IR (cm^{-1}, CH_2Cl_2) $\nu_{N{\equiv}O}$ 1642 s; ^1H NMR (δ, $CDCl_3$) 7.4 (m, 15 H), 5.22 (s, 5 H), 2.42 (s, 3 H); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) PPh_3 at[31] 134.7 (d, J_{CP} = 53.7 Hz, ipso), 133.7 (d, J_{CP} = 10.7 Hz, ortho), 130.3 (d, J_{CP} = 2.4 Hz, para), 128.3 (d, J_{CP} = 10.7 Hz, meta), 91.3 (s, C_5H_5), 27.0 (d, J_{CP} = 8.4 Hz, CH_3); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 19.9 (s); high resolution mass spectrum (m/e), 591.08071 (M^+; calcd ^{187}Re 591.07678), 589.06768 (M^+; calcd ^{185}Re 589.07178), 329 ($M^+ - PPh_3$), 262 ($^+PPh_3$). Anal. Calcd for $C_{24}H_{23}NOPReS$: C, 48.80; H, 3.92; N, 2.37. Found: C, 48.6; H, 3.8; N, 2.4.

X-ray Crystal Structure of 1. X-ray data were collected as described in Table I on an Enraf-Nonius CAD-4 automated diffractometer. Of 7560 reflections collected with $\theta \leq 30°$, 5440 with $I \geq 3\sigma(I)$ were used in the final refinement. Lorentz and polarization corrections were applied, but absorption corrections (μ = 49.94 cm^{-1}) were not made. The structure solution proceeded smoothly by using standard heavy-atom techniques and was refined by full-matrix least-squares calculations. All calculations were performed on a Vax 11/780 computer with the Enraf-Nonius SDP proram library.[34] All non-hydrogen and non-fluorine atoms were refined with anisotropic Gaussian amplitudes. Anomolous dispersion corrections were applied throughout the refinement. The positions of all non-thioformaldehyde hydrogens were calculated with C-H bond distances set at 0.95 Å and idealized sp^2 geometry. The η^2-$H_2C{=}S$ thioformaldehyde hydrogens were located from a difference Fourier synthesis. All hydrogen atom contributions were included in structure factor calculations, but their positions were not refined.

MO Calculations. Extended Hückel calculations[35] were conducted with weighted H_{ij} formula. The rhenium and phosphorus atoms of $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}S)]^+$ were assigned idealized octahedral and tetrahedral geometries, respectively. The η^2-$H_2C{=}S$ carbon and sulfur atoms were assigned bond lengths (below) and angles (below) on the basis of the X-ray crystal structure of 1. The C-Re-S angle was bisected by an axis perpendicular to the Re-P and Re-N vectors. The η^2-$H_2C{=}S$ ligand was rotated about this axis while the Re-C-S bond distances and angles were held constant. The axis intersected the C-S bond at a distance of 0.837 Å from carbon. The η^2-$H_2C{=}S$ hydrogen atoms were positioned such that the H-C-H plane was normal to the $\overline{\mathrm{Re{-}C{-}S}}$ plane and formed an angle of 157.4° with the C-S vector, thus tilting the hydrogen atoms ca. 23° from ideal sp^2 geometry. Bond lengths used for η^2-$H_2C{=}S$ were as follows (Å): Re-C, 2.199; Re-S, 2.381; C-S, 1.742; C-H, 1.090. The parameters used for sulfur were as follows: 3s, H_{ii} = -20.00 eV, ζ = 1.817; 3p, H_{ii} = -13.30 eV, ζ = 1.817. The remaining bond lengths and parameters were the same as described previously.[17,36]

Acknowledgment. We thank the Department of Energy for support of this research. FT NMR spectra were obtained on instruments acquired via NSF departmental instrumentation grants.

Registry No. 1, 84369-18-6; 2, 71763-23-0; 3, 71763-25-2; 5, 84369-19-7; (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3), 71763-18-3.

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Phosphasilenes: Synthesis and Spectroscopic Characterization

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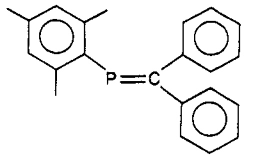
Received October 23, 1986

A number of phosphasilenes as representatives of a new class of compounds containing π-bonded silicon is described. Several phosphasilenes ArP=SiR′R″ (**3**, Ar = 2,4,6-tri-*tert*-butylphenyl; R′, R″ = phenyl, 2,4,6-trimethylphenyl, 2,4,6-triethylphenyl, 2,4,6-triisopropylphenyl, *tert*-butyl, or certain combinations thereof) were synthesized by the reaction of ArPHLi (**8**) and the corresponding dichlorosilanes $R'R''SiCl_2$ (**4**), followed by elimination of HCl. Depending on R′ and R″, several side reactions were encountered; for this reason, and because of the low stability of **3**, their isolation in pure form was not achieved. Compounds **3** were characterized as phosphasilenes by their unique ^{31}P and ^{29}Si NMR data, in particular by the strongly deshielded $\delta(^{29}Si)$ value (148-176 ppm) and the large ^1J(PSi) coupling constant (ca. 150 Hz). The (thermal) stability of **3** increases with increasing steric protection. Reactions of **3** with methanol and tellurium are briefly described.

Introduction

Heteroalkenes that contain an element of the third or a higher period in a pπ-hybridized state violate the classical double bond rule[1] which states that such compounds are unstable under ordinary conditions. Indeed, stable derivatives have only been obtained by special precautions, e.g., by resonance stabilization or by steric protection of the double bond.

An early example of the use of steric effects is the stabilization of the P=C unit by a mesityl and two phenyl groups in the phosphaalkene **1**.[2] Highly successful was the use of the 2,4,6-tri-*tert*-butylphenyl group that is one of the sterically most demanding groups. It permitted the isolation of the first stable diphosphene **2** by Yoshifuji et al.[3] and has since led to the preparation of a number of compounds with otherwise evasive functionalities[4] as well



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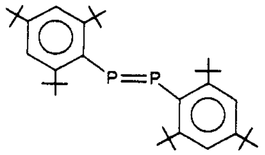

2

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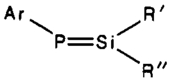
as to the synthesis of compounds with a double bond between phosphorus and other third or higher row elements: phosphorus (P=P),[5] arsenic (P=As),[5] antimony (P=Sb),[5] silicon (P=Si),[6] germanium (P=Ge),[7] and tin (P=Sn).[8]

In a preliminary report,[6] we have described the synthesis of the first phosphasilene (or phosphasilaalkene) **3a** that turned out to have a limited stability in solution and to be exceptionally reactive toward air.

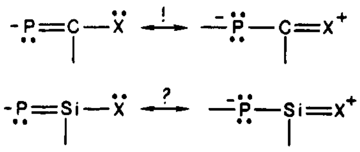


3a: R' = R'' = Mes[9]
b: R' = R'' = Es[9]
c: R' = Ph, R'' = Is[9]
d: R' = Mes, R'' = Is[9]
e: R' = *t*-Bu, R'' = Is[9]
(**f**: R' = R'' = Is[9])

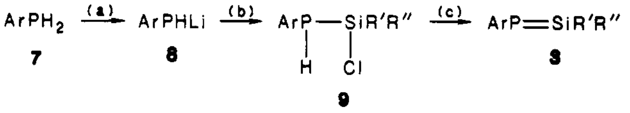
In this paper, we disclose the experimental details of the synthesis of **3a** and of the four other phosphasilenes **3b–e**. Due to better steric protection, some of these show a higher degree of stability, in particular **3d** and **3e**.

Results and Discussion

Before our results are presented, a general consideration concerning our strategy seems appropriate. When first attempting the synthesis of **3**, we realized that the P=Si bond would be a rather difficult target. In the first place, phosphorus and silicon are two elements that are notoriously reluctant to form p(π) double bonds,[5,10,11] with silicon being particularly close to the diagonal in the Periodic System that roughly separates the elements with some tendency to form double bonds in the upper right region from those in the lower left which do not. An additional handicap of P=Si systems is the following. There are two established strategies for the stabilization of reactive double bond systems, i.e. delocalization (sometimes combined with introduction of a positive charge) and steric protection. Of these, only the second is fully applicable for P=Si bonds because delocalization would create (partial) double-bond character at one or both of the two constituent atoms. This is illustrated by a comparison of the effect of a heteroatom X (oxygen, nitrogen) on a P=C or a P=Si bond. The resonance structure at the right is much more favorable in the first case because its double bond is of the well-known, stable type between two elements of the second period; in the second case, one of the two heavy atoms, i.e. silicon, is still involved in double bonding.



