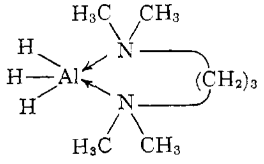
The soluble product fraction is dimeric in benzene (observed degree of association 1.88). It melts at 120° with decomposition as evidenced by the evolution of hydrogen and the formation of finely divided aluminum. Davidson and Wartik report that the TMED alane adduct is dimeric in the vapor phase and prefer a chelate structure (I) in which the aluminum atom is hexacoordinate. However, the TMED alane adduct exhibits an Al–H stretching band[3] at 1710 cm.$^{-1}$, *i.e.*, identical with the Al–H frequency in both the polymeric and dimeric forms of TMPD alane as well as in $AlH_3 \cdot 2N(CH_3)_3$.[3] Previous papers[4,6–8] have correlated Al–H frequency with the coordination number of aluminum in alane–Lewis base adducts. Such complexes with pentacoordinated aluminum atoms absorb between 1690 and 1724 cm.$^{-1}$. We suggest, therefore, that the alternative dimeric bridge structure proposed by Davidson and Wartik (structure II) should be preferred to structure I.

The sublimate obtained from both the polymeric and dimeric forms of TMPD alane by heating *in vacuo* above 90° is a transparent crystalline solid which melts sharply at 135° without decomposition. We believe this to be the monomeric form of TMPD alane (structure IV). In benzene, however, a 0.3 wt. % solution of the sublimate exhibited a degree of association of 1.44. The Al–H absorption observed for the sublimate also occurs at 1710 cm.$^{-1}$, which is evidence of pentacoordinate aluminum as in structure IV.



IV

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Raymond N. Storey in obtaining infared spectra of TMPD alane samples.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF CANTERBURY,
CHRISTCHURCH, NEW ZEALAND

Tertiary Phosphine Oxide and Arsine Oxide Metal Carbonyl Complexes

BY L. CHANDRASEGARAN AND G. A. RODLEY

Received February 18, 1965

The reactions of iron pentacarbonyl, cobalt tetracarbonyl, and vanadium hexacarbonyl with triphenylphosphine oxide and triphenylarsine oxide have been found to give ionic products (*e.g.*, $[Fe((C_6H_5)_3PO)_2][Fe_2(CO)_8]$ and $[V((C_6H_5)_3AsO)_4][V(CO)_6]_2)$.[1–4] Apparently direct substitution of carbon monoxide does not occur for these carbonyls because of the ease of valence disproportionation. A phosphine oxide carbonyl complex of composition $Mo((C_6H_5)_3PO)(CO)_3$ has been isolated from the reaction of the phosphine oxide with the hydride, $[Mo_2(CO)_6(OH)_3H_3]$.[5]

We have found that direct reaction of molybdenum hexacarbonyl with the oxides yields products of the compositions $Mo((C_6H_5)_3PO)_2(CO)_4$, $Mo((C_6H_5)_3AsO)_2(CO)_4$, and $Mo((C_6H_5)_3PO)_3(CO)_3$. The reaction of tungsten hexacarbonyl with triphenylphosphine oxide in the presence of diglyme gives $W((C_6H_5)_3PO)_3(CO)_3$. X-Ray, infrared, and conductivity studies indicate that these products are substituted carbonyl complexes and not ionic compounds. The molybdenum compounds (both tricarbonyl and tetracarbonyl) were more readily prepared from reactions of the oxides with the intermediates $Mo(C_7H_8)(CO)_3$ and $Mo(CH_3CN)_3(CO)_3$, although the precise conditions for obtaining one type of substituted phosphine oxide complex in preference to the other were not determined.

A single crystal X-ray study of $Mo((C_6H_5)_3PO)_2(CO)_4$ has been made and the unit cell found to be monoclinic with a = 16.79 Å., b = 12.38 Å., c = 17.13 Å., β = 105°. From the cell volume and the density (ρ = 1.44 g./cc.) the molecular weight was calculated as 746 for four molecules per unit cell. The theoretical value for $Mo((C_6H_5)_3PO)_2(CO)_4$ is 764. The possible ionic formulation of $[Mo((C_6H_5)_3PO)_4][Mo(CO)_5]$ for this compound is inconsistent with the space group of the crystal (C2/c). Moreover, the complex is a nonelectrolyte in acetone. X-Ray powder photographs show that the arsine oxide complex $Mo((C_6H_5)_3AsO)_2(CO)_4$ is isomorphous with $Mo((C_6H_5)_3PO)_2(CO)_4$. The complexes $Mo((C_6H_5)_3PO)_3(CO)_3$ and $W((C_6H_5)_3PO)_3(CO)_3$ are also isomorphous.

