Phosphine Complexes of Main Group Elements: Phosphinomethyl Substituted Aluminates as Anionic Phosphine Ligands to Lithium and *X*-Ray Structure of $Me_2Al(CH_2PMe_2)_2Li(Me_2NCH_2CH_2NMe_2)$

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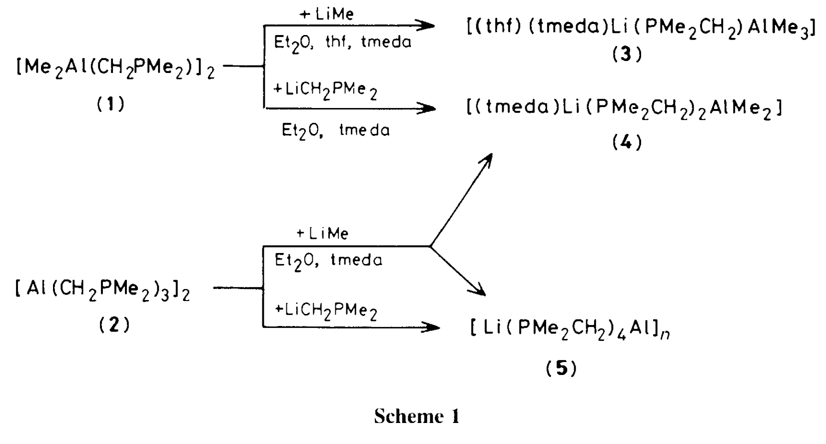
Anionic aluminates of the type $[Me_xAl(CH_2PMe_2)_{4-x}]^-$ were synthesized and shown to co-ordinate to a Li^+ ion; according to an *X*-ray structure determination $[Me_2Al(CH_2PMe_2)_2Li(Me_2NCH_2CH_2NMe_2)]$ contains a six-membered $Al(C-P)_2Li$ heterocycle.

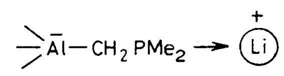
We are currently interested in phosphine co-ordination to main group elements.[1] At present, two features appear to promote this type of co-ordination: the introduction of the phosphine as an anionic ligand, and/or the formation of a ring system upon co-ordination, either by chelating or bridging phosphine ligands. Both criteria are met by phosphinomethanides.[2] Two recent structure determinations of this class of compounds have revealed co-ordination of the phosphorus atoms to a lithium ion, *i.e.* in $[LiCH_2PMe_2{\cdot}tmeda]_2$, (tmeda = $Me_2NCH_2CH_2NMe_2$),[3] and $[LiC(PMe_2)_3{\cdot}thf]_2$, (thf = tetrahydrofuran).[1]

A similar approach makes use of phosphinomethyl-substituted aluminates which are obtained from the recently described aluminium dimers $[Me_2Al(CH_2PMe_2)]_2$, (**1**) and $[Al(CH_2PMe_2)_3]_2$, (**2**)[4] by reaction with LiMe and $LiCH_2PMe_2$,[5] respectively (Scheme 1).

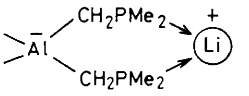
Because of rapid exchange of substituents, the reaction of (**2**) with LiMe does not yield the expected aluminate, but rather (**4**) and (**5**) are formed in a disproportionation reaction. Complex (**3**) is also unstable with respect to disproportionation; in the course of a few days, solutions of (**3**) decompose to (**4**) and $[(tmeda)_2Li]^+[AlMe_4]^-$. Compounds (**3**) and (**4**)



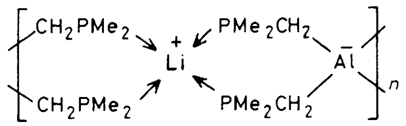
Scheme 1



I



II



III

may be isolated as colourless, crystalline solids in donor solvents such as thf or tmeda, whereas (**5**) is obtained as a sparingly soluble white powder.[†] The composition of (**3**)—(**5**) is not affected by the addition of excess tmeda to the solution prior to isolation. Thus co-ordination modes of type I (**3**), II (**4**), and III, (**5**), respectively, seem likely. To establish this novel type of phosphine co-ordination to lithium, an *X*-ray structure determination of (**4**) was undertaken.

