A metallated primary arsine; synthesis and structure of [PhAsHLi·2thf]$_\infty$

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The lithium primary arsenide [PhAsHLi·2thf]$_\infty$, obtained by reaction of ^{n}BuLi with PhAsH$_2$ in toluene–thf, crystallises in the form of helical polymers; the structure of the right-hand enantiomorph has been obtained.

Amido alkali metal compounds have been intensively investigated in the past few decades and the key factors governing their preferred structures, whether existing as uncomplexed oligomers $[R_2NM]_n$ or Lewis base solvated species $[R_2NM{\cdot}xL]_n$ (M = Li–Cs), have been uncovered.[1] Although the structural patterns found in related alkali metal complexes containing Group 15 anions of the type R_2E^- (E = P, As, Sb, Bi) appear to be similar to those found for the amido complexes, far fewer complexes have been characterised in the solid state.[2] Recent attention in this area has focused on the structures adopted by alkali metal complexes containing primary amido and phosphido groups (RNH^- [3] and RPH^- [4] anions). However, to date only a handful of these species have been structurally characterised and no examples have been reported for the heavier Group 15 elements (As–Bi). Our interest in species containing REH^- anions stems from their use as precursors in the synthesis of heterometallic imido and phosphinidene cage complexes,[5] such as $[\{Sb(PCy)_3\}_2Li_6{\cdot}6Me_2NH]$ {obtained from the metallation reaction of [CyPHLi] with $Sb(NMe_2)_3$}.[6] During recent attempts to extend this work to related systems containing $[E(AsR)_3]^{3-}$ (E = As–Bi), we had cause to investigate the structure of the lithiate of PhAsH$_2$.

The reaction of PhAsH$_2$ in toluene with ^{n}BuLi yields a yellow precipitate at room temperature which was dissolved in a minimum of thf. Storage at –25 °C gives colourless crystalline rods of [PhAsHLi·2thf]$_\infty$ **1** suitable for X-ray crystallography.† The low-temperature [180(2) K] structure of **1**‡ shows that the complex is composed of PhAsHLi·2thf monomer units linked together by Li–As–Li bridges into infinite helical polymer chains (Fig. 1).

This structural arrangement is similar to that occurring in the primary phosphido lithium complex [(Mes)PHLi·2thf]$_\infty$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$)[7] and in the related secondary phosphido complexes [Ph$_2$PLi·*n*L]$_\infty$ (*n*L = Et$_2$O, 2thf) and [Cy$_2$PLi·thf]$_\infty$.[8] A noteworthy feature of **1** is the presence exclusively of only the right-hand helical chain in the solid state structure. Although there is little doubt that the other (left-hand) form is also present in samples of **1**, the crystallisation of separate enantiomorphs is rare for polymeric alkali metal complexes of this type. Generally, as in the cases of [(Mes)PHLi·2thf]$_\infty$[7] and [LiNPr$^i_2$]$_\infty$,[9] co-crystallisation of both helical elements occurs and, to our knowledge, only for [Cy$_2$PLi·thf]$_\infty$[8] has a chiral structure been identified in the solid state (however, unlike **1** it did not prove possible to assign the absolute configuration in this case). Although a number of other As–Li bonded complexes have been structurally characterised,[10,11] all of these have molecular (rather than polymeric) arrangements in the solid state as a result of high degrees of Lewis base solvation of the Li$^+$ cations and/or the presence of sterically demanding substituents. Complex **1** is the first example of an alkali metal primary arsenide to be structurally characterised.

