As–As Bond Forming and As–C Bond Cleavage in the Formation of $[Li(thf)\{As(Bu^t)As(Bu^t)_2\}]_2$ (thf = tetrahydrofuran). *X*-Ray Structure of an Unusual Lithium Organoarsenide

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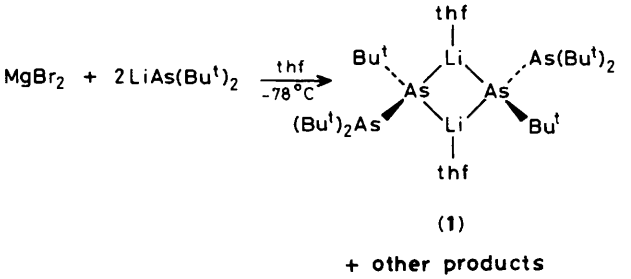
$[Li(thf)\{As(Bu^t)As(Bu^t)_2\}]_2$ (thf = tetrahydrofuran), produced from the interaction of $LiAs(Bu^t)_2$ with $MgBr_2$ (2 : 1) in thf, is a dimer with two Li atoms bridging two $-As(Bu^t)As(Bu^t)_2$ groups and with a planar Li_2As_2 core [Li–As 2.58(2), As–As 2.403(2), Li · · · Li 3.290(3) Å].

Lithium diorganophosphides and arsenides ($LiER_2$, E = P or As) are of importance as useful synthetic reagents in organic and inorganic chemistry.[1] N.m.r. studies[2] have suggested that these species exist in solution as dimers or tetramers, and the solid-state structures of a number of lithium diorganophosphides have recently been reported.[3] We report here the synthesis and *X*-ray structure of $[Li(thf)\{As(Bu^t)As(Bu^t)_2\}]_2$ (**1**) (thf = tetrahydrofuran) which is one of the first lithium organoarsenides to be structurally characterized.[4]

Reaction of $LiAs(Bu^t)_2$[5] with carefully dried anhydrous $MgBr_2$ (2 : 1) in thf at −78 °C yields a pale yellow suspension from which pale yellow crystals of (**1**) can be isolated in *ca.* 65% yield following evaporation to dryness and recrystallization from hexane (Scheme 1).†

The process by which (**1**) is formed is clearly complex. Other products are formed in the reaction although we have so far failed to identify or characterize them. However, the mechanism of formation of (**1**) clearly involves As–As bond formation and As–C bond cleavage. Related processes have been observed in a number of other organoarsenic systems.[6] Also, such carbon–group 15 (Ölander numbering) element bond cleavages may be relevant to the deactivation of homogeneous catalysts.[7] The ^1H n.m.r. spectrum of (**1**) in $C_6D_5CD_3$ exhibits three sharp singlets at δ 1.27, 1.32, and 1.36 and is consistent with the structure determined by a single crystal *X*-ray diffraction study.‡

The molecular structure of (**1**) is shown in Figure 1. The central unit of the molecule consists of a planar Li_2As_2 core. There is a crystallographically imposed centre of inversion at the mid-point of As(2)–As(2′). The bridging Li atoms each bear one co-ordinated thf molecule. The arsenido As atoms [As(2), As(2′)] have a pseudotetrahedral geometry consisting of two Li atoms, a Bu^t group, and an $-As(Bu^t)_2$ unit. The As atoms of these latter groups have a pyramidal geometry indicating that they posess stereochemically active lone pairs of electrons.



Scheme 1

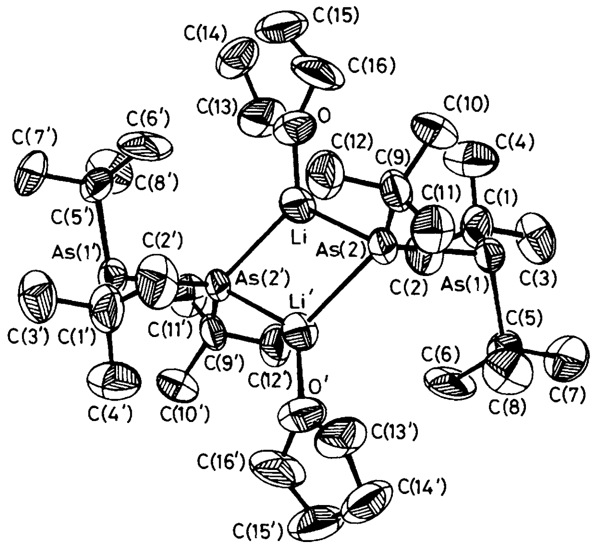


Figure 1. ORTEP view of (**1**). Key bond lengths (Å) and angles (°) not in text: Li–O 1.89(2), As(2)–C(9) 2.045(12), As(1)–C(1) 2.067(14), As(1)–C(5) 2.066(12); Li–As(2)–Li′ 79.4(3), As(2)–Li–As(2′) 100.6(3), Li–As(2)–C(9) 113.9(6), C(9)–As(2)–As(1) 100.7(3), Li–As(2)–As(1) 128.6(5), As(2)–As(1)–C(1) 101.4(3), As(2)–As(1)–C(5) 104.1(3).

To our knowledge, compound (**1**) is one of the first lithium organoarsenides to have been structurally characterized.[4] The two Li–As lengths are the same to within experimental error [both 2.58(2) Å] and are slightly shorter than those recently determined by Power and co-workers in $Li(1,4\text{-dioxane})_3AsPh_2$ [Li–As 2.66(1) Å] and $[Li(thf)_2AsPh_2]_2$ [Li–As 2.708(9) and 2.757(9) Å].[4] The As(1)–As(2) distance [2.403(2) Å] is comparable with other As–As single bond distances[8] [*e.g.* $(AsPh)_6$, As–As 2.459 Å (av.)].[9] The Li · · · Li′ distance of 3.290(3) Å] indicates the absence of significant Li–Li bonding.

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† The complex decomposes slowly over the range 150—200 °C, and gave satisfactory elemental analyses (C, H); ^1H n.m.r. ($C_6D_5CD_3$): δ 1.27 (s, 9H), 1.32 (s, 9H), 1.36 (s, 9H) [all $As(Bu^t)$]; 1.50 (br. m, 4H, thf), 3.56 (br., m, 4H, thf); ($\nu_{max.}$Nujol mull, NaCl plates): 1360s, sh., 1260m, 1150m, 1040m, br., 890w, br., 800w cm^{-1}.

‡ *Crystal data:* (**1**), $C_{16}H_{35}As_2LiO$, *M* = 400.24, monoclinic, space group $P2_1/c$ (No. 14), a = 9.526(2), b = 15.357(4), c = 15.094(3) Å, β = 107.909(2)°, U = 2101.2(5) $Å^3$, D_c = 1.265 g cm^{-3}, Z = 4, λ(Mo-K_α) = 0.71073 Å (graphite monochromator), μ(Mo-K_α) = 31.68 cm^{-1}. Methods: MULTAN, difference Fourier, full-matrix least-squares. Refinement of 936 reflections [$I > 3\sigma(I)$], collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C, out of 3286 unique observed reflections gave R and R_w values of 0.0520 and 0.0596 respectively. All non-hydrogen atoms anisotropic, hydrogen atoms not located. Highest peak in final difference Fourier = 0.462 e $Å^{-3}$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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