Phosphonium Ylides with Functionalized Silyl Substituents

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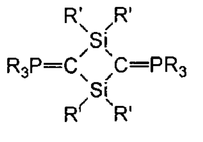
Received March 23, 1994

Key Words: Silicon compounds / Ylides / NMR, ^{13}C, ^{17}O, ^{29}Si

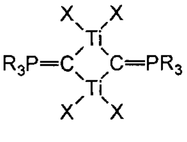
Two series of aminophosphonium ylides with reactive alkoxychlorosilyl substituents $(R_2N)_3P{=}CHSi(OR')_2Cl$ (**1**–**8**, R = Me, Et/R' = Me, Et, *i*Pr, *t*Bu) have been prepared by reaction of the aminophosphonium ylides $(R_2N)_3P{=}CH_2$ with the corresponding dialkoxydichlorosilanes $Cl_2Si(OR')_2$. Substituent effects have been investigated by heteronuclear solution NMR studies of the nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, and ^{31}P. These studies show an alternating shielding effect along the C–O–Si–C backbone. Further reactions of the chlorosilylated ylides with the aminomethylenephosphorane $(Me_2N)_3P{=}CH_2$ lead to the formation of the bis-ylidic compounds $[(Me_2N)_3P{=}CH]_2Si(OR')_2$ (**9**, **10**), which are also available in one-pot syntheses. The molecular structure of $[(Me_2N)_3P{=}CH]_2Si(O\textit{i}Pr)_2$ (**9**) has been confirmed by single-crystal X-ray diffraction. In the crystal the molecules have two ylidic carbon centers with planar configuration, which are bridged by a nearly tetrahedral silicon atom. Short P–C- and Si–C distances indicate a stabilizing effect of the carbanionic centers.

Phosphonium ylides with *silyl* substituents at the carbanionic center have been known for a considerable period of time[1]. In these compounds the silicon atoms exercise a stabilizing effect on the carbanionic function, decreasing their basicity and their specific nucleophilic ylide reactivity[2]. However, the silyl groups also act as efficient leaving groups in many organic reactions of the ylides[3–8]. Trimethylsilyl groups in particular have been employed in most cases for this purpose, while *Si*-functional substituents have been largely ignored. Of special interest are cyclic compounds **A** with silicon as a bridging atom between the ylidic groups[9–11].

Recently, a series of *titanyl*-substituted phosphonium ylides bearing halogen, alkoxy, or amido substituents X at the titanium atoms (**B**) have been presented[12], complementing earlier work with bifunctional, ylidic titanyl compounds[13,14].



A



B

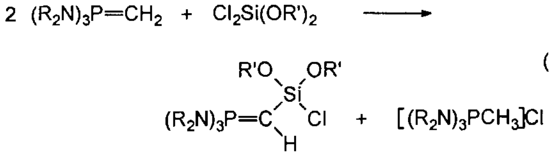
These compounds have been found to react with aromatic aldehydes to give allenes. Titanyl-substituted ylides can thus serve as transfer reagents for "naked" carbon atoms. A nucleophilic substitution at the titanium center has been proposed for the primary reaction-inducing step.

In order to introduce a silicon functionality into compounds of type **A** and their precursors, two series of alkoxychlorosilyl species have now been prepared, which would give access to interesting derivatives and complexes of silicon-functionalized phosphonium ylides.

Results

Syntheses of Monoylides

The chlorosilylated phosphonium ylides **1**–**8** are prepared by the reaction of the methylene-phosphoranes $(R_2N)_3P{=}CH_2$ with dialkoxydichlorosilanes. In the first step of these reactions silylated phosphonium salts are generated and subsequently deprotonated in a transylidation process[15] by a second equivalent of the unsubstituted methylenephosphorane.



$$2\ (R_2N)_3P{=}CH_2 + Cl_2Si(OR')_2 \longrightarrow (R_2N)_3P{=}C(H){-}Si(OR')_2Cl + [(R_2N)_3PCH_3]Cl \qquad (1)$$

R' =	Me	Et	iPr	tBu
R = Me	**1**	**2**	**3**	**4**
Et	**5**	**6**	**7**	**8**

Compounds **1**–**8** are purified by kugelrohr distillation in vacuo. They are obtained as colorless, clear and viscous liquids, which are sensitive to oxidation by air and to hydrolysis. Although the compounds can be distilled without decomposition, the pure substances undergo rearrangement reactions upon storage at ambient temperature leading to complex mixtures of products. This decomposition is avoided by cooling the compounds immediately after distillation to −78°C and keeping them at this temperature.

Solution NMR Studies

The compounds **1**–**8** have been fully characterized by NMR measurements (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, and ^{31}P). The data for the ylidic carbon and the silicon atoms of the ylides **1**−**8** are listed in Table 1.

