Disiloxanes, Disilazanes and Related Compounds Derived from 1,8-Disilylnaphthalene[☆]

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The synthesis, spectroscopic data and molecular structures of heterocycles derived from 1,8-disilylnaphthalene are reported. The key intermediate for the preparation of the title compounds is 1,8-bis[(trifluoromethylsulfonyl)silyl]naphthalene (**3**), which is prepared from 1,8-bis[(4-methoxyphenyl)silyl]naphthalene (**2**) by treatment with two equivalents of triflic acid in toluene at −20 °C. The resulting silyl triflate is stable only below this temperature and was not isolated. Its reactions with water, ammonia, amines, and sulfane give the corresponding disiloxane, disilazanes and disilthiane. The molecular structure of *Si,Si'*-(Naphthalene-1,8-diyl)-*N*-phenyldisilazane (**8**) was determined by X-ray diffraction. Treatment of **2** with substoichiometric amounts of triflic acid and subsequent reaction of the resulting monosilyl triflate with *tert*-butylamine gives a related chiral *N*-tert-butyl-*Si*-(4-methoxyphenyl)disilazane **10**. Its molecular structure was proven by X-ray diffraction. A cyclic phosphonium bis(silyl)methylide (**11**) was synthesized by a transylidation process using **3** and $CH_2{=}P(NMe_2)_3$. The structure of **11** was also determined by X-ray diffraction.

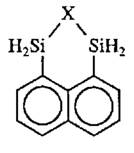
Cyclic siloxanes, silazanes and carbosilanes are important monomers for the preparation of silicones and materials based on silicon nitride or silicon carbide systems[1]. Monomer/polymer interconversion is generally facile for the siloxanes (Si−O−Si) and silazanes (Si−N−Si), and a variety of catalysts are available for reaching equilibrium[2]. Much higher activation energies are required for carbosilanes (Si−C−Si), and only high-temperature activation or action of strong Lewis acids allow a non-destructive oligomerization[3].

Cyclic monomers can be activated for chemical conversion by the application of structural ring strain, as present in small rings or in fused systems with serious distortions of the standard configuration at one or more of the ring members. This strategy was widely used with a variety of small ring compounds, but conformational strain has previously not been probed systematically for medium ring sizes with inflexible substitution patterns.

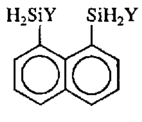
An interesting and useful model system for a more detailed investigation of the structural effects of *flattening "strait-jackets"* is the *naphthalene* system with its various modes of substitutional isomerism. Based on the results of our own recent studies of simple polysilylated naphthalenes[4], we now investigated the title compounds, focusing again on their structural characteristics. To avoid any steric or electronic influence by other substituents, the *hydrido*silanes were chosen as the more fundamental reference systems. This approach resembles the concept followed in related work on polysilylated benzenes[5], anthracenes[6], alkenes[7], and alkanes[8].

Preparation and Properties of the Compounds

A consideration of the various synthetic pathways to the heterocyclic systems in question (**A**) suggested that the final ring closure between the silicon atoms should be particularly straightforward if a convenient access could be found to *Si,Si'*-difunctionalized precursors (**B**).



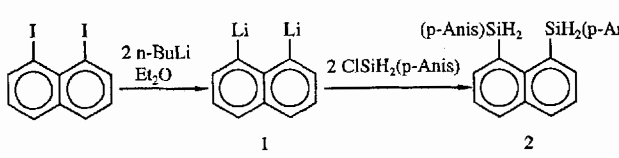
A



B

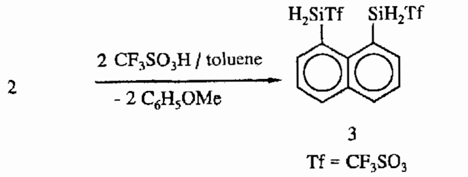
The method proposed in our initial studies was still unsatisfactory regarding the yields and the selectivity of the synthesis[4]. These disadvantages were now avoided by starting from 1,8-dilithionaphthalene[9] (**1**). Treatment of this reagent with two equivalents of chloro(4-methoxyphenyl)silane affords the 1,8-disilylated intermediate **2**, which could be isolated as very pure crystals in 80% yield (Eq. 1). Protodearylation using *two* equivalents of trifluoromethanesulfonic acid ("triflic" acid, in toluene at −20 °C) gives stable solutions of the *Si,Si'*-bis-triflate **3**, which can be used for all further cyclization reactions (Eq. 2).

It should be noted that the regioselective protodearylation of compound **2** requires the presence of activating 4-methoxy substituents (in the anisyl group) in order to rule out the cleavage of the naphthyl substituents from the silicon atoms[4]. Neither phenyl nor *p*-tolyl substituents are applicable if complete regioselectivity is required. Also, the reaction mixture must not reach room temperature, in order



