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Phosphasilene synthesis and reactivity: an improved route to 1-(2,4,6-tri-tert-butylphenyl)-2-tert-butyl-2-(2,4,6-tri-isopropylphenyl)phosphasilene

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Abstract

A new route was developed for the synthesis of a specific phosphasilene, 1-(2,4,6-tri-tert-butylphenyl)-2-tert-butyl-2-(2,4,6-tri-isopropylphenyl)phosphasilene (**1e**). Several novel phosphasilenes (**1**) with various substituents on phosphorus have been synthesized. The influence of the substituents on the phosphorus and silicon chemical shifts and the stability of the phosphasilenes is analyzed. The chemical reactivity of **1e** has been investigated.

Introduction

For a long time it was believed phosphaheteroalkenes and other heteroalkenes of the third or higher period elements could not be made. This was explained by the so called "Classical Double Bond Rule", which, as shown by a survey of the recent literature [1], is no longer valid in its original formulation. In the light of these developments, it seems more realistic to state that elements in the lower left part of the Periodic Table have a lower tendency to form double bonds. Phosphasilenes (**1**), i.e. compounds with a phosphorus–silicon double bond (P=Si), involve a $p\pi$-bonded phosphorus and a $p\pi$-bonded silicon atom and are therefore of interest as inherently highly unstable representatives of the phosphaheteroalkenes. In 1984, we reported the first moderately stable phosphasilene [2]; since then several others have been synthesized, and their stability and spectroscopic properties were studied [3,4].

We now report our studies of an alternative, improved route to phosphasilenes. Furthermore, we have synthesized several new phosphasilenes with various substituents on phosphorus and analyzed the influence on the phosphorus and silicon chemical shifts as well as on the stability of these compounds. By this improved procedure it was possible to obtain the very crowded **1e** as an almost pure compound. Several reactions were carried out with **1e**.

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Results and discussion

Alternative route to phosphasilenes

Our original procedure for the preparation of phosphasilenes involved the sequence outlined below (eq. 1). Combination of the lithium phosphide **2** with a suitable dichlorosilane **3** in THF gives **4**, which on elimination of HCl gives **1**.

$$\underset{\mathbf{2}}{R^1PHLi} + \underset{\mathbf{3}}{R^2R^3SiCl_2} \xrightarrow[-LiCl]{} \underset{\mathbf{4}}{R^1P(H)-SiR^2R^3(Cl)} \xrightarrow[-HCl]{base} \underset{\mathbf{1}}{R^1P=SiR^2R^3} \quad (1)$$

However, several difficulties were encountered with this procedure. The major problem was that **2** is not only a reactant but also a highly efficient base for the elimination of HCl from sterically congested representatives of **4**. Thus, the yield of **1** could be increased by employing the stoichiometry **2** : **3** = 2 : 1 (eq. 2).

$$2\ \underset{\mathbf{2}}{R^1PHLi} + \underset{\mathbf{3}}{R^2R^3SiCl_2} \longrightarrow \underset{\mathbf{1}}{R^1P=SiR^2R^3} + \underset{\mathbf{5}}{R^1PH_2} \quad (2)$$

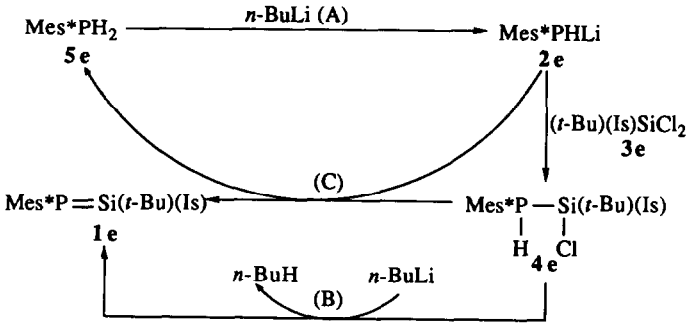
This method, however, has the drawback of yielding equimolar amounts of **5**, which so far have not been separated from the sensitive **1**. We therefore investigated the alternative approach outlined below (eq. 3). Two equivalents of n-butyllithium were treated with **5** in order to obtain dilithiophosphide **6**; **6** was expected to combine with a dichlorosilane **3** to give phosphasilene **1**, with lithium chloride as the only and easily-separable by-product.

$$\underset{\mathbf{5}}{R^1PH_2} \xrightarrow[-2\ n\text{-BuH}]{2\ n\text{-BuLi}} \underset{\mathbf{6}}{R^1PLi_2} \xrightarrow[-2\ LiCl]{R^2R^3SiCl_2\ (3)} \underset{\mathbf{1}}{R^1P=SiR^2R^3} \quad (3)$$

This procedure turned out to be successful as a one-pot reaction, combining both steps for the synthesis of one specific phosphasilene, i.e. **1e** (R^1 = Mes* [5*], R^2 = Is [5*], R^3 = ^{t}Bu). However, contrary to the concept behind this procedure, isolation, detection by NMR or trapping with D_2O of the interesting "intermediate" dilithiophosphide **6e** (Mes*PLi_2) proved to be impossible; only the formation of the monolithiophosphide **2e** was observed. Though disappointing, this was not totally unexpected; Cowley reported failure in attempts to make **6e** [6]. Thus, the course of events leading to **1e** must be different from that depicted in eq. 3.

