DALTON
FULL PAPER

Synthesis, structures and coordination behaviour of $[As(NR)_3]^{3-}$ trianions

Allan Bashall,[a] Andrew D. Bond,[b] Alexander D. Hopkins,[b] Sara J. Kidd,[b] Mary McPartlin,[a] Alexander Steiner,[c] Robert Wolf,[b] Anthony D. Woods[b] and Dominic S. Wright*[b]

[a] *School of Applied Chemistry, University of North London, London, UK N7 8DB*
[b] *Chemistry Department, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: dsw1000@cus.cam.ac.uk*
[c] *Chemistry Department, University of Liverpool, Crown Street, Liverpool, UK L69 7ZD*

Received 31st July 2001, Accepted 2nd November 2001
First published as an Advance Article on the web 9th January 2002

Re-examination of the X-ray structure of the imido As(III) complex previously formulated as $[\{As(N^tBu)_3\}_2Li_6]\cdot$benzene (**1**·benzene) indicates that the disorder within the $[\{As(N^tBu)_3\}_2Li_6]$ cage can be better explained by the molecular formulae $[\{As(N^tBu)_3\}_2Li_6]\cdot[LiNH^tBu]_6$ or $[\{As(N^tBu)_3\}Li_3\cdot(^tBuNHLi)_3]$. The syntheses and X-ray structures of the new complexes $[\{As(N(2\text{-}MeO\text{-}C_6H_4)_3)\}_2Li_6\cdot 2TMEDA]$ (**3**) and $[As\{N(2\text{-}py)\}_3\cdot LiN(2\text{-}py)\cdot 3thf]_2\cdot 2thf$ (**4**·2thf), containing $[As(NR)_3]^{3-}$ anions, are reported. Attempts to prepare the heteroleptic trianion $[As(NCy)_2(NCH_2Ph)]_3^-$ *via* reaction of the arsazane dimer $[CyNHAs(\mu\text{-}NCy)]_2$ (**5**) with $PhCH_2NHLi$ (1 : 6 equivalents) led to the unexpected formation of Zintl compounds containing the As_7^{3-} anion. The X-ray structure of $[As_7Li_3\cdot 3(CyNH_2)\cdot 3thf]$ **6** is also reported.

In recent years the chemistry of Group 15 imido anions, such as the trianions $[E(NR)_3]^{3-}$ [1] and the dianions $[E_2(NR)_4]^{2-}$ (E = P–Bi),[2,3] has been the focus of considerable attention.[3,4] We have developed a general synthetic methodology for the synthesis of several distinct classes of Group 15 imido anion frameworks, involving reactions of the Group 15 dimethylamido reagents $E(NMe_2)_3$ (E = As, Sb, Bi) with primary amines (RNH_2) and primary amido alkali metal compounds (RNHM; M = alkali metal).[4] Anions of this type have been shown to act as highly flexible ligands to an extensive range of main group and transition metals.[4]

So far the majority of our studies have concentrated on the heavier Group 15 elements (Sb and Bi). However, motivated by the observation that the coordination characteristics of these ligand systems can be dramatically modified by varying the Group 15 element present within them,[5] we have more recently begun to explore the synthesis and coordination chemistry of the P and As analogues. In a preliminary report, we showed that $[\{As(N^tBu)_3\}_2Li_6]$, containing the $[As(N^tBu)_3]^{3-}$ trianion, can be obtained in unsolvated and benzene solvated forms (**1** and **1**·benzene, respectively) from the reaction of $As(NMe_2)_3$ with $^tBuNH_2$ and ^tBuNHLi (1 : 3 : 3 equivalents).[6] More recently, Russell and coworkers have used a modified procedure, involving reaction of $AsCl_3$ with RNH_2 followed by lithiation of the proposed intermediate $As(HNR)_3$ with ^nBuLi, in the preparation of similar cage complexes containing $[As(NR)_3]^{3-}$ trianions.[7]

We report here a full account of our preliminary studies of the preparation of trianions of this type using $As(NMe_2)_3$. The syntheses and structures of the new cage complexes $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6\cdot 2TMEDA$ (**3**) [TMEDA = $(Me_2NCH_2)_2$] and $[As(N\text{-}2\text{-}py)_3Li_3\cdot LiNH(2\text{-}py)\cdot 3thf]_2\cdot 2thf$ (**4**·2thf) (2-py = 2-pyridyl) are presented, with a re-examination of the previously reported complex $[\{As(N^tBu)_3\}_2Li_6]\cdot$benzene (**1**·benzene). Attempts to prepare a cage complex containing the heteroleptic trianion $[As(NCy)_2(NCH_2Ph)]^{3-}$ (Cy = cyclohexyl) from the reaction of the arsazane dimer $[CyNHAs(\mu\text{-}NCy)]_2$ (**5**) with excess $[PhCH_2NHLi]$ led to the surprising formation of Zintl compounds containing the As_7^{3-} anion. The crystal structure of the new Zintl compound $[As_7Li_3\cdot 3H_2NCy\cdot 3thf]$ (**6**) is reported.

Results and discussion

In contrast to $Sb(NMe_2)_3$, $As(NMe_2)_3$ does not react with ^tBuNHLi (1 : 3 equivalents) to give the desired trianion, $[As(N^tBu)_3]^{3-}$.[6] This difference can be attributed to the lower reactivity of the As(III) reagent, stemming from the lower polarity of As–N bonds compared to Sb–N bonds. In order to circumvent this problem, the reaction of $As(NMe_2)_3$ (1 equivalent) with a mixture of $^tBuNH_2$ and ^tBuNHLi (3 : 3 equivalents) in hexane solvent was used in the preparation of $[\{As(N^tBu)_3\}_2Li_6]$ (**1**). We also reported that the benzene solvate $[\{As(N^tBu)_3\}_2Li_6]\cdot$benzene (**1**·benzene) can be obtained by recrystallisation of unsolvated **1** from benzene. Presumably, the synthesis of **1** involves the initial formation of $As(NH^tBu)_3$, which is then metallated by ^tBuNHLi (Scheme 1). This sequence is similar to that employed by Russell in the later synthesis of two other cages of this type, $[\{As(NCH_2Ph)_3\}_2Li_6]$ and $[As\{N(2\text{-}MeOC_6H_4)\}_3]Li_6\cdot n$thf (*n* = 1 and 2), only using ^nBuLi as the metallating source.

$$As(NMe_2)_3 \xrightarrow{^tBuNH_2} As(NH^tBu)_3 \xrightarrow[-3^tBuNH_2]{+3^tBuNHLi} {}^1/_2[\{As(N^tBu)_3\}_2Li_6]$$

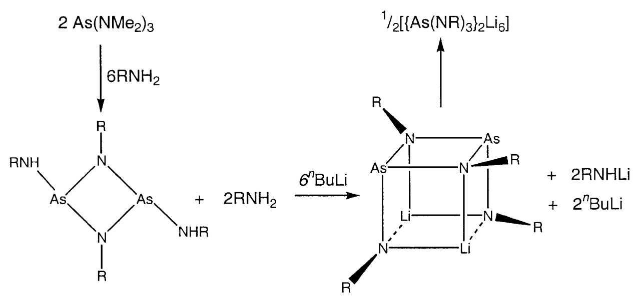
Scheme 1

Both the solid-state structures of **1** and **1**·benzene were extensively disordered. This was initially attributed to the similarity of the As–N and Li–N bond lengths and to the similar trigonal pyramidal coordination environments for Li and As, resulting in 50 : 50 site disorder between the As centre and three symmetry-related Li^+ cations of their $As_2N_6Li_6$ cores (corresponding to random rotation of the cores, which leave the ^{t}Bu groups in the same sites). However, we now report that reinvestigation of the structure of **1**·benzene reveals a far more complicated situation.

Prompted by a desire to improve the quality of the data on

DOI: 10.1039/b106913f

these species, the new solvate '$[\{As(N^tBu)_3\}_2Li_6]$·toluene' (**1**·toluene) was prepared by the reaction of $As(NMe_2)_3$ (in toluene) with $^tBuNH_2$ (1 : 3 equivalents), followed by addition of ^nBuLi (3 equivalents) in hexane (Scheme 2). The low-temperature (180 K) X-ray structure of the toluene solvate reveals that it is isomorphous and isostructural with **1**·benzene (with disordered toluene replacing benzene on the $\bar{3}$m site), crystallising in the same rhombohedral space group, $R\bar{3}m$. Refinement of the structure of the $[\{As(N^tBu)_3\}_2Li_6]$ cage (Fig. 1a) in the same manner as that undertaken previously for **1**·benzene led to a high R_1 ($I > 2\sigma$) value of 0.095, but with the data apparently being of good quality (R_{int} = 0.043) (*cf.* a similar situation occurs for **1**·benzene, with R_1 = 0.095 and R_{int} = 0.076). By varying the occupancy of the As(III) centre and the Li^+ cations, it is found that there is no partial occupancy of the six symmetry-related Li^+ sites by As. Instead, a better model for this situation is that the As(III) centre alone is assigned half occupancy. This refinement results in a significant reduction of R_1 ($I > 2\sigma$) to 0.065, with more reasonable displacement factors for the As atoms. Similar refinement of the data for **1**·benzene leads to a reduction in R_1 from 0.095 to 0.059, strongly indicating that this complex has a similar composition to the toluene solvate. The exact composition of the arene (benzene and toluene) solvates cannot be ascertained on the basis of their X-ray structures alone, since both a co-crystallised mixture of $[\{As(N^tBu)_3\}_2Li_6]$ with the hexamer $[^tBuNHLi]_6$ (shown in Fig. 1b) (*i.e.*, **1**·$[^tBuNHLi]_6$·2arene) and the single compound $[\{As(N^tBu)_3\}Li_3·(^tBuNHLi)_3]$·arene (illustrated in Fig. 1c) represent possible overall formulae which, if disordered, would explain the observed crystal structure. Attempts to refine the unsolvated complex $[\{As(N^tBu)_3\}_2Li_6]$ (**1**) in a similar way failed, and the original formulation and model for the disorder of this complex proposed by us earlier appears to be correct.



