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FULL PAPER

Syntheses and X-ray crystal structures of tris(imido)arsenate anions†

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Lithium salts of tris(imido)arsenate anions are produced by the reaction of 3 equivalents of RNH_2 with $AsCl_3$ in thf–NEt_3 followed by metallation with 3 equivalents of Bu^nLi. These complexes form ion-contacted dimers in the solid-state whereby two $As(NR)_3{}^{3-}$ trianions sandwich six lithium cations in irregular 14 membered core configurations whose degrees of distortion are dictated by the differing ways in which the lithium cations are solvated.

Introduction

The development of new ligands based on imido complexes of the p block elements has been a subject which has excited considerable recent interest. Chivers and Stalke have reported imido chalcogenide anions which have been found to act both as ligands to other metals or as imido transfer reagents to other species.[1–3] An alternative synthetic route to both the imido and related phosphinidene ligands of the heavier Groups 14 and 15 elements has been investigated by Wright *et al.* which utilises transmetallation of primary (amido)lithium (or phosphidolithium) with dimethylamido complexes of main group elements.[4] The imido complexes have found applications both as ligands and as precursors to the deposition of antimony/alkali metal phases,[5] whereas the phosphinidene complexes have recently found applications in the synthesis of zintl anions.[6] Our own interest in this area has focussed on the study of imido analogues of the Group 15 oxoanions. Hence, we succeeded in synthesising the imido analogues of both the orthophosphate and phosphite anions {*i.e.*, $[P(NR)_4]^{3-}$ and $[H–P(NR)_3]^{2-}$ respectively} from the reactions of P_nX_m ($n = 2$, $m = 4$, X = I; $n = 1$, $m = 3$, X = Cl) with m equivalents of primary amine followed by lithiation using m equivalents of Bu^nLi.[7,8] We have now turned our attention to investigations of imido anions of the Group 15 element congeners.

Compounds containing As–N bonds have a long and varied history dating back to the 1840's.[9] More recent studies have begun to reveal the precise nature of the products from the relatively simple reactions that were carried out by these early pioneers. Of particular relevance to the current report has been a recent account from Wright *et al.* which describes the synthesis and structure of the first example of a tris(imido) arsenic trianion, $[Li_3As(Bu^tN)_3]_2$ from the metallation of $Bu^tN(H)Li$ with $As(NMe_2)_3$ in the presence of Bu^tNH_2 (3 : 1 : 3 equivalents) in hexane.[10] However, the structural data serves only to confirm the assignment of the compound since it is heavily disordered, negating the calculation of precise bond dimensions. We report here an alternative synthesis of tris(imido)arsenate trianions and present single crystal X-ray diffraction analyses on two such compounds.

Results and discussion

Our recent studies have shown that the reaction of PCl_3 with 3 equivalents of *o*-anisidine in thf–NEt_3 and subsequent metallation with Bu^nLi (2 or 3 equivalents) gives $[Li_2HP(NR)_3]_2$, resulting from proton exchange from an amido centre to a phosphorus centre accompanied by metallation of the remaining NH protons.[8] Equivalent reactions using $AsCl_3$ in place of PCl_3 give notably different products. The colourless crystalline solids of general formula $[Li_3As(NR)_3]_2$, are produced from the reactions of $AsCl_3$ with 3 equivalents of RNH_2 {R = 2-OMePh (**1**), R = CH_2Ph (**2**)} in thf–NEt_3 followed by metallation with 3 equivalents of Bu^nLi.

Table 1 Selected bond lengths and angles for **1**·thf, **1**·2thf and **2**·2thf

	1·thf	**1**·2thf	**2**·2thf
As–N(1)	1.8652(14)	1.885(3)	1.876(2)
As–N(2)	1.8869(14)	1.871(3)	1.882(2)
As–N(3)	1.8626(15)	1.853(2)	1.885(2)
N(1)–Li(1)	2.016(3)	2.065(6)	2.086(5)
N(1)–Li(2)	2.161(3)	2.122(6)	2.024(5)
N(1)–Li(3)	2.143(3)	2.128(6)	2.078(5)
N(2)–Li(1)	2.109(3)	2.229(6)	2.105(5)
N(2)–Li(2)	2.054(3)	2.030(6)	2.026(5)
N(2)–Li(3)	2.147(4)	2.123(6)	2.088(5)
N(3)–Li(1)	1.973(3)	1.955(6)	2.061(5)
N(3)–Li(2)	1.962(3)	1.987(6)	2.018(5)
N(3)–Li(3)	2.588(4)	2.767(6)	2.058(5)
N(2)–As(1)–N(1A)	92.48(6)	92.10(11)	98.90(9)
N(1A)–As(1)–N(3A)	94.00(6)	95.83(11)	99.65(9)
N(2)–As(1)–N(3A)	96.10(6)	93.44(11)	99.61(9)

