# Phenylsilyl Chalcogenides, (Phenylsilyl)amines and Related Phosphonium (Phenylsilyl)methylides

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The synthesis of 1,3-diphenyldisiloxane (**1**) by hydrolysis of chloro(phenyl)silane is optimized, 1,3-diphenyldisilthiane (**2**) is made available by the reaction of $H_2S$ with $PhH_2SiCl$ and triethylamine. 1,3-Diphenyldisilselenane (**3**) is prepared from $K_2Se$ and $PhH_2SiBr$. Selective ammonolysis of $PhH_2SiBr$ leads either to bis(phenylsilyl)amine (**4**) or to tris(phenylsilyl)amine (**5**). (Phenylsilyl)bis(trimethylsilyl)amine (**6**) is prepared by the reaction of 1,1,1,3,3,3-hexamethyldisilazane with chloro(phenyl)silane and triethylamine. According to a crystal structure determination the molecule of **6** features a planar $Si_3N$ skeleton. Phenylsilylated phosphonium methylides are available by two synthetic pathways: Transsilylation of phosphonium (trimethylsilyl)methylides and direct silylation of unsubstituted phosphonium methylides $R_3P = CH_2$.The structure of the molecule $Me_3P = C(SiH_2Ph)_2$ (**11**) in the crystal also exhibits a virtually planar $PCSi_2$ skeleton, isoelectronic with $Si_3N$.

Silicon-containing thin layers have widespread use in modern electrotechnology. Hydrogenated amorphous silicon (a-Si: H) and silicon carbide (a-SiC: H) find applications as semiconductors in solar cells and photoreceptors. Thin films of $SiO_2$, $Si_3N_4$, and $Si_2ON_2$ are employed as diffusion barriers in integrated circuits, as protective layers, and for passivation. Silicon carbide serves as an abrasive-resistant coating.

In most cases thin films of this kind are presently generated by plasma-enhanced chemical vapor deposition (PECVD)[1] using mixtures of silane gas with hydrocarbons (for SiC), with carbon or nitrogen oxides (for $SiO_2$), and with nitrogen gas or ammonia (for $Si_3N_4$). Since handling of silane is hazardous and deposition depends markedly on many parameters, mainly the partial pressure of the different gases, a high standard in apparatus technology is indispensable. It appears highly desirable to reduce some of these problems by using specially designed molecules as feedstock sources containing all elements for deposition in the right ratio.

According to this concept it should also be possible to influence the chemical structure of the deposited layer. Thus, for example fragments in a-SiC: H-layers containing C–H bonds can be diminished by using feedstock gases like polysilylmethanes having no or only a reduced number of C–H bonds present in the PECVD starting compounds[2].

For deposition of the majority of silicon-containing materials the most promising compounds are highly hydrogenated silane derivatives. The difficulties in handling halosilanes, $H_3SiX$, which have low boiling points, are inflammable in air, and tend to disproportionate are strongly reduced by using phenylsilyl compounds, $PhH_2SiX$, as synthons for silyl compounds, $H_3SiX$. The phenyl group can readily be displaced by a hydrogen atom in a two-step synthesis, in the first step according to the method of Fritz and Kummer[3] (Eq. 1) and in the second by hydride reduction of the corresponding halo- or pseudohalosilane (Eq. 2).

$$PhH_2Si-R + HX \rightarrow PhH + R-H_2Si-X \quad (1)$$

$$4\,R-H_2Si-X + LiAlH_4 \rightarrow 4\,R-SiH_3 + LiX + AlX_3 \quad (2)$$

Since only very few phenylsilyl reagents are available, we report here on the syntheses of phenylsilyl compounds of the chalcogenes, of nitrogen, and of phosphorus ylides which represent carbanionic reagents.

## 1,3-Diphenyldisiloxane (1)

Disiloxane **1** has first been prepared by Nebergall et al.[4] Hydrolysis of bromo(phenyl)silane led to **1** in 78% yield with formation of 2,4,6-triphenylcyclotrisiloxane as the main byproduct. This preparative method could now be optimized by using chloro(phenyl)silane (Eq. 3), which is less reactive than the bromo compound.

$$2\,PhH_2SiCl + H_2O \rightarrow \underset{\mathbf{1}}{(PhH_2Si)_2O} + 2\,HCl \quad (3)$$

Hydrolysis of chloro(phenyl)silane in THF by slowly adding a stoichiometric amount of water affords only low yields of **1** and a complex mixture of cyclic siloxanes $(PhHSiO)_n$ ($n$ = 5 is dominating). We found the optimum conditions with yields of **1** over 90% by pouring a solution of chloro(phenyl)silane in diethyl ether rapidly on a large excess of finely crushed ice. Only traces of higher siloxanes are detectable in the product, and there are only small losses in the workup procedure.

Apart from the confirmation of the reported physical data of **1**[4], the compound has been further identified by IR, NMR and mass spectral studies (see Experimental).

### 1,3-Diphenyldisilthiane (2)

Compound **2** has first been synthesized by Horn and Hemecke[5] by a transsilylation reaction of hexamethyldisilthiane with chloro(phenyl)silane (Eq. 4).

$$(Me_3Si)_2S + 2\,PhH_2SiCl \rightarrow \underset{\mathbf{2}}{(PhH_2Si)_2S} + 2\,Me_3SiCl \tag{4}$$

$$2\,PhH_2SiCl + H_2S + 2\,Et_3N \rightarrow \mathbf{2} + 2\,[HNEt_3]Cl \tag{5}$$

Since this is an equilibrium reaction, only moderate yields (41%) are obtained after a reaction time of 21 days, as also confirmed by our own investigations. Even after six months the yield does not exceed 40%.

According to an alternative route, **2** could now be prepared by the reaction of chloro(phenyl)silane with $H_2S$ in THF in the presence of triethylamine as a dehydrohalogenating reagent (Eq. 5).

Like other disilthianes[6], **2** is sensitive to hydrolysis and produces a distasteful odor. Analytical and spectroscopic data confirm the identity of the product (see Experimental).

### 1,3-Diphenyldisilselenane (3)

In the syntheses of disilselenanes described in ref.[7] complex seleno-aluminates are used as selenium sources, which are treated with halosilanes.

