New Diazasilaphosphetidines and their Precursors

Bettina Eichhorn and Heinrich Nöth

Department of Chemistry, Inorganic Chemistry, University of Munich, Butenandtstr. 5 - 13 (D), D-81 377 München, Germany

Reprint requests to Prof. Dr. Heinrich Nöth. E-mail: H.Noeth@lrz.uni-muenchen.de

Dedicated to Prof. Dr. R. Schmutzler on the occasion of his 65th birthday

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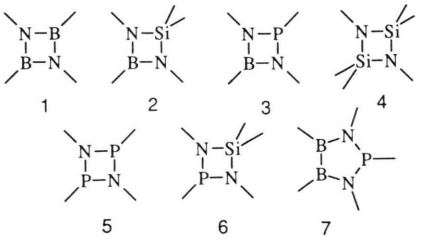
Bis(monoorganylamino)diorganylsilanes, 1,3,2,4-Diazasilaphosphetinides

A series of aminosilanes $(R'HN)_2SiR_2$ have been prepared. In case of bulky substituents R' the aminolysis of Ph_2SiCl_2 stops at the $(R'HN)ClSiPh_2$ stage. Replacement of the Cl atom is achieved with LiNHR' which allows the synthesis of mixed bisaminosilanes $(R'HN)(R''HN)SiPh_2$. The X-ray structures of three of these compounds have been determined. There are no intermolecular N-H···N hydrogen bonds in these compounds in the solid state. Several 1,3,2,4-diazaphosphetidines have been synthesized using bis(N-lithioamino)silanes and bis(N-lithioamino)phosphanes . Amongst these the heterocycle **18** possesses an almost planar four membered N_2SiP ring system.

Introduction

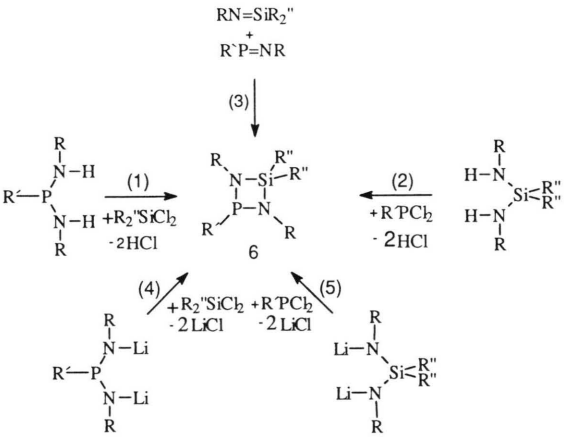
Heterocyclic systems are still an attractive field of research particularly in relation to the question of electron delocalisation. From the six formally related four membered ring systems **1** to **6** only **1** can be considered to be a 4π electron system, **1** being isoelectronic and isostructural with cyclobutadiene while **2** is reminiscent of a 4π allylic system. The diazaphosphaboretidine **3** can be formally viewed as a 6π electron system provided that the P atom is in a planar environment. As far as we know [1, 2] this is not the case. Therefore it is electronically akin to **2**. The heterocycles **4** to **6** are best considered as having localized lone pairs of electrons at the nitrogen and phosphorus centers. The five membered ring **7** can be looked at as being a 4π electron system. However, the first member of this class of heterocycles clearly shows no electron delocalization for the NBBN unit because there is a considerable twist of its BN units against one another [3].



Bis(monoorganylamino)diorganylsilanes

Synthesis and NMR characterization

Several routes to diazasilaphosphetidines can be envisaged. They are summarized in Scheme 1. Route (1) requires bis(monoorganylamino)diorganylsilanes while route (2) needs bis(monoorganylamino)phosphanes. For a condensation to **6** hydrogen chloride must be removed. This is usually achieved by triethylamine as an auxiliary base. Route (3) is a typical cycloaddition reaction between low coordinated silicon and phosphorus



Scheme 1. Routes to 1,3,2,4-diazasilaphosphetidines.

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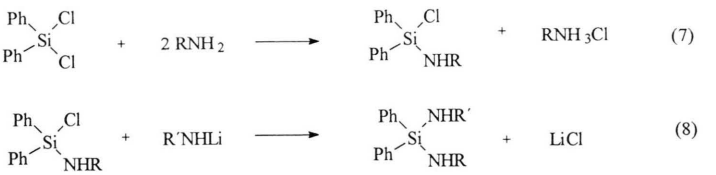


species. Routes (4) and (5) may be more effective than routes (1) and (2) because of the higher nucleophilicity of the lithium compounds and the thermodynamic driving force of LiCl formation.

Both routes, (1) and (5) require bis(monoorganylamino)diorganylsilanes. Compounds **8** to **10** were prepared according to [1] by aminolysis of the respective diorganyldichlorosilane with an excess of a primary amine. In order to prevent condensation reactions to cyclosilazanes sufficiently bulky groups R and R' are required to kinetically stabilize these compounds.

