

REACTIONS OF COORDINATED LIGANDS

II. REACTIONS OF (CHLORODIMETHYLPHOSPHINE)- AND (CHLORO-DIPHENYLPHOSPHINE) PENTACARBONYLMOLYBDENUM WITH SELECTED ALCOHOLS, ETHANETHIOL, HYDROGEN SULFIDE, AMMONIA AND SEVERAL AMINES

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SUMMARY

The compounds $(ClR_2P)(CO)_5Mo$, where R is CH_3 or C_6H_5 , react readily with a variety of nucleophilic reagents to yield new $(R_2PX)(CO)_5Mo$ complexes. The complexes $(R_2POR')(CO)_5Mo$, $[R_2P(NR''R''')](CO)_5Mo$ and $(R_2PSC_2H_5)(CO)_5Mo$ are obtained in good yield from the reactions with $R'OH$ ($R' = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7$), $R''R'''NH$ ($R'' = R''' = H, R'' = R''' = CH_3$, and $R'' = H$ with $R''' = CH_3$), and C_2H_5SH , respectively. Hydrogen sulfide and $(C_2H_5)_3N$ react with the chlorophosphine complexes to give $[(CH_3)_2PSH]Mo(CO)_5$ and $(C_2H_5)_3NH^+ [(C_6H_5)_2PO](CO)_5Mo^-$. Also, $(CH_3)_3SiCl$ reacts with $(C_2H_5)_3NH^+ [(C_6H_5)_2PO](CO)_5Mo^-$ to generate $[(C_6H_5)_2POSi(CH_3)_3](CO)_5Mo$. 1H NMR and infrared spectral properties of the new complexes are given.

INTRODUCTION

Although reports of hydrolysis and alcoholysis of coordinated halo-phosphine ligands are found scattered through the literature of the past century, neither the scope nor synthetic utility of these reactions has been studied systematically¹⁻⁹. In our first paper in this series, we reported on the facile hydrolysis of the phosphorus-chlorine bond in $(R_2PCl)Mo(CO)_5$, where R is methyl or phenyl, to yield complexes of dimethyl- and diphenylphosphinous acids¹⁰. Here, we report on our investigations of the reactions of these same two molybdenum complexes with a variety of nucleophilic reagents. The reagents employed include alcohols, thiols, primary and secondary amines, ammonia and hydrogen sulfide.

EXPERIMENTAL

Molybdenum hexacarbonyl was a generous gift from the Climax Molybdenum Co. Syntheses of (chlorodiphenylphosphine)- and (chlorodimethylphosphine)pentacarbonylmolybdenum have been reported¹⁰. Aniline and triethylamine were stored

over solid potassium hydroxide and distilled before use. Methylamine and dimethylamine were dried by passage through columns of solid potassium hydroxide. Commercial anhydrous ammonia and hydrogen sulfide were used directly. Alcohols and ethanethiol were fractionally distilled. Hexane, methylcyclohexane and toluene were