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

Preliminary investigations were undertaken to establish the identities of **1** and **2** using elemental analyses (C, H, N), IR and ^1H NMR spectroscopies. Of particular note was the absence of a signal for the NH resonance in either the IR or ^1H NMR spectra. This indicated that full metallation of the amine protons had indeed occurred. However, in order to probe the nature of the bonding within these complexes, more detailed investigations using diffraction techniques were necessary.

Low-temperature X-ray structure experiments on complexes **1** and **2** reveal that both complexes have ion-contacted dimeric structures whereby two $[As(NR)_3]^{3-}$ anions are linked together by six lithium cations in 14 membered $As_2N_6Li_6$ cages (see Figs. 1a and 1b). This is similar to the cage motif observed in the earlier example of Wright *et al.*[10] but the absence of significant disorder in **1** and **2** (compared to the serious site disorder in the earlier example) allows access to detailed geometrical data (see Table 1 for selected bond lengths and angles).

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† Dedicated to the memory of Ron Snaith.

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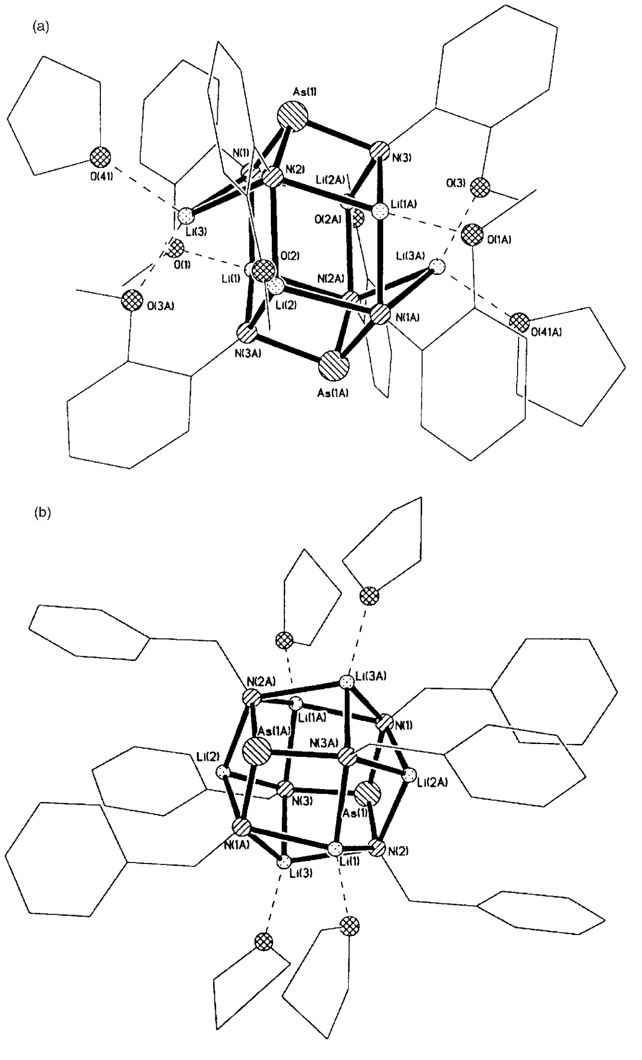


Fig. 1 The crystal structures of complexes **1**·thf (a) and **2**·2thf (b). Hydrogen atoms have been omitted for clarity. The structure of **1**·2thf (which is similar to **1**·thf but with an additional molecule of thf included in the crystal lattice) is not shown.

