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# Synthesis and structure of [{MeAl($\mu$-PMes)(PMes)}$_2$Li$_4$]$_2\cdot$7thf, containing a [MeAl($\mu$-PMes)(PMes)]$_2^{4-}$ tetraanion (Mes = 2,4,6-Me$_3$C$_6$H$_2$)

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*Received (in Cambridge, UK) 14th May 2003, Accepted 18th June 2003*
*First published as an Advance Article on the web 9th July 2003*

**The reaction of MeAlCl$_2$ with MesPHLi (1:4 equivalents) in thf/toluene gives the cage complex [{MeAl($\mu$-PMes)(PMes)}$_2$Li$_4$]$_2\cdot$7thf (1), containing an [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanion which is valence-isoelectronic with extensively studied Group 15 anions of the type [E($\mu$-NR)(NR)]$_2^{2-}$**

Our recent interest in p-block element phosphides stems from the discovery that Group 15 heterometallic compounds decompose at low temperatures to give Zintl compounds,[1] *e.g.*, the cage [{Sb(PCy)$_3$}$_2$Li$_6\cdot$6Me$_2$NH],[2] containing the [Sb(PCy)$_3$]$^{3-}$ trianion, decomposes at *ca.* 30–40 °C into Sb$_7$(Li$\cdot$2Me$_2$NH)$_3$.[3] This process, which is driven thermodynamically by the formation of P–P bonds, provides the basis for a potentially general approach to an extensive range of alloy coatings. However, the extension of this approach to other main group elements has so far been limited by the rarity of related heterometallic phosphide complexes of Groups 13 (Al–In) and 14 (Sn, Pb). As a basis for further developments in this area, we are attempting to establish a new range of p-block metal phosphide anions in these groups that are valence-isoelectronic with well-established, Group 14 and 15 imido counterparts, allowing well-defined changes in the ratio of the p-block element to the alkali metal in the resulting heterometallic cage complexes (and consequently in the alloy deposited by their thermal decomposition). The most extensively studied class of Group 14 and 15 imido anions are dianions of the type [E($\mu$-NR)(NR)]$_2^{2-}$ (Group 14, E = MeSi;[4] Group 15 E = P,[5] As,[6] Sb,[7] Bi[8]) (Fig. 1a), which exhibit a rich coordination chemistry with a broad range of main group and transition metal ions.[4,9] We present here the synthesis and structure of the cage [{MeAl($\mu$-PMes)(PMes)}$_2$Li$_4$]$_2\cdot$7thf (**1**), containing an [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanion (Fig. 1b) that is valence-isoelectronic with these key classes of Group 14/15 anions. This is the first valence analogue of [E($\mu$-NR)(NR)]$_2^{2-}$ for Group 13.

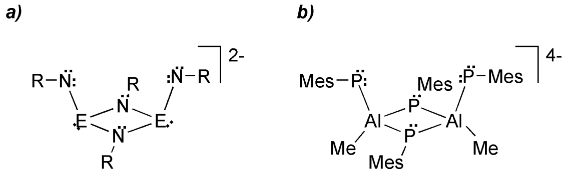

**Fig. 1** *(a)* Structure of [E($\mu$-NR)(NR)]$_2^{2-}$ (E = MeSi, P, As, Sb, Bi) and *(b)* the valence-isoelectronic [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanion.

Complex **1** was obtained by the reaction of MeAlCl$_2$ with MesPHLi (1:4 equivalents) in thf/toluene (47% yield) (eqn. (1)).† This result is different from that observed previously in

$$4MeAlCl_2 + 16MesPHLi \xrightarrow[-8MesPH_2]{-8LiCl} \underset{\mathbf{1}}{[\{MeAl(\mu\text{-}PMes)(PMes)\}_2Li_4]_2.7thf} \qquad (1)$$