	Me_2Si-$(NHiPr)_2$ (**8**)	Me_2Si-$(NH^tBu)_2$ (**9**)	Me_2Si-$(NHPh)_2$ (**10**)
δ^{29}Si (ppm)	8.9	–16.2	–10.8
δ^1H(N) (ppm)	0.4	0.6	3.23
	Ph_2Si-$(NHPh)_2$ (**11**)	Ph_2Si-$(NHiPr)_2$ (**12**)	Ph_2Si-(Cl)NHiPr (**13**)
δ^{29}Si (ppm)	–30.2	–27.9	–13.5
δ^1H(N) (ppm)	4.1	0.97, 0.98	1.75
	Ph_2Si-$(NH^tBu)_2$ (**14**)	$Ph_2Si(NHiPr)$-NH^tBu (**15**)	
δ^{29}Si (ppm)	–35.4	–31.7	
δ^1H(N) (ppm)	1.4	1.3 (br)	

Compounds **9** to **11** are already known [4, 5] and are readily accessible. In contrast the aminolysis of diphenyldichlorosilane with isopropylamine or *tert*-butylamine proceeds readily only as shown in eq. (7) allowing the synthesis of monoorganylamino(chloro)diphenylsilanes, *e. g.* **13**. Replacement of the Cl atom by an amino group is readily achieved by using lithium amides. Consequently the reaction of Ph_2SiCl_2 with LiHNR leads directly to $Ph_2Si(NHR)_2$. On the other hand, aminolysis of Ph_2SiCl_2 with an amine followed by reaction with a lithium amide of a different amine allows the preparation of "mixed" bis(amino)diphenylsilanes as exemplified for compound **15**. Compound **11** was first described by Anderson [4].

The ^{1}H and ^{13}C NMR spectra of compounds **8** to **15** are unexceptional. And this is true also for ^{29}Si NMR data, the ^{29}Si nucleus being most deshielded in compound **13** obviously due to the inductive effect of the Cl atom. A much larger variation results for the ^{1}H resonance of the NH group. Once again, amongst the series of the alkylamino compounds **12** to **15** this proton is least shielded for the chloride **13**. In compound **15** the two different NH proton signals could not be separated. Also, the ^{1}H NMR signal of the NH protons is rather broad for **14** while two signals could be observed for **12**. We were unable to decide whether this indicates the presence of two different NH groups (which is actually unlikely in terms of the ^{13}C resonances) or is due to $^3J(^1H,^1H)$ with the isopropyl's CH group.

However, it should be noted that there is a ^{29}Si shift difference of 25.1 ppm between compounds **8** and **9**, in contrast to only 3.7 ppm between **14** and **15**.

Molecular structures

The diaminodiphenylsilanes **12**, **14** and **15** crystallize well. Single crystals of these compounds were subjected to X-ray structure analysis in order to study the influence of increasing size of the amino groups on the molecular structures. These

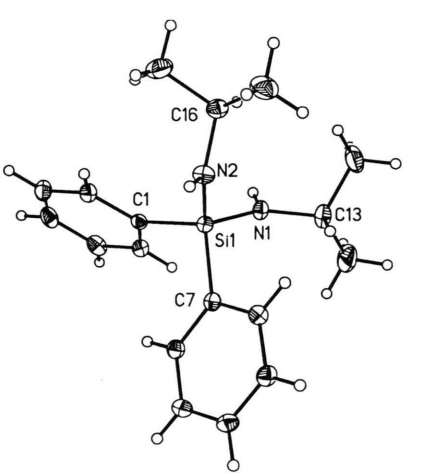


Fig 1. Molecular structure of $Ph_2Si(NHiPr)_2$ in ORTEP description. Thermal ellipsoids are depicted on a 25% probability scale.

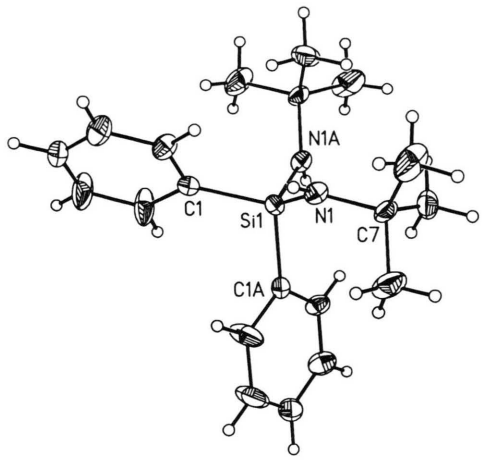


Fig 2. Molecular structure of $Ph_2Si(NH^tBu)_2$ in ORTEP description. Thermal ellipsoids are depicted on a 25% probability scale.

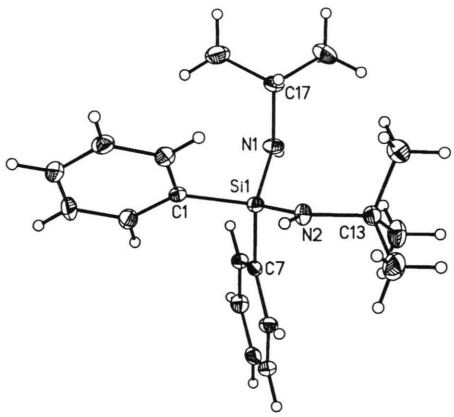


Fig 3. Molecular structure of $Ph_2Si(NH^tBu)(NHiPr)$ in ORTEP description. Thermal ellipsoids are depicted on a 25% probability scale.

structures are depicted in Figures 1 - 3. The most important structural parameters are summarized in Table 1.

The Si-N bond lengths of the three compounds can be considered as equal, the mean distance being 1.705 Å. As expected, the N-Si-N bond angle is largest for compound **15** and smallest for compound **13**. The small difference (2.5°) is nevertheless significant, and is reflected also in the C-Si-C bond angle which is largest for compound **13** and smallest for compound **14**. No influence of the amino groups on the Si-C bond lengths is noted. However, the interplanar angles between the two phenyl groups vary significantly. They are 68.7 and 73.2°, respectively,

Tab 1. Selected bonding distances (in Å) and angles (in °) of the bis(monoorganylamino)diphenylsilanes.