The infrared data for the carbonyl complexes are given in Table I. For the trisubstituted compounds two main ν(C–O) bands are observed and they can be assigned as the A_1 and E modes corresponding to the *cis* configuration. The splitting of the lower energy bands is presumably associated with a lowering of the molecular symmetry in the solid state. For the disubstituted compounds the bands can be assigned as the $2A_1$, B_1, and B_2 modes of a *cis* compound with C_{2v} symmetry. This is consistent with the point symmetry of one of the 4-fold special positions of the space group (C2/c).

Some idea of the bonding properties of the oxide ligands can be obtained from an examination of the carbonyl frequencies and also the ν(P–O) and ν(As–O) values. The ν(C–O) values for the phosphine oxide and arsine oxide complexes are generally low by com-

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TABLE I

INFRARED DATA[a]

ν(C–O), cm.$^{-1}$		ν(M–O) (M = P or As), cm.$^{-1}$	
cis-$Mo((C_6H_5)_3PO)_2(CO)_4$			
2006 w, 1878 vs, 1845 s, 1797 vs		1156 m 1148 s	1152
cis-$Mo((C_6H_5)_3AsO)_2(CO)_4$			
2003 w, 1883 vs, 1850 s, 1792 vs		880 m 868 s	874
cis-$Mo((C_6H_5)_3PO)_3(CO)_3$			
1898 m, 1757 s 1733 s	1745	1206 sh 1192 s 1185 sh 1171 s	1188
cis-$W((C_6H_5)_3PO)_3(CO)_3$			
1883 m, 1745 s 1721 s	1733	1183 s 1161 m	1172

[a] ν(P–O) for $(C_6H_5)_3PO$ is 1190 cm.$^{-1}$, ν(As–O) for $(C_6H_5)_3AsO$ is 880 cm.$^{-1}$. The spectra were recorded as Nujol mulls.

parison with values for other complexes of the same compositions.[6–8] This indicates that the phosphine and arsine oxides have relatively low π accepting capacities. Two ν(P–O) and ν(As–O) absorptions are found for the complexes $Mo((C_6H_5)_3PO)_2(CO)_4$ and $Mo((C_6H_5)_3AsO)_2(CO)_4$, as expected for a *cis* configuration. In the case of the phosphine oxide complexes of molybdenum the average ν(P–O) frequency increases from 1152 cm.$^{-1}$ in $Mo((C_6H_5)_3PO)_2(CO)_4$ to 1188 cm.$^{-1}$ in $Mo((C_6H_5)_3PO)_3(CO)_3$. This latter value is high by comparison with other transition metal phosphine oxide complexes[9] and is probably associated with weak σ bonding from the P–O group to the zerovalent molybdenum.

Experimental

Cycloheptatrienemolybdenum tricarbonyl and tricarbonyltris(methyl cyanide)molybdenum were prepared by methods previously reported in the literature.[10,11] Triphenylarsine oxide was prepared by oxidation of Eastman triphenylarsine with hydrogen peroxide. Triphenylphosphine oxide, molybdenum hexacarbonyl, and tungsten hexacarbonyl were obtained from L. Light and Co. Ltd.

Tricarbonyltris(triphenylphosphine oxide)molybdenum.—A hot saturated solution of 0.58 g. of $(C_6H_5)_3PO$ in benzene was added to a cold saturated solution of 0.19 g. of cycloheptatrienemolybdenum tricarbonyl in benzene and refluxed under nitrogen for 4 hr. A yellow product separated on the sides of the flask. The impure product was recrystallized by heating with benzene (15 ml.) to 110° for 6 hr. in an evacuated sealed tube.

