REACTIONS OF COORDINATED LIGANDS

VIII [*]. SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM CARBONYL COMPLEXES OF DIPHENYLPHOSPHINOUS ACID AND DIPHENYLPHOSPHINOUS ACID DERIVATIVES

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Summary

Several unexpected reactions have led to syntheses of *cis*-[Mo(CO)$_4$((PPh$_2$)$_2$-E)] in which E = O, S, NH. The E = O complex was obtained from the reactions of several acid chlorides (CH$_3$C(O)Cl, PCl$_3$, (MeO)P(O)Cl$_2$ and [Mo(CO)$_5$-(PMe$_2$Cl)]) with [Et$_3$NH]$^+$ *cis*-[Mo(CO)$_4$((PPh$_2$O)$_2$H)]$^-$. The E = NH analog arose from the reaction of BF$_3 \cdot$O(C$_2$H$_5$)$_2$ with *cis*-[Mo(CO)$_4$(PPh$_2$NH$_2$)$_2$] and the E = S complex resulted from the reaction of H$_2$S with *cis*-[Mo(CO)$_4$(PPh$_2$-Cl)$_2$]. The unsymmetrically substituted complex *cis*-[Mo(CO)$_4$(PPh$_2$OH)-(PPh$_2$OCH$_2$CH$_3$)] was obtained from the reaction of *cis*-[Mo(CO)$_4$(PPh$_2$Cl)$_2$] with excess sodium ethoxide in ethanol. Cleavage of a P—S bond in *cis*-[Mo-(CO)$_4$((PPh$_2$)$_2$S)] with NaOH in the presence of Et$_4$N$^+$Cl$^-$ yielded the unsymmetrical complex [Et$_4$N]$^+$ *cis*-[Mo(CO)$_4$((PPh$_2$O)(PPh$_2$S)H)]$^-$. Synthesis of *cis*-[Mo(CO)$_4$((PPh$_2$O)$_2$P(O)CH$_2$Cl)] was accomplished by reacting (ClCH$_2$)-P(O)(OH)$_2$ with *cis*-[Mo(CO)$_4$(PPh$_2$Cl)$_2$]. Multinuclear NMR (^{1}H, ^{13}C, ^{17}O, ^{31}P) and IR spectroscopy assisted in complex characterization. Conductance measurements on acetone solutions proved the complexes [Et$_3$NH]$^+$ *cis*-[Mo(CO)$_4$-((PPh$_2$O)$_2$E)]$^-$, where E = H$^+$, BF$_2$$^+$, and [Et$_4$N]$^+$ *cis*-[Mo(CO)$_4$((PPh$_2$O)-(PPh$_2$Y)H)]$^-$, where Y = O, S, to be 1/1 electrolytes.

Introduction

Among the known complexes with diorganophosphinous acid (R$_2$POH) and phosphinito (R$_2$PO$^-$) ligands [1], those complexes which contain the presumably symmetrical ring system $\overline{M-PR_2-O\cdots H\cdots O-PR_2}$ have proved to be of

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[*] For part VII see Ref. 8.

special interest [2—6]. Formation of this ring system appears to be thermo-dynamically favorable as both *cis*- and *trans*-[Mo(CO)$_4$(PPh$_2$Cl)$_2$] are reported to hydrolyze to the *cis* product, [Et$_3$NH]$^+$ *cis*-[Mo(CO)$_4$((PPh$_2$O)$_2$H)]$^-$ [5]. Platinum(II) complexes of thio analogs of this ring system in which one or both of the oxygen atoms is replaced by sulfur have been reported recently [7].

This continuation of our work on the reactions of coordinated phosphorus donor ligands [2] reports several new reactions leading to complexes with diphenylphosphinous acid and/or derivatives of diphenylphosphinous acid as ligands. The complexes included in the study are: *cis*-[Mo(CO)$_4$((PPh$_2$)$_2$E)] in which E = O, S or NH; *cis*-[Mo(CO)$_4$(PPh$_2$OH)(L)], where L is Ph$_2$POEt or Ph$_2$POCH$_2$CH$_2$NMe$_2$; *cis*-[Mo(CO)$_4$((PPh$_2$O)$_2$P(O)Cl)]; and [Et$_4$N]$^+$ *cis*-[Mo-(CO)$_4$((PPh$_2$O)(PPh$_2$S)H)]$^-$. A conductivity study of this last-mentioned complex and other anionic complexes *cis*-[Mo(CO)$_4$((PPh$_2$O)$_2$G)]$^-$ where G = H$^+$ or BF$_2$$^+$ is included. Infrared spectroscopy and multinuclear NMR are employed in the characterization of the complexes.

Experimental

Reagents and solvents. *cis*-Bis(chlorodiphenylphosphine)tetracarbonylmolyb-denum(0) (I), (chlorodimethylphosphine)pentacarbonylmolybdenum(0), *cis*-bis-(diphenylphosphinamide)tetracarbonylmolybdenum(0), [NHEt$_3$]$^+$[Mo(CO)$_4$-((PPh$_2$O)$_2$H)]$^-$ (II), [NEt$_4$]$^+$[Mo(CO)$_4$((PPh$_2$O)$_2$H)]$^-$ (VI) [8], [NHEt$_3$]$^+$ [Mo-(CO)$_4$((PPh$_2$O)$_2$BF$_2$)]$^-$ (VII) and [Mo(CO)$_4$(PPh$_2$OH)(PPh$_2$OCH$_2$CH$_2$NMe$_2$)] (VIII) were prepared by literature methods [1,7—9]. Diethylether, tetrahydro-furan and triethylamine were distilled from calcium hydride under dry nitrogen. Chlorodiphenylphosphine (Aldrich) was vacuum distilled prior to use. Other solvents and reagents were used as received from various suppliers.

