHEME 4



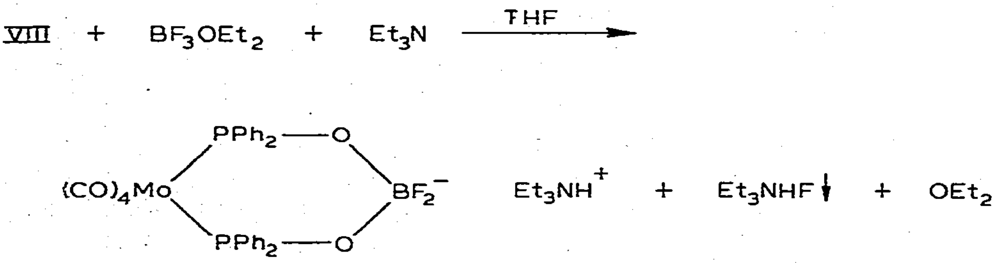
(VIII)

The structure assigned to VIII can be rationalized in part from the earlier work of Kraihanzel and Bartish [7] on the hydrolysis of complexes of the general type $[Mo(CO)_5(PR_2Cl)]$ with water and triethylamine. When R = phenyl, an ionic product, $[Et_3NH]^+[Mo(CO)_5(PPh_2O)]^-$, was obtained. When R = methyl the product obtained was the covalent complex, $[Mo(CO)_5(PMe_2OH)]$. Thus, in I the first chlorodiphenylphosphine ligand may react to form an ionic ligand such as was noted for the pentacarbonyl complex. However, the second ligand reacts as the chlorodimethylphosphine ligand in the pentacarbonyl complex. Most likely, the reduced acidity of the second P—O—H formed can be ascribed to hydrogen bridging with the P—O$^-$ already present. Alternatively, the negative charge from the diphenylphosphinite ligand may be redistributed through the metal and onto the diphenylphosphonic acid ligand as well as the carbonyl ligands.

The symmetrical hydrogen bonded system proposed for VIII is identical to that reported by Dixon and Rattray [4,5] to be present in a series of *cis*-platinum and *cis*-palladium complexes containing hydrolyzed chlorodiphenylphosphine ligands. Their proposal was arrived at on the basis of conductivity measurements, elemental analyses, and infrared spectral data. Confirmation of a symmetrical hydrogen bond in $[Pd_2(SCN)_2((PPh_2O)_2H)]$ by an X-ray diffraction study was carried out by Naik, Palenik, Jacobson, and Carty [11].

Several reactions of VIII are of interest as they offer further confirmation of the proposed structure for the complex as well as generating new complexes containing unusual heterocyclic rings. Reaction of VIII with boron trifluoride diethyl etherate led to the substitution of a BF_2 group for the proton as is shown in Scheme 5.

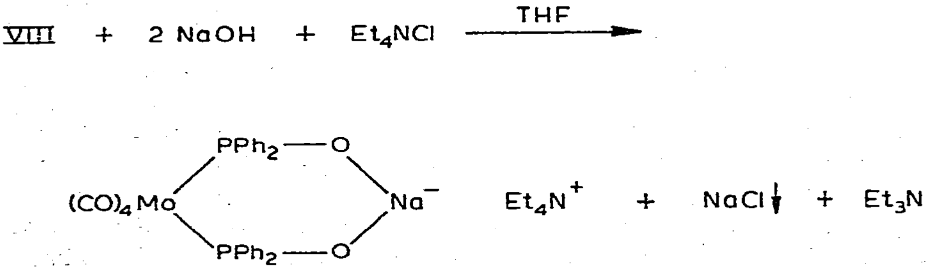
SCHEME 5



(X)

It seems reasonable that both fluorine atoms are attached to the boron, since if one of the fluorides were ionic, triethylammonium fluoride would have precipitated during the purification procedures. This is in contrast to structures proposed by Austin [3] for the products of reactions between boron trifluoride diethyl etherate and *cis*-platinum complexes containing bis(diphenylphosphinito)hydrogen(1-) ligands which contain a one covalent and one ionic fluorine. Reaction of VIII with sodium hydroxide and tetraethylammonium chloride, as shown in Scheme 6, led to substitution of the sodium ion for the remaining proton. It is proposed that the sodium ion is two-coordinate and occupies a bridging position similar to that of the hydrogen in VIII. The reaction of VIII with chlorosilanes gave the expected products which were identical to those produced by the reaction of *cis*-$[Mo(CO)_4(PPh_2NHLi)_2]$ with the chlorosilanes, except that the NH was replaced by O. These reactions are summarized in