Scheme 2

The realisation of the more complicated nature of the benzene and toluene solvates prompted us to undertake an extensive reinvestigation of the formation of the $[As(N^tBu)_3]^{3-}$ trianion. Various reactions of $As(NMe_2)_3$ with $^tBuNH_2$ and ^nBuLi (1 : 3 : 3 equivalents) in hexane/toluene were performed, with reaction times (after addition of ^nBuLi) from 5 min to 72 h at reflux. These extensive studies reveal that the isolated product contains significant amounts of $[^tBuNHLi]_n$. This is seen in the IR spectra of samples by the presence of a N–H stretching band at 3215 cm^{-1}, which (owing to its low intensity) was overlooked in the original study. The room-temperature ^1H NMR behaviour of isolated crystalline samples (in benzene) is highly complicated and several minor resonances in the region δ 1.00 and 1.60, which intensify with prolonged reaction, appear to result from thermal decomposition. However, despite this complexity, some fundamental conclusions can still be drawn from these studies. Only very minor traces of the free octamer $[^tBuNHLi]_8$ can generally be observed in the room-temperature ^1H NMR spectra (in D_6-benzene) of the products [δ = −1.46 (s, N–H), 1.38 (s, ^tBu); *cf.* values of δ = −1.45 and 1.37 reported previously for this species[8]]. Instead, a new ^tBuNHLi-containing species forms one of the major components [δ = −0.85 (s, N–H) and 1.29 (s, ^tBu); relative integral 1 : 9, respectively]. The identity of this solution species is uncertain. However, it seems unlikely that the free hexamer $[^tBuNHLi]_6$ (possibly present in the solid-state as **1**·$[^tBuNHLi]_6$) would have a stable existence in solution, and no similar resonance has been observed for $[^tBuNHLi]_8$ in the same solvent.[8] The other major resonance [δ = 1.51 (s)] can be assigned to the $[As(N^tBu)_3]^{3-}$ trianion. A variable-temperature ^1H NMR study in toluene solution shows that the two major resonances [*i.e.*, δ = 1.29 and 1.51] dominate the spectrum, down to −60 °C. The ratio of the $[As(N^tBu)_3]^{3-}$ trianion resonance to the

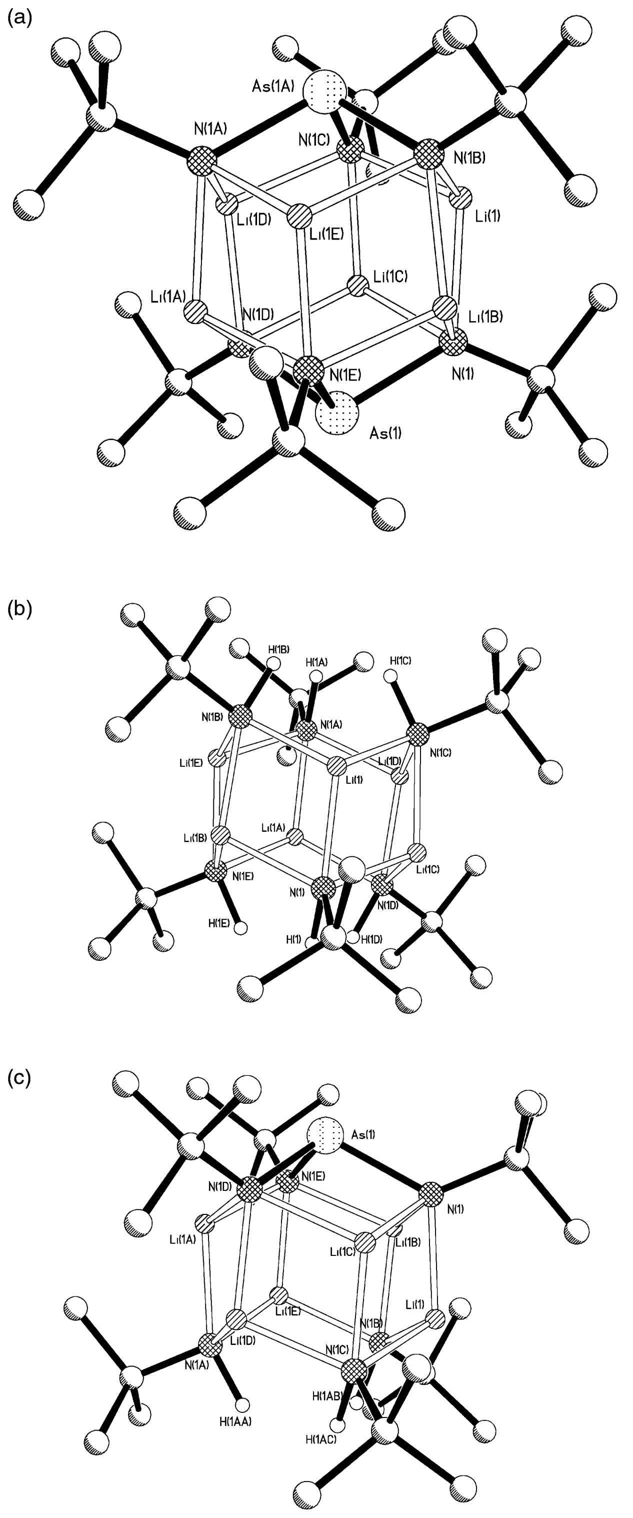
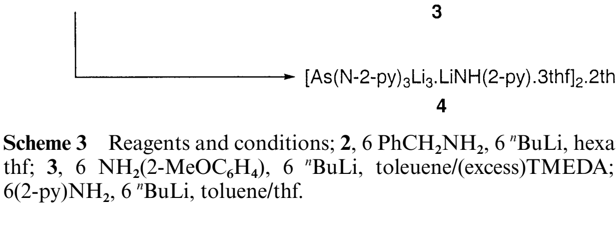


Fig. 1 (a) Structure of $[\{As(N^tBu)_3\}_2Li_6]$; the possible components of the disorder: (b) the hexamer of $[^tBuNHLi]_6$; (c) the complex $[\{As(N^tBu)_3Li_3·(^tBuNHLi)_3]$.

resonance for the unidentified ^{t}BuNHLi-containing species is approximately 1–1.2 : 1 (depending on reaction time). Significantly, the room-temperature ^{7}Li NMR spectrum is dominated by two very distinct Li resonances [δ = 0.83, 1.15 (relative to LiCl/D_2O)], in *ca.* 1 : 1 ratio, and these resonances dominate the spectrum down to −60 °C. Our original suggestion that the presence of different ^{t}Bu resonances in the ^{1}H NMR spectrum of **1** at room temperature may be due to restricted rotation of the ^{t}Bu groups within the $As_2N_6Li_6$ core therefore appears to be in error. Thus, although the amount of $[As(N^tBu)_3]^{3-}$ trianion formed increases with reaction time, the new formulation of the benzene solvate (indicated by the reassessment of the solid-state molecular disorder, above) in fact appears to be more representative of the major product of this reaction. The isolation of crystalline unsolvated **1** or of the ^{t}BuNHLi-containing benzene or toluene solvates therefore appears to be the result of preferential crystallisation in the presence or absence of an arene solvent.