	8	**9**	**10**
S1-N1	1.700(2)	1.710(5)	1.704(4)
S1-N2/N1A	1.709(3)	1.709(5)	1.710(4)
Si1-C1	1.879(2)	1.875(5)	1.877(5)
S1-C7/C1A	1.881(2)	1.875(5)	1.878(5)
N1-Si1-N2/N1A	111.6(9)	114.2(4)	113.1(2)
C1-Si1-C7/C1A	110.02(8)	109.2(3)	109.5(2)*

* C9-Si1-C15.

for the two independent molecules of compound **14**, 71.4° for the bis(isopropylamino) compound **13** and 68.7° for compound **15**. This does not reflect a uniform trend, although the twist of the phenyl groups is less for the diphenylsilanes containing isopropylamino groups.

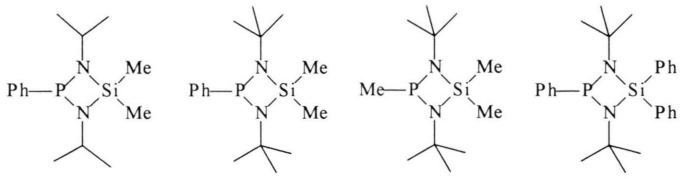
The sum of bond angles at the nitrogen atoms is close to 360° for all compounds, and there are no intermolecular N-H···N interactions in the solid state.

1,3,2,4-Diazasilaphosphetidines

Synthesis and Characterization

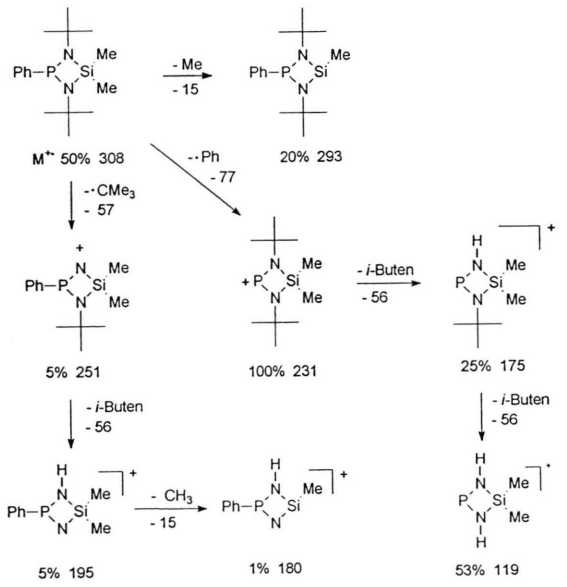
Four membered diazasilaphosphetidines are known for a number of derivatives obtained by reactions (3) to (5) (see Scheme 1). A new route is described by eq. (4). The reaction of bis(monoorganylamino)organylphosphanes, after metallation with LiBu, with diorganyldichlorosilanes yielded compounds **16** to **18**. Yields were, however, unsatisfactory. Therefore, the "reverse" reaction route has been used [1], metallation of di(monoorganylamino)diorganylsilanes followed by reaction with organyldichlorophosphanes. Application of this method provided good yields of **18** and **19**.

The NMR spectra of the products show a considerable deshielding of the ^{31}P nuclei compared with the $R'P(NHR)_2$ starting materials. The shift differences $\Delta^{31}P$ range from 78.6 to 83.7 ppm. This is most likely due to changes in the N-P-N bond angle on going from the bis(aminoorganyl)phosphane to the diazasilaphosphetidine (v. i.). For compounds **16** and **17** there are two signals in the ^1H and ^{13}C-NMR spectra for the MeSi groups which indicate that the P atom is not in a planar environment. Both of them show $^3J(^{31}P^1H)$ coupling which is 5.1 Hz for **16** and 5.5 Hz for **17**.



16 **17** **18** **19**

	16	**17**	**18**	**19**
δ^{29}Si	16.6	13.9	13.5	13.9
δ^{31}P	137.5	125.7	137.3	130.2
δ^{15}N	-325.8	-317	-319.5	-



Scheme 2. Fragmentation pattern for the diazasilaphosphetidine **17**.

Ring formation leads to a better shielding of the ^{15}N nuclei amounting to shift differences of Δ^{15}N = 21 ppm for **16** and 24.9 ppm for **19** compared with $PhP(NHR)_2$ (R = *i*Pr, *t*Bu) [3]. This may be due to the introduction of the more electropositive Si atom as well as to the smaller P-N-Si bond angle in comparison with the noncyclic counterparts giving the bonds of the N atoms more s-character. This suggestion is supported by a decrease of the coupling constant $^1J(^{31}P^{15}N)$ which is 33.1 Hz for **16** and 33.4 Hz for **17**. The same trends are also observed for the P,Si-phenyl derivatives **18** and **19**. In these cases, the assignment of all ^{13}C NMR signals of the phenyl groups is not unequivocal in the absence of special decoupling experiments.

