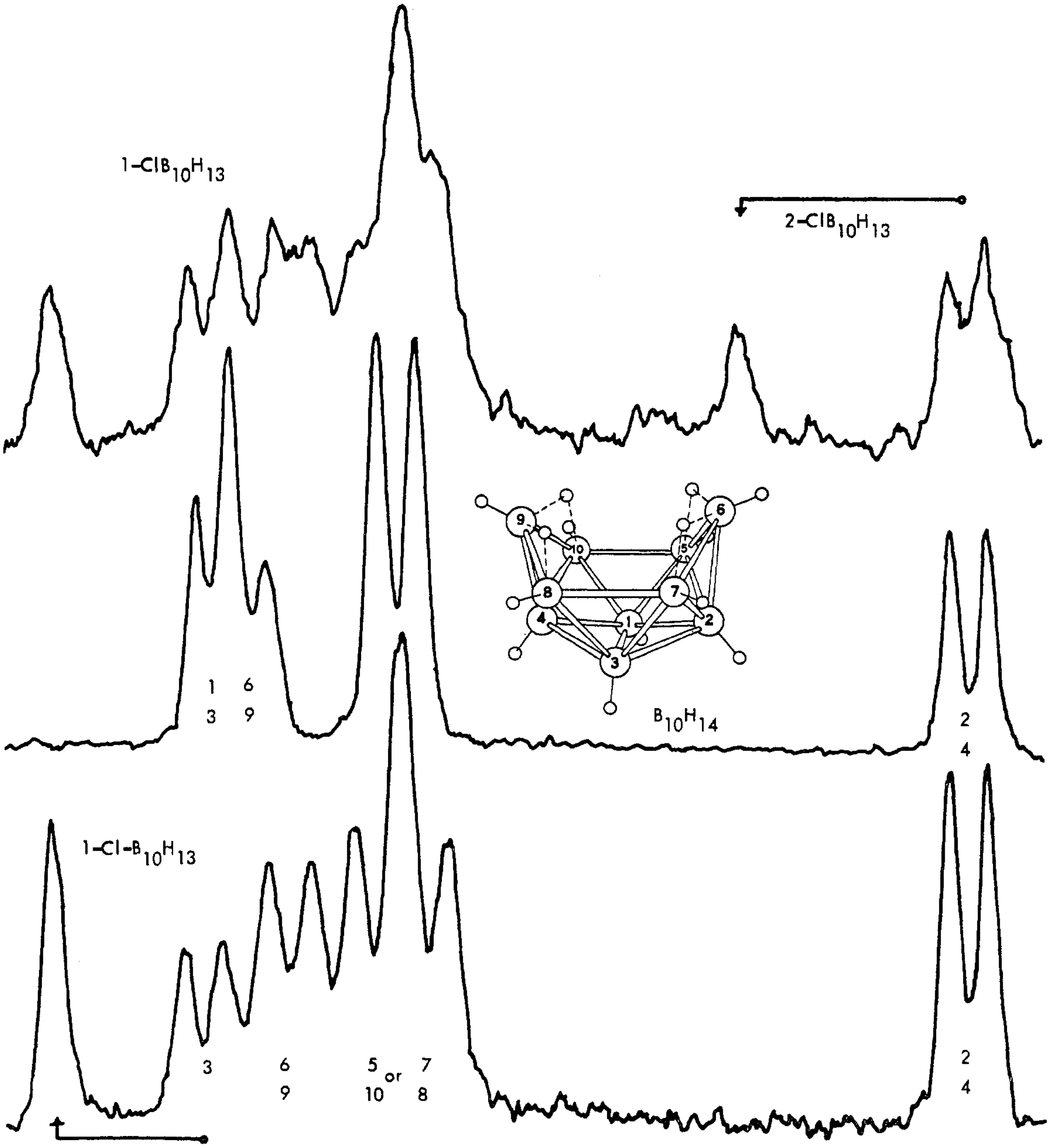

Figure 1.—B^{11} n.m.r. spectra (64.2 Mc.) of a 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$ mixture, $B_{10}H_{14}$, and pure 1-$ClB_{10}H_{13}$ in CS_2 solution.

of 1-$ClB_{10}H_{13}$ is detected. Thus, the presumed $ClB_{10}H_{13}$ isomer (m.p. 59°) is in reality a mixture of two isomers.