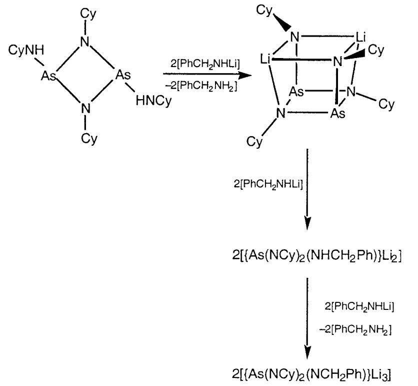
A fundamental problem in obtaining 'pure' **1** (*i.e.*, in isolation from $[{}^tBuNHLi]_n$) may well be the large steric demands of the primary amine precursor, making the formation of the likely intermediate in this reaction, the tris(amido) As(III) species $[As(NH^tBu)_3]$, less favourable. This conclusion can be drawn from the result of attempts to generate the $[As(NCy)_3]^{3-}$ anion from the reaction of $As(NMe_2)_3$ with $CyNH_2$ (1 : 3 equivalents), followed by lithiation with ^{n}BuLi (3 equivalents) (in hexane). Only the previously reported complex $[\{As_2(NCy)_4\}_2Li_4]_2$ (containing the $[As_2(NCy)_4]^{2-}$ dianion)[4a] could be isolated in this case (as confirmed by X-ray analysis), suggesting that the formation of $[As(NHCy)_3]$ is less favourable than the arsazene dimer $[CyNHAs(\mu\text{-}NCy)]_2$ under these conditions. Where sterically demanding organic substituents (R) are present, an alternative mechanism for the generation of the $[As(NR)_3]^{3-}$ anions may be envisaged (Scheme 2). It is noteworthy in this regard that reaction of this mixture with ^{n}BuLi results in the precipitation of hexane-insoluble CyNHLi, which is therefore not available for the formation of $[As(NCy)_3]^{3-}$ under these conditions. However, in contrast, ^{t}BuNHLi is soluble in hexane and further addition can therefore lead more easily to the formation of $[As(N^tBu)_3]^{3-}$, *via* the mechanism outlined in Scheme 2. An attempt to force the formation of $[As(NH^tBu)_3]$ (in a 1 : 3 reaction of $As(NMe_2)_3$ with ^{t}BuNH$_2$ in hexane for 3 h at reflux), prior to reaction with ^{n}BuLi (3 equivalents) (12 h at reflux), again failed to generate 'pure' $[\{As(N^tBu)_3\}Li_6]$ **1**.

In contrast to the complicated situation observed in the reaction of $As(NMe_2)_3$ with ^{t}BuNH$_2$, analogous reactions of $As(NMe_2)_3$ with other, less sterically demanding amines, followed by metallation with ^{n}BuLi, generally occur far more smoothly. The complexes $[\{As(NCH_2Ph)_3\}_2Li_6\cdot 4thf]$ (**2**), $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6\cdot 2TMEDA$ (**3**), and $[As(N\text{-}2\text{-}py)_3Li_3\cdot LiNH(2\text{-}py)\cdot 3thf]_2\cdot 2thf$ (**4**·2thf) have been prepared using this method; the yields being 28.5% for **2**, 35% for **3** and 85% for **4**·2thf (Scheme 3). All of these complexes were initially characterised by elemental analysis and ^{1}H NMR and IR spectroscopy, which confirmed that in the cases of **2** and **3** complete deprotonation of the amines had occurred. However, in the case of **4**·2thf these preliminary studies showed that singly-deprotonated (2-py)NH groups were present in the structure of the complex (N–H str 3481–3283cm^{-1}). This observation is clearly relevant to our reappraisal of the outcome of the reaction of $As(NMe_2)_3$ with ^{t}BuNH$_2$/^{n}BuLi (described above). However, the nature of the association of the N(2-py) and (2-py)NH components and the elaborate structure of **4** could not be fully appreciated until a later X-ray crystallographic study. During the course of these studies the syntheses and structures of **2** (18% yield) and $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6\cdot n$thf ($n$ = 1 and 2) (30% yield) [containing the same $N(2\text{-}MeOC_6H_4)$ ligand as that present in **3**] were reported.[7] No valid comparisons regarding the relative efficiencies of the different methods of the synthesis of this type of cage [employing $AsCl_3$ or $As(NMe_2)_3$] can be drawn at this stage, particularly bearing in mind the different conditions for crystallisation of the products used and/or Lewis base ligands present, and there are obvious advantages in either method of synthesis. Thus, whereas $AsCl_3$ is a more accessible and cheaper reagent than $As(NMe_2)_3$, the reaction times necessary in the preparation of **2**, **3** and **4**·2thf are of the order of a few minutes at reflux (compared to 16 h at room temperature). The synthesis of **2** is described in detail in the Experimental section, however, since the structural features of the complex obtained by us are identical to those reported earlier, it would not be appropriate to discuss the nature of the complex further here.



Scheme 3 Reagents and conditions; **2**, 6 $PhCH_2NH_2$, 6 ^{n}BuLi, hexane/thf; **3**, 6 $NH_2(2\text{-}MeOC_6H_4)$, 6 ^{n}BuLi, toleuene/(excess)TMEDA; **4**, 6(2-py)NH$_2$, 6 ^{n}BuLi, toluene/thf.

As part of this study, we began to explore the potential generation of heteroleptic (mixed-ligand) As(III) trianions of this type. The one-pot reaction of arsazane dimer [prepared *in situ* from $As(NMe_2)_3$ and $CyNH_2$ (1 : 2 equivalents)][9] with excess $PhCH_2NHLi$ (3 equivalents) was undertaken in an attempt to prepare the $[As(NCy)_2(NCH_2Ph)]^{3-}$ anion (Scheme 4). Briefly bringing the reaction mixture to reflux resulted in an intensification of the colour, from pink-red to a deep red-purple. Remarkably, instead of obtaining the desired heteroleptic anion (or indeed any other As–N bonded imido or amido arrangement) only the Zintl compound $[As_7Li_3\cdot 3H_2NCy\cdot 3thf]$ (**6**) could be isolated from this reaction (although in moderately low yield of 17%). Repeating the reaction in the presence of TMEDA results in the formation and solation of the previously characterised Zintl compound $[As_7Li_3\cdot 3TMEDA]$ (**7**).[10] Owing to surface degradation of crystals of **6** and **7** once isolated from solution (a long-recognised feature of Zintl compounds, which is associated with desolvation of the Lewis base ligands and reversion to the intermetallic 'alloy' phase[11]), satisfactory analytical and spectroscopic data on them was difficult to obtain. The identity of **7** was finally confirmed by obtaining the unit cell parameters of a crystalline sample (the data being identical with that reported in the literature).[10a] A full X-ray crystallographic data collection was obtained on the new complex **6**, which confirmed its identity. Previously, we have shown



Scheme 4

Table 1 Crystal data for $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6{\cdot}2TMEDA$ (**3**), and $[As(N\text{-}2\text{-}py)_3Li_3{\cdot}LiNH(2\text{-}py){\cdot}3thf]_2{\cdot}2thf$ (**4**) and $[As_7Li_3{\cdot}3H_2NCy{\cdot}3thf]$ (**6**)

	3	**4**	**6**
Empirical formula	$C_{54}H_{74}As_2Li_6N_{10}O_6$	$C_{72}H_{98}As_2Li_8N_{16}O_8$	$C_{30}H_{63}As_7Li_3N_3O_3$
M	1150.71	1521.02	1059.09
T/K	180(2)	180(2)	180(2)
λ/Å	0.7107	0.7107	0.7107
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	14.1001(5)	11.8168(6)	11.3301(3)
b/Å	12.9517(3)	13.2090(6)	14.5022(5)
c/Å	15.8827(5)	14.3578(5)	15.8403(6)
α/°	90	82.657(3)	116.203(2)
β/°	101.239(2)	71.871(3)	98.386(2)
γ/°	90	69.363(2)	103.745(2)
V/Å^3	2844.9(2)	1992.8(2)	2172.5(1)
Z	2	1	1
ρ_{calc}/g cm^{-3}	1.343	1.267	1.691
Total data	17280	19493	25432
Unique data (R_{int})	6470 (0.059)	6933 (0.047)	9891 (0.063)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.035, 0.082	0.049, 0.114	0.042, 0.085
$R1$, $wR2$ [all data]	0.048, 0.088	0.063, 0.120	0.066, 0.093
S	1.032	1.042	1.034

Data in common: λ = 0.71073 Å.

that Zintl compounds containing E_7^{3-} anions (E = As, Sb) can be obtained by thermolysis of Group 15 phosphide arrangements, such as $[\{Sb(PCy)_3\}_2Li_6{\cdot}6Me_2NH]$ (containing the $[Sb(PCy)_3]^{3-}$ trianion).[12] However, the indication from these studies is that this type of reaction is driven thermodynamically by the formation of P–P single bonds (205 kJ mol^{-1}), and that the lower single N–N bond energy (167 kJ mol^{-1}) therefore underpins the greater thermal stability of the imido analogues. Although the mechanism of formation of **6** and **7** is not understood at this stage, their formation appears to indicate a completely different pathway (possibly involving As-centred radical intermediates[13]). Since there is some indication that $[\{As(NCH_2Ph)_3\}_2Li_6{\cdot}4thf]$ (**2**) is thermally unstable (turning red at *ca.* 50 °C[7]), we investigated the use of this complex as a potential precursor for **6** and **7**.[7] However, no products could be isolated from thermolysis reactions of **4** in the presence of TMEDA or $CyNH_2$.