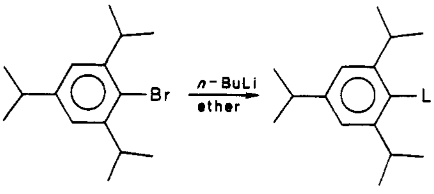
Scheme I



$$\underset{\mathbf{7}}{ArPH_2} \xrightarrow{(a)} \underset{\mathbf{8}}{ArPHLi} \xrightarrow{(b)} \underset{\mathbf{9}}{ArP(H){-}SiR'R''(Cl)} \xrightarrow{(c)} \underset{\mathbf{3}}{ArP{=}SiR'R''}$$

As the P=Si bond is also expected to be rather polarized due to the electronegativity difference ($x(P) - x(Si) = 0.3$),[12] a low-energy pathway for dimerization is available and particular care must be taken to maximize the only remaining protection strategy, i.e. steric hindrance around the double bond.

Dichlorodiorganylsilanes 4. For the synthesis of the phosphasilenes **3a–e** (see next section), we needed the corresponding dichlorosilanes **4a–e**. The choice of the 2,4,6-triisopropylphenyl group (= Is[9]) was based on the following considerations. While the Ar[9] group might be expected to furnish the highest possible protection at silicon, the preparation of the required Ar_2SiCl_2 has proven impossible so far. Perhaps the relatively large size of chlorine is detrimental, as the compounds Ar_2SiF_2[13a] and $ArSiF_3$[13] have recently been prepared, while neither Weidenbruch[13a] nor we were able to obtain $ArSiCl_3$. The Is[9] group seemed to be the next best candidate for our purpose. A great advantage of this group is the clean and easy availability of many Is-substituted compounds because we could obtain $IsLi{\cdot}OEt_2$ (**5**) in pure form. According to eq 1, the bromine–lithium exchange reaction



(1)

5

was performed at 20 °C in ether/hexane; when this solution is cooled to –60 °C, crystals of pure **5** separated. The crystal structure of **5** is under investigation. The dichlorosilanes **4** were prepared by the reactions of eq 2–5 as indicated.

$$2RLi + SiCl_4 \rightarrow \underset{\mathbf{4a,b,f}}{R_2SiCl_2} \tag{2}$$

$$\underset{\mathbf{5}}{IsLi{\cdot}OEt_2} + SiCl_4 \rightarrow \underset{\mathbf{6}}{IsSiCl_3} \tag{3}$$

$$\mathbf{5} + RSiCl_3 \rightarrow \underset{\mathbf{4c,d,f}}{RIsSiCl_2} \tag{4}$$

$$RLi + \underset{\mathbf{6}}{IsSiCl_3} \rightarrow \underset{\mathbf{4e,f}}{RIsSiCl_2} \tag{5}$$

Compound **4a** is known;[14a] the others are new, but the close analogue of **4b**, bis(2,6-diethylphenyl)dichlorosilane, has been described.[14b] Compounds **4d–f** are unusually stable; e.g., **4e** survives boiling for 3 h in water or in THF/H_2O solution unchanged. Similarly, **6** is rather stable

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(9) For simplicity, we use the following short-hand notations in this paper: Mes = mesityl (2,4,6-trimethylphenyl); Es = "esityl" (2,4,6-triethylphenyl); Is = "isityl" (2,4,6-triisopropylphenyl); Ar = "supermesityl" (2,4,6-tri-*tert*-butylphenyl).

(10) For a review on phosphaalkenes, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem.* **1981**, *93*, 771.

(11) For a review on three-coordinated silicon compounds, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(12) (a) $x(P) = 2.1$ and $x(Si) = x(Ge) = x(Sn) = 1.8$ have been proposed by Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Probably more realistic, but still within small limits, are the electronegativities $x(P) = 2.19$, $x(Si) = 1.90$, $x(Ge) = 2.01$, and $x(Sn) = 1.96$ proposed by: Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215 and references cited therein.

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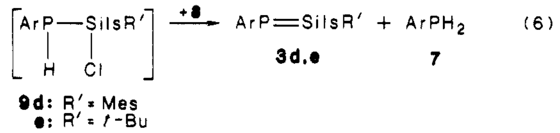
toward air and appears to be the most sterically protected aromatic trichlorosilane. As far we we know, only $(Me_3Si)_3CSiCl_3$[14c] is more stable than **6**.

Preparation of Phosphasilenes 3. Our original procedure for the preparation of **3** followed the sequence outlined in Scheme I. However, depending on the nature of R′ and R″, several problems were encountered.

For example, it was disappointing though not totally unexpected that the combination of Is_2SiCl_2 (**4f**) and the lithium phosphide **8**[15] was impossible. In THF solution, the two compounds did not react, not even after 3 h at 55 °C in THF (^{31}P NMR). Obviously, the combination of one Ar and two Is groups in the molecule of **9f** would have implied too much crowding. Nevertheless, it is surprising that not even decomposition occurred, e.g. by single electron transfer. It may be pointed out incidentally that our lack of success in preparing Ar_2SiCl_2 appears less disappointing in this light; its combination with **8** may be predicted to be equally unsuccessful. Another unforeseen, and so far insurmountable, difficulty was encountered in the reactions of **8** with **4d** and **4e**. The coupling reactions to **9d** and **9e** were apparently achieved, but **9d** and **9e** could not be detected, even when we screened the reaction mixture directly by means of ^{31}P NMR spectroscopy. Instead, the signals of **3d** and **3e**, respectively, were observed, together with that of **7**. One must conclude that in this case, **8** is a highly efficient base for promoting the elimination of HCl from initially formed **9** (eq 6).



$$\left[\begin{array}{c}ArP\text{—}SiIsR'\\ |\quad\ \ |\\ H\quad Cl\end{array}\right] \xrightarrow{+8} \underset{3d,e}{ArP{=}SiIsR'} + \underset{7}{ArPH_2} \qquad (6)$$

9d: R′ = Mes
e: R′ = *t*-Bu

We believe that the strongly increased susceptibility of **9d** and **9e** to elimination is another illustration of the steric congestion in these compounds. Elimination of HCl relieves this strain. A close analogy may be found in the relief of B-strain[16] in crowded aliphatic compounds which favors elimination over nucleophilic substitution.[17]

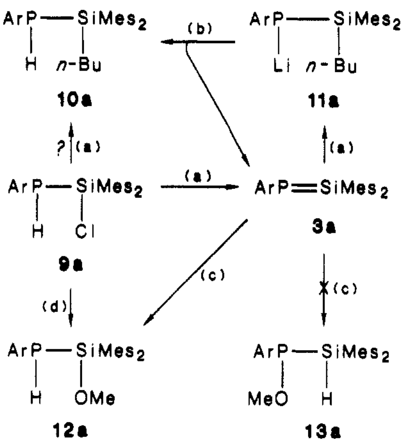
After realizing that, in the conversion of **9** to **3**, 1 equiv of **8** is consumed as a base, we could increase the yield of **3d** and **3e** by employing the stoichiometry **8**:**4** = 2:1 (eq 7). Actually, this method is successful for the in situ

$$\underset{8}{2ArPHLi} + \underset{4}{R'R''SiCl_2} \rightarrow \underset{3}{ArP{=}SiR'R''} + \underset{7}{ArPH_2} \qquad (7)$$

synthesis of all phosphasilenes **3a–e**, but it has the obvious drawback of yielding equimolar amounts of **7** that could so far not be separated from the sensitive **3**.

Only in the sterically least crowded cases of **4a** and **4c** could the coupling with **8** be successfully stopped at the stage of **9**; **9a** and **9c** were isolated in pure form and subjected to elimination with base in a separate step. The steric congestion seems to be intermediate in **9b**, which was obtained together with **3b** (ratio 1:2) from the reaction of a 1:1 mixture of **8** and **4b** (Scheme I); the product ratio was hardly influenced by changing the reaction conditions, e.g. by adding **8** to **4b** or vice versa.