Table 1. NMR data for the ylidic carbon and silicon atoms of the compounds **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$\delta(^{13}C$, ylidic)	-0.32	0.26	0.68	4.58	3.23	3.84	4.44	8.62
$\delta(^{29}Si)$	-28.14	-31.60	-34.62	-46.80	-28.90	-32.41	-35.30	-47.71

The characteristic resonances for the ylidic carbon atoms appear in a range from $\delta = -0.32$ (**1**) to 4.58 (**4**) for the *N*-Me compounds, and from $\delta = 3.23$ (**5**) to 8.62 (**8**) for the *N*-Et compounds. The differences $\Delta(\delta)$ within these series (**1**−**4** and **5**−**8**) are about 5 ppm. This can be attributed to the increasing inductive and steric effects of the alkyl substituents bound to the oxygen atoms. The $^1J(^{13}C^{31}P)$ values are as large as 170 Hz. Comparable values for silylated phosphonium ylides are only found in the case of tris(dialkylamino)methylenephosphoranes[11]. The stepwise replacement of amino groups by an alkyl or phenyl group leads to a decrease of $^1J(^{13}C^{31}P)$. One-bond P-C coupling constants for ylides with alkyl- or phenyl-substituted phosphonium atoms are smaller than 100 Hz. This difference can be ascribed to the higher electronegativity of nitrogen as compared to carbon. The opposite effect is found in the ^{29}Si-NMR spectra. $\delta(^{29}Si)$ decreases with increasing inductive effect of the oxygen-bound alkyl substituents. $\delta(^{29}Si)$ has been found to be -28 for the *O*-methyl compounds **1** and **5** and to shift to -47 for the *O*-*tert*-butyl derivatives **4** and **8**. The chemical shifts $\delta(^{17}O)$ cover the range from 7 to 88, which is similar to that of the corresponding alcohols (MeOH: $\delta = -37$, *t*BuOH: 62)[16]. With increasing inductive effect of the alkyl group R′, $\delta(^{17}O)$ of the series **1**−**4** and **5**−**8** and of the corresponding alcohols increases in steps of comparable magnitude. These results are compiled in Table 2.

Table 2. ^{17}O Chemical shifts for alcohols and the ylides **1**−**8**

	δ(**5** - **8**)	Δ(δ)	δ(**1** - **4**)	Δ(δ)	δ(R = H)	Δ(δ)
MeO-R	8		7		-37	
EtO-R	43	35	44	37	6	43
^{i}PrO-R	72	29	71	27	38	32
^{t}BuO-R	88	16	88	17	62	24

The resonances of the ^{15}N and ^{31}P nuclei are independent of changes in the alkoxy substituents. In summary, the change of the alkyl group results in an alternation of shielding and deshielding along the C−O−Si−C skeleton. This behavior is the same in both series of compounds (R = Me, Et). The results are illustrated in Figure 1.

Syntheses of Bis-ylidic Compounds

The reactivity of the chlorosilylated phosphonium ylides **3** and **4** has been tested by treating them with another two equivalents of tris(dimethylamino)methylenephosphorane. A transylidation process leads to silicon-bridged, noncyclic bis-ylides **9** and **10**, respectively. The products can also be generated in a direct way by reaction of one equivalent of dialkoxydichlorosilane with four equivalents of tris(dimethylamino)methylenephosphorane.

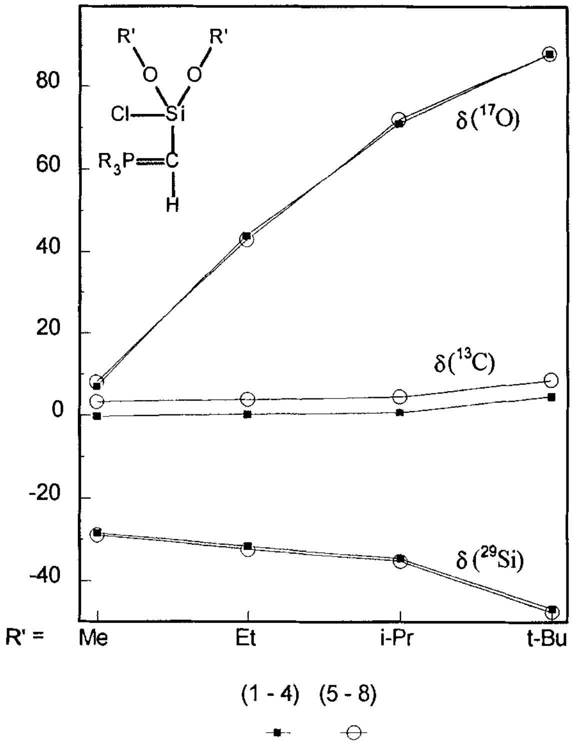
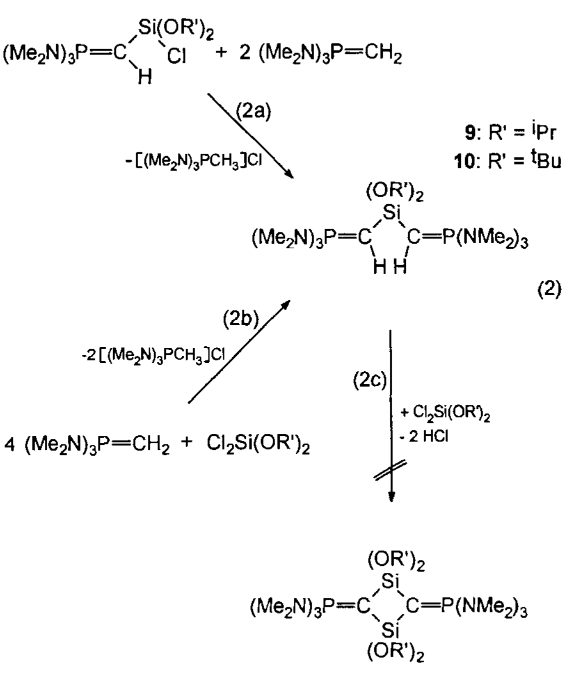


