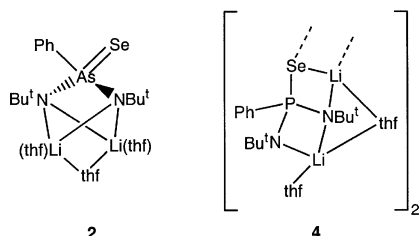


The molecular structures of **1**·(THF)₃ and **2** are depicted in Figs. 1 and 2, respectively. The structures show similar features with the PhAs(NBu^t)₂ framework chelating each of the two lithium centres in an *N,N'* manner. Each Li⁺ ion is further coordinated by one terminal and one asymmetrically bridging THF molecule. The mean As–N bond lengths in **2** are *ca.* 0.10 Å shorter than those in **1**·(THF)₃ as a result of the oxidation of the As(III) centre to As(V). In addition, the N–As–N bond angle is *ca.* 6° smaller in **1**·(THF)₃ than that in **2**, presumably reflecting the stereochemical influence of the lone pair on arsenic. The As=Se bond distance of 2.272(1) Å in **2** is slightly longer than those reported for Et₃As=Se and PhPr₂As=Se [2.234(1) and 2.227(1) Å, respectively].⁵ The difference is probably attributable to the partial ionic character of **2**.

The monomeric structure of **2**, with a terminal As=Se bond, is in distinct contrast to the dimeric aggregation of the phosphorus analogue {(THF)₂Li₂[PhP(Se)(NBu^t)₂]}₂ (**4**).⁹ The absence of the third coordinating THF ligand in **4** results in *N,Se* chelation of the second Li⁺ ion and dimerization *via* Li–Se interactions.



Attempts to grow X-ray quality crystals of **3** were unsuccessful, but the NMR data are consistent with a structure similar to that of **2**. The reaction of **1** with elemental tellurium proceeds readily at *ca.* 25 °C (but not at lower temperatures). However, ¹H and ¹²⁵Te NMR spectra of the reaction mixture indicate the formation of several Te-containing compounds as a result of the decomposition of the initial product {(THF)₃Li₂[PhAs(Te)(NBu^t)₂]}₂. Details of the characterization of these compounds will be given elsewhere.

In summary, we have described a new method for generating As=Se bonds under mild conditions, and a rare structural characterization of this functionality. Similar approaches are being investigated for the generation of chalcogenides of related antimony- and bismuth-centred systems.

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Notes and references

† Synthesis of **1**: A solution of 2.5 M LiBuⁿ in hexanes (8.10 mL, 20.28 mmol) was added dropwise to a solution of PhAs(NHBu^t)₂¹⁰ (3.003 g, 10.14 mmol) in diethyl ether (30 mL) at 0 °C to give a cloudy yellow mixture, which was allowed to warm to 23 °C. After 5 h, the solvent was removed under vacuum. The resulting product was washed with *n*-hexane (3 × 5 mL) to give **1** as a white powder (2.002 g, 6.50 mmol, 64%), which was recrystallized from diethyl ether–hexane at –15 °C. Anal. calc. for C₁₄H₂₃AsLi₂N₂: C, 54.57; H, 7.52; N, 9.09. Found C, 55.83; H, 7.44; N, 8.98%. NMR data (THF-*d*₈, 25 °C): ¹H NMR: δ 1.04 (s, 18 H, CMe₃), 6.95 (t, 1 H, AsPh-*p*), 7.06 (t, 2 H, AsPh-*o*), 7.60 (d, 2 H, AsPh-*m*); ¹³C{¹H} NMR: δ 38.2 (NCMe₃), 53.5 (NCMe₃), 126.0, 127.5, 131.1 (AsPh). The *ipso* carbon resonances for **1**–**3** were not observed.

