

Phosphorus(III and V)- and Arsenic(III)-Nitrogen Metallacycles derived from the Bulky Arylamido Ligand $\overline{\text{N}}\text{HAr}$ ($\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$); X-Ray Structures of $\text{Ar}\overline{\text{N}}\overline{\text{P}}\overline{\text{N}}(\text{Ar})\text{AlMe}_2$ and $\text{PAr}(\text{NHAr})_2$ †

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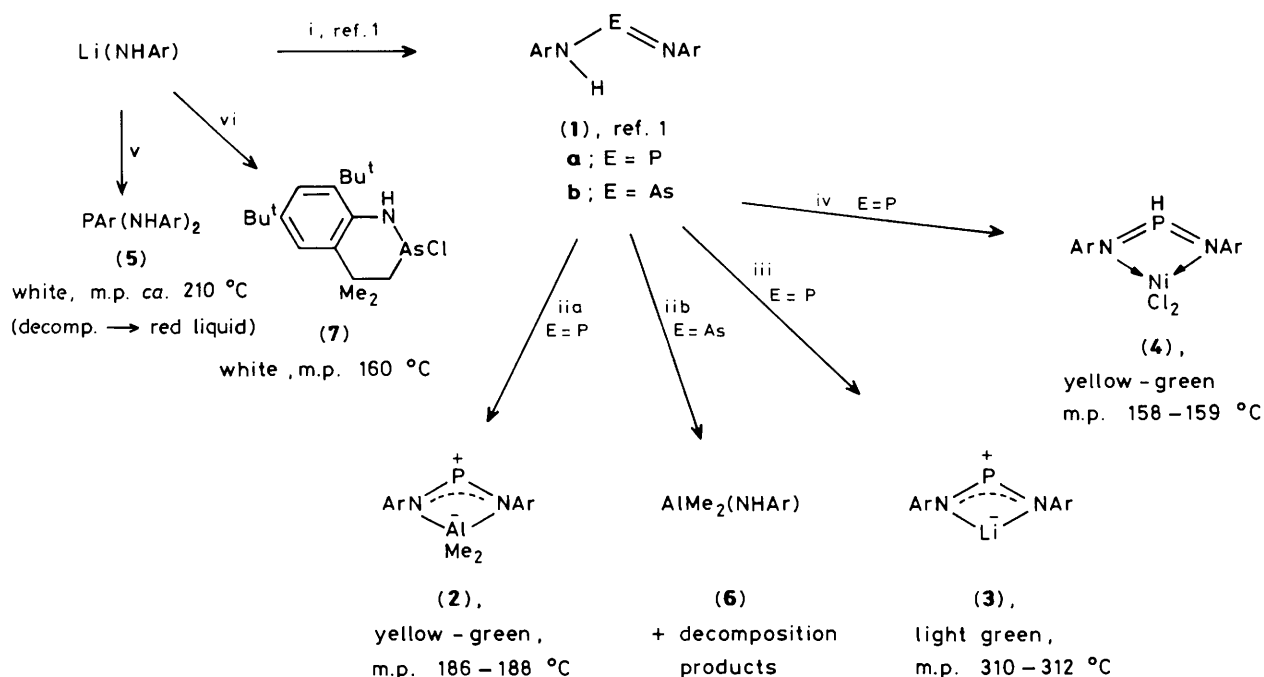
In its co-ordination chemistry $\text{P}(=\text{NAr})(\text{NHAr})$ ($\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$) (**1a**) behaves either as (i) a source of its conjugate base yielding $\text{Ar}\overline{\text{N}}\overline{\text{P}}\overline{\text{N}}(\text{Ar})\overline{\text{ML}}_n$ (**2**) [$\overline{\text{ML}}_n = \text{AlMe}_2$, from $(\text{AlMe}_3)_2$] and (**3**) ($\overline{\text{ML}}_n = \text{Li}$, from LiBu^n), or (ii) as a neutral hydrido- P^{V} ligand in $[\overline{\text{Ni}}\text{Cl}_2\{(\text{ArN})_2\text{PH}\}]$, but the arsa(III)azene (**1b**) [the As analogue of (**1a**)] undergoes facile As-NHAr bond-scission with $(\text{AlMe}_3)_2$; whereas (**1b**) is obtained from $2\text{Li}(\text{NHAr}) + \text{AsCl}_3$ in OEt_2 at 20°C , prolonged reflux in PhMe of the same reagents furnishes a cyclometallated product; $\langle\text{P}-\text{N}\rangle$ in (**2**) [$1.617(4)\text{ \AA}$] is intermediate between the P=N and P-N bond lengths in (**1a**), and is significantly shorter than the $1.74(1)\text{ \AA}$ for $\langle\text{P}-\text{N}\rangle$ in $\text{PAr}(\text{NHAr})_2$ [obtained from $\text{PArCl}_2 + 2\text{Li}(\text{NHAr})$].