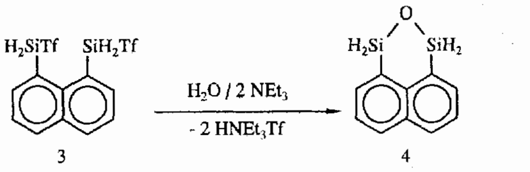
(1)

p-Anis = 4-methoxyphenyl

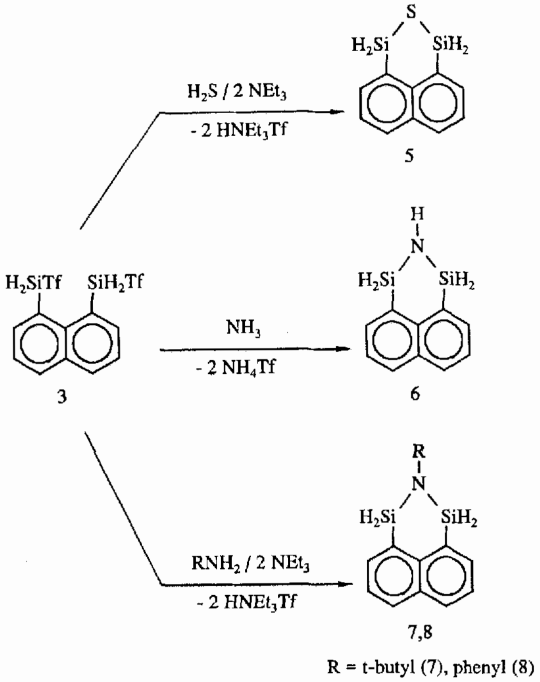


(2)

$$2\,RSiH_2Tf \rightleftharpoons RSiH_3 + RSiHTf_2 \qquad (3)$$



(4)



(5)

(6)

(7)

R = t-butyl (7), phenyl (8)

to avoid rearrangement with redistribution of the triflate functions (Eq. 3).

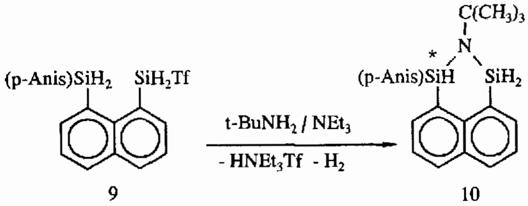
Ring closure of compound **3** to the corresponding *disiloxane* **4** is achieved by simple hydrolysis in the presence of a base (triethylamine) (Eq. 4)[10]. The product is a colorless oil, which could not be crystallized.

The analogous *disilthiane* **5** is generated by passing gaseous hydrogen sulfide into the solution of **3** and triethylamine (Eq. 5). It forms a colorless, malodorous solid sensitive to hydrolysis.

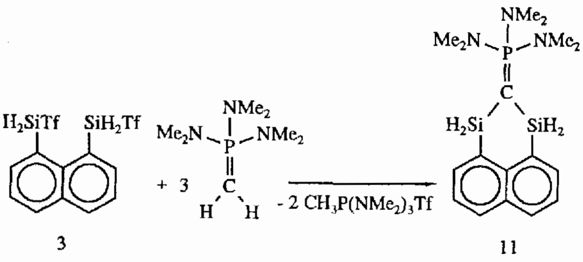
Three different *disilazanes* were prepared through cyclization of precursor **3** by reaction with ammonia (Eq. 6), *tert*-butylamine, and aniline (Eq. 7). The auxiliary base triethylamine proved unnecessary in the ammonia reaction[11]. The unsubstituted disilazane **6** (40% yield) is a colorless solid, quite sensitive to hydrolysis, while the liquid *tert-butyl* derivative (**7**, 50% yield) is more stable owing to the steric protection of the disilazane linkage. The *phenyl* homolog (**8**, 75% yield) was obtained as colorless single crystals, the structure of which was determined (below).

The reaction of *equi*molar quantities of compound **2** with triflic acid yields a solution of the *mono*-triflate[12] **9** bearing still one *p*-anisyl substituent at the non-functionalized silicon atom. Addition of a mixture of *tert*-butylamine and triethylamine to this product (at −20°C) and warming of the reaction mixture to ambient temperature afford the disilazane **10** (Eq. 8). Obviously, the substitution of the triflate anion at one of the two silicon atoms is quickly followed by a nucleophilic attack of the *tert*-butylamino nitrogen atom at the second silicon atom, which leads to ring closure with the elimination of hydrogen. The product is obtained in 60% yield as colorless single crystals, the structure of which could also be determined (below).

A *carbon* bridge between the two silicon atoms can be formed by the reaction of compound **3** with *three* equivalents of tris(dimethylamino)phosphonium methylide. In this process, two equivalents of the ylide function as a base to bind the triflic acid produced in the cyclization. According to the classical scheme of transylidation reactions, two molar quantities of tris(dimethylamino)methylphosphonium triflate are formed as the by-product[13] (Eq. 9). The product (**11**) is obtained as pale yellow single crystals (75% yield), which are very sensitive to air and moisture. The molecular structure could be elucidated on the basis of the single-crystal X-ray data.



(8)



(9)

Analytical and Spectroscopic Characterization

The composition and basic structural features of the new compounds could be confirmed by standard analytical and spectroscopic techniques (Experimental). Only a few details are noteworthy.

For the *disiloxane* **4**, both the ^{29}Si- and ^{17}O-NMR signals could be detected ($\delta_{Si} = -26.4$, $^{1}J_{Si,H} = 227$ Hz; $\delta_{O} =$

-9.5). Their parameters are consistent with standard disiloxane bonding characteristics[8c]. The ^{29}Si- (and ^{15}N)-NMR data of the analogous *disilthiane* **5** ($\delta_{Si} = -31.8$, $^{1}J_{Si,H} = 226$) and *disilazane* **6** ($\delta_{Si} = -36.9$, $^{1}J_{Si,H} = 210$; $\delta_{N} = -398.4$) are also indicative of a largely strain-free cyclic structure if compared with known reference compounds[14]. The number and multiplicity of the signals of all three compounds support the presence of virtually symmetrical structures (C_{2v} point group). If there are e.g. significant deviations of the basic skeleton from planarity (below), the structure is flexible in solution to render the substituents NMR-equivalent.This is also true for the *N-tert*-butyl and *N*-phenyl compounds (**7**, **8**).