In a separate experiment, it was observed that n-butyllithium does not react with **1e** at room temperature. In view of the high reactivity of less crowded phosphasilenes, this was very surprising and illustrates the importance of steric protection. The conclusion was therefore drawn that the synthesis of the very crowded **1e** followed the reaction path shown in Scheme 1, in which n-butyllithium has the double function of metallating **5e** (step A) and of eliminating HCl from **4e** (step B);

* Reference number with an asterisk indicates a note in the list of references.



Scheme 1

the latter step in which **1e** is formed, takes the place of the previous HCl elimination from **4e** by **2e** (step C [3a]).

On the other hand it was possible to synthesize two other dilithiophosphides, **6g** ($IsPLi_2$) and **6k** ($PhesPLi_2$), bearing the isityl and phesityl group [5*], respectively, on phosphorus. Apparently, steric hindrance by the very large supermesityl group prevents the second metallation of **2e**; aggregation of such a lithium phosphide may be an additional factor. The dilithiophosphides **6g** and **6k** do react with D_2O and Me_3SiCl to give the expected RPD_2 and $RP(SiMe_3)_2$ derivatives, respectively. Unexpectedly, they did not react at all with $Cl_2Si(^tBu)(Is)$ (**3e**) (see Experimental). The reactions of **6g** with $IsPCl_2$ and $IsAsCl_2$ did not give the expected diphosphene or phosphaarsene, but presumably mixtures of cyclophosphines [7] due to halogen–metal exchange reactions (see Experimental). Reaction with Ph_2CCl_2 yielded, besides the same cyclophosphines, a compound (ca. 10% yield) which gave a typical low field ^{31}P NMR signal (δ +235.7 in THF) [8] and was tentatively assigned the formulation $IsP{=}CPh_2$. The lower reactivity of 1,1-dimetallophosphines than of their monometallated analogues finds a parallel in the behaviour of 1,1-diorganometallic compounds [9].

New phosphasilenes

The new approach employing **5** and two equivalents of n-butyllithium (*vide supra*) was not applicable for primary phosphines with a group smaller than supermesityl (Mes*), probably because of the rapid formation of highly unreactive dilithiophosphides **6**. Therefore, several new phosphasilenes could only be synthesized (Table 1) following the original procedure (see eq. 2). However, the yields were significantly lower, and an increasing number of unidentified side products were formed as the substitution on phosphorus became less sterically demanding. Purification turned out to be very difficult. Due to these problems, the compounds were only, but unambiguously, characterized by their unique ^{31}P and ^{29}Si NMR data, in particular by the strongly deshielded $\delta(^{29}Si)$ values and the large $^1J(PSi)$ coupling constants. In Table 1 known (**1a–1e** [3]) as well as new compounds and their ^{31}P and ^{29}Si NMR data are summarized. The ^{31}P NMR chemical shifts are somewhat scattered and surprisingly shielded [3]; together with the ^{29}Si NMR chemical shifts, they show a certain compensatory tendency in the sense that the sum of $\delta(^{31}P) + \delta(^{29}Si)$ is approximately constant ($\langle\Sigma[\delta(^{31}P) + \delta(^{29}Si)]\rangle = 272 \pm 15$ ppm, if one excludes **1c**). The phosphorus shift becomes shielded and the silicon shift deshielded

Table 1

^{31}P [a] and ^{29}Si [b] NMR data for $R^1P{=}SiR^2R^3$ (1)

Compound	R^1	R^2	R^3	$\delta(^{31}P)$ (ppm)	$\delta(^{29}Si)$ (ppm)	$^1J(PSi)$ (Hz)
1a	Mes*	Mes	Mes	136.0	151.2	149
1b	Mes*	Es	Es	133.7	150.1	152
1c	Mes*	Ph	Is	93.5	153.0	151
1d	Mes*	Mes	Is	122.7	148.7	152
1e	Mes*	^{t}Bu	Is	105.4	175.9	155
1f	Mes*	Es	Es′	134.2	149.2 [c]	153
	Mes*	Es′	Es	135.8	149.0 [c]	153
1g	Is	^{t}Bu	Is	66.2	190.3	153
1h	Es	^{t}Bu	Is	65.8	194.1	153
1i	Mes	^{t}Bu	Is	69.0	196.8	153
1j	R″	^{t}Bu	Is	69.7	199.0	154
1k	Phes	^{t}Bu	Is	86.7	180.0	151

[a] Standard: ext. 85% H_3PO_4. [b] Standard: ext. Me_4Si. [c] The assignment for the $\delta(^{29}Si)$ signal to one of the $\delta(^{31}P)$ signals is arbitrary and may have to be reversed.

when the substituent on phosphorus is smaller; this trend is most obvious within a set having identical substituents at silicon (i.e. **1e**, **1g–1h**). Highly diagnostic are the ^{29}Si NMR chemical shifts which are amongst the most deshielded ones ever reported for silicon: to our knowledge, **1j** ($\delta(^{29}Si) = 199$ ppm) has the most deshielded chemical shift reported so far for a silene. Even more diagnostic are the large coupling constants $^1J(PSi)$ in the range of 149–155 Hz, attributed to the high *s*-character in the σ-component of the P=Si bond.