Scheme II



We have briefly reported in our preliminary communication[6] that the elimination of HCl from **9a** with *n*-butyllithium afforded besides **3a** also **10a** in a ratio of 1:1 (Scheme II). Compound **10a** may be formed by direct nucleophilic substitution of chlorine at silicon, assuming that the chlorine–silicon bond in **9a** is insufficiently protected by steric hindrance. We feel, however, that this course of events is less likely because, in our experience, the reaction of **4** with *n*-butyllithium was slow at –60 °C. By extrapolation, it may expected to be even slower in **9** which, being a monochlorosilane, should be less reactive than the dichlorosilane **4**; moreover, **9** is sterically more congested than **4**. Therefore, another conceivable reaction sequence appears to be more attractive, i.e. HCl elimination from **9a** to give **3a**, followed by addition of *n*-butyllithium to the latter. In this case, the formation of **11a** would require 2 mol of *n*-butyllithium/mol of **9a**, but **11a** (like **8**, vide supra) is probably an efficient base for the elimination of HCl from the remaining **9a** (Scheme II). In fact, this sequence would nicely explain the 1:1 ratio of **3a** and **10a**, which is expected if the conversion of **9a** to **3a** is slower than that of **3a** to **11a**. Though not extensively investigated, the reaction of **9a** with *tert*-butyllithium gave inferior yields of **3a**, probably because this lithium reagent added even faster to **3a**. On the other hand, $(Me_3Si)_3SiLi$[19] proved to be an efficient base to effect a clean conversion of **9a** to **3a** (preliminary results; ^{31}P NMR data only).

The marginal protection of **3a** by the two mesityl groups on silicon is also illustrated by its high reactivity. In the reaction mixture (Scheme II), its half-life was approximately 1 week at –60 °C and 1 day at 25 °C. The product(s) of decomposition have not been identified. In contrast to the more protected **3** of this series, **3a** reacted instantaneously with minute traces of air; it proved too unstable to be separated from **10a**. The structure of **3a** was therefore chemically corroborated by addition of methanol; **3a** disappeared immediately and gave **12a** which was also obtained from **9a** with sodium methoxide. The regioisomer **13a** of **12a** was not observed; this is in line with the expected polarity of the P=Si bond in which silicon is the positive pole (see next section).

In a similar fashion, treatment of **9c** with *n*-butyllithium gave **3c** as one of the products. However, the yield was

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(16) (a) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 2892. (b) Bartlett, P. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1968**, *90*, 4421.

(17) It is noteworthy that a carbon analogue of **3a**, $MesP{=}CMes_2$,[18] could not be prepared. It has even less steric crowding at phosphorus than **3a** (Mes vs. Ar), and the same substituents at the second atom involved in double bonding ($CMes_2$ vs. $SiMes_2$). Nevertheless, $MesP{=}CMes_2$ could not be synthesized because the shorter bonds emanating from carbon increase the steric hindrance and probably prevent the eliminating base from approaching the precursor.

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Table I. NMR Spectra of Phosphasilenes $ArP{=}SiR'R''$ (3)[a]

compd[a]			^{31}P[b]		^{29}Si[c]	
	R′	R″	δ	$^1J(PSi)$, Hz	δ	$^1J(SiP)$, Hz
3a[d]	Mes	Mes	136.0	149	151.2[e]	149
3b[d]	Es	Es	133.7	152	150.1	152
3c[d]	Ph	Is	93.5	151	153.0	151
3d[d]	Mes	Is	122.7	152	148.7	152
3e[f]	*t*-Bu	Is	105.4	154	175.9	155

[a] For the nomenclature see ref 9. [b] Measured at 101.2 MHz. [c] Measured at 49.7 MHz. [d] In THF. [e] In our preliminary communication,[6] an erroneous value of $\delta(^{29}Si)$ 76.7 was published; this was actually a folded-in signal, because we had not anticipated[11] the extremely deshielded chemical shift of **3a** and stopped scanning around +110 ppm. [f] In C_6D_6.

Table II. ^{31}P Chemical Shifts of Phosphaheteraalkenes of Group 15

compd	δ
$ArP{=}NSiMe_3$	476[a]
$ArP{=}PCH(SiMe_3)_2$	493[b]
$ArP{=}AsCH(SiMe_3)_2$	575[c]
$ArP{=}SbCH(SiMe_3)_2$	620[c]

[a] Reference 20. [b] Reference 21a. [c] Reference 21b.

only 5%. Side reactions prevailed, one of them being probably substitution at silicon (see Experimental Section). Better results were obtained with **8** and **4c** (ratio 2:1); this gave a mixture of **3c** and **7**, from which the NMR data could be obtained.

So far, we have not succeeded in isolating **3** in pure, crystalline form. Besides the instability of some members, the large amount of impurities (e.g. **7**) in combination with a surprisingly high solubility even in *n*-pentane thwarted all our attempts to obtain crystals; column chromatography even under the most careful conditions (removal of water and oxygen) led to decomposition. The compounds are, however, characterized beyond any doubt as phosphasilenes by their spectral properties, in particular their NMR spectra (see next section). Characteristic for all **3** is also a (light) yellow color (cf. the yellow color of triarylphosphaalkenes[2b]).

NMR Spectra of Phosphasilenes. The ^{31}P and ^{29}Si NMR data of **3** are collected in Table I.

The phosphorus chemical shifts are found at unexpectedly high field. Initially, we were even misled as to the identity of **3** because $P{=}X$ compounds where X is an element of group 15 show a monotonic increase of $\delta(^{31}P)$ with increasing period number of X. The trend shown in Table II may be considered representative; although the substituents at the $P{=}X$ group are not (fully) identical, their influence on the phosphorus chemical shift is expected to be small in relation to the effect of X.

Making the (in retrospect unjustified) assumption of a corresponding trend for phosphaheteraalkenes of group 14, we extrapolated from $\delta(^{31}P)$ 234 for $MesP{=}CPh_2$[2] a value of $\delta(^{31}P)$ 250–300 for **3a**; the experimental value $\delta(^{31}P)$ 136.0 thus seemed by far too much shielded.

Quite unique and highly diagnostic, however, are the extremely deshielded values of $\delta(^{29}Si)$ and the large coupling constants $^1J(PSi)$. In general, compounds containing tetracoordinated silicon have chemical shift values not exceeding +50 ppm;[22] larger downfield shifts have only been observed in a few transition-metal complexes such as $[Cp_2(CO)_2Fe]_2SiCl_2$ ($\delta(^{29}Si)$ 146.4).[23] On the other hand, tricoordinated silicon is strongly deshielded. While the chemical shift range depends to some extent on the double-bond partner in $Si{=}X$ and on the substituents at the double bond, it usually falls between 40 and 100 ppm. The two most deshielded values are found for silaalkenes that do not carry a heteroatom capable of conjugation (Table III, entry 2): $Me(Me_3SiO)Si{=}C(SiMe_2\text{-}t\text{-}Bu)(adamantyl)$ ($\delta(^{29}Si)$ 126.5)[24] and $Me_2Si{=}C(SiMe_2\text{-}t\text{-}Bu)(SiMe_3)$ ($\delta(^{29}Si)$ 144.2).[25] However, a glance at Table III reveals that for the phosphasilenes **3**, $\delta(^{29}Si)$ ranges from 148 to 176 ppm, and thus silicon is even more deshielded. To our knowledge, **3e** ($\delta(^{29}Si)$ 175.9; Table I) has the most deshielded shift value ever reported for a silicon compound.

Table III. ^{29}Si Chemical Shifts of Tricoordinated Silicon

type of compds	range of $\delta(^{29}Si)$
$R_2Si{=}CR(OR)$	38–74[a]
$R_2Si{=}CR_2$	126.5,[b] 144.2[c]
$R_2Si{=}SiR_2$	62–95[a]
$R_2Si{=}NR$	60.3,[d] 78.3[e]
3	148–176[f]

[a] Reference 11. [b] Reference 24. [c] Reference 25. [d] Reference 26b. [e] Reference 26a. [f] Table I.

