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Tetrafluorocyclodisilazanes: synthesis, crystal structure, and molecular orbital ab initio calculations ☆

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Abstract

The bis(silylamino)difluorosilane $(RHN)_2SiF_2$, **1** and the (silylamino)-trifluorosilane $(RHN)SiF_3$ with $R = {}^tBu_2PhSi$, **2**, were prepared by reaction of lithiated di-tert-butylphenylsilylamine with tetrafluorosilane. Reaction of **1** with two molar equivalents of ${}^tBuLi$ yields the dilithiated **3**, which when brought into reaction with SiF_4, gives the tetrafluoro-substituted four-membered (SiNSiN) ring species $RNSiF_2NRSiF_2$ **4**. Reaction of **1** with PF_3 yields the cyclic four-membered ring 1,3-diaza-2-phospha-4-sila-cyclobutane, $RNSiF_2NRPF$ **5**. The bis-(silylamino)difluorosilanes **1**, and the related $R'NHSiF_2NHR'$, $R' = {}^tBu_2Me\text{–}Si$, **6**, are also synthesized by treatment of **2** with lithiated di-tert-butylsilylamines. The X-ray crystal structure of **4** reveals the shortest *trans*-annular Si ··· Si ring distance (237.6 pm) observed in cyclodisilazanes. Molecular orbital ab initio calculations on the model cyclodisilazanes **8a–8d** were performed at the HF/6-31G* level of theory in order to account for short observed Si ··· Si distance in **4** and the analogous species $F_2SiNR'SiF_2NR'$, $R' = {}^tBu_2MeSi$, **7**. The calculation reveals a very large effect of the fluorine and silyl substituents on the Si ··· Si separation. They also show that the (SiNSiN) ring is extremely flexible in respect of bending of the endocyclic N–Si–N bond angles. Steric interactions associated with the bulky substituents or lattice effects in the crystal may therefore strongly influence the geometry of the (SiNSiN) cycle. The calculations demonstrate that despite the very short Si ··· Si separation in **4** and **7** there is no bonding interaction between the ring silicon atoms.

Keywords: Silicon; Silazanes; Ab initio calculations; Crystal structure; Anomeric effects

1. Introduction

The ammonolysis of dialkyl- and diaryl-chlorosilanes and the condensation of aminosilanes give well-established methods of making four-, six- and eight-membered cyclosilazanes [1]. A new method for the preparation of cyclodisilazanes involves the (2 + 2)-cycloaddition of reactive iminosilanes and their adducts [1,2], but the reaction is often accompanied by rearrangements [2].

Relative to organic substituted cyclosilazanes only a few (Si–N) ring systems with inorganic substituents are known [1,3,4]. Ammonolysis of $SiCl_4$ leads only to small yields of the cyclic tetramer $(Cl_2SiNSiCl_3)_4$, the trimer $(Cl_2SiNH)_3$ and the dimer $(Cl_2SiNSiCl_3)_2$ [4]. Ammonolysis of SiF_4 stops at the ammonia adduct $SiF_4 \cdot (NH_3)_2$, the oldest known Si–N compound [5,6], probably because of the high Si–F bond energy. Tetrafluorosilane does not react with the less basic silylamines, but with silyl-amides fluorinated Si–N compounds are obtained [6].

In this paper we report that by starting from bis(silylamino)difluorosilanes we were able to isolate a Si-fluorinated cyclodisilazane and the first 1,3-diaza-2-phospha-4-silacyclobutane fully fluorinated at Si and P. An X-ray diffraction study of the Si-fluorinated cyclodisilazane shows along with one other known tetrafluoro-substituted cyclodisilazane [7], the shortest transannular Si ··· Si distances (237.6 pm) known for cyclodisilazanes. The reasons for this short Si ··· Si separation are investigated by quantum-mechanical ab initio calculations.

☆ Dedicated to Prof. N. Wiberg on the occasion of his 60th birthday.

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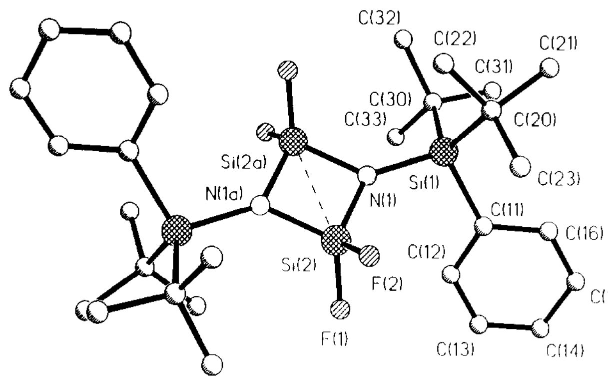
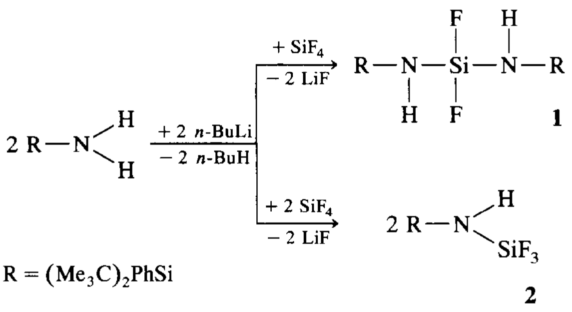


Fig. 1. PLUTO drawing of the X-ray crystal structure of 4.