For the generation of **3** a suspension of freshly prepared potassium selenide[8] in THF has now been silylated with bromo(phenyl)silane (Eq. 6).

$$2\,PhH_2SiBr + K_2Se \rightarrow \underset{\mathbf{3}}{(PhH_2Si)_2Se} + 2\,KBr \tag{6}$$

The reaction does not proceed to completion (23% yield) at room temperature owing to partial decomposition to give elementary selenium.

Compound **3** is a colorless liquid of disgusting odor, which can be distilled in vacuo (135°C/1 mbar). It is moisture- and air-sensitive. **1** and $H_2Se$, or selenium are formed in the decomposition, respectively.

The $^1H$-NMR spectrum of **3** in $CDCl_3$ shows a resonance for the silyl protons at $\delta = 4.93$ with one pair of satellites according to HSi coupling to the $^{29}Si$ nucleus ($^1J$ = 233.4 Hz), and another satellite pair with a HSiSe coupling to the $^{77}Se$ nucleus ($^2J$ = 17.1 Hz). The $^{29}Si$-NMR spectrum shows a triplet resonance at $\delta = -31.36$ owing to the coupling to both silyl protons. Since the spectrum was recorded in the INEPT technique[9], it was possible to observe the $^1J$(SiSe) coupling of 112.1 Hz in characteristic satellites. This value is in the same range as that of $(H_3Si)_2Se$ [$^1J$(SiSe) = 110.6 Hz][10]. In the same way the SiC coupling constant is observed ($^1J$ = 73.1 Hz) to be somewhat greater than in phenylsilane, $PhSiH_3$ [$^1J$(SiC) = 70.0 Hz][11]. The two disilselenanes should therefore have similar bonding characteristics.

Attempts to prepare 1,3-diphenyldisiltellurane in the same manner as described for **3** have not been successful. The products obtained consist of a mixture of several compounds exhibiting $H_2Si$ triplets and HSi doublets in the $^{29}Si$-NMR spectrum. The components could not be separated by distillation owing to decomposition to elementary tellurium and hydrogen telluride.

### Bis(phenylsilyl)amine (4) and Tris(phenylsilyl)amine (5)

Bis(phenylsilyl)amine has been mentioned in the patent literature[12] as a pyrolysis product of cyclic silazanes, but has not been isolated and characterized. Compound **4** is available, together with **5**, by ammonolysis of bromo(phenyl)silane dissolved in diethyl ether (Eqs. 7 and 8).

$$2\,PhH_2SiBr + 3\,NH_3 \rightarrow \underset{\mathbf{4}}{(PhH_2Si)_2NH} + 2\,NH_4Br \tag{7}$$

$$3\,PhH_2SiBr + 4\,NH_3 \rightarrow \underset{\mathbf{5}}{(PhH_2Si)_3N} + 3\,NH_4Br \tag{8}$$

$$3\ \mathbf{4} \not\longrightarrow 2\ \mathbf{5} + NH_3 \tag{9}$$

The course of the reaction can be controlled by the rate of the ammonia admission to the bromo(phenyl)silane solution. Formation of **4** is favored by a rapid stream of ammonia, while a slow stream of ammonia favors the formation of **5**. Mixtures of **4** and **5**, or relatively pure raw products, can be separated and purified, respectively, by distillation in vacuo without decomposition or disproportionation in contrast to disilazane[13] and other disilylamines[14], which readily undergo disproportionation, suggesting a process as written in Eq. (9).

Both **4** and **5** are colorless liquids, which are stable for some time in dry air. They are readily hydrolyzed by water to ammonia and **1**.

### (Phenylsilyl)bis(trimethylsilyl)amine (6)

The known **6** was prepared first by a dehydrocondensation reaction from 1,1,1,3,3,3-hexamethyldisilazane and phenylsilane in the presence of a catalytic amount of potassium trimethylsilanolate[15].

The NH function in hexamethyldisilazane can also be silylated by the action of chloro(phenyl)silane and triethylamine according to Eq. (10).

$$\begin{gathered}(Me_3Si)_2NH + PhH_2SiCl + NEt_3 \rightarrow \\ \underset{\mathbf{6}}{(Me_3Si)_2N-SiH_2Ph} + [HNEt_3]Cl\end{gathered} \tag{10}$$

A similar silylation with chlorotrimethylsilane is not observed owing to sterical hindrance.

*Crystal and Molecular Structure of* **6**: The molecular geometry is shown in Figure 1.

Since this is the first crystal structure of a trisilylamine having no electronegative substituents (F, O, or another N atom) bound to a Si atom, it can only be compared with electron diffraction data of other simple trisilylamines like $(H_3Si)_3N$[126] or $(MeSiH_2)_3N$[17]. Like in these trisilylamines, the $NSi_3$ group in **6** is completely planar within the experimental error (the sum of angles at the N atom is 359.7°).

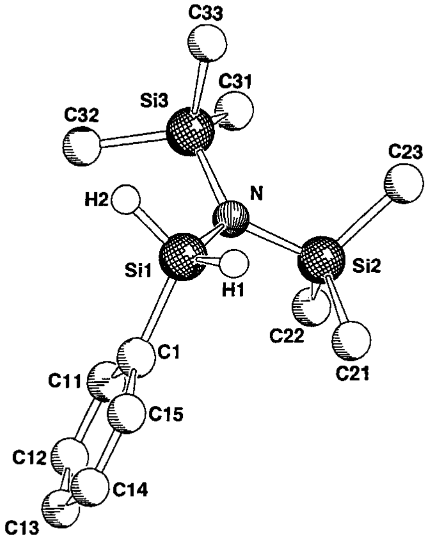

Figure 1. Molecular structure of compound **6** with atomic numbering (SCHAKAL). Distances [Å] and angles [°]: Si1 – N 1.723(2), Si2 – N 1.751(3), Si3 – N 1.750(3), Si1 – C1 1.864(3), Si2 – C23 1.861(4); Si1 – N – Si2 119.4(1), Si2 – N – Si3 123.4(1), Si1 – N – Si3 116.9(1), N – Si1 – C1 113.4(1), N – Si2 – C21 109.8(1)

The angle Si2 – N – Si3 (123.4°) is somewhat greater than those angles Si – N – Si containing the Si1 atom of the phenylsilyl group according to the higher space requirement of the bulky trimethylsilyl groups. The two $Me_3Si$ groups are placed relative to each other in such a way, that a maximum distance between the methyl groups is achieved. The bonds Si2 – N and Si3 – N (1.751 and 1.750 Å) are longer than the Si1 – N bond (1.723 Å), because of the different electronic effects of the two sorts of silyl groups. All Si – N bond lengths are in the same range as those in $(MeSiH_2)_3N$ and $(H_3Si)_3N$ and indicate a partial multiple bond character. The conformation of the molecule as a whole does not have a mirror plane or any other symmetry element. The plane of the phenyl ring is not vertical to the $NSi_3$ plane.