The *disilazane* **10** is the only asymmetrical species in this series, with a center of chirality at one of the silicon atoms. The product is a mixture of enantiomers. Through the loss of symmetry, the protons of the SiH_2 group are non-equivalent, and the silicon atoms and all C(H) units of the naphthalene ring show separate signals. The signals of the *tert*-butyl group are unaffected as compared to compound **8**.

The heterocycle **11** shows NMR spectra typical of *ylidic* species: The carbon atom in the bridgehead position between the phosphorus and the two silicon atoms has its ^{13}C resonance at very high field ($\delta = -12.9$) with a large $^{1}J_{P,C}$ coupling constant of 148 Hz, indicating (planar) sp^2 hybridization.

Crystal and Molecular Structures

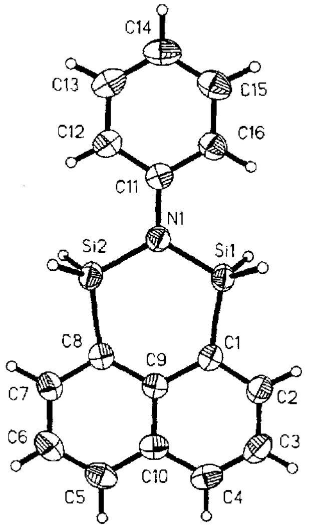
Crystals of the *N-phenyldisilazane* **8** (from hexane) are monoclinic, space group $P2_1/c$, with six molecules in the unit cell. In the asymmetric unit there is one complete molecule (I, with no crystallographically imposed symmetry, Figure 1) and one half molecule, which is symmetry-related to another half in the neighboring asymmetric unit (II).

Table 1. Crystal data, structure solution, and refinement of compounds **8**, **10**, and **11**

	8	**10**	**11**
Formula	$C_{16}H_{15}NSi_2$	$C_{21}H_{25}NOSi_2$	$C_{17}H_{28}N_3PSi_2$
Formula mass [g/mol]	277.47	363.60	361.57
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	15.882(3)	14.987(1)	15.718(3)
b [Å]	7.350(1)	10.494(1)	9.357(2)
c [Å]	18.783(3)	13.634(1)	14.218(3)
α [°]	90	90	90
β [°]	106.73(1)	113.29(1)	111.84(3)
γ [°]	90	90	90
V [^{3}]	2099.8	1969.5	1941.0
ρcalc [gcm^{-3}]	1.317	1.226	1.240
Z	6	4	4
μ(Mo-K_α) [cm^{-1}]	2.40	1.89	2.70
T [°C]	-62	-68	-62
hkl range	±22 / -9 / $+17$	-18 / $+12$ / ±15	$+19$ / $+11$ / ±17
Measured reflections	4901	3818	4168
Unique reflections	4412	3813	3520
Observed reflections with $F_o > 4 F_o$	3455	3081	3132
R_{int}	0.0135	0.0000	0.0395
Refined parameters	317	326	300
$wR2$ / $R_{based\ on\ F}$ (OMIT4)	0.1480 / 0.0513	0.1014 / 0.0344	–
R	–	–	0.0364 (unit weights)
ρ_{fin}(max/min) [e $^{-3}$]	+0.74 / -0.30	+ 0.31 / -0.25	+0.40 / -0.28
Weighting parameters a/b	0.0724 / 1.9921	0.0525 / 0.7554	

This unexpected situation arises owing to a disorder of molecule II over two orientations, which could be accounted for by a split model. The molecular dimensions of molecules I and II are very similar.

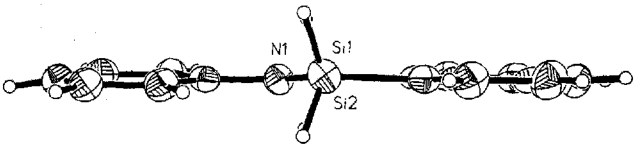
Figure 1. Molecular structure of compound **8** with atomic numbering (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitary radii for hydrogen atoms). Selected bond lengths [A] and bond angles [°]: Si1–N1 1.734(2), Si2–N1 1.739(2), Si1–C1 1.855(3), Si2–C8 1.857(3), N1–C11 1.425(3), Si–H (average) 1.38; Si1–N1–Si2 120.7(1), Si1–N1–C11 119.2(2), Si2–N1–C11 119.9(2), N1–Si1–C1 111.5(1), Si1–C1–C9 126.9(2), H01–Si1–H02 107(2), N1–Si1–H02 110.7(14), N1–Si1–H01 108.2(13)



The configuration at the nitrogen atom is planar, with the sum of the angles at 359.8°. All atoms of the two naphthalene rings are coplanar, and the nitrogen and the silicon atoms are also in this molecular plane (Figure 2). Significant ring strain is suggested, however, by the angles C2–C1–Si1 = 114.4(2) and C7–C8–Si2 = 114.5(2)° (Figure 1), which are clearly much smaller than the ideal 120° reference value. The plane of the *N*-phenyl ring is only slightly tilted relative to the naphthalene plane.