Figure 1. Substituent effects along the molecular backbone in ylides **1**−**8** (δ values)

The compounds **9** and **10** can be purified by kugelrohr distillation in vacuo. They are colorless solids with melting points near room temperature. Probably owing to the absence of a chloro function no rearrangements are observed. Therefore, the pure products are stable under nitrogen at ambient temperature, but decompose in air and moisture.



(2)

In the synthesis following pathway (2b) the chlorosilane is added to an excess of tris(dimethylamino)methylenephosphorane. We also have carried out the reversed pathway by adding the methylenephosphorane slowly to the chlorosilane. The products are the same in both cases. Again the silicon-bridged derivative is formed exclusively, and no indication of a *doubly* silylated species (**A**) has been found in the reaction mixture (2c). Sterical hindrance and the low basicity of the monosilylated ylides are held responsible for this observation.

Crystal Structure of the Bis-ylidic Compound 9

Crystals of **9** have been grown by cooling the melt slowly to 10°C. They belong to the orthorhombic system, space group $P2_12_12_1$ (No. 19), and contain $Z = 4$ formula units in the unit cell. The molecules show no crystallographic symmetry. The molecular structure is shown in Figure 2.

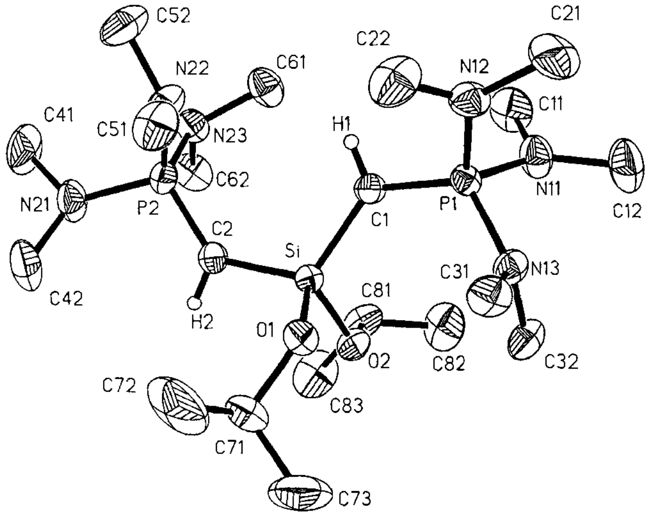


Figure 2. Molecular structure of diisopropoxybis[tris(dimethylamino)-phosphoranylidenemethyl]silane (**9**) in the crystal (hydrogen atoms except for ylidic protons have been omitted for clarity). – Selected bond distances [Å] and angles [°]: P1–C1 1.658(2), P2–C2 1.656(2), C1–Si 1.797(2), C2–Si 1.810(2); P1–C1–Si 129.2(1), P2–C2–Si 134.9(1), C1–Si–C2 114.7(1), O1–Si–O2 100.4(1), Si–C1–H1 120.0(2), Si–C2–H2 112.0(2), P1–C1–H1 111.0(2), P2–C2–H2 112.0(2)

The ylidic carbon atoms exhibit a planar configuration (sum of angles 360.2° at C1, 358.9° at C2). The two planes defined by P1–C1–H1 and P2–C2–H2 are twisted by an angle of 18.2°. As expected for the sp^2-carbon geometry the double bond character of P=C is confirmed by short P–C bond lengths [P1–C1 = 1.658(2), P2–C2 = 1.656(2) Å]. These data are the shortest P–C distances known for silylated phosphonium ylides. For a mono-trimethylsilylated ylide Appel et. al. have reported a P–C distance of 1.674 Å[17]. In doubly silylated compounds this bond length increases to as much as 1.69 Å[17,18]. The silicon-carbon bonds show distances of 1.797(2) and 1.810(2) Å, respectively. The coordination at the silicon atom is nearly tetrahedral with a slightly widened C1–Si–C2 angle and a narrowed O1–Si–O2 angle. The different configurations of the six dimethylamino groups are noteworthy. The coordination of the nitrogen atoms varies from nearly planar (358.8° and 357.0° at N11 and N21, respectively) to pyramidal (336.4° at N23). Similar differences have been reported for a cyclic (dimethylamino)phosphonium ylide[9].