### Phenylsilylated Phosphorus Ylides

A number of ways of generating silylated phosphorus ylides have been described[18]. Some of these methods have now been applied successfully to the preparation of the phenylsilylated derivatives of trimethylmethylenephosphorane (**7**) and methylenetriphenylphosphorane (**8**).

$$\underset{\mathbf{7}}{Me_3P{=}CH_2} \quad \underset{\mathbf{8}}{Ph_3P{=}CH_2} \quad \underset{\mathbf{9}}{Me_3P{=}C(SiMe_3)_2}$$

*Preparation According to the Transsilylation Method:* The most important process for the formation of silicon functional phosphorus ylides is the transsilylation reaction[19]. The two well established [bis(trimethylsilyl)methylene]triorganophosphoranes $Me_3P{=}C(SiMe_3)_2$ (**9**) and $Ph_3P{=}C(SiMe_3)_2$ (**10**)[20,21] serve as starting materials. The latter compound is available by direct silylation of **8** in a slow reaction, whereby it is formed together with triphenyl[(trimethylsilyl)methylene]phosphorane, $Ph_3P{=}CHSiMe_3$ (Eqs. 11 and 12). The compounds can be separated by distillation in vacuo.

$$3\,\underset{\mathbf{8}}{Ph_3P{=}CH_2} + 2\,Me_3SiCl \longrightarrow 2\,[Ph_3PMe]Cl + \underset{\mathbf{10}}{Ph_3P{=}C(SiMe_3)_2} \tag{11}$$

$$2\,\mathbf{8} + Me_3SiCl \longrightarrow [Ph_3PMe]Cl + Ph_3P{=}CHSiMe_3 \tag{12}$$

Transsilylation of **9** or **10** with chloro(phenyl)silane affords [bis(phenylsilyl)methylene]trimethylphosphorane (**11**) (Eq. 13) and [bis(phenylsilyl)methylene]triphenylphosphorane (**12**) (Eq. 14), respectively.

$$\underset{\mathbf{9}}{Me_3P{=}C(SiMe_3)_2} + 2\,PhH_2SiCl \longrightarrow \underset{\mathbf{11}}{Me_3P{=}C(SiH_2Ph)_2} + 2\,Me_3SiCl \tag{13}$$

$$\underset{\mathbf{10}}{Ph_3P{=}C(SiMe_3)_2} + 2\,PhH_2SiCl \longrightarrow \underset{\mathbf{12}}{Ph_3P{=}C(SiH_2Ph)_2} + 2\,Me_3SiCl \tag{14}$$

However, these procedures lead to product mixtures, and it was found difficult to separate the compounds.

*Direct Silylation of* **7** *and* **8**: The ylide **7** can be silylated directly with chloro(phenyl)silane to yield **11** (Eq. 15) in good yield and high purity.

$$3\,\underset{\mathbf{7}}{Me_3P{=}CH_2} + 2\,PhH_2SiCl \longrightarrow 2\,[Me_4P]Cl + \underset{\mathbf{11}}{Me_3P{=}C(SiH_2Ph)_2} \tag{15}$$

Since the reaction proceeds in two steps, affording the monosilylated species ($Me_3P{=}CHSiH_2Ph$) as the primary product which reacts more slowly, it is necessary to allow the mixture to stand for about 10 days at ambient temperature. The direct silylation of **8** proceeds in the same manner, but the equilibrium appears to be less in favor of the product side, such that a mixture of the mono- and bissilylated phosphoranes is formed, which cannot be separated by distillation.

The $^1$H-NMR spectrum of **11** shows three groups of signals. The methyl resonance at $\delta = 0.80$ and the $SiH_2$ resonance at $\delta = 5.25$ are split into doublets by $^{31}$P couplings, while the phenyl protons produce the common multiplet structure at $\delta = 7$.

The proton-decoupled $^{13}$C-NMR spectrum shows the resonance of the ylidic C atom as a doublet at $\delta = -10.89$ [$^1J$(CP) = 73.1 Hz]. This coupling constant is much smaller than that in unsilylated **7** [$^1J$(CP) = 90.3 Hz at $\delta = -2.55$] indicating reduced multiple bond character in **11** as compared to **7**[22].

The $^{29}$Si-NMR spectrum shows the expected triplet resonance which is further split into multiplets by couplings to $^{31}$P and the *o*-phenyl protons.

The $^{31}$P-NMR resonance of **11** ($\delta = 9.20$) is shifted downfield as compared to **7** by about 11.5 ppm. It suggests a more limited transfer of negative charge from the ylidic C atom to the P atom. This trend was noted already for the trimethylsilylated phosphoranes[23]. The $^{31}$P resonances of silylated ylides can thus be put in the following order:

$\delta[Me_3P=C(SiMe_3)_2,\mathbf{9}] > \delta(Me_3P=CHSiMe_3) > \delta(Me_3P=CH_2,\mathbf{7})$

$\delta[Ph_3P=C(SiH_2Ph)_2,\mathbf{12}] > \delta[Ph_3P=CH(SiH_2Ph)] > \delta(Ph_3P=CH_2,\mathbf{8})$

*Crystal and Molecular Structure of* **11**: The molecule contained in the asymmetric unit is shown in Figure 2, in which also the molecular dimensions are summarized.