In the case of **1f**, a 1 : 1 mixture of the expected *E*/*Z* isomers has been observed, whereas for **1c–1e** and **1g–1k**, only one stereoisomer seems to be formed according to ^{29}Si and ^{31}P NMR spectroscopy. Apparently, only the stable *E*-isomer is produced due to the difference in bulk between the large isityl group and the smaller second substituent at silicon.

A particularly interesting feature of phosphaheteroalkenes is the thermal *E*/*Z* isomerization barrier. In principle, *E*/*Z* isomerization of phosphasilenes, like that of other phosphaheteroalkenes (or the corresponding imines), can proceed by inversion at phosphorus or by rotation around the double bond. If a rotation mechanism were observed, it would yield information on the strength of the π-component of the double bond, because in the transition state the *p*-orbitals on phosphorus and silicon are orthogonal and their overlap is zero. However, no *E*/*Z* isomerization of **1f** was observed up to 80 °C [10]. Therefore, we can only estimate an experimental lower limit for $\Delta G^{\ddagger}$ of approximately 84 kJ/mol for this transformation; this is well below the calculated value for $HP{=}SiH_2$ of 121 kJ/mol [11].

In general, the stability of **1** was found to increase with increasingly bulky substitution. A closer look at the thermal stability leads to the conclusion that protection by bulky substituents is more important at silicon than at phosphorus. For example, the ^{31}P NMR spectrum of **1a** shows a 50% decrease in the signals after 6 hours, while **1e**, with the same (supermesityl) group at phosphorus but sterically more demanding ligands at the silicon atom, was stable for several weeks at room temperature. On the other hand **1e** and **1i** have the same substituents on the Si atom

but different ones on the P atom (Mes* and Mes, respectively), and their thermal stabilities in solution are the same.

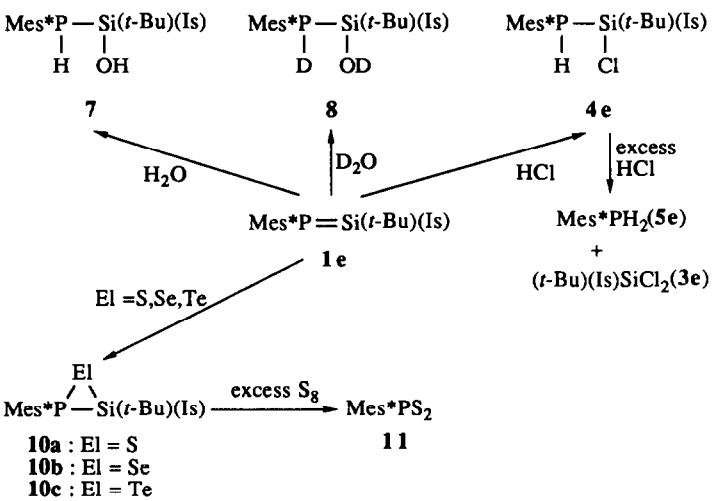
Reactions of **1e**

So far, investigation of the chemical reactivity of the phosphasilenes has been restricted because they could not be isolated pure. By the improved approach depicted in Scheme 1, it was possible to obtain **1e** in nearly pure form (^{1}H NMR spectra showed small amounts of impurities, but only one signal was observed in the ^{31}P NMR spectrum). Nevertheless, attempted crystallization, sublimation, or purification by column chromatography did not give a 100% pure or crystalline product.

Several reactions (see Scheme 2) with **1e** were performed using the salt-free reaction mixture containing at least 95% of the phosphasilene (see Experimental). Although most of the products could be characterized by ^{31}P, ^{29}Si NMR and high resolution mass spectrometry, purification by standard procedures again turned out to be impossible because of the sensitive nature of these compounds, which were too unstable under the reaction conditions.

The reactivity pattern of **1e** reflects the polarization expected on the basis of electronegativities [3a]; phosphorus is the negative end of the P=Si dipole and adds electrophiles, whereas nucleophiles attack at silicon. Adducts **7**, **8**, and **4e** resulted by the reaction of **1e** with water, deuterium oxide, and hydrogen chloride, respectively. They were obtained as diastereomeric pairs (about 1.5 : 1). Thus we conclude that the addition is stepwise with loss of stereospecificity in the intermediate. With an excess of hydrogen chloride, **4e** is cleaved to form **3e** and **5e**.

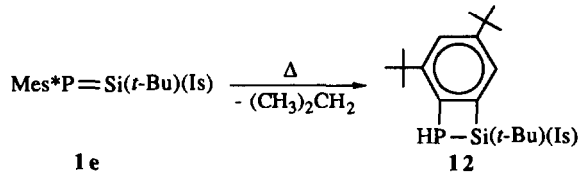
By analogy with the behavior of phosphaalkenes and related compounds [12], **1e** adds chalcogens (sulphur, selenium, and tellurium) to form unstable three-membered ring compounds **10**. When stoichiometric amounts of chalcogen were used the reaction proceeded too slowly and could not be completed before decomposition began, and so the reactions had to be performed with an excess of chalcogen. This had the drawback of leading to partial over-oxidation of the initially formed **10**. The



Scheme 2

silathiaphosphirane **10a** for example was readily cleaved to give the known compound **11** [12,13]. Therefore, **10a–c** were identified by their characteristic high field chemical shifts only.