Analyses. Elemental analyses were provided by Baron Consulting Company, Orange, CT. Infrared spectra were obtained with a Perkin—Elmer Model 283B instrument. Conductivities of acetone solutions of the complexes were measured using a standard conductivity cell with 1 cm^2 platinum electrodes separated by 1 cm and coated with platinum black. Melting points were determined by sam-ples sealed in glass capillary tubes under nitrogen. Multinuclear (^{1}H, ^{13}C, ^{17}O, ^{31}P) NMR spectra were taken of saturated solutions of the complexes using a JEOL FX90Q NMR spectrometer. The operating parameters are summarized in Table 1. Physical properties of the complexes are listed in Tables 2—4.

Synthesis and isolation procedure. Recrystallizations were carried out with mixed solvents according to the following general procedure. A saturated solu-tion (r.t.) of the impure product in the more polar solvent was heated to boiling whereupon the less polar solvent was added to the point of incipient precipita-tion. The hot solution was filtered under nitrogen pressure through a 1 cm layer of chromatography grade silica gel on the frit of a glass funnel. The filtrate was heated to boiling and an additional amount of the less polar solvent was added to the cloud point. Cooling in a refrigerator (—10°C) and subsequent workup yielded one or more crops of crystalline product.

cis-Tetracarbonyl(tetraphenyldiphosphathiane)molybdenum(0), cis[Mo(CO)$_4$-((PPh$_2$)$_2$S)] (III)

A solution of 4.00 g (6.10 mmol) of I in 25 ml of THF was stirred at room

TABLE 1

NMR INSTRUMENT PARAMETERS AND STANDARDS

Nucleus	Center of spectrum (MHz)	Data point resolution (Hz)	Spectrum width (Hz)	Pulse angle (°)	Delay	Number of pulses	Standards
^{1}H	89.60475 ($CD Cl_3$) 89.60450 (CD_2Cl_2) 89.60425 (CD_3COCD_3)	0.1	1000	90	—	1	TMS internal
^{13}C	22.53330	0.7	6000	30	2.5 sec	2×10^2 — 6×10^3	TMS internal
^{17}O	12.15050	5	10,000	90	40 msec	3×10^5 — 3×10^6	H_2O external
^{31}P	36.27758	2.4	10,000	90	—	1	85% H_3PO_4 external

temperature as hydrogen sulfide was bubbled into the solution for 5 min. The flow of hydrogen sulfide was maintained during the dropwise addition of a solution of 2.00 ml of triethylamine in 15 ml of THF and for an additional 10 min. The reaction mixture was filtered through a 1 cm pad of chromatography grade silica gel on a sintered glass funnel. Evaporation of the filtrate left an oily, brown residue which was recrystallized from diethyl ether/hexane to yield 2.20 g of the yellow crystalline product (59%). A second recrystallization yielded analytically pure product, m.p. 145—146°C. (Found: C, 55.10; H, 3.30. $C_{28}H_{20}MoO_4P_2S$ calcd.: C, 55.10; H, 3.56%).

cis-Tetracarbonyl(tetraphenyldiphosphoxane)molybdenum(0), cis-[Mo(CO)$_4$- ((PPh$_2$)$_2$O)] (IV)

Procedure 1. A solution of 0.18 ml (2.00 mmol) of phosphorus trichloride in 20 ml of THF was added dropwise to a stirred room temperature solution of 1.43 g (2.00 mmol) of II and 0.30 ml of triethylamine in 15 ml of THF over a 25 min period. After an additional 30 min, the reaction mixture was filtered to remove the precipitated triethylammonium chloride. The filtrate was evaporated to dryness. Recrystallization of the yellow, oily residue from dichloromethane/ hexane yielded 0.47 g (40%) of analytically pure, yellow, crystalline product, m.p. 197—199°C (dec.). (Found: C, 56.27; H, 3.57. $C_{28}H_{20}MoO_5P_2$ calcd.: C, 56.58; H, 3.39%).

Procedure 2. Triethylamine (0.67 ml, 4.8 mmol) was added to a stirred, room temperature solution of 1.50 g (2.10 mmol) of II and 1.00 g (2.41 mmol) of [Mo(CO)$_5$(PMeCl$_2$)] in 25 ml of THF. After 1 h, the solution was filtered to remove precipitated triethylamine hydrochloride and the filtrate was evaporated to dryness. The yellow solid residue was recrystallized from dichloromethane/hexane to yield 1.34 g (100%) of yellow crystalline product with the same m.p., ¹H NMR and infrared spectra as the pure product obtained by procedure 1.

Procedure 3. Methyl dichlorophosphonate (0.19 ml, 1.80 mmol) was added to a solution of 1.30 g (1.82 mmol) of II and 0.26 g (1.80 mmol) of triethylamine in 30 ml of THF. The isolation method of procedure 2 was followed and yielded 0.63 g (58%) of the same yellow product.