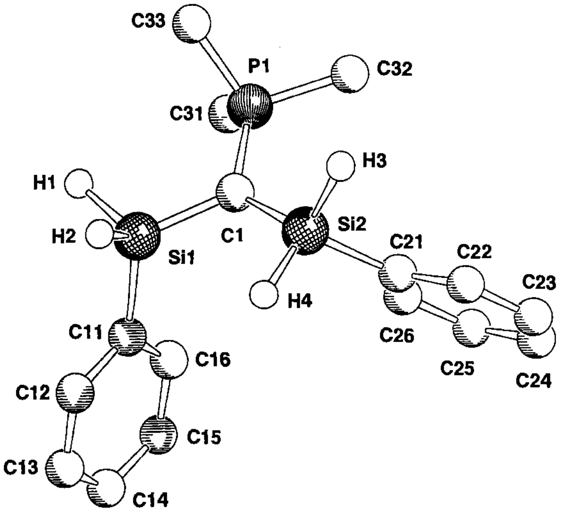

Figure 2. Molecular structure of compound **11** with atomic numbering (SCHAKAL). Distances [Å] and angles [°]: P–C1 1.685(3), P–C31 1.795(5), P–C32 1.789(5), P–C33 1.797(5), Si1–C1 1.811(3), Si2–C1 1.809(3), Si1–C11 1.878(3), Si2–C21 1.884(3), Si1–H1 1.55(3), Si1–H2 1.49(3); C1–P–C31 114.1(2), P–C1–Si1 119.1(2), P–C1–Si2 116.9(2), Si1–C1–Si2 116.9(2), C1–Si1–C11 115.9(1), C1–Si2–C21 115.9(1)

The ylidic P–C1 bond is about 0.1 Å shorter than the reference P–C bonds in this molecule, and in good agreement with data for **8**[24]. The trimethylphosphane group has approximately $C_{3v}$ symmetry with a distorted tetrahedral geometry, the methylene group clearly requiring more space than the methyl groups. The carbanionic C atom C1 is not quite trigonal-planar, as suggested by theoretical studies[25]. The angle between the two planes PC1Si1 and PC1Si2 amounts to as much as 23°, clearly placing the ylidic C atom C1 out of the PSi1Si2 plane. Similar distortions have also been observed for other ylides[26,27]. As compared with the unsilylated ylide **8**, the carbanion geometry in **11** is closer to planarity owing to the stabilizing electronic effects and steric requirements of the silyl substituents. This geometry is not unlike the structure of isolectronic silylamines: While one silyl substituent is not always sufficient to planarize the nitrogen atom, two or more such substituents are[28] (see compound **6**). The angle Si1–C1–Si2 in **11** is sterically compressed by the expansion of the P–C1–Si angles. The average bond length for Si1–C1 and Si2–C1 is 1.810 Å, placing them 0.075 Å shorter than e.g. in the tetrakis(phenylsilyl)methane molecule[2]. This effect can be attributed to the higher bond order of the silicon-carbanion linkage.

The two phenyl groups in molecule **11** are oriented towards one side of the P(C)Si$_2$ system, at variance with the conformation of $Ph_3P=C(SPh)(SePh)$[29] in the crystal. It is likely, however, that crystal effects are mainly responsible for this discrepancy.

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## Experimental

All experiments were carried out under dry purified nitrogen. Solvents and glassware were dried and kept under nitrogen. – NMR: Jeol GX 270, Jeol GX 400 spectrometers. – IR: Film between KBr plates, Nicolet 5 DX. – MS: Mat 311 (EI).

*Starting Materials:* Chloro(phenyl)silane was obtained by chlorination of phenylsilane[30], bromo(phenyl)silane by analogous bromination[4]. Trimethylmethylenephosphorane was prepared by treatment of tetramethylphosphonium bromide with potassium hydride in boiling THF[31].

*1,3-Diphenyldisiloxane* (**1**): A solution of 10.4 ml of chloro(phenyl)silane (0.070 mol) in 30 ml of diethyl ether is poured rapidly onto 50 g of finely crushed ice. After melting of all the ice, the organic layer is separated from the aqueous phase and washed twice with 20 ml of water to remove HCl. The solution is dried with magnesium sulfate, the solvent removed under reduced pressure, and the remaining colorless liquid distilled in vacuo to yield 7.3 g (91%) of **1**, b.p. 85°C/1 mbar. – $^1$H NMR (270.17 MHz, CDCl$_3$, TMS, 20°C): $\delta = 5.14$ [s, 4H, $^1J$(HSi) = 221.7 Hz, SiH$_2$], 7.33–7.42 and 7.45–7.61 (m, 10H, C$_6$H$_5$). – $^{29}$Si NMR (79.34 MHz, CDCl$_3$, TMS, 20°C): $\delta = -25.21$ [tt, $^1J$(SiH) = 220.6, $^3J$(SiCCH) = 6.4 Hz]. – MS (EI, 70 eV): *m/z* (%) = 230 [M$^+$], 152 (100) [C$_6$H$_8$O$_2$Si], 151, 107 [C$_6$H$_7$Si], 105 [C$_6$H$_5$Si], 74. – IR (film): $\tilde{\nu} = 3071$ cm$^{-1}$, 3050 w, 3008 w, 2150 vs ($\nu$SiH), 1890 w, 1833 w, 1813 w, 1771 w, 1686 w, 1588 m, 1482 w, 1426 s, 1075 s ($\nu_{as}$SiOSi), 980 s, 948 s, 906 s, 871 s, 765 w, 735 m, 645 s, 639 s, 456 m.