the reaction of MeAlCl$_2$ with 2,6-$^i$PrC$_6$H$_3$NHLi (Dipp = 2,6-$^i$PrC$_6$H$_3$) which gives the [Al(NHDipp)$_4$]$^-$ anion *via* further reaction of the Al-bonded Me group.[10] During the present study we showed that the related P anion ([Al(PHMes)$_4$]$^-$) is produced by the (4:1 stoichiometric) reaction of MesPHLi with AlCl$_3$, in the ion-separated complex Li(thf)$_4^+$[Al(PHMes)$_4$]$^-$ (**2**). The most closely related Group 13 anion frameworks to the [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanion of **1** are the cyclic [{MeAl($\mu$-PCy)}$_2$($\mu$-PCy)]$_2^{4-}$ tetraanion[11] and the [($^t$BuN)$_2$Al($\mu$-N$^t$Bu)Al(NH$^t$Bu)(N$^t$Bu)]$^{3-}$ trianion.[12] The latter complex is formed by the deprotonation of the dimer [($^t$BuNH)$_2$Al($\mu$-HN$^t$Bu)]$_2$ with $^n$BuLi. However, unlike the [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanion of **1** the previously reported [{MeAl($\mu$-PCy)}$_2$($\mu$-PCy)}]$_2^{4-}$ and [($^t$BuN)$_2$Al($\mu$-N$^t$Bu)Al(NH$^t$Bu)(N$^t$Bu)]$^{3-}$ anions have no direct Group 15 relatives.

A low-temperature crystallographic study of **1**‡ shows the complex to be the heterobimetallic cage [{MeAl($\mu$-PMes)(PMes)}$_2$Li$_4$]$_2\cdot$7thf (Fig. 2a), resulting from the coordination of eight Li$^+$ cations by two, symmetry-related [{MeAl($\mu$-PMes)(PMes)}$_2$]$^{4-}$ tetraanions (the core of which is shown in Fig. 2b). The complex has $C_2$ symmetry with the vector Li(3)$\cdots$Li(5)$\cdots$O(4) lying on the symmetry axis and the

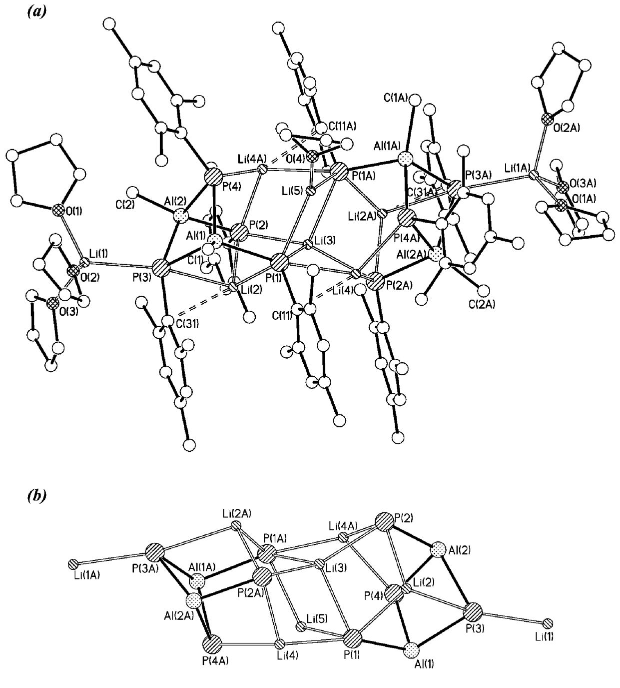

**Fig. 2** (a) Structure of the cage **1** that has crystallographic $C_2$ symmetry. Lattice toluene molecules and disorder of coordinated thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°); Al(1)–C(1) 1.994(8), Al(1)–P(1) 2.379(2), Al(1)–P(3) 2.416(3), Al(1)–P(4) 2.428(3), Al(2)–C(2) 1.991(7), Al(2)–P(2) 2.364(2), Al(2)–P(3) 2.424(3), Al(2)–P(4) 2.441(3), P(3)–Li(1) 2.600(11), Li(1)–O 1.937(12)–1.968(12), P(1)–Li(2) 2.495(11), P(2)–Li(2) 2.453(11), P(3)–Li(2) 2.720(10), Li(2)$\cdots$C(31) 2.473(12), P(1)–Li(3) 2.623(9), P(2)–Li(3) 2.528(5), P(1)–Li(4) 2.537(11), P(2A)–Li(4) 2.487(12), C(11)$\cdots$Li(4) 2.472(12), P(1)–Li(5) 2.565(12), Li(5)–O(4) 1.94(2), P(3)–Al(1)–P(4) 90.96(9), P(1)–Al(1)–P(3) 110.57(10), P(1)–Al(1)–P(4) 95.67(9), P(3)–Al(2)–P(4) 90.46(9), P(2)–Al(2)–P(3) 114.03(9), P(2)–Al(2)–P(4) 99.32(9), Al(1)–P(3)–Al(2) 85.76(8), Al(1)–P(4)–Al(2) 85.13(9); (b) the core structure of **1**.

