

A bis(imido)organoarsenate dianion incorporating *n*-butyllithium

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Reaction of  $\text{AsCl}_3$  with 3 equivalents of  $(2\text{-OPh})\text{C}_6\text{H}_4\text{NH}_2$  in toluene/ $\text{NEt}_3$ , followed by metallation with 3 equivalents of  $\text{Bu}^n\text{Li}$  produces a bis(imido)organoarsenate dianion as a lithium salt which co-complexes  $\text{Bu}^n\text{Li}$  to form a dimeric cage with a 14 membered core.

Recently we have been interested in the development of anionic ligands involving p-block elements and imido groups. We have succeeded in synthesising the imido analogues of both the orthophosphate and phosphite anions from reactions of phosphorus halides with primary amines, followed by metallation using *n*-butyllithium.<sup>1,2</sup> The lithium salt of the imidophosphite dianion  $[\text{Li}_2\text{HP}(\text{NR})_3]_2$  is produced from reaction of  $\text{PCl}_3$  with 3 equivalents of 2-methoxyaniline in  $\text{thf}/\text{NEt}_3$  and subsequent metallation with  $\text{Bu}^n\text{Li}$  (3 equivalents).<sup>2</sup> Use of more elaborate NH sources such as hydrazones give significantly different products. Similar reaction to that described above with benzophenone hydrazone in place of 2-methoxyaniline produces a salt that contains the bis(imido)organo dianion  $[\text{Li}_2\text{Bu}^n\text{P}(\text{NR})_2]_2 \cdot 4\text{thf}$ .<sup>3</sup> A more straightforward synthesis of comparable bis(imido)phosphine dianions is the reaction of  $\text{PhPCl}_2$  with benzophenone hydrazone (1:2 equivalents) in  $\text{thf}/\text{NEt}_3$ , followed by metallation of the reaction mixture with 2 equivalents  $\text{Bu}^n\text{Li}$  giving  $[\text{Li}_2\text{PhP}(\text{NR})_2]_2 \cdot 6\text{thf}$  in good yield.<sup>3†</sup>

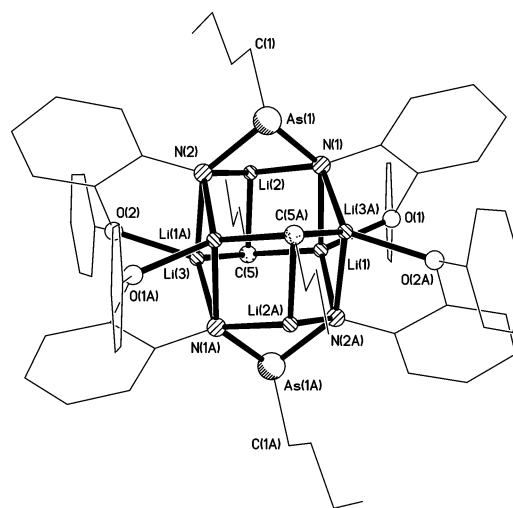
Reports of comparable imido arsenic anions are more scarce. Chivers *et al.* recently reported that bis(imido)organoarsenate dianions may be prepared from metallation of  $\text{RAs}\{\text{N}(\text{H})\text{R}'\}_2$  with  $\text{Bu}^n\text{Li}$ ,<sup>4,5</sup> and that subsequent reaction with chalcogens oxidises the arsenic centre rather than inserting in the Li–N bonds.<sup>4</sup> Wright *et al.* have prepared imido arsenate  $[\text{As}(\text{NR})_3]_3^{3-}$  and  $[\text{E}_2(\text{NR})_4]_2^{2-}$  dianions by reaction of  $\text{As}(\text{NMe}_2)_3$  with primary amines and their lithium salts.<sup>6</sup> We have shown that similar trianions may be prepared from the reaction of  $\text{AsCl}_3$  with 3 equivalents of  $\text{RNH}_2$  ( $\text{R} = (2\text{-OMe})\text{C}_6\text{H}_4$ ,  $\text{CH}_2\text{Ph}$ ) in  $\text{thf}/\text{NEt}_3$ , followed by metallation with 3 equivalents of  $\text{Bu}^n\text{Li}$ .<sup>7</sup> Using related chemistry, we report here a synthesis of the lithium salt of the bis(imido)organoarsenate dianion that cocomplexes *n*-butyllithium to give a complex that demonstrates a new structural motif in the rapidly expanding field of imido p-block anions.<sup>8</sup>

Reaction of a toluene/ $\text{NEt}_3$  solution of  $\text{AsCl}_3$  with 2-phenoxyaniline (1:3 equivalents) followed by metallation with 3 equivalents of  $\text{Bu}^n\text{Li}$ , does not produce the expected  $[\text{As}(\text{NR})_3]_3^{3-}$  trianion. Instead the resulting complex  $\text{Li}_6\text{Bu}_2^{n-}[\text{Bu}^n\text{As}(\text{NR})_2]_2$  (**1**), contains a lithium bis(imido)organoarsenate salt which forms a cocomplex with *n*-butyllithium.