*1,3-Diphenyldisilthiane* (**2**): 10.4 ml of chloro(phenyl)silane (0.070 mol), 10.7 ml of triethylamine (dried with CaH$_2$ and distilled, 0.077 mol, 10% excess), and 100 ml of THF are placed in a 250-ml two-necked flask equipped with a gas inlet tube and a reflux condenser with a gas outlet. A low stream of hydrogen sulfide is admitted through the gas inlet tube and continued with vigorous stirring while white triethylammonium chloride is precipitating. The solid is filtered, and the solvent and the excess of triethylamine are removed from the filtrate in vacuo. The remaining product is purified by distillation to yield 7.15 g of **2** (83%), b.p. 114°C/1 mbar, m.p. –24°C. – $^1$H NMR (270.17 MHz, CDCl$_3$, TMS, 20°C): $\delta = 5.03$ [s, 4H, $^1J$(HSi) = 222.7 Hz, SiH$_2$], 7.27–7.37 and 7.54–7.58 (m, 10H, C$_6$H$_5$). – $^{29}$Si NMR (79.43 MHz, CDCl$_3$, TMS, 20°C): $\delta = -24.95$ [tt, $^1J$(SiH) = 223 Hz, $^3J$(SiCCH) not resolved]. – IR (film): $\tilde{\nu} = 3046$ cm$^{-1}$ m, 3050 m, 3015 m, 2261 w, 2157 vs ($\nu$SiH), 1953 w, 1883 w, 1813 w, 1588 m, 1482 m, 1425 s, 1334 m, 1300 w, 1189 w, 1120 s, 1064 m, 932 vs, 864 vs, 815 vs, 745 s ($\nu$SiC), 697 s, 586 s, 559 s, 503 s ($\nu_{as}$SiSSi). – MS (EI, 70 eV): *m/z* (%) = 246 [M$^+$], 169 (100) [M$^+$ – Ph].

*1,3-Diphenyldisilselenane* (**3**): Potassium selenide is prepared freshly according to a literature procedure[8] from 10.55 g of potassium (0.27 mol) and 10.65 g of selenium (0.135 mol). After completion of the reaction in liquid ammonia the solvent is volatilized and the remaining solid warmed to 100°C for 4 h. The slightly brown $K_2Se$ thus obtained is pulverized and suspended in 250 ml of THF. A solution of 50.5 g of bromo(phenyl)silane in 50 ml of THF is added dropwise to the suspension. The mixture is stirred for 12 h, then the precipitate is filtered and the solvent removed in vacuo. The remaining liquid is fractionally distilled over a 7-cm Vigreux column to yield 9.1 g of **3** (23%), b.p. 135°C/1 mbar. – $^{1}H$ NMR (399.78 MHz, $CDCl_3$, TMS, 20°C): $\delta$ = 4.93 [s, 4H, $^{1}J$(HSi) = 223.4, $^{2}J$(HSiSe) = 17.1 Hz, $SiH_2$], 7.31–7.42 and 7.56–7.60 (m, 10H, $C_6H_5$). – $^{29}Si$ NMR (53.67 MHz, $CDCl_3$, TMS, 20°C): $\delta$ = –31.36 [tm, $^{1}J$(SiH) = 223.5, $^{1}J$(SiC) = 73.1, $^{1}J$(SiSe) = 112.1 Hz]. – MS (EI, 70 eV): *m/z* (%) = 294 [$M^+$], 216 [$M^+ - H_2 -$ Ph], 141, 74 (100). – IR (film): $\tilde{\nu}$ = 3068 $cm^{-1}$ m, 2150 s ($\nu$SiH), 1952 w, 1877 w, 1815 w, 1588 w, 1480 w, 1427 s, 1332 w, 1303 w, 1121 m, 1104 m, 926 s, 870 m, 840 s, 798 vs, 736 m, 695 s, 641 w, 563 m, 455 m, 414 m, 350 m ($\nu_{as}$SiSeSi).

*Bis(phenylsilyl)amine* (**4**): 150 ml of bromo(phenyl)silane and 1.3 l of diethyl ether are placed in a 2-l two-necked flask equipped with an efficient reflux condenser and a gas inlet tube. A vigorous steam of dry ammonia is admitted into the intensely stirred solution. The flow rate of the ammonia stream is chosen such, that after a 5-min initial period no gas is escaping through a mercury valve attached to the condenser. After 2 h the solution absorbs only little ammonia and the excess escapes through the valve. This state is maintained for half an hour. The ammonium bromide precipitate is filtered and the diethyl ether distilled from the filtrate. The remaining colorless liquid is fractionally distilled in vacuo to yield 9.9 g of **5** (4%), b.p. 136°C/1 mbar) and 120 g of **4** (91%), b.p. 114°C/1 mbar. – $^{1}H$ NMR (399.78 MHz, $C_6D_6$, TMS, 20°C): $\delta$ = 0.12 (broad, 1H, NH), 5.06 [d, 4H, $^{3}J$(HSiNH) = 3.7, $^{1}J$(HSi) = 208.1 Hz, $SiH_2$], 7.12–7.19 (m, 6H, *m,p*-H), 7.47–7.53 (m, 4H, *o*-H). – $^{29}Si$ NMR (53.67 MHz, $C_6D_6$, TMS, 20°C): $\delta$ = –28.60 [t, $^{1}J$(SiH) = 207.8 Hz]. – MS (EI, 70 eV): *m/z* (%) = 229 [$M^+$], 228 [$M^+ -$ H], 183, 150 (100) [$C_6H_8NSi_2$], 107 [$C_6H_7Si$]. – IR (film): $\tilde{\nu}$ = 3325 $cm^{-1}$ s ($\nu$NH), 3000 m, 2110 s ($\nu$SiH), 1950 w, 1880 w, 1585 m, 1480 w, 1425 m, 1375 w, 1330 w, 1175 s ($\nu$NH), 1115 s, 930 vs ($\nu_{as}$SiNSi), 850 vs, 725 m, 695 s, 665 m, 600 m, 460 m, 390 m.

$C_{12}H_{15}NSi_2$ (229.4)
Calcd. C 62.82 H 6.59 N 6.10
Found C 62.16 H 6.71 N 6.28

