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Preliminary communication

SYNTHESIS, STRUCTURE, AND REACTIONS OF THE FIRST HOMOLEPTIC LITHIUM-ARSENIC COMPOUND, $[Li(\mu\text{-}AsR_2)]_3$ ($R = CH(SiMe_3)_2$) *

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Summary

Reaction of Li with $AsClR_2$ ($R = CH(SiMe_3)_2$) affords $[Li(\mu\text{-}AsR_2]_3$ (I), the first structurally characterised dialkylarsenide, which in OEt_2 at 25°C yields $AsHR_2$, $AsMeR_2$, $AsHR_2$, or $\dot{A}sR_2$ (II) with HCl, MeCl, Bu^tCl, or $SnCl_2$, respectively; upon removal of solvent, II furnishes As_2R_4 (III), which readily dissociates into II: the As_3Li_3 ring of I has a boat conformation and the average Li–As bond distance is 2.60(4) Å.

Organic lithium compounds $(LiX)_n$ are of considerable importance as X^- transfer agents, for example to transition metal (M) sites to yield complexes containing an M–X bond [1]. They are also often of theoretical and structural interest [2].

We now report the synthesis, characterisation, and some features of the chemistry of the first homoleptic Li–As compound $[Li(\mu\text{-}AsR_2)]_3$ (I) ($R = CH(SiMe_3)_2$) (Scheme 1), and its X-ray structure (Fig. 1). The lithium dialkylarsenide I is evidently capable of functioning either (a) as a strong reducing agent, or (b) as an As-centred nucleophile.

Treatment of I in OEt_2 with $SnCl_2$ gave metallic tin and $\dot{A}sR_2$ (II) (ii in Scheme 1). The tin(II) compound $Sn(AsR_2)_2$ may well have been an intermediate along the reaction pathway, Scheme 2. The persistent radical II had previously been obtained in PhMe solution, by reduction of $AsClR_2$ with the bis(imidazolidinylid-2-ene) $\{=\overline{CN(Et)(CH_2)_2N}Et\}_2$ [3].

Reactions of type (b) are illustrated by the formal $Cl^-/^-AsR_2$ displacement upon exposing I to ethereal HCl or MeCl to furnish $AsHR_2$ (III) or $AsMeR_2$ (IV), respectively (iii and iv in Scheme 1).

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* No reprints available

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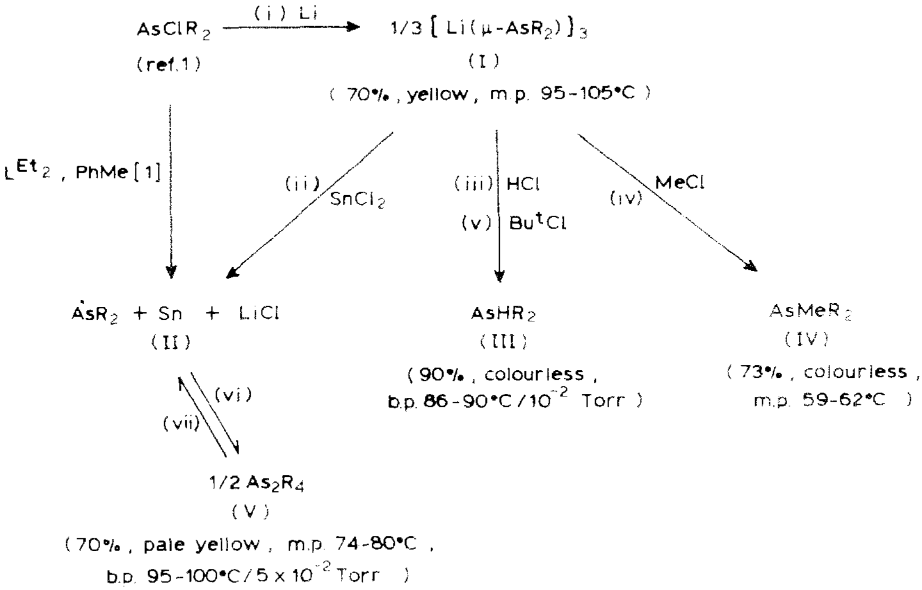