TABLE 1

 $(R_2PX)(CO)_5Mo$ COMPLEXES: PHYSICAL PROPERTIES AND ANALYSES

X	M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)		
			C	H	N
$R = C_6H_5$					
OCH ₃	43-44	87	48.06 (47.78)	3.08 (2.87)	
OC ₂ H ₅	47-49	80	48.87 (48.93)	3.31 (3.22)	
O-n-C ₃ H ₇	47-48	55	49.53 (50.00)	3.36 (3.54)	
O-i-C ₃ H ₇	47-48	67	50.14 (50.00)	3.32 (3.54)	
NH ₂	100-101 (dec.)	92	46.88 (46.68)	2.89 (2.75)	3.53 (3.20)
NH(CH ₃)	88-90 (dec.)	87	47.61 (47.89)	3.41 (3.13)	3.09 (3.12)
N(CH ₃) ₂	114-116 (dec.)	85	49.26 (49.04)	3.97 (3.44)	3.15 (3.02)
NH(C ₆ H ₅)	153-154 (dec.)	89	53.79 (53.80)	2.95 (3.12)	2.65 (2.73)
SC ₂ H ₅	76-78	83	47.25 (47.30)	3.35 (3.12)	
S ⁻ (C ₂ H ₅) ₃ NH ⁺	116-117 (dec.)	77	50.00 (49.75)	4.85 (4.69)	2.66 (2.52)
	B.p. (°C/mmHg)				
$R = CH_3$					
OCH ₃	40-42/0.05	89	29.55 (29.27)	2.75 (2.74)	
OC ₂ H ₅	40-42/0.03	86	31.51 (31.58)	2.91 (3.21)	
O-n-C ₃ H ₇	62-64/0.03	63	33.32 (33.72)	3.41 (3.65)	
O-i-C ₃ H ₇	66-67/0.03	67	33.06 (33.72)	3.71 (3.65)	
NH ₂	74-75/0.05 ^a	87	26.56 (26.81)	2.11 (2.56)	4.44 (4.46)
NH(CH ₃)	70-71/0.03	74	29.61 (29.34)	3.27 (3.07)	4.12 (4.28)
N(CH ₃) ₂	83-84/0.04	66	31.45 (31.64)	3.81 (3.52)	4.46 (4.11)
SC ₂ H ₅	^b	51	30.43 (30.17)	3.19 (3.07)	

^a M.p. 33-35°. ^b B.p. uncertain; m.p. 33°.

dried by distillation from phosphorus(V) oxide. Diethyl ether was a commercial anhydrous grade solvent.

All reactions, filtrations and recrystallizations were carried out under an atmosphere of prepurified nitrogen. Elemental analyses were performed by Baron Consulting Co., Orange, Conn., and are listed with other pertinent data in Table 1. Proton magnetic resonance spectra were obtained with an Hitachi Perkin-Elmer Model R20A spectrometer. Infrared bands were determined with a Perkin-Elmer Model 621 instrument.

Reactions of $(R_2PCl)Mo(CO)_5$ ($R = CH_3$ or C_6H_5) with alcohols

A mixture of $(R_2PCl)Mo(CO)_5$ (1 g) and an alcohol (10 ml) was heated at reflux for 1–1.5 h. The resulting dark coloured solution was added to water (50 ml) and the product extracted with two 10 ml portions of hexane. The combined hexane extracts were dried over anhydrous magnesium sulfate, decolorized with 2 g of alumina and then filtered. Crude products were obtained by evaporating the hexane from the filtrate under a stream of nitrogen. Crystallization of the (alkyldiphenylphosphinite)pentacarbonylmolybdenum complexes was induced by scratching. These white solids were purified by recrystallization from hexane. The pale yellow or colorless (alkyl dimethylphosphinite)pentacarbonylmolybdenum complexes were purified by vacuum distillation in a micro distillation apparatus. A short-path distillation head (Kontes K-287100) was employed.

Reaction of $(R_2PCl)Mo(CO)_5$ ($R = CH_3$ or C_6H_5) with ethanethiol

An excess of ethanethiol (10 ml) was added to 1 g of $(R_2PCl)Mo(CO)_5$ dissolved in 5 ml of hexane. The solution was stirred well and 1 ml of triethylamine was added slowly. The resultant precipitate of triethylammonium chloride was removed by filtration. Excess ethanethiol and hexane were removed under aspirator vacuum to yield the crude products. Pure (ethyl diphenylthiophosphinite)pentacarbonylmolybdenum was obtained as a white crystalline solid upon recrystallization from hexane. Colorless (ethyl dimethylthiophosphinite)pentacarbonylmolybdenum was obtained by high vacuum distillation.

Preparation of triethylammonium (diphenylthiophosphito)pentacarbonylmolybdenum

Anhydrous hydrogen sulfide was bubbled through a solution of 1 g of $[(C_6H_5)_2PCl]Mo(CO)_5$ and 1 ml of triethylamine in 15 ml of diethyl ether for approximately 15 min. Removal of the solvent under aspirator vacuum left a solid mixture which was slurried with 25 ml of water to dissolve the triethylammonium chloride. The water insoluble product was collected by filtration, dissolved in hot hexane/acetone and treated with charcoal. The filtrate obtained after removal of the charcoal was concentrated in a stream of nitrogen until a good quantity of white crystalline product had precipitated.