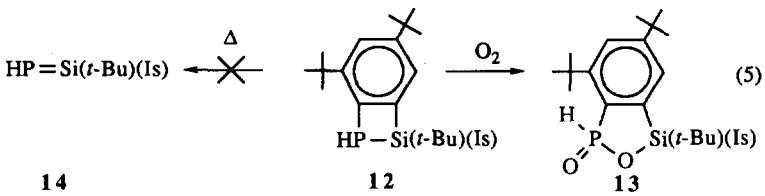
Upon heating a solution of **1e** in benzene or toluene at 60 °C for several hours, isobutene was eliminated with the formation of the phosphasiletene **12** (eq. 4).



(4)

1e **12**

Although the reaction was performed in perdeuterated solvents, no deuterium was incorporated. Abstraction of the hydrogen on phosphorus from the solvent, such as was suggested for the formation of a related phosphagermene [14], can therefore be excluded; the hydrogen is apparently derived from the tert-butyl group. The mechanism of this reaction is still unclear. Two isomers (*cis*/*trans*) of **12** were found, and shown by NMR spectroscopy [10] not to be in equilibrium. These isomers must therefore have been formed during the reactions. This excludes a concerted reaction and points to a stepwise process, either ionic or radical. Compound **12** is, like its germanium analogue [14], thermally very stable: it was recovered unchanged after 12 h at 150 °C and did not give phosphasilene **14** (or dimers thereof), in contrast to the behaviour of the tin analogue of **12** [14]. With elementary oxygen, **11** gave two stereoisomers (about 1 : 1) of the five-membered ring compound **13** (eq. 5).



(5)

14 **12** **13**

As observed for several other heteroalkenes (P=Ge [15], P=P [16], Si=Si [17]), phosphasilene **1e** is thermochromic; a solution of **1e** (1 *M*) in perdeuterated toluene is yellow at −80 °C, orange at room temperature, and deep-orange at +80 °C. This thermochromism was also reflected in the ^{31}P NMR spectrum of **1e**. The ^{31}P NMR chemical shift is deshielded with increasing temperature (see Table 2); both phenomena are reversible.

Table 2

Temperature dependence of the ^{31}P chemical shift of **1e**

T (°C):	−70	−50	−35	0	+27	+60	+105
δ(ppm) [a]	+100.5	+101.6	+102.5	+104.1	+105.5	+107.2	+109.2

[a] In toluene-d_8

Satisfactory UV and IR spectra could only be recorded for **1e** because the other compounds contained impurities. The UV spectrum of **1e** shows two bands at 327 (log $\epsilon = 2.3$) and 255 nm (log $\epsilon = 2.6$) and is quite similar to the UV spectra of the phospha- and arsa-alkenes [18]. The band at 327 is probably due to the $n\pi^*$ transition. Both bands disappear upon addition of water (formation of **7**).

The IR spectrum of **1e** shows a strong band at 706 cm^{-1}. We tentatively assign this absorption to the P=Si stretching vibration; this assignment is supported by theoretical calculations by Gordon et al. [11], predicting 673 cm^{-1} for $HP{=}SiH_2$.

Experimental

General procedures

The syntheses of air-sensitive starting materials were performed under argon or nitrogen; small scale experiments (i.e. preparation of the phosphasilenes and reactions with **1e**) were performed in sealed, evacuated systems [19]. THF, diethyl ether, and n-pentane were distilled from sodium-potassium alloy. The NMR spectra were recorded on a Bruker WH-90 NMR spectrometer at 90 MHz (^1H) and on a Bruker WM-250 NMR spectrometer at 250 MHz (^1H), 62.89 MHz (^{13}C), 49.69 MHz (^{29}Si), or 101.2 MHz (^{31}P). Chemical shifts (ppm) were measured relative to external Me_4Si or 85% H_3PO_4. Elemental analyses were performed by the Mikroanalytisches Labor Pascher, Remagen–Bandorf, Germany. HR EI mass spectra were recorded on a Finnigan MAT 90 mass spectrometer. UV spectra were recorded on a Beckman DU-70 spectrophotometer. IR spectra were recorded on a Matteson Galaxy 6030 FT–IR spectrometer.

*Dichloro(2,6-diethylphenyl)(2,4,6-triethylphenyl)silane (**3f**) (Es'EsSiCl$_2$)*