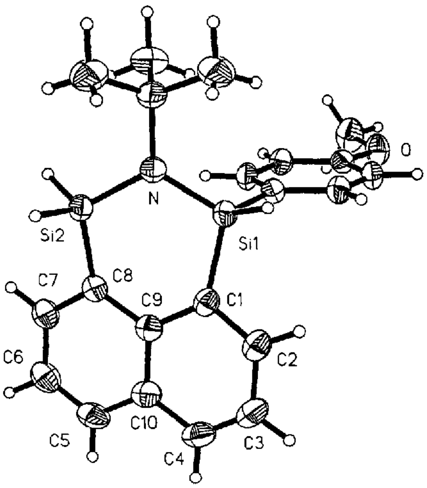
Crystals of the *anisyl-substituted disilazane* **10** (from tetrahydrofuran) are monoclinic, space group $P2_1/c$ with four formula units in the unit cell. The molecule has no crystallographically imposed symmetry (Figure 3). Associated with the crystallographic center of inversion in the lattice, the crystal contains both enantiomers. The two rings of the naphthalene part are again fully (co)planar, and the nitrogen atom is in a planar configuration (sum of the angles 359.9°).

Figure 2. Molecular structure of compound **8**, side projection



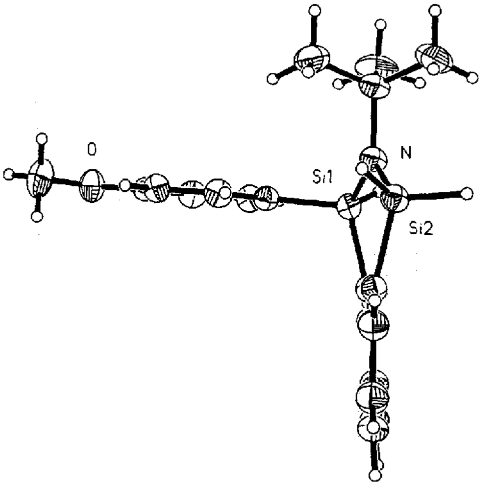
By contrast with the findings in compound **8**, however, the two silicon atoms are *not* in the naphthalene plane of compound **10**, but displaced on opposite sides of the mo-

Figure 3. Molecular structure of compound **10** with atomic numbering (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond lengths [Å] and angles [°]:Si1–N 1.721(2), Si2–N 1.723(2), Si1–C1 1.875(2), Si2–C8 1.863(2), N–C11 1.515(2), Si–H (average) 1.40; Si1–N–Si2 119.0(1), Si1–N–C11 122.47(2), Si2–N–C11 118.4(1), N–Si1–C1 110.2(1), N–Si2–C8 112.3(1), Si1–C1–C9 124.9(1), Si2–C8–C9 123.4(1)



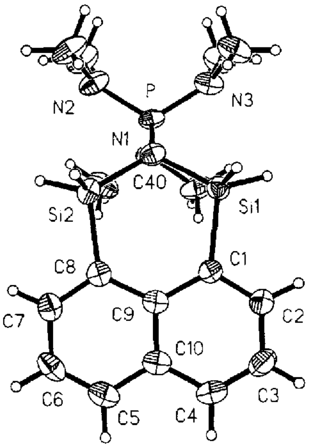
lecular reference plane (Figure 4). The six-membered ring containing the disilazane unit is thus twisted in compound **10**, while it is planar in compound **8**. This difference may be a consequence of the steric bulk of the *tert*-butyl substituent, which is better accommodated in a twist form, whereas the planar phenyl ring fits perfectly between the four *Si*-bound hydrogen atoms in a planar form of **8**. The deviations of the C2–C1–Si1 and C7–C8–Si2 angles from 120° (Figure 3), which indicate molecular strain, are about the same in **8** and **10**. The *p*-anisyl substituent shows no anomalies. Its methoxy group is coplanar with the phenyl ring.

Figure 4. Molecular structure of compound **10**, side projection



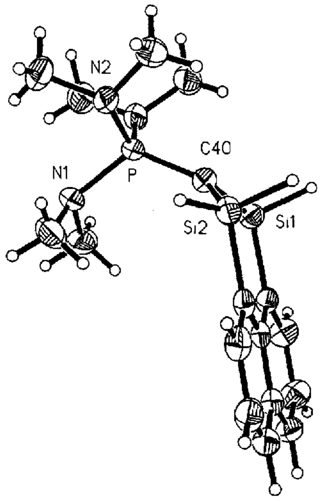
Crystals of the *ylide* **11** (from hexane/diethyl ether) are monoclinic, space group $P2_1/c$, with four formula units in the unit cell. The molecules have no crystallographically imposed symmetry, but the coordinates of the atoms are closely obeying mirror symmetry (Figure 5).

Figure 5. Molecular structure of compound **11** with atomic numbering (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond lengths [Å] and angles [°]: Si1–C40 1.808(2), P–C40 1.668(2), Si1–C1 1.883(2), Si2–C8 1.879(2), N1–P 1.688(2), N2–P 1.658(2), Si–H (average) 1.42; Si1–C40–Si2 108.9(1), Si1–C40–P 123.5(1), Si2–C40–P 123.0(2), C40–Si1–C1 111.8(1), Si1–C1–C9 125.2(1), N1–P–N2 100.6(1), N1–P–N3 102.1(1), N2–P–N3 114.3(1), N1–P–C40 117.9(1), N2–P–C40 111.1(1), N3–P–C40 110.5(1)



The structure has two prominent features, which are at variance with the situation in both compounds **8** and **10**: First, the silicon-containing six-membered ring is strongly tilted at the silicon atoms to give what can be described as an envelop conformation (Figure 6). Second, the ylidic carbon atom is not in a planar configuration, but clearly pyramidal with a *sum of the angles of 355.4°*. This structural detail is quite common in phosphorus ylide chemistry[14,15], and most modern theoretical treatments can account for the deviation from planarity (from full sp^2 hybridization)[15].