Preparation of (dimethylthiophosphinous acid)pentacarbonylmolybdenum

Dry hydrogen sulfide was bubbled through a solution of 1 g of $[(CH_3)_2PCl]Mo(CO)_5$ in 25 ml of diethyl ether. Addition of 1 ml of triethylamine to the solution during passage of the hydrogen sulfide led to formation of a gummy precipitate. After acidification of the mixture with dilute hydrochloric acid, the ether layer was separated

and dried with anhydrous magnesium sulfate. Removal of the ether under vacuum left an oil which had spectral properties in accord with those predicted for the desired product. The compound was not successfully distilled or recrystallized. The acid did not form readily isolable quaternary salts with triethylamine or pyridine.

Reactions of $(R_2PCl)Mo(CO)_5$ ($R = CH_3$ or C_6H_5) with ammonia and amines

Anhydrous ammonia, dry methylamine or dimethylamine was bubbled through a solution of 1 g of $(R_2PCl)Mo(CO)_5$ in 25 ml of diethyl ether for about 15 min. The resulting mixture was filtered to remove the precipitated amine hydrochloride. Removal of the ether from the filtrate under aspirator vacuum left either a white solid ($R = C_6H_5$), which was recrystallized from ethanol, or a clear liquid ($R = CH_3$), which was vacuum distilled. [Anilino(diphenylphosphine)]pentacarbonylmolybdenum was prepared directly from $[(C_6H_5)_2PCl]Mo(CO)_5$ and aniline (1/3 mole ratio) in diethyl ether. The white solid product was isolated and purified according to the procedure used for the other solid complexes.

(Trimethylsilyl diphenylphosphinite)pentacarbonylmolybdenum

A mixture of 1.4 g (2.6 mmoles) of $(C_2H_5)_3NH [(C_6H_5)_2PO]Mo(CO)_5^{10}$ and 0.9 g (8.0 mmoles) of trimethylchlorosilane in 15 ml of anhydrous ether was allowed to stir at room temperature for 0.5 h. Filtration of the mixture to remove precipitated triethylammonium chloride yielded a yellow filtrate. The residue obtained upon evaporation of the filtrate was recrystallized from hexane to give the product as a waxy, white solid, m.p. 69–70°. The minimum yield is 65%. The complex was identified by its infrared and 1H NMR spectral properties.

RESULTS AND DISCUSSION

Metal complexes of organophosphorus ligands are usually prepared by the direct reaction of a tertiary phosphine, phosphite ester or other phosphorus compound with a precursor metal compound. Obviously, such procedures depend upon the availability of the free phosphorus compound. However, as we have pointed out earlier, complexes of diphosphoxanes, alkyl phosphinites and dimethyl phosphinous acid may not be obtained directly owing to the thermodynamic instability of the free phosphorus ligands. Complexes of these ligands may be prepared indirectly by exploiting the chemical reactivity of the P–Cl bond in coordinated halo-phosphine ligands¹⁰. Listed in Table 1 are the products of further reactions of two coordinated organophosphorus ligands which we have now carried out. In none of the reactions cited was any evidence noted for cleavage of the P–Mo bond. The reactions of the complexes with hydrogen sulfide and ethanethiol proceeded best in the presence of triethylamine.

Several of the new complexes listed in Table 1 contain organophosphorus ligands which either have not been reported to exist in the free state or are known to be thermodynamically unstable with respect to rearrangement to a four-covalent phosphorus(V) compound. Specific attention may be drawn to $(CH_3)_2POCH_3$, which is reported to rearrange readily to $(CH_3)_3PO^{11}$, and the hitherto unknown $(CH_3)_2PSH$, $(CH_3)_2PNH_2$ and $(CH_3)_2PNH(CH_3)$.