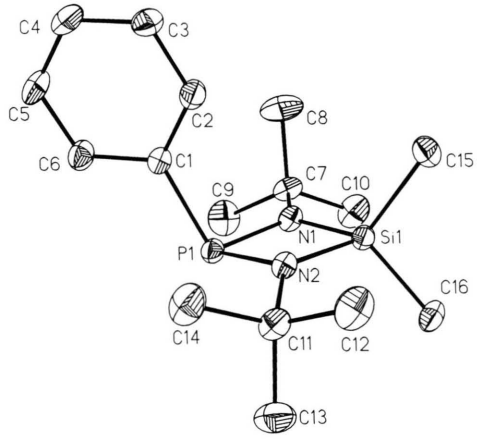
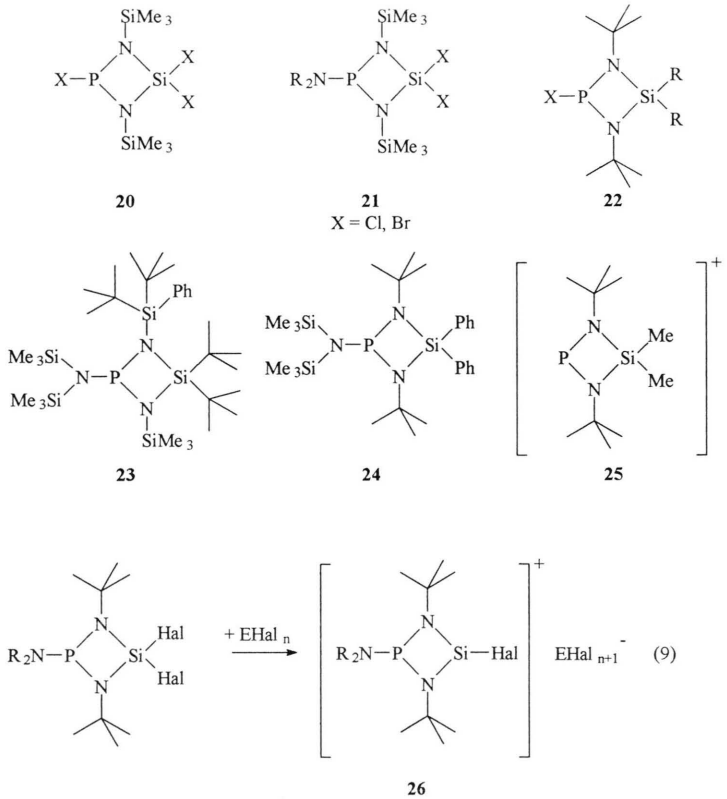


Fig 4. a) Molecular structure of the diazasilaphosphetidine **18**. Thermal ellipsoids represent a 25% probability. H atoms have been omitted for clarity. b) A view along the P-Si axis to demonstrate ring folding and orientation of the quartenary C atoms bonded to N atoms. Selected bond lengths (in Å): P1-N1 1.736(2), P1-N2 1.736(2), P1-C1 1.862(2), N1-C7 1.480(3), N2-C11 1.488(3), N1-Si1 1.735(2), N2-Si1 1.739(2), Si1-C15 1.867(3), Si1-C16 1.870(3). – Selected bond angles (in °, all esd's are 0.1°): N1-P1-N2 84.0, N1-P1-C1 104.4, N2-P1-C1 103.6, N1-Si1-N2 83.9, N1-Si1-C15 116.6, N1-Si1-C16 116.3, N2-Si1-C15 116.7, N2-Si1-C16 116.1, P1-N1-Si1 95.9, P1-N2-Si1 95.9.

Mass spectrometric characterization of the diazasilaphosphetidines was performed only for compound **17**. Scheme 2 shows the most important fragmentations. The molecular ion is fairly abundant (appr. 5%). However, the most abundant ion is that of the phosphenium cation. Thus, breaking the P-C bond is preferred over breaking the Si-C bonds. Obviously a nitrenium based fragment is much less favored than the phosphenium type ion. This cannot be rationalized only by the weaker P-C bond compared to the N-C bond but particularly by better stabilization of the $N\text{-}P^+\text{-}N$ unit.



20 **21** **22**

X = Cl, Br

23 **24** **25**

26

Molecular Structure

The NMR spectra indicated that the P atoms of diazasilaphosphetidines do not reside in a planar environment. This has been ascertained by an X-ray structure determination on compound **17** as depicted in Fig. 4.

The four-membered ring is almost planar, as the folding angle between the planes SiN_2 and PN_2 amounts to only 5°. One of the N atoms exhibits a planar environment (sum of bond angles 360°), the other, N2, is slightly pyramidal (sum of bond angles 354°). It is worth noting that the P-N and Si-N bond lengths are similar.

Discussion

Bis(monoorganylamino)silanes were first reported by Anderson [4] including a number of bis(anilino)diorganylsilanes. However, bis(methylamino)diorganylsilanes are also accessible [8]. These were of interest as intermediates for the formation of 1,3,2,4-diazadisiletidines [9]. Amongst these compounds $(^tBuHN)_2SiMe_2$ [10] was best studied e. g. as a reagent for the preparation of $[Me_2Si(N^tBu)_2Sn]$ or for spirocyclic titanium amides [5]. The thermal stability of $(RHN)_2SiR'_2$ compounds clearly increases with the steric demand of the organyl substituents.

The amination of diorganyldichlorosilanes proceeds stepwise, and many "asymmetrically" substituted diaminodiorganylsilanes may be prepared by the route described by eq. (6). It would be interesting to see whether $Ph_2Si(NH^tBu)NH_2$ or even $Me_2Si(NH^tBu)NH_2$ are accessible. Both of them would be versatile reagents. Two compounds akin to these have been described by P. P. Power *et al.* [11], $Mes_2Si(NH_2)_2$ and $Triph_2Si(NH_2)_2$ (Mes = mesityl, Triph = 2,4,6-triphenylphenyl), which demonstrate that condensation by loss of NH_3 can be kinetically prevented by introducing sufficiently bulky organyl groups, and indicate that the condensation process proceeds intermolecularly.