It had been demonstrated that 2-$IB_{10}H_{13}$ melts higher (116°,[2] 117° [14]) than 1-$IB_{10}H_{13}$ (72°,[2] 98° [14]). 1-$ClB_{10}H_{13}$ melts at 73°, pure 2-$ClB_{10}H_{13}$ would be expected to have a higher melting point; however, mixtures rich in 1-$ClB_{10}H_{13}$ may be expected to have lower melting points, thus accounting for the (59°) melting point of the 2-$ClB_{10}H_{13}$-containing mixture.

Acknowledgment.—This research was supported by the Office of Naval Research. We also express our appreciation to Drs. Manny Hillman and D. J. Mangold, who furnished the samples of $ClB_{10}H_{13}$, and to Prof. Riley Schaeffer, who revealed[13] to us the comlete B^{11} n.m.r. assignment of $B_{10}H_{14}$.

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[14] M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960).

CONTRIBUTION FROM THIOKOL CHEMICAL CORPORATION,
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The Chemistry of Alane. V.[1] N,N,N′,N′-Tetramethylpropanediamine Alane[2]

BY ARCHIE R. YOUNG, II, AND ROBERT EHRLICH

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Davidson and Wartik[3] have reported the synthesis of a dimeric, 1:1 complex of N,N,N′,N′-tetramethyl-

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[1] Paper IV: A. R. Young, II, and R. Ehrlich, *J. Am. Chem. Soc.*, **86**, 5359 (1964).

[2] This research was supported by the Advanced Research Projects Agency under ARPA Order No. 24-60 and by the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, Calif., under Contract AF33(616)-5935 (1960).

[3] J. M. Davidson and T. Wartik, *J. Am. Chem. Soc.*, **82**, 5506 (1960).

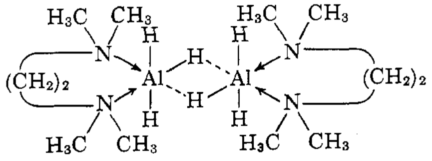
TABLE I

ANALYSES OF TMPD ALANE

	Calcd. for $AlH_3 \cdot C_7H_{18}N_2$	Found		
		Precipitate	Solution fraction	Sublimate
Active H, %	1.89	1.99	2.01	2.03
Al, %	16.84	15.60	17.78	17.03
TMPD, %	81.27	82.44	80.23	79.60
Mol. wt.[a]	160	1725 (concn. = 0.6 wt. %)	301 (concn. = 0.6 wt. %)	231 (concn. = 0.3 wt. %)
H:Al:TMPD	3:1:1	3.41:1:1.09	3.03:1:0.94	3.19:1:0.97

[a] Determined by measuring freezing points of benzene solutions.

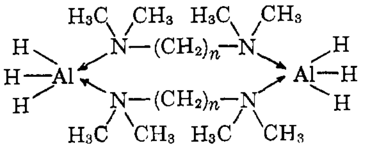
ethylenediamine (TMED) with alane which has much greater thermal stability than trialkylamine complexes of alane. These authors suggested that the superior thermal stability of TMED alane is a consequence of a chelate structure (I) in which the aluminum atoms are hexacoordinate. During the



I

course of a study of the thermal stabilities of alane–Lewis base adducts we have synthesized a 1:1 adduct of N,N,N′,N′-tetramethylpropanediamine (TMPD) with alane. Two forms of the TMPD alane adduct were readily isolable under ambient conditions, namely, a benzene-soluble dimer, analogous to the aforementioned TMED adduct, and a sparingly soluble form which has a molecular weight of 1725. Both forms upon heating above 90° *in vacuo* yield a sublimate which melts sharply at 135°. The molecular weight of the sublimate indicates a degree of association of 1.44 in benzene.

On the basis of the observed Al–H frequencies in the infrared spectra of diamine–alane adducts,[3] we believe that structure I is probably not correct for the dimers. The alternative bridge structure (II) (also proposed by Davidson and Wartik) in which the aluminum atoms are pentacoordinate is more consistent with available data on diamine–alane adducts.



II

Experimental

During the preparation and subsequent handling of TMPD alane care was taken to exclude air and moisture from the material. Solvents were dried over $LiAlH_4$, distilled, and stored over $LiAlH_4$. Analyses were obtained by quantitative hydrolysis followed by standard wet chemical methods for aluminum and tertiary amine.