There are considerable variations from regular D_{3d} symmetry in the As/Li/N networks that form the cores of these polyhedral cages. Whereas the core of complex **2** is probably best viewed as a single $As_2Li_6N_6$ cage, complex **1** is significantly distorted and perhaps should be represented as an $As_2Li_4N_6$ rectangular parallelopiped with two N–N vectors each being capped by additional "pendant" lithium atoms (see Fig. 2). The ready flexibility of the $As(NR)_3{}^{3-}$ trianion unit in accommodating these distortions is seen in the fact that complex **1** crystallises in the same space group {*P*2(1)/*c*} with two different unit cells. In both crystalline forms of **1**, one molecule of thf coordinates to each monomer unit. An additional molecule of thf is included in one of the lattices. Furthermore, the differences between the two forms of **1** are evident not only from the different solvation of the crystal lattice but from subtle differences in the bonding within the structures. The principal difference is that the lithium atoms described as "pendant" to the central core of **2** (as shown in Fig. 2) adopt different positions relative to the core. Hence, the distance (labelled x in Fig. 2) between the pendant Li cation and the imido N on the other $As(NR)_3{}^{3-}$ anion is 2.588(4) Å in **1**·thf and 2.767(6) Å in **1**·2thf. There are also some subtle differences in the binding within each of the cores in the two different forms of **1** and these are outlined in the structure descriptions below.

Within each of the structures, the arsenic centres are coordinated by three imido groups in a highly distorted trigonal pyramidal geometry. An examination of the mean bond lengths and angles about the arsenic centres reveal differences between **1** and **2** {av. N–As–N 93.8° in **1**·2thf, 94.2° in **1**·thf, 99.4° in **2**; av. As–N 1.870 Å in **1**·2thf, 1.872 Å in **1**·thf, 1.881 Å in **2**}. The approximately 5° difference in the mean N–As–N angles between the structures of **1** and **2** highlights the flexibility of the $As(NR)_3$ units in accommodating the distortions of the core structures described above. Additionally, whilst similar phosphorus complexes have distorted tetrahedral geometries about the pnictide centre {*e.g.*, av. N–P–N 108.8° in $[Li_2HP(NR)_3]_2$;[8] av. N–P–N 104.2° in $[Li_3P(NR)_4]_2$[11]}, this is far less pronounced for the imido arsenic anions reported here. This trend continues for the corresponding imido antimony anions {in $[Li_3Sb(NR)_3]_2$ av. N–Sb–N 91.8° for $R = Bu^t$, 90.8° for R = 2,4-dimethoxyphenyl, 93.4° for R = cyclohexyl,[4,12] 94.5° for $R = CH_2CH_2Ph$},[12] and probably reflects increasing p orbital usage in the imido pnictide bond as the group is descended.

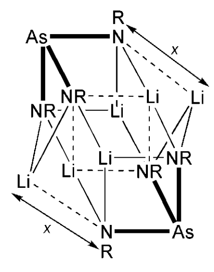


Fig. 2 Schematic of the core configuration of **1**.

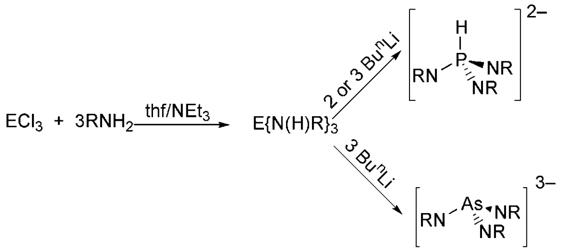
There are considerable variations in the Li–N distances within the complexes. This is more enhanced in the structures of **1** than **2** {varying between 1.955(6)–2.229(6) Å in **1**·2thf, 1.962(3)–2.161(3) Å in **1**·thf and 2.018(5)–2.105(5) Å in **2**}. This is probably the result of lithium solvation of **2** being composed of solely Li–N and Li–O(thf) interactions whereas in the structures of **1**, there is competition for binding to Li from not only imido N centres and thf ligands but additionally from the methoxy sidearms of the anisyl groups. This competition results in the lithium atoms being less tightly held in the 14 membered core of **1** compared to **2** and probably dictates greater distortion in the core of **1**.

Each lithium atom in the structures of **1** (both with one and two thf ligands) is in a chemically distinct environment. In one environment {Li(2)}, the lithium cation has a distorted five coordinate geometry, being bound to two imido nitrogen atoms from one $[As(NR)_3]^{3-}$ unit, a long distance {Li(2)–O(27) 2.623(6) Å} contact with the oxygen centre of a methoxy sidearm from one of these imido centres and to another imido nitrogen centre and its corresponding methoxy sidearm from the other $[As(NR)_3]^{3-}$ unit. A second Li environment {Li(1)} is bound by two imido centres of one $[As(NR)_3]^{3-}$ unit and by an imido centre and its corresponding methoxy sidearm of the other $[As(NR)_3]^{3-}$ unit to give a distorted tetrahedral geometry. The third Li environment also possesses distorted tetrahedral geometry, being solvated by two imido ligands from one $[As(NR)_3]^{3-}$ unit, a thf ligand and a methoxy sidearm from the other $[As(NR)_3]^{3-}$ unit. The nitrogen centres of the imido groups similarly show varied coordination, although not to the same extent as the lithium centres. Two of the nitrogen centres have distorted square based-pyramidal geometries, being coordinated by an arsenic centre, three lithium atoms and the carbon atom of a methoxyphenyl group. The remaining nitrogen centre has a distorted tetrahedral geometry, being coordinated to one less lithium centre.