The reactions employed here have several attractive features in addition to

their importance in leading to complexes of thermodynamically unstable ligands. Firstly, the need for preparation of n different complexes does not demand the availability of n different phosphorus ligands. A single complex such as $[\text{Cl}(\text{CH}_3)_2\text{P}(\text{CO})_5\text{Mo}]$ can serve as a starting material for an essentially limitless number of complexes. Secondly, uncomplexed phosphines, especially low molecular weight alkyl derivatives, are extremely toxic. The fewer of such materials which need to be handled in the laboratory the better. In the present work the only free phosphines employed were $\text{Cl}(\text{CH}_3)_2\text{P}$ and $\text{Cl}(\text{C}_6\text{H}_5)_2\text{P}$. Thirdly, the processes developed here are relatively inexpensive in terms of the quantities of reagents required to obtain sufficient amounts of products for physical measurement types of investigations. Lastly, in comparison to thermal substitution and photochemical procedures which can often lead to more highly substituted products as well as thermal or photochemical decomposition products, the reactions of coordinated ligands cited here proceed without any significant side reactions.

In addition to pointing out the advantages of the synthetic procedures presented here, we must also note some of the limitations in reactions of coordinated halo-phosphine ligands. In particular, the $(\text{ClR}_2\text{P})(\text{CO})_5\text{Mo}$ compounds employed here show little reactivity toward Grignard reagents under classical reaction conditions. In several attempts with a variety of Grignard reagents, only CH_3MgI gave the desired product, $[(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{P}](\text{CO})_5\text{Mo}$, and this only in 20% yield. Attempts to form the diphenylphosphine and diphenylfluorophosphine complexes by reacting the diphenylchlorophosphine complex with lithium aluminum hydride and antimony trifluoride, respectively, proved to be unsuccessful as the starting complex was recovered in good yield in each instance. To further illustrate the relatively low reactivity of the complexed ligands, we examined the relative rates of cleavage of the P-Cl bond in $\text{Cl}(\text{C}_6\text{H}_5)_2\text{P}$ and in the complexes $(\text{ClR}_2\text{P})\text{Mo}(\text{CO})_5$. Equimolar amounts of the phosphine complex or phosphine and methanol were dissolved in benzene and the methanolysis followed by ^1H NMR. The relative rates of methanolysis followed the order: $\text{Cl}(\text{C}_6\text{H}_5)_2\text{P} > [\text{Cl}(\text{C}_6\text{H}_5)_2\text{P}](\text{CO})_5\text{Mo} > [\text{Cl}(\text{CH}_3)_2\text{P}](\text{CO})_5\text{Mo}$. In general, $\text{PR}_2(\text{O})\text{Cl}$ and ClR_2P react with alcohols at comparable rates. Seemingly then, differences in reactivity of the free ligand and complexed ligand are not related directly to a change in coordination number of phosphorus from three to four. Possibly, the significant change in rate upon complexation may reflect a major difference between the P-O and P-Mo bonds. Removal of electron density on molybdenum by phosphorus through $d_\pi-d_\pi$ bonding should lower the positive character of phosphorus and thereby lower its susceptibility to nucleophilic attack. Alternatively, one might say that partial population of the $3d$ levels of phosphorus by way of $d_\pi-d_\pi$ bonding will make the $3d$ levels less available for forming a five coordinate intermediate in a presumed $\text{S}_\text{N}2\text{-P}$ rate determining step. Of course, steric crowding about the phosphorus atom by the large pentacarbonylmolybdenum moiety may also play an important role in controlling the rate of esterification. A precise analysis of the mechanism of the reactions of the coordinated ligands will have to be based upon planned kinetic studies.

Characterization of the complexes is based upon the positions and intensities of the $\bar{\nu}(\text{CO})$ bands listed in Table 2, the simplified force constants calculated therefrom¹², and the ^1H NMR signals of the complexed ligands shown in Table 3.