Conclusion

Silylated aminophosphonium ylides with electronegative substituents (chlorine, alkoxy) at the silicon atom have been made accessible according to the transylidation route from ylides $(R_2N)_3P{=}CH_2$ and silanes $(R'O)_2SiCl_2$. Both monosilylated and silicon-bridged bisylides have been obtained in this process in high yields. We have not succeeded in accomplishing ring closure to bifunctional cyclic ylides, however, probably owing to severe steric hindrance. The ylides of the types $(R_2N)_3P{=}CHSi(OR')_2Cl$ and $[(R_2N)_3P{=}CH]_2Si(OR')_2$ have been designed as synthons for carbon transfer in organic reactions. Both the SiCl/OR′ and the only remaining SiC bonds are expected to be broken in such reactions owing to the excellent leaving group properties of ylidic moieties at silicon (desilylation). With the aid of fluorine catalysts this mode of reaction should be even more promising. Pertinent work analogous to the investigations with the corresponding titanium compounds is in progress.

This work has been supported by *Fonds der Chemischen Industrie*.

Experimental

All reactions were carried out under dry and purified nitrogen. The solvents were dried with CaH_2, distilled, and stored under nitrogen. All glassware was heated to 150°C, evacuated and filled with nitrogen. – NMR: Jeol GX 400. References: Tetramethylsilane for ^1H, ^{13}C, and ^{29}Si spectra, external H_3PO_4 (85% in H_2O) for ^{31}P, external D_2O for ^{17}O, and external nitromethane for ^{15}N. The spectra were recorded as 25% solutions in C_6D_6 at 25°C. ^1H (399.78 MHz), ^{13}C (100.53 MHz), ^{15}N (40.51 MHz), ^{17}O (54.21 MHz), ^{29}Si (79.43 MHz), ^{31}P (161.85 MHz). – MS: Varian MAT90 (CI, Isobutane) and Varian MAT311A (EI, 70 eV). The peaks of the chlorinated species show correct isotope patterns and are given with respect to the isotope ^{35}Cl.

Reagents: Tris(dialkylamino)methylenephosphoranes $(R_2N)_3P{=}CH_2$ were obtained by deprotonation of the corresponding phosphonium salts with potassium hydride[19]. Dialkoxydichlorosilanes $Cl_2Si(OR')_2$ were prepared by the reactions of silicon tetrachloride with alcohols[20]. All yields are based on the respective silanes.

Synthesis of [(Chlorodialkoxysilyl)methylene]tris(dialkylamino)phosphoranes. – General Procedure: To 30 ml of *n*-pentane were added at 0°C at the same time and in the same volume 2 equiv. (30 mmol) of tris(dialkylamino)methylenephosphorane and 1 equiv. (15 mmol) of the dialkoxydichlorosilane. The mixture was refluxed for 3 h, and the white phosphonium salt was filtered off. After removal of the solvent from the filtrate in vacuo the products were purified by kugelrohr distillation.

[(Chlorodimethoxysilyl)methylene]tris(dimethylamino)phosphorane (**1**): Yield 41%, b.p. kugelrohr distillation at 130°C air bath temp./0.01 mbar. – ^1H NMR: $\delta = -0.10$ [d, ^2J(HCP) = 10.1 Hz, 1H, PCH], 2.37 [d, ^3J(HCNP) = 9.8 Hz, 18H, NCH_3], 3.54 (s, 6H, OCH_3). – ^{13}C NMR: $\delta = -0.32$ [dd, ^1J(CP) = 169.6, ^1J(CH) = 135.6 Hz, PC], 37.36 [qquint, ^1J(CH) = 136.0, ^2J(CNP) = 4.1, ^3J(CNCH) = 4.1 Hz, NC], 50.64 [q, ^1J(CH) = 142.0 Hz, OC]. –

^{15}N{^{1}H} NMR (DEPT): δ = −363.55 [d, ^1J(NP) = 13.5 Hz]. − ^{17}O{^{1}H} NMR: δ = 7 (s). − ^{29}Si NMR (DEPT): δ = −28.14 [ddsept, ^2J(SiCP) = 35.4, ^2J(SiCH) = 7.3, ^3J(SiOCH) = 4.7 Hz]. − ^{31}P{^{1}H} NMR: δ = 65.88 (s). − MS (CI), *m/z*: 302 (100%) [M$^+$ + 1], 301 [M$^+$], 266 [M$^+$ − Cl], 258 [M$^+$ + 1 − NMe$_2$], 257 [M$^+$ − NMe$_2$], 251 [266 − Me], 119 [P(NMe$_2$)$_2$].