According to the literature the standard Si-N single bond length is 1.80 Å and the standard Si=N double bond 1.56 Å [12]. Thus the Si-N bond lengths found for compounds **8** to **10** correspond to single

bonds and are very similar to data of many other aminosilanes [13]. The longest Si-N bond, so far, has been observed for $Mes_2Si(NH_2)_2$ (1.78(7) Å). This bond length is closest to the calculated single bond length. The shortening of the Si-N bonds is currently explained by the bond polarity [13] while π-bonding is no longer considered to be essential. Moreover, it should be noted that the presence of planar tricoordinated N atoms will also lead to a shortening of the Si-N single bond length.

The first 1,3,2,4-diazasilaphosphetidines have been obtained by Fink [9] by reacting octamethyltrisilazane with LiBu followed by $RPCl_2$. Obviously, the reaction intermediate is $Me_2Si(NLiMe)_2$, which, however, was not characterized at this time. A route, which provided Si- and P-functional diazasilaphosphetidines was designed by Niecke *et al.* [14]. Addition of $SiCl_4$ or $SiBr_4$ to the iminophosphane $(Me_3Si)_2N{=}PR$ followed by Me_3SiHal elimination led to the four membered rings **20** and **21**.

Aminolysis reactions performed by Klingebiel *et al.* [15] demonstrated that the P-X bond of diazasilaphosphetidines is more reactive than the Si-X bond. The resulting P-aminosubstituted diazasilaphosphetidines arouse interest because they formed rotational isomers, and this aspect has been studied in depth by O. J. Scherer *et al.* [1]. Asymmetrically substituted diazasilaphosphetidines can also be made by a [2+2} cycloaddition between iminosilanes $RN{=}SiR'_2$ and iminophophanes RN=PR' [7]. This makes asymmetrically substituted species available. N-Metallated bis(amino)phosphanes and bis(amino)silanes now provide alternative routes to the four membered N_2SiP ring system, and it is quite apparent that these two routes can be considerably extended in order to prepare new kinds of P- or Si-functional diazasilaphosphetidines.

Compound **17** is so far the only diazasilaphosphetidine with an *almost* planar ring configuration showing a folding angle of only 5.4°. Much stronger folding is observed for the diazasilaphosphetidines **23** and **24** namely 24 and 22°, respectively [1, 2]. Moreover, both compounds show no truly planar coordination at their nitrogen atoms. Thus, the sum of bond angles around the nitrogen atoms of **22** is 357 and 355°, and for **23** the values are 350 and 352° [1, 2]. Formation of the cation $Me_2Si(N^tBu)_2P^+$ [16] leads to a totally planar system.

In this context it would be of interest to study the halide abstraction of compound **24** which might lead to a silenium cation **26**, representing a 6π electron system provided that the lone pair at the P atom becomes available for electron delocalization.

Experimental

All manipulation were carried out under anhydrous conditions using the Schlenk technique and dinitrogen as a protecting atmosphere. All reagents were used as supplied. Mass spectra: Atlas CH7 at 70eV ionisation energy; NMR: Bruker WP200, Jeol GSX 270 and FX 400 (^1H, ^{13}C, ^{29}Si, ^{31}P); internal lock: C_6D_6.

Di(isopropylamino)dimethylsilane (**8**): A stirred solution of isopropylamine (54.8 g, 0.93 mol) in diethyl ether (250 ml) was cooled in an ice bath, and dichlorodimethylsilane (26.6 g, 210 mmol) was slowly added. A white precipitate formed. After addition stirring of the suspension was continued for 1 h. Then the insoluble material was removed by filtration. From the filtrate all volatiles were removed at 10 Torr, and the remaining liquid subjected to distillation. Yield: 14 g of **8** (40%), b. p. 35°C/5 Torr.

NMR ($CDCl_3$): δ^1H: –0.02 (s, 6 H, Si*Me*), 0.4 (s, broad, 2 H, NH), 1.03 (d, $^3J(HH) = 6.1$ Hz, 12 H CH*Me*), 2.9 - 3.1 (m, 2 H C*H*Me). – $\delta^{13}C$: –0.4 (s, Si*Me*), 27.9 (s, CH*Me*), 42.3 (s, *C*HMe); – $\delta^{29}Si$: 8.9 s. $C_8H_{22}N_2Si$ (174.36): Calcd C 55.1, H 12.72, N 16.07. Found C 54.76, H 12.73, N 15.85%.

Di(tert-butylamino)dimethylsilane (**9**): Prepared as described for **8** from $^tBuNH_2$ (30.0 g, 410 mmol) and Me_2SiCl_2 (11.6 g, 90 mmol). Yield: 9.3 g of **9** (51%), b. p. 65°C/7 Torr, colorless, moisture sensitive liquid.

NMR ($CDCl_3$): δ^1H: 0.005 (s, 6 H, SiMe), 0.6 (s, broad, 2 H, NH), 1.15 (s, 18 H, CMe); – $\delta^{13}C$: 3.5 (s, Si*Me*), 33.8 (s, C*Me*), 49.1 (s, *C*Me); – $\delta^{29}Si$: –16.2 s. $C_{10}H_{26}N_2Si$ (202.42): Calcd C 59.34, H 12.95, N 13.84. Found C 57.11, H 13.02, N 13.11%.

Bis(anilino)dimethylsilane (**10**): Prepared in analogy to **8** from aniline (34.4 g, 370 mmol) and Me_2SiCl_2 (11.9 g, 90 mmol) in diethyl ether (200 ml). The filtrate was reduced in volume to about 80 ml and the solution layered with pentane. After several hours compound **10** had separated and was isolated. Yield: 18.1 g (81%), m. p. 113 - 116 °C.