Figure 6. Molecular structure of compound **11**, side projection



The P=C bond length [1.668(2) Å] is very short, but in the range generally observed for ylides[15,16]. The Si–C(ylide) bond lengths are also unusually short [Si1–C40

1.808(2) and Si2–C40 1.806(2) Å], even as compared to the internal reference values [Si1–C1 1.883(2), Si2–C8 1.879(2) Å], where standard sp^2 carbon atoms are involved. These phenomena are also quite typical of the special bonding situation of third-row elements (P, Si) at electron-rich second-row elements (with N and C lone pairs)[17].

There is yet another structural peculiarity in molecule **11**. The coordination geometry at the nitrogen atoms of the dimethylamino groups is quite different: At N1 there is a strongly pyramidal configuration (sum of the angles 337.8°!), while at N2 and N3 (quasi-related by mirror symmetry) it is closer to planar (352.7 and 352.9°, respectively). Also, the distance P–N1 is longer [1.668(2) Å] than P–N2 and P–N3 [1.658(2) and 1.652(2) Å]. These differences are also observed in tris(dimethylamino)phosphane [$(Me_2N)_3P$] as well as in the free ylide $(Me_2N)_3P{=}CH_2$, and are nicely reproduced by ab initio calculations of these simple homologues[18].

Conclusion

Our studies of derivatives of 1,8-disilylnaphthalene have given access to heterocyclic molecules containing the corresponding poly(hydridosilyl)arene units by regioselective protodearylation reactions employing triflic acid. These hydridosilyltriflate precursors are not easy to handle due to ready isomerization, but stable up to −10°C. Current investigations are focusing now on related compounds containing the 1,2-disilylbenzene unit. Molecules of this type containing both $SiH_2{-}X{-}SiH_2$ units and SiH_3 groups suitable for further reactions (e.g. dehydrogenative coupling) are expected to widen the scope of this expanding field.

Experimental

All experiments were carried out under dry purified nitrogen. Solvents and glassware were dried and kept under nitrogen. – NMR: Jeol GX 400. – MS: Mat 311 (EI 70 eV) or GC/MS with mass-selective detector HP 5971 A (EI 70 eV).

1,8-Bis[(4-methoxyphenyl)silyl]naphthalene[4] (**2**): A solution of 1,8-dilithionaphthalene[9] (0.013 mol, from 4.94 g of 1,8-diiodonaphthalene) in 120 ml of diethyl ether is slowly added with stirring to a solution of chloro(4-methoxyphenyl)silane (4.48 g, 0.026 mol) in 70 ml of diethyl ether at 0°C. After further stirring for 1 h at room temp., the solution is poured onto crushed ice mixed with $NaHCO_3$ for neutralization. The organic layer is separated and washed three times with 50 ml of water, then dried with $MgSO_4$. After evaporation of the solvent the crude product is recrystallized from diethyl ether. Colorless needles, 4.2 g (80%).

1,8-Bis[(trifluoromethylsulfonyl)silyl]naphthalene (**3**): A solution of **2** (1.72 g, 4.3 mmol) in 50 ml of toluene is cooled to −20°C, and triflic acid (0.76 ml, 8.6 mmol) is added. The solution is stirred for 1 h at this temp. and then used for further reactions without isolation of the product.

Siloxane **4**: To a solution of **3** (from 2.20 g, 5.5 mmol of **2**) in 50 ml of toluene kept at −20°C a solution of water (0.10 ml, 5.5 mmol) and NEt_3 (1.53 ml, 11.0 mmol) in 15 ml of diethyl ether is added. The reaction mixture is allowed to warm slowly to room temp. The oily triethylammonium triflate is separated and the solvent removed in vacuo. The remaining product is purified by sublimation (30°C/0.05 Torr). Colorless oil, 0.5 g (45%), m.p. 4°C. – ^1H NMR (400 MHz, C_6D_6, 20°C): δ = 5.43 (s, $^1J_{Si,H}$ = 226 Hz, 4H, SiH_2), 7.16 (dd, $^3J_{H,H}$ = 7, $^3J_{H,H}$ = 8 Hz, 2H, 3/6-H), 7.28 (d, $^3J_{H,H}$ = 7 Hz, 2H, 2/7-H), 7.58 (d, $^3J_{H,H}$ = 8 Hz, 2H, 4/5-H). – ^{13}C NMR (100 MHz, C_6D_6, 20°C): δ = 125.3 (d, $^1J_{H,C}$ = 162 Hz, C-3/6), 127.6 (m, C-1/8), 131.5 (dt, $^1J_{H,C}$ = 159, $^3J_{H,C}$ = 9 Hz, C-4/5), 132.1 (dd, $^1J_{H,C}$ = 156, $^3J_{H,C}$ = 9 Hz, C-2/7), 133.6 (tm, $^3J_{H,C}$ = 8 Hz, C-10), 142.4 (m, C-9). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): δ = −26.4 (tdm, $^1J_{Si,H}$ = 227, $^3J_{Si,H}$ = 8 Hz, SiH_2). – ^{17}O NMR (54 MHz, C_6D_6, 20°C): δ = −9.5 (s). – IR (nujol): ṽ = 2159 cm^{-1} (SiH), 1030 (Si–O–Si). – MS, *m/z*: 202 [M^+], 155 [$M^+ - SiH_2O$], 128 [$C_{10}H_8$]. – $C_{10}H_{10}OSi_2$ (202.4): calcd. C 59.3, H 5.0, Si 27.8; found C 58.6, H 5.1, Si 28.0.