Quantitative Hydrolysis.—The sample to be hydrolyzed was attached to a Toepler pump system, cooled to −196°, and evacuated. Then approximately 20 ml. of water was distilled onto the sample and the mixture was allowed to warm to room temperature. When hydrolysis was complete the noncondensable gases were pumped through two −196° traps into a calibrated collection system. A sample of the gas was submitted for mass spectroscopic identification and the quantity of hydrogen was calculated by means of the ideal gas equation. The hydrolysis residue was submitted for aluminum analysis and determination of amine content by acid–base titration.

Preparation of TMPD Alane.—To a solution of 0.12 mole of $AlH_3 \cdot N(C_2H_5)_3$ in 200 ml. of benzene[4] was added 0.12 mole of TMPD dropwise with stirring at room temperature. Precipitation occurred immediately on addition of the amine. The mixture was stirred at room temperature overnight and the white, crystalline precipitate was filtered and dried *in vacuo* at room temperature. The yield was 8.7 g. of solid which did not melt up to 200° and which was only slightly soluble in benzene. Cryoscopic molecular weight determination in benzene gave a value of 1725 for a 0.6 wt. % solution.

The clear filtrate was freeze-dried to obtain 4.6 g. of white solid, melting at 120° with decomposition and having a molecular weight of 301 by freezing point depression measurement of a 0.6 wt. % solution in benzene.

Both the polymer and the dimer (insoluble and soluble fractions, respectively) sublimed readily above 90° at pressures of less than 0.1 mm., producing a transparent crystalline sublimate, m.p. 135°.

Results of analysis of the three product fractions are presented in Table I.

Infrared spectra of the polymer, the dimer, and the sublimate were obtained at 2–15 μ as KBr pellets. The spectra were identical, showing an Al–H absorption at 1710 cm.⁻¹.

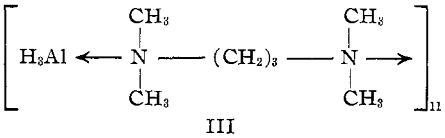
Discussion

The two product fractions obtained in the reaction of TMPD with triethylamine alane (eq. 1), as well as the

$$\mathrm{TMPD} + H_3Al \cdot N(C_2H_5)_3 \longrightarrow H_3Al \cdot \mathrm{TMPD} + (C_2H_5)_3N \quad (1)$$

sublimate, are 1:1 adducts. They have identical infrared spectra, which exhibit an Al–H stretching band at 1710 cm.⁻¹. However, they have distinctly different physical properties.

The sparingly soluble fraction (about 65% of the total yield of solid products) exhibits no melting point upon heating to above 200°. Its molecular weight in benzene (Table I) is 1725. This fraction is clearly not a dimeric chelate analogous to the TMED alane adduct reported by Davidson and Wartik,[3] but is most probably a linear coordination polymer[5] having approximately eleven repeat units (structure III).



$$\left[H_3Al \longleftarrow \underset{CH_3}{\overset{CH_3}{N}} \text{---} (CH_2)_3 \text{---} \underset{CH_3}{\overset{CH_3}{N}} \longrightarrow \right]_{11}$$

III

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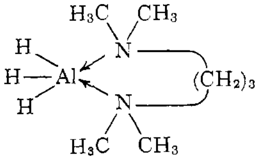
[4] R. Ehrlich, *et al.*, *Inorg. Chem.*, **2**, 650 (1963).

[5] N. R. Fetter and D. W. Moore, *Can. J. Chem.*, **42**, 885 (1964). These authors report the synthesis of a 1:1 TMPD–alane complex by amine exchange using TMPD as a solvent. No molecular weight was reported for the product.

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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[6] W. Zeil, R. Dautel, and W. Honsburg, *Z. Elektrochem.*, **60**, 1131 (1956).

[7] E. Hoffman and G. Schomburg, *ibid.*, **61**, 1100, 1101 (1957).

[8] R. Dautel and W. Zeil, *ibid.*, **64**, 1234 (1960).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Tertiary Phosphine Oxide and Arsine Oxide Metal Carbonyl Complexes

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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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[1] W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2075 (1959).

[2] G. Franz, Dissertation, Technischen Hoschschule München, 1959.

[3] W. Hieber, J. Peterhans, and E. Winter, *Chem. Ber.*, **94**, 2572 (1961).

[4] W. Hieber, E. Winter, and E. Schubert, *ibid.*, **95**, 3070 (1962).

[5] W. Hieber, K. Englert, and K. Rieger, *Z. anorg. allgem. Chem.*, **300**, 295 (1959).