SCHEME 6



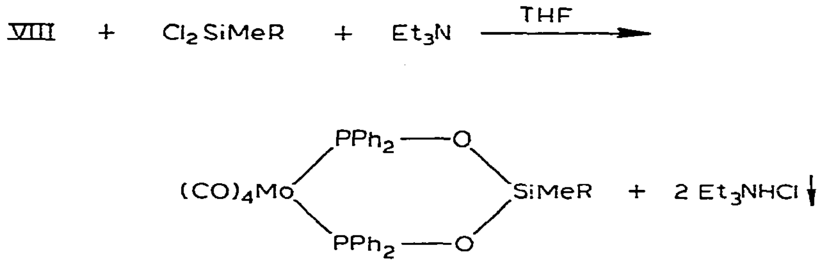
Schemes 7—9. Compound XIV is especially unique because of the proposed spiro-geometry at silicon.

SCHEME 7

$$\text{VIII} + 2\text{ClSiMe}_3 + \text{Et}_3\text{N} \xrightarrow{\text{THF}} cis\text{-}[\text{Mo(CO)}_4(\text{PPh}_2\text{OSiMe}_3)_2] + 2\ \text{Et}_3\text{NHCl}\downarrow$$

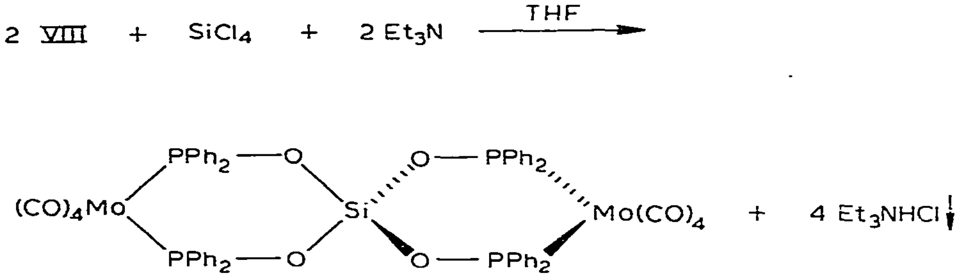
(XI)

SCHEME 8



(XII) R = Me
(XIII) R = Ph

SCHEME 9



(XIV)

Nuclear magnetic resonance spectra

The ^{1}H NMR spectra for these complexes have been obtained and the chemical shifts and coupling constants are reported in Table 1. The spectra are unusual in that, although the complexes have a *cis*-geometry, there is evidence of "virtual" coupling of the E—H and E—CH$_n$ protons (E = N, O, S) to both of the phosphorus nucleii. The theoretical aspects of this type of spin system have been elucidated by Harris [12] and by Hägele and Harris [13]. The results of the "virtual" coupling in the present complexes is to give a "virtual coupled triplet" (vct) in which the center peak is shorter and broader than the outer ones. The separation between the outer lines for resonances due to E—H protons is equal to ^2J(PH) + ^4J(PH) and for the resonances due to E—CH$_n$ protons is

TABLE 1

^{1}H NMR DATA [a]

Complex	$\tau(CH_n-E)$ (ppm)	$\|^2J(HP) + {}^5J(HP)\|$ (Hz)	$\tau(H_n-E)$ (ppm)	$\|^2J(HP) + {}^4J(HP)\|$ (Hz)	$\tau(CH_3-Si)$ (ppm)	$\tau(CH_3-R)$ (ppm)	$\|J^3(HH)\|$ (Hz)
II			7.55bs				
III	7.87vct	12.1	7.78s				
IV			5.56vct	18.2		7.86s	
V	6.78vct	12.0					
VI						7.81s	
VII	7.94qvct	5.2 $\|^3J(HH)\|$ 7.3				9.13t	7.3
VIII	6.93q [b]	$\|^3J(HH)\|$ 7.3 [b]				8.81t [b]	7.3 [b]
IX	6.68q [c]	$\|^3J(HH)\|$ 7.3 [c]				8.78tt [c]	7.3 [c] $\|^3J(NH)\|$ 2.0 [c]
X	7.39q [b]	$\|^3J(HH)\|$ 7.3 [b]				9.00t [b]	7.3 [b]
XI					10.10s		
XII					9.70s		
XIII					9.55s		
XV			8.60bs		10.33s		
XVI			7.80vct	8.8	9.72s		
XVII			7.30vct	8.5	9.48s		
XVIII	6.95q [b]	$\|^3J(HH)\|$ 7.3 [b]	1.30bs [d]			8.73t [b]	7.3 [b]

