

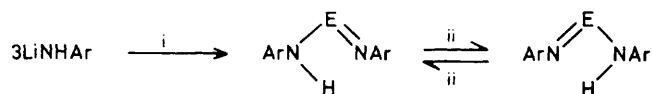
## Novel Arylimides of Phosphorus(III) and Arsenic(III) [the Arsazene being the First Stable Compound containing an As<sup>III</sup>N Double Bond]; X-Ray Structures of E(=NAr)(NHAr) (E = P or As, Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>)†

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Treatment of PCl<sub>3</sub> or AsCl<sub>3</sub> with 3Li(NHAr) (Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>) affords the novel two-co-ordinate P<sup>III</sup> or As<sup>III</sup> imides E(=NAr)(NHAr) [E = P (1) or E = As (2)] which undergo slow prototropy in C<sub>6</sub>D<sub>6</sub>; for the isomorphous compounds (1) and (2), *J*(EN) and ∠ NEN for (1) [in square brackets for (2)] are 1.573(8) and 1.633(8) Å [1.714(7) and 1.745(7) Å] and 103.8(5)° [98.8(3)°], respectively.

We have recently introduced the bulky ligand <sup>-</sup>NHAr (Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>), and have described unusual amides of *inter alia* lithium<sup>1,2</sup> and boron.<sup>3</sup> We now report on an extension into the realm of P<sup>III</sup> and As<sup>III</sup> chemistry.

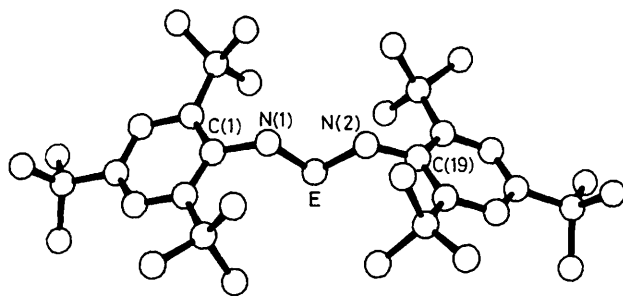


(1), E = P, orange, m.p. 203–205 °C

(2), E = As, dark red, m.p. 173–175 °C

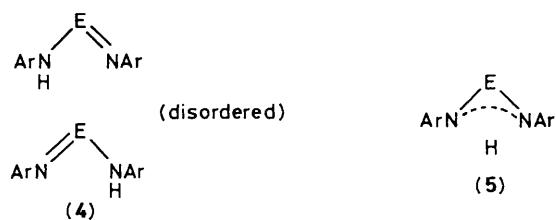
**Scheme 1.** Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>; E = P or As. *Reagents and conditions:* i, ECl<sub>3</sub>, OEt<sub>2</sub>, reflux, and subsequent isolation of crystalline (1) or (2); ii, C<sub>6</sub>D<sub>6</sub>, 30 °C, <sup>1</sup>H n.m.r. spin-saturation-transfer experiments [these involved the selective irradiation of either *o*-Bu<sup>t</sup> or *p*-Bu<sup>t</sup> protons of (a) imido- and (b) amido-aryls and observing any changes in intensity of the non-irradiated signals]. *Characterisation:* C/H/N analyses, as well as i.r. and n.m.r. data, for each of (1) and (2); selected n.m.r. chemical shifts (C<sub>6</sub>D<sub>6</sub>; 30 °C): <sup>1</sup>H (1): δ 1.68 and 1.62 (*o*-Bu<sup>t</sup>), 1.50 and 1.40 (*p*-Bu<sup>t</sup>), and 4.6 [d, *J*(<sup>31</sup>P–<sup>1</sup>H) 84 Hz, NH]; (2): 1.65 and 1.54 (*o*-Bu<sup>t</sup>), 1.44 and 1.30 (*p*-Bu<sup>t</sup>); <sup>13</sup>C (1): δ 36.9, 36.7, 35.0, and 34.8 (CBu<sup>t</sup>); (2): 36.85, 36.75, 35.0, and 34.7 (CBu<sup>t</sup>); <sup>31</sup>P{<sup>1</sup>H} (rel. to H<sub>3</sub>PO<sub>4</sub>): (1), 268.4 p.p.m.; and X-ray data for (1) and (2) (Figure 1).