NMR ($CDCl_3$): δ^1H: 0.13 (s, 6 H SiMe), 3.23 (broad, 2 H, NH), 6.7 - 7.1 (m, 10 H, Ph); – $\delta^{13}C$: –1.4 (s, Si*Me*), 115.0, 117.1, 118.8, 129.5, 146.5 (s, ipso C); – $\delta^{29}Si$: –10.8. $C_{14}H_{18}N_2Si$ (242.40): Calcd C 69.37, H 7.48, N 11.56. Found C 68.34, H 7.36, N 11.31%.

Di(isopropylamino)diphenylsilane (**12**): Isopropylamine (76.5 g, 0.9 mol) was dissolved in diethyl ether (250 ml) and the solution cooled in an ice bath. To the stirred solution was slowly added Ph_2SiCl_2 (50.6 g,

0.2 mol). The precipitate was filtered off after 5 h of stirring. Then ether was removed *in vacuo* from the filtrate and the residue distilled. B. p. 110 °C/0.05 Torr, Yield: 40 g of **12** (68%). The liquid solidifies on standing, m. p. 123 - 125 °C.

NMR (C_6D_6): δ^1H: 0.97 (s, broad, 1 H, NH), 0.98 (broad, 1 H, NH), 1.03 (d, ^3J(H,H) = 6.4 Hz, 12 H, CH*Me*), 3.3 (m, 2 H, C*H*Me), 7.2 - 7.7 (m, 10 H, Ph); – δ^{13}C: 27.9 (s, CH*Me*), 42.6 (s, *C*HMe), 127.5 (s, *p*-Ph), 129.1 (s, *m*-Ph), 134.7 (s, *o*-Ph), 138.0 (*ipso*-Ph); – δ^{29}Si: –27.9. $C_{18}H_{26}N_2Si$ (298.51): Calcd C 72.43, H 8.78, N 9.38. Found C 72.33, H 8.23, N, 9.35%.

Chloro-tert-butylamino(diphenyl)silane (**13**)*: tert*-Butylamine (13.9 g, 0.19 mmol) was dissolved in a 1:1 mixture of pentane and diethyl ether (200 ml). After cooling the stirred solution to –20 °C Ph_2SiCl_2 (12.1 g, 0.08 mol) was added drop wise. The suspension was then warmed to ambient temperature and kept under reflux for 1 h. Solid material was filtered off and washed with pentane. From the united filtrates all volatiles were removed *in vacuo* and the residue distilled. The fraction at b. p. 112 °C/0.03 Torr – yield 10.9 g of **13** (50%) – was a colorless oily liquid.

NMR (C_6D_6: δ^1H: 1.25 (s, 9 H, C*Me*), 1.75 (broad, 1 H, NH) 7.3 - 7.8 (m, 10 H, Ph); – δ^{13}C: 33.2, (s, CH*Me*), 50.8 (*C*Me), 127.7 (s, *p*-Ph), 130.3 (s, *m*-Ph), 134.5 (s, *o*-Ph), 135.3 (*ipso*-Ph); – δ^{29}Si: –13.5. $C_{16}H_{20}NClSi$ (289.88): Calcd C 66.30, H 6.95, N 4.83. Found C 66.32, H 7.49, N 4.97%.

Bis(tert-butylamino)diphenylsilane (**14**)*: tert*-Butylamine (4.24 ml) was dissolved in a mixture of pentane and THF (70, 20 ml). Then 25.8 ml of *n*-LiBu (0.04 mol) was slowly added with stirring. To the yellow solution was added **13** (10.9 g, 0.04 mol). After heating to reflux for 1 h, 10 ml of water was added and the two phased liquid transferred into a separation funnel. The ether phase was separated and dried with sodium sulfate. Then ether was removed and the residue distilled. B. p. 116 °C/0.03 Torr. Crystals formed in a few days, m. p. 140 - 144 °C. Yield: 8.3 g (25%).

NMR ($CDCl_3$): δ^1H: 1.2 (s, 18 H, C*Me*), 1.4 (broad, 2 H, NH), 7.3 - 7.6 (m, 10 H, Ph); – δ^{13}C: 33.6 (s, C*Me*), 49.9 (s, *C*Me), 127.4 (s, *p*-Ph), 128.7 (s. *m*-Ph), 134.9 (s, *o*-Ph) 140.1 (*ipso*-Ph); – δ^{29}Si: -35.4. $C_{20}H_{30}N_2Si$ (326.56): Calcd C 73.56, H 9.26, N 8.58. Found C 73.14, H 9.01, N 8.21 %.

tert-Butylamino-isopropylamino(diphenyl)silane (**15**)*:* Isopropylamine (1.17 ml, 14 mmol) dissolved in 20 ml of pentane and 5 ml of THF was metallated with 8.9 ml of a pentane solution of LiBu (0.014 mol). To the reaction mixture was added with stirring **13** (3.73 g, 0.013 mol) and the mixture was kept at reflux for 1 h. LiCl was filtered off, the volatile materials removed *in vacuo* and the residue subjected to distillation. **15** distilled at 130 °C/1 Torr. Yield: 1.28 g (32%). The oil crystallized rapidly, m. p. 133 - 135 °C.

NMR ($CDCl_3$): δ^1H: 1.1 (d, ^3J(H,H) = 6.4 Hz, 6 H, CH*Me*), 1.2 (s, 9 H, C*Me*), 1.3 (s, broad, 2 H, NH), 3.3 (m, ^3J(H,H) = 6.2 Hz, CH*Me*), 7.3 - 7.6 (m, 10 H, Ph); – δ^{13}C: 27.7 (s, CH*Me*), 33.6 (s, C*Me*), 42.5 (s, *C*HMe), 49.6 (*C*Me), 127.5, 128.9, 134.8, 139.0 (*ipso*-Ph); – δ^{29}Si: –31.7. $C_{19}H_{28}N_2Si$ (312.53): Calcd C 73.02, H 9.03, N 8.96. Found C 72.96, H 8.33, N 8.94%.