*Tris(phenylsilyl)amine* (**5**): 25 ml of bromo(phenyl)silane and 100 ml of diethyl ether are placed in a 250-ml two-necked flask equipped with a reflux condenser and a gas inlet tube. A slow stream of ammonia is admitted through the gas inlet tube into the vigorously stirred solution. After displacement of the nitrogen by ammonia no gas is escaping through a mercury valve. When the ammonia stream is no longer completely absorbed, the admittance of ammonia is discontinued. The white suspension is stirred for additional 2 h, then the precipitated ammonium bromide is filtered, the diethyl ether removed by distillation, and the remaining liquid fractionally distilled in vacuo to give a fraction of unreacted bromo-(phenyl)silane and 13.95 g of **5** (69%), b.p. 136°C/1 mbar, m.p. 14°C. – $^{1}H$ NMR (399.78 MHz, $C_6D_6$, TMS, 30°C). $\delta$ = 5.25 [s, 6H, $^{1}J$(HSi) = 211.2 Hz, $SiH_2$], 7.05–7.14 (m, 9H, *m,p*-H), 7.44–7.47 (m, 6H, *o*-H). – $^{29}Si$ NMR (53.67 MHz, $C_6D_6$, TMS, 30°C): $\delta$ = –23.63 [tm, $^{1}J$(SiH) = 210.3 Hz]. – MS (EI, 70 eV): *m/z* (%) = 335 [$M^+$], 334 [$M^+ -$ H], 257 [$C_{10}H_{14}NSi_3$], 179 (100) [$C_6H_9NSi_3$]. – IR (film): = 3045 $cm^{-1}$ m, 2910 m, 2120 s ($\nu$SiH), 1950 w, 1880 w, 1810 w, 1585 w, 1483 w, 1425 m, 1375 m, 1330 w, 1300 w, 1265 w, 1115 s, 940 vs ($\nu_{as}$SiNSi), 840 vs, 755 m, 720 s, 690 s, 620 m, 465 m, 380 w.

$C_{18}H_{21}NSi_3$ (335.6)
Calcd. C 64.43 H 6.31 N 4.17
Found C 63.45 H 6.28 N 4.55

*(Phenylsilyl)bis(trimethylsilyl)amine* (**6**): 10.0 ml of chloro(phenyl)silane (0.073 mol) is added to 10.2 ml of triethylamine (0.073 mol) and 15.4 ml of 1,1,1,3,3,3-hexamethyldisilazane. The mixture is heated to 130°C for 3 h without a solvent. After cooling to ambient temperature the product is suspended in 50 ml of pentane and the suspension stirred for 0.5 h. The pentane is removed under reduced pressure and the residue distilled in vacuo to yield 10.39 g (53%) of **6**, b.p. 45–49°C (0.1 mbar), m.p. 7–8°C. – $^{1}H$ NMR (399.78 MHz, $C_6D_6$, TMS, 25°C): $\delta$ = 0.21 [s, $^{2}J$(HCSi) = 6.1 Hz, 18H, $(H_3C)_3Si$], 5.14 (s, 2H, $H_2Si$), 7.17–7.19 (m, 2H, *m,p*-H), 7.59–7.61 (m, 2H, *o*-H). – $^{13}C\{^{1}H\}$ NMR (100.54 MHz, $C_6D_6$, TMS, 25°C): $\delta$ = 3.58 (s, $CH_3$), 128.24 (s, *o*-C), 129.87 (s, *p*-C), 133.99 (s, *i*-C), 136.69 (s, *m*-C). – $^{15}N\{^{1}H\}$ NMR (INEPT, 40.51 MHz, $C_6D_6$, $CH_3NO_2$ external, 25°C): $\delta$ = –358.4 (s). – $^{29}Si$ NMR (INEPT, 79.43 MHz, $C_6D_6$, TMS, 25°C): $\delta$ = –35.86 [tt, $^{1}J$(SiH) = 205.1, $^{3}J$(SiCCH) = 6.3 Hz, $SiH_2$], 6.07 [dec, $^{2}J$(SiCH) = 6.1 Hz, $SiMe_3$].

*[Bis(trimethylsilyl)methylene]triphenylphosphorane* (**10**) *and Triphenyl[(trimethylsilyl)methylene]phosphorane:* 0.28 mol of methylenetriphenylphosphorane is freshly prepared by treating 100 g (0.28 mol) of commercially available methyltriphenylphosphonium bromide, suspended in 500 ml of diethyl ether, with the equivalent amount of a 1.6 M *n*-butyllithium solution in hexane. 20.28 g of chlorotrimethylsilane (0.19 mol) is slowly added to the phosphorane solution. The mixture is allowed to react for 26 d with short vigorous stirring after every 6 h. The precipitate is filtered, and the solvents are removed by evaporation in vacuo. An orange-red oil remains, which is fractionally distilled in vacuo by using a 5-cm Vigreux column. The first fraction (b.p. 150–155°C/1 mbar) is a mixture containing 95% of triphenyl[(trimethylsilyl)methylene]-phosphorane (yield 19.3 g, 40%) and 5% of **10**. – $^{1}H$ NMR (270.17 MHz, $C_6D_6$, 20°C): $\delta$ = –0.06 [d, 1H, $^{2}J$(HCP) = 8.6 Hz, HCP], 0.23 (s, 9H, $H_3C$), 7.03–7.20 (m, 9H, *m,p*-H), 7.70–7.83 (m, 6H, *o*-H). The second fraction (b.p. 178–180°C/1 mbar) consists predominantly of **10** ⟨ca. 94% purity, with 6% of triphenyl[(trimethylsilyl)methylene]phosphorane⟩, yield 34.4 g (44%). – $^{1}H$ NMR (270.17 MHz, $C_6D_6$, 20°C): $\delta$ = 0.20 (s, 18H, $CH_3$), 7.03–7.21 (m, 9H, *m,p*-H), 7.72–7.85 (m, 6H, *o*-H). – $^{13}C\{^{1}H\}$ NMR (64.97 MHz, $C_6D_6$, 20°C): $\delta$ = –1.08 [d, $^{1}J$(CP) = 94.9 Hz, $PCSi_2$], 4.40 [d, $^{3}J$(CSiCP) = 3.9 Hz, $CH_3$], 128.30 [d, $^{2}J$(CCP) = 11.25 Hz, *o*-C], 130.73 [d, $^{4}J$(CCCCP) = 2.90 Hz, *p*-C], 132.97 [d, $^{3}J$(CCCP) = 9.78 Hz, *m*-C], 134.74 [d, $^{1}J$(CP) = 84.1 Hz, *i*-C].