2. Results and discussion

The bis(silylamino)difluorosilane **1** and (silylamino) trifluorosilane **2**, containing the bulky R = $(Me_3C)_2PhSi$ group substituent on nitrogen are obtained by the reaction of monolithiated di-tert-butyl-phenylsilylamine with SiF_4 [8]. Reaction in a 1 : 1 molar ratio leads to **1** (Eq. 1a), while use of a two molar proportion of SiF_4 gives **2** (Eq. 1b).



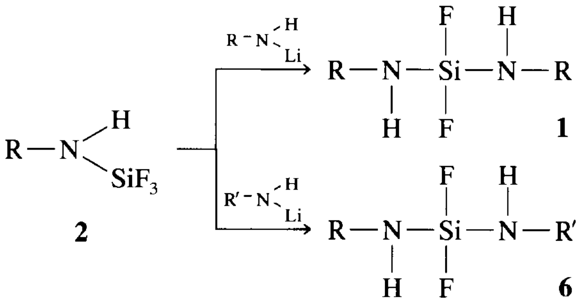
(1a)

(1b)

R = $(Me_3C)_2PhSi$

Treatment of **1** with two equivalents of tert-butyllithium yields the dilithium derivative **3**. A compound with a similar conformation to that of **3** has been described recently [7]. Compound **3** reacts with SiF_4 at 0°C to give the cyclodisilazane **4** (Eq. 2) and with PF_3 at −78°C to give the 1,3-diaza-2-phospha-4-silacyclobutane **5** (Eq. 3).

The reactions of **2** with monolithiated di-tert-butylmethyl- and di-tert-butylphenylsilylamine, respectively, yields the bis(silylamino)difluorosilanes **1** and **6** (Eq. 4).



(4)

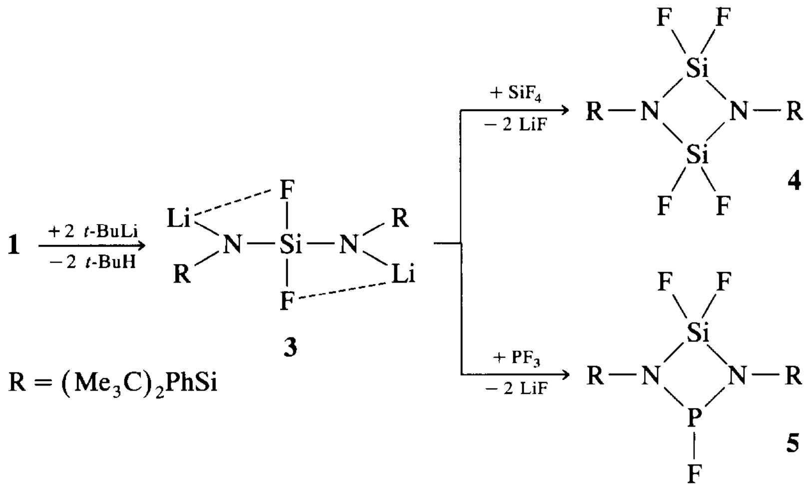
R = $(Me_3C)_2PhSi$; R′ = $(Me_3C)_2MeSi$

2.1. X-ray structure of the cyclodisilazane 4

The molecular structure of **4** was determined by X-ray crystallography and a PLUTO drawing of the structure is given in Fig. 1. The geometrical parameters are shown in Tables 1–3.

2.2. Crystal data

4: $C_{28}H_{46}N_2F_4Si_4$, $M = 599.0$, orthorhombic, space group *Pbca*, $a = 1126.7(2)$ pm, $b = 1640.1(3)$ pm, $c = 1749.2(3)$ pm, $V = 3.232$ nm^3, $Z = 4$, $D_c = 1.231$ Mg cm^{-3}, $F(000) = 1280$, λ (Mo-Kα) = 71.073 pm, $\mu = 0.221$ mm^{-1}, crystal size 0.3 × 0.5 × 0.9 mm^3, data collection on a Stoe-Siemens AED diffractometer at 293 K, 2391 reflections with $2\Theta < 45°$, 1437 unique data with $F > 3.0\ \sigma(F)$: $R = 0.07$, $wR = 0.074$, $w^{-1} =$



(2)

(3)

R = $(Me_3C)_2PhSi$

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$)