Complex **2** has a more regular structure than **1** whereby each lithium centre binds to three imido nitrogen atoms {two from one $[As(NR)_3]^{3-}$ unit and one from the other}. Two of the lithium centres further coordinate a molecule of thf whereas the remaining lithium centre is tri-coordinate. This unusual aggregation feature reflects the largely ionic bonding in the core.

The hard O-donors of thf ligands bind to two lithium centres {Li(1) and Li(3)} in the monomer unit, but steric crowding leads to the packing of the benzyl groups in a cavity around the other Li centre {Li(2)}. Thus, binding of further thf to this centre is sterically unfavourable. Each nitrogen centre within **2** is in a distorted square-based pyramidal geometry, being bound to an arsenic atom, three lithium atoms and the carbon atom of the benzyl group.

The dimensions of the $[As(NR)_3]^{3-}$ moiety may provide an insight into the nature of this trianion. It is interesting to note that, whereas comparable imido phosphorus complexes possess P–N bond lengths that are intermediate in length between commonly accepted values for single and double bonds,[7,8] the corresponding As–N distances observed in this work are very much in the realm for the commonly accepted values for single bonds. This interesting contrast may account for the observed difference in reactivity in the equivalent phosphorus and arsenic reactions. This difference in reactivity is highlighted in Scheme 1.



Scheme 1 Amination of ECl_3 (E = P, As) with RNH_2 followed by metallation with Bu^nLi.

For both reactions, one would postulate an $E\{N(H)R\}_3$ intermediate prior to metallation. For the phosphorus reaction, metallation results in a proton shift from an amide {N(H)R} centre to the phosphorus centre, giving the observed $[Li_2HP(NR)_3]_2$ fragment on metallation. However, for the corresponding arsenic reactions that produce complexes **1** and **2**, only $[Li_3As(NR)_3]_2$ fragments are observed. This may be due to the increased weakness of As=N when compared to P=N double bonds, thus disfavouring the migration of a proton from nitrogen to the heavier Group 15 element. Hence, metallation of the intermediate yields the trianionic $[As(NR)_3]^{3-}$ seen in **1** and **2** rather than the dianionic $[HAs(NR)_3]^{2-}$.

Conclusions

The syntheses and structures of complexes **1** and **2** illustrate that tris(imido)arsenate anions are readily accessible from the amination of arsenic(III) chloride followed by metallation with Bu^nLi. A comparison of structural data for these complexes demonstrate the flexibility of the $As(NR)_3{}^{3-}$ trianion with the degree of distortion dictated by intramolecular Lewis base solvation of the lithium centres.

Experimental

General

Compounds **1** and **2** 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 N_2.[13] Toluene, thf and diethyl ether were dried by distillation over sodium–benzophenone prior to the reactions. The products were isolated and characterized with the aid of an argon-filled Saffron Beta glove box. Melting points were determined by sealing samples in capillaries under argon and then using a conventional apparatus. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer 1600 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 a Perkin-Elmer 240 Elemental Analyser. ^1H NMR spectra were recorded on a Jeol Lambda 300 MHz Multinuclear FT spectrometer in dry deuterated benzene (using the solvent resonances as the internal reference standard).

Syntheses of 1 and 2

Both complexes were prepared by the following method. To an ice-cooled stirred solution of $AsCl_3$ (0.17 ml, 2 mmol) in 10 ml of thf and NEt_3 (4 ml, 28.7 mmol) was added 3 molar equivalents of the primary amine {for **1**, 2-methoxyaniline (0.68 ml, 6 mmol); for **2**, benzylamine (0.66 ml, 6 mmol)}. A white solid was observed in solution, which was filtered (porosity 3 sinter with celite) after stirring for 16 h at room temperature. To the resulting solution was added Bu^nLi (1.88 ml, 1.6 mol l^{-1}, 6 mmol) which caused the solution to turn a very distinctive colour (for **1**, a bright yellow solution; for **2**, a bright pink solution was observed). Colourless cubic crystalline blocks of complex **1** were made by removal of solvent *in vacuo* followed by dissolution in toluene (5 ml) with a minimum thf (*ca.* 1 ml), followed by storage for 24 h at 5 °C. Complex **2** also crystallises as colourless cubic blocks which were made by removal of solvent to *ca.* 3 ml followed by layering with diethyl ether (10 ml). Crystals of **2** turn a pink/purple colour after *ca.* 6 h storage at room temperature or with mild heating (30 seconds at *ca.* 50 °C).