A suspension of 2,6-diethylphenyllithium (34 mmol; prepared from 1-bromo-2,6-diethylbenzene [20] and n-butyllithium as described previously for 2,4,6-tri-isopropylphenyllithium and 2,4,6-triethylphenyllithium [3]) in benzene (100 ml) was added at 0 °C during 2 h to a solution of trichloro(2,4,6-triethylphenyl)silane [3] (9.2 g, 31 mmol) in benzene (20 ml). After the addition was complete, the mixture was allowed to warm to room temperature. After 48 h, very little reaction had taken place and so THF (50 ml) was added, and the reaction was then complete after 3 h at room temperature. The salt was filtered off, and the filtrate evaporated to dryness. The light yellow residue was distilled in vacuum (b.p. 153 °C/$3 \cdot 10^{-2}$ mbar), yielding **3f** (9.1 g, 75%) as a colorless oil. ^1H NMR ($CDCl_3$): δ 1.04 (t, 6 H, $J = 7.3$ Hz, *o*-CH_2CH_3), 1.07 (t, 6 H, $J = 7.3$ Hz, *o*-CH_2CH_3), 1.24 (t, 3 H, $J = 7.5$ Hz, *p*-CH_2CH_3), 2.62 (q, 2 H, $J = 7.4$ Hz, *p*-CH_2CH_3), 2.84 (q, 4 H, $J = 7.4$ Hz, *o*-CH_2CH_3), 2.90 (q, 4 H, $J = 7.4$ Hz, *o*-CH_2CH_3), 6.92 (s, 2 H, Es*H*), 7.08 (d, 2 H, $J = 7.5$ Hz, *m*-Es'*H*), 7.08 (t, 1 H, $J = 7.7$ Hz, *p*-Es'*H*); ^{13}C NMR ($CDCl_3$): δ 15.02 (q, $^1J(CH) = 127$ Hz), 16.20 (q, $^1J(CH) = 127$ Hz), 16.26 (q, $^1J(CH) = 127$ Hz), 28.61 (t, $^1J(CH) = 129$ Hz), 29.48 (t, $^1J(CH) = 127$ Hz), 29.52 (t, $^1J(CH) = 127$ Hz), 127.24 (d, $^1J(CH) = 155$ Hz), 127.53 (d, $^1J(CH) = 159$ Hz), 130.03 (s), 130.94 (d, $^1J(CH) = 160$ Hz), 133.34 (s), 147.13 (s), 149.28 (s), 149.33 (s); ^{29}Si NMR ($CDCl_3$): δ 0.46 (s); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 392 ($M^{+\cdot}$, 4), 363 (18), 162 (100), 133 (19); MS, $M^{+\cdot}$ (^{35}Cl) found: 392.1494, calcd.: 392.1494. Anal. Found: C, 67.80; H, 7.80; Cl, 17.00; Si, 7.36. $C_{22}H_{30}Cl_2Si$ calcd.: C, 67.16; H, 7.69; Cl, 18.02; Si, 7.14%.

2,4,6-Tri-isopropylphenylphosphine (5g) ($IsPH_2$)

A solution of 1-bromo-1,4,6-tri-isopropylbenzene [20] (35.4 g, 0.125 mol) in THF (150 ml) was added to magnesium (4.25 g, 0.175 mol) in THF (10 ml). After 1.5 h reflux, the formation of the Grignard reagent was quantitative (D_2O-quench), and the solution was slowly (1.5 h) added to a solution of trichlorophosphine (18.5 g, 0.134 mol) in diethyl ether (150 ml) at −60 °C. After overnight stirring, the mixture was warmed to 10 °C. After filtration to remove the magnesium salts the solution of dichloro-2,4,6-tri-isopropylphenylphosphine was slowly added to a suspension of $LiAlH_4$ (7.0 g, 0.19 mol) in diethyl ether (40 ml) at 0 °C. After overnight stirring, the excess of $LiAlH_4$ was destroyed by addition of aqueous NH_4Cl (200 ml). The mixture was filtered and the organic layer separated and dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was distilled in vacuum to give **5g** (17.1 g, 58%) as a colorless liquid (b.p. 77 °C/4 · 10^{-3} mbar). ^{1}H NMR (C_6D_6): δ 1.23 (d, 12 H, J = 6.8 Hz, *o*-CH(CH_3)$_2$), 1.24 (d, 6 H, J = 6.9 Hz, *p*-CH(CH_3)$_2$), 2.81 (sep, 1 H, J = 6.8 Hz, *p*-CH(CH$_3$)$_2$), 3.47 (sep, 2 H, J = 6.8 Hz, *o*-CH(CH$_3$)$_2$), 3.87 (d, 2 H, ^1J(PH) = 204 Hz, PH_2), 7.11 (d, 2 H, ^4J(PH) = 2.3 Hz, IsH); ^{31}P NMR (C_6D_6): δ −158.2 (t, ^1J(PH) = 203 Hz); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 236 ($M^{+\cdot}$, 32), 235 (8), 205 (18), 204 (11), 203 (100); MS, $M^{+\cdot}$ found: 236.169, calcd.: 236.1688. Anal. Found C, 76.19; H, 10.70; P, 12.96. $C_{15}H_{25}P$ calcd.: C, 76.23; H, 10.66; P, 13.11%.

2,4,6-Triethylphenylphosphine (5h) ($EsPH_2$)

This was prepared as described for **5g** from 1-bromo-2,4,6-triethylbenzene [20] (30.0 g, 0.124 mol). After distillation, **5h** (14.5 g, 60%) was obtained as a colorless liquid (b.p. 77 °/4 · 10^{-3} mbar). ^{1}H NMR (C_6D_6): δ 1.21 (t, 6 H, J = 7.3 Hz, *o*-CH_2CH_3), 1.22 (t, 3 H, J = 7.3 Hz, *p*-CH_2CH_3), 2.53 (q, 2 H, J = 7.3 Hz, *p*-CH_2CH_3), 2.75 (q, 4 H, J = 7.3 Hz, *o*-CH_2CH_3), 3.78 (d, 2 H, ^1J(PH) = 203 Hz, PH_2), 6.89 (d, 2 H, ^4J(PH) = 2 Hz, EsH); ^{31}P NMR (C_6D_6): δ −158.1 (t, ^1J(PH) = 203 Hz); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 194 ($M^{+\cdot}$, 38), 165 (8), 162 (11), 161 (100), 133 (10), 105 (10); MS, $M^{+\cdot}$ found: 194.123, calcd.: 194.1220. Anal. Found: C, 74.06; H, 9.87; P, 15.6. $C_{12}H_{19}P$ calcd.: C, 74.20; H, 9.86; P, 15.94%.

