First Structural Characterization of Silicon–Arsenic and Silicon–Phosphorus Multiple Bonds in Silylated Silylidene-arsanes and -phosphanes; X-Ray Structure of a Tellura-arsasilirane Derivative

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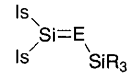
The molecular structures of the 1-*tert*-butyl-1-isityl-3,3,3-triisopropyldisilaphosphene **4** (isityl = 2,4,6-triisopropylphenyl), the analogous disilaarsene **5**, and the corresponding tellura-arsasilirane **6** (formed by reaction of **5** with elemental tellurium) are established by X-ray crystallographic analysis.

In 1991, we reported on a simple synthesis of the stable phosphasilene derivatives **1**, in which a triorganylsilyl group is attached to the phosphorus atom.[1] In addition, we have shown that thermally stable arsasilenes **2**, *i.e.* compounds with a Si=As bond, are, surprisingly, easily accessible by a multiple-step reaction, starting from Is_2SiF_2 (Is = isityl = 2,4,6-triisopropylphenyl) and $[LiAsH_2(dme)]$.[2] The remarkably high thermal stability of **1** and **2** (up to 110 °C), which is due to electronic influences of the SiR_3 groups,[2] enabled us to study the reactivity of the Si=P[3] and Si=As[4] bonds. However, none of the derivatives **1** and **2** were isolated in crystalline form. Recently, Niecke and coworkers reported on the isolation of the first crystalline phosphasilene **3**, whose structure was elucidated by single-crystal X-ray diffraction.[5]

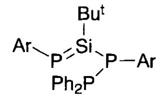
Here we report the unusual ^{31}P and ^{29}Si NMR data and molecular structure of the phosphasilene **4**, which differ substantially from that obtained for **3**. Moreover, we describe the first X-ray structure of a crystalline arsasilene, namely **5**, and its tellurium-oxidation product, that is the tellura-arsasilirane **6**.

Compounds **4** and **5** were prepared in a multiple-step reaction analogous to that used for the synthesis of **1** and **2**, starting from $Is(Bu^t)SiF_2$ **7** and 2 equiv. of $[LiEH_2(dme)]$ (E = P, As), proceeding *via* **8**, **9** and **10**, **11** as isolable intermediates, respectively (see Scheme 1).

The thermolysis of solutions of **10** and **11** in hexane at 60 °C yielded orange–red, clear solutions from which **4** (75%) and **5** (88%) were isolated as yellow and orange crystals, respectively. Compounds **4** and **5** are extremely sensitive to air and moisture. Their constitutions were determined by MS and NMR spectroscopy.† The phosphasilene **4** shows an unusually high-field singlet signal at δ −29.9 in the ^{31}P NMR spectrum, untypical for a two-coordinate phosphorus centre. Evidently, this corresponds to the large deshielding of the three-coordinate silicon atom at δ 213.2 in the ^{29}Si NMR spectrum, the lowest value known to date in the Si=P series.[5,6] On the other hand, for the ^{29}Si nucleus of the $SiPr^i_3$ group a resonance signal is observed in the normal range for silyl compounds at δ 21.0. In comparison with this finding the phosphasilene **1a** (SiR_3 = $SiPr^i_3$) gives resonance signals in the ^{31}P and ^{29}Si NMR spectra at δ 11.1 (Si=*P*) and 167.8 (*Si*=P), respectively.[1] Even larger differences in the ^{31}P chemical shifts are observed in the cases of the derivatives **3** (δ 128.7, Si=*P*)[5] and **12** (δ 105.4).[6] The identical chemical shifts in the ^{31}P CP-MAS solid-state and solution NMR spectra of **4** prove that only one isomer occurs; the X-ray structure determination of **4** (see below) reveals this to be the (*Z*)-form.‡ The unusually large shielding of the phosphorus atoms in **1** and **4** is attributed to the strong σ-donor influence of the silyl group. However, the characteristically large $^1J_{(Si=P)}$ coupling constants of **1**, **4** and **12** (149–160 Hz) clearly indicate the similar electronic situation of the three-coordinate Si atom and the Si–P π-bond. In contrast, the exceptionally large $^1J_{(Si=P)}$ value of 203 Hz of **3** demonstrates the special electronic nature of this derivative. In line with this, the X-ray structure analysis of **3** revealed a non-planar trigonal coordination of silicon and a Si=P distance of 2.094(3) Å, which is significantly longer than the value predicted by calculations (2.04–2.06 Å).[5,7,8] Phosphasilenes of type **1** and **4** however, are expected to represent Si=P bonds with trigonal-planar coordinated silicon, in which the Si–P π-bonds are strengthened by the silyl group attached to phosphorus. This is supported by *ab initio* calculations performed on the parent compounds $H_2Si{=}PH$ and $H_2Si{=}P(SiH_3)$.[8] The clear difference between the bond angles in **4** and the calculated values of $H_2Si{=}P(SiH_3)$ is revealed by an X-ray structure determination of **4** (see Fig. 1).§ The angle at the two-coordinate phosphorus [112.79(4)°] is considerably larger than the value predicted for $H_2Si{=}P(SiH_3)$ (100°), and that observed in **3** (104.2°). The