The origin of these chemical shift values is only partly understood. Undoubtedly, the deshielding is largely caused by paramagnetic contributions to the shielding tensor.[27] These are to a large extent inversely proportional to the HOMO–LUMO energy gap, which is generally small in alkene-type compounds (π–π^*). Thus, deshielded shifts are diagnostic for the involvement of silicon in $p(\pi)p(\pi)$ bonding. Returning to the ^{31}P chemical shifts, we note that they are unexpectedly shielded; still, they are not completely outside of the rather broad range found for dicoordinated phosphorus.[5,10] This upfield shift must be a consequence of the electronegativity difference between phosphorus ($x = 2.1$) and silicon ($x = 1.8$); phosphaalkenes (carbon: $x = 2.5$) have phosphorus shifts that are approximately 100 ppm more deshielded.[2,10] A confirmation for the inductive effect as the cause of these upfield shifts may be derived from the observation that a qualitatively similar upfield shift occurs in tertiary phosphines when replacing a phosphorus carbon bond by a phosphorus–silicon bond.[28]

We have, however, at present no satisfactory explanation for the substituent effects on $\delta(^{31}P)$ and $\delta(^{29}Si)$ in **3**. With the exception of **3e**, these effects are small for ^{29}Si but rather large for ^{31}P. Possibly, conformational differences with concomitant long-range anisotropic effects of the silicon substituents are responsible; another possibility consists of sterically enforced variations of the valence angle at phosphorus with concomitant rehybridization. One interesting conclusion can be drawn from the practical absence of a solvent effect on the silicon chemical shift and silicon–phosphorus coupling constant of **3a** (in THF, $\delta(^{29}Si)$ 151.2 ($^1J(SiP) = 149$ Hz (Table I)); in C_6D_6, $\delta(^{29}Si)$ 151.0 ($^1J(SiP) = 149$ Hz)). In the corresponding silanimines $R_2Si{=}NR$, the silicon chemical shift in THF ($\delta(^{29}Si)$ -2.55[26c]) is much more shielded than that in C_6D_6 ($\delta(^{29}Si)$ 78.29[26a]) because THF coordinates to the unsaturated

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Table IV. ^{31}P Chemical Shifts of Phosphaheteraalkenes of Group 14

compd	$\delta(^{31}P)$
MesP=CPh$_2$	234[a]
ArP=SiMes$_2$ (**3a**)	136[b]
ArP=GeMes$_2$	175.4[c]
ArP=Sn[CH(SiMe$_3$)$_2$]$_2$	204.7[d]

[a] Reference 2. [b] Table I. [c] Reference 7. [d] Reference 8.

silicon. The ^{29}Si NMR data clearly eliminate the possibility of such coordination in **3a**. Presumably both steric hindrance in **3a** and the smaller polarity of the Si=P bond as compared to the Si=N bond are responsible.

Finally, it is of interest to point out that the downfield trend for phosphorus chemical shifts with increasing atomic weight of X (X = element of group 15) in RP=XR (Table II) is restored for group 14 elements Y in RP=YR′R″ after the opposite step from Y=C to Y=Si. This follows from the data in Table IV. Apparently, in the later periods, electronegativity differences become less important,[12] and other factors such as the decreasing HOMO–LUMO gap prevail.

We feel that the deshielded silicon chemical shifts furnish sufficient evidence for the proposed structure of **3** as phosphasilenes, but the evidence derived from the ^1J(PSi) coupling constants is at least equally compelling. For phosphorus–silicon bonds involving tetracoordinated, sp^3-hybridized silicon, ^1J(PSi) values above 100 Hz have not been observed,[22] with the remarkable exception of LiP(SiH$_3$)$_2$ (^1J(PSi) = 256 Hz).[29] For **3**, the ^1J(PSi) coupling constants have the unusually high value of 149–155 Hz (Table I). This may be taken as evidence for a high s character in the P–Si bond, as expected for sp^2-hybridization of both elements involved.

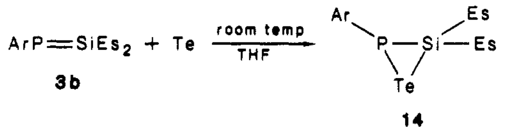
Another observation from the NMR spectra is that in those phosphasilenes that bear two different substituents on silicon and could therefore occur as two isomers of *Z* and *E* configuration (i.e. **3c**–**3e**), no indications were obtained for the presence of more than one isomer; the ^{31}P NMR spectra are expected to be particularly sensitive for the detection of such stereoisomerism. We assume that the large difference in size between the Is group (2,4,6-triisopropylphenyl) and the other groups makes the isomer with the Is group in the *E* position much more stable. It should be pointed out that if this explanation is correct, *tert*-butyl is "smaller" than isityl, at least in these compounds.

The ^{1}H NMR spectra of **3** could not be fully assigned as many signals were obscured by overlapping signals of byproducts or impurities. Interesting features are the aryl proton signals of **3a** and **3b** and the Si-*t*-Bu signal of **3e**. In **3a**, the aryl protons of the two mesityl groups gave separate singlets at δ 6.84 and 6.54 which we tentatively ascribe to the (*E*)- and (*Z*)-mesityl groups, respectively. This assignment is based on the rather shielded value for the latter group (cf. δ 6.83 for **4a** and δ 6.69 for **9a**); it can be explained by additional shielding of the (*Z*)-mesityl group by the P–Ar group in the presumably propeller-shaped **3a** (cf. the geometry of the phosphaalkene **1**[2b]). A similar argument can be derived for the aryl protons of the two diastereomeric esityl groups of **3b** (see Experimental Section). This reasoning is supported by the observation of a rather shielded value for the Si-*t*-Bu group of **3e**: $\delta(^1H)$ 0.71. The limited number of compounds that bear the *tert*-butyl group on sp^2-hybridized silicon shows $\delta(^1H)$ values in the range of 1–1.5 ppm.[26a,30] Interestingly, and in line with our reasoning, such *tert*-butyl groups in disilenes[30] are more shielded by about 0.3 ppm when they are oriented cis to the aryl group at the other silicon atom. Both this high-field shift and the fact that only one sharp signal is observed are in line with the presence of one diastereoisomer with the *tert*-butyl group in the *Z* position (vide supra).

Chemical Reactions of 3. The chemical investigation of **3** was so far handicapped because, as discussed in a previous paragraph, they could not be isolated in pure form. Several attempted reactions gave ambiguous results due to the presence of impurities.

The reactivity of **3** decreases with increasing steric protection in the sequence **3a**, **3c** > **3b** > **3d**, **3e**. While **3a** and **3c** are destroyed immediately by even short contact with air (e.g. short opening of a NMR tube), **3b** survived such conditions; **3d** and **3e** are even more stable. They can be kept in solution indefinitely in the absence of air.

The reaction of **3a** with methanol to furnish **12a** has already been mentioned (Scheme II). A rather clean reaction was observed between **3b** and elemental tellurium (eq 8).



(8)

The product **14** was formed within 48 h. It is a new type of three-membered heterocycle that was characterized by its $\delta(^{31}P)$ −126 with ^1J(PTe) = 222 Hz; these values are in line with those of the only other three-membered ring containing both phosphorus and tellurium, *t*-BuP–P(*t*-Bu)–Te [$\delta(^{31}P)$ −69 (^1J(PTe) = 229 Hz)].[31] On standing under air, the yellow THF solution of **14** decomposed under formation of a gray precipitate, probably metallic tellurium.

Experimental Section

All reactions with air-sensitive materials were carried out under a nitrogen atmosphere. Sampling of solutions containing phosphasilenes into NMR tubes was performed in a nitrogen-filled glovebox of high quality. Solvents were dried and distilled before use from LiAlH$_4$ (THF, diethyl ether, pentane) or potassium (benzene).

^{1}H NMR measurements were performed at 90 MHz on a Bruker WH90 spectrometer; chemical shifts were measured relative to internal solvent signals that were calibrated separately with internal Me$_4$Si. ^{29}Si and ^{31}P NMR measurements were performed on a Bruker WM250 spectrometer at 49.7 and 101.2 MHz, respectively; chemical shifts were measured relative to external Me$_4$Si or 85% H$_3$PO$_4$, respectively. Mass spectra were recorded on a Varian Mat CH5-DF mass spectrometer or a Hewlett-Packard 5890 MSD mass spectrometer; the expected isotope patterns were observed.

