

Preliminary communication

THE MOLECULAR STRUCTURE OF A TRIMERIC ALUMINIUM PHOSPHAMIDE, $[(CH_3)_2AlP(CH_3)_2]_3$, DETERMINED BY GAS ELECTRON DIFFRACTION

ARNE HAALAND, JENS HOUGEN, HANS V. VOLDEN,

Department of Chemistry, University of Oslo, P.b. 1033, Blindern 0315 Oslo 3 (Norway)

GERHARD HANIKA and HANS H. KARSCH

Anorganisch-chemisches Institut, Technische Universität München, D 8046 Garching (G.F.R.)

(Received November 20th, 1986)

In an article, "The Polymerization of Some Derivatives of Trimethylaluminium", published in 1942 Davidson and Brown described the syntheses and characterization of a series of organoaluminium compounds [1]. Over the years we have determined the molecular structure of several of them by gas electron diffraction, viz. Me_3AlNMe_3 [2], Me_3AlPMe_3 [3], Me_3AlOMe_2 [4] and Me_3AlSMe_2 [5], $(Me_2AlOMe)_3$ [6], $(Me_2AlSMe)_2$ [7] and $(Me_2AlCl)_2$ [8] *. In this note, which we dedicate to Davidson and Brown, we report the structure of the eighth compound, $(Me_2AlPMe_2)_3$.

Within a series of trimeric, dimeric and monomeric diorganoaluminium phosphides, prepared by the reaction of the appropriate diorganoaluminium chloride with a lithium diorgano phosphide [11], we have prepared $[Me_2AlPMe_2]_3$ as colorless crystals (m.p. 145°C). The 1H NMR spectrum shows two quartets of equal intensity at +0.61 and -0.89 ppm ($(X_6A)(A'X'_6)_2$ spin system).

The gas electron diffraction pattern was recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of about 170°C. Exposures were made with nozzle-to-plate distances of 50 and 25 cm. Six plates from the first set and five from the second were photometered and the data processed by standard procedures. The intensity data thus obtained ranged from $s = 20$ to 250 nm^{-1} .

Structure refinements were based on a chair model of C_{3v} symmetry as indicated in Fig. 1. In addition it was assumed that: (i) Me_2AlP_2 and Me_2PA_2 fragments have C_{2v} symmetry. (ii) Me groups have C_{3v} with symmetry axes coinciding with the C–Al or C–P bonds. (Al)C–H and (P)C–H bond lengths were assumed equal. The valence angle PCH could not be refined and was fixed at 110.7°, as in PMe_3 [12]. Finally the methyl groups were fixed in staggered positions as indicated in Fig. 1.

* $(Me_2AlNMe_2)_2$ has been studied by X-ray crystallography [9,10].

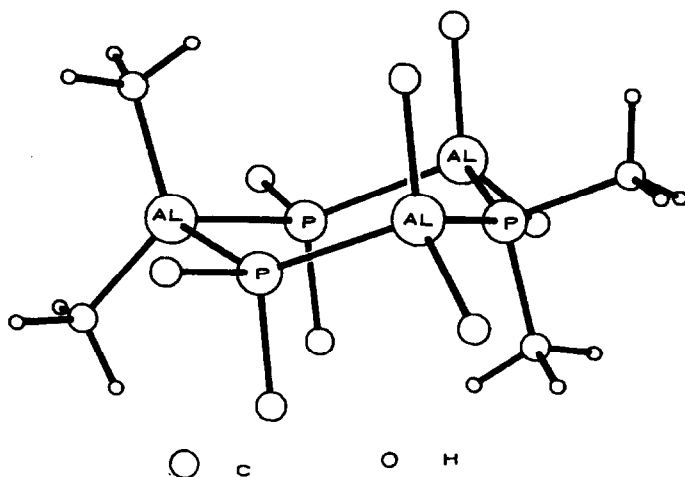
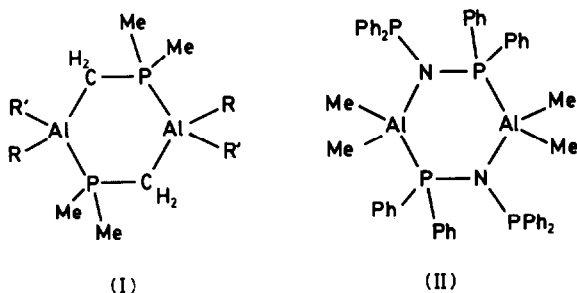


Fig. 1. Molecular model of $(\text{Me}_2\text{AlPMe}_2)_3$. Symmetry C_{3v} . Most of the hydrogen atoms have been omitted for clarity.