2,4,6-Triphenylphenylphosphine (5k) ($PhesPH_2$)

This was prepared as described for **5g** from 1-bromo-2,4,6-triphenylbenzene (43.4 g, 0.113 mol). After distillation **5k** (26.0 g, 68%) was obtained as colorless crystals (m.p. 64 °C, b.p. 198 °C/4 · 10^{-3} mbar). ^{1}H NMR (C_6D_6): δ 3.87 (d, 2 H, ^1J(PH) = 201 Hz, PH_2) 7.15–7.53 (m, 17 H, ArH). ^{31}P NMR (C_6D_6): δ −132.6 (t, ^1J(PH) = 201 Hz). Anal. Found: C, 85.28; H, 5.64; P, 9.18. $C_{24}H_{19}P$ calcd.: C, 85.19; H, 5.66; P, 9.15%.

2,6-Dimethyl-4-octoxyphenylphosphine (5j) ($R''PH_2$)

A solution of (2,6-dimethyl-4-octoxyphenyl)diethoxyphosphine [21] (14.8 g, 46.0 mmol) was slowly added to a suspension of $LiAlH_4$ (2.0 g, 59 mmol) in diethyl ether (100 ml). After 0.5 h reflux and overnight stirring, the excess $LiAlH_4$ was destroyed by addition of aqueous NH_4Cl (100 ml) at 0 °C. Work-up as described for **5g** yielded **5j** (9.0 g, 84%) as a colorless oil (b.p. 120 °C/2 · 10^{-3} mbar). ^{1}H NMR (C_6D_6): δ 0.96 (t, 3 H, J = 6.5 Hz, $-OCH_2CH_2(CH_2)_5CH_3$), 1.30–1.42 (m, 10 H,

$-OCH_2CH_2(CH_2)_5CH_3$), 1.71 (t of t, 2 H, $J = 6.5$ Hz, $-OCH_2CH_2(CH_2)_5CH_3$), 2.32 (s, 6 H, *o*-CH_3), 3.64 (d, $^1J(PH) = 201$ Hz, PH_2), 3.75 (t, 2 H, $J = 6.5$ Hz, $-OCH_2CH_2(CH_2)_5CH_3$), 6.69 (d, 2 H, $^4J(PH) = 2$ Hz, Ar*H*); ^{31}P NMR (C_6D_6): δ -156.1 (t, $^1J(PH) = 201$ Hz); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 266 ($M^{+\cdot}$, 63), 234 (3), 154 (100), 122 (30), 121 (81); MS, $M^{+\cdot}$, found 266.178, calcd.: 266.1793, Anal. Found: C, 72.39; H, 10.40; O, 5.95, P, 11.6. $C_{16}H_{27}OP$ calcd.: C, 72.15; H, 10.22; O, 6.01, P, 11.63%.

2,4,6-Tri-isopropylphenyldilithiophosphide (6g) ($IsPLi_2$)

To a solution of **5g** (0.25 mmol) in diethyl ether (1 ml) at room temperature was added a solution of n-butyllithium (0.5 mmol) in n-pentane (2 ml). The mixture was stirred for 1 h and to the resulting orange solution of **6g** was added an excess of chlorotrimethylsilane (or deuterium oxide). After complete decolorization, the solvents were evaporated and the colorless residue was dissolved in perdeuterated benzene, filtered and washed into a connected NMR tube. $IsPD_2$: ^{31}P NMR (C_6D_6): δ -160.4 (quint, $^1J(PD) = 32$ Hz). $IsP(SiMe_3)_2$: -169.3 (s, $^1J(PSi) = 21$ Hz); ^{29}Si (C_6D_6): δ 0.77 (d, $^1J(PSi) = 21$ Hz); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 380 ($M^{+\cdot}$, 100), 365 (4), 84 (45), 73 (81); MS, $M^{+\cdot}$ found: 380.247, calcd.: 380.247.

Reaction of 6g with dichlorodiphenylmethane

To a solution of **6g** (0.8 mmol) in THF (10 ml) at room temperature was added a solution of dichlorodiphenylmethane (0.67 mmol) in diethyl ether (3 ml). The mixture immediately turned deep-red. After 2.5 h stirring the color had changed to orange. ^{31}P NMR (THF): δ 235.7 (s, 10%), 79.1 (s, 2%), -26.5 (s, 5%), -98.8 (d, $^1J(PP) = 179$ Hz, 2 P) and -132.8 (t, $^1J(PP) = 179$ Hz, 1 P) (traces of tri(2,4,6-tri-isopropylphenyl)cyclotriphosphine [22]), -100.2 (s, 83%).