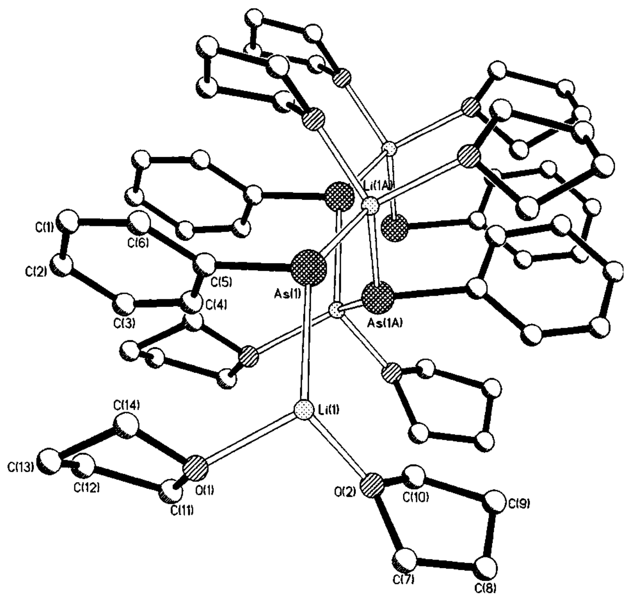

Fig. 1 Polymeric structure of **1**. H atoms and the disorder of the thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°): As(1)–Li(1) 2.70(3), As(1)–Li(1A) 2.69(3), As(1)–C(5) 1.95(2), Li–O (average) 1.94; Li(1)–As(1)–Li(1A) 143.4(5), As(1A)–Li(1)–As(1) 116(1), C(5)–As(1)–Li(1) 103.3(7), C(5)–As(1)–Li(1A) 91.0(7).

In the chains of **1** the As–Li bonds in the Li–As–Li bridges are of equal lengths within statistical error [mean 2.70 Å] and are in the range of values previously observed for other As–Li bonded complexes (2.46–2.76 Å).[10] The Li$^+$ cations adopt a distorted tetrahedral geometry, with the most marked distortion occurring in the As–Li–As angle [116(1)°]. The As centres also exhibit a large distortion in the chain Li–As–Li angle [143.4(5)°; *cf.* 103.3(7) and 91.0(7)° for the C–As–Li angles]. The pattern of expanded Li–As–Li and As–Li–As angles in **1** is similar to that observed in the polymeric phosphides [(Mes)PHLi·2thf]$_\infty$ [Li–P–Li 130.0(2), P–Li–P 122.3(2)°][7] and [Ph$_2$PLi·2thf]$_\infty$ [Li–P–Li 135.0(5), P–Li–P 123.1(8)°],[8] in which bis solvation of Li$^+$ by thf is also present. However, the almost linear Li–P–Li bridge (177°) observed in the structure of [H$_2$PLi·2thf]$_\infty$[12] suggests that (where the Lewis base and extent of solvation are comparable) the steric bulk of the organic substituents has the major influence over the P geometries. On this basis, the large Li–As–Li angle in **1** is probably steric in origin rather than providing evidence for any fundamental change in hybridisation of the As centre.

In conclusion, the first alkali metal primary arsenide [PhAsHLi·2thf]$_\infty$ exhibits an interesting helical structure in the solid state. The structure of this species provides a rare insight into the nature of aggregation for an arsenide with very low steric demands, and suggests a link with the structural patterns found for related polymeric phosphorus complexes.

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Notes and references

† Synthesis of **1**. $PhAsH_2$ was prepared by the reduction of phenylarsonic acid with Hg–Zn amalgam and HCl. Using half the quantity of Hg–Zn amalgam as that suggested in the literature[13] leads to more reproducible yields (*ca.* 40–50%). ^1H NMR (+25 °C, d_6-benzene, 250 MHz): δ 7.34 (2H, m, *o*-C–H), 7.07 (3H, m, *p*- and *m*-C–H), 3.52 (2H, s, AsH_2). To a solution of $PhAsH_2$ (0.91 ml, 8.0 mmol) in toluene (20 ml) at −78 °C was added ^{n}BuLi (5.3 ml, 1.5 mol dm^{-3} in hexanes, 8.0 mmol). A yellow precipitate was formed which was dissolved by addition of thf (10 ml). The solution was concentrated under vacuum until precipitation commenced. The solid was dissolved by heating and storage at −25 °C gave colourless crystalline rods (1.48 g, 61% on the basis of the empirical formula [PhAsHLi·2thf]). Isolation of **1** under vacuum (10^{-1} atm) leads to loss of some of the coordinated thf (*ca.* 0.75 equiv.). ^1H NMR (+25 °C, d_6-benzene, 250 MHz): δ 7.29 (2H, d, *o*-C–H), 7.07 (2H, t, *m*-C–H), 6.93 (1H, t, *p*-C–H), 3.62 (5H, m, thf CH_2O) and 1.36 (5H, m, thf CH_2), 2.07 (1H, s, As–H) {Found: C, 52.5; H 6.8. Calc. for [PhAsHLi·*x*thf] ($x = 1.25$): C, 52.8; H, 6.4%}.