The novel arylimides of phosphorus(III) and arsenic(III) $\text{E}(=\text{NAr})(\text{NHAr})$ [$\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$ and $\text{E} = \text{P}$ (**1a**) or $\text{E} = \text{As}$ (**1b**)] have recently been prepared from $2\text{Li}(\text{NHAr})$ and ECl_3 under mild conditions (i in Scheme 1).^{1‡} We now provide the following interesting extensions (a)–(f) of this chemistry.

† No reprints available.

‡ Satisfactory C, H, N microanalyses, and i.r. and n.m.r. data for compounds (**2**)–(**7**); selected chemical shifts (δ in p.p.m., in C_6D_6 at 30°C): $^{31}\text{P}\{^1\text{H}\}$ (rel. to 85% H_3PO_4): (**1a**) 268.4, (**2**) 359.2, (**3**) 337.0, (**4**) 11.2 [$J(^{31}\text{P}^1\text{H})$ 603 Hz], (**5**) 82.0 [$^2J(^{31}\text{P}^1\text{H})$ 406 Hz]; see X-ray data for (**2**) (Figure 1) and (**5**) (Figure 2).

(a) Compound (**1a**) has an acidic NH hydrogen, as evident from (1) its facile reactions (iia or iii in Scheme 1) with $(\text{AlMe}_3)_2$ or LiBu^n [but not $\text{Li}(\text{NHAr})$] to yield the two-coordinate phosphorus(III) metallacycles $\text{Ar}\overline{\text{N}}\overline{\text{P}}\overline{\text{N}}(\text{Ar})\overline{\text{ML}}_n$ (**2**) ($\overline{\text{ML}}_n = \text{AlMe}_2$) or (**3**) ($\overline{\text{ML}}_n = \text{Li}$), respectively; or (2) the characterisation of the neutral P^{V} -ligated complex $[\overline{\text{Ni}}\text{Cl}_2\{(\text{ArN})_2\text{PH}\}]$ (**4**), obtained from (**1a**) and NiCl_2 . (b) In contrast, compound (**1b**) undergoes As-N, rather than N-H, bond-scission upon treatment with $(\text{AlMe}_3)_2$ (iib in Scheme 1) to yield $\text{AlMe}_2(\text{NHAr})$ (**6**). (c) The N-H bond also remains intact after prolonged heating under reflux in PhMe of $2\text{Li}(\text{NHAr})$ and AsCl_3 , hydrogen atom abstraction from a Bu^t



Scheme 1. Abbreviations: Ar = $\text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$; E = P or As. Reagents and conditions: i, ECl_3 , OEt_2 , 20 °C, and isolation of (**1**) as crystals;¹ ii, $\frac{1}{2}(\text{AlMe}_3)_2$, C_6H_{14} , 20 °C; iii, LiBu^n , C_6H_{14} , 20 °C; iv, NiCl_2 (anh.), OEt_2 , 20 °C; v, PArCl_2 , tetrahydrofuran, 20 °C (then reflux 4 h); vi, $\frac{1}{2}\text{AsCl}_3$, PhMe, 80 °C, 3 days.

group being preferred (vi in Scheme 1) to afford the cyclometallated arsaza-tetrahydronaphthalene derivative (**7**). (d) Despite the bulk of Ar, we have prepared (v in Scheme 1) the highly hindered bis(arylamino)phosphine $\text{PAr}(\text{NHAr})_2$ (**5**), which resists thermal elimination to yield $\text{P}(\text{=NAr})\text{Ar}$ [*cf.*² $\text{P}(\text{=NSiMe}_3)\text{Ar}$, the first stable $\text{C}-\text{P}^{\text{III}}=\text{N}$ compound]. (e) X-Ray data on (**2**)[§] show (Figure 1) the P–N bonds to be short and the N–Al–N angle to be remarkably acute. (f) The P–N bonds in (**5**) (Figure 2)[§] are exceptionally long for a P^{III} amide; but, despite the bulk of the Ar and NHAr groups, the sum of the angles at P is only ca. 311°.