Procedure 4. A solution of 0.29 ml (4.0 mmol) of acetyl chloride in 20 ml of THF was added dropwise to a stirred, room temperature solution of 1.43 g (2.00 mmol) of II and 0.30 ml (2.0 mmol) of triethylamine over a 20 min period. Thirty min after the addition was completed, the reaction mixture was filtered and the procedure of product isolation followed that used above. The light green residue yielded 1.20 g (~100%) of yellow product identical to the pure material obtained by procedure 1.

cis-Tetracarbonyl(tetraphenyldiphosphazane)molybdenum(0), cis-[Mo(CO)$_4$- ((PPh$_2$)$_2$NH)] (V)

A solution of 0.49 ml (4.00 mmol) of boron trifluoride diethyletherate in 10 ml of THF was added to a solution of 1.22 g (2.00 mmol) of *cis*-[Mo(CO)$_4$- (PPh$_2$NH$_2$)$_2$] in 15 ml of THF over a 0.5 h period. The reaction mixture was evaporated to dryness to yield a solid brown residue. Recrystallization of the residue from methylenechloride/hexane yielded 0.40 g of crude product. The

TABLE 2

INFRARED SPECTRA (2200—1800 cm^{-1}) FOR cis-[Mo(CO)$_4$(L—L)] AND cis-[Mo(CO)$_4$LL'] ^{a}

L—L or LL'		$\nu_{A_1}(1)$	$\nu_{A_1}(2)$	ν_{B_1}	ν_{B_2}
[(PPh$_2$O)$_2$H]$^-$	II	2016m	1896s	1915s	1873m
[(PPh$_2$O)$_2$BF$_2$]$^-$	VII	2023m	1919s	1908s	1879m
[(PPh$_2$O)(PPh$_2$S)H]$^-$	IX	2016m	1896m	1913s	1860m
PPh$_2$SPPh$_2$	III	2029m	1930sh	1923s	1898m
PPh$_2$OPPh$_2$	IV	2030m	1940sh	1927s	1904sh
PPh$_2$NHPPh$_2$	V	2024m	1924sh	1914s	1891m
(PPh$_2$O)$_2$P(O)CH$_2$Cl	X	2042m	1949sh	1936s	1923sh
(PPh$_2$OH)(PPh$_2$OCH$_2$CH$_2$NMe$_2$)	VIII	2023m	1924sh	1907s	1888sh
(PPh$_2$OH)(PPh$_2$OEt)	XI	2030m	1932sh	1917s	1902sh

^{a} Solvent is CH$_2$Cl$_2$.

crude material was recrystallized from THF/cyclohexane to yield analytically pure product, m.p. 206—209°C (dec) (lit. 204—205°C [10]) (Found: C, 57.41; H, 4.45; N, 2.26; C$_{32}$H$_{29}$MoNO$_5$P$_2$ calcd.: C, 57.76; H, 4.39; N, 2.10%).

Tetraethylammonium cis-tetracarbonyl((diphenylphosphinite)(diphenylthio-phosphinite)hydrogen(—1))molybdenum(0), [Et$_4$N]$^+$ cis-[Mo(CO)$_4$((PPh$_2$O)-(PPh$_2$S)H)]$^-$ (IX)

A mixture of 0.61 g (1.0 mmol) of III, 0.10 g (2.5 mmol) of sodium hydroxide, 1.00 ml of distilled water, and 0.32 g (2.0 mmol) of tetraethyl-ammonium chloride in 25 ml of acetone was stirred at room temperature for 6 h before being evaporated to dryness. The residue was washed with two 25 ml portions of distilled water and one 10 ml portion of methanol and then dissolved in dichloromethane. The filtered solution was reduced in volume to 40 ml and cooled to —10°C. After several hours 0.35 g of analytically pure, white crystalline product was obtained which slowly decomposes above 150°C. (Found: C, 56.94; H, 5.53. C$_{36}$H$_{41}$MoNO$_5$P$_2$S calcd.: C, 57.07; H, 5.45%). Concentration of the filtrate to 10 ml followed by cooling to —10°C yielded a second crop of 0.06 g for a total yield of 54%.

cis-Tetracarbonyl[bis(diphenylphosphino)(chloromethyl)phosphonate:P,P'] - molybdenum(0) - 0.5 dichloromethane, cis-[Mo(CO)$_4$((PPh$_2$O)$_2$P(O)CH$_2$Cl)] · 0.5 CH$_2$Cl$_2$ (X)

Triethylamine (0.83 ml, 6.0 mmol) was added to a well-stirred, room temperature solution of 1.95 g (3.00 mmol) of I and 0.39 g (3.0 mmol) of (chloro-methyl)phosphonic acid in 30 ml of THF. After 25 min, the reaction mixture was evaporated to dryness. The residue was recrystallized from dichloro-methane/diethylether to yield 1.10 g (49%) of analytically pure, white crystal-line product, m.p. 195.5—199.0°C. (Found: C, 47.34; H, 3.22. C$_{29.5}$H$_{23}$ClMo-O$_7$P$_3$ calcd.: C, 47.28; H, 3.09%).

cis-Tetracarbonyl(ethyl diphenylphosphinite)(diphenylphosphinous acid)-molybdenum(0) - 0.5 dichloromethane, cis-[Mo(CO)$_4$(PPh$_2$OEt)(PPh$_2$OH)] · 0.5 CH$_2$Cl$_2$ (XI)