Anal. Calcd. for $Mo((C_6H_5)_3PO)_3(CO)_3$: C, 67.50; H, 4.44; Mo, 9.46. Found: C, 67.02; H, 4.71; Mo, 9.96.

This complex was also isolated from the direct reaction of $(C_6H_5)_3PO$ with $Mo(CO)_6$ (3:1) in a benzene–petroleum ether mixture. The complex is stable in air for several days.

Tetracarbonylbis(triphenylphosphine oxide)molybdenum.—A hot saturated solution of 3.2 g. of $(C_6H_5)_3PO$ in diethylene glycol dimethyl ether (diglyme) was added to a hot saturated solution of 1 g. of $Mo(CO)_6$ in benzene. The solution was refluxed under nitrogen for 1.5 hr. A yellow-brown product separated from the solution. This product was recrystallized from benzene (15 ml.) in a sealed tube heated to 120°.

Anal. Calcd. for $Mo((C_6H_5)_3PO)_2(CO)_4$: C, 62.90; H, 3.93; Mo, 12.59. Found: C, 62.82; H, 4.08; Mo, 12.49.

This compound was also isolated from the reaction of tricarbonyltris(methyl cyanide)molybdenum with $(C_6H_5)_3PO$ in benzene under nitrogen and the reaction of $(C_6H_5)_3PO$ with an excess of $Mo(CO)_6$ in a benzene–petroleum ether mixture. The complex is stable in air for several days.

Tricarbonyltris(triphenylphosphine oxide)tungsten.—A hot saturated solution of 2.38 g. of $(C_6H_5)_3PO$ in diglyme was added to a hot saturated solution of 1 g. of $W(CO)_6$ in benzene and the solution refluxed under nitrogen for 5 hr. A small amount of an orange compound separated on the sides of the reaction flask. Insufficient material was obtained for analyses, but an X-ray powder photograph of the compound showed that it was isomorphous with tricarbonyltris(triphenylphosphine oxide)-molybdenum. The complex is less stable in air than the corresponding molybdenum compound.

Tetracarbonylbis(triphenylarsine oxide)molybdenum.—A mixture of 0.96 g. of $(C_6H_5)_3AsO$ and 0.3 g. of tricarbonyltris(methyl cyanide)molybdenum was refluxed in benzene (40 ml.) under nitrogen for about 10 min. A small amount of an orange solid separated. The X-ray powder photograph of this solid showed that it was isomorphous with the corresponding $(C_6H_5)_3PO$ complex, tetracarbonylbis(triphenylphosphine oxide)molybdenum. The compound is less stable in air than the phosphine oxide complex.

Microanalyses for carbon and hydrogen were carried out by Dr. A. D. Campbell at the Microanalytical Laboratory, University of Otago. Molybdenum was determined by fusing 0.1 g. of compound with 0.2 g. of NaOH, 0.5 g. of Na_2CO_3, and 0.25 g. of Na_2O_2 in a nickel crucible, extracting the residue with water, and precipitating the molybdenum as the oxime with 8-hydroxyquinoline.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 221 spectrometer, except that in the case of $Mo((C_6H_5)_3AsO)_2(CO)_4$ the ν(C–O) values were determined on a Perkin-Elmer Infracord.

The X-ray powder photographs were recorded with a Philips Debye–Scherrer powder camera (diameter 11.483 cm.) and the cell dimensions and space group for $Mo((C_6H_5)_3PO)_2(CO)_4$ were determined from oscillation, Weissenberg, and precession photographs. The density was determined by flotation.

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CONTRIBUTION NO. 1792 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA,
AND FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO

Raman Studies of Hydrido- and Deuteriorhenium Tetracarbonyl Trimer[1]

BY J. M. SMITH,[2] W. FELLMANN,[2] AND L. H. JONES[3]

Received March 17, 1965

In a previous study the trimer of rhenium tetracarbonyl was found to be diamagnetic, suggesting the

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[1] This work was supported by the Atomic Energy Commission and by Grant GP 4175, National Science Foundation, which was used for partial support for two of the authors (J. M. S. and W. F.) in connection with their work in collaboration with Prof. H. D. Kaesz, U.C.L.A.

[2] Department of Chemistry, U.C.L.A.

[3] Los Alamos Scientific Laboratory.