As for (a), the formation of the P^{III} heterocycles (**2**) and (**3**) is surprising in the light of the observations that $\text{P}(\text{=NR})(\text{NR}_2)$ ($\text{R} = \text{SiMe}_3$) yields with (i) $(\text{AlMe}_3)_2$ the P^{V} compound $\text{RNP}(\text{Me})_2\text{N}(\text{R})\text{AlMe}_2$ (**8**),³ and (ii) BCl_3 the three-co-ordinate P^{III} compound $\text{RNP}(\text{Cl})\text{N}(\text{R})\text{BCl}$ (**9**);⁴ however, with $(\text{AlCl}_3)_2$, $\text{R}_2\text{NPN}(\text{R})\text{AlCl}_3$ (**10**) was obtained, which on heating gave $\text{R}_2\text{NPN}(\text{R})\text{AlCl}_2$ (**11**).⁵ The broad band decoupled ^{31}P n.m.r. chemical shift, $\delta^{31}\text{P}\{^1\text{H}\}$ in p.p.m. rel. to H_3PO_4 , is clearly structurally diagnostic, as evident from

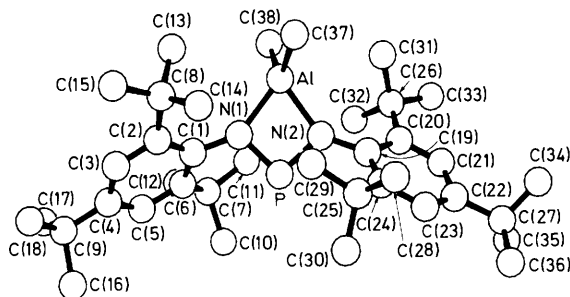


Figure 1. The molecular structure and atom numbering scheme for $\text{ArNPN}(\text{Ar})\text{AlMe}_2$ (Ar = $\text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$) (**2**). Important distances and angles defining the heterocyclic environment are as follows: P–N(1) 1.619(4), P–N(2) 1.615(4), Al–N(1) 1.974(4), Al–N(2) 1.981(4), $\angle\text{Al-C}$ 1.970(6), N(1)–C(1) 1.463(5), N(2)–C(19) 1.452(5) Å; N(1)–P–N(2) 96.2(2), N(1)–Al–N(2) 74.9(1), P–N(1)–Al 94.5(2), P–N(2)–Al 94.4(2), N(1)–Al–C(37) 124.2(2), N(2)–Al–C(38) 123.2(2), N(1)–Al–C(38) 109.1(2), N(2)–Al–C(37) 108.4(2), $\angle\text{C-N-P}$ > 118.9(4)°.

[§] Crystal data for (**2**): $\text{C}_{36}\text{H}_{64}\text{AlN}_2\text{P}$, monoclinic, space group $P2_1/c$, $a = 12.576(1)$, $b = 10.563(1)$, $c = 30.061(2)$ Å, $\beta = 101.08(1)^\circ$, $U = 3918.9$ Å³, $Z = 4$, $D_c = 1.03$ g cm⁻³. (**5**): $\text{C}_{54}\text{H}_{89}\text{N}_2\text{P}$, triclinic, space group $P\bar{1}$, $a = 11.247(2)$, $b = 14.756(3)$, $c = 18.749(3)$ Å, $\alpha = 68.53(1)$, $\beta = 73.44(1)$, $\gamma = 77.35(2)^\circ$, $U = 2752.5$ Å³, $Z = 2$, $D_c = 0.96$ g cm⁻³. The structure of (**2**) was solved by routine heavy atom methods and refined to $R = 0.064$, $R' = 0.077$, using 3297 reflections with $|F^2| > \sigma(F^2)$ measured on a CAD-4 diffractometer with $\text{Cu-K}\alpha$ radiation. The structure of (**5**) was solved by direct methods and refined to $R = 0.139$, $R' = 0.183$, using 3855 reflections with $|F^2| > \sigma(F^2)$ measured on the CAD-4 with $\text{Mo-K}\alpha$ 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.