DOI: 10.1039/b305259a

remaining atoms in general positions. The five crystallographically unique $Li^+$ sites thus result in a total of eight lithium cations in the dimeric unit of **1**. In addition there are three and a half molecules of toluene for each of the cages of **1** in the lattice. Similarly to the geometry of the isoelectronic $[E(\mu\text{-}NR)(NR)]_2{}^{2-}$ dianions within the lithium cages $[\{E(\mu\text{-}NR)(NR)\}_2Li_2]_2$ (E = MeSi, P–Bi)[4–8] the $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanions of **1** are puckered about the $Al_2P_2$ ring and adopt a *cis* conformation, with the pendent PMes groups [associated with P(1) and P(2)] pointing towards the centre of the cage and with the Al-bonded Me groups being directed *exo*. The roughly *trans* disposition of the μ-PMes groups of the $Al_2(\mu\text{-}PMes)_2$ rings [attached to P(3,3′) and P(4,4′)] allows the coordination of $Li^+$ cations by P(3,3A) not only within the central core of **1** but also two thf-solvated $Li^+$ cations [Li(1) and Li(1A)] at the periphery of the cage. This bonding mode is unlike that found in the Group 14 analogues $[MeSi(\mu\text{-}NR)(NR)]_2Li_2$,[4] or the Group 15 analogues $[\{E(\mu\text{-}NR)(NR)\}_2Li_2]_2$ (E = P–Bi)[5a–8] or in any other metal complexes involving these Group 14 or 15 ligands, where metal coordination occurs using the NR groups alone within the core. This difference possibly results from the greater polarity of Al–P bonds and the consequent higher development of negative charge on the P centres of the $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanion.

The $Al_2P_2$ rings of the $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanions in **1** are almost rectangular in shape (Al–P–Al mean 85.4°, P–Al–P mean 90.7°), with the terminal Al–P bonds being significantly shorter [Al(1,2)–P(1,2) range 2.364(2)–2.379(2)Å] than the Al–P bonds within the $Al_2(\mu\text{-}P)_2$ units [Al(1,2)–P(3,4) range 2.416(3)–2.441(2)Å].[13a] The $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanions coordinate the $Li^+$ cations of the cage using a combination of their μ-PMes and pendent PMes groups, as well as by π-arene interactions with the Mes rings. The large range of P–Li bond lengths found in the cage [2.453(11)–2.720(10)Å] reflects the differing coordination numbers of the $Li^+$ cations present and their mode of coordination by the $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanions.[13b] For Li(2) and Li(4), the relatively low coordination number of three offered by P centres within the core of **1** is compensated for by short C···Li contacts to the *ipso*-C atom of Mes groups [C(11,31)···Li(4,2) mean 2.47(1)Å]. In the case of Li(2), the C···Li interaction also appears to make up for the presence of a weak P–Li bond to the μ-P centre [P(3)] of the tetraanion [P(3)–Li(2) 2.720(10)Å]. Presumably the reason for this long P–Li bond (which is by far the longest in the structure of **1**) is that P(3) is also involved in *exo*-bonding to Li(1) [P(3)–Li(1) 2.600(11)Å]. No C···Li interactions are involved in the coordination environment of Li(5), despite its three coordinate (trigonal-planar) geometry. The remaining $Li^+$ cations [Li(1,1′) and Li(3)] are four coordinate, with Li(3) being bonded solely to the pendent PMes groups of the both $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanions of the cage and with Li(3) being coordinated by one P centre and three thf ligands outside the cage structure.