Crystal data: $C_{14}H_{38}AlLiN_2P_2$, M = 295.06, orthorhombic, space group $Cmc2_1$ (No. 36), a = 10.652(3), b = 16.209(5), c = 12.761(4) Å, U = 2203.3 Å^3, D_c = 0.889 g/cm^3 for Z = 4 at −40 °C. 1249 Reflections were collected on a Syntex $P2_1$ automated four-circle diffractometer (ω-scans, $1 \leq \theta \leq 25°$, graphite-monochromated Mo-K_α radiation, λ = 0.71069 Å, temperature −40 °C) of which 1082 were unique ($R_{int.}$ = 0.026). Data were corrected for Lorentz and polarization effects, but not for those of absorption [μ(Mo-K_α) = 2.22 cm^{-1}]. The structure was solved by direct methods (MULTAN 80) and completed by Fourier syntheses. Full-matrix least-squares refinement of 110 parameters on 954 statistically significant reflections [$F_o \geq 4.0\sigma(F_o)$] led to a final R = 0.04, R_w = 0.04 with $w = k/\sigma^2(F_o)$, k = 2.0 in the last cycle (non-H atoms anisotropic, with the exception of two disordered methyl groups which were refined isotropically, H atoms fixed with U = 0.05 Å^2, SHELX-76). A final difference map was qualitatively featureless, $\Delta\rho_{max./min.}$ = 0.23/−0.22 e/Å^3.[‡]

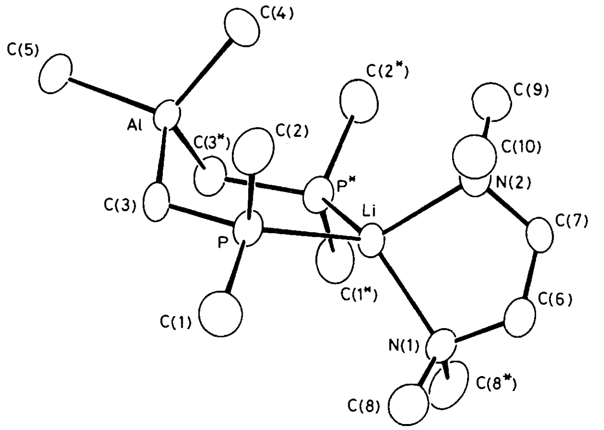


Figure 1. Molecular structure of [(tmeda)Li(PMe$_2$CH$_2$)$_2$AlMe$_2$] (**4**) (ORTEP, vibrational ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Crystallographic mirror symmetry relates the starred atoms to the unstarred atoms. The mirror plane bisecting the molecule and containing atoms Al,C(4),C(5),Li,N(1),N(2),C(6) necessitates two-fold positional disorder of atoms C(7),C(9),C(10) of the (nonplanar) tmeda ligand. Only one alternative is shown.

As Figure 1 shows, the phosphorus atoms of both $-CH_2PMe_2$ substituents of the aluminate ion are co-ordinated to the Li^+ ion; thus it is acting as a chelating ligand. A slightly distorted tetrahedral co-ordination geometry of the lithium ion is completed by one molecule of tmeda, also co-ordinating in a chelating fashion [angles P–Li–P* 105.7(3)°, N(1)–Li–N(2) 87.3(5)°]. Whereas the structural parameters of the five-membered Li·tmeda ring resemble closely those observed in a variety of other tmeda complexes of Li^+,[3,6] those of the six-membered $Al(CH_2PMe_2)_2Li$ heterocycle formed upon complexation of the aluminate, show some interesting differences. The C(3),C(3*), P,P*,Li portion of the ring is almost planar; the Li atom deviates only 0.14 Å from the plane through the other four atoms. The Al atom is situated on the opposite side of the C(3),C(3*),P,P* plane at a distance of 1.16 Å. This pseudo-envelope conformation also follows from the angles between the planes Al,C(3),C(3*)/C(3),C(3*),P,P* and C(3),C(3*),P,P*/P,P*,Li, 66.7° and 5.0°, respectively. The reason for this considerable flattening is reflected in the bonding parameters of the chelating phosphino groups with the Li^+ ion. The P–Li bond length of 2.606(5) Å is comparable to that found in the phosphinomethanides.[1,3] However, the accommodation of two such bonds to the same central atom in a six-membered ring results in a (nonbonding) P–P* distance of 4.155(3) Å [angle P–Li–P* 105.7(3)°]. This distance is contrasted by a separation of only 3.193(8) Å of the ring carbon atoms C(3)/C(3*). Apparently, this rather large discrepancy can only be accounted for by the observed ring flattening. The Al · · · Li distance across the six-membered ring is 4.020(5) Å. Although the direct electrostatic attractive interaction between anionic and cationic centres should be fairly small, it cannot be ruled out that Coulomb forces, together with chelate formation, play a decisive role in the formation of (**4**) even in the presence of excess of tmeda.

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[†] ^{31}P N.m.r. data (referenced to external 85% H_3PO_4): (**3**) ($C_6D_5CD_3$) δ −49.2 p.p.m.; (**4**) (C_6D_6) δ −50.8 p.p.m.; (**5**) (C_6D_6, thf, tmeda) δ −50.2 p.p.m. Broad signals were observed for all compounds.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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