Reaction of 6g with dichloro(2,4,6-tri-iso-propylphenyl)arsine

To a solution of **6g** (0.8 mmol) in THF (10 ml), at $-60\,^\circ C$ was added dichloro(2,4,6-tri-isopropylphenyl)arsine (0.8 mmol). The reaction mixture immediately turned deep-brown. It was allowed to warm to room temperature. After stirring for 2.5 h the color had changed to light-green. The mixture was evaporated to dryness and the residue dissolved in perdeuterated benzene (2.5 ml). The ^{31}P NMR spectrum (C_6D_6) showed no signals in the low-field region (thus, formation of a phosphaarsene can be excluded [23]); δ -60.3 (s, 20%), -68.4 and -119.5 (AB-system, $J(AB) = 213$ Hz, 39%) (probably tri(2,4,6-tri-isopropylphenyl)difosfaarsiraan), -84.0 (s, 2%), -98.8 (d, $^1J(PP) = 179$ Hz, 2 P) and -132.8 (t, $^1J(PP) = 179$ Hz, 1 P) (30% tri(2,4,6-tri-isopropylphenyl)cyclotriphosphine [22]), 106.3 (s, 8%) (probably tri(2,4,6-tri-isopropylphenyl)phosphadiarsiraan).

2,4,6-Triphenylphenyldilithiophosphide (6k) ($PhesPLi_2$)

To a solution of **5k** (0.5 mmol) in diethyl ether (4 ml) at room temperature was added a solution of n-butyllithium (1.8 mmol) in n-hexane (1.2 ml). A red precipitate was immediated formed, and later became orange; after 27 h stirring an excess of chlorotrimethylsilane (or deuterium oxide) was added to the suspension. Rapid decolorization occurred with deuterium oxide, but with chlorotrimethylsilane the resulting reaction mixture turned light orange. In both cases the mixture was

evaporated to dryness. The residue was dissolved in perdeuterated benzene and the solution filtered and washed into a connected NMR tube. $PhesPD_2$: ^{31}P NMR (C_6D_6): δ −135.0 (quint, $^1J(PD) = 33$ Hz); MS, $M^{+\cdot}$ found: 340.132, calcd.: 340.1346. $PhesP(SiMe_3)_2$: ^{31}P NMR (C_6D_6): δ −146.2 (s, $^1J(PSi) = 21$ Hz); ^{29}Si NMR (C_6D_6): δ 0.46 (d, $^1J(PSi) = 21$ Hz); mass spectrum (EI, 70 eV), *m/z* (relative intensity) 482 ($M^{+\cdot}$, 100), 410 (34), 335 (33), 306 (65); *MS*, $M^{+\cdot}$ found: 482.201, calcd.: 482.2051.

1-(2,4,6-Tri-tert-butylphenyl)-2-(2,4,6-tri-isopropylphenyl)-2-tert-butylphosphasilene (1e)

To a solution of 2,4,6-tri-tert-butylphenylphosphine (2.22 g, 8.0 mmol) in diethyl ether (20 ml) at room temperature was added n-butyllithium (16 mmol) in hexane (10 ml). After 1.5 h reflux the solution was evaporated and a solution of dichloro(2,4,6-tri-isopropylphenyl)-tert-butylsilane (2.86 g, 8 mmol) in THF (20 ml) was added to the residue at −20 °C. The mixture was stirred for 5 min, allowed to warm to room temperature, and then heated for 15 min at 50 °C. The solvent was evaporated, the orange-colored sticky oil dissolved in n-pentane (20 ml) and the lithium chloride removed by filtration. The salt-free n-pentane solution of **1e** was divided into ten equal portions containing about 0.8 mmol of **1e**. Attempts to crystallize **1e** from various solvents or solvent mixtures (e.g. toluene, pentane, hexane, benzene, diethyl ether, THF) or chromatography under nitrogen were unsuccessful.

1-(2,4,6-Tri-tert-butylphenyl)-2-(2,6-diethylphenyl)-2-(2,4,6-triethylphenyl)phosphasilene (1f)

To a solution of 2,4,6-tri-tert-butylphenylphosphine **5e** (0.25 g, 0.9 mmol) in diethyl ether (10 ml) at −60 °C was added a solution of n-butyllithium (0.9 mmol) in hexane (2.5 ml). After 10 h stirring a solution of dichloro(2,6-diethylphenyl)(2,4,6-triethylphenyl)silane (**3f**) (160 mg, 0.45 mmol) in THF (5 ml) was added. The mixture was stirred for 5 min at −60 °C then warmed to room temperature. After 1 h stirring the solvent was evaporated. The orange residue was dissolved in perdeuterated benzene (2.5 ml) and the solution filtered to remove the lithium salt.

Phosphasilenes 1g–1k

A solution of n-butyllithium (0.8 mmol) in hexane (2 ml) was added to a solution of **5** (0.8 mmol) and dichloro(2,4,6-tri-isopropylphenyl)-tert-butylsilane (0.4 mmol) in THF (5 ml) at −60 °C. The mixture was slowly warmed to room temperature and stirred for 20 min. The solvent was evaporated, and the orange residue was dissolved in perdeuterated benzene (2.5 ml) and the solution was filtered. For ^{31}P and ^{29}Si NMR see Table 1.

