

# A novel route to chalcogenides of heavy pnictogens: synthesis and X-ray structure of $\{(THF)_3Li_2[PhAs(Se)(NBu^t)_2]\}$

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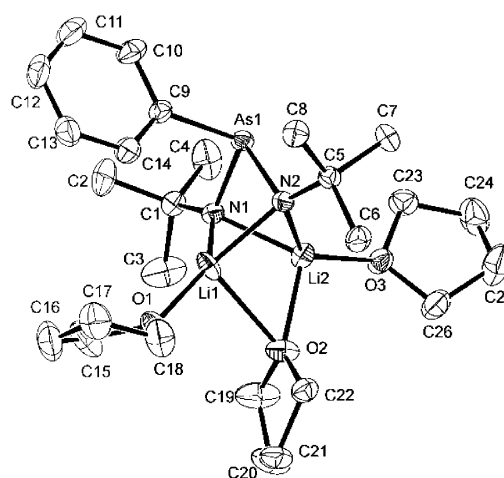
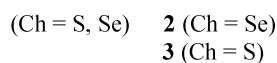
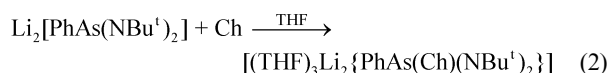
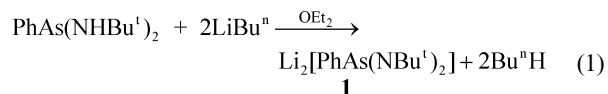
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The rapid reaction of  $Li_2[PhAs(NBu^t)_2]$  with elemental selenium in THF at 23 °C produces  $\{(THF)_3Li_2[PhAs(Se)(NBu^t)_2]\}$ , which contains a formal As=Se double bond.

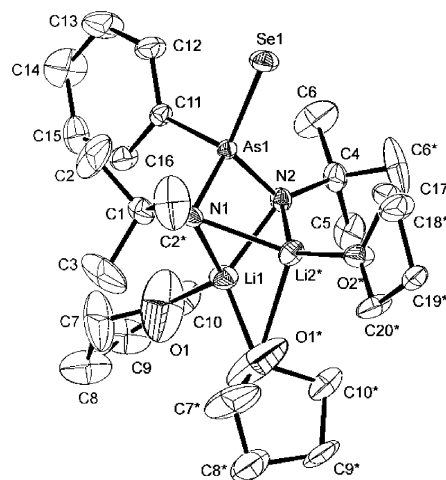
Triorganyl pnictogen chalcogenides of the type  $R_3E=Ch$  ( $E = P, As$ ;  $Ch = S, Se, Te$ ) exhibit decreasing stability as the size of (a) the pnictogen and (b) the chalcogen increases. For the phosphorus series, this trend is illustrated by the increased lability of P=Te bonds compared to P=Se or P=S linkages.<sup>1</sup> In the case of arsenic, several  $R_3As=S$  derivatives have been prepared and structurally characterized.<sup>2</sup> However, there are relatively few examples of arsine selenides,<sup>3,4</sup> only two of which have been structurally characterized,<sup>5</sup> while the corresponding arsine tellurides are not known.<sup>4</sup> This paucity of information is due, in part, to the method of synthesis, which involves reaction of an arsine  $R_3As$  with elemental chalcogen at elevated temperatures. Such conditions oppose the preservation of thermally labile As=Ch bonds.

Recently we have described a different route to previously inaccessible phosphine tellurides, *e.g.*  $[(TMEDA)Na][N\{P(Te)Ph_2\}_2]$ , that involves metallation of the phosphorus(III/III) precursor  $HN(PPh)_2$  prior to the reaction with tellurium.<sup>6</sup> Theoretical calculations indicate that the increased reactivity may be attributed to a higher electron density at the phosphorus(III) centre upon metallation.<sup>7</sup> In addition, Woollins *et al.* have provided evidence that suggests that the electron density at phosphorus is maximized in derivatives of the type  $RP(NR')_2$  ( $R, R' = \text{alkyl, aryl}$ ).<sup>8</sup> These findings sparked our interest in the preparation of chalcogenides of heavier pnictogens. We report here the facile synthesis and X-ray structure of  $\{(THF)_3Li_2[PhAs(Se)(NBu^t)_2]\}$  (**2**) from the reaction of  $Li_2[PhAs(NBu^t)_2]$  (**1**) and elemental selenium.