Details of the data collections and refinements for the X-ray structures of complexes **3**, **4** and **6** are given in Table 1. Key bond lengths and angles for **3** and **4** are listed in Tables 2 and 3, and those for **6** are reported in Table 4.

A low-temperature (180 K) crystallographic study of **3** shows that it consists of centrosymmetric cage molecules, of formula $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6{\cdot}2TMEDA$ (Fig. 2). The overall composition of the complex is similar to all other Group 15/Li$^+$ compounds containing $[E(NR)_3]^{3-}$ anions so far structurally characterised, the molecular structure arising from the association of two $[As\{N(2\text{-}MeOC_6H_4)\}_3]^{3-}$ anions by six Li$^+$ cations into a fourteen-membered cage arrangement. However, although a number of similar Group 15 complexes of this type, containing variable amounts of Lewis base solvation of the Li$^+$ cations, have been reported, the structure of **3** presents the first opportunity to assess the structural impact of coordination by a bidentate donor (TMEDA) in such a system.

Comparison of the structure of **3** with the closely related cage complexes $[Sb\{N\text{-}2,4\text{-}(MeO)_2C_6H_3\}_3]Li_6{\cdot}2thf$[3] and $[As\{N(2\text{-}MeOC_6H_4)\}_3]Li_6{\cdot}n\text{thf}$ (n = 2 and 4)[7] is particularly informative. In both of the latter, the 2-MeO groups of the anisidine ligands are involved in extensive intramolecular O–Li solvation of the Li$^+$ cations of their cores. This, and the additional solvation of two of the Li$^+$ cations by thf ligands, results in large distortions in the N_6Li_6 core arrangements from the more symmetrical ('stack-like') structures observed in less solvated cages (such as $[\{Sb(NCy)_3\}_2Li_6{\cdot}2NHMe_2]$[3] and $[\{As(NCH_2Ph)_3\}_2Li_6{\cdot}2thf]$[7]). Although the resulting pattern of intra- and inter-molecular solvation in these species is similar

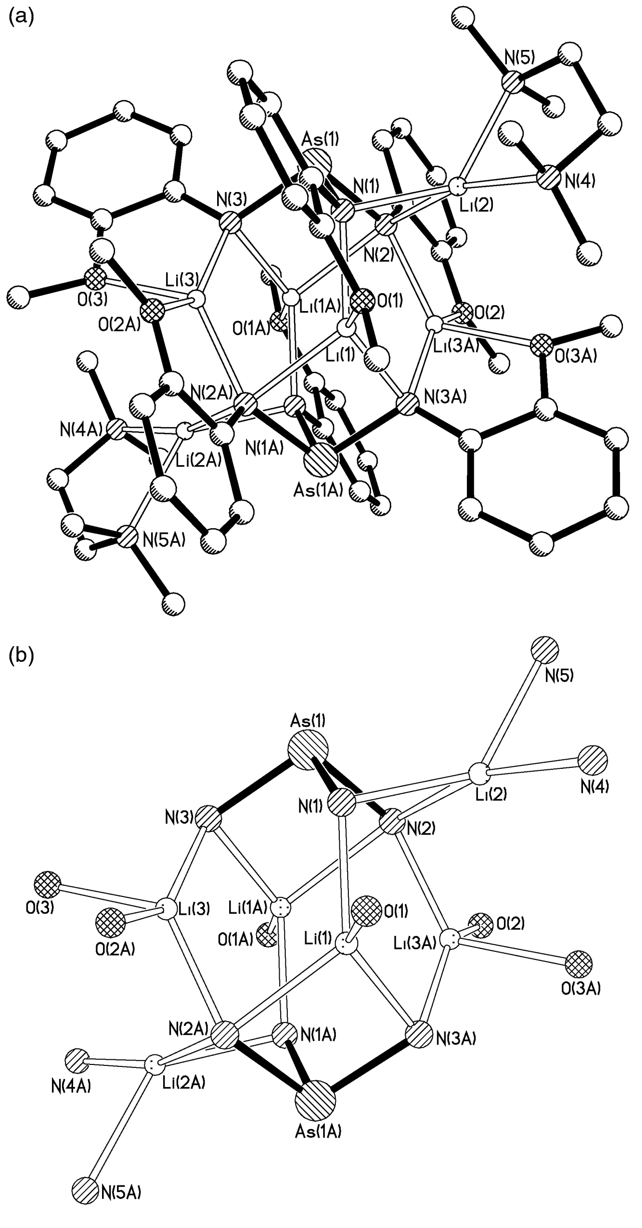


Fig. 2 Structure of cage molecules of $[As\{N(2\text{-}MeOC_6H_4)\}_3]_2Li_6{\cdot}2TMEDA$ (**3**).

in many respects (containing three chemically distinct $\mathrm{Li^+}$ environments within each symmetry-related $[\mathrm{E(NR)_3Li_3}]$ half of the cages), a key difference is the absence of one N–Li core bond in the As complexes. This most probably arises from the relative compactness (smaller ligand bite) of the $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]^{3-}$ anion (As–N mean 1.87 Å [7]) compared to its Sb counterpart (Sb–N mean 2.05 Å [3]).

The core structures present in $[\mathrm{Sb\{N\text{-}2,4\text{-}(MeO)_2C_6H_3\}_3}]_2\mathrm{Li_6}\cdot\mathrm{2thf}$[3] and $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]_2\mathrm{Li_6}\cdot n\mathrm{thf}$[7] and **3** are shown in Fig. 3. The chelation of two of the $\mathrm{Li^+}$ cations of the core in **3** (Fig. 3c) by TMEDA has a dramatic effect on the resulting pattern of intramolecular MeO–Li bonding; giving a core structure which is very different to those observed in $[\mathrm{Sb\{N\text{-}2,4\text{-}(MeO)_2C_6H_3\}_3}]_2\mathrm{Li_6}\cdot\mathrm{2thf}$ and $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]_2\mathrm{Li_6}\cdot n\mathrm{thf}$ (Fig. 3a and 3b, respectively). This TMEDA coordination effectively excludes intramolecular MeO–Li bonding to the chelated Li centre [Li(2)] (Fig. 2), providing the underlying reason for the extensive rearrangement of the pattern of intramolecular MeO–Li bonding within the core. Coordination by TMEDA is also responsible for the extremely large distortion of the $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]^{3-}$ anion {N(1)–As(1)–N(2) 88.88(7)°; *cf.* N(1)–As(1)–N(3) 98.05(8) and N(2)–As(1)–N(3) 99.00(8)°, and 92.1(1)–99.61(9)° in $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]_2\mathrm{Li_6}\cdot n\mathrm{thf}]$[7]}. The bonding of Li(2) to two of the N centres of an $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]^{3-}$ anion [Li(2)–N(1) 2.069(4), Li(2)–N(2) 2.474(4) Å], in addition to coordination by TMEDA, gives this $\mathrm{Li^+}$ ion a highly distorted tetrahedral geometry. A distorted tetrahedral environment also occurs for Li(1), arising from bonding to two of the imido N centres of one of the $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]^{3-}$ anions [Li(1)–N(2A) 2.235(4), Li(1)–N(3A) 2.000(4) Å], one imido N centre of the other anion [Li(1)–N(1) 2.002(4) Å], and anisidine-MeO coordination [Li(1)–O(1) 1.972(4) Å]. This bonding pattern and $\mathrm{Li^+}$ coordination environment is dominant within the structures of $[\mathrm{Sb\{N\text{-}2,4\text{-}(MeO)_2C_6H_3\}_3}]_2\mathrm{Li_6}\cdot\mathrm{2thf}$[3] and $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]_2\mathrm{Li_6}\cdot n\mathrm{thf}$.[7] However, the coordination environment of Li(3) has not been observed previously for any of the Group 15 cage compounds of this type. This $\mathrm{Li^+}$ cation is coordinated only by *one* of the imido N centres of each of the $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]^{3-}$ anions [Li(3)–N(2A) 2.037(4), Li(3)–N(3) 1.965(4)Å] and by *one* of the MeO groups of each of the trianions. The Li centre spans the two anions at the centre of the cage. A very distorted tetrahedral geometry for this $\mathrm{Li^+}$ cation results [N(3)–Li(3)–N(2A) 127.9(2), O(3)–Li(2)–O(2A) 98.1(2)°]. The large range of Li–N bond lengths found in **3** [range 2.000(4)–2.474(4) Å] reflects the presence of three very different coordi-

Table 2 Selected bond distances (Å) and angles (°) for $[\mathrm{As\{N(2\text{-}MeOC_6H_4)\}_3}]_2\mathrm{Li_6}\cdot\mathrm{2TMEDA}$ (**3**)

As(1)–N(1)	1.865(2)	Li(2)–N(2)	2.474(4)
As(1)–N(2)	1.888(2)	Li(2)–N(4)	2.165(4)
As(1)–N(3)	1.858(2)	Li(2)–N(5)	2.192(4)
Li(1)–N(1)	2.002(4)	Li(3)–N(3)	1.965(4)
Li(1)–N(2A)	2.235(4)	Li(3)–N(2A)	2.037(4)
Li(1)–N(3A)	2.000(4)	Li(3)–O(3)	2.083(4)
Li(1)–O(1)	1.972(4)	Li(3)–O(2A)	1.940(4)
Li(2)–N(1)	2.069(4)		
N(1)–As(1)–N(2)	88.88(7)	N(1)–Li(1)–N(3A)	129.4(2)
N(1)–As(1)–N(3)	98.05(8)	N(1)–Li(2)–N(3)	70.0(1)
N(2)–As(1)–N(3)	99.00(8)	N(4)–Li(2)–N(5)	83.6(1)
N(2A)–Li(1)–N(3A)	84.4(1)	N(3)–Li(3)–N(2A)	127.9(2)
N(1)–Li(1)–N(2A)	122.7(2)	O(3)–Li(2)–O(2A)	98.1(2)

Symmetry operations used to generate equivalent atoms labelled A, $-x$, $-y + 1$, $-z$.