Least-squares refinement of nine structure parameters and thirteen r.m.s. amplitudes of vibration led to satisfactory agreement between experimental and calculated intensity values: $R_2 = [\sum w(I_{\text{exp}} - I_{\text{calc}})^2 / \sum w I_{\text{exp}}^2] = 0.044$. The best values obtained for bond distances and valence angles were: Al-P 243.4(4), P-C 184.6(3), Al-C 196.9(7), and C-H 109.1(5) pm; PAIP 96.4(7), AlPAI 131.7(8), CAIC 124(2), CPC 99(2), and AlCH 112(2)°.

The Al-P bonds in $(\text{Me}_2\text{AlPMe}_2)_3$ may be regarded as 50% dative and 50% covalent. They are a few pm shorter than the purely dative bonds in Ia (R = R' = Me); Al-P 245.1(2) pm [13], II (Ph = phenyl); Al-P 252.6(3) and 254.3(3) pm [14]



and in $\text{Me}_3\text{AlPMe}_3$; Al-P 253(4) pm [3]. The dative bonds in Ib (R = Cl, R' = CH_2PMe_2); Al-P 242.5(1) pm [13] are shorter, perhaps owing to the inductive effect of the electronegative Cl atoms.

The coordination around Al and P is distorted from ideal tetrahedral in the direction predicted by the Valence Shell Electron Pair Repulsion Model.

Acknowledgements. We are grateful to Ms. Snefrid Gundersen for technical assistance and to the Norwegian Research Council for Science and the Humanities (NAVF), as well as to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

- 1 N. Davidson and H.C. Brown, *J. Am. Chem. Soc.*, 64 (1942) 316.
- 2 G.A. Anderson, F.R. Forgaard and A. Haaland, *Acta Chem. Scand.*, 26 (1972) 1947.
- 3 A. Almenningen, L. Fernholt, A. Haaland and J. Weidlein, *J. Organomet. Chem.*, 145 (1978) 109.
- 4 A. Haaland, S. Samdal, O. Stokkeland and J. Weidlein, *J. Organomet. Chem.*, 134 (1977) 165.
- 5 L. Fernholt, A. Haaland, M. Hargittai, R. Seip and J. Weidlein, *Acta Chem. Scand. A*, 35 (1981) 529.
- 6 D.A. Drew, A. Haaland and J. Weidlein, *Z. Anorg. Allg. Chem.*, 398 (1973) 241.
- 7 A. Haaland, O. Stokkeland and J. Weidlein, *J. Organomet. Chem.*, 94 (1975) 353.
- 8 K. Brenhaugen, A. Haaland and D.P. Novak, *Acta Chem. Scand.*, A, 28 (1974) 45.
- 9 H. Hess, A. Hinderer and S. Steinhauser, *Z. Anorg. Allg. Chem.*, 377 (1970) 1.
- 10 G.M. McLaughlin, G.A. Sim and J.D. Smith, *J. Chem. Soc. Dalton*, (1972) 2197.
- 11 H.H. Karsch and G. Hanila, to be submitted.
- 12 L.S. Bartell and L.O. Brockway, *J. Chem. Phys.*, 32 (1960) 512.
- 13 H.H. Karsch, A. Appelt, F.H. Köhler and G. Müller *Organometallics*, 4 (1985) 231.
- 14 H. Schmidbaur, S. Lauteschläger and B. Milewski-Mahrla, *Chem. Ber.*, 116 (1983) 1403.