Reaction of 1e with water and deuterium oxide

An excess of water (deuterium oxide) was added at room temperature to a solution of **1e** (0.8 mmol, *vide supra*) in n-pentane (2 ml). The orange color gradually disappeared, and after 2 h shaking the mixture was almost colorless. It was washed into a connected NMR tube. **7**: ^{31}P NMR (n-pentane): δ −122.7 (d, $^1J(PH) = 223$ Hz), −124.7 (d, $^1J(PH) = 206$ Hz), ratio about 1:1; ^{29}Si NMR (n-pentane): δ 19.1 (d, $^1J(PSi) = 43$ Hz), 16.9 (d, $^1J(PSi) = 38$ Hz); MS, $M^{+\cdot}$ found: 582.4408, calcd.: 582.4386. **8**: ^{31}P NMR (n-pentane): δ −124.2 (t, $^1J(PD) = 34$ Hz),

-126.7 (t, ^1J(PD) = 32 Hz); ^{29}Si NMR (n-pentane): δ 19.2 (d, ^1J(PSi) = 39 Hz), 16.9 (d, ^1J(PSi) = 39 Hz); MS, $M^{+\cdot}$ found: 584.4435, calcd.: 584.4511.

Reaction of ***1e*** *with hydrogen chloride*

To a solution of **1e** (0.8 mmol) in n-pentane (2 ml) gaseous hydrogen chloride (40 ml at 0.5 bar; 0.8 mmol) was added by distillation. After 30 min shaking, the initial orange color had disappeared. The solvent was evaporated and the residue was dissolved in perdeuterated benzene (2.5 ml), and the solution washed into a connected NMR tube. **4e** (two isomers in the ratio of 1 : 2): ^{31}P NMR (C_6D_6): δ -115.9 (d, ^1J(PH) = 232 Hz), -119.0 (d, ^1J(PH) = 213 Hz); ^{29}Si NMR (C_6D_6): δ 11.5 (d, ^1J(PSi) = 55 Hz), 11.0 (d, ^1J(PSi) = 53 Hz); MS, $M^{+\cdot}$ found 600.402, calcd.: 600.4032.

Attempted reaction of ***1e*** *with n-butyllithium*

To a solution of **1e** (0.8 mmol) in diethyl ether (2.0 ml) at room temperature was added to a solution of n-butyllithium (0.8 mmol) in n-hexane (2.0 ml). The ^{31}P NMR spectrum after 30 min showed that only **1e** was present. After 2 days' stirring no color change had occurred. Subsequently, the reaction mixture was treated with deuterium oxide and washed into a connected NMR tube. Only the diastereomers **8**, resulting from of the deuterium oxide to the double bond (*vide supra*) were detected.

Thermolysis of ***1e***

The thermolysis was carried out without solvent (A) or in solution (B). (A) Phosphasilene **1e** (0.8 mmol) was heated for 72 h at 60 °C. The volatile products were distilled into a connected NMR tube and dissolved in perdeuterated benzene (0.5 ml). The only detectable product was pure isobutene (^{1}H NMR (C_6D_6): δ 1.61 (t, 6 H, J = 0.15 Hz, $=C(CH_3)_2$), 4.74 (septet, 2 H, J = 0.15 Hz, $=CH_2$). The oily residue was dissolved in perdeuterated benzene (2.5 ml); the ^{31}P NMR spectrum did not differ from that obtained after thermolysis in solution, *vide infra*. (B) A solution of **1e** (0.8 mmol) in perdeuterated benzene (toluene) was heated in a sealed tube during 72 h at 60 °C. The phosphasilene was completely converted into the isomeric pair of phosphasiletenes **12** (in the ratio of 1 : 1). ^{31}P NMR (C_6D_6): δ -114.9 (d, ^1J(PH) = 175 Hz), -125.6 (d, ^1J(PH) = 165 Hz); ^{29}Si NMR (C_6D_6): δ 3.4 (d, ^1J(PSi) = 14 Hz), -0.7 (d, ^1J(PSi) = 10 Hz); MS, $M^{+\cdot}$ found: 508.361, calcd.: 508.3654. The phosphasiletenes were oxidized with elementary oxygen (20 h at room temperature) to give the isomeric pair of the five-membered ring compounds **13** (in the ratio of 1 : 1). ^{31}P NMR (Tol-d_8) δ 26.1 (d, ^1J(PH) = 575 Hz), 25.8 (d, ^1J(PH) = 577 Hz); ^{29}Si NMR (Tol-d_8) δ 13.3 (s), 12.8 (s); MS, $M^{+\cdot}$ found: 540.352, calcd.: 540.3553.

Reactions of ***1e*** *with the chalcogens*

To a solution of **1e** (0.8 mmol) in THF (5 ml) at -20 °C was added a ten-fold excess of sulphur (selenium, tellurium). After 30 min stirring at this temperature, the color had changed from orange to pale-yellow. The solution was washed into a connected NMR tube: ^{31}P NMR (THF): δ -88.5 (**10a**), -90.0 (^1J(PSe) = 112 Hz) (**10b**), -116.3 (**10c**). Due to the (unexpected) instability of these compounds under the reaction conditions, a ^{29}Si NMR spectrum could not be recorded. Compound **10a** was readily cleaved, and Mes*PS_2 was found, δ ^{31}P (THF) 297 ppm.

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