Is = 2,4,6-$Pr^i_3C_6H_2$
1 E = P
2 E = As



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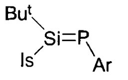

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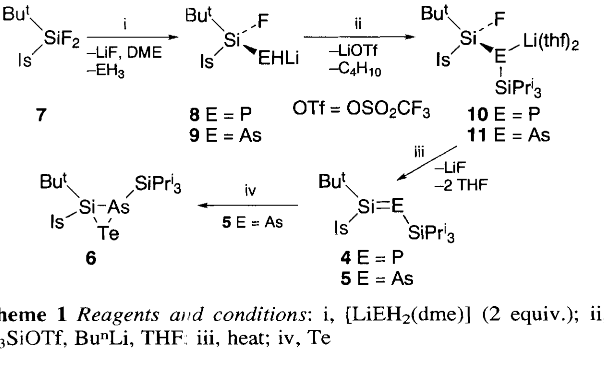
Ar = 2,4,6-$Bu^t_3C_6H_2$



Scheme 1 *Reagents and conditions*: i, $[LiEH_2(dme)]$ (2 equiv.); ii, Pr^i_3SiOTf, Bu^nLi, THF; iii, heat; iv, Te

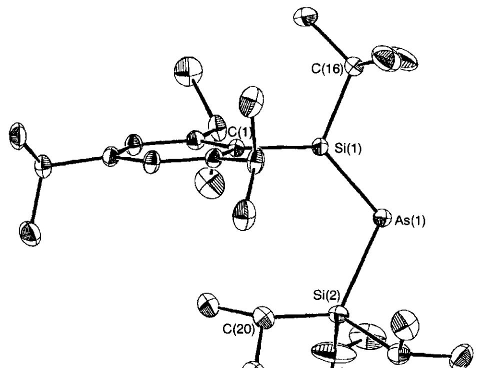


Fig. 1 Molecular structure of **5** which is isotypic to **4**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **5**: As(1)–Si(1) 2.164(1), As(1)–Si(2) 2.363(2), Si(1)–C(1) 1.874(2), Si(1)–C(16) 1.911(3); Si(1)–As(1)–Si(2) 110.92(4), As(1)–Si(1)–C(16) 114.67(9), As(1)–Si(1)–C(1) 131.78(9), C(1)–Si(1)–C(16) 113.4(1). Selected bond lengths (Å) and angles (°) for **4**: Si(1)–P(1) 2.062(1), Si(2)–P(1) 2.255(1), Si(1)–C(1) 1.871(2), Si(1)–C(16) 1.904(2); Si(1)–P(1)–Si(2) 112.79(4), P(1)–Si(1)–C(16) 114.59(7), P(1)–Si(1)–C(1) 131.99(9), C(1)–Si(1)–C(16) 113.36(9).

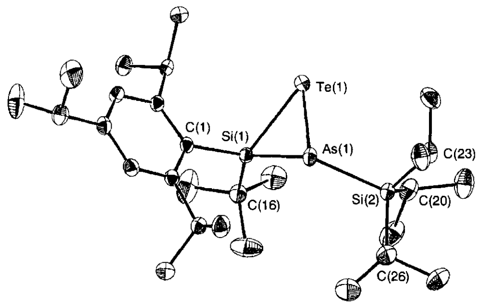


Fig. 2 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): As(1)–Si(1) 2.354(4), As(1)–Si(2) 2.396(1), Si(1)–Te(1) 2.491(1), As(1)–Te(1) 2.635(1); Si(1)–As(1)–Te(1) 59.60(4), Te(1)–Si(1)–As(1) 65.83(4), Si(1)–Te(1)–As(1) 54.58(4), Si(1)–As(1)–Si(2) 121.12(4), Te(1)–As(1)–Si(2) 103.07(5).