[(Chlorodiethoxysilyl)methylene]tris(dimethylamino)phosphorane (**2**): Yield 81%, b.p. kugelrohr distillation at 135°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = 0.02 [d, ^2J(HCP) = 10.1 Hz, 1H, PCH], 1.23 [t, ^3J(HCCH) = 7.0 Hz, 6H, OCH$_2$C*H*$_3$], 2.38 [d, ^3J(HCNP) = 9.8 Hz, 18H, NCH$_3$], 4.00 [q, ^3J(HCCH) = 7.0 Hz, 4H, OC*H*$_2$CH$_3$]. − ^{13}C NMR: δ = 0.26 [dd, ^1J(PC) = 169.6, ^1J(CH) = 135.1 Hz, PCH], 18.38 [qt, ^1J(CH) = 125.5, ^2J(CCH) = 2.3 Hz, OCH$_2$*C*H$_3$], 37.44 [qquint, ^1J(CH) = 136.0, ^2J(CNP) = 4.1, ^3J(CNCH) = 4.1 Hz, NCH$_3$], 58.85 [tq, ^1J(CH) = 141.6, ^2J(CCH) = 4.6 Hz, O*C*H$_2$CH$_3$]. − ^{15}N{^{1}H} NMR (DEPT): δ = −363.52 [d, ^1J(NP) = 13.1 Hz]. − ^{17}O{^{1}H} NMR: δ = 44 (s). − ^{29}Si NMR (DEPT): δ = −31.60 [ddquint, ^2J(SiCP) = 34.6, ^2J(SiCH) = 7.5, ^3J(SiOCH) = 3.8 Hz]. − ^{31}P{^{1}H} NMR: δ = 66.38 (s). − MS (CI), *m/z*: 330 [M$^+$ + 1], 329 [M$^+$], 294 [M$^+$ − Cl], 251 (100%) [M$^+$ + 1 − NMe$_2$ − Cl], 119 [(Me$_2$N)$_2$P].

[(Chlorodiisopropoxysilyl)methylene]tris(dimethylamino)phosphorane (**3**): Yield 76%, b.p. 97°C/0.01 mbar. − ^{1}H NMR: δ = −0.02 [d, ^2J(HCP) = 10.4 Hz, 1H, PCH], 1.29 [d, ^3J(HCCH) = 6.1 Hz, 6H, CHC*H*$_3$ a], 1.31 [d, ^3J(HCCH) = 6.1 Hz, 6H, CHC*H*$_3$ b], 2.40 [d, ^3J(HCNP) = 9.8 Hz, 18H, NCH$_3$], 4.54 [sept, ^3J(HCCH) = 6.1 Hz, 2H, OCH]. − ^{13}C NMR: δ = 0.68 [dd, ^1J(CP) = 168.7, ^1J(CH) = 134.7 Hz, PC], 25.71 [qquint, ^1J(CH) = 125.2, ^2J(CCH) = 3.9, ^3J(CCCH) = 3.9 Hz, CH*C*H$_3$], 37.54 [qquint, ^1J(CH) = 135.9, ^2J(CNP) = 4.1, ^3J(CNCH) = 4.1 Hz, NCH$_3$], 65.52 [dsept, ^1J(CH) = 141.6, ^2J(CCH) = 4.1 Hz, OCH]. − ^{15}N{^{1}H} NMR (DEPT): δ = −363.61 [d, ^1J(NP) = 12.8 Hz]. − ^{17}O{^{1}H} NMR: δ = 71 (s). − ^{29}Si NMR (DEPT): δ = −34.62 [ddt, ^2J(SiCP) = 34.2, ^2J(SiCH) = 7.3, ^3J(SiOCH) = 3.5 Hz]. − ^{31}P{^{1}H} NMR: δ = 66.71 (s). − MS (CI), *m/z*: 358 [M$^+$ + 1], 357 (100%) [M$^+$], 322 [M$^+$ − Cl], 313 [M$^+$ − NMe$_2$], 119 [(Me$_2$N)$_2$P].

[(Di-tert-butoxychlorosilyl)methylene]tris(dimethylamino)phosphorane (**4**): Yield 83%, b.p. kugelrohr distillation at 145°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = −0.09 [d, ^2J(HCP) = 10.1 Hz, 1H, PCH], 1.51 (s, 18H, CCH$_3$), 2.42 [d, ^3J(HCNP) = 9.8 Hz, 18H, NCH$_3$]. − ^{13}C NMR: δ = 4.58 [dd, ^1J(CP) = 165.5, ^1J(CH) = 133.7 Hz, PC], 31.90 [qsept, ^1J(CH) = 125.0, ^2J(CNP) = 4.14 Hz, C*C*H$_3$], 37.66 [qquint, ^1J(CH) = 136.0, ^2J(CNP) = 4.14, ^3J(CNCH) = 4.14 Hz, NCH$_3$], 73.47 [dez, ^2J(CCH) = 4.14 Hz, *C*CH$_3$]. − ^{15}N{^{1}H} NMR (DEPT): δ = −363.47 [d, ^2J(NP) = 11.9 Hz]. − ^{17}O{^{1}H} NMR: δ = 88 (s). − ^{29}Si NMR (DEPT): δ = −46.80 [dd, ^2J(SiCP) = 31.1, ^2J(SiCH) = 6.7 Hz]. − ^{31}P{^{1}H} NMR: δ = 66.26 (s). − MS (CI), *m/z*: 386 (100%) [M$^+$ + 1], 385 [M$^+$], 350 [M$^+$ − Cl], 119 [(Me$_2$N)$_2$P].