While there is considerable temptation to explain all of the differences in the

simplified force constants in terms of the relative electron withdrawing capabilities of the ligands, the actual spread in calculated values is too small to permit extensive speculation. However, a general order of apparent electron withdrawing ability for the R_2PX ligands is: $X=Cl > OR' > NR'_2 \geq CH_3$ or C_6H_5 . This order is based mainly on the trends in k_1 which is more sensitive to the phosphorus donor ligand than is k_2 . Although the overall ranges of k_1 and k_2 are quite small, the small differences for the alkoxy and trimethylsiloxy derivatives are surprising. Much evidence has been accumulated which supports $O(p_\pi) \rightarrow Si(d_\pi)$ bonding in organosilicon compounds. A similar type of delocalization from oxygen to silicon in $[(C_6H_5)_2POSi(CH_3)_3](CO)_5Mo$ would be expected to diminish $O(p_\pi) \rightarrow P(d_\pi)$ bonding in the silicon derivative and thereby enhance its π -acceptor capability as a ligand relative to the alkoxy derivatives. Conceivably, $O(p_\pi) \rightarrow P(d_\pi)$ bonding is minimal, if important at all, owing to the unavailability of the phosphorus $3d$ levels which may be used more effectively in π -bonding to the metal. A similar proposal for the bonding in $[(CH_3)P(OCH_3)_2](CO)_5Mo$ was made by Jones and Coskran¹³. A second notable observation

TABLE 2

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

$X(R=C_6H_5)$	Freq. (cm^{-1})				Force constants ($mdyn/\text{Å}$)		
	$A_1(1)$	B_1	$A_1(2)$	E	k_1	k_2	k_i
Cl	2079	1989	1965	1957	15.81	16.01	0.30
OCH ₃	2074	1991	1961	1951	15.75	15.97	0.30
OC ₂ H ₅	2074	1991	1960	1952	15.73	15.98	0.30
O- <i>n</i> -C ₃ H ₇	2074	1990	1959	1950	15.71	15.96	0.30
O- <i>i</i> -C ₃ H ₇	2073	1990	1958	1949	15.70	15.94	0.30
OSi(CH ₃) ₃	2073	1987	1956	1947	15.67	15.92	0.30
NH ₂	2073	1987	1955	1947	15.65	15.92	0.30
NH(CH ₃)	2073	1988	1954	1946	15.64	15.91	0.31
N(CH ₃) ₂	2073	1988	1950	1941	15.59	15.85	0.32
NH(C ₆ H ₅)	2074	1988	1951	1946	15.59	15.91	0.31
SC ₂ H ₅	2075	1990	1958	1950	15.70	15.96	0.30
S ⁻ (C ₂ H ₅) ₃ NH ⁺	2066			1934	15.32	15.74	0.32
CH ₃	2072	1985	1952	1945	15.61	15.89	0.31
$X(R=CH_3)$							
Cl	2080	1989	1971	1956	15.92	16.05	0.30
OCH ₃	2077	1990	1962	1948	15.78	15.94	0.31
OC ₂ H ₅	2077	1988	1962	1949	15.78	15.96	0.31
O- <i>n</i> -C ₃ H ₇	2074	1990	1962	1949	15.77	15.94	0.30
O- <i>i</i> -C ₃ H ₇	2074	1988	1957	1942	15.71	15.86	0.32
NH ₂	2073	1986	1957	1946	15.69	15.90	0.31
NH(CH ₃)	2073	1986	1957	1948	15.68	15.93	0.30
N(CH ₃) ₂	2074	1990	1952	1943	15.62	15.88	0.32
SC ₂ H ₅	2074	1987		1950	15.56	15.96	0.30
SH	2074	1988		1945	15.50	15.91	0.31
CH ₃ ^c	2071		1952	1943	15.61	15.87	0.31

^a Hexane employed as solvent. B_1 modes are weak and placed with an uncertainty of several wave numbers. The $A_1(2)$ and E bands overlap to varying extents and the band maxima were determined by graphical resolution. ^b Ref. 12. ^c Ref. 18.