Bis(anilino)diphenylsilane (**11**)*:* To a solution of diphenyldichlorosilane (10.0 g (0.04 mol) in toluene (20 ml), cooled in an ice bath, was added with stirring aniline (25 g (0.27 mol). The suspension was then heated to reflux for 1 h and stirring was continued for 12 h at ambient temperature. The precipitate was filtered off and extracted with 60 ml of almost boiling toluene. The volume of the toluene solution was reduced *in vacuo* to about 30 ml and then 30 ml of pentane were placed on top of the solution. Cooling to –30 °C yielded 3.2 g of **11** (26%). The compound was washed with pentane and dried *in vacuo*.

NMR ($CDCl_3$): δ^1H: 4.1 (s, broad, 2 H, NH), 7.3 - 8.0 (m, 20 H, Ph); – δ^{13}C: 117.2, 118.9, 128.2, 129.2, 130.4, 133.8, 134.7, 145.7. $C_{24}H_{22}N_2Si$ (366.52): Calcd C 78.64, H 6.05, N 7.64%. Found C 77.92, H 6.09, N 7.33%.

1,3-Di(isopropyl)-2,2-dimethyl-4-phenyl-1,3,2,4-diazasilaphosphetidine (**16**): $PhP(NHiPr)_2$ [3] (0.69 g, 3.07 mmol) dissolved in toluene (10 ml) was metallated with BuLi at –30 °C (4.02 ml, 6.4 mmol). The solution was kept under reflux for 1 h and transferred into a dropping funnel. From there the solution was dropped into a stirred solution of Me_2SiCl_2 (0.41 g, 3.2 mmol) in toluene (10 ml). After warming to ambient temperature and stirring over night the solid was removed by filtration, toluene evaporated *in vacuo* and the residue distilled, b. p. 80 °C/0.13 Torr. Yield: 0.37 g of **16** (43 %). Yellow oil. NMR (C_6D_6): δ^1H: 0.37 (s, 3 H Si*Me*), 0.44 (s, 3 H, Si*Me*), 09.1 (d, ^3J(H,H) 6.4 Hz, 6 H, CH*Me*), 1.04 (d, ^3J(H,H) 6.3 Hz, 6 H, CH*Me*), 3.09 (sept. ^3J(H,H) 6.4 Hz, 2 H, C*H*Me), 7.15 - 8.0 (m, 5 H, Ph); – δ^{13}C: 4.9 (s, Si*Me*), δ^{15}N: –325.8 (d, ^1J(P,N) = 34.8 Hz); – ^{29}Si: 16.6 (d, ^2J(P,Si) = 2.6 Hz); – ^{31}P: 137.5 s. $C_{14}H_{25}N_2PSi$ (280.43): Calcd C 59.96, H 8.99, N 9.99. Found C 58.91, H 9.23, N 10.02%.

1,3-Di(tert-butyl)-2,2-dimethyl-4-phenyl-1,3,2,4-diazasilaphosphetidine (**17**)*:* $PhP(NH^tBu)_2$ [3] (12.1 g, 50 mmol) in toluene (50 ml) was metallated as described for **16** with 63 ml of a 1.56 M LiBu solution in hexane. The solution was added to Me_2SiCl_2 (6.81 g, 50 mmol) in 20 ml of toluene at –78 °C. Work up was carried out as described for **16**. **17** distills at b. p. 86 °C/0.13 Torr as an oil which solidifies, m. p. 71 °C. Yield: 7.7 g (52%).

Tab 2. Crystallographic data and data related to data collection, structure solution and refinement for compounds **12**, **13**, **15**, and **17**.

Compound	**12**	**14**	**15**	**17**
Chem. formula	$C_{18}H_{26}N_2Si$	$C_{20}H_{30}N_2Si$	$C_{19}H_{28}N_2Si$	$C_{16}H_{29}N_2PSi$
Form wght.	298.50	316.55	312.52	308.47
Cryst. size [mm]	0.08 × 0.3 × 0.7	0.1 × 0.1 × 0.2	0.1 × 0.15 × 0.15	0.19 × 0.3 × 0.32
Cryst. system	monoclinic	orthothombic	monoclinic	monoclinic
Space group	P2(1)/n	$P\bar{4}2(1)c$	P2(1)/n	P2(1)/c
a [Å]	10.2643(9)	15.3312(2)	10.3382(3)	9.3091(1)
b [Å]	18.2853(14)	15.3312(2)	18.2646(6)	11.4431(1)
c [Å]	10.3445(8)	17.0722(3)	10.5648(1)	18.2046(2)
β [°]	112.482(1)	90	109.89(1)	101.34(1)
V [Å]^3	1794.0(3)	4012.75(10)	1875.87(8)	1901.41(3)
Z	4	8	4	4
ρ (calc.) [Mg/m^3]	1.105	1.081	1.107	1.078
μ [mm^{-1}]	0.128	0.119	0.125	0.202
F(000)	648	1414	680	672
Index range	$-12 \leq h \leq 12$, $-19 \leq k \leq 23$, $-12 \leq k \leq 13$	$-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-15 \leq k \leq 22$	$-12 \leq h \leq 12$, $-24 \leq k \leq 13$, $-12 \leq k \leq 12$	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-21 \leq k \leq 22$
2 θ [°]	56.18	58.36	58.50	57.04
Temp. [K]	183(5)	193	193	233
Refl. collected	7616	22129	10546	9101
Refl. unique	3320	4097	3250	3878
Refl. observed (4σ)	1907	2274	2125	2309
R (int.)	0.0655	0.1077	0.0984	0.1227
No. variables	200	223	212	189
Weighting scheme[a] x/y	0.0614/0.8811	0.0000/3.7854	0.0000/3.2910	0.0705/0.9923
GOOF	1.291	1.280	1.292	1.084
Final R (4σ)	0.0523	0.0803	0.0988	0.0593
Final $wR2$	0.1275	0.1194	0.1365	0.1361
Larg. res. res. peak [e/Å^3]	0.261	0.201	0.279	0.277