[(Chlorodimethoxysilyl)methylene]tris(diethylamino)phosphorane (**5**): Yield 43%, b.p. kugelrohr distillation at 135°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = −0.04 [d, ^2J(HCP) = 11.0 Hz, 1H, PCH], 0.91 [t, ^3J(HCCH) = 7.3 Hz, 18H, CH$_2$C*H*$_3$], 2.92 [dq, ^3J(HCNP) = 10.4, ^3J(HCCH) = 7.3 Hz, 12H, NCH$_2$], 3.56 (s, 6H, OCH$_3$). − ^{13}C NMR: δ = 3.23 [dd, ^1J(CP) = 171.9, ^1J(CH) = 133.3 Hz, PCH], 14.31 [qq, ^1J(CH) = 125.5, ^2J(CCH) = 2.8, ^3J(CCNP) = 2.8 Hz, CH$_2$*C*H$_3$], 40.29 [tquint, ^1J(CH) = 135.4, ^2J(CNP) = 4.6, ^2J(CCH) = 4.1 Hz, NCH$_2$], 50.57 [q, ^1J(CH) = 142.0 Hz, OCH$_3$]. − ^{15}N{^{1}H} NMR (DEPT): δ = −336.94 [d, ^1J(NP) = 12.4 Hz]. − ^{17}O{^{1}H} NMR: δ = 8.54 (s). − ^{29}Si NMR (DEPT): δ = −28.90 [ddsept, ^2J(SiCP) = 36.6, ^2J(SiCH) = 8.1, ^3J(SiOCH) = 4.7 Hz]. − ^{31}P{^{1}H} NMR: δ = 64.31 (s). − MS (CI), *m/z*: 386 (100%) [M$^+$ + 1], 385 [M$^+$], 350 [M$^+$ − Cl], 314 [M$^+$ + 1 − NEt$_2$], 175 [(Et$_2$N)$_2$P].

[(Chlorodiethoxysilyl)methylene]tris(diethylamino)phosphorane (**6**): Yield 89%, b.p. kugelrohr distillation at 185°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = 0.08 [d, ^2J(HP) = 11.3 Hz, 1H, PCH], 0.94 [t, ^3J(HCCH) = 7.0 Hz, 18H, NCH$_2$C*H*$_3$], 1.26 [t, ^3J(HCCH) = 7.0 Hz, 6H, OCH$_2$C*H*$_3$], 2.98 [dq, ^3J(HCCH) = 7.0, ^3J(HCNP) = 10.1 Hz, 12H, NCH$_2$], 4.03 [q, ^3J(HCCH) = 7.0 Hz, 4H, OCH$_2$]. − ^{13}C NMR: δ = 3.84 [dd, ^1J(CP) = 171.0, ^1J(CH) = 132.4 Hz, PC], 14.27 [qq, ^1J(CH) = 125.0, ^2J(CCH) = 2.8, ^3J(CCNP) = 2.8 Hz, NCH$_2$*C*H$_3$], 18.36 [qt, ^1J(CH) = 125.9, ^2J(CCH) = 2.8 Hz, OCH$_2$*C*H$_3$], 40.26 [tquint, ^1J(CH) = 136.0, ^2J(CCH) = 4.6, ^2J(CNP) = 3.7 Hz, NCH$_2$], 58.84 [tq, ^1J(CH) = 142.5, ^2J(CCH) = 4.6 Hz, OCH$_2$]. − ^{15}N{^{1}H} NMR (DEPT): δ = −336.91 [d, ^1J(NP) = 12.1 Hz]. − ^{17}O{^{1}H} NMR: δ = 43 (s). − ^{29}Si NMR (DEPT): δ = −32.41 [d; ^2J(SiCP) = 36.3 Hz]. − ^{31}P{^{1}H} NMR: δ = 64.73 (s). − MS (EI), *m/z*: 413 [M$^+$], 384 [M$^+$ − Et], 342 [M$^+$ − NEt$_2$], 270 [M$^+$ − 2 NEt$_2$], 175 (100%) [(Et$_2$N)$_2$P], 104.

[(Chlorodiisopropoxysilyl)methylene]tris(diethylamino)phosphorane (**7**): Yield 68%, b.p. kugelrohr distillation at 200°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = −0.03 [d, ^2J(HCP) = 11.6 Hz, 1H, PCH], 0.95 [t, ^3J(HCCH) = 7.0 Hz, 18H, NCH$_2$C*H*$_3$], 1.28 [d, ^3J(HCCH) = 6.0 Hz, 6H, OCH$_2$C*H*$_3$ a], 1.30 [d, ^3J(HCCH) = 6.0 Hz, 6H, OCH$_2$C*H*$_3$ b], 2.89 [dq, ^3J(HCNP) = 10.1, ^3J(HCCH) = 7.0 Hz, 12H, NCH$_2$], 4.52 [sept, ^3J(HCCH) = 6.0 Hz, 2H, OCH]. − ^{13}C NMR: δ = 4.44 [dd, ^1J(CP) = 171.0, ^1J(CH) = 131.9 Hz, PCH], 14.28 [qq, ^1J(CH) = 125.6, ^2J(CCH) = 2.8, ^3J(CCNP) = 2.8 Hz, NCH$_2$*C*H$_3$], 25.65 [qquint, ^1J(CH) = 125.0, ^2J(CCH) = 4.6, ^3J(CCCH) = 4.6 Hz, OCH(*C*H$_3$)$_2$], 40.25 [tquint, ^1J(CH) = 135.6, ^2J(CCH) = 4.6, ^2J(CNP) = 4.6 Hz, NCH$_2$], 65.49 [dsept, ^1J(CH) = 141.6, ^2J(CCH) = 4.6 Hz, OCH]. − ^{15}N{^{1}H} NMR (DEPT): δ = −337.09 [d, ^1J(NP) = 12.1 Hz]. − ^{17}O{^{1}H} NMR: δ = 72 (s). − ^{29}Si NMR (DEPT): δ = −35.30 [ddt, ^2J(SiCP) = 35.7, ^2J(SiCH) = 8.5, ^3J(SiOCH) = 3.6 Hz]. − ^{31}P{^{1}H} NMR: δ = 64.73 (s). − MS (CI), *m/z*: 442 [M$^+$ + 1] (100%), 441 [M$^+$], 413 [M$^+$ + 1 − Et], 406 [M$^+$ − Cl], 370 [M$^+$ + 1 − NEt$_2$], 340, 207, 175 [(Et$_2$N)$_2$P].