The features of interest are as follows. (a) We have obtained (Scheme 1, reaction i) the first disubstituted phosphazene P(=NAr)(NHAr) (1). (b) The isomorphous arsenic analogue As(=NAr)(NHAr) (2) is the first stable arsenic(III) compound containing an As=N double bond, and as a crystalline two-co-ordinate arsenic complex it has no forerunner. (c)



**Figure 1.** The molecular structures and atom numbering schemes for the phosphorus(III) and arsenic(III) aryylimides E(=NAr)(NHAr) [Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>, and E = P (1) or As (2)]. Some relevant dimensions for compounds (1) and (2) [in square brackets] are as follows: E–N(1) 1.573(8) [1.714(7)], E–N(2) 1.633(8) [1.745(7)], N(1)–C(1) 1.475(11) [1.422(10)], N(2)–C(19) 1.413(10) [1.438(9)] Å; N(1)–E–N(2) 103.8(5) [98.8(3)]°, E–N(1)–C(1) 126.1(7) [123.2(6)], E–N(2)–C(19) 126.5(7) [124.6(5)]°.

† No reprints available.



Although single crystal *X*-ray analysis of the phospho- and arsa-azenes (**1**) and (**2**) failed to identify the site of protonation of the conjugate base  $^{-}E(NAr)_2$  ( $E = As$  or  $P$ ), n.m.r. data ( $^1H$  and  $^{13}C$ ) showed that the two aryl groups are magnetically distinct (up to at least 400 K). (d) The slow exchange process  $E(=NAr)(NHAr) \rightleftharpoons E(NHAr)(=NAr)$  (ii in Scheme 1) for the compounds (**1**) and (**2**), has, however, now been demonstrated to occur (using spin-saturation-transfer nuclear Overhauser n.m.r. studies on each of the pair of *o*- and *p*-Bu $^t$   $^1H$  signals); these are unprecedented examples of prototropic tautomerism. (e) *X*-Ray data for compounds (**1**) and (**2**) reveal that the two E–N distances are unequal (although this is more pronounced for  $E = P$  than  $E = As$ ) and the NEN angle decreases in the sequence  $P > As$ .

Phospha-azenes  $P(=NR)(NR^1R^2)$  (**3**) were first obtained in 1973,<sup>4</sup> and *X*-ray data for one such compound ( $R = R^1 = Bu^t$ ,  $R^2 = SiMe_3$ ) are available<sup>5</sup> and are similar to those now found for compound (**1**) (Figure 1). Each of the substituents  $R$ ,  $R^1$ , and  $R^2$  in (**3**) has invariably, in the past, been bulky.<sup>6</sup> Attempts to prepare  $As(=NR^2)(NR^2_2)$  by thermolysis of  $AsCl(NR^2_2)_2$  failed.<sup>7</sup>

As for (c), the *X*-ray data for (**1**) and (**2**) do not distinguish between the disordered structure (**4**) and a delocalised

alternative (**5**).<sup>‡</sup> The As–N bond lengths in  $As^{III}$  amides have been in the range 1.79–1.88 Å.<sup>8</sup>

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<sup>‡</sup> *Crystal data* for (**1**) [(**2**) square brackets]  $C_{36}H_{50}N_2P$  [ $C_{36}H_{50}N_2As$ ], orthorhombic [orthorhombic], space group  $P2_12_12_1$  [ $P2_12_12_1$ ],  $a = 9.747(5)$  [9.661(7)],  $b = 15.787(9)$  [15.959(5)],  $c = 22.958(10)$  [23.101(8)] Å,  $U = 3533$  [3562] Å<sup>3</sup>,  $Z = 4$  [4],  $D_c = 1.04$  [1.11] g cm<sup>-3</sup>,  $F(000) = 1216$  (1288). The structures of the isomorphous compounds (**1**) and (**2**) were solved by direct methods and refined to  $R = 0.095$  [0.055],  $R_w = 0.098$  [0.064], using 1213 [2463] reflections with  $|F^2| > \sigma(F^2)$  measured on an Enraf–Nonius CAD-4 diffractometer with Mo- $K_\alpha$  radiation. 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.