Table 3 Key bond distances (Å) and angles (°) for $[\mathrm{As(N\text{-}2\text{-}py)_3Li_3\cdot LiNH(2\text{-}py)\cdot 3thf}]_2\cdot\mathrm{2thf}$ (**4**·2thf)

As(1)–N(1)	1.854(2)	Li(2)–N(7)	2.028(6)
As(1)–N(2)	1.855(2)	Li(3)–N(7)	2.051(7)
As(1)–N(3)	1.860(2)	Li(4)–N(8)	2.061(6)
Li(2)–N(1)	2.135(6)	Li–O(1,2)	mean 1.98
Li(2)–N(2)	2.100(6)	Li(1)–N(4A)	2.089(6)
Li(3)–N(1)	2.060(6)	Li(1)–N(6)	2.097(6)
Li(3)–N(3)	2.079(6)	Li(1)–N(5A)	2.087(6)
Li(4)–N(2)	2.069(6)	As(1) ··· As(1A)	4.271(2)
Li(4)–N(3)	2.120(6)	Li(1) ··· Li(1A)	3.600(9)
		As(1) ··· Li(1)	2.714(6)
		As(1A) ··· Li(1)	2.871(5)
N(1)–As(1)–N(2)	96.3(1)	N(1)–Li(2,3)–N(7)	mean 99.4
N(1)–As(1)–N(3)	91.5(1)	Li(2)–N(7)–Li(3)	78.8(3)
N(2)–As(1)–N(3)	91.2(1)	N(8)–Li(4)–N(2)	120.2(3)
N(1)–Li(2)–N(2)	81.5(2)	N(8)–Li(4)–N(3)	122.3(3)
N(1)–Li(3)–N(3)	80.0(2)	N(6)–Li(1)–N(4)	108.9(3)
N(2)–Li(4)–N(3)	78.6(2)	N(6)–Li(1)–N(5A)	108.7(3)
As(1)–N(1,2,3)–Li	range 90.3(2)–95.9(2)	N(4)–Li(1)–N(5A)	119.0(3)
Li–N(1,2,3)–Li	range 76.2(2)–90.3(2)		

Symmetry transformations used to generate equivalent atoms labelled A, $-x$, $-y$, $-z$.

Table 4 Key bond distances (Å) and angles (°) for $[\mathrm{As_7Li_3\cdot 3H_2NCy\cdot 3thf}]$ (**6**)

As(2)–As(1)	2.4100(6)	As(1)–Li(1)	2.705(7)
As(2)–As(3)	2.4114(6)	As(4)–Li(1)	2.659(7)
As(2)–As(4)	2.4147(6)	As(1)–Li(2)	2.667(8)
As(1)–As(6)	2.3806(6)	As(3)–Li(2)	2.721(8)
As(3)–As(5)	2.3776(6)	As(3)–Li(3)	2.680(8)
As(4)–As(7)	2.3814(6)	As(4)–Li(3)	2.749(1)
As(5)–As(6)	2.4732(6)	Li–N	range 2.036(8)–2.055(8)
As(5)–As(7)	2.4781(6)	Li–O	range 1.946(9)–1.955(7)
As(6)–As(7)	2.4753(6)		
As–As(2)–As	mean 100.9	As–As–As ($\mathrm{As_3}$ ring)	60.0
As–As(1,3,4)–As	mean 99.5	As–Li–As	mean 87.2
As–As(5,6,7)–As	mean 105.2	O–Li–N	range 108.1(4)–114.0(4)

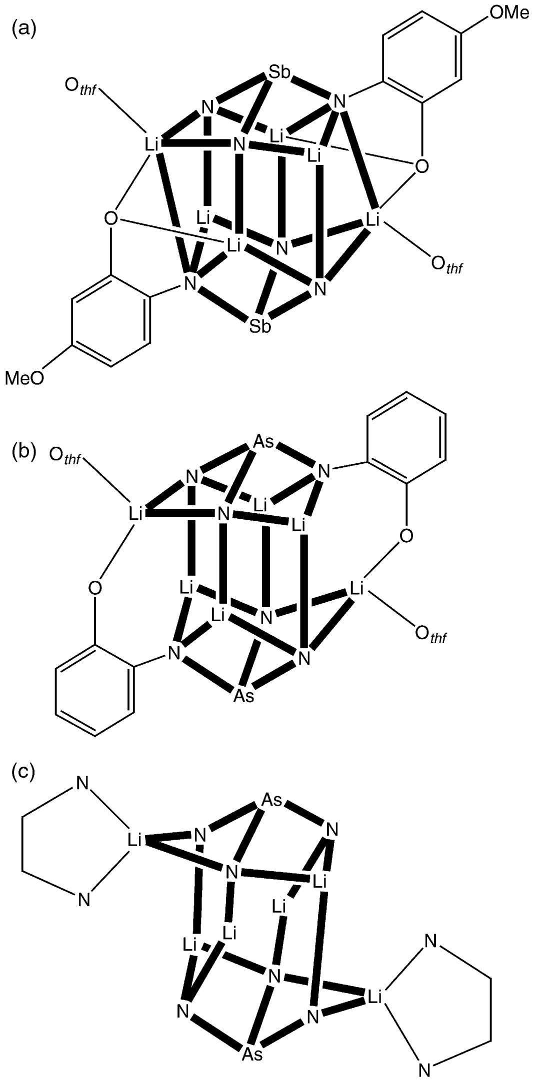


Fig. 3 The core structures and Li$^+$ coordination environments present in (a) [Sb{N-2,4-(MeO)$_2$C$_6$H$_3$}$_3$]$_2$Li$_6$·2thf, (b) [As{N(2-MeOC$_6$H$_4$)}$_3$]$_2$Li$_6$·*n*thf, and (c) [As{N(2-MeOC$_6$H$_4$)}$_3$]$_2$Li$_6$·2TMEDA (**3**).

nation environments for the Li$^+$ cations found in the complex, as well as the strain induced by TMEDA coordination of this arrangement.

The preliminary spectroscopic investigations of **4**·2thf, indicating the presence of 2-pyNH groups, are confirmed by the structural characterisation of this complex (180 K). The structure is best regarded as a co-complex between [As(N-2-py)$_3$Li$_3$] and LiNH(2-py), which then dimerises into an elaborate, centrosymmetric arrangement, *via* ring py-N–Li bonding (Fig. 4a). In addition, there are two uncoordinated thf molecules in the lattice. The aggregation of the [As(N-2-py)$_3$Li$_3$] and LiNH(2-py) units of **4** produces a metallacyclic cavity at the centre of the molecule, defined by As(1) ··· As(1A) [4.271(2) Å] and Li(1) ··· Li(1A) [3.600(9) Å]. Only one related co-complex of a Group 15 [E(NR)]$_3$$^{3-}$ anion has been structurally characterised previously, [{Sb(NCy)$_3$Li$_3$}$_2$(K^{t}BuO)$_3$].[13] This complex results from symmetrical insertion of a [KO^{t}Bu]$_3$ trimeric ring into the N$_6$Li$_6$ core of [{Sb(NCy)$_3$}$_2$Li$_6$·2NHMe$_2$].[13] The 'back-to-back' mode of aggregation found here in the structure of [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·3thf]$_2$ (**4**) represents a new structural type in this area.