Preliminary investigations were undertaken to establish the identity of (**1**) using elemental analyses (C, H, N), IR and  $^1\text{H}$  NMR spectroscopy. It was observed that the signal for the NH resonance in both the IR and  $^1\text{H}$  NMR spectra was absent, indicating that full metallation of the amide protons had occurred. However, the  $^1\text{H}$  NMR spectrum showed several multiplets in the low frequency region that we took to show the presence of alkyl groups. On the basis of this observation, a more detailed crystallographic investigation was undertaken.

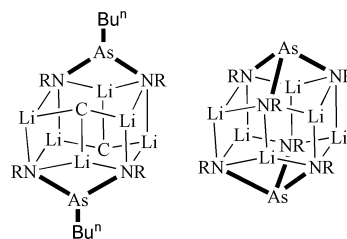
A low-temperature X-ray crystallographic study of the product shows it to be an ion-contacted dimeric structure

that lies about an inversion centre and comprises two  $[\text{Bu}^n\text{As}(\text{NR})_2]_2^{2-}$  dianions and two  $\text{Bu}^n$  monoanions linked together by six lithium cations to form a 14 membered  $\text{As}_2\text{N}_4\text{-C}_2\text{Li}_6$  cage (Fig. 1).



**Fig. 1** Crystal structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) include: As(1)–N(1) 1.875(2), As(1)–N(2) 1.879(2), As(1)–C(1) 1.993(2), N(1)–Li(1) 2.111(5), N(1)–Li(2) 2.022(5), N(2)–Li(2) 2.054(5), N(2)–Li(3) 2.128(5), Li(1)–C(5) 2.166(5), Li(2)–C(5) 2.137(5), Li(3)–C(5) 2.187(5); N(1)–As(1)–N(2) 88.30(9), N(1)–As(1)–C(1) 101.72(10), N(2)–As(1)–C(1) 99.95(10). Symmetry equivalents used to generate equivalent atoms labelled “A”:  $1 - x, 2 - y, 1 - z$ .

At first glance, this appears related to the 14 membered  $\text{As}_2\text{N}_6\text{Li}_6$  cages often seen in the structures of the lithium salts of triimido arsenate trianions,<sup>6,7</sup> whereas in fact the two systems are quite different (Fig. 2).



**Fig. 2** The core structures of **1** and  $D_{3d}$   $\text{Li}_6\text{As}_2\text{N}_6$ .

Both are formed around *pseudo* hexagonal prismatic lithium/heteroatom cores. However, in  $[\text{Li}_3\text{As}(\text{NR})_3]_2$ , two pyramidal  $[\text{As}(\text{NR})_3]_3^{3-}$  units interlink with six Li atoms to form a core structure of approximately  $D_{3d}$  symmetry. In contrast, **1** consists of six  $\text{Li}^+$  cations and two  $[\text{Bu}^n\text{As}(\text{NR})_2]_2^{2-}$  dianions (each of which contribute  $\text{AsN}_2$  vertices to the core structure as described) and the remaining vertices coming from separate *n*-butyl anions. Hence two As–N vectors of  $[\text{Li}_3\text{As}(\text{NR})_3]_2$  are not matched by corresponding As–C vectors in **1**. The  $[\text{Bu}^n\text{As}(\text{NR})_2]_2^{2-}$  dianion units of **1** closely resemble those in the

previously reported bis(imido)organoarsenate dianions, that of  $[\text{PhAs}(\text{NBU})_2]^{2-}$  which was isolated both as a thf solvated monomeric lithium salt,<sup>4</sup> and as an unsolvated dimeric species.<sup>5</sup> The As centres in **1** have extremely distorted trigonal pyramidal geometries. The N–As–N angles of 88.30(9)° and the N–As–C angles of 99.95(10)° and 101.72(10)° are extremely compressed from the ideal tetrahedral bond angle which underlines the flexibility of the imido arsenic units to accommodate distortions to the predicted geometry imposed by the core structure. The As–N bond lengths of 1.875(2) and 1.879(2) Å are characteristic of As–N single bonds as has been previously observed in other imido and amido As(III) compounds.<sup>6,7</sup>

There are two separate lithium environments in the molecule; Li(1) and Li(3) are four coordinate, being bound to one imido nitrogen atom from each  $[\text{Bu}^n\text{As}(\text{NR})_2]^{2-}$  unit {Li–N distances range from 2.103(5) to 2.168(5) Å} and have additional shorter Li–O contacts with an oxygen centre from a phenoxy sidearm {Li–O 1.980(5) and 1.973(5) Å} and to a carbon atom from the *n*-butyl moiety {Li–C 2.166(5) and 2.187(5) Å}. The other lithium environment is three coordinate, more strongly bonded than the other lithium atoms to both the imido nitrogen centres {Li–N 2.022(5) and 2.054(5) Å} and the *n*-butyl group {Li–C 2.137(5) Å}. Correspondingly, the imido centres are five coordinate, being bound to three Li centres, a carbon atom of the aromatic ring and the arsenic centre. The  $\alpha$ -carbon of the *n*-butyl anion is six coordinate, being bound to two H atoms and a C atom of the *n*-butyl chain and to a further three Li centres. The coordination environment of this carbon atom is very similar to that seen for the equivalent C centre in parent  $(\text{Bu}^n\text{Li})_6$ .<sup>9</sup>