$\delta^{31}\text{P}\{^1\text{H}\}$ for compounds (**8**)–(**11**): 42.05,³ 171.7,⁴ 452.7,⁵ and 379.3, respectively, *cf.*, data on compounds (**1a**) and (**2**)–(**4**).[‡]

Our formulation of the Ni^{II} complex (**4**) (see Scheme 1) as derived from $\text{PH}(\text{=NAr})_2$, a tautomer of (**1a**) (the metal-free three-co-ordinate P^{V} hydrides are still unknown) rather than $\text{P}(\text{=NAr})(\text{NHAr})$ is based on n.m.r. data. Firstly, ^1H and ^{13}C n.m.r. spectra show that the two groups Ar in (**4**) are equivalent. Secondly, the value for $\delta^{31}\text{P}\{^1\text{H}\}$ in (**4**) is appropriate: *cf.*, (i) the data cited above, (ii) $\delta -55.0$ p.p.m. found for $\text{P}(\text{=NR})_2(\text{NR})$ ($\text{R} = \text{SiMe}_3$),⁶ and (iii) $\delta 325$ p.p.m. in $[\text{PtL}_3]$ [$\text{L} = \text{P}(\text{=NR})(\text{NR}_2)$],^{7a} $\delta 297.5$ p.p.m. in $[\text{Pt}_3(\mu\text{-CNBu}^t)(\mu\text{-L})_2(\text{CHBu}^t)_3]$ ^{7b} and $\delta 262.4$ p.p.m. in $[\text{NiL}_3]$.^{7c}

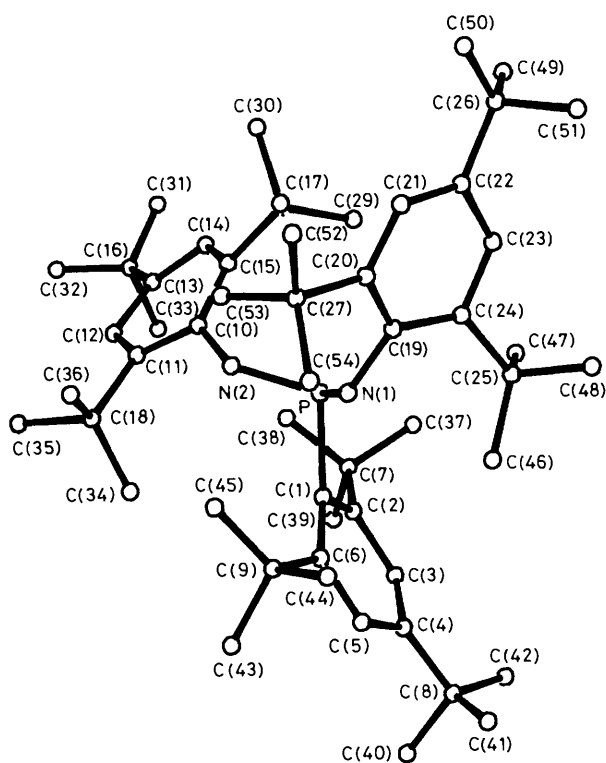


Figure 2. The molecular structure and atom numbering scheme for $\text{PAr}(\text{NHAr})_2$ ($\text{Ar} = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6}$) (**5**). Selected parameters are: $\text{P-N}(1)$ 1.73(1), $\text{P-N}(2)$ 1.75(1), $\text{P-C}(1)$ 1.90(1), $\text{N}(1)\text{-C}(19)$ 1.45(2), $\text{N}(2)\text{-C}(10)$ 1.47(2) Å; $\text{N}(1)\text{-P-N}(2)$ 104.6(6), $\text{N}(1)\text{-P-C}(1)$ 98.7(6), $\text{N}(2)\text{-P-C}(1)$ 108.0(5), $\text{P-N}(1)\text{-C}(19)$ 118.7(8), $\text{P-N}(2)\text{-C}(10)$ 123.5(8)°.

Finally, the high value for $^1J(^{31}\text{P}^1\text{H})$, 603 Hz, is appropriate for the presence of a $\text{P}^{\text{V}}\text{-H}$ bond [cf.,⁸ $\text{P}(\text{=NR})(\text{NR}_2)_2\text{H}$ with δ -13 p.p.m. and $^1J(\text{PH})$ 543 Hz].

The present results indicate that the phospho(III)azene has a potentially rich co-ordination chemistry. The lipophilic lithium compound (**3**) is a convenient transfer agent for the ligand $[\text{P}(\text{NAr})_2]^-$.

The closest comparisons relating to the X-ray data for (**2**) are with (i) the parent phospho(III)azene $\text{P}(\text{=NAr})(\text{NHAr})$ which has P-N bond lengths of 1.573(8) and 1.633(8) Å and $\angle\text{N-P-N} = 103.8(5)^\circ$; and (ii) the P^{V} ring compound $\text{RNP}(\text{Cl})(\text{NR}_2)\text{N}(\text{R})\text{TiCl}_3$ for which the ring parameters include P-N bond lengths of 1.597(5) and 1.613(5) Å and $\angle\text{N-P-N} = 97.8(3)^\circ$.⁸

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