Silthiane **5**: Dry hydrogen sulfide gas is passed into a solution of **3** (from 1.60 g, 4.0 mmol of **2**) in toluene (40 ml) at −20°C, while NEt_3 (1.11 ml, 8.0 mmol) is simultaneously added. After 30 min the solution is allowed to warm to room temp., the oily NEt_3HTf separated, and the solvent evaporated. The residue is purified by sublimation (50°C/0.05 Torr) and recrystallization from hexane. Colorless solid, 0.7 g (80%), m.p. >200°C (dec.). – ^1H NMR (400 MHz, C_6D_6, 20°C): δ = 5.35 (s, $^1J_{Si,H}$ = 226 Hz, 4H, SiH_2), 7.06 (dd, $^3J_{H,H}$ = 8/9 Hz, 2H, 3/6-H), 7.44 (d, $^3J_{H,H}$ = 9 Hz, 2H, 2/7-H), 7.55 (d, $^3J_{H,H}$ = 8 Hz, 2H, 4/5-H). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20°C): δ = 125.1 (C-3/6), 129.0 (C-1/8), 132.5 (C-4/5), 134.8 (C-2/7), 137.0 (C-10), 140.8 (m, C-9). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): δ = −31.8 (tm, $^1J_{Si,H}$ = 226 Hz, SiH_2). – IR (nujol): ṽ = 2165 cm^{-1} (SiH). – MS, *m/z*: 218 [M^+], 155 [$M^+ - SiH_2S$], 128 [$C_{10}H_8$]. – $C_{10}H_{10}SSi_2$ (218.4): calcd. C 55.0, H 4.6, Si 25.7; found C 54.3, H 4.5, Si 25.6.

Silazane **6**: Through a solution of **3** (from 1.60 g, 4.0 mmol of **2**) in toluene (40 ml) a stream of gaseous ammonia is passed at −20°C for 30 min. Then bubbling is stopped, and the reaction mixture is allowed to warm to room temp. The precipitated salt is filtered off, and the residue is sublimed in vacuo (50°C/0.05 Torr). Colorless microcrystalline solid, 0.3 g (40%), m.p. >200°C (dec.). – ^1H NMR (400 MHz, C_6D_6, 20°C): δ = 0.02 (s broad, 1H, NH), 5.19 (s, $^1J_{Si,H}$ = 210 Hz, 4H, SiH_2), 7.13 (dd, $^3J_{H,H}$ = 7/8 Hz, 2H, 3/6-H), 7.49 (d, $^3J_{H,H}$ = 7 Hz, 2H, 2/7-H), 7.55 (d, $^3J_{H,H}$ = 8 Hz, 2H, 4/5-H). – ^{13}C NMR (100 MHz, C_6D_6, 20°C): δ = 125.2 (d, $^1J_{H,C}$ = 160 Hz, C-3/6), 129.2 (m, C-1/8), 131.3 (dt, $^1J_{H,C}$ = 159, $^3J_{H,C}$ = 7 Hz, C-4/5), 133.8 (dd, $^1J_{H,C}$ = 156, $^3J_{H,C}$ = 8 Hz, C-2/7), 133.9 (tm, $^3J_{H,C}$ = 8 Hz, C-10), 142.3 (m, C-9). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): δ = −36.9 (tdm, $^1J_{Si,H}$ = 210, $^3J_{Si,H}$ = 8 Hz, SiH_2). – $^{15}N\{^1H\}$ NMR (41 MHz, C_6D_6, 20°C): δ = −398.4 (s). – IR (nujol): ṽ = 3440 cm^{-1} (NH), 2126 (SiH), 930 (Si–N–Si). – MS, *m/z*: 201 [M^+], 155 [$M^+ - SiH_2N$], 128 [$C_{10}H_8$]. – $C_{10}H_{11}NSi_2$ (201.4): calcd. C 59.6, H 5.5, N 7.0, Si 27.9; found C 59.4, H 5.8, N 6.9, Si 28.3.

N-tert-Butyldisilazane **7**: To a solution of **3** (from 1.60 g, 4.0 mmol of **2**) at −20°C in toluene (40 ml) a mixture of *tert*-butylamine (0.42 ml, 4.0 mmol) and NEt_3 (1.11 ml, 8.0 mmol) is added. After 30 min the reaction mixture is warmed to room temp. and the oily triethylammonium triflate separated. The solvent is removed in vacuo and the residue purified by sublimation (60°C/0.05 Torr). Colorless oil, 0.5 g (50%). – ^1H NMR (400 MHz, C_6D_6, 20°C): δ = 1.39 (s, 9H, CH_3), 5.34 (s, $^1J_{Si,H}$ = 210 Hz, 4H, SiH_2), 7.22 (dd, $^3J_{H,H}$ = 7/8 Hz, 2H, 3/6-H), 7.61 (d, $^3J_{H,H}$ = 8 Hz, 2H, 2/7-H), 7.55 (d, $^3J_{H,H}$ = 7 Hz, 2H, 4/5-H). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20°C): δ = 30.5 (CH_3), 53.2 (CN), 125.5 (C-3/6), 130.8 (C-4/5), 131.6 (C-1/8), 132.4 (C-10), 133.8 (C-2/7), 141.6 (C-9). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): δ = −42.8 (tdm, $^1J_{Si,H}$ = 210, $^3J_{Si,H}$ = 8 Hz, SiH_2). – IR (nujol): ṽ = 2160 cm^{-1} (SiH), 937 (Si–N–Si). – MS, *m/z*: 257 [M^+], 242 [$M^+ - CH_3$], 201 [M^+ –