Si(1)–P(1) distance in **4** [2.062(1) Å] is clearly shorter than the length of the adjacent Si(2)–P(1) single bond [2.255(1) Å]. These distances are in very good agreement with the respective calculated values.[7,8] The sum of the bond angles at the Si(1) atom is 359.9°, *i.e.* this centre is trigonal-planar coordinated. Of considerable interest also are the distinct P(1)–Si(1)–C(1) [131.36(9)°] and P(1)–Si(1)–C(16) bond angles [114.59(7)°], which probably differ for steric reasons. The Si(2)–P(1)–Si(1)–C(1) (−13.7°) and Si(2)–P(1)–Si(1)–C(16) torsion angles (169.5°) of **4** are also a result of the influence of steric hindrance. This geometry in **4** compared to that in **3** clearly indicates that the Si=P distance and the coordination geometry at silicon are more strongly influenced by electronic than steric effects. Thus, the non-planar environment of silicon (sum of angles 356.7°) and the relatively long Si=P distance [2.094(3) Å] in **3** is probably better explained in terms of a second-order Jahn–Teller distortion.[10]

The molecular structure of the arsasilene **5**§ (Fig. 1) was also determined by X-ray diffraction analysis, showing that **5** is isotypic to the phosphasilene homologue **4**. The Si(1)–As(1) distance (Si=As) of 2.164(1) Å is in perfect agreement with the value calculated for the parent compound,[8] and the Si(1) atom is in a trigonal-planar surrounding (359.9°). The length of the Si(2)–As(1) single bond [2.363(2) Å] is similar to the values in $As(SiH_3)_3$ [2.355(1) Å][11] and in other silylarsanes.[2] The electronically-related conditions in **4** and **5** are also expressed by their similar ^{29}Si chemical shifts: the three-coordinate Si centre shows a large deshielding at δ 228.8.†

Oxidation of **5** with elemental tellurium at 25 °C yields the tellura-arsasilirane **6** which was isolated in form of orange crystals. Its composition and constitution were confirmed by MS and NMR spectroscopy.‡ Interestingly, the ^{125}Te and ^{29}Si NMR spectra of **6** show two sets of resonance signals at 20 °C, indicating that both diastereoisomeric forms are present in solution, whereas only one diastereoisomer (racemic mixture *R,R* and *S,S* configured) was observed in the crystal. Compound **6** represents the first compound of this type; its final molecular structure was established by X-ray crystallography as shown in Fig. 2.§ The Si(1)–Te(1) and As(1)–Te(1) bond lengths in **6** are in good agreement with the sums of the covalent radii of these elements. As expected for a three-membered ring, the endocyclic Si(1)–As(1) single bond distance [2.354(1) Å] is significantly shorter than the exocyclic Si(2)–As(1) bond [2.396(1) Å].

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Footnotes

† *Selected data for* **4**: ^{31}P NMR (81 MHz, [$^2H_6$]benzene $\delta_{P(1)}$ −29.9 (s); ^{29}Si NMR (39.7 MHz, [$^2H_6$]benzene) $\delta_{Si(1)}$ 213.2 [d, Si=P, ^1J(SiP) 161 Hz], $\delta_{Si(2)}$ 21.0 [d, Pr^iSi, ^1J(SiP) 75 Hz]; *m/z* (%) 476 (M^+, 6), 433 ($[M - Pr^i]^+$, 8), 419 ($[M - Bu]^+$, 24) 305 ($[M - Bu - SiPr^i_2H_2]^+$, 100). For **5**: ^{29}Si NMR (39.7 MHz, [$^2H_6$]benzene $\delta_{Si(1)}$ 228.7 (s, Si=As), $\delta_{Si(2)}$ 25.4 (s, Pr^iSi); MS *m/z* (%): 520 (M^+, 15), 477 ($[M - Pr^i]^+$, 4), 463 ($[M - Bu]^+$, 2), 287 ($[Is(Bu^t)SiH]^+$, 100).

‡ *Selected data for* **6**: ^{29}Si NMR (39.7 MHz, [$^2H_6$]benzene) $\delta_{Si(1)}$ −23.3 (s), −17.6, $\delta_{Si(2)}$ 17.9 (s), 13.5; ^{125}Te NMR [$^2H_6$]benzene, ref. Me_2Te) $\delta_{Te(1)}$ −550.1 (s), −547.4 (s); MS *m/z* (%) 650 (M^+, 19), 520 ($[M - Te]^+$, 9), 157 ($SiPr^i_3{}^+$, 80), 115 ($SiPr^i_2H^+$, 94).