(2,4,6-Triisopropylphenyl)lithium Etherate (IsLi·OEt$_2$, 5). According to Whitesides et al.,[32] 1,3,5-triisopropylbenzene (IsH) was brominated to IsBr and the latter in diethyl ether (0.25 mol per 300 mL) converted to **5** with *n*-butyllithium in hexane (*caution*: the reagents are mixed at −60 °C and the reaction is completed by warming to room temperature; it is highly *exothermic*). After the solution was stirred for 2 h at room tem-

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perature, **5** may either be used directly in solution or isolated by crystallization. For this latter purpose, the reaction mixture was cooled to −60 °C; after 1 night, white crystals of **5** were formed (50%), and after 1 week 80% of **5** had crystallized. The mother liquor was siphoned off; the crystals of **5** have been kept for months at room temperature under nitrogen. The crystals of **5** were moderately soluble in pentane or benzene; ^{1}H NMR analysis revealed the composition IsLi·OEt$_2$: (C_6D_6) δ 7.11 (s, 2 H, Is-H), 3.28–2.61 (m, 3 H, $CH(CH_3)_2$), 2.83 (q, J = 7 Hz, 4 H, OCH_2CH_3), 1.54 (d, J = 7 Hz, 12 H, ortho $CH(CH_3)_2$), 1.36 (d, J = 7 Hz, 6 H, para $CH(CH_3)_2$), 0.59 (t, J = 7 Hz, 6 H, OCH_2CH_3).

Trichloro(2,4,6-triisopropylphenyl)silane (IsSiCl$_3$, 6). A solution of IsLi·OEt$_2$ (**5**) (30.18 g, 106 mmol) in benzene (200 mL) was cooled to 5 °C, and the solution of $SiCl_4$ (17.9 g, 105 mmol) in benzene (40 mL) was slowly added. According to ^{1}H NMR, **6** (80%) and **4f** (20%) were formed. The reaction mixture was filtered, the filtrate evaporated, and the residue distilled to yield colorless crystals of **6** (18.65 g, 52%): mp 70–71 °C; bp 133 °C (6 mbar); ^{1}H NMR ($CDCl_3$) δ 7.13 (s, 2 H, Is-H) 3.81 (sept, J = 7 Hz, 2 H, ortho $CH(CH_3)_2$), 2.91 (sept, J = 7 Hz, 1 H, para $CH(CH_3)_2$), 1.28 (d, J = 7 Hz, 12 H, ortho $CH(CH_3)_2$), 1.26 (d, J = 7 Hz, 6 H, para $CH(CH_3)_2$); ^{29}Si NMR ($CDCl_3$) δ −4.09; MS, m/z (relative intensity) 336 (30, $M^{\bullet+}$), 321 (40, $[M - Me]^+$), 203 (83, $[M - SiCl_3]^+$), 43 (100, i-Pr^+); HRMS calcd for $C_{15}H_{23}{}^{35}Cl_3Si$ 336.0635, found 336.0639.

Dichlorosilanes 4. Dichlorobis(2,4,6-trimethylphenyl)silane (Mes$_2$SiCl$_2$, 4a). 4a was prepared as described by Wiberg et al.[14a]. **4a** was crystallized from n-pentane, mp 119–120 °C (lit.[14a] mp 120–121 °C); if kept for longer periods of time, it must be stored under nitrogen: ^{1}H NMR ($CDCl_3$) δ 6.83 (s, 4 H, Mes-H), 2.43 (s, 12 H, ortho CH_3), 2.26 (s, 6 H, para CH_3).

Dichlorobis(2,4,6-triethylphenyl)silane (Es$_2$SiCl$_2$, 4b). 1,3,5-Triethylbenzene (EsH) was brominated by the method of Whitesides[32] for IsH (vide supra) to give EsBr as a colorless liquid: bp 80 °C (2 mbar) (lit.[33] bp 99 °C (3 mbar)); ^{1}H NMR ($CDCl_3$) δ 6.93 (s, 2 H, Es-H), 2.77 (q, J = 7.5 Hz, 4 H, ortho CH_2CH_3), 2.56 (q, J = 7.5 Hz, 2 H, para CH_2CH_3), 1.22 (t, J = 7.5 Hz, 9 H, CH_3). EsBr (25 g, 104 mmol) in diethyl ether was lithiated with n-BuLi in hexane as described for **5** (vide supra). To the resulting solution of EsLi was added during 1 h at 0 °C neat $SiCl_4$ (7.96 g, 47 mmol). After being stirred for 1 h at room temperature, the reaction mixture was filtered and the filtrate concentrated and distilled to yield **4b** as a colorless liquid that is stable toward air for several hours but colors faintly yellow when kept at daylight: bp 135 °C (0.05 mbar); ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 4 H, Es-H), 2.86 (q, J = 7.3 Hz, 8 H, ortho CH_2CH_3), 2.60 (q, J = 7.3 Hz, 4 H, para CH_2CH_3), 1.22 (t, J = 7.3 Hz, 6 H, para CH_2CH_3), 1.04 (t, J = 7.3 Hz, 12 H, ortho CH_2CH_3); ^{29}Si NMR ($CDCl_3$) δ 1.0; MS, m/z (relative intensity) 420 (0.4, $M^{\bullet+}$), 391 (24, $[M - Et]^+$), 162 (100, $EsH^{\bullet+}$), 133 (27, $[EsH - Et]^+$). **Trichloro(2,4,6-triethylphenyl)silane** (EsSiCl$_3$) can be obtained by crystallizing EsLi·(OEt$_2$)$_n$ (n has not been determined) as described for **5** and performing the reaction with $SiCl_4$ in benzene and 1:1 stoichiometry. EsSiCl$_3$: ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 2 H, Es-H), 3.13 (q, J = 7.3 Hz, 4 H, ortho CH_2CH_3), 2.70 (q, J = 7.5 Hz, 2 H, para CH_2CH_3), 1.35 (t, J = 7.3 Hz, 6 H, ortho CH_2CH_3), 1.32 (t, J = 7.5 Hz, 3 H, para CH_2CH_3).

Dichlorophenyl(2,4,6-triisopropylphenyl)silane (IsPhSiCl$_2$, 4c). At room temperature, trichlorophenylsilane (0.888 g, 4.2 mmol) was added by a syringe to the stirred solution of **5** (1.18 g, 4.2 mmol) in n-pentane. After 20 h, the reaction mixture was filtered and evaporated. By molecular distillation, pure **4c** was obtained as a colorless liquid that for longer periods should be stored under nitrogen: ^{1}H NMR ($CDCl_3$) δ 7.89–7.40 (m, 5 H, Ph-H), 7.08 (s, 2 H, Is-H), 3.50 (sept, J = 7 Hz, 2 H, ortho $CH(CH_3)_2$), 2.89 (sept, J = 7 Hz, 1 H, para $CH(CH_3)_2$), 1.26 (d, J = 7 Hz, 6 H, para $CH(CH_3)_2$), 1.10 (d, J = 7 Hz, 12 H ortho $CH(CH_3)_2$); ^{29}Si NMR ($CDCl_3$) δ 3.7; MS, m/z (relative intensity) 378 (55, $M^{\bullet+}$), 300 (76, $[M - C_6H_6]^{\bullet+}$), 285 (100, $[M - C_6H_6 - Me]^+$), 257 (54), 175 (26, $[M - Is]^+$); HRMS calcd for $C_{21}H_{28}{}^{35}Cl_2Si$ 378.1337, found 378.1344. Anal. Calcd for $C_{21}H_{28}SiCl_2$: C, 66.47; H, 7.44; Cl, 18.69; Si, 7.40. Found: C, 66.30; H, 7.59; Cl, 17.81; Si, 7.47.

Dichloro(2,4,6-triisopropylphenyl)(2,4,6-trimethylphenyl)silane (IsMesSiCl$_2$, 4d). To the solution of **5** (1.537 g, 5.4 mmol) in n-pentane (25 mL) was added trichloromesitylsilane.[34] After 1 h, very little reaction had taken place. Therefore THF (5 mL) was added. Now the reaction was complete after 3 h at room temperature. The reaction mixture was evaporated to dryness. The residue was extracted with pentane and filtered and the filtrate evaporated to dryness. The residue (2.161 g, 95%) was crystallized from pentane to give white crystals of **4d**; mp 75–77 °C; **4d** is rather stable in air in the crystalline form, but less so in solution: ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 2 H, Is-H), 6.81 (s, 2 H, Mes-H), 3.66 (sept, J = 7 Hz, 2 H, ortho $CH(CH_3)_2$), 2.88 (sept, J = 7 Hz, 1 H, para $CH(CH_3)_2$), 2.41 (s, 6 H, ortho CH_3(Mes)), 2.25 (s, 3 H, para CH_3(Mes)), 1.24 (d, J = 7 Hz, 6 H, para $CH(CH_3)_2$), 1.08 (d, J = 7 Hz, 12 H, ortho $CH(CH_3)_2$); MS, m/z (relative intensity) 420 (2.5, $M^{\bullet+}$), 377 (23, $[M - i\text{-}Pr]^+$), 300 (39, [M − MesH]), 120 (100, $MesH^{\bullet+}$); HRMS calcd for $C_{24}H_{34}{}^{35}Cl_2Si$ 420.1807, found 420.1811.

