Synthesis of a Phospha-arsene and a Phosphastibene; the First Compounds with Phosphorus–Arsenic and Phosphorus–Antimony Double Bonds

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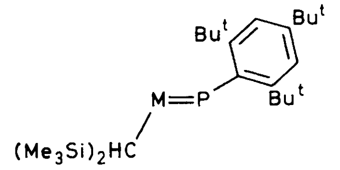
The reaction of $(Me_3Si)_2CHMCl_2$ (M = As or Sb) with $(2,4,6\text{-}Bu^t{}_3C_6H_2)PH_2$ in the presence of 1,5-diazabicyclo[5.4.0]undec-5-ene affords the double-bonded compounds, $(2,4,6\text{-}Bu^t{}_3C_6H_2)P{=}MCH(SiMe_3)_2$ (M = As or Sb).

In a recent communication[1] we described a new synthetic route to phosphorus–phosphorus double bonds. We now report that the same type of reaction has been used to prepare compounds with phosphorus–arsenic and phosphorus–antimony double bonds. These species represent the first examples of heteronuclear multiple bonding between the heavier main-group elements.

The new stibine, $(Me_3Si)_2CHSbCl_2$, was prepared by treat-



(1) M = As
(2) M = Sb

ment of $SbCl_3$ with $(Me_3Si)_2CHMgCl$ in Et_2O solution.† Treatment of $(Me_3Si)_2CHMCl_2$, M = As[2] or Sb, with (2,4,6-$Bu^t_3C_6H_2)PH_2$ in tetrahydrofuran in the presence of excess of 1,5-diazabicyclo[5.4.0]undec-5-ene afforded the phospha-arsene (**1**) and phosphastibene (**2**) as orange crystalline materials. Compound (**1**) was characterised by ^{31}P n.m.r. spectroscopy, and high resolution mass spectrometry (h.r.m.s.). The mass spectrum showed the expected molecular ion at 510.2256 (calc. 510.2248) whilst the $^{31}P\{^1H\}$ n.m.r. spectrum exhibited a characteristically low-field resonance at δ 575 p.p.m. (ref. ext. H_3PO_4 85%) indicative of P=P double bonding.[3] The presence of the $(Me_3Si)_2CH$ group was confirmed by the ^1H-coupled ^{31}P spectrum δ 575 p.p.m. (d, $^3J_{PH}$ 8.9 Hz). In order to fully characterise (**1**) an *X*-ray crystallographic study was undertaken.

Crystal data: $C_{25}H_{48}AsPSi_2$, M = 510.22, triclinic, space group $P\bar{1}$ (No. 2), a = 9.991(4), b = 10.452(9), c = 15.140(15) Å, α = 89.72(7), β = 85.03(5), γ = 77.72(5)°, U = 1539(3) Å^3, D_c = 1.310 g cm^{-3}, Z = 2, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 12.8 cm^{-1}. The structure, shown in Figure 1 together with the atom numbering scheme, was solved by conventional heavy atom methods (Patterson and difference Fourier) using data collected on an Enraf-Nonius CAD-4 diffractometer. Refinement (full matrix, least squares) using 3862 unique observed data [$I > 3\sigma(I)$] converged smoothly to give final residuals R = 0.0624 and R_w = 0.0791.‡ All non-hydrogen atoms were refined using anisotropic thermal parameters. The three hydrogen atoms H(01), H(3) [on C(3)], and H(5) [on C(5)] were located and refined positionally with fixed isotropic thermal parameters.

RP=PR
(3) R = 2,4,6-$Bu^t_3C_6H_2$
(4) R = $(Me_3Si)_3C$
(5) R = H

The structure consists of isolated neutral molecules of (**1**) with no short intermolecular contacts. The phosphorus–arsenic separation of 2.124(2) Å is consistent with its formulation as a double bond and is significantly shorter than the sum of the covalent radii (2.35 Å).[4] The phosphorus is bonded to a 2,4,6-$Bu^t_3C_6H_2$ group [P(1)–C(1) = 1.847(5) Å] while the arsenic bonds to a $(Me_3Si)_2CH$ ligand [As(1)–C(01) = 1.995(5) Å]. The central atoms, C(01), As(1), P(1), and C(1) are essentially planar [mean deviation 0.010(7) Å] and *trans*, similar to the structure found for the two structurally characterised RP=PR complexes (**3**) (R = 2,4,6-$Bu^t_3C_6H_2$)[3a] and (**4**) [R = $(Me_3Si)_3C$].[3k] *Ab initio* MO calculations[5] on the model compound (**5**) (R = H) reveal that the *trans* geometry is more stable than the *cis* by *ca.* 12 kJ mol^{-1} although in compounds (**1**)—(**4**) the *trans* preference is probably required by the presence of bulky groups. The bond angle at phosphorus in (**1**) [96.4(2)°] is much smaller than that in (**3**) [102.8(1)°][3a] presumably owing to decreased steric effects.

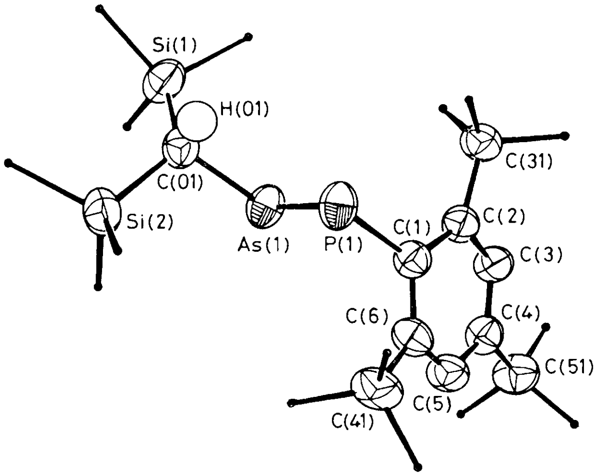


Figure 1. Molecular structure of (**1**) showing the atom numbering scheme. Important parameters are As(1)–P(1) 2.124(2), As(1)–C(01) 1.995(5), P(1)–C(1) 1.847(5) Å; C(01)–As(1)–P(1) 101.2(2), As(1)–P(1)–C(1) 96.4(2)°.

Compound (**2**) was characterised by h.r.m.s. (found 556.2092, calc. 556.2070) and by $^{31}P\{^1H\}$ n.m.r. spectroscopy. The ^{31}P chemical shift of (**2**) is δ 620.0 p.p.m. and is the lowest field ^{31}P resonance so far reported. In solution (**2**) is unstable and decomposes to the diphosphene, (**3**). The decomposition of (**2**) → (**3**) can be followed by ^{31}P n.m.r. spectroscopy and suggests that (**2**) is a source of free phosphinidene, which in the absence of a capturing group, dimerises to give (**3**).

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† Whilst the present manuscript was in preparation, a publication appeared describing the synthesis of $(Me_3Si)_2CHSbCl_2$ by a similar route. H. J. Breunig, W. Kanig, and A. Soltani-Neshan, *Polyhedron*, 1983, **2**, 291.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.