To a solution of sodium ethoxide prepared from 0.15 g (6.5 mmol) of

sodium in 10 ml of absolute ethanol was added 1.30 g (2.00 mmol) of I. After 3 h, the reaction mixture was evaporated to dryness and the residue was recrystallized from dichloromethane/hexane to yield 0.39 g (31%) of product. A second recrystallization yielded analytically pure product, m.p. 145—147°C (dec.). (Found: C, 53.64; H, 4.17%. $C_{30.5}H_{27}ClMoO_6P_2$ calcd.: C, 53.64; H, 3.99%).
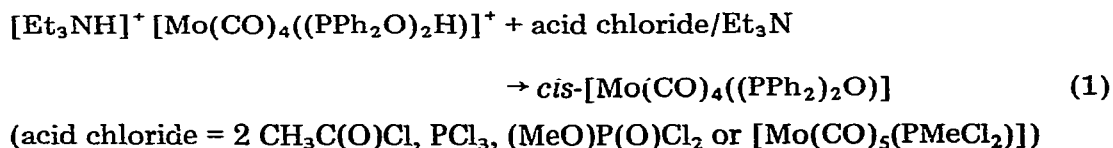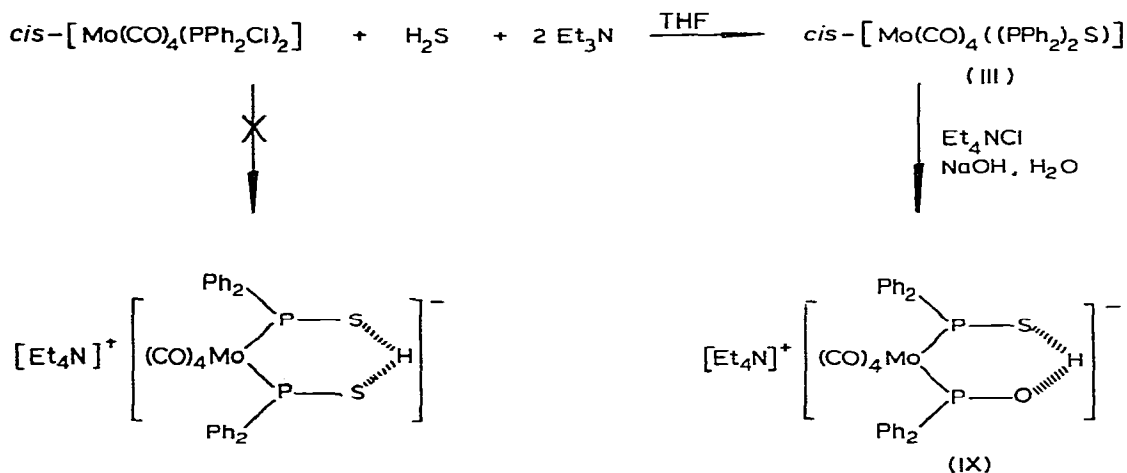
Results and discussion

cis-[Mo(CO)₄((PPh₂)₂E)] complexes (E = O, S, NH)

Although metal complexes containing the $\bar{M}$—PR_2—O···H···O—$\overline{PR}_2$ ring have been known for several years, the first analogous thiophosphinite complexes have only recently been reported and were obtained from reactions of diphenylphosphane sulfide with platinum(II) N,N-dialkyldithiocarbamates [7]. Inasmuch as earlier work from this laboratory had shown [Mo(CO)₅(PPh₂Cl)] to react with both water and hydrogen sulfide in the presence of triethylamine to yield [Et₃NH]⁺ [Mo(CO)₅(PPh₂E)]⁻ (E = O and S respectively) [9], an attempt was made to synthesize [Et₃NH]⁺ [Mo(CO)₄((PPh₂S)₂H)]⁻, the thiophosphinite analog of [Et₃NH]⁺ [Mo(CO)₄((PPh₂O)₂H)]⁻ (II) by reacting cis-[Mo(CO)₄(PPh₂Cl)₂] (I) with H₂S in the presence of triethylamine. Instead, cis-[Mo(CO)₄((PPh₂)₂S)] (III), was obtained as the only molybdenum containing complex. This air stable, yellow crystalline solid has good solubility in common organic solvents. The formulation of the complex as cis-[Mo(CO)₄-((PPh₂)₂S)] is supported by ¹H, ¹³C and ³¹P NMR, infrared spectra in the metallocarbonyl stretching region, elemental analysis and a cryoscopic molecular weight of 607 ± 20 measured in 1,2-dibromoethane.

As shown in Scheme 1, complex III undergoes hydrolysis with aqueous sodium hydroxide in the presence of tetraethylammonium chloride to yield IX as a white crystalline solid which is poorly soluble in diethyl ether, benzene and chloroform but is soluble in dichloromethane, tetrahydrofuran and acetone. The formulation of IX as a mixed diphenylphosphinito-diphenylthiophosphinito complex with a hydrogen bridge is based on elemental analyses, the confirmation of a cis configuration as evidenced by the nature of the bands in the metallocarbonyl stretching region, infrared bands at 2650, 2300 and 850 cm⁻¹ indicative of a P—O—H linkage, and nonequivalence of the two ³¹P nuclei to be discussed later.