‡ Crystal data for **1**. $C_{14}H_{22}AsLiO_2$, $M = 304.18$, monoclinic, space group $P2_1$, $Z = 2$, $a = 8.150(2)$, $b = 8.564(2)$, $c = 11.278(2)$ Å, $\beta = 101.87(3)°$, $V = 770.3(3)$ Å^3, μ(Mo-Kα) = 1.311 mm^{-1}, $T = 180(2)$ K. Data were collected on an Siemens-Stoe AED diffractometer. Of a total of 2438 reflections collected, 2004 were independent ($R_{int} = 0.051$). Final $R1 = 0.104$ [$I>2\sigma(I)$] and $wR2 = 0.244$ (all data). The high residual R value is the result of poor crystal quality (resulting from very high air-sensitivity) and from the extensive disorder in both of the thf molecules, which could only be modelled approximately. C(12)–C(14) and O(1) of one thf molecule, and C(9) and C(10) of the other were modelled over two sites with *ca.* 50:50 occupancy. CCDC reference number 186/1464. See http:/www.rsc.org/suppdata/dt/1999/1921/ for crystallographic files in .cif format.

1 K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1994, **37**, 47; R. E. Mulvey, *Chem. Rev.*, 1991, **20**, 167.

2 F. Pauer and P. P. Power, *Lithium Chemistry, A Theoretical and Experimental Overview*, eds. A.-M. Sapse and P. v. R. Schleyer, Wiley, New York, 1995, ch. 9, pp. 295; M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, 1995, vol. 1, ch. 1, p. 1.

3 R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339.

4 J. D. Smith, *Angew. Chem.*, 1998, **110**, 2181; *Angew. Chem., Int. Ed.*, 1998, **37**, 2071.

5 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373.

6 M. A. Beswick, J. M. Goodman, C. N. Harmer, A. D. Hopkins, M. A. Paver, P. R. Raithby, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1997, 1897.

7 E.-M. Hey and F. Weller, *J. Chem. Soc., Chem. Commun.*, 1992, 220.

8 R. A. Bartlett, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1986, **25**, 1243.

9 N. D. R. Barnett, R. E. Mulvey, W. Clegg and P. A. O'Neil, *J. Am. Chem. Soc.*, 1991, **113**, 8187.

10 For As–Li bonded complexes, see (*a*) G. Becker and C. Whitthauer, *Z. Anorg. Allg. Chem.*, 1982, **492**, 28; (*b*) A. M. Arif, R. A. Jones and K. B. Kidd, *J. Chem. Soc., Chem. Commun.*, 1986, 1440; (*c*) R. A. Barlett, H. V. R. Dias, H. Hope, B. D. Murray, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1986, **108**, 6921; (*d*) M. Driess and H. Pritzkow, *Angew. Chem.*, 1992, **104**, 350; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 316; (*e*) L. Zsolnai, G. Huttner and M. Driess, *Angew. Chem.*, 1993, **105**, 1549; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1439; (*f*) L. J. Jones, A. T. McPhail and R. L. Wells, *J. Coord. Chem.*, 1995, **34**, 119; (*g*) M. Driess, H. Pritzkow, S. Martin, S. Rell, D. Fenske and G. Baum, *Angew. Chem.*, 1996, **35**, 986; *Angew. Chem., Int. Ed. Engl.*, 1996, **108**, 1064; (*h*) M. Driess, K. Merz, H. Pritzkow and R. Janoschek, *Angew. Chem.*, 1996, **108**, 2688; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2507.

11 For other As–M bonded complexes, see A. Belforte, F. Calderazzo, A. Morvillo, G. Pelizzi and D. Vitali, *Inorg. Chem.*, 1984, **23**, 1504.

12 R. A. Jones, S. U. Koschmieder and C. M. Nunn, *Inorg. Chem.*, 1987, **26**, 3610; G. Becker, H. M. Hartmann and W. Z. Schwarz, *Z. Anorg. Allg. Chem.*, 1989, **577**, 9.

13 C. S. Palmer and R. Adams, *J. Am. Chem. Soc.*, 1922, **44**, 1356.

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