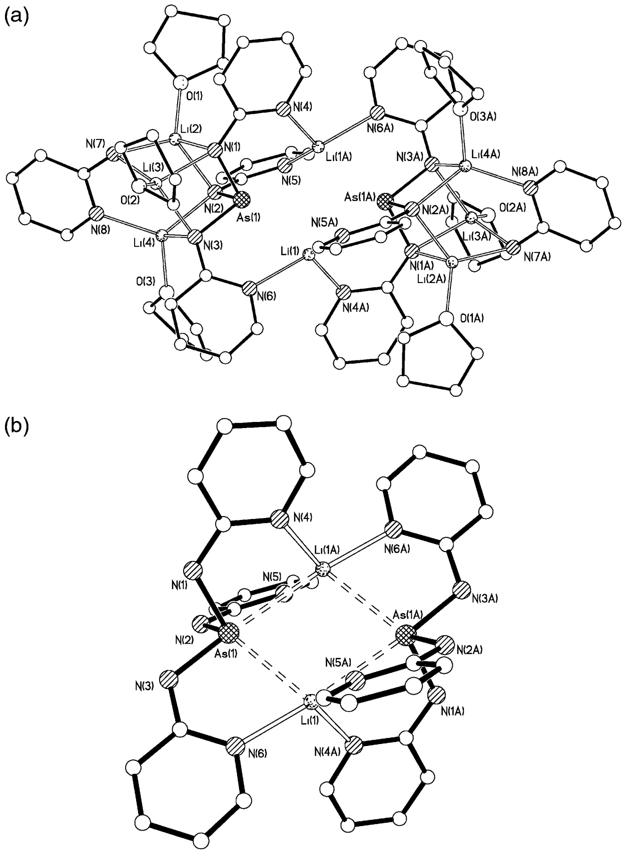


Fig. 4 (a) Structure of centrosymmetric cage molecules of [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·3thf]$_2$·2thf (**4**). (b) Central, metallocyclic ring of **4**, showing the As–Li interactions.

Within the symmetry-related [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·2thf] halves of **4**, the Li$^+$ cations [Li(2), Li(3) and Li(4)] are bonded to the [As(N-2-py)$_3$]$^{3-}$ anion in a similar manner to that found in the majority of fourteen-membered Group 15 cages of the type [{E(NR)$_3$}$_2$Li$_6$].[14] The relatively large range of Li–N bond lengths observed in this [As(N-2-py)$_3$Li$_3$] fragment [2.060(6)–2.135(6) Å] results (in part) from the mode of coordination of the 2-pyNH anion to the three Li$^+$ cations. The μ-bridging of Li(2) and Li(3) by the N(H) centre of the 2-pyNH anion [Li(2)–N(7) 2.028(6), Li(3)–N(7) 2.051(7) Å], and their coordination by thf ligands, gives these Li$^+$ cations similar distorted tetrahedral geometries. The four coordinate Li(4), being bonded to the pyridyl-ring N centre of the 2-pyNH anion [Li(4)–N(8) 2.061(6) Å], has a unique environment. However, it is clear from further examination of the distortion of the [As(N-2-py)$_3$]$^{3-}$ anion itself that the chelation of Li(1,1A) by two of the pyridyl-ring N centres [Li(1)–N(4A) 2.089(6), Li(1)–N(5A) 2.087(6) Å] has a large impact on the bond lengths and angles found in the [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·2thf] units of **4**. This coordination results in a significant expansion of the associated N–As–N angle within the [As(N-2-py)$_3$]$^{3-}$ anion [N(1)–As(1)–N(2) 96.3(1)°], compared to the other N–As–N angles (both *ca.* 91°). Despite this distortion, the As–N bond lengths found in this anion [range 1.854(2)–1.860(2) Å] are similar to those observed in **3** [range 1.858(2)–1.888(2) Å], and in other [As(NR)$_3$]$^{3-}$ anions [1.853(2)–1.887(1) Å[7]].

Li(1) and Li(1A) are located within the central, metallacyclic core of **4** (Fig. 4b), and are responsible for the association of the two [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·2thf] halves of the complex *via* further pyridyl N–Li bonding [Li(1)–N(6) 2.097(6) Å]. At first sight, the coordination of these Li centres by the three pyridyl-N ligands gives them a distorted trigonal pyramidal geometry [N–Li(1)–N range 108.7(3)–119.0(3)°]. However, closer examination reveals that relatively short As ··· Li contacts with As(1) and As(1A) are also present, which further reinforce the dimerisation of the [As(N-2-py)$_3$Li$_3$·LiNH(2-py)·2thf] halves of **4**, within the central As$_2$Li$_2$ ring. The As(1) ··· Li(1) separation [2.714(6) Å] is well within the range of values found for As$_{\text{anion}}$–Li bonds in lithium diorgano–arsanes (range *ca.* 2.48–2.80 Å; values of *ca.* 2.70 Å being typical),[15] while the longer As(1A) ··· Li(1) contact [2.871(5) Å] appears to be less significant. This is the first time that the Group 15 element (E) in an $[E(NR)_3]^{3-}$ anion (or, indeed, any other related imido anion of this class) has been observed to bond to the alkali metal counter cation.

Unequivocal proof of the surprising formation of Zintl compounds in the reactions of the arsazane dimer **5** with excess $PhCH_2NHLi$ is provided by the structure of the isolated complex $[As_7Li_3\cdot3H_2NCy\cdot3thf]$ (**6**) (Fig. 5a). The structural features of the As_7^{3-} anion of **6** are similar to those reported for the toluene solvate of $[As_7Li_3\cdot3TMEDA]$.[10b] Like this solvate, each of the As atoms of **6** are crystallographically independent, with the pattern of As–As bond lengths found within the As_7^{3-} anion of **6** being almost the same [*i.e.*, As(2)–As(1,3,4) mean 2.41, As(1,3,4)–As(6,5,7) mean 2.38, and As(5,6,7)–As(6,7,5) mean 2.48 Å; *cf.* 2.40, 2.37 and 2.48 Å for the corresponding mean bond lengths in $[As_7Li_3\cdot3TMEDA]\cdot1.5(toluene)$[10b]]. This pattern is typical of heterosubstituted cluster anions having a nortricyclic structure.[16]

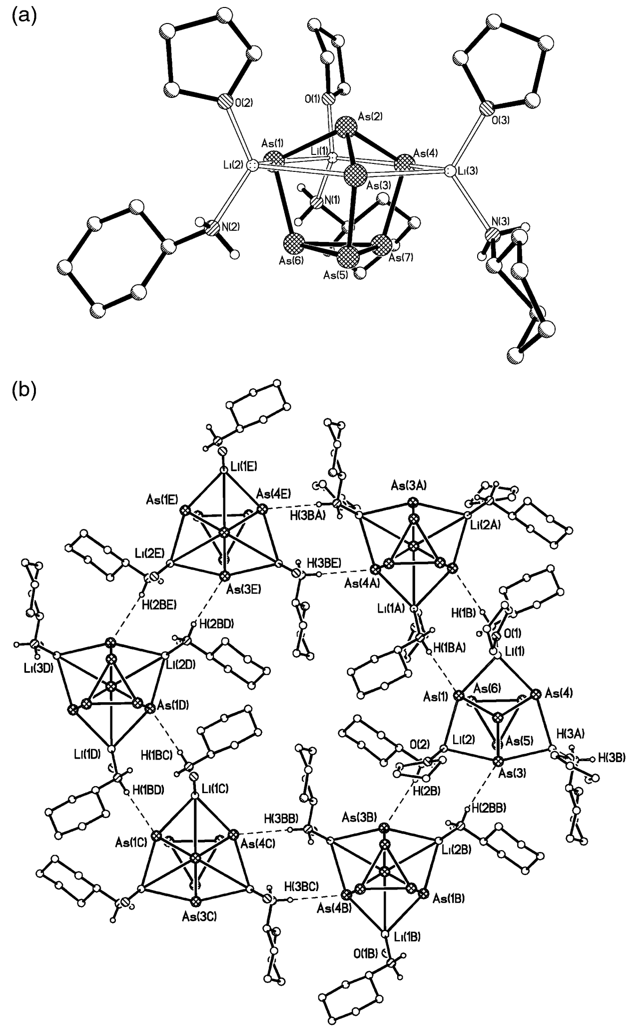


Fig. 5 (a) Structure of the Zintl compound $[As_7Li_3\cdot3H_2NCy\cdot3thf]$ (**6**). (b) Association of molecules in the lattice into cyclic units *via* N–H ··· As bonding. Symmetry operations generating the arsenic atom labels, A: $2 - x, 2 - y, 1 - z$; B: $2 - x, 2 - y, 2 - z$; C: $-1 + x, -1 + y, z$; D: $1 - x, 1 - y, 1 - z$; E: $-1 + x, -1 + y, -1 + z$.

Although unusual, the presence of three coordinated primary amine ($CyNH_2$) ligands in **6** is similar to the coordination of Me_2NH ligands within the structure of the related Sb complex $[Sb_7Li_3\cdot6NHMe_2]$.[12b] In addition, the coordination of two different Lewis base ligands within such an arrangement has been observed in the structure of $[Sb_7Na_3\cdot3TMEDA\cdot3thf]$.[10b] These similarities apart, a surprising consequence of the presence of the coordinated $CyNH_2$ in **6** is the unusual nature of intermolecular association in the crystal lattice. The presence of relatively short N–H ··· As interactions between the Li-coordinated $CyNH_2$ ligands and the three anionic As centres of the As_7^{3-} anions [As(1), As(3) and As(4)] (range 2.78–2.83 Å; N–H ··· As range 168.8–177.2°), results in the association of molecules of **6** into cyclic hexamers (Fig. 5b). These units then aggregate further into infinite ('graphite-like') honeycomb sheets.

