DALTON
COMMUNICATION

Build-up of an $Al_4P_6Li_4$ cage from an Al_4N_4 cubane: synthesis and structure of $[Li(OC_4H_8)]_4[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6H_{11})\}]_2\cdot C_6H_5Me$

Robert E. Allan, Michael A. Beswick, Paul R. Raithby, Alexander Steiner and Dominic S. Wright *

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

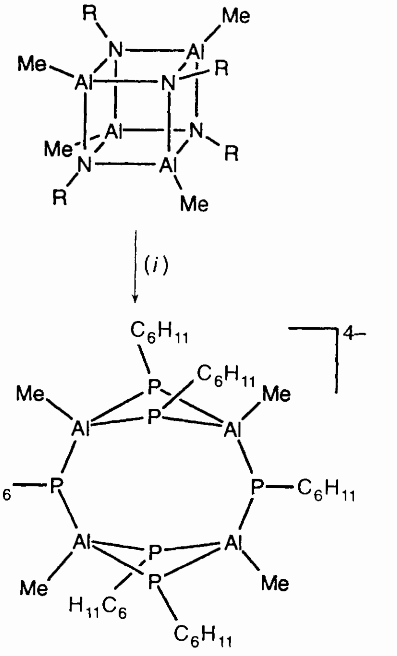
The acid–base reaction of the Al^{III} imido cubane $[AlMe(Nmes)]_4$ (mes = 2,4,6-$Me_3C_6H_2$) with $Li[PH(C_6H_{11})]$ yielded the heterobimetallic cage complex $[Li(OC_4H_8)]_4[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6H_{11})\}]_2\cdot C_6H_5Me$, the metallacyclic tetraanion of which is the first example of an Al^{III} phosphinidine anion.

A major focus of our current work has been the development of new ligand systems containing p-block metals. We recently employed the step-wise metallation of monolithiated primary amines, Li(NHR), with Group 15 metal dimethylamido compounds in the preparation of a variety of imido metal anions.[1] These species function as versatile ligands to a range of transition and main-group metals.[2] Attempts to extend this synthetic strategy to related Group 14 metal ligands proved unsuccessful. However, we found that the transmetallation reactions of the cubane $[Sn(NBu^t)]_4$ with monolithiated primary amines and phosphines [Li(EHR), E = N or P] furnish a new route to cage complexes containing tin(II) imido and phosphinidine anions.[3]

We here report the synthesis of $[Li(thf)]_4[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6H_{11})\}]_2\cdot C_6H_5Me$ **1** (thf = tetrahydrofuran) from the reaction of $[AlMe(Nmes)]_4$ (mes = 2,4,6-$Me_3C_6H_2$)[4] with $Li[PH(C_6H_{11})]$ (1:6 equivalents) (Scheme 1).† The preparation of complex **1** illustrates that Group 13 metal imido cubanes can be used as general precursors to the synthesis of a new class of Group 13 metal phosphinidine anions.

Despite the poor quality of the data, owing to weak diffraction at high angles, the low-temperature crystal structure of complex **1** ‡ shows unequivocally that it is a mixed-metal cage complex, $[Li(thf)]_4[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6H_{11})\}]_2\cdot C_6H_5Me$, consisting of a 14-membered $\{Al_4P_6Li_4\}$ core (Fig. 1). In addition, there is one lattice-bound toluene molecule per molecule of **1**. Although the core of **1** is identical to the arrangement found in $[Li(thf)]_4[\{Sn_2[P(C_6H_{11})]_3\}_2]\cdot 2thf$[3] {generated from the reaction of $[Sn(NBu^t)]_4$ with $Li[PH(C_6H_{11})]$}, its structure is unique for any Group 13 metal compound. Other examples of polyhedral cage arrangements with the same core shape as **1** are those of the Sb^{III} complex $[(PhCH_2CH_2NLi)_3Sb\cdot thf]_2$,[1b] and the Ge^{IV} and Si^{IV} complexes $[\{(Pr^i{}_3Si)AsLi\}_3GeBu^t]_2$[7a] and $[(RNLi)_3SiR']_2$ (R = Me_3Si, R′ = Me, Bu^t or Ph;[7b] R = Bu^t, R′ = Ph;[7a] R = Me, R′ = Bu^t[7d]).[8]