SCHEME 1. Abbreviations: $R = CH(SiMe_3)_2$, $L^{Et}_2 = \{=\overline{CN(Et)(CH_2)_2N}Et\}_2$. Reaction conditions: each of i–v was carried out in OEt_2 at ca. 25 °C; vi, removal of solvent in vacuo; vii, distil. or PhMe at 75 °C or at 25 °C under UV irradiation (medium pressure Hg lamp). Characterisation: (a) microanalysis and ^1H and ^{13}C NMR spectra (in C_6D_6) for I and III–V (diastereotopic $SiMe_3$'s for III–V)); (b) ^7Li NMR for I: $\delta = +1.62$ ppm in C_6D_6, rel. to aq. $LiNO_3$; (c) mass spectra (highest m/e peaks (P^+ = parent ion)): I: $(2P/3 - 114)^+$, III: (P^+), IV: $(P)^+$, V: $(P/2 - 1)^+$; and (d) X-ray diffraction for I (see Fig. 1).

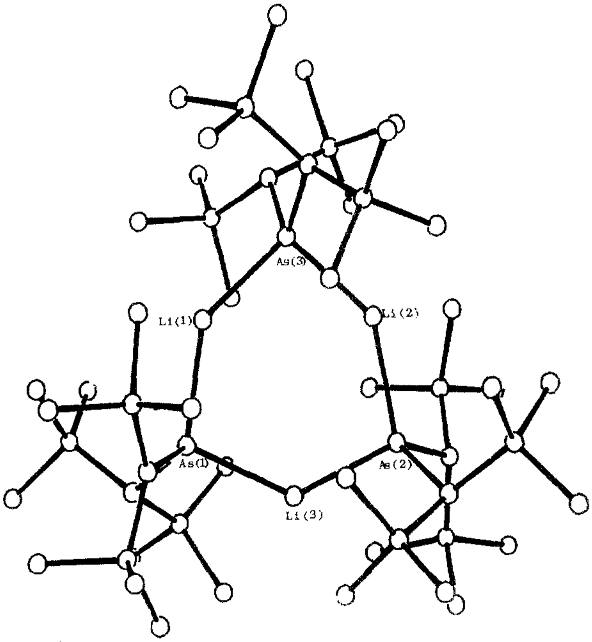
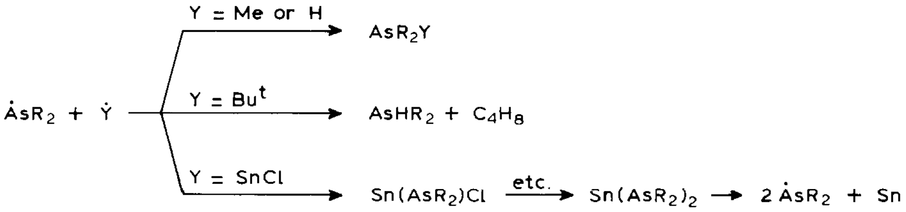


Fig. 1. The molecular structure and atom numbering scheme for μ-tris[bis{bis(trimethylsilyl)-methyl}arsenido]trilithium (I). Some relevant dimensions are: Li(1)–As(1) 2.58(4), Li(1)–As(3) 2.58(4), Li(2)–As(2) 2.63(4), Li(2)–As(3) 2.57(4), Li(3)–As(1) 2.66(4), Li(3)–As(2) 2.58(4) Å; Li(1)–As(3)–Li(2) 98(1), As(3)–Li(2)–As(2) 142(1), Li(2)–As(2)–Li(3) 103(1), As(2)–Li(3)–As(1) 131(1), Li(3)–As(1)–Li(1) 105(1), As(1)–Li(1)–As(3) 140(2)°.



SCHEME 2.

The reaction of $[Li(\mu\text{-}AsR_2)]_3$ (I) with Bu^tCl to yield $AsHR_2$ (III) (v in Scheme 1) is unexpected in the light of the formation of $\dot{P}R_2$ from $[Li(\mu\text{-}PR_2)]_2$ and Bu^tCl [4]. However, $AsHR'_2$ was obtained from $[Li(\mu\text{-}AsR'_2)(dme)]_2$ and Bu^tCl ($R' = SiMe_3$, dme = $MeO[CH_2]_2OMe$) [5]; it was proposed that $AsBu^tR'_2$ was an intermediate which decomposed by β-elimination. We consider this pathway to be unlikely, at any rate for reaction v of Scheme 1, because the formation of the sterically hindered $AsBu^tR_2$ is implausible; $AsBu^tR'_2$ is known [5].