***tert*-Butyldichloro(2,4,6-triisopropylphenyl)silane (Is-*t*-BuSiCl$_2$, 4e).** The solution of *tert*-butyllithium (21 mmol) in pentane was added during 30 min at room temperature to the solution of **6** (7.00 g, 20.7 mmol) in benzene (50 mL). After being stirred for 3 h, the reaction mixture was evaporated. The residue was dissolved in pentane and water. The pentane layer was dried ($MgSO_4$), filtered, and evaporated to dryness, yielding **4e** (7.00 g, 94%) which was crystallized from n-pentane to give colorless crystals; mp 98–99 °C. Compound **4e** is completely stable toward air: ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 2 H, Is-H), 3.52 (sept, J = 7 Hz, 2 H, ortho $CH(CH_3)_2$), 2.90 (sept, J = 7 Hz, 1 H, para $CH(CH_3)_2$), 1.28 (d, J = 7 Hz, 18 H, $CH(CH_3)_2$), 1.24 (s, 9 H, $SiC(CH_3)_3$); ^{29}Si NMR ($CDCl_3$) δ 25.3; MS, m/z (relative intensity) 358 (23, $M^{\bullet+}$), 301 (100, $[M - t\text{-}Bu]^+$), 265 (88), 203 (42); HRMS calcd for $C_{19}H_{32}{}^{35}Cl_2Si$ 358.1649, found 358.1629. Treatment of **4e** with AgF in THF converted it to Is-t-BuSiF$_2$, mp 73–74 °C, which was identical (melting point, ^{29}Si NMR) with a product prepared by Sakurai et al.[13b]

Dichlorobis(2,4,6-triisopropylphenyl)silane (Is$_2$SiCl$_2$, 4f). Compound **4f** was obtained by two routes, both of which were not optimized. In the first place, **4f** was a side product of the synthesis of **6** (vide supra). For its isolation, the residue obtained after distillation of **6** was crystallized from n-pentane to furnish colorless crystals of **4f**, mp 108 °C. In a qualitative NMR tube experiment, **4f** was prepared by adding **6** to a solution of **5** in C_6D_6. The conversion **6** to **4f** was slow; it was complete only after 5 h at 50 °C: ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 4 H, Is-H), 3.66 (sept, J = 7 Hz, 4 H, ortho $CH(CH_3)_2$), 2.83 (sept, J = 7 Hz, 2 H, para $CH(CH_3)_2$), 1.19 (d, J = 7 Hz, 12 H, para $CH(CH_3)_2$), 1.01 (d, J = 7 Hz, 24 H, ortho $CH(CH_3)_2$); MS, m/z (relative intensity) 504 (3), $M^{\bullet+}$), 300 (19, $[M - IsH]^{\bullet+}$), 204 (100, $IsH^{\bullet+}$), 189 (49, $[IsH - Me]^+$); HRMS calcd for $C_{30}H_{46}{}^{35}Cl_2Si$ 504.2746, found 504.2723.

Other Dichlorosilanes. Five other sterically crowded dichlorosilanes were synthesized by analogous procedures but characterized only by their typical ^{1}H NMR spectra that are fully diagnostic for the R groups in R′R″SiCl$_2$. They are briefly described below. (1) **Mes-*t*-BuSiCl$_2$** (known compound;[35] from MesSiCl$_3$ and t-BuLi in benzene): ^{1}H NMR ($CDCl_3$) δ 6.89 (s), 2.61 (s), 2.28 (s), 1.16 (s). (2) **MesXySiCl$_2$** (Xy = 2,6-dimethylphenyl; from MesSiCl$_3$ and XyLi in benzene): ^{1}H NMR ($CDCl_3$) δ 7.04 (s), 6.84 (s), 2.51 (s), 2.46 (s), 2.31 (s). (3) **MesEsSiCl$_2$** (from MesSiCl$_3$ and EsLi in benzene): ^{1}H NMR ($CDCl_3$) δ 6.92 (s), 6.84 (s), 2.86 (q), 2.62 (q), 2.43 (s), 2.27 (s), 1.24 (t), 1.08 (t). (4) **Es-*t*-BuSiCl$_2$** (from EsSiCl$_3$, vide supra, and t-BuLi in benzene): ^{1}H NMR ($CDCl_3$) δ 7.02 (s), 2.93 (q), 2.65 (q), 1.31 (t), 1.27 (t), 1.19 (s). (5) **EsIsSiCl$_2$** (from **6** and EsLi in benzene): ^{1}H NMR ($CDCl_3$) δ 7.00 (s), 6.89 (s), 3.70 (sept, ortho $CH(CH_3)_2$), 2.85 (q, CH_2CH_3), 1.06 (d, ortho $CH(CH_3)_2$); other signals not assignable.

The Reaction of ArPHLi (8) with Dichlorosilanes (4). General Remarks. As explained in Results and Discussion (Preparation of Phosphasilenes), the reactions did not proceed in a straightforward, uniform way; in no case was a stable,

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crystalline phosphasilene **3** isolated in pure form. A typical run was as follows.

Under nitrogen, **7**[15] and **4** (ratio 1:1); scale 1–2 mmol) were dissolved in anhydrous THF (10 mL). The solution was cooled to –60 °C. Then *n*-BuLi (1.6 M in *n*-hexane; 1.05 mmol of BuLi per mmol of **7**) was added; the mixture turned immediately wine-red due to the formation of **8**. The formation of **8** appears to be much faster than its coupling with **4** or the reaction of *n*-BuLi with **4**.[36] Then the in situ mixture of **8** and **4** was slowly warmed from –60 °C to room temperature and stirred for another 90 min. At this stage, a NMR sample was taken (drybox!); the ^{31}P NMR spectrum was highly diagnostic to distinguish between unreacted **8** (δ(^{31}P) –106 (^{1}J(PH) = 167 Hz); THF) and **9** (typically δ(^{31}P) –95/–120 ^{1}J(PH) = ca. 220 Hz). Depending on the substituents (see below) three types of reaction were encountered: no reaction (**4f**: 3 h at 55 °C!), slow reaction (**4e**: 2 h at 40 °C), and complete reaction.

Product formation also strongly depended on **4**. Only in the case of **4a** and **4c**, the desired coupling products **9a** and **9c**, respectively, were obtained; **4d** and **4e** gave no **9**, but directly **3**; **4b** showed an intermediate behavior. Compounds **9a–c** were unstable toward air, probably due to facile cleavage of the P–Si bond, and tended to stick and foam in the workup procedure, especially when the byproduct LiCl and residual THF had not been carefully removed. In some cases, ArH and unidentified phosphorus compounds were formed in variable amounts (δ(^{31}P) 55, –63, and –72, respectively). The greatest possible care in using pure products and intermediates and excluding air and moisture was found to be strictly necessary. On the other hand, the direct reaction of *n*-BuLi with **4** was not a major problem at –60 °C.

As mentioned in the general discussion, the most convenient and reliable manner of preparing **3** (in the presence of **7**!) for spectroscopic investigations was that of eq 7, using 2 equiv of preformed **8** per mol of **4**; it worked in all cases (**3a–e**).

In the following, the best results and conditions obtained so far are described for the different products.

[Chlorobis(2,4,6-trimethylphenyl)silyl](2,4,6-tri-*tert*-butylphenyl)phosphine (ArPHSiClMes$_2$, 9a) was obtained in solution as described under general remarks: ca. 85% yield; ^{1}H NMR (CDCl$_3$) δ 7.24 (b s, 2 H, Ar-H), 6.69 (s, 4 H, Mes-H), 5.02 (d, ^{1}J(PH) = 223 Hz, 1 H, PH), 2.21 (s, 6 H, para CH$_3$), 2.14 (s, 12 H, ortho CH$_3$), 1.31 (b s, 27 H, *t*-Bu); ^{31}P NMR (THF) δ –106.7 (d, ^{1}J(PH) = 224 Hz); ^{29}Si NMR (CDCl$_3$) δ 8.9 (d, ^{1}J(SiP) = 58 Hz).