Overall, complex **1** can be regarded as constructed from the association of the metallacyclic Al^{III} phosphinidine tetraanion $[\{(AlMe)[\mu\text{-}P(C_6H_{11})]\}_2\{\mu\text{-}P(C_6H_{11})\}]_2{}^{4-}$ with four thf-solvated Li^+ cations. The tetraanion is composed of two puckered



Scheme 1 R = 2,4,6-$Me_3C_6H_2$. (*i*) $6[PH(C_6H_{11})]^-$, $-2[NHR]^-$ $-2NH_2R$

---

† Synthesis of **1**. The salt $Li[PH(C_6H_{11})]$ (15 mmol) was prepared by treating $PH_2(C_6H_{11})$ (1.99 cm^3, 15 mmol) with $LiBu^n$ (in hexanes, 10.0 cm^3, 15 mmol, 1.5 mol dm^{-3}) in toluene (45 cm^3) and thf (5 cm^3) under argon. Heating to reflux (2 min) gave a darker yellow solution of the monolithiate. To this solution was added $[AlMe(Nmes)]_4$ (1.75 g, 2.5 mmol) and the mixture brought to reflux (48 h). The pale yellow solution was filtered to remove a white precipitate (Celite) and the filtrate was reduced under vacuum to *ca.* half volume. The yellow precipitate was gently heated back into solution and storage (5 °C, 12 h) gave yellow-green diamond-shaped crystals of **1**, yield 0.98 g (31%); decomp. > 320 °C (Found: C, 58.3; H, 9.4; P, 14.3. Calc.: C, 60.0; H, 9.4; P, 14.8). IR (solid, Nujol): $\tilde{\nu}_{max}/cm^{-1}$ major bands at 1275, 1103 and 1051. ^1H NMR [250 MHz, +25 °C, $DCON(CD_3)_2$]: δ 7.20 (m, toluene), 3.60 (16 H, m, thf), 2.80 [6 H, d of m, H_α C_6H_{11} ($^2J_{P-H}$ *ca.* 51 Hz)], 2.10 (s, Me of toluene), 1.76 (16 H, m, thf), 1.65 (m), 1.20 (m, 60 H, CH_2 of C_6H_{11}), −1.13 (12 H, br s, Me). ^{31}P NMR [101.3 MHz, +25 °C, $DCON(CD_3)_2$, relative to H_3PO_4] δ 86.7 (s).

‡ Crystal data for **1**. $C_{63}H_{118}Al_4Li_4O_4P_6$, $M = 630.54$, monoclinic, space group $P2_1/n$, $a = 13.430(3)$, $b = 16.990(3)$, $c = 16.730(3)$ Å, $\beta = 94.80(3)°$, $U = 3804.0(13)$ Å^3, $Z = 2$, $D_c = 1.101$ Mg m^{-3}, $\lambda = 0.710\,73$ Å, $T = 153(2)$ K, μ(Mo-Kα) = 0.227 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.11 × 0.16 × 0.17 mm in an oil drop[5] by the θ–ω method ($8.06 \leqslant 2\theta \leqslant 45.04°$). Of a total of 6218 collected reflections, 4941 were independent. The data were corrected for absorption by a semi-empirical method based on ψ scans. The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1$ [$F > 4\sigma(F)$] = 0.1188 and $wR2$ = 0.3614 (all data) $\{R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{0.5}$, $w = 1/[\sigma^2(F_o{}^2) + (xP)^2 + yP]$, $P = F_o{}^2 + (2F_c{}^2/3)\}$;[6] largest peak and hole in the final difference map 0.795 and −0.725 e Å^{-3}. Symmetry transformations used to generate equivalent atoms: 1a $-x$, $-y$, $-z + 1$; 2a $-x$, $-y - 1$, $-z + 1$. The H atoms were restricted geometrically. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/281.