For 1. The product obtained is a mixture of **1**·thf and **1**·2thf. The latter appears to readily lose one molecule of thf per monomer unit when isolated under vacuum (10^{-2} torr, +25 °C, 10 min) and the following data were collected using this mono-solvated material. Yield 0.32 g (30%); mp: no melting or decomposition up to 240 °C; IR (Nujol mull) ν/cm^{-1} 3070 (C–H str., $-C_6H_4OMe$); ^1H NMR (+25 °C, 250 MHz, $[D_6]$-benzene): δ = 7.8–6.3 (collection of m, 12H, $-NC_6H_4OMe$), 3.60 (m, 4H, thf), 2.83 (s, 9H, $-OCH_3$), 1.73 (m, 4H, thf). Found: C, 56.59%; H, 5.79%; N, 7.94%. $Li_3As(NC_6H_4OCH_3)_3\cdot(C_4H_8O)$ requires C, 56.50%; H, 5.46%; N, 7.91%.

For 2. Yield 0.20 g (18%); mp 124–128 °C to a purple oil; IR (Nujol mull) ν/cm^{-1} 3046 (C–H str., $-C_6H_5$); ^1H NMR (+25 °C, 250 MHz, $[D_6]$-benzene): δ = 7.42–6.90 (15H, collection of m, $-NCH_2C_6H_5$), 4.42 (6H, s, $-CH_2C_6H_5$), 3.60 (m, 8H, thf), 1.73 (m, 8H, thf); Found: C, 62.50%; H, 6.51%; N, 7.59%. $Li_3As(NCH_2C_6H_5)_3\cdot(C_4H_8O)_2$ requires C, 62.70%; H, 6.67%; N, 7.57%.

X-Ray crystallographic studies

Data collection for 1·thf, 1·2thf and 2·2thf. Data were collected on a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å)[14] using a crystal mounted on a glass fibre in a rapidly cooled perfluoropolyether.[15] Details of the data collection, refinement and crystal data are listed in Table 2. The instrument used was a Siemens SMART-CCD diffractometer. The structure was solved by direct methods and refined by least squares on F^2 values for all reflections.[16] Absorption corrections were applied, based on multiple and symmetry equivalent measurements.[17]

CCDC reference numbers 153207–153209.

See http://www.rsc.org/suppdata/dt/b0/b009240l/ for crystallographic data in CIF or other electronic format.

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Table 2 Crystal data and refinements of **1**·thf, **1**·2thf and **2**·2thf

Compound	**1**·thf	**1**·2thf	**2**·2thf
Chemical formula	$C_{25}H_{29}AsLi_3N_3O_4$	$C_{29}H_{37}AsLi_3N_3O_5$	$C_{29}H_{37}AsLi_3N_3O_2$
M	531.25	604.36	555.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
a/Å	10.4043(6)	10.500(2)	10.238(3)
b/Å	12.4742(7)	17.511(3)	15.458(4)
c/Å	20.2378(11)	16.330(3)	17.674(5)
β/°	104.8070(10)	102.62(2)	90.938(5)
V/Å^3	2539.3(2)	2929.8(9)	2796.8(13)
Z	4	4	4
μ/mm^{-1}	1.374	1.202	1.245
T/K	173(2)	173(2)	173(2)
Reflections collected	16090	18250	17608
Independent reflections [R_{int}]	5851 [0.0231]	6617 [0.0613]	6405 [0.0315]
R indices [$F > 4\sigma(F)$]	$R1 = 0.0270$ $wR2 = 0.0692$	$R1 = 0.0458$ $wR2 = 0.0920$	$R1 = 0.0450$ $wR2 = 0.1199$
R indices (all data)	$R1 = 0.0390$ $wR2 = 0.0719$	$R1 = 0.0908$ $wR2 = 0.1018$	$R1 = 0.0546$ $wR2 = 0.1242$

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