[Chlorobis(2,4,6-triethylphenyl)silyl](2,4,6-tri-*tert*-butylphenyl)phosphine (ArPHSiClEs$_2$, 9b). Formation described with **3b**: ^{1}H NMR (CDCl$_3$) δ 7.22 (b s, 2 H, Ar-H), 6.77 (s, 4 H, Es-H), 5.01 (d, ^{1}J(PH) = 223 Hz, 1 H, PH), 2.70–2.22 (m, 12 H, C*H*$_2$CH$_3$), 1.31 (b s, 27 H, *t*-Bu), 1.00–0.69 (m, 18 H, CH$_2$C*H*$_3$); ^{31}P NMR (THF) δ –106.3 (d, ^{1}J(PH) = 224 Hz); ^{29}Si NMR (C$_6$D$_6$) δ 6.8 (d, ^{1}J(SiP) = 63 Hz).

[Chlorophenyl(2,4,6-triisopropylphenyl)silyl](2,4,6-tri-*tert*-butylphenyl)phosphine (ArPHSiClPhIs, 9c). Compound **9c** was obtained according to the general procedure as a mixture of two diastereoisomers (ca. 2.6:1), yield ca. 85%. Contrary to **9a** and **9b**, **9c** could be crystallized from pentane, but the isomer ratio was not changed significantly: white crystals; mp 149–150 °C; ^{1}H NMR (CDCl$_3$) δ 7.65–6.92 (m, 9 H, aryl-H), 5.0 (d, ^{1}J(PH) = 231 Hz, 1 H, PH), 3.31–2.66 (m, 3 H, C*H*(CH$_3$)$_2$), 1.37–0.93 (m, 45 H, CH$_3$; *t*-Bu as highest peak at δ 1.34); ^{31}P NMR (C$_6$D$_6$) δ –107.3 (d, ^{1}J(PH) = 231 Hz), –113.4 (d, ^{1}J(PH) = 233 Hz), ratio 72:28. Anal. Calcd for C$_{39}$H$_{58}$ClPSi: C, 75.38; H, 9.41; Cl, 5.71; P, 4.99; Si, 4.52. Found: C, 74.84; H, 9.49; Cl, 5.70; P, 4.66; Si, 4.70.

1-(2,4,6-Tri-*tert*-butylphenyl)-2,2-bis(2,4,6-trimethylphenyl)phosphasilene (ArP═SiMes$_2$, 3a). (a) From 9a. As described above, **9a** (1.63 mmol) was prepared in situ from **8** and **4a**. This solution was cooled to –60 °C, and *n*-BuLi (1.63 mmol, in *n*-hexane) was added. The reaction mixture turned deep red immediately. When the solution was slowly warmed to room temperature, the color changed to orange. After 1 h at room temperature, a ^{31}P NMR spectrum (careful sampling!) revealed the signals of **3a** and **10a** (Scheme II). Compound **10a** was isolated by flash chromatography (6 cm of Al$_2$O$_3$, pentane) and identified by its spectral data: ^{1}H NMR (CDCl$_3$) δ 7.17 (b s, 2 H, Ar-H), 6.69 (s, 4 H, Mes-H), 4.63 (d, ^{1}J(PH) = 217 Hz, 1 H, PH), 2.20 (s, 6 H, para CH$_3$), 1.94 (s, 12 H, ortho CH$_3$), 1.40–0.60 (m, 9 H, *n*-Bu), 1.31 (b s, 27 H, *t*-Bu); ^{31}P NMR (THF) δ –116.6 (d, ^{1}J(PH) = 216 Hz). **(b) According to Eq 7.** Compound **4a** (ca. 1 mmol) was reacted in THF solution at –60 °C with **8** (2 mmol). For this purpose we made first a solution of **8** by the usual procedure (**7** + *n*-BuLi, in THF, 5 mL), in the absence of **4a**, and checked the complete conversion of **7** into **8** by ^{31}P NMR at room temperature. The solution was cooled again to –60 °C, and **4a** was added in pure form. When the solution was warmed to room temperature, the red color of **8** was replaced by an orange color. This solution was ready for ^{31}P and ^{29}Si NMR measurement (in THF). Evaporation of solvent and extraction into C$_6$D$_6$ or CDCl$_3$, followed by filtration, made complementary measurements possible: ^{29}Si NMR (C$_6$D$_6$) δ 151.0 (d, ^{1}J(SiP) = 149 Hz); ^{29}Si NMR (THF; Table I) δ 151.2 (d, ^{1}J(SiP) = 149 Hz). Although **3a** was not sufficiently pure to analyze the ^{1}H NMR spectrum completely, we could discern two separate signals for the aryl protons of the (*E*)- and (*Z*)-mesityl group: δ 6.84 and 6.54. **(c) DBU as a Base.** With DBU as a base, there was no indication for the formation of **3a**. In C$_6$D$_6$, **9a** and DBU gave no color; the signal of **9a** (δ –106 (^{1}J(PH) = 224 Hz)) was replaced by a signal at δ –112 (^{1}J(PH) = 217 Hz). In THF, the addition of DBU to a mixture of **7** and **4a** resulted in a reaction between DBU and **4a** (without coloration), while **7** stayed unchanged.

1-(2,4,6-Tri-*tert*-butylphenyl)-2,2-bis(2,4,6-triethylphenyl)phosphasilene (ArP═SiEs$_2$, 3b). The reaction of **8** (1.4 mmol) and **4b** (1.4 mmol) in THF (10 mL) at –60 °C gave, according to ^{31}P NMR, a mixture of products: **3b** (δ 133; 39%), **9b** (δ –106; 18%), and **7** (δ –131; 43%). The yield of **9b** was higher when an excess of **4b** was used: **8** (7.84 mmol) and **4b** (13.32 mmol) (ratio 1:1.7) gave **3** (26%), **9b** (48%), and **7** (26%). No indications for the presence of ArPHSiBuEs$_2$ were found. Compound **3b** showed, in analogy to **3a**, two diastereometric esityl groups as indicated by the aryl-H signals: δ 6.94 (*E* ?) and 6.65 (*Z* ?).

1-(2,4,6-Tri-*tert*-butylphenyl)-2-phenyl-2-(2,4,6-triisopropylphenyl)phosphasilene (ArP═SiIsPh, 3c). (a) From 9c. The solution of **9c** (718 mg, 1.15 mmol) in THF (25 mL) was cooled to –70 °C, and *n*-BuLi (1 mmol, hexane solution) was injected. A yellow color developed that turned red orange on warming to room temperature. The ^{31}P NMR spectrum showed eight signals: δ 93.5 (**3c**; 5%), –72 (31%), –107 (43%), –113 (15%), –118 (d, ^{1}J(PH) = ca. 230 Hz; 10%), –123 (d, ^{1}J(PH) = ca. 230 Hz; 12%), –134.4 (s; 8%), –134.6 (s, 5%). We tentatively assign the signals at –118/–123 ppm to ArP(H)SiBuIsPh and at –134 ppm to ArP(Li)SiBuIsPh, both occurring in diastereomeric pairs. **(b) According to Eq 7.** The reaction was performed as described for **3a** and gave **3c** in a sufficiently high concentration to measure the ^{29}Si NMR spectrum. In the ^{31}P spectrum we observed a 1:1 ratio for **3c** and **7**, while in the ^{29}Si spectrum the signal of **3c** (δ 153.0) was the only major resonance.

1-(2,4,6-Tri-*tert*-butylphenyl)-2-(2,4,6-triisopropylphenyl)-2-(2,4,6-trimethylphenyl)phosphasilene (ArP═SiIsMes, 3d). Only one experiment was performed in this case. The reaction of **8** (0.59 mmol) and **4d** (0.57 mmol) was performed as described in general remarks. ^{31}P NMR spectroscopy indicated the formation of **3d** and **7** only, but not of **9d**. The signal of **3d** was found at +122.7 ppm; the signal of **7** was of comparable intensity.