Another synthetic goal related to complexes of phosphinous acid ligands was the generation of complexes containing the $\overline{Mo}$—PPh_2—O—PR—$\overline{OPPh}_2$ ring system according to previously developed procedures which led to bridged diphosphoxane complexes [9]. Several reactions are shown in eq. 1 which did not lead to the desired ring system. Instead, cis-[Mo(CO)₄((PPh₂)₂O)] (IV) was isolated as the common product of these reactions. Wong and coworkers [11] have shown that conversion of II to IV can also be achieved with trifluoroacetic acid

[Et₃NH]⁺ [Mo(CO)₄((PPh₂O)₂H)]⁺ + acid chloride/Et₃N

$$\rightarrow \textit{cis-}[Mo(CO)_4((PPh_2)_2O)] \qquad (1)$$

(acid chloride = 2 CH₃C(O)Cl, PCl₃, (MeO)P(O)Cl₂ or [Mo(CO)₅(PMeCl₂)])

$cis-[Mo(CO)_4(PPh_2Cl)_2]$ + H_2S + $2 Et_3N$ $\xrightarrow{\text{THF}}$ $cis-[Mo(CO)_4((PPh_2)_2S)]$

(III)

Et_4NCl
$NaOH . H_2O$

$[Et_4N]^+$ structure

$[Et_4N]^+$ structure (IX)

SCHEME 1

in methylene chloride [11]. These same workers have obtained the crystal structure of IV. The compression of the P—O—P bond angle required for chelate ring formation can be expected to have a profound effect on the P—O—P stretching modes. In fact, two bands at 781 and 766 cm^{-1} have been tentatively assigned to the symmetric and asymmetric stretching modes, respectively. These values correspond to very substantial shifts from previously reported ranges of 980—930 cm^{-1} and 720—680 cm^{-1} [12]. The mechanism(s) leading to formation of the chelating diphosphoxane complex are as yet unknown but may be viewed as a dehydration leading to formation of an acid anhydride. As shown in Scheme 2, the originally sought ring system has been obtained by another means. Complex X is a white, air-stable crystalline solid which turns blue when exposed to light and has good solubility in chloroform, dichloromethane, tetrahydrofuran and acetone.

$cis-[Mo(CO)_4(PPh_2Cl)_2]$ + $(ClCH_2)P(O)(OH)_2$ $\xrightarrow{\text{Et}_3\text{N}}$ structure (X)
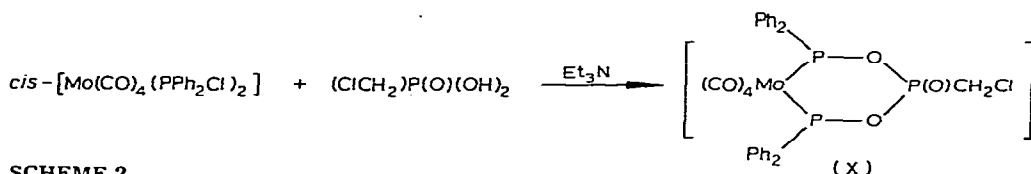
SCHEME 2

The ease of cyclization noted in Scheme 1 and eq. 1 leading to the chelate complexes III and IV has also been found in the reaction of cis-[Mo(CO)$_4$-(PPh$_2$NH$_2$)$_2$] with boron trifluoride diethyletherate. As shown in eq. 2 the product of this reaction is the tetraphenyldiphosphazane complex V and not the expected cis-[(CO)$_4$Mo(PPh$_2$NH)$_2$BF]. The melting point, infrared spectrum and ^{31}P NMR spectrum of V agree with published data [10]. The fate of the boron trifluoride in the reaction is unknown.

$$cis\text{-}[Mo(CO)_4(PPh_2NH_2)_2] + BF_3 \cdot OEt_2 \rightarrow cis\text{-}[Mo(CO)_4((PPh_2)_2NH)] \qquad (2)$$
$$(V)$$
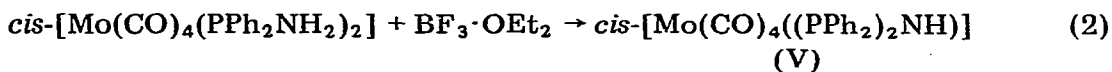
The carbonyl ligand carbon atoms and the phosphorus nuclei in cis-[Mo(CO)$_4$-L$_2$], in which L$_2$ are mono- or bi-dentate phosphorus donor ligands, constitute

TABLE 3

^{13}C. ^{17}O AND ^{31}P NMR DATA FOR cis-[Mo(CO)$_4$(L—L)] AND cis-[Mo(CO)$_4$LL'] COMPLEXES ^{a}

L—L or LL'		^{13}C(trans CO ^{b})		
		δ ^{c} (ppm)	$|^2J(CP) + {}^2J(CP')|$ (Hz)	$|^2J(CP)|, |^2J(CP')|$ (Hz)
(PPh$_2$O)$_2$H$^-$ Et$_3$NH$^+$	(II)	220.05at	15	—
(PPh$_2$O)$_2$H$^-$ Et$_4$N$^+$	(VI)	220.84at	13	—
(PPh$_2$O)$_2$BF$_2$$^-Et_3NH^+$	(VII)	219.86at	15	—
(PPh$_2$O)(PPh$_2$S)H$^-$Et$_4$N$^+$	(IX)	229.23dd	—	23, 8
		219.26dd	—	29, 9
PPh$_2$SPPh$_2$	(III)	217.98dd	—	32, 13
PPh$_2$OPPh$_2$	(IV)	217.20at	15	—
PPh$_2$NHPPh$_2$	(V)	218.61dd	—	25, 10
(PPh$_2$O)$_2$P(O)CH$_2$Cl	(X)	212.22at	21	—
(PPh$_2$OH)(PPh$_2$OCH$_2$CH$_2$NMe$_2$)	(VIII)	215.87dd	—	26, 8
		215.68dd	—	30, 8
(PPh$_2$OH)(PPh$_2$OEt)	(XI)	215.01dd	—	30, 8
		214.01dd	—	25, 8

^{a} at = apparent triplet; dd = doublet of doublets; t = triplet; s = singlet; d = doublet; m = multiplet. ^{b} (cis CO) and (trans CO) refer to CO ligands trans to another carbonyl and trans to a phosphorus donor ligand, respectively. ^{c} See Table 1 for instrument parameters and standards. ^{d} Actual signal is accidental 1/2/1

two different spin systems. For the ^{13}C nucleus of a carbonyl ligand cis to both phosphorus donor ligands, the spin system is AX$_2$ and in each case the ^{13}C signal is a 1/2/1 triplet with $|^2J(CP)|$ 9—11 Hz as shown in Table 3 for complexes II—VII. For complex X, the two different substituents on the central phosphorus atom in the chelate chain lead to a structural differentiation of the two cis carbonyl ligands and two 1/2/1 triplets separated by 1.17 ppm are observable.