C_4H_8], 155 [$M^+ - SiH_2NC_4H_9$], 128 [$C_{10}H_8$]. – $C_{14}H_{19}NSi_2$ (257.5): calcd. C 65.3, H 7.4, N 5.4, Si 21.8; found C 64.5, H 7.6, N 5.2, Si 21.5.

N-Phenyldisilazane **8**: Preparation as described for **7** by using aniline (0.36 ml, 4.0 mmol). The product is isolated by sublimation (65°C/0.05 Torr) and recrystallisation from hexane. Colorless crystals, 0.8 g (75%), m.p. 83–84°C. – ^1H NMR (400 MHz, C_6D_6, 20°C): $\delta = 5.36$ (s, $^1J_{\mathrm{Si,H}} = 217$ Hz, 4H, SiH_2), 6.91 (t, $^3J_{\mathrm{H,H}} = 7$ Hz, 1H, 14-H), 7.13 (dd, $^3J_{\mathrm{H,H}} = 7/8$ Hz, 2H, 3/6-H), 7.16 (dd, $^3J_{\mathrm{H,H}} = 7/9$ Hz, 2H, 13/15-H), 7.31 (dd, $^3J_{\mathrm{H,H}} = 9/1$ Hz, 2H, 12/16-H), 7.46 (d, $^3J_{\mathrm{H,H}} = 7$ Hz, 2H, 2/7-H), 7.53 (d, $^3J_{\mathrm{H,H}} = 8$ Hz, 2H, 4/5-H). – ^{13}C NMR (100 MHz, C_6D_6, 20°C): $\delta = 122.3$ (dt, $^1J_{\mathrm{H,C}} = 157$, $^3J_{\mathrm{H,C}} = 7$ Hz, C-12/16), 123.0 (dt, $^1J_{\mathrm{H,C}} = 159$, $^3J_{\mathrm{H,C}} = 7$ Hz, C-14), 125.5 (d, $^1J_{\mathrm{H,C}} = 160$ Hz, C-3/6), 129.5 (m, C-1/8), 130.0 (dd, $^1J_{\mathrm{H,C}} = 159$, $^3J_{\mathrm{H,C}} = 8$ Hz, C-13/15), 131.4 (dt, $^1J_{\mathrm{H,C}} = 159$, $^3J_{\mathrm{H,C}} = 6$ Hz, C-4/5), 133.5 (t, $^3J_{\mathrm{H,C}} = 7$ Hz, C-10), 134.2 (dd, $^1J_{\mathrm{H,C}} = 157$, $^3J_{\mathrm{H,C}} = 8$ Hz, C-2/7), 141.3 (m, C-9), 147.4 (t, $^3J_{\mathrm{H,C}} = 8$ Hz, C-11). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): $\delta = -37.0$ (td, $^1J_{\mathrm{Si,H}} = 217$, $^3J_{\mathrm{Si,H}} = 8$ Hz, SiH_2). – IR (nujol): $\tilde{\nu} = 2130\ \mathrm{cm^{-1}}$ (SiH), 940 (Si–N–Si). – MS, *m/z*: 277 [M^+], 198 [$M^+ - C_6H_5 - 2H$], 186 [$M^+ - NC_6H_5$], 155 [$M^+ - SiH_2NC_6H_5$], 128 [$C_{10}H_8$]. – $C_{16}H_{15}NSi_2$ (277.5): calcd. C 69.3, H 5.5, N 5.0, Si 20.2; found C 69.0, H 5.5, N 5.1, Si 20.5.