[a] s = singlet, bs = broad singlet, t = triplet, tt = triplet of triplets, vct = "virtual" coupled triplet, q = quartet, q vct = quartet of "virtual" couplet triplets. τ values are in ppm with TMS as internal standard. Solvent in $DCCl_3$ in all cases except for VIII, IX and XVIII for which the solvent is d^6-acetone. [b] For protons of triethylammonium counter ion. [c] For protons of tetraethylammonium counter ion. [d] Due to NH and OH proton exchange.

TABLE 2

INFRARED SPECTRA OF THE CARBONYL REGION [a]

<table>
<tr><th>Complex</th><th>ν(CO)$A_1^{(1)}$</th><th>ν(CO)$A_1^{(2)}$</th><th>ν(CO)B_1</th><th>ν(CO)B_2</th><th>Solvent</th></tr>
<tr><td>II</td><td>2023</td><td>1930</td><td colspan="2">1906</td><td>CS_2</td></tr>
<tr><td>III</td><td>2021</td><td>1928</td><td colspan="2">1905</td><td>CS_2</td></tr>
<tr><td>IV</td><td>2019</td><td>1934</td><td colspan="2">1906</td><td>CS_2</td></tr>
<tr><td>V</td><td>2026</td><td>1932</td><td colspan="2">1915</td><td>CS_2</td></tr>
<tr><td></td><td>2026</td><td>1935(sh)</td><td colspan="2">1912</td><td>$CHCl_3$</td></tr>
<tr><td>VI</td><td>2028</td><td>1939</td><td>1923</td><td>1908(sh)</td><td>CS_2</td></tr>
<tr><td>VII</td><td>2028</td><td>1935</td><td>1921</td><td>1906</td><td>CS_2</td></tr>
<tr><td>VIII</td><td>2013</td><td>1920</td><td colspan="2">1894</td><td>$CHCl_3$</td></tr>
<tr><td>IX</td><td>2008</td><td>1913</td><td colspan="2">1876</td><td>$CHCl_3$</td></tr>
<tr><td>X</td><td>2021</td><td>1925</td><td colspan="2">1898</td><td>$CHCl_3$</td></tr>
<tr><td>XI</td><td>2024</td><td>1931</td><td colspan="2">1909</td><td>CS_2</td></tr>
<tr><td>XII</td><td>2030</td><td>1939</td><td colspan="2">1918</td><td>CS_2</td></tr>
<tr><td>XIII</td><td>2031</td><td>1941</td><td colspan="2">1924</td><td>CS_2</td></tr>
<tr><td>XIV</td><td>2033</td><td>1946</td><td colspan="2">1927</td><td>CS_2</td></tr>
<tr><td>XV</td><td>2019</td><td>1919</td><td>1904</td><td>1877(sh)</td><td>CH_2Cl_2</td></tr>
<tr><td>XVI</td><td>2027</td><td>1935</td><td colspan="2">1909</td><td>CS_2</td></tr>
<tr><td>XVII</td><td>2026</td><td>1933</td><td>1905(sh)</td><td>1898</td><td>CS_2</td></tr>
</table>

[a] 2050 to 1850 cm^{-1}. All complexes are *cis*; (sh) = shoulder.

equal to ^3J(PH) + ^5J(PH). "Virtual" coupling was observed in all complexes containing an E—CH_n group and in some of the complexes containing an E—H group. Johannsen, Stelzer, and Unger [6] also observed "virtual" coupling for both the P—methyl and N—CH_n protons in complexes of the type *cis*-[$Mo(CO)_4$-$(PMe_2NMeR)_2$]. The coupling constants sums observed in this work for the N—methyl protons are comparable to those reported earlier [6].

All the silicon-methyl proton resonances observed were sharp singlets. For XII and XVI, the presence of a sharp singlet indicates that the heterocyclic rings are either fluxional at the ambient temperature of the instrument or have a rigid planar configuration.