The ^{13}C chemical shift of a carbonyl ligand trans to a phosphorus donor ligand is invariably greater than the chemical shift of a cis carbonyl in the same complex [13]. Inasmuch as the two ^{31}P nuclei in cis-[Mo(CO)$_4$L$_2$] are magnetically non-equivalent relative to a ^{13}C nucleus of a carbonyl ligand trans to one of the phosphorus donor ligands, these three nuclei constitute an AXX' spin system and analysis of the band shape of the A = ^{13}C portion of the spectrum requires recourse to the work of Redfield, Nelson and Cary [14,15]. This band shape may range from a 1/2/1 triplet, with separation between the outer lines equal to $|^2J(CP) + {}^2J(CP')|$ for a very large $|^2J(PP')|$ to a first order doublet of doublets when $|^2J(PP')| \to 0$. For intermediate values of $|^2J(PP')|$ a five line multiplet is expected which can be analyzed to give all three coupling constants. Unfortunately, the two outermost peaks in the five line multiplet are weak in many cases and are not observable even over long accumulation times. As a result, the commonly observed multiplet is an apparent triplet with the separation of the outer lines equal to $|^2J(CP) + {}^2J(CP')|$ [16]. Of the complexes reported in this section of the paper, it is interesting to note that apparent

$^{13}C(cis$ CO $^b)$		$^{17}O(trans$ CO $^b)$	$^{17}O(cis$ CO $^b)$	^{31}P—Mo		Solvent
δ ^{c} (ppm)	$|^2J(CP)|$ (Hz)	δ ^{c} (ppm)	δ ^{c} (ppm)	δ ^{c} (ppm)	$|^2J(PP')|$ (Hz)	
211.94t	11	366.5	356.8	113.3s	f	$(CD_3)_2CO$
211.67t	11	366.1	356.8	107.1s	f	$(CD_3)_2CO$
211.83t	11	366.9	358.5	114.3s	f	$(CD_3)_2CO$
211.80dd	11, 11 ^{d}	e	e	114.4d 57.8d	31 31	$(CD_3)_2CO$
210.01t	9	380.5	363.7	31.8s	f	CD_2Cl_2
208.97t	9	378.1	359.3	135.3s	f	CD_2Cl_2
209.93t	9	373.3	357.6	70.0s	f	CD_2Cl_2
207.22t 206.05t	10 11	371.3	358.8	155.9d ^{g}	f	$CDCl_3$
209.78dd	11, 11 ^{d}	362.1 361.3	356.8	148.2d 120.5d	39 39	$CDCl_3$
208.55ddd	11,11 ^{d}	366.9 362.5	356.4	149.6d 125.4d	39 39	$CDCl_3$

triplet with both $|^2J(CP)|$ values equal within measurement error. ^{e} Not observable owing to poor solubility. ^{f} Not determinable from available data. ^{g} δ = 8.6 ppm for medial phosphorus: triplet with $|^2J(P)|$ 11 Hz.

triplets are noted for the two phosphoxane derivatives IV and X, but for the thia (III) and aza (V) analogs of IV doublets of doublets are observed from which both $|^2J(CP)|$ and $|^2J(CP')|$ may be measured directly. If the signs of $|^2J(CP)|$ and $|^2J(CP')|$ are different for $[cis$-Mo(CO)$_4$L$_2]$, as has been suggested earlier [16], the values of $|^2J(CP) + ^2J(CP')|$ for II and V compare favorably with the line separations noted for IV and X and other complexes as well. The observance of a doublet of doublets for the *trans* carbonyl ^{13}C signal suggests that $|^2J(PP')|$ values for II and V must equal or approach zero. That $|^2J(PP')|$ is not zero in III is demonstrated by the apparent triplets observed for C(1), C(2) and C(3) of the aromatic carbons. On the other hand, $|^2J(PP')|$ in V must be very small, if not zero, inasmuch as the signals for C(1) (a doublet of doublets) and C(2) and C(3) (doublets) show no sign of virtual coupling to the more distant phosphorus nucleus.

Unsymmetrical cis-[Mo(CO)₄LL'] complexes

In an earlier publication, the reaction of cis-[Mo(CO)$_4$(PPh$_2$Cl)$_2$] (I) with N,N-dimethylethanolamine was reported to yield cis-[Mo(CO)$_4$(PPh$_2$OH)-(PPh$_2$OCH$_2$CH$_2$NMe$_2$)] (VIII) [7]. Our further efforts to synthesize unsymmetrically substituted cis-[Mo(CO)$_4$LL'] complexes have resulted in the isolation of cis-[Mo(CO)$_4$(PPh$_2$OH)(PPh$_2$OEt)] (XI) from the reaction of I with excess sodium ethoxide in ethanol as shown in eq. 3. The mechanism which leads to formation of VIII and XI is not known, and further studies in this area are planned.