*[Bis(phenylsilyl)methylene]trimethylphosphorane* (**11**): A solution of 95.95 g of methylenetrimethylphosphorane (1.05 mol) in 500 ml of diethyl ether is cooled to 0°C. 99.80 g of chloro(phenyl)silane (0.70 mol) is slowly added to the solution. A white precipitate is formed immediately. The mixture is stirred for 10 d. Then the solid is filtered and the solvent removed from the filtrate in vacuo to leave 52.28 g (50%) of **11**, which can be further purified either by crystallization from diethyl ether or by sublimation in vacuo, b.p. 158°C/1 mbar, m.p. 62°C. – $^{1}H$ NMR (399.78 MHz, $C_6D_6$, TMS, 20°C): $\delta$ = 0.80 [d, 9H, $^{2}J$(HCP) = 12.8 Hz, $CH_3$], 5.29 [d, 4H, $^{3}J$(HSiCP) = 14.0, $^{1}J$(HSi) = 188.6 Hz, $SiH_2$], 7.19–7.28 (m, 6H, *m,p*-H), 7.80–7.82 (m, 4H, *o*-H). – $^{13}C\{^{1}H\}$ NMR (100.54 MHz, $C_6D_6$, TMS, 20°C): $\delta$ = –10.89 [d, $^{1}J$(CP) = 73.1 Hz, $PCSi_2$], 17.57 [d, $^{1}J$(CP) = 59.1 Hz, $CH_3$], 128.05 (s, *m*-C), 128.97 (s, *p*-C), 135.07 (s, *o*-C), 140.14 (s, *i*-C). – $^{29}Si$ NMR (53.67 MHz, $C_6D_6$,

20°C): $\delta$ = −39.60 [tm, $^1J$(SiH) = 189.0 Hz]. – $^{31}$P NMR (109.37 MHz, $C_6D_6$, $H_3PO_4$ external, 20°C): $\delta$ = 9.20 [dec quint, $^2J$(PCH) = 12.8, $^3J$(PCSiH) = 14.1 Hz]. – MS (EI, 70 eV): $m/z$ (%) = 302 [M$^+$], 301 (100) [M$^+$ − H], 271, 195 [$Me_3PCSiH_2Ph$], 119, 105 [PhSi]. – IR (Nujol): $\tilde{\nu}$ = 2362 cm$^{-1}$ s, 2102 m (νSiH), 2066 s, 1418 m, 1413 w, 1305 w, 1289 w, 1108 w, 1077 s (νP=C), 985 m, 875 s, 855 s, 834 s, 725 s, 701 m ($\nu_{as}C_3P$), 669 m ($\nu_sC_3P$), 594 m, 574 w.

$C_{16}H_{23}PSi_2$ (302.5) Calcd. C 63.53 H 7.66
Found C 62.41 H 7.33

*Triphenyl[(phenylsilyl)methylene]phosphorane and [Bis(phenylsilyl)methylene]triphenylphosphorane* (**12**): As described for **10**, 0.275 mol of methylenetriphenylphosphorane dissolved in diethyl ether is treated with 26.15 g of chloro(phenyl)silane (0.18 mol) at 0°C. The mixture is allowed to react for 21 d with some vigorous stirring every 6 h. The white precipitate is filtered, and the solvents are removed in vacuo. Petroleum ether (60−90°C) is added to the residue, the precipitate formed is filtered and the petroleum ether evaporated from the filtrate in vacuo. A yellow-orange oil remains containing triphenyl[(phenylsilyl)methylene]phosphorane and **12** in the ratio 20:80. The spectroscopic data are assigned as follows: Triphenyl[(phenylsilyl)methylene]phosphorane: $^1$H NMR (399.78 MHz, $C_6D_6$, TMS, 35°C): $\delta$ = 0.56 [dt, 1H, $^2J$(HCP) = 7.4, $^3J$(HCSiH) = 4.6 Hz, P=CH], 5.24 [dd, 2H, $^3J$(HSiCP) = 9.3, $^3J$(HSiCH) = 4.6 Hz, $SiH_2$], 6.95−7.08 and 7.59−7.70 (m, 15H, $C_6H_5P$), 7.12−7.29 and 7.88−7.93 (m, 5H, $C_6H_5Si$). – $^{31}$P{$^1$H} NMR (161.85 MHz, $C_6D_6$, TMS, 35°C): $\delta$ = 25.43 (s). – **12**: $^1$H NMR (399.78 MHz, $C_6D_6$, TMS, 35°C): $\delta$ = 5.31 [d, 4H, $^3J$(HSiCP) = 12.8 Hz, $SiH_2$], 6.95−7.08 and 7.59−7.70 (m, 15H, $C_6H_5P$), 7.12−7.29 and 7.88−7.93 (m, 10H, $C_6H_5Si$). – $^{31}$P{$^1$H} NMR (161.85 MHz, $C_6D_6$, 30°C): $\delta$ = 27.32 (s).

Table 1. Crystal data, structure solution and refinement for compounds **6** and **11**

| | **6** | **11** |
|---|---|---|
| Formula | $C_{12}H_{25}NSi_3$ | $C_{16}H_{23}PSi_2$ |
| $M_r$ | 267.598 | 302.507 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$ [Å] | 8.463(1) | 7.905(1) |
| $b$ [Å] | 17.135(1) | 12.455(1) |
| $c$ [Å] | 11.945(1) | 18.219(2) |
| $\beta$ [°] | 101.08(1) | 91.73(1) |
| $V$ [Å$^3$] | 1699.9 | 1792.9 |
| $\varrho_{calc.}$ [gcm$^{-3}$] | 1.046 | 1.120 |
| $Z$ | 4 | 4 |
| $F$(000) [e] | 584 | 648 |
| $\mu$(Mo-$K_\alpha$) [cm$^{-1}$] | 2.532 | 2.674 |
| $T$ [°C] | −60 | −50 |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| Scan | $\omega$ | $\omega$ |
| Scan width [°, in $\omega$] | 0.8 | 0.8 |
| $hkl$ range | +9, +19, ±13 | ±9, +14, +21 |
| $\sin(\Theta/\lambda)_{max}$ [Å$^{-1}$] | 0.583 | 0.594 |
| Measured reflections | 3137 | 3549 |
| Unique reflections | 2828 | 3150 |
| $R_{int}$ | 0.0202 | 0.0199 |
| Observed reflections | 2184 | 2496 |
| $F_o \geqslant$ | $4\sigma(F_o)$ | $4\sigma(F_o)$ |
| Refined parameters | 153 | 264 |
| H atoms (found/calcd.) | 17/8 | 23/0 |
| $R$ | 0.0517 | 0.0452 |
| $R_w$ | 0.0523 | 0.0412 |
| (shift/error)$_{max}$ | 0.001 | 0.001 |
| $\varrho_{fin}$(max/min) [eÅ$^{-3}$] | +0.29, −0.33 | +0.46, −0.35 |

*[Bis(phenylsilyl)methylene]trimethylphosphorane* (**11**) *and [Bis(phenylsilyl)methylene]triphenylphosphorane* (**12**) *by Transsilylation of* **9** *and* **10**: The phosphorane **9** or **10** is dissolved in benzene. Two equivalents of chloro(phenyl)silane are added. The mixture is stirred at 50°C for 24 h. The solvent, the chlorotrimethylsilane and unreacted chloro(phenyl)silane are removed in vacuo. The residue is dissolved in $C_6D_6$ and studied by NMR spectroscopy. A mixture of the starting compound (**9** or **10**) with **11** or **12**, respectively, is detected. The products have not been separated.