Conclusions

The synthetic and structural studies reported here show that reactions of $As(NMe_2)_3$ with $RNH_2/RNHLi$ can be used to prepare a broad range of $[As(NR)_3]^{3-}$ anions. It is clear, however, that incomplete reaction in the case of $^tBuNH_2/^nBuLi$ provides a major complication to the synthesis of 'pure' $[As(N^tBu)_3]^{3-}$, which is yet to be overcome. The unexpected formation of Zintl compounds in one of these systems (involving $PhCH_2NHLi$) appears to suggest that the thermodynamic stability of these cage compounds, with respect to the 'alloy' phase, *can* be dependent on the organic substituent present. Work is in progress to further explore the coordination chemistry of $[As(NR)_3]^{3-}$ anions and their thermal decomposition.

Experimental

General

Compounds **1**–**6** are air- and moisture-sensitive. They were handled on a vacuum line (in an efficient fume cupboard) using standard inert-atmosphere techniques and under dry/oxygen-free argon.[17] $As(NMe_2)_3$ was prepared using the literature route, by transmetallation of $AsCl_3$ with $LiNMe_2$ (1 : 3 equiv).[18] It was purified by distillation [35.5 °C, 2.0 mmHg; $\delta = 2.56$ ($CCl_4/SiMe_4$), 2.60 (D_8-toluene)] and stored as a standardised solution in toluene. Tetrahydrofuran, toluene and hexane were dried by distillation over sodium/benzophenone prior to the reactions. TMEDA was distilled over CaH_2 and stored over molecular sieves (13X). The products were isolated and characterised with the aid of a nitrogen-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system and equipped with an O_2 meter (reading *ca.* 1–10 ppm while in use). Melting points (uncorrected) were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440. ^1H NMR and ^7Li NMR spectra were recorded on a Bruker AM400 MHz spectrometer in dry deuterated D_6-benzene and/or D_8-toluene (using the solvent resonances as the internal reference standards for ^1H NMR, and a saturated solution of $LiCl/D_2O$ as the external standard for ^7Li NMR).

Synthesis of 1·toluene. To a solution of $^tBuNH_2$ (3.15 ml, 30.0 mmol) in hexane (20 ml) was added a solution of $As(NMe_2)_3$ (5.0 ml, 2.0 mol dm^{-3} in toluene, 10 mmol), and the mixture heated to reflux (*ca.* 5 min). After this time some white precipitate had formed. ^nBuLi (18.8 ml, 1.6 mol dm^{-3} in hexanes, 30.0 mmol) was added at ambient temperature and the mixture heated to reflux briefly (*ca.* 3 min). A clear yellow solution was formed. The solvent was reduced *in vacuo* until a yellow precipitate formed. This was dissolved by heating and storage at room temperature gave colourless crystals of $\mathbf{1}\cdot[^tBuNHLi]_6$. Yield (typical) 1.45 g (41.6%, on the basis of $^tBuNH_2$ supplied). IR (Nujol, NaCl), ν/cm^{-1} = 3215 (w) (N–H str), 1376 (s), 1349 (s), 1260 (m), 1204 (s), 1183 (s), 1091 (w), 1017 (m), 945 (s), 891 (m), 754 (m), 720 (s). ^{1}H-NMR (400.16 MHz, +25 °C, C_6D_6), (typical) $\delta = -1.46$ (variable traces, [^{t}BuNHLi]$_8$), −0.85 (br s, 1H), 1.29 (s, *ca.* 9H, [^{t}BuNHLi]$_n$), 1.38 (variable traces, [^{t}BuNHLi]$_8$), 1.51 (s, *ca.* 9–12H, [{As(N^{t}Bu)$_3$}$_2$Li$_6$]) (other minor unidentified species at $\delta = 1.07$ (s), 1.40 (s), 1.41 (s), 1.45 (s) may also be observed, depending on reaction time). ^{7}Li NMR (100.16 MHz, +25 °C, D$_8$-toluene), (typical) $\delta = 0.83$ (s), 1.15 (d) (*ca.* 1 : 1) [other minor resonances at $\delta = 1.41$ (s) and 1.84 (s); cooling to −60 °C results in broadening of these resonances]. Elemental analysis (C, H, N) (eighteen analyses on a total of seven reaction products) was highly variable owing to the variability of the amount of [^{t}BuNHLi]$_n$ in samples and the partial removal of the toluene of solvation from the lattice once the complex is isolated under vacuum (2.0 mmHg, 10–15 min).

Synthesis of 2. To a solution of As(NMe$_2$)$_3$ (2.0 ml, 2.5 mol dm^{-3} in toluene, 5.0 mmol) in 10 ml hexane was added freshly distilled benzylamine (1.64 ml, 15.0 mmol). On addition, the solution became slightly cloudy. The mixture was heated to reflux (5 min). ^{n}BuLi (9.5 ml, 1.6 mol dm^{-3}, 15.0 mmol) was added at ambient temperature. On addition the solution became orange and an orange-red precipitate formed. All the solvent was removed *in vacuo* and the residue dissolved in thf (40 ml), to give a deep wine-red solution. Pink crystals of **2** were obtained on storing the solution overnight at room temperature. Yield 0.80 g (28.5% on the basis of As supplied). Melting point: 125–127 °C (lit.,[7] 125–126 °C). IR (Nujol, NaCl) ν/cm^{-1} = 3160 (w) (arom. C–H-str), 1594 (w) (arom. C–C-str), 1457 (s), 1377 (s), 1297 (w), 1255 (m), 1075 (s), 1014 (s), 906 (s), 797 (s), 736 (s), 698 (m). ^{1}H-NMR (400.16 MHz, +25 °C, C_6D_6), $\delta = 1.47$ (m, 8H, CH$_2$ of thf), 3.67 (t, 8H, O–CH$_2$), 4.59 (s, 8H, CH$_2$ of benzylamide), 7.09–7.43 (m, 15H, CH of benzylamide). Elemental analysis: found C 61.7, H 6.6, N 6.8; calc. C 62.2, H 6.7, N 7.6%.

Synthesis of 3. To a solution of *o*-anisidine (0.85 ml, 7.5 mmol) in 10 ml toluene was added As(NMe$_2$)$_3$ (1.0 ml, 2.5 mol dm^{-3}, 2.5 mmol). The slightly cloudy mixture was brought briefly to reflux. To this mixture at −78 °C was added ^{n}BuLi (5 ml, 1.5 mol dm^{-3}, 7.5 mmol). The mixture was allowed to warm to room temperature and a white precipitate appeared. The precipitate was dissolved by addition of 10 ml TMEDA and heating briefly to reflux. Crystals suitable for X-ray structural analysis were obtained by storing the solution at room temperature. Yield 0.50 g (34.9% based on As supplied). Melting point, decomposes slowly beyond 250 °C. IR (Nujol, NaCl), ν/cm^{-1} = 1373 (s), 1259 (s), 1226 (m), 1203 (mw), 1165 (w), 1108 (s), 1047 (w), 1019 (s), 858 (m), 797 (s), 726 (s). ^{1}H-NMR (400.16 MHz, +25 °C, C_6D_6), $\delta = 2.04$ (s, 12H, CH$_3$ of TMEDA), 2.34 (s, 4H, CH$_2$ of TMEDA), 2.51 (s, 3H, OCH$_3$), 2.89 (s, 3H, OCH$_3$), 3.11 (s, 3H,,OCH$_3$), 6.38–7.80 (overlapping m, 12 H, arom. C–H of 2-MeO–C$_6$H$_4$–N). Elemental analysis: found C 55.9, H 6.6, N 12.4; calc. C 56.4, H 6.5, N 12.2%.

Synthesis of 4. To a solution of 2-aminopyridine (1.129 g, 12.0 mmol) in toluene (10 ml) was added As(NMe$_2$)$_3$ (2.0 ml, 2.0 mol dm^{-3}, 4.0 mmol). The slightly cloudy solution was heated briefly to reflux. ^{n}BuLi (8.0 ml, 1.5 mol dm^{-3}, 12.0 mmol) was added to the mixture at −78 °C and the reaction mixture allowed to warm to room temperature. The clear yellow solution produced was brought to reflux briefly (2 min), then all solvent was removed *in vacuo*. The white solid residue was recrystallised from thf (3 ml). Crystals formed on storing the solution at ambient temperature. Yield 1.93 g (85% based on 2-pyNH$_2$ supplied). decomp. 225 °C. IR (Nujol, NaCl), ν/cm^{-1} = 3481–3283 (m) (N–H str), other bands at 1349 (s), 1278 (s), 1047 (ms), 981 (s), 877 (ms) 835 (m), 764 (s), 731 (s), 693 (s) 646 (w). ^{1}H NMR (400.16 MHz, +25 °C, C_6D_6), $\delta = 1.32$ (mult, 2H, CH$_2$ of thf), 3.45 (t, 2H, OCH$_2$ of thf), 5.85–8.14 (overlapping mult, 4H,,CH of N–2-pyr). Elemental analysis, found C 55.6, H 6.4, N 15.5; calc. C 56.9, H 6.4, N 14.8%.