TABLE 4

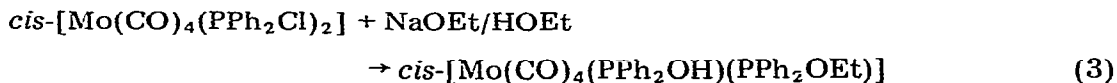^{13}C NMR DATA FOR THE NON-CARBONYL CARBON NUCLEI IN cis-[Mo(CO)$_4$(L–L)] AND cis-[Mo(CO)$_4$LL']

L–L or LL'		C(1)		C(2,6)	
		δ (ppm)	$\|^1J(CP) + {}^3J(CP')\|$ [b] (Hz)	δ (ppm)	$\|^2J(CP) + {}^4J(CP')\|$ [b] (Hz)
(PPh$_2$O)$_2$H$^-$ Et$_3$NH$^+$ [c]	(II)	148.24at	33	130.26at	13
(PPh$_2$O)$_2$H$^-$ Et$_4$N$^+$ [c]	(VI)	149.02at	33	129.35at	13
(PPh$_2$O)$_2$BF$_2^-$ Et$_3$NH$^+$ [c]	(VII)	147.94at	33	130.26at	13
(PPh$_2$O)(PPh$_2$S)H$^-$ Et$_4$N$^+$ [c]	(IX)	148.14d / 146.95d	41 / 71	134.10d / 130.48d	12 / 13
PPh$_2$SPPh$_2$ [d]	(III)	138.22at	31	131.59at	15
PPh$_2$OPPh$_2$	(IV)	139.26at	37	129.87at	16
Ph$_2$NHPh$_2$·THF [d]	(V)	139.03dd	23, 7	130.52d	15
(PPh$_2$O)$_2$P(O)CH$_2$Cl [e]	(X)	139.88ddat / 139.32dat	19,2 / 20,5 [f]	129.80at	16
(PPh$_2$OH)(PPh$_2$OCH$_2$CH$_2$NMe$_2$) [e]	(IX)	144.84d / 137.77d	33 / 28	131.57d / 129.77d	14 / 13
(PPh$_2$OH)(PPh$_2$OCH$_2$CH$_2$CH$_3$) [e]	(XI)	142.40d / 135.90d	39 / 29	131.38d / 129.51d	14 / 15

TABLE 4 (contd.)

L—L or LL'		C(3,5)		C(4)		Other ^{13}C nuclei	
		δ (ppm)	$|^{3}J(CP) + {}^{5}J(CP')|$ (Hz) [b]	δ (ppm)	$|^{4}J(CP)|$ (Hz)	δ (ppm)	J (indicated) (Hz)
$(PPh_2O)_2H^{-}$ Et_3NH^{+} [c]	(II)	128.31at	9	129.12s	—	46.72s (CH_2) 8.94s (CH_3)	—
$(PPh_2O)_2H^{-}$ Et_4N^{+} [c]	(VI)	127.33t	8	127.85s	—	52.22t (CH_2) 6.93s (CH_3)	3 $|^{1}J(CN)|$ —
$(PPh_2O)_2BF_2^{-}$ Et_3NH^{+} [c]	(VII)	128.34at	9	129.18s	—	46.97s (CH_2) 8.94s (CH_3)	— —
$(PPh_2O)(PPh_2S)H^{-}$ Et_4N^{+} [c]	(IX)	128.30d 127.44d	9 8	129.34d 127.80d	1 2	52.84t (CH_2) 7.67s (CH_3)	3 $|^{1}J(CN)|$ —
PPh_2SPPh_2 [d]	(III)	129.70at	10	131.78s	—	—	—
PPh_2OPPh_2	(IV)	128.50at	11	130.94s	—	—	—
$Ph_2NHPh_2 \cdot THF$ [d]	(V)	128.76d	10	130.60s	—	67.94s (CH_2)-THF 25.77s (CH_2)-THF	— —
$(PPh_2O)_2P(O)CH_2Cl$ [e]	(X)	128.57at	10	131.04s	—	35.15d (CH_2)	67 $|^{2}J(CP)|$
$(PPh_2OH)(PPh_2OCH_2CH_2NMe_2)$ [e]	(IX)	128.06d 127.75d	9 9	130.26s 129.53d	— 1	62.10d (OCH_2) 58.48d (NCH_2)	10 $|^{2}J(CP)|$ 7 $|^{3}J(CP)|$
$(PPh_2OH)(PPh_2OCH_2CH_3)$ [e]	(XI)	128.47d 128.06d	7 8	130.70s 129.61d	— 1	64.14d (CH_2) 16.50d (CH_3)	12 $|^{2}J(CP)|$ 5 $|^{3}J(CP)|$

[a] at = apparent triplet, d = doublet, dd = doublet of doublets, dat = doublet of apparent triplets, t = triplet, s = singlet. [b] Where apparent triplets are observed, the listed values are $|^{n}J(CP) + {}^{n+2}J(CP')|$. For doublets, the listed value is $^{n}J(CP)$. For a doublet of a doublet, the two values $|^{n}J(CP)|$ and $|^{n+2}J(CP')|$ are both given. [c] Solvent chloroform-d_3. [d] Solvent dichloromethane-d_2. [e] Solvent acetone-d_6. [f] C(1), but not C(2), (3), (4), of the phenyl rings are differentiated (see text).

