Novel Arylimides of Phosphorus(III) and Arsenic(III) [the Arsazene being the First Stable Compound containing an As^{III}N Double Bond]; *X*-Ray Structures of E(=NAr)(NHAr) (E = P or As, Ar = $C_6H_2Bu^t{}_3$-2,4,6)†

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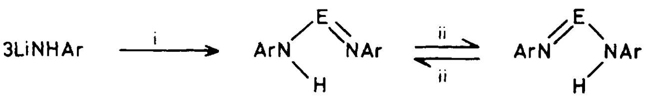
Treatment of PCl_3 or $AsCl_3$ with 3Li(NHAr) (Ar = $C_6H_2Bu^t{}_3$-2,4,6) affords the novel two-co-ordinate P^{III} or As^{III} imides E(=NAr)(NHAr) [E = P (**1**) or E = As (**2**)] which undergo slow prototropy in C_6D_6; for the isomorphous compounds (**1**) and (**2**), *l*(EN) and ∠ NEN for (**1**) [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 $^-$NHAr (Ar = $C_6H_2Bu^t{}_3$-2,4,6), and have described unusual amides of *inter alia* lithium[1,2] and boron.[3] We now report on an extension into the realm of P^{III} and As^{III} chemistry.



(**1**), E = P, orange, m.p. 203-205 °C
(**2**), E = As, dark red, m.p. 173-175 °C

Scheme 1. Ar = $C_6H_2Bu^t{}_3$-2,4,6; E = P or As. *Reagents and conditions:* i, ECl_3, OEt_2, reflux, and subsequent isolation of crystalline (**1**) or (**2**); ii, C_6D_6, 30 °C, ^1H n.m.r. spin-saturation-transfer experiments [these involved the selective irradiation of either *o*-Bu^t or *p*-Bu^t 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_6D_6; 30 °C): ^1H (**1**): δ 1.68 and 1.62 (*o*-Bu^t), 1.50 and 1.40 (*p*-Bu^t), and 4.6 [d, $J(^{31}P-^1H)$ 84 Hz, NH]; (**2**): 1.65 and 1.54 (*o*-Bu^t), 1.44 and 1.30 (*p*-Bu^t); ^{13}C (**1**): δ 36.9, 36.7, 35.0, and 34.8 (*C*Bu^t); (**2**): 36.85, 36.75, 35.0, and 34.7 (*C*Bu^t); $^{31}P\{^1H\}$ (rel. to H_3PO_4): (**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)

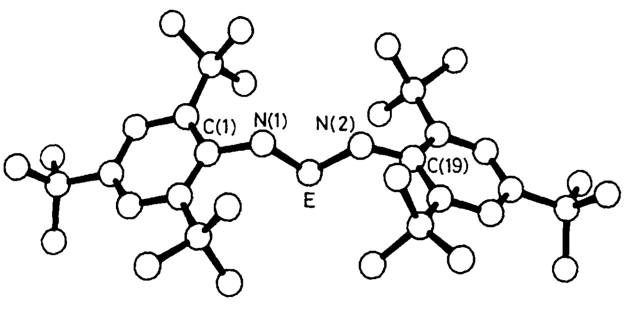


Figure 1. The molecular structures and atom numbering schemes for the phosphorus(III) and arsenic(III) arylimides E(=NAr)(NHAr) [Ar = $C_6H_2Bu^t{}_3$-2,4,6, and E = P (**1**) or As (**2**)]. Some relevant dimensions for compounds (**1**) and (**2**) [in square brackets] are as follows: E–N(1) 1.573(8) [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)]°.

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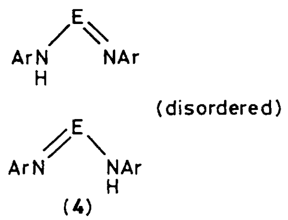
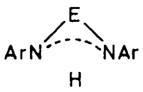
† No reprints available.



(4)



(5)

Although single crystal *X*-ray analysis of the phospha- 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,[4] and *X*-ray data for one such compound (R = R^1 = Bu^t, R^2 = SiMe$_3$) are available[5] 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.[6] Attempts to prepare $As(=NR^2)(NR^2{}_2)$ by thermolysis of $AsCl(NR^2{}_2)_2$ failed.[7]

As for (c), the *X*-ray data for (**1**) and (**2**) do not distinguish between the disordered structure (**4**) and a delocalised alternative (**5**).‡ The As–N bond lengths in As^{III} amides have been in the range 1.79—1.88 Å.[8]

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‡ *Crystal data* for (**1**) [(**2**) square brackets] $C_{36}H_{59}N_2P$ [$C_{36}H_{59}N_2As$], 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^3, Z = 4 [4], D_c = 1.04 [1.11] g cm^{-3}, $F(000)$ = 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_α 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.