The reagent **1** is prepared by the reaction of  $PhAs(NHBu^t)_2$  with two equivalents of  $LiBu^t$  in diethyl ether [eqn. (1)].<sup>†</sup> The reaction of **1** with a stoichiometric amount of selenium in THF results in immediate reaction at *ca.* 23 °C to give **2** [eqn. (2)]. The sulfur analogue **3** is prepared in a similar manner.<sup>†</sup> No reaction occurs between  $PhAs(NHBu^t)_2$  and selenium under these conditions. Complexes **2** and **3** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra and, in the case of **2**, also by <sup>7</sup>Li and <sup>77</sup>Se NMR spectra and by an X-ray structural determination.<sup>‡</sup> The X-ray structure of **1**·(THF)<sub>3</sub> was also determined for comparison.<sup>‡</sup>



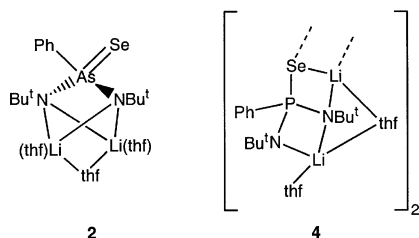
**Fig. 1** Structure of **1**·(THF)<sub>3</sub>. Probability ellipsoids are drawn at the 30% level. Selected bond lengths (Å) and angles (°) include: As(1)–C(9) 2.023(5), As(1)–N(1) 1.844(4), As(1)–N(2) 1.849(5), Li(1)–N(1) 1.98(1), Li(1)–N(2) 2.02(1), Li(2)–N(1) 2.026(9), Li(2)–N(2) 2.070(9), Li(1)–O(1) 1.927(7), Li(2)–O(3) 1.929(8), Li(1)–O(2) 2.398(10), Li(2)–O(2) 2.036(9); C(9)–As(1)–N(1) 103.0(2), C(9)–As(1)–N(2) 104.9(2), N(1)–As(1)–N(2) 85.5(2), N(1)–Li(1)–N(2) 77.7(3), N(1)–Li(2)–N(2) 75.5(3).



**Fig. 2** Structure of **2**. Only one position for the disordered atoms is shown for clarity. Probability ellipsoids are drawn at the 30% level. Selected bond lengths (Å) and angles (°) include: As(1)–Se(1) 2.272(1), As(1)–C(11) 1.985(4), As(1)–N(1) 1.724(4), As(1)–N(2) 1.768(5), Li(1)–N(1) 2.03(1), Li(1)–N(2) 1.99(1), Li(2)\*–N(1) 2.21(2), Li(2)\*–N(2) 2.14(2); C(11)–As(1)–N(1) 105.0(2), C(11)–As(1)–N(2) 107.8(2), N(1)–As(1)–N(2) 91.6(2), Se(1)–As(1)–C(11) 105.2(1) Se(1)–As(1)–N(1) 124.1(1), Se(1)–As(1)–N(2) 121.3(1), N(1)–Li(1)–N(2) 77.1(4), N(1)–Li(2)\*–N(2) 70.3(2). Symmetry operation for the starred atoms:  $x, -y + \frac{1}{2}, z$ .