cis-[Mo(CO)$_4$(PPh$_2$Cl)$_2$] + NaOEt/HOEt

$$\rightarrow cis\text{-}[Mo(CO)_4(PPh_2OH)(PPh_2OEt)] \qquad (3)$$

Few NMR studies of *cis*-[Mo(CO)$_4$LL'] complexes such as VIII, IX and XI have been reported. As a result of the low symmetry of these molecules, there are three types of carbonyl ^{13}C nuclei and the ^{31}P nuclei are chemical shift inequivalent. Each different ^{13}C nucleus constitutes the A portion of an AMX system where M and X are the ^{31}P nuclei. As expected, a doublet of doublets is seen for each carbonyl ^{13}C nuclei *trans* to a phosphorus ligand. Values of the coupling constants are: |^2J(CP)| (*trans*) 23—30 Hz and |^2J(CP)| (*cis*) 8—9 Hz. For the ^{13}C nuclei which are mutually *cis* to the two different phosphorus nuclei, apparent 1/2/1 triplets are observed for all three compounds. These apparent triplets can be most simply accounted for by assuming the occurrence of overlapping doublets with both |^2J(CP)| 11 Hz. Interpretation of these triplets as apparent triplets arising from AXX' type coupling is possible but not necessary inasmuch as the separation of the outer lines would equal |^2J(CP) + ^2J(CP')| = 2|^2J(PC)| = 22 Hz.

As expected, the [31]P {[1]H} spectrum for each of the unsymmetrical *cis* complexes VIII, IX and XI consists of a doublet of doublets with |^2J(PP')| = 31—39 Hz. For the two complexes VIII and XI, the more deshielded signals at δ 148 and δ 150 fall in the range noted for *cis*-[Mo(CO)$_4$(PPh$_2$OR)$_2$] complexes [16] and can be assigned to the phosphinite ester ligand. The higher field δ 120—125 chemical shifts of VIII and XI approach the chemical shifts of δ 107—114 seen for the anionic complex ions II, VI and VII. Two signals separated by 56 ppm are observed for the phosphinite-thiophosphinite complex. The less deshielded signal at δ 114 is assigned to the phosphinite phosphorus and the more shielded signal at δ 58 is assigned to the thiophosphinite phosphorus. This last assignment is supported by the ^{31}P chemical shift observations for *cis*-[Mo(CO)$_4$((PPh$_2$)$_2$S)] and *cis*-[Mo(CO)$_4$(PPh$_2$SEt)$_2$] [16].

Although ^{13}C resonance signals for aromatic nuclei of chelating phosphorus donor ligands have not been reported routinely in the past, these data can be structurally informative. The data summarized in Table 4 clearly shows that separate signals may be observed for the phenyl groups on the different ligands in complexes VIII, IX and XI. Also, as we have shown in numerous other cases [17] aromatic rings on the same donor atom are also differentiable by ^{13}C NMR in compounds such as X. Further, the appearance of doublets, apparent triplets, etc., for C(1) and C(2), 3 in some instances, allows for interpretation which parallels the treatment of the carbonyl carbon nuclei.

Natural abundance ^{17}O NMR is being increasingly employed in studies of metal carbonyl complexes [16,18—20]. The inherent NMR characteristics of [17]O together with the low natural concentration of this isotope make data collection difficult and the lack of detectable internuclear coupling to nuclei such as ^{31}P adds to the uncertainty of assignments of chemical shifts. For [M(CO)$_5$L] complexes, the assignment of [17]O signals to carbonyl group *cis* and *trans* to L is simplified by the relative signal areas [20]. However, there has been some uncertainty in the assigning of *cis* and *trans* carbonyl [17]O signals in *cis*-[Mo(CO)$_4$-L$_2$] based on the halfwidths of these signals. We believe our observations of the unsymmetrically disubstituted complexes VIII and XI leads to a clarification of

TABLE 5

MOLAR CONDUCTIVITIES OF [Et₃NR][(CO)₄Mo$\overline{PPh_2O}$···M···$\overline{EPPh_2}$] IN ACETONE

Compound	R	E	M	λ_m (mol l^{-1} ohm^{-1})
II	H	O	H	96
VI	E	O	H	140
VII	H	O	BF$_2$	149
IX	Et	S	H	135
	Reference NaI			144

assignments. For both of these complexes three ^{17}O NMR signals are expected and as shown in Table 3 are seen. The two low field ^{17}O signals of the different *trans* carbonyls are just barely resolved for compound VIII but are clearly resolved for XI. The positioning of the ^{17}O *trans* carbonyl signals downfield of the *cis* carbonyl signals and the slightly narrower halfwidths of the former signals confirms the assignment made earlier [16]. The assignment of the sharper resonance signals to the carbonyls *trans* to the phosphorus donor ligands contrasts with an earlier suggestion for *cis*-[Mo(CO)₄L₂] complexes [19].

Conductance measurements

Crystallographic studies of complexes such as [Pd(PPh₂S₂)((PPh₂O)₂H)] [21] and [Pt((P(OMe)₂O)₂BF₂)₂] [22] have proven conclusively that the H⁺ and BF₂⁻ moieties are tightly held between the *cis*-phosphorus donor anionic ligands. A similar type of binding has been proposed for our complexes II, VI, VII and IX. As such, these complexes ought to be ionic and in fact are 1/1 electrolytes as is clearly demonstrated by the conductance data in Table 5. The apparent depressed conductance value for complex II could be a reflection of ion pairing which might occur by proton bridging between the Et₃NH⁺ cation and the negative phosphinito oxygen sites.

Acknowledgements

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