The reaction used to prepare **1** has evidently not followed the predicted pathway observed in our previous studies. Presumably, complex **1** results from one of two pathways in a similar fashion to that observed for both related phosphorus and boron species.<sup>3,10</sup> Either, the  $\text{Bu}^n\text{Li}$  may act as both a nucleophile and a base and may substitute an amide group of a fully aminated intermediate,  $\text{As}\{\text{N}(\text{H})\text{R}\}_3$ , which accompanied by metallation of the remaining amide protons and complexation of additional  $\text{Bu}^n\text{Li}$  would produce **1**. Alternatively, amination in the first step is incomplete giving  $\text{ClAs}\{\text{N}(\text{H})\text{R}\}_2$ ; reaction of this with  $\text{Bu}^n\text{Li}$  would be expected to deprotonate the amido protons and to eliminate LiCl. Complexation of additional  $\text{Bu}^n\text{Li}$  would then produce **1**. Further investigation will be required to assign the mechanism that is operating. The reasons for the difference in reactivity between the 2-phenoxyaniline {which produces the bis(imido)organo arsenate dianion seen here} and 2-methoxyaniline {which yields  $[\text{As}(\text{NR})_3]^{3-}$ } are unclear. It may simply be a case of preferential crystallisation of a specified product although the additional steric bulk of the phenoxy sidearm may play a role.

Whilst cocomplexation of  $\text{Bu}^n\text{Li}$  is rare, it is not completely unprecedented. Several other examples are known in which lithiated anions form complexes with organolithium reagents. Snaith *et al.* found that by treating diphenylamine with a sixfold excess of  $\text{Bu}^n\text{Li}$  led to an unusual product involving both lithiated amine and the organolithium reagent.<sup>11</sup> More recently, Chivers *et al.* reported that *unsolvated*  $\text{Bu}^n\text{Li}$  and  $\text{Bu}^t\text{Li}$  are incorporated within group 13 amido/imido anions in a similar way as observed in this current Communication.<sup>12,13</sup>

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## Notes and references

† Synthesis of **1**:  $\text{AsCl}_3$  (0.22 ml, 2.5 mmol) was added dropwise to an ice-cooled stirred solution of (2-OPh) $\text{C}_6\text{H}_4\text{NH}_2$  (1.39 g, 7.5 mmol) in toluene (30 ml) and  $\text{NEt}_3$  (3 ml) and stirred for 1 h at room temperature. A white solid was observed, the solution was filtered (porosity 3 sinter with celite).  $\text{Bu}^n\text{Li}$  (4.69 ml, 1.6 mol l<sup>-1</sup> in hexanes, 7.5 mmol) was added dropwise to give a bright yellow solution. Colourless crystalline blocks of complex **1** were obtained by removal of approximately 10 ml solvent *in vacuo* and storage of the resulting solution for 16 h at 25 °C.

Yield: 0.78 g (54% wrt  $\text{AsCl}_3$ ); mp 156 °C; decomposes to a brown oil at 165 °C; Anal. calc. for  $\text{C}_{32}\text{H}_{36}\text{AsLi}_3\text{N}_2\text{O}_2$ : C, 66.68; H, 6.30; N, 4.86. Found C, 66.57; H, 6.53; N, 4.66%; <sup>1</sup>H NMR data (thf-d<sup>8</sup>, 25 °C, 300 MHz):  $\delta$  = 5.55–7.2 (collection of m, 18H,  $-\text{NC}_6\text{H}_4\text{OC}_6\text{H}_5$ ), 0.6–2.2 (series of overlapping m, 18H,  $\text{AsCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{LiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); IR (Nujol mull) no distinguishing absorptions.

Crystal data for **1**:  $\text{C}_{64}\text{H}_{72}\text{As}_2\text{Li}_6\text{N}_4\text{O}_4$ ,  $M = 1150.74$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.996(2)$ ,  $b = 21.075(4)$ ,  $c = 12.603(3)$  Å,  $\beta = 95.78(3)^\circ$ ,  $V = 2905.8(1)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 1.201$  mm<sup>-1</sup>, 20448 reflections measured, 6664 unique ( $R_{\text{int}} = 0.053$ ), final  $R = 0.0422$  for  $I > 2\sigma(I)$ . X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å).<sup>14</sup> The structure was solved by direct methods and refined by least squares on  $F^2$  values for all reflections.<sup>15</sup> Absorption corrections were applied, based on multiple and symmetry equivalent measurements.<sup>16</sup> CCDC reference number 208893. See <http://www.rsc.org/suppdata/dt/b3/b304307j/> for crystallographic data in CIF or other electronic format.

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