Synthesis of 6. To a solution As(NMe$_2$)$_3$ (1.0 ml, 2.5 mol dm^{-3}, 2.5 mmol) was added CyNH$_2$ (0.57 ml, 5 mmol). The slightly cloudy mixture was briefly heated to reflux (producing **5**). A suspension of the monolithiate of benzylamine was prepared by the reaction of ^{n}BuLi (5.0 ml, 7.5 mmol) with freshly distilled benzylamine (0.82 ml, 7.5 mmol) in hexane (10 ml). This suspension was added at room temperature to the reaction mixture. The orange suspension of the lithiate dissolved immediately and the solution became a deep red colour, which intensified as the mixture was brought to reflux (2 min). After all the solvent had been removed *in vacuo*, thf (5 ml) was added to the residue (a dark-red oil). Crystals of **6** formed on storage at −10 °C (12 h). Yield 0.063 g (17.1%, on the basis of As supplied). IR (Nujol, NaCl), ν/cm^{-1} = 3292 (w) (N–H str), 1462 (s), 1373 (m), 1307 (w), 1255 (m), 1090 (m), 1019 (m), 797 (m), 722 (m). ^{1}H-NMR (400.16 MHz, +25 °C, C_6D_6), $\delta = 0.76$–1.64 (overlapping mult, 10H, CH$_2$-groups of cyclohexyl), 1.50 (mult, 4H, CH$_2$ of thf), 2.35 (mult, 1H, α-C–H of cyclohexyl), 3.66 (mult, 4H, O–CH$_2$ of THF), 4.79 (br s, 2 H, H$_2$N of cyclohexyl). Elemental analysis: found C 36.3, H 5.6, N 4.5; calc. C 34.2, H 5.4, N 4.0%.

X-Ray crystallographic studies

Data collection. Crystals of **1**·toluene, **3**, **4** and **6** were mounted directly from solution under argon using an inert fluorocarbon oil which protects them from atmospheric oxygen and moisture.[19] Data for all of the compounds were collected on a Nonius Kappa CCD diffractometer, using an Oxford Cryosystems N$_2$ Cryostream cooling unit. Details of the data collection, refinement and crystal data are listed in Table 1.

Structure solution and refinement. The structures were all solved by direct methods[20] and refined by full-matrix least squares on F^2.[21] Satisfactory refinement of "**1**·toluene" could only be obtained by assigning half occupancy to the arsenic atom sites; attempts to redistribute the missing arsenic over the lithium sites in all cases resulted in an marked increase of R_1. A possible explanation is that the lithium salt of the trianion (Fig. 1a) had co-crystallised with a previously unknown virtually isostructural hexamer [^{t}BuNHLi]$_6$ (Fig. 1b) and that the two species were randomly distributed throughout the crystal in equivalent sites resulting in the two structures being superimposed in the observed structure. A possible formulation was therefore **1**·[^{t}BuNHLi]$_6$·2toluene. Alternatively the monoarsenic complex [{As(N^{t}Bu)3}Li$_3$(^{t}BuNHLi)$_3$] (Fig. 1c) might be present with a random distribution of orientation, the arsenic atom pointing up in half the molecules and down in the others. The toluene molecule was disordered on the site of $\bar{3}$m symmetry.

Some of the thf ligands in both **4** and **6** showed evidence of conformational disorder. In **4**, each thf ligand bonded to Li was refined in two orientations with *ca.* 50% site occupancy. In **6**, one of the three thf ligands was refined in two orientations with *ca.* 50% site occupancy. Additionally, in **6** the cyclohexyl rings bonded to N(2) and N(3) showed some disorder with one carbon atom in each refined as two components with site occupancies *ca.* 75 : 25% and 65 : 35% for the two rings respectively. In **4**, H(1N) associated with the (2-py)NH group, was located in a difference Fourier map and refined freely with the N–H distance restrained to be 0.88(1) Å. All other hydrogen atoms in **3**, **4** and **6** were placed geometrically and allowed to ride during subsequent refinement. In the final cycles of full-matrix least-squares refinement, all full-occupancy non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC reference numbers 169732–169735.

See http://www.rsc.org/suppdata/dt/b1/b106913f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge the EPSRC (A.D.B., S.J.K., M.McP., A.S., A.D.W., D.S.W.), the Leverhulme Trust (D.S.W.), Evangelisches Studienwerk Villigst (R.W.) and Churchill and Fitzwilliam College (Fellowship for A.D.H.) for financial support. We also thank Dr J. Davies (Cambridge) for collecting X-ray data on all the complexes reported in this work.

References

1 M. A. Beswick, N. Choi, C. N. Harmer, A. D. Hopkins, M. A. Paver, M. McPartlin, P. R. Raithby, A. Steiner, M. Tombul and D. S. Wright, *Inorg. Chem.*, 1998, **37**, 2177.

2 (*a*) M. A. Beswick, E. A. Harron, A. D. Hopkins, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1999, 107; (*b*) R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, M.-A. Rennie, C. A. Russell, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1994, 1481; (*c*) D. Barr, M. A. Beswick, A. J. Edwards, J. R. Galsworthy, M. A. Paver, M.-A. Rennie, C. A. Russell, P. R. Raithby, K. L. Verhorevoort and D. S. Wright, *Inorg. Chim. Acta*, 1996, **248**, 9.

3 L. Stahl, *Coord. Chem. Rev.*, 2000, **210**, 203.

4 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373; M. A. Beswick, M. E. G. Mosquera and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 2437.

5 A. Bashall, M. A. Beswick, E. A. Harron, A. D. Hopkins, S. J. Kidd, M. McPartlin, P. R. Raithby, A. Steiner and D. S. Wright, *Chem. Commun.*, 1999, 1145.

6 M. A. Beswick, S. J. Kidd, M. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Inorg. Chem. Commun.*, 1999, **2**, 612.

7 L. T. Burke, J. C. Jeffery, A. P. Leedham and C. A. Russell, *J. Chem. Soc., Dalton Trans.*, 2001, 423.

8 N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Linsay, Q.-Y. Liu, F. M. MacKenzie, R. E. Mulvey and P. G. Williard, *Chem. Commun.*, 1996, 2321.

9 $[CyNHAs(\mu\text{-}NCy)]_2$ has been characterised by elemental analysis, ^1H NMR and EI mass spectrometry, see: A. D. Bond, A. D. Hopkins, R. Wolf, A. D. Woods and D. S. Wright, *Organometallics*, 2001, **20**, 4454.

10 (*a*) M. Driess, K. Metz, H. Pritzkow and R. Janoschek, *Angew. Chem.*, 1996, **106**, 2688; M. Driess, K. Metz, H. Pritzkow and R. Janoschek, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2507; (*b*) A. Bashall, M. A. Beswick, N. Choi, A. D. Hopkins, S. J. Kidd, Y. G. Lawson, M. E. G. Mosquera, M. McPartlin, P. R. Raithby, A. E. H. Wheatley, J. A. Wood and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2000, 479.

11 J. D. Corbett, *Chem. Rev.*, 2985, **85**, 383; H.-G. von Schnering, *Angew. Chem.*, 1981, **93**, 44; H.-G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 33.

12 (*a*) 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; (*b*) M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin and D. S. Wright, *Science*, 1998, **281**, 1500; (*c*) A. D. Hopkins, J. A. Wood and D. S. Wright, *Coord. Chem. Rev.*, 2001, **216–217**, 155–172.

13 Stable As radicals have been observed in specific cases, for example see M. J. S. Gynane, A. Hudson, M. F. Lappert and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1980, 2423.

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

15 For example, see M. Driess and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 316; L. J. Jones, A. T. McPhail and R. L. Wells, *J. Coord. Chem.*, 1995, **34**, 119; M. Driess, S. Kuntz, K. Merz and H. Pritzkow, *Chem. Eur. J.*, 1998, **4**, 1628.

16 (*a*) W. Hönle, H. G. von Schnering, A. Schmidpeter and G. Burget, *Angew. Chem.*, 1984, **96**, 796; W. Hönle, H. G. von Schnering, A. Schmidpeter and G. Burget, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 817; (*b*) W. Schmettow and H. G. von Schnering, *Angew. Chem.*, 1977, **89**, 895; W. Schmettow and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 857.

17 D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 2nd edn., 1986.

18 K. Moedritzer, *Inorg. Chem.*, 1964, **3**, 609.18.

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

20 SIR-92, A. Altomare, G. Cascarano, C. Giacovazzo, A. Guargliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

21 SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany, 1997.