*Crystal Structure Analyses:* Suitable single crystals of compound **6** were obtained from the melt or from a solution in pentane (0.3 × 0.45 × 0.45 mm) and of **11** by sublimation in vacuo (0.25 × 0.45 × 0.45 mm). They were sealed in glas capillaries under argon and mounted on a four-circle Syntex-P2$_1$ diffractometer with a graphite monochromator. Crystal data and data concerning collection and refinement are compiled in Table 1. Reduced cell calculations did not indicate any higher cell symmetry. The measured intensities were not corrected for absorption or extinction effects. The structures were solved by direct methods (SHELXS-86) and completed by difference Fourier syntheses. After refinement of all

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **6**. [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where $U_1$, $U_2$, and $U_3$ are the eigenvalues of the $U_{ij}$ matrix; e.s.d. values in parentheses]

| ATOM | X/A | Y/B | Z/C | U(eq.) |
|---|---|---|---|---|
| SI1 | 0.1154(1) | 0.42659(6) | 0.36887(8) | 0.044 |
| SI2 | 0.4122(1) | 0.40986(6) | 0.26831(8) | 0.044 |
| SI3 | 0.1991(1) | 0.55693(6) | 0.22842(8) | 0.048 |
| N | 0.2410(3) | 0.4630(2) | 0.2837(2) | 0.035 |
| C1 | -0.0073(4) | 0.3418(2) | 0.3045(3) | 0.039 |
| C11 | -0.0571(4) | 0.3334(2) | 0.1868(3) | 0.048 |
| C12 | -0.1531(5) | 0.2714(2) | 0.1410(3) | 0.056 |
| C13 | -0.2030(4) | 0.2169(2) | 0.2110(3) | 0.054 |
| C14 | -0.1544(4) | 0.2240(2) | 0.3275(3) | 0.055 |
| C15 | -0.0590(4) | 0.2854(2) | 0.3730(3) | 0.046 |
| C21 | 0.4274(5) | 0.3194(2) | 0.3573(3) | 0.060 |
| C22 | 0.3990(5) | 0.3774(3) | 0.1189(3) | 0.071 |
| C23 | 0.5987(5) | 0.4668(3) | 0.3180(4) | 0.076 |
| C31 | 0.3145(5) | 0.5792(3) | 0.1148(4) | 0.071 |
| C32 | -0.0161(5) | 0.5654(2) | 0.1575(4) | 0.069 |
| C33 | 0.2466(7) | 0.6303(2) | 0.3436(4) | 0.080 |

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **11**. [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where $U_1$, $U_2$, and $U_3$ are the eigenvalues of the $U_{ij}$ matrix; e.s.d. values in parentheses]

| ATOM | X/A | Y/B | Z/C | U(eq.) |
|---|---|---|---|---|
| C1 | 0.5885(4) | 0.0966(2) | 0.8156(1) | 0.036 |
| SI2 | 0.2289(1) | 0.44651(7) | 0.39001(4) | 0.043 |
| SI1 | 0.1263(1) | 0.45839(7) | 0.22558(4) | 0.043 |
| P1 | -0.0950(1) | 0.33897(7) | 0.32983(4) | 0.038 |
| C11 | 0.8134(4) | 0.0977(2) | 0.6775(1) | 0.033 |
| C12 | 0.8578(4) | 0.2052(3) | 0.6825(2) | 0.043 |
| C13 | 0.9883(5) | 0.2476(4) | 0.6442(2) | 0.055 |
| C14 | 1.0809(5) | 0.1819(4) | 0.5996(2) | 0.060 |
| C15 | 1.0431(5) | 0.0753(4) | 0.5941(2) | 0.061 |
| C16 | 0.9099(4) | 0.0337(3) | 0.6320(2) | 0.050 |
| C21 | 0.8486(4) | 0.1632(2) | 0.9403(1) | 0.034 |
| C22 | 0.9244(4) | 0.1454(3) | 1.0096(2) | 0.041 |
| C23 | 1.5152(4) | 0.2760(3) | 0.5462(2) | 0.043 |
| C24 | 1.0335(4) | 0.3236(3) | 1.0151(2) | 0.045 |
| C25 | 0.9604(5) | 0.3440(3) | 0.9476(2) | 0.049 |
| C26 | 0.8699(4) | 0.2649(3) | 0.9104(2) | 0.042 |
| C31 | 0.3702(7) | 0.2763(4) | 0.7722(3) | 0.066 |
| C32 | -0.1072(7) | 0.2912(5) | 0.4221(2) | 0.064 |
| C33 | -0.2847(6) | 0.4158(5) | 0.3132(4) | 0.073 |

non-hydrogen atoms with anisotropic displacement parameters all hydrogen atoms (23) and 17 hydrogen atoms out of 25 could be located in the difference Fourier maps for **11** and **6**, respectively, and were included with fixed atomic contributions ($U_{\mathrm{iso(fix)}}$ = 0.05 Å$^2$), except the two H atoms at silicon in compound **6** and seven H-atoms in **11**, which were refined isotropically. The remaining 8H atoms in **6** were calculated at idealized geometrical positions and also included with fixed atom contributions ($U_{\mathrm{iso(fix)}}$ = 0.05 Å$^2$) (SHELX-76). The fractional atomic coordinates and isotropic displacement parameters are listed in Tables 2, 3.

Further information on the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55946, the names of the authors, and the journal citation.

## CAS Registry Numbers

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