§ *Crystal data*: **4**, monoclinic, space group $P2_1/a$, $a = 18.427(4)$, $b = 9.329(2)$, $c = 20.085(3)$ Å, $\beta = 116.20(2)°$, $V = 3098.0(10)$ Å^3, $Z = 4$, $D_c = 1.02$ g cm^{-3}, $T = 173$ K, 5621 measured reflections, 5451 unique, 342 parameters, $R1 = 0.046$ for 4355 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.119$ {all reflections, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$}.

5, monoclinic, space group $P2_1/a$, $a = 18.412(8)$, $b = 9.356(5)$, $c = 20.268(8)$ Å, $\beta = 116.26(4)°$, $V = 3131(3)$ Å^3, $Z = 4$, $D_c = 1.11$ g cm^{-3}, $T = 173$ K; 5666 measured reflections, 5494 unique, 339 parameters, $R1 = 0.038$ for 4490 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.098$ {all reflections, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$}. Intensity data for **4** and **5** were collected on a Nicolet R3 diffractometer (Mo-Kα radiation, ω-scans, $\theta_{max} = 25°$) and for **6** on a Siemens-Stoë AED 2 (Mo-Kα radiation, ω-scan, $\theta_{max} = 27°$).

6, monoclinic, space group $P2_1/a$, $a = 11.263(7)$, $b = 17.879(11)(2)$, $c = 16.229(10)$ Å, $\beta = 98.21(5)°$, $V = 3235(4)$ Å^3, $Z = 4$, $D_c = 1.331$ g cm^{-3}, $T = 218$ K; 6505 unique reflections, 310 parameters, $R1 = 0.0326$ [$I > 2\sigma(I)$], $wR2 = 0.0902$ {all data, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2\Sigma(wF_o^4)]^{1/2}$}. The structures were solved by direct methods[12a] and refined on F^2 with all measured reflections.[12b] Anisotropic atomic displacement factors were used for all non-hydrogen atoms. Methyl H atoms were refined as part of a rigid group. The other H atoms were inserted in calculated positions (C–H of isopropyl groups at Si) or refined freely (H atoms of the phenyl ring). One of the isopropyl groups is disordered in **4** and **5**.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. Driess, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1022.

2 M. Driess and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 316.

3 M. Driess and H. Pritzkow, *Phosphorus, Sulfur, Silicon Rel. Elem.*, 1993, **76**, 57; M. Driess and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 751; M. Driess, *Adv. Organomet. Chem.*, in the press.

4 M. Driess, H. Pritzkow and W. Sander, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 283; M. Driess and H. Pritzkow, *J. Chem. Soc., Chem. Commun.*, 1993, 1585; see also refs. 3.

5 H. R. G. Bender, E. Niecke and M. Nieger, *J. Am. Chem. Soc.*, 1993, **115**, 3314.

6 C. N. Smit and F. Bickelhaupt, *Tetrahedron Lett.*, 1984, **25**, 3011; *Organometallics*, 1987, **6**, 1156; Y. van den Winkel, H. Bastiaans and F. Bickelhaupt, *J. Organomet. Chem.*, 1991, **405**, 183; *Phosphorus, Sulfur, Silicon Rel. Elem*, 1990, **49/50**, 333.

7 K. J. Dykema, T. N. Truong and M. Gordon, *J. Am. Chem. Soc.*, 1985, **107**, 4535; L.-J. Lee, J. E. Boggs and A. H. Cowley, *J. Chem. Soc., Chem. Commun.*, 1985, 773; P. v. R. Schleyer and D. Kost, *J. Am. Chem. Soc.*, 1988, **110**, 2105.

8 M. Driess and R. Janoschek, *J. Mol. Struct. (Theochem)*, 1994, **313**, 129.

9 Review: W. Kutzelnigg, U. Fleischer and M. Schindler, in *NMR–Basic Principles and Progress*, vol. 23, Springer, Berlin, Heidelberg, New York, 1991.

10 T. A. Albright, J. K. Burdett and M.-H. Whangbo, in *Orbital Interactions in Chemistry*, Wiley, New York, 1985, p. 95.

11 B. Beagley, A. G. Robiette and G. M. Sheldrick, *J. Chem. Soc. A*, 1968, 3006.

12 (*a*) G. M. Sheldrick, SHELXS86, Göttingen, 1986; (*b*) G. M. Sheldrick, SHELXL93, Göttingen, 1993.