The molecular structures of **1**·(THF)<sub>3</sub> and **2** are depicted in Figs. 1 and 2, respectively. The structures show similar features with the PhAs(NBu<sup>t</sup>)<sub>2</sub> framework chelating each of the two lithium centres in an *N,N'* manner. Each Li<sup>+</sup> 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)<sub>3</sub>, 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)<sub>3</sub> 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 Et<sub>3</sub>As=Se and PhPr<sub>2</sub>As=Se [2.234(1) and 2.227(1) Å, respectively].<sup>5</sup> 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)<sub>2</sub>Li<sub>2</sub>[PhP(Se)(NBu<sup>t</sup>)<sub>2</sub>]<sub>2</sub>}<sub>2</sub> (**4**).<sup>9</sup> The absence of the third coordinating THF ligand in **4** results in *N,Se* chelation of the second Li<sup>+</sup> 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, <sup>1</sup>H and <sup>125</sup>Te 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)<sub>3</sub>Li<sub>2</sub>[PhAs(Te)(NBu<sup>t</sup>)<sub>2</sub>]}<sub>2</sub>. 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 LiBu<sup>n</sup> in hexanes (8.10 mL, 20.28 mmol) was added dropwise to a solution of PhAs(NHBu<sup>t</sup>)<sub>2</sub><sup>10</sup> (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 C<sub>14</sub>H<sub>23</sub>AsLi<sub>2</sub>N<sub>2</sub>: C, 54.57; H, 7.52; N, 9.09. Found C, 55.83; H, 7.44; N, 8.98%. NMR data (THF-*d*<sub>8</sub>, 25 °C): <sup>1</sup>H NMR: δ 1.04 (s, 18 H, *CMe*<sub>3</sub>), 6.95 (t, 1 H, *AsPh-p*), 7.06 (t, 2 H, *AsPh-o*), 7.60 (d, 2 H, *AsPh-m*); <sup>13</sup>C{<sup>1</sup>H} NMR: δ 38.2 (NCMe<sub>3</sub>), 53.5 (NCMe<sub>3</sub>), 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 Li<sub>2</sub>[PhAs(NBu<sup>t</sup>)<sub>2</sub>] (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*<sub>8</sub>, 25 °C): <sup>1</sup>H NMR: δ 1.09

(s, *CMe*<sub>3</sub>), 1.77 (m, OCH<sub>2</sub>CH<sub>2</sub>), 3.62 (m, OCH<sub>2</sub>CH<sub>2</sub>), 7.10–7.21, 8.19 (m, *AsPh*). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 26.3 (OCH<sub>2</sub>CH<sub>2</sub>), 36.3 (*CMe*<sub>3</sub>), 54.0 (*CMe*<sub>3</sub>), 68.2 (OCH<sub>2</sub>CH<sub>2</sub>), 127.1, 128.1, 131.8 (*AsPh*). <sup>7</sup>Li: δ 3.92. <sup>77</sup>Se: 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 S<sub>8</sub> (0.021 g, 0.082 mmol) under conditions similar to those described for **2**. NMR data (THF-*d*<sub>8</sub>, 25 °C): <sup>1</sup>H NMR: δ 1.08 (*CMe*<sub>3</sub>), 1.77 (OCH<sub>2</sub>CH<sub>2</sub>), 3.62 (OCH<sub>2</sub>CH<sub>2</sub>), 7.14–7.23, 8.24 (*AsPh*). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 26.5 (CH<sub>2</sub>CH<sub>2</sub>), 36.5 (*CMe*<sub>3</sub>), 54.0 (*CMe*<sub>3</sub>), 68.4 (CH<sub>2</sub>CH<sub>2</sub>), 127.5, 128.4, 132.7 (*AsPh*).

‡ Crystal data for **1**·(THF)<sub>3</sub>: Yellow, X-ray quality crystals were obtained by recrystallization of **1** from THF at –50 °C. *M* = 524.46, orthorhombic, space group *Pna*2<sub>1</sub>, *a* = 18.7419(6), *b* = 10.7469(3), *c* = 14.6045(5) Å, *V* = 2941.6(2) Å<sup>3</sup>, *T* = 173(2) K, *Z* = 4, μ(Mo-Kα) = 1.184 mm<sup>–1</sup>, 6230 reflections measured, 3472 unique (*R*<sub>int</sub> = 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*<sup>2</sup> using SHELXL97.<sup>12</sup> 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*<sub>1</sub>/*m*, *a* = 9.8072(4), *b* = 15.1468(6), *c* = 10.8128(5) Å, β = 102.933(2)°, *V* = 1565.5(1) Å<sup>3</sup>, *T* = 173(2) K, *Z* = 2, μ(Mo-Kα) = 2.27 mm<sup>–1</sup>, 9855 reflections measured, 3077 unique (*R*<sub>int</sub> = 0.068), final *R* = 0.053 for 2280 observed data with *I* > 2σ(*I*). Data collection and solution were as described for **1**·(THF)<sub>3</sub>. 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)<sub>3</sub>] and 190560 (**2**). See <http://www.rsc.org/suppdata/dt/b2/b207302a/> for crystallographic data in CIF or other electronic format.

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