Infrared spectra

Infrared spectra in the 2200—1800 cm^{-1} region were taken of solutions of the complexes in either chloroform or carbon disulfide and the results are reported in Table 2. For *cis*-octahedral complexes with a local site symmetry of C_{2v} at the molybdenum, four carbonyl stretching bands corresponding to the $A_1^{(1)}$, $A_1^{(2)}$, B_1, and B_2 symmetry modes are expected. In all cases a weak, sharp band corresponding to the $A_1^{(1)}$ mode was observed above 2000 cm^{-1} while one or more overlapped bands corresponding to the other three symmetry modes were found between 1950 and 1850 cm^{-1}. The bands for the three charged complexes were found at lower frequencies than those for the neutral complexes in the order $\nu(OBF_2O) > \nu(OHO) > \nu(ONaO)$. This trend is consistent with an increasingly ionic nature of the O—X—O bonds since the most ionic (Na^+) would lead to the greatest charge delocalization onto the molybdenum carbonyl system. Although no other major trends are apparent in the carbonyl spectra of these complexes, it is interesting to note that the nitrogen—phosphorus complexes show slightly lower frequency values than the isoelectronic oxygen—phosphorus complexes in all cases.

TABLE 3

INFRARED DATA 4000—600 cm^{-1} [a]

Complex	ν[(P)—E—H] (cm^{-1})	δ_3(CH$_3$Si) (ppm)	ν[(P)—E—R] (cm^{-1})		ν[P—E—(R)] (cm^{-1})			Other
II	3425(sh), 3410s 3342w, 3322w				970 mb	839s		δ(NH$_2$) 1583s
III	3417s		1087s			784m		δ(NCH$_3$) 1392m
IV	3386s		910s			807s		δ(PNC) 1297s, 1226m
V			1034s			758s		δ(POC) 1177w
VI			889s, 874s		830sh,	814m, 794w		δ(POC) 1216s, 1194s
VII						604s		δ(CH$_2$ wag) 1259m
VIII	2797wb, 2400mvb				925sb,	870m		
IX						970mb		
X						972sb		ν(BF$_2$) 1031sb
			ν(P—E—Si) [b] (cm^{-1})					
XI		1267s	1010sb,	990s,		850sb		
XII		1265s	1002s,	990s,	929s,	840mb,	816m	
XIII		1264m	1003s,	944s,	892s,		800m	
XIV			1012s,	996s,				
XV	3330s	1264sb		925sb		845sb		
XVI	3357m	1257s, 1229m	945s,	919sh,	910m,	850mb,	795m	
XVII	3330w, 3318w	1250m, 1231m		933sb,	818w,	802m,	782w	

[a] All samples in KBr disks; s = strong, m = medium, w = weak, b = broad, vb = very broad, (sh) = shoulder. [b] Contains bands due to P—E—(Si) and (P)—E—Si.

Infrared spectra in the 4000—350 cm^{-1} region were taken of KBr discs of the complexes and the results are given in Table 3. The assignment of the bands due to the phosphorus—ligand vibrations is not straightforward. An unequivocal assignment of the bands arising from the P—E—Si (E = O, NH) structure is especially difficult as very few infrared studies of compounds containing this grouping have been published [2—4,15]. A second problem with this assignment arises because the known P—O and Si—O stretches lie in approximately the same position. Thus, for compounds containing the P—E—Si linkage, it is only possible to state that two sets of bands in 1010—910 cm^{-1} region and in the 850—790 cm^{-1} region appear to arise from the stretching vibrations of P—E and E—Si bonds. The bands in the first region are strong to very strong while those in the second region are medium to strong in intensity. The number and shape of the bands in these regions are variable and dependent upon the complex being observed.

The assignment of bands due to the P—N—C system is also subject to question. Corbridge [14] assigns absorptions between 850 and 650 cm^{-1} to P—N stretching and absorptions between 1150 and 870 cm^{-1} to N—C(aliphatic) stretching. These assignments are similar to those made by both Corbridge [14] and Thomas [15] for the stretching bands arising from a P—O—C(aliphatic) system. Thomas [15], however, assigns the P—N stretch between 1102 and 789 cm^{-1} and the N—C(aliphatic) stretch between 1144 and 1087 cm^{-1}. The same inconsistencies appear in the regions assigned for the stretching bands arising from the P—N—C-(aromatic) system. The assignments given in Table 3 for the stretching bands arising from the P—E—C systems were arrived at by comparison of isoelectronic pairs of complexes. The assignments made are in good agreement with the ranges assigned by Corbridge [14].

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