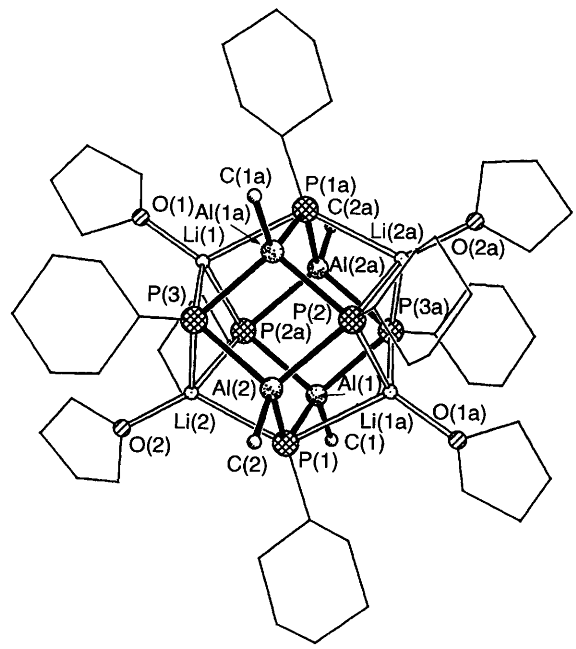


Fig. 1 Molecular structure of complex **1**. Hydrogen atoms and lattice-bound toluene of solvation have been omitted for clarity. Key bond lengths (Å) and angles (°): Al(1)–P(1) 2.374(6), Al(1)–P(2a) 2.393(6), Al(1)–P(3a) 2.421(5), Al(2)–P(1) 2.381(5), Al(2)–P(2) 2.406(5), Al(2)–P(3) 2.411(6), P(1)–Li(1a) 2.77(3), P(1)–Li(2) 2.58(2), P(2)–Li(1a) 2.52(2), P(2)–Li(2a) 2.59(2), P(3)–Li(1) 2.48(3), P(3)–Li(2) 2.56(2), Li(1)–O(1) 1.95(3), Li(2)–O(2) 1.92(2), Al(1)–C(1) 1.99(1), Al(2)–C(2) 1.99(1); P(1)–Al(1)–P(2a) 100.6(2), P(1)–Al(1)–P(3a) 111.2(2), P(2a)–Al(1)–P(3a) 99.9(2), P(1)–Al(2)–P(2) 109.9(2), P(1)–Al(2)–P(3) 104.1(2), P(2)–Al(2)–P(3) 99.8(2), average angles about Al 109.2, average angles about Li 108.4

$[\mathrm{Al}\{\mu\text{-P}(C_6H_{11})\}]_2$ rings which are linked by two bridging $P(C_6H_{11})$ units. Within this anion the Al–P bonds are all of similar lengths [2.374(6)–2.421(5) Å] and all the Al centres adopt similar pseudo-tetrahedral geometries (average angle about Al 109.2°). Each of the four Li^+ cations are bound, in the equator of the $[\{(\mathrm{AlMe})[\mu\text{-P}(C_6H_{11})]\}_2\{\mu\text{-P}(C_6H_{11})\}]_2{}^{4-}$ anion, to one P centre of each of the $[\mathrm{Al}\{\mu\text{-P}(C_6H_{11})\}]_2$ rings and to one of the P centres of the bridging $P(C_6H_{11})$ groups [P–Li 2.48(3)–2.77(3) Å]. The P–Li distances are characteristic of those seen in numerous lithium phosphide complexes.[9] The thf solvation of the Li^+ cations ensures that each adopts a favourable pseudo-tetrahedral configuration (Li–O average 1.94 Å, average angle about Li 108.4°). Within the cage, the P atoms have similar square-based pyramidal geometries, each $P(C_6H_{11})$ unit being bonded to two Al and two Li centres.

A few cage complexes containing imido Al^{III} anions have been characterised, using metallation reactions of AlH_3 or $LiAlH_4$, *e.g.*, $[(Bu^tN)_4(AlH)_3M(thf)_n]$[10a] (M = Ca, $n = 3$; M = Mg, $n = 1$) and $[\mathrm{AlH}\{N(CH_2)_3NMe_2\}]_6\cdot 2LiH$.[10b] Recently, the metallation reaction of primary amido Al^{III} complexes, $[AlR_2(NHR')]_2$, with organolithium compounds has been employed in the preparation of complexes containing $[AlR_2(NR')]^-$ anions.[11] However, only a handful of Group 13 phosphinidine compounds have been structurally characterised[12] and the only complex containing a Group 13 phosphinidine anion is that of $[Li(Et_2O)_2(Bu^tGa)(\mu\text{-}PBu^t)_2(GaBu^t{}_2)_2]$.[12b]

The use of imido cubanes as synthetic precursors is a novel approach to compounds containing Group 13 phosphinidine anions. Previous approaches to phosphinidine compounds of Group 13 metals (E) have mainly involved transmetallation of organometallic halides (EX_2R) or metallation using organometallics (ER_3).[12] We believe that this new strategy points the way to a large area of chemistry involving Group 13 cage compounds that has previously been inaccessible. Similar reactions of larger imido Al cages {*e.g.* $[AlMe(NMe)]_8$[13]} with monolithiated primary phosphines may allow the preparation of a range of phosphinidine anions related to **1**. In addition, preliminary investigations show that **1** reacts with various transition and main-group metal halides (*e.g.*, CuCl, $SnCl_4$ or $AlCl_2Me$). Metal exchange provides a promising route to a range of complexes containing the $[\{(\mathrm{AlMe})[\mu\text{-P}(C_6H_{11})]\}_2\{\mu\text{-P}(C_6H_{11})\}]_2{}^{4-}$ anion.