It is probable that the initial step in each of the above reactions of the dialkylarsenide (I) with the appropriate chloride YCl (Y = SnCl, H, Me, or Bu^t, ii–v in Scheme 1) is a one-electron transfer, followed by the elimination of LiCl and formation of the radical pair ($\dot{A}sR_2 + \dot{Y}$). We suggest that the nature of the ultimate product is finally determined by steric effects, Scheme 2.

Although $\dot{A}sR_2$ is indefinitely stable at ca. 25°C in PhMe [3], or in OEt_2, we now, surprisingly, find that removal of solvent yields the crystalline dimer As_2R_4 (V) (vi in Scheme 1). The As–As bond in V must be exceedingly weak, because ready dissociation into the monomer $\dot{A}sR_2$ (II) was achieved upon distillation, or in PhMe by heating or irradiation (vii in Scheme 1). The boiling point of As_2R_4 is of the same order as that of $AsHR_2$ (see Scheme 1) and $AsClR_2$ (b.p. 142–144°C/3 Torr [3]), consistent with the vapour being that of the monomer II, as is confirmed by preliminary gas phase electron diffraction (g.e.d.) data.

The six membered As_3Li_3 ring in I does not have 3-fold symmetry, since the Li–As(3)–Li angle is significantly smaller than those at the other two As atoms. There is a plane of mirror symmetry through As(3) and Li(3) perpendicular to the ring but this does not extend to the $CH(SiMe_3)_2$ substituents. The atoms As(1), As(2), Li(1), and Li(2) are essentially co-planar (± 0.03 Å), whilst As(3) and Li(3) are both slightly below this plane by -0.12 and -0.24 Å, respectively.

X-Ray quality crystals of $[Li(\mu\text{-}AsR_2)]_3$ (I) were grown from n-C_5H_{12} at -30°C. *Crystal data for (I)*: $C_{42}H_{114}As_3Li_3Si_{12}$ triclinic, space group $P\bar{1}$, a 11.542(6), b 14.230(2), c 23.865(6) Å; α 85.98(2), β 79.95(3), γ 70.96(3)°; U 3642.9 Å^3; $Z = 2$, D_c 1.09 g cm^{-3}.

The structure of I (Fig. 1) was solved by standard heavy atom methods and refined to $R = 0.098$, $R' = 0.128$ *, using 3600 reflections with $|F^2| > \sigma(F^2)$ measured on a CAD-4 diffractometer with Cu-K_α radiation.

The present results on $[Li(\mu\text{-}AsR_2)]_3$ (I) may be compared with those for $[Li(\mu\text{-}PR_2)]_2$ [4], which retains its dimeric integrity in the gas phase, and perhaps

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

for steric reasons affords $\dot{P}R_2$, rather than PHR_2, with Bu^tCl. The nitrogen congener, $Li(NR_2)$, is unknown (as is NHR_2). A near analogue, $[Li(\mu\text{-}NR'_2)]_3$ ($R' = SiMe_3$), like I, forms an alternant $(LiE)_3$ ring in the crystal [6], but differs from I in being planar, and behaving as a milder reducing agent but a much stronger Brønsted base. Further comparisons are (Li–As distances in parentheses) with (i) $[Li(\mu\text{-}AsR'_2)(dme)]_2$ (2.59(2) Å) [7], (ii) $Li(AsPh_2)(1,4\text{-dioxane})_3$ (2.66(1) Å) [8], and (iii) $[Li(\mu\text{-}AsPh_2)(OEt_2)_2]_2$ [(2.708(9) Å) [8], in each of which the lithium atom is four-coordinate; (iv) $[Li(12\text{-crown-}4)_2][AsPh_2] \cdot thf$ [9], which contains well separated, non-interacting cations and anions, with the C–As–C angle of 108.6(2)° significantly wider than the 98.1(8) and 100.8(9)° found in I; and (*added in proof*) (v) $[Li\{\mu\text{-}As(AsBu^t_2)Bu^t\}(THF)_2]_2$ [10].

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