In conclusion, compound **1** is of importance in being the first Group 13 anion system of its type (containing nitrogen or phosphorus functionality) that is directly related to a well-established and extensively studied family of Group 14 and 15 anions of the type $[E(\mu\text{-}NR)(NR)]^{2-}$ (E = MeSi, P–Bi). This complex has a unique cage structure and composition (containing a 1:2 ratio of Al to Li). The applications of **1** as a source of the $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2]^{4-}$ tetraanion and its thermal decomposition are under investigation.

We gratefully acknowledge the EPSRC (A.B., R.H., F.G., M.McP., D.S.W) and The Cambridge European Trust (F.G.) for financial support. We also thank Dr J. E. Davies for collecting X-ray data for **1**.

## Notes and references

† *Synthesis of* **1**: A solution of $MesPH_2$ (1.74 ml, 12.0 mmol) in toluene (20 ml) and thf (20 ml) was lithiated with $^nBuLi$ (7.7ml, 1.6 mol $dm^{-3}$ in hexanes, 12 mmol) at −78 °C. After stirring at room temperature for 1 h an orange solution was obtained. To this solution was added $MeAlCl_2$ (3.0 ml, 1.0 mol $dm^{-3}$ in hexanes, 3.0 mmol) at −78 °C. A yellow solution was obtained at room temperature and the reaction mixture was stirred for a further 24 h. The solvent was removed under vacuum and replaced by toluene (60 ml). The reaction mixture was filtered to remove LiCl (Celite, porosity 3 sinter) and the volume of the filtrate reduced to *ca.* 50 ml under vacuum. Storage at −10 °C (48 h) gave light yellow crystals of **1**·3.5toluene. Yield 0.80 g (47% based on Al). $^1H$ NMR (+25 °C, 400.16 MHz, $d_6$-benzene), $\delta$ = 7.2–6.8 (m, $C_6H_5$, toluene), 3.51 (br s, 28H, $CH_2$, thf), 2.31 (s, 48H, *o*-Me of Mes), 2.27 (s, 24H, *p*-Me of Mes), 2.10 (s, Me, toluene), 1.35 (br s, 28H, $CH_2$–O, thf), 0.40 (s, 12H Me–Al) (there are *ca.* 3–4 molecules of toluene per cage molecule of **1**). $^{31}P$ NMR (+27 °C, $d_6$-benzene, 161.9 MHz), $\delta$= −106.8 (s) (minor resonances at $\delta$ −61.7 and −68.8). Variable-temperature $^{31}P$ NMR studies ($d_8$-toluene) suggest a complicated, concentration-dependent set of equilibrium processes is occurring in solution. However, even at −80 °C the static (*i.e.*, solid-state) structure of **1** could not be frozen out. Elemental analysis, found C 68.6, H 7.7, P 12.4, calcd. for **1**·3.5toluene C 68.5, H 8.2, P 11.0%.

‡ *Crystal data for* **1**·3.5toluene; $C_{128.50}H_{184}Al_4Li_8O_7P_8$, $M$ = 2251.96, monoclinic, space group $P2/n$, $Z$ = 2, $\alpha$ = 16.1493(3), $b$ = 15.1393(2), $c$ = 28.7338(5) Å, $\beta$ = 90.0630(10)°, $V$ = 7025.1(2) Å$^3$, μ(Mo–Kα) = 0.172 $mm^{-1}$, $\rho_{calc}$ = 1.065 Mg $m^{-3}$, $T$ = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 30091 reflections collected, 6443 were unique ($R_{int}$ = 0.062). The structure was solved by direct methods and refined by full-matrix least squares on $F^2$.[14] Final $R1$ = 0.087 [$I > 2\sigma(I)$] and $wR2$ = 0.234 (all data). CCDC 210709. See http://www.rsc.org/suppdata/cc/b3/b305259a/ for crystallographic data in .cif or other electronic format. The structure exhibited extensive disorder of the thf ligands and partial occupancy of the toluene solvate sites. These factors accounted for the poor diffraction by the crystal, resulting in the relatively high $R$ values. All four thf ligands showed conformational disorder with the oxygen and carbon atom being resolved into sites of approximately half occupancy. The thf ligand associated with O(4) was disordered across the $C_2$ axis. There are three half toluene solvated molecules in general positions in the asymmetric unit and one half occupancy toluene rotational disordered across an inversion centre, giving a total of 3.5 toluene molecules per unit of **1**.

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