Acknowledgements

We gratefully acknowledge the EPSRC (R. E. A., M. A. B., P. R. R. and D. S. W.), the Royal Society (P. R. R. and D. S. W.) and the EU (fellowship for A. S.) for financial support.

References

1 A. J. Edwards, M. A. Paver, M.-A. Rennie, P. R. Raithby, C. A. Russell and D. S. Wright, (*a*) *J. Chem. Soc., Chem. Commun.*, 1994, 1481; (*b*) *Angew. Chem.*, 1994, **106**, 1334; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1277.

2 A. J. Edwards, M. A. Paver, M.-A. Rennie, C. A. Russell, P. R. Raithby and D. S. Wright, *Angew. Chem.*, 1994, **106**, 1960; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1875; *Angew. Chem.*, 1995, **107**, 1088; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1012.

3 R. E. Allan, M. A. Beswick, N. L. Cromhout, M. A. Paver, P. R. Raithby, A. Steiner, M. Trivithick and D. S. Wright, *Chem. Commun.*, 1996, 1501.

4 P. P. Power and K. M. Waggoner, *J. Am. Chem. Soc.*, 1991, **113**, 3385.

5 D. Stalke and T. J. Kottke, *Appl. Crystallogr.*, 1993, **26**, 615.

6 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

7 (*a*) L. Zsolnai, G. Huttner and M. Dreiss, *Angew. Chem.*, 1993, **105**, 1549; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1439; (*b*) D. J. Brauer, H. Bürger, G. L. Liewald and J. Wilkie, *J. Organomet. Chem.*, 1985, **287**, 305; (*c*) D. J. Brauer, H. Bürger and G. L. Liewald, *J. Organomet. Chem.*, 1986, **308**, 119; (*d*) F. Gross, V. Huch, J. Pöhlmann, A. Spaniol and M. Veith, *Chem. Ber.*, 1993, **126**, 2625.

8 M. Veith, *Chem. Rev.*, 1990, **90**, 3.

9 W. Setzer and P. von Ragué Schleyer, *Adv. Organomet. Chem.*, 1995, **24**, 353; K. Gregory, P. von Ragué Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry II*, ed. C. E. Housecroft, Pergamon, Oxford, 1995, vol. 1, ch. 1.

10 (*a*) G. Del Piero, M. Cesari, S. Cucinella and A. Muzzei, *J. Organomet. Chem.*, 1977, **137**, 265; (*b*) G. Perego and G. Dozzi, *J. Organomet. Chem.*, 1981, **205**, 21; (*c*) M. Cesari, G. Perego, G. Del Piero and M. Corbellini, *J. Organomet. Chem.*, 1975, **87**, 43.

11 D. A. Atwood and D. Rutherford, *Organometallics*, 1996, **15**, 436.

12 (*a*) R. L. Wells, A. P. Purdy, A. T. McPhail and C. G. Pitt, *J. Chem. Soc., Chem. Commun.*, 1986, 487; (*b*) M. P. Petrie and P. P. Power, *Organometallics*, 1993, **12**, 1592; (*c*) A. H. Cowley, R. A. Jones, M. A. Mardones, J. L. Atwood and S. G. Bott, *Angew. Chem.*, 1991, **103**, 1163; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1141; (*d*) K. M. Waggoner, S. Parkin, D. C. Pestana, H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 3597; (*e*) A. R. Barron and M. A. Power, *Angew. Chem.*, 1991, **103**, 1403; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1353; (*f*) D. A. Atwood, A. H. Cowley, R. A. Jones and M. A. Mardones, *J. Organomet. Chem.*, 1993, **449**, C1; (*g*) A. H. Cowley, R. A. Jones, M. A. Mardones, J. L. Atwood and S. G. Bott, *Angew. Chem.*, 1990, **102**, 1504; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1409.

13 S. Amirkhalili, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1979, 1206.

Received 8*th August* 1996; *Communication* 6/05541I