1-(2,4,6-Tri-*tert*-butylphenyl)-2-*tert*-butyl-2-(2,4,6-triisopropylphenyl)phosphasilene (ArP═SiIs-*t*-Bu, 3e). Because of the considerable stability of **3e**, even on short exposure to air, the formation of this compound was extensively studied with the aim of isolation in pure state, including changes of stoichiometry, temperature, and solvent. Never was any **9e** observed. The best procedure to obtain **3e** in high yield has so far been the following (see eq 7).

To the solution of **7** (1.093 g, 3.9 mmol) and **4e** (0.702 g, 1.95 mmol) in THF (10 mL) was added *n*-BuLi (3.9 mmol, hexane solution) at –65 °C. The solution was slowly warmed to 40 °C and stirred for 1.5 h. According to ^{1}H and ^{31}P NMR, **3e** and **7**

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[36] For this reason, it was not necessary to perform the reaction in a two-step fashion by first preparing **8** from **7** and *n*-BuLi, followed by coupling of **8** and **4**. This was experimentally confirmed in a number of cases by executing the reaction in both versions; the results were essentially identical.

were the only products (ratio 1:1). Inspite of the stability of **3e**, attempted separation from **7** was not successful. Column chromatography of 718 mg of **3e** + **7** on specially dried Al$_2$O$_3$ (length 23 cm, diameter 2 cm) with anhydrous diethyl ether under nitrogen led to decolorization of the yellow band halfway; only **7** and ArH were eluted from the column. Fractional crystallization of **3e** and **7** was thwarted by the high solubility of **3e** in a number of suitable solvents; e.g., from *n*-pentane at −60 °C, a precipitate was formed with an unchanged ratio. However, from the mixture, the ^{1}H NMR spectrum could be determined by abstraction of the signals of **7**: ^{1}H NMR (CDCl$_3$) δ 7.34 (d, ^{4}J(PH) = 1.7 Hz, 2 H, Ar-H), 6.99 (s, 2 H, Is-H), 3.32–2.65 (m, 3 H, C*H*(CH$_3$)$_2$), 1.68 (s, 18 H, ortho *t*-Bu), 1.40–1.21 (m, 27 H, para *t*-Bu and CH(C*H*$_3$)$_2$), 0.71 (s, 9 H, SiC(C*H*$_3$)$_3$); MS, *m/z* (relative intensity) 564 (2, M$^{\bullet+}$), 508 (18, [M − C$_4$H$_8$]$^{\bullet+}$), 451 (62, [M − C$_4$H$_8$ − C$_4$H$_9$]$^{+}$), 323 (77), 231 (100); HRMS calcd for C$_{37}$H$_{61}$PSi 564.4280, found 564.4311; HRMS calcd for C$_{33}$H$_{53}$PSi 508.5057, found 508.5066.

Solutions containing **3e** showed after extended exposure to air in the ^{31}P NMR spectrum two new signals at δ −122 and −125 (CDCl$_3$; both d, ^{1}J(PH) = 220 Hz). We ascribe these signals to the two diastereoisomers of ArPHSi(OH)Is-*t*-Bu, the hydrolysis products of **3e**.

Reactions of 3. Reaction of 3a with Methanol. As described for **3a**, a mixture of **3a** and **10a** (1:1) was prepared by route a. Addition of a drop of methanol to an NMR tube containing this mixture resulted in immediate disappearance of the yellow color of **3a**. While the signal of **10a** was unchanged, that of **3a** was replaced by a new signal at δ(^{31}P) −112.6 (d, ^{1}J(PH) = 219 Hz). The reaction mixture was evaporated to dryness and the residue dissolved in pentane. Filtration and evaporation of the filtrate gave a mixture of **10a** and **12a** that could be analyzed by means of ^{1}H NMR spectroscopy. **10a**: ^{1}H NMR identical with that of the product isolated from **3a** (vide supra). **12a**: ^{1}H NMR (CDCl$_3$) δ 7.17 (d, ^{4}J(PH) = 2 Hz, 2 H, Ar-H), 6.65 (s, 4 H, Mes-H), 4.62 (d, ^{1}J(PH) = 220 Hz, 1 H, PH), 3.15 (s, 3 H, OCH$_3$), 2.20 (s, 6 H, para CH$_3$), 2.02 (s, 12 H, ortho CH$_3$), 1.35 (s, 18 H, ortho *t*-Bu), 1.30 (s, 9 H, para *t*-Bu); ^{31}P NMR (THF) δ −112.6 (d, ^{1}J(PH) = 219 Hz). The ^{1}H NMR and ^{31}P NMR spectra of **12a** were identical with those of a sample that was independently synthesized as follows. While **9a** (0.5 mmol) in THF solution did not react with a large excess of methanol (1 h, room temperature) addition of sodium methoxide (1 mmol, concentrated solution in methanol) effected conversion to **12a**: MS, *m/z* (relative intensity) 574 (7.5, M$^{\bullet+}$), 325 (21), 297 (100, [M − ArPH]$^{+}$), 277 (35, [M − Si(OMe)Mes$_2$]$^{+}$); HRMS calcd for C$_{37}$H$_{55}$OPSi 574.3589, found 574.3560.

Reaction of 3b with Tellurium. One of the preparations described for **3b** had afforded a mixture with the following composition: **3b** (55%), ArPHR (?, δ(^{31}P) −72; 25%), and ArPHSi(OH)Es$_2$ (?, δ(^{31}P) −112; 20%). Stirring this mixture with metallic tellurium gradually led to disappearance of the ^{31}P signal of **3b**; it was replaced by a new signal at δ −126 (no *J*(PH), ^{1}J(PTe) = 222 Hz) which we ascribe to **14**.

2-(2,4,6-Tris-*tert*-butylphenyl)-3,3-bis(2,4,6-triethylphenyl)telluraphosphasilirane (14). After 48 h, the composition of the mixture was **14** (55%), "δ −72" (25%), and "δ −112" (20%). On flash column chromatography (Al$_2$O$_3$, *n*-pentane, no exclusion of air), a yellow band was eluted which was shown to be **14** (^{31}P NMR); it decomposed within 10 min on exposure to air and deposited a blackish, metallic material (tellurium?). Slow chromatography caused blackening of the yellow band on the column.

Acknowledgment. We thank F. M. Lock, U. H. Verkerk, and H. Derlagen for experimental contributions. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid (C.N.S.) from the Netherlands Organization for the Advancement of Pure Science (ZWO).[37]

Registry No. **3a**, 92753-10-1; **3b**, 107742-50-7; **3c**, 107742-51-8; **3d**, 107742-53-0; **3e**, 107742-54-1; **4a**, 5599-27-9; **4b**, 107742-35-8; **4c**, 107742-36-9; **4d**, 107742-37-0; **4e**, 107742-38-1; **4f**, 107742-39-2; **5**, 107742-58-5; **6**, 107742-40-5; **7**, 83115-12-2; **9a**, 92753-11-2; **9b**, 107742-47-2; **9c** (isomer 1), 107742-48-3; **9c** (isomer 2), 107742-49-4; **10a**, 92753-12-3; **12a**, 92753-13-4; **14**, 107742-57-4; EsBr, 91-06-5; EsLi·OEt$_2$, 107742-59-6; EsSiCl$_3$, 107742-41-6; MesSiCl$_3$, 17902-75-9; Is-*t*-BuSiF$_2$, 107742-42-7; MesXySiCl$_2$, 107742-43-8; XyLi, 63509-96-6; MesEsSiCl$_2$, 107742-44-9; Es-*t*-BuSiCl$_2$, 107742-45-0; EsIsSiCl$_2$, 107742-46-1; ArP(H)SiBuIsPh (isomer 1), 107742-52-9; ArP(H)SiBuIsPh (isomer 2), 107768-19-4; ArP(Li)SiBuIsPh (isomer 1), 107742-60-9; ArP(Li)SiBuIsPh (isomer 2), 107742-61-0; ArP(H)Si(OH)Is-*t*-Bu (isomer 1), 107742-55-2; ArP(H)Si(OH)-Is-*t*-Bu (isomer 2), 107742-56-3; EsH, 102-25-0; PhSiCl$_3$, 98-13-5; ^{29}Si, 14304-87-1.

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(37) After submission of this manuscript, related work on phosphasilenes by Russian authors (Romanenko, V. D.; Ruban, A. V.; Drapailo, A. B.; Markovskii, L. N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1985**, *55*, 2486) has become available. We thank a reviewer for drawing our attention to this publication.