Synthesis of **2**: THF (6 mL) was added to a vessel containing Li₂[PhAs(NBu^t)₂] (0.200 g, 0.649 mmol) and selenium powder (0.051 g, 0.649 mmol). After stirring at 23 °C for 1 h, the solution was heated to 50 °C to dissolve the product. Concentration of the reaction mixture to 2.5 mL and storage at –15 °C for 2 d gave colourless crystals of **2** (0.206 g, 0.341 mmol, 53%). NMR data (THF-*d*₈, 25 °C): ¹H NMR: δ 1.09

(s, CMe₃), 1.77 (m, OCH₂CH₂), 3.62 (m, OCH₂CH₂), 7.10–7.21, 8.19 (m, AsPh). ¹³C{¹H} NMR: δ 26.3 (OCH₂CH₂), 36.3 (CMe₃), 54.0 (CMe₃), 68.2 (OCH₂CH₂), 127.1, 128.1, 131.8 (AsPh). ⁷Li: δ 3.92. ⁷⁷Se: δ 46.1. Satisfactory CHN analyses of **2** and **3** could not be obtained owing to facile loss of coordinated THF.

Synthesis of **3**: Colourless crystals of **3** were obtained in *ca.* 30% yield by the reaction of **1** (0.200 g, 0.649 mmol) with S₈ (0.021 g, 0.082 mmol) under conditions similar to those described for **2**. NMR data (THF-*d*₈, 25 °C): ¹H NMR: δ 1.08 (CMe₃), 1.77 (OCH₂CH₂), 3.62 (OCH₂CH₂), 7.14–7.23, 8.24 (AsPh). ¹³C{¹H} NMR: δ 26.5 (CH₂CH₂), 36.5 (CMe₃), 54.0 (CMe₃), 68.4 (CH₂CH₂), 127.5, 128.4, 132.7 (AsPh).

‡ Crystal data for **1**·(THF)₃: Yellow, X-ray quality crystals were obtained by recrystallization of **1** from THF at –50 °C. *M* = 524.46, orthorhombic, space group *Pna*2₁, *a* = 18.7419(6), *b* = 10.7469(3), *c* = 14.6045(5) Å, *V* = 2941.6(2) Å³, *T* = 173(2) K, *Z* = 4, μ(Mo-Kα) = 1.184 mm^{–1}, 6230 reflections measured, 3472 unique (*R*_{int} = 0.035), final *R* = 0.041 for 2812 observed data with *I* > 2σ(*I*). Data were collected on a Nonius Kappa CCD diffractometer and the structure was solved and refined against *F*² using SHELXL97.¹² The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in geometrically idealized positions and were not refined.

Crystal data for **2**: *M* = 603.42, monoclinic, space group *P2*₁/*m*, *a* = 9.8072(4), *b* = 15.1468(6), *c* = 10.8128(5) Å, β = 102.933(2)°, *V* = 1565.5(1) Å³, *T* = 173(2) K, *Z* = 2, μ(Mo-Kα) = 2.27 mm^{–1}, 9855 reflections measured, 3077 unique (*R*_{int} = 0.068), final *R* = 0.053 for 2280 observed data with *I* > 2σ(*I*). Data collection and solution were as described for **1**·(THF)₃. The atoms Se1, Li1, N1, N2, C1, C3, C4, and C5 lie on the mirror plane while the As atom lies off the mirror plane and is disordered. A THF-attached to Li1 was disordered with its atoms located over two sites and had unequal site occupancy factors. Due to the mirror symmetry, the second Li/THF moiety (Li2, O2, C17–20) and the phenyl ring were also disordered and scrambled across the mirror. The non-hydrogen atoms were refined anisotropically with the exception of the atoms of the smaller fraction of the first THF, which were allowed isotropic displacement parameters. The phenyl ring was constrained as a regular hexagon with C–C 1.39 Å and C–C–C 120°. CCDC reference numbers 190559 [**1**·(THF)₃] and 190560 (**2**). See <http://www.rsc.org/suppdata/doi/b207302a/> for crystallographic data in CIF or other electronic format.

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