[(Di-tert-butoxychlorosilyl)methylene]tris(diethylamino)phosphorane (**8**): Yield 77%, b.p. kugelrohr distillation at 215°C air bath temp./0.01 mbar. − ^{1}H NMR: δ = −0.08 [d, ^2J(HCP) = 11.9 Hz, 1H, PCH], 0.98 [t, ^3J(HCCH) = 7.0 Hz, 18H, CH$_2$C*H*$_3$], 1.52 (s, 18H, CCH$_3$), 3.00 [dq, ^3J(HCNP) = 10.1, ^3J(HCCH) = 7.0 Hz, 12H, NCH$_2$]. − ^{13}C{^{1}H} NMR: δ = 8.62 [d, ^1J(CP) = 167.9 Hz, PC], 14.35 [d, ^3J(CCNP) = 3.2 Hz, CH$_2$*C*H$_3$], 31.88 (s, C*C*H$_3$), 40.31 [d, ^2J(CNP) = 5.1 Hz, NCH$_2$], 73.55 (s, *C*CH$_3$). − ^{15}N{^{1}H} NMR (DEPT): δ = −337.24 [d, ^1J(NP) = 11.5 Hz]. − ^{17}O{^{1}H} NMR: δ = 88 (s). − ^{29}Si NMR (DEPT): δ = −47.71 [dd, ^2J(SiCP) = 32.9, ^2J(SiCH) = 8.0 Hz]. − ^{31}P{^{1}H} NMR: δ = 63.79 (s). − MS (CI), *m/z*: 470 [M$^+$ + 1], 469 [M$^+$], 434 [M$^+$ − Cl], 398 [M$^+$ + 1 − NEt$_2$], 262 (100%), 175 [(Et$_2$N)$_2$P].

Diisopropoxybis[tris(dimethylamino)phosphoranylidenemethyl]silane (**9**). − *Route (2a):* 2.0 g (6 mmol) of **3** was dissolved in 60 ml of *n*-hexane. After cooling of this solution to 0°C, 2.6 ml (13.4 mmol) of a solution of tris(dimethylamino)methylenephosphorane in hexane (20 ml) was added dropwise. The mixture was warmed up to room temp. and refluxed for 3 h. The colorless precipitate was filtered off, and the solvent was removed from the filtrate in vacuo. Kugelrohr distillation of the crude product at 210°C air bath temp./0.01 mbar yielded 2.0 g (68%) of **9**. − *Route (2b):* 10 ml (51 mmol) of tris(dimethylamino)methylenephosphorane was added to 150 ml of *n*-hexane. At 0°C 2.5 ml (12.5 mmol) of dichlorodiisopropoxysilane was added from a dropping funnel. To complete the reaction the mixture was refluxed for 6 h. The phosphonium salt was filtered off and the solvent removed from the filtrate in vacuo. Purification of **9** by kugelrohr distillation (210°C air bath temp./0.01 mbar) gave 4.0 g (64%) of a colorless solid, m.p. 27°C. – ^{1}H NMR: $\delta = -0.42$ [dd, ^{2}J(HP) = 9.2, ^{4}J(HCSiCP) = 1.5 Hz, 2H, HCP], 1.43 [d, ^{3}J(HCCH) = 6.1 Hz, 12H, H_3CC], 2.60 [d, ^{3}J(HCNP) = 9.2 Hz, 36H, H_3CN], 4.63 [sept, ^{3}J(HCCH) = 6.1 Hz, 2H, $HCCH_3$]. – ^{13}C NMR: $\delta = 0.09$ [ddd, ^{1}J(CP) = 154.2, ^{1}J(CH) = 128.9, ^{3}J(CSiCP) = 6.1 Hz, CP], 26.74 [qq, ^{1}J(CH) = 124.1, ^{3}J(CCCH) = 4.6 Hz, H_3CC], 38.18 [qquint, ^{1}J(CH) = 135.1, ^{2}J(CNP) = 3.9, ^{3}J(CNCH) = 3.9 Hz, H_3CN], 62.97 [dquint, ^{1}J(CH) = 138.3, ^{2}J(CCH) = 4.4 Hz, CCH_3]. – ^{15}N{^{1}H} NMR (DEPT): $\delta = -362.77$ [d, ^{1}J(NP) = 8.5 Hz]. – ^{17}O{^{1}H} NMR: $\delta = 71$ (s). – ^{29}Si NMR (DEPT): $\delta = -19.12$ [ttt, ^{2}J(SiCP) = 25.0, ^{2}J(SiCH) = 3.2, ^{3}J(SiOCH) = 3.2 Hz]. – ^{31}P{^{1}H} NMR: $\delta = 67.80$ (s). – MS (CI), *m/z*: 499 [M$^+$ + 1], 498 [M$^+$], 454 [M$^+$ – NMe_2], 439 [M$^+$ – O*i*Pr], 411 (100%) [M$^+$ + 1 – 2 NMe_2], 368 [411 – *i*Pr]. – $C_{20}H_{52}N_6O_2P_2Si$ (498.7): calcd. C 48.17, H 10.51, N 16.85; found C 47.83, H 10.26, N 16.92.