TABLE 3

¹H NMR DATA FOR (XR₂P)(CO)₅MO COMPLEXES^a

X	$\tau\text{CH}_3\text{-P}^b$ (ppm)	$ ^2J(\text{HP}) $ (Hz)	$\tau\text{CH}_n\text{-E}^b$ (E=O,N,S)	$ ^3J(\text{HP}) $ (Hz)	Other ^b
(R=CH ₃)					
OCH ₃	8.23d	5.0	6.49d	13.6	
OC ₂ H ₅	8.28d	5.0	6.28 ^c	7.9 ^c	CH ₃ C: τ 8.73t [³ J(HH)=7.0 Hz]
O-n-C ₃ H ₇	8.25d	4.9	6.40 ^d	7.7 ^d	CH ₃ : τ 9.07t CCH ₂ C: τ 8.35m
O-i-C ₃ H ₇	8.32d	4.7	5.87 ^e	12.4 ^e	CH ₃ C: τ 8.77d [³ J(HH)=5.9 Hz] NH ₂ : τ 8.0br
NH ₂	8.38d	6.4			
NH(CH ₃)	8.43d	5.7	7.41d	10.8	
N(CH ₃) ₂	8.42d	5.4	7.45d	12.3	
SC ₂ H ₅	8.18d	4.3	7.26 ^c	7.8 ^c	CH ₃ C: τ 8.65t [³ J(HH)=7.5 Hz] SH: τ 7.84
SH	8.08d	4.8			
(R=C ₆ H ₅)					
OCH ₃			6.56d	13.2	
OC ₂ H ₅			6.36 ^c	6.5 ^c	CH ₃ C: τ 8.75t [³ J(HH)=6.9 Hz]
O-n-C ₃ H ₇			6.50 ^d	6.4 ^d	CH ₃ C: τ 9.09t CCH ₂ C: τ 8.40m
O-i-C ₃ H ₇			5.56 ^e	10.8 ^e	CH ₃ C: τ 8.92d [³ J(HH)=6.2 Hz] CH ₃ Si: τ 9.95s NH ₂ : τ 7.54br
OSi(CH ₃)					
NH ₂					
NH(CH ₃)			7.68d	10.1	
N(CH ₃) ₂			7.40d	11.7	
SC ₂ H ₅			7.74 ^c	6.4 ^c	CH ₃ C: τ 8.99 [³ J(HH)=7.5 Hz]

^a CS₂ solutions. τ values relative to internal TMS at τ 10 ppm. ^b Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^c Apparent quintet; coupling constant measured from doublet obtained upon spin decoupling from the CH₃C group. ^d Apparent quartet; coupling constant measured from doublet obtained upon spin decoupling from the CCH₂ protons. ^e Apparent septet; coupling constant measured from doublet obtained upon spin decoupling from the CH₃C groups.

is the fact the OR' and SC₂H₅ groups have approximately equal effects on the apparent π -acceptor abilities of their respective ligands. Closely related are the observations on the two anionic complexes [(C₆H₅)₂PY](CO)₅Mo⁻, where Y is S or O¹⁰. Here again, no expected differences between the π -bonding capabilities of O and S are able to manifest themselves, perhaps for the same reason cited above.

The various ¹H NMR chemical shift values and $|^2J(\text{P-H})|$ coupling constants given in Table 3 support the assigned structures. Although $|^2J(\text{P-H})|$ for the CH₃-P group of tertiary phosphines is positive¹⁴, the sign apparently reverses in all recorded instances when the three-covalent phosphorus is converted to a four-covalent species as in an oxide, sulfide, or quaternary salt¹⁵⁻¹⁷. Presumably, the sign of $|^2J(\text{P-H})|$ for the methylphosphine ligands in the molybdenum complexes is also negative. No acceptable relationships can be cited between τ and the $|^2J(\text{P-H})|$ values or between

either of these properties and various classical sets of resonance and inductive parameters of substituents. We have noted a smooth relationship between $|^2J(P-H)|$ values for the free and complexed ligands where both values are available. This relationship will be discussed in more detail when additional pertinent data has become available.

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