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

NMR (C_6D_6): δ^1H: 0.47 (s, 3 H, Si*Me*) , 0.52 (s, 3 H, Si*Me*), 1.02 (s, 18 H, C*Me*), 7.3 - 7.8 (m, 5 H, Ph), – δ^{13}C: 6.2 (2, Si*Me*), 8.7 (d, ^3J(P,C) = 5.5 Hz, Si*Me*), 32.4 (d, ^3J(P,C) = 5.5 Hz, C*Me*), 50.8 (d, ^2J(P,C) = 10.0 Hz, *C*Me), 128.0 (s, *p*-Ph), 129.9 (s, *m*-Ph), 130.0 (s, *o*-Ph), 151.8 (d, ^1J(P,C) = 8.3 Hz, *ipso*-Ph); - δ^{15}N: –317 (d, ^1J(P,N) = 34.8 Hz); – δ^{29}Si: 13.9 (d, ^2J(P,Si) = 2.6 Hz); – δ^{31}P: 125.7 s. $C_{16}H_{29}N_2PSi$ (308.48): Calcd C 62.30, H 9.48, N 9.08. Found C 61.00, H 9.37, N 8.43 %.

1,3-Di(tert-butyl)-2,2,4-trimethyl-1,3,2,4-diazasilaphosphetidine (**18**)*:* A solution of $Me_2Si(NH^tBu)_2$ (2.91 g, 10 mmol) in toluene (20 ml) was metallated at –78 °C with LiBu (18.6 ml, 1.56 M solution in hexane). After heating shortly to reflux this solution was dropped into a stirred solution of $MePCl_2$ (1.68 g, 10 mmol) dissolved in toluene (10 ml). Work up was carried out as described for **17**. B. p. 55 - 57 °C/ 0.1 Torr. Yield: 1.2 g (34%).

NMR (C_6D_6): δ^1H: 0.28 (s, 3 H, Si*Me*), 0.34 (s, 3 H, SP*Me*), 1.1 (s, 18 H, C*Me*), 1.24 (d, ^2J(P,H) = 6.1 Hz, 3 H, P*Me*); – δ^{13}C: 5.8 (s, Si*Me*), 9.1 (d, ^3J(P,C) = 3.8 Hz, Si*Me*), 32.3 (d, ^3J(P,C) = 6.1 Hz, CH*Me*), 33.0 (d, ^1J(P,C) = 45.0 Hz, P*Me*), 50.1 (d, ^2J(P,C) = 10.7 Hz, *C*Me); – δ^{15}N: –319.5 (d, ^1J(P,N) = 34.7 Hz); – δ^{29}Si: 13.5 (d, ^2J(P,Si) = 2.9 Hz); – ^{31}P: 137.3 s. $C_{11}H_{27}N_2PSi$ (246.41): Calcd C 53.62, H 11.04, N 11.37. Found C 52.43, H 10.87, N 11.00%.

1,3-Di(tert-butyl)-2,2,4-triphenyl-1,3,2,4-diazasilaphosphetidine (**19**)*:* $Me_2Si(NH^tBu)_2$ (1.05 g, 3.2 mmol) in toluene (10 ml) was metallated with LiBu (4.4 ml, 1.56 M) and reacted with $PhPCl_2$ (0.68 g, 3.2 mmol). Distillation yielded a mixture of **19** with the aminosilane (approximately 10:1). Therefore, the compound was only characterized by NMR spectroscopy.

NMR (C_6D_6): δ^1H: 1.0 (s, C*Me*), 7-2 - 8.0 (m, Ph); – δ^{13}C: 32.5 (d, ^3J(P,C) = 6.0 Hz, CH*Me*), 51.5 (d, ^2J(P,C) = 9.2 Hz, *C*Me), 125 - 140 Ph; – δ^{29}Si: 13.9 (d, ^2J(P,Si) = 2.6 Hz); – δ^{31}P: 130.2 s.

X-ray structure determinations

The selected single crystal was mounted in perfluoroether oil on the tip of a glass fiber and put on a gonio-

meter head which was placed on the support of a Siemens P4 four circle diffractometer equipped with a low temperature device LT2 and an area detector CCD. MoKα-radiation and a graphite monochromator were used as radiation source. All measurements were performed at 193 K. The unit cell dimensions were calculated from at total of 60 frames taken at 4 different setting angles with $\Delta\phi = 0.3°$. Data collection was performed in the hemisphere mode collecting data on 1300 frames at two different χ-setting with $\Delta\phi = 0.3°$. Data reduction was performed with the program SAINT [17] and the structures solved with direct methods as implemented in the program SHEXTL [17]. Non hydrogen atoms were refined in anisotropic description including hydrogen atoms in calculated positions as riding on the respective atom in isotropic description. Relevant data are summarized in Table 2. Further information (without structure factor tables) are deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 142860 to 142863. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. by quoting the authors and the journal citation [Fax: intern)+44-1223/336-033; E-mail: deosit@ccdc.cam.uk].

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