Di-tert-butoxybis[tris(dimethylamino)phosphoranylidenemethyl]silane (**10**) was synthesized according to route (2b) with a 20% excess of tris(dimethylamino)methylenephosphorane [6 ml (31 mmol) of ylide, 1.1 ml (6.5 mmol) of silane]; reflux time: 12 h. Purification by kugelrohr distillation at 215°C air bath temp./0.01 mbar yielded 2.0 g (58%) of colorless, crystalline **10**, m.p. 29°C. – ^{1}H NMR: $\delta = -0.43$ [dd, ^{2}J(HCP) = 9.2, ^{4}J(HCSiCP) = 1.8 Hz, 2H, $Si(CH)_2$], 1.65 [s, 18H, $C(CH_3)_3$], 2.62 [d, ^{3}J(HCNP) = 9.8 Hz, 36H, $N(CH_3)_2$]. – ^{13}C NMR: $\delta = 5.42$ [dddd, ^{1}J(CP) = 152.1, ^{1}J(CH) = 127.8, ^{3}J(CSiCP) = 6.4, ^{3}J(CSiCH) = 1.6 Hz, PC], 32.7 [qsept, ^{1}J(CH) = 124.6, ^{3}J(CCCH) = 4.1 Hz, $C(\mathit{C}H_3)_3$], 38.37 [qquint, ^{1}J(CH) = 133.1, ^{2}J(CNP) = 4.1, ^{3}J(CNCH) = 4.1 Hz, $N(\mathit{C}H_3)_2$], 70.61 [dez, ^{2}J(CCH) = 4.1 Hz, $\mathit{C}(CH_3)_3$]. – ^{15}N{^{1}H} NMR (DEPT): $\delta = -362.63$ [d, ^{1}J(NP) = 7.3 Hz]. – ^{17}O{^{1}H} NMR: $\delta = 89$ (s). – ^{29}Si NMR (DEPT): $\delta = -29.87$ [tt, ^{2}J(SiCP) = 24.7, ^{2}J(SiCH) = 6.6 Hz]. – ^{31}P{^{1}H} NMR: 66.77 (s). – MS (CI), *m/z*: 527 [M$^+$ + 1], 526 (100%) [M$^+$], 483 [M$^+$ + 1 – NMe_2], 439 [M$^+$ + 1 – 2 NMe_2]. – $C_{22}H_{56}N_6O_2P_2Si$ (526.8): calcd. C 50.16, H 10.72, N 15.95; found C 49.66, H 10.59, N 15.72.

Crystal and Structure Solution Data for $C_{20}H_{52}N_6O_2P_2Si$ (**9**): $M_r = 498.71$ orthorhombic, $a = 10.706(1)$, $b = 11.581(1)$, $c = 23.821(2)$ Å, space group $P2_12_12_1$ (No. 19, Int. Tables), $V = 2953.4$ Å^3, $Z = 4$, $D_c = 1.122$ g cm^{-3}, $T = -62$°C, $\mu(\text{Mo-}K_\alpha) = 2.1$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, CAD4 diffractometer, 6232 reflections measured, 6009 unique and 5629 observed [$F_o \geqslant 4\sigma(F_o)$]. Structure solution by direct methods with the ylidic hydrogen atoms ($U_{iso} = 0.08$) and all missing non-hydrogen atoms located by successive difference Fourier syntheses; refinement of 287 parameters converged at $R = 0.031$ ($R_w = 0.035$) ($R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/[\Sigma w F_o^2]^{1/2}$ with $w = [\sigma^2(F_o) + 0.001611\ F_o^2]^{-1}$) including the aliphatic hydrogen atoms in idealized, fixed positions ($U_{iso} = 0.08$); maximum and minimum residual electron densities in the difference Fourier map were 0.451 and –0.355 e Å^{-3}, respectively. Supplementary material may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58257, the names of the authors, and the journal citation.

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