N-tert-Butyl-Si-(4-methoxyphenyl)disilazane **10**: A solution of 1,8-bis[(4-methoxyphenyl)silyl]naphthalene (2.00 g, 5.0 mmol) in toluene (25 ml) is treated with triflic acid (0.44 ml, 5.0 mmol) at −20°C. After the mixture has been kept at this temp. for 1 h, a mixture of *tert*-butylamine (0.52 ml, 5.0 mmol) and NEt_3 (0.72 ml, 5.0 mmol) is added, and the solution is allowed to warm to room temp. The oily ammonium salt is removed, the solvent evaporated, the residue washed with pentane, and the crude product recrystallized from tetrahydrofuran. Pale yellow crystals, 1.1 g (60%), m.p. 127–128°C. – ^1H NMR (400 MHz, C_6D_6, 20°C): $\delta = 1.38$ (s, 9H, CCH_3), 3.16 (s, 3H, OCH_3), 5.47 and 5.66 (d each, $^1J_{\mathrm{Si,H}} = 213$, $^2J_{\mathrm{H,H}} = 16$ Hz, 2H, SiH_2), 5.88 (d, $^1J_{\mathrm{Si,H}} = 212$ Hz, 1H, SiH), 6.64 and 7.52 (d each, $^3J_{\mathrm{H,H}} = 8$ Hz, 4H, $C_6\mathit{H}_4$), 7.13 and 7.23 (dd each, $^3J_{\mathrm{H,H}} = 7/8$ Hz, 2H, 3/6-H), 7.52 and 7.59 (d each, $^3J_{\mathrm{H,H}} = 7$ Hz, 2H, 2/7-H), 7.66 and 7.76 (d each, $^3J_{\mathrm{H,H}} = 8$ Hz, 2H, 4/5-H). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20°C): $\delta = 31.6$ ($C\mathit{C}H_3$), 54.0 ($\mathit{C}CH_3$), 54.4 (CH_3O), 114.2, 125.4, 135.7, 161.3 (C_6H_4), 125.7 (C-3/6), 130.4, 130.9 (C-4/5), 131.7, 131.8 (C-1/8), 133.3, 133.9 (C-2/7), 135.9 (C-10), 141.2 (C-9). – ^{29}Si NMR (79 MHz, C_6D_6, TMS, 20°C): $\delta = -41.7$ (dddd, $^1J_{\mathrm{Si,H}} = 211/210$, $^3J_{\mathrm{Si,H}} = 8/1$ Hz, SiH_2), −24.8 (dqm, $^1J_{\mathrm{Si,H}} = 212$, $^3J_{\mathrm{Si,H}} = 6$ Hz, SiH). – IR (nujol): $\tilde{\nu} = 2125\ \mathrm{cm^{-1}}$ (SiH), 993 (Si–N–Si). – MS, *m/z*: 363 [M^+], 348 [$M^+ - CH_3$], 306 [$M^+ - (CH_3)_2C{=}CH_2$], 274 [$M^+ - OCH_3 - CH_3)_2C{=}CH_2$], 240 [$M^+ - CH_3OC_6H_4 - Me$], 198 [$M^+ - CH_3OC_6H_4 - C(Me)_3$] 155 [$M^+ - CH_3OC_6H_4SiH - NC(CH_3)_3$]. – $C_{21}H_{25}NOSi_2$ (363.6): calcd. C 69.4, H 6.9, N 3.9, Si 15.4; found C 69.0, H 7.1, N 3.7, Si 15.7.

Ylide **11**: To a solution of **2** (2.00 g, 5.0 mmol) in 50 ml of toluene triflic acid (0.88 ml, 10.0 mmol) is added at −20°C. The reaction mixture is stirred for 1 h at this temp., and subsequently 2.66 g (15.0 mmol) of $H_2C{=}P(NMe_2)_3$ diluted with 10 ml of toluene is added and the mixture slowly warmed to room temp. After 30 min the solvent is removed in vacuo, and the residue is washed three times with hexane (30 ml each). The combined hexane solutions are concentrated in vacuo to yield the crude product. The ylide is purified by recrystallization from hexane. Pale yellow crystals, 1.4 g (75%), m.p. >200°C (dec.). – ^1H NMR (400 MHz, C_6D_6, 20°C): $\delta = 2.36$ (d, $^3J_{\mathrm{P,H}} = 10$ Hz, 18H, $P[N(CH_3)_2]_3$), 5.48 (s, $^1J_{\mathrm{Si,H}} = 192$ Hz, 4H, SiH_2), 7.33 (t, $^3J_{\mathrm{H,H}} = 7$ Hz, 2H, 3/6-H), 7.70 (d, $^3J_{\mathrm{H,H}} = 7$ Hz, 2H, 2/7-H), 8.03 (d, $^3J_{\mathrm{H,H}} = 7$ Hz, 2H, 3/5-H). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20°C): $\delta = -12.9$ (d, $^1J_{\mathrm{P,C}} = 148$ Hz, P=C), 37.9 (d, $^2J_{\mathrm{P,C}} = 4$ Hz, $P[N(CH_3)_2]_3$), 125.0 (C-3/6), 128.3 (C-1/8), 130.5 (C-4/5), 134.3 (C-10), 134.4 (C-2/7), 143.5 (C-9). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20°C): $\delta = 63.9$ (s). – ^{29}Si NMR (79 MHz, C_6D_6, 20°C): $\delta = -46.1$ (tm, $^1J_{\mathrm{Si,H}} = 191$, $^2J_{\mathrm{Si,P}} = 7$ Hz (observed in the $^{29}Si\{^1H\}$ NMR spectrum), SiH_2). – MS, *m/z*: 361 [M^+], 287 [$M^+ - NMe_2 - 2\,Me$], 239 [$M^+ - P(NMe_2)_2$], 199 [$M^+ - P(NMe_2)_3$], 186 [$C{=}P(NMe_2)_3$], 119 [$P(NMe_2)_2$].

Crystal Structure Determinations: Suitable crystals of compounds **8**, **10**, and **11** were sealed in glass capillaries and examined with an Enraf Nonius CAD 4 diffractometer. Graphite-monochromator Mo-K_α radiation ($\lambda = 0.71069$) was used. The structures were solved by direct methods (SHELXTL[19]). All heavy atoms were refined with anisotropic displacement parameters (compound **8**, **10**: SHELXLTL-93[20]; compound **11**: SHELXTL-PLUS[19]). All hydrogen atoms were found. – Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-59200, the names of the authors, and the journal citation.

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