Atom	x	y	z	U_{eq}
Si(1)	1963(1)	741(1)	4072(1)	40(1)
C(11)	1277(5)	1482(4)	3377(3)	49(2)
C(12)	274(6)	1922(4)	3549(3)	54(2)
C(13)	−194(6)	2504(4)	3060(4)	65(3)
C(14)	351(7)	2660(5)	2376(4)	74(3)
C(15)	1362(8)	2227(5)	2189(4)	77(3)
C(16)	1816(6)	1659(4)	2674(3)	65(3)
C(20)	2709(5)	−154(4)	3554(3)	53(2)
C(21)	3956(6)	26(4)	3255(3)	72(3)
C(22)	2794(7)	−894(4)	4098(4)	75(3)
C(23)	1928(7)	−419(4)	2862(3)	74(3)
C(30)	2971(5)	1371(4)	4722(3)	50(2)
C(31)	3894(6)	1842(4)	4255(4)	74(3)
C(32)	3632(6)	853(4)	5321(3)	72(3)
C(33)	2228(6)	2021(4)	5141(3)	63(3)
N(1)	782(4)	342(3)	4638(2)	43(2)
Si(2)	−613(1)	1(1)	4447(1)	48(1)
F(1)	−1546(3)	654(3)	4189(2)	77(2)
F(2)	−705(3)	−642(3)	3801(2)	78(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$\sigma^2(F) + 0.0004\ F^2$. The structure solution was by direct methods and refinement by full-matrix least-squares, with non-hydrogen atom anisotropic and H-atoms in riding mode with fixed isotropic μ values using SHELXTL-Plus.

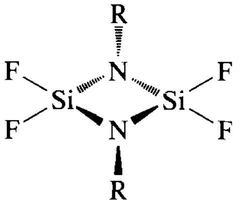
The tetrafluorocyclodisilazane **4** has essentially a planar (SiNSiN) four-membered ring possessing an inversion centre (Fig. 1). The sums of the angles around N(1) and N(1a) is 359.3°, so that the nitrogen atoms have essentially a planar environment, and the substituents at N(1) and N(1a) are in the (SiNSiN) plane. Other known 1,3-cyclodisilazanes also have essentially planar four-membered rings with planar arrangements around the nitrogen atoms [9,10]. The bulky R-substituents on Si(1) and Si(1a) force these silicon atoms out of the N(1) · · · N(1a) line (5.8°) in a *trans* fashion in the direction of Si(2) and Si(2a) (Fig. 1). The endocyclic Si–N bonds (Si(2)–N(1): 170.1 pm, Si(2a)–N(1): 170.6 pm) are considerably shorter than the exocyclic N–Si bonds (Si(1)–N(1): 178.3 pm). This contrasts with the situation in other 1,3-cyclodisilazanes, for which the opposite trend is observed [9,10]. The Si(2)–N(1)–Si(2a) ring angle is smaller than 90°, (while the N(1)–Si(2)–N(1a) ring angle is larger than 90°) (Fig. 1), whereas in other known 1,3-cyclodisilazanes these angles are larger and smaller, respectively, than 90° [9,10]. This brings the ring silicon atoms in **4** into close proximity. The transannular Si · · · Si ring distance in **4** is 237.6 pm, a distance very close to that of a normal Si–Si single bond (ca. 235 pm) [11]. The analogous tetrafluorocyclodisilazane **7** has also a short transannular Si · · · Si ring distance of 237.8 pm [7]. Similarly short Si · · · Si ring distances were found in several 1,3-cyclodisiloxanes [12,13]

Table 2
Bond lengths (pm)

Si(1)–C(11)	188.5(6)	Si(1)–C(20)	192.0(6)
Si(1)–C(30)	191.1(6)	Si(1)–N(1)	178.3(4)
C(11)–C(12)	137.5(9)	C(11)–C(16)	140.3(8)
C(12)–C(13)	138.5(9)	C(13)–C(14)	136.9(10)
C(14)–C(15)	138.1(11)	C(15)–C(16)	135.9(10)
C(20)–C(21)	152.7(9)	C(20)–C(22)	154.4(9)
C(20)–C(23)	155.9(8)	C(30)–C(31)	153.2(9)
C(30)–C(32)	154.0(9)	C(30)–C(33)	154.1(9)
N(1)–Si(2)	170.1(5)	N(1)–Si(2A)	170.6(4)
Si(2)–F(1)	156.7(4)	Si(2)–F(2)	155.0(4)
Si(2)–N(1A)	170.6(4)	Si(2)–Si(2A)	237.6(3)

Table 3
Bond angles (°)

C(11)–Si(1)–C(20)	111.6(2)	C(11)–Si(1)–C(30)	106.2(3)
C(20)–Si(1)–C(30)	115.7(3)	C(11)–Si(1)–N(1)	106.8(2)
C(20)–Si(1)–N(1)	108.0(2)	C(30)–Si(1)–N(1)	108.2(2)
Si(1)–C(11)–C(12)	122.3(4)	Si(1)–C(11)–C(16)	121.5(5)
C(12)–C(11)–C(16)	116.0(5)	C(11)–C(12)–C(13)	122.7(6)
C(12)–C(13)–C(14)	119.8(6)	C(13)–C(14)–C(15)	118.7(7)
C(14)–C(15)–C(16)	121.0(6)	C(11)–C(16)–C(15)	121.7(6)
Si(1)–C(20)–C(21)	114.6(4)	Si(1)–C(20)–C(22)	109.7(4)
C(21)–C(20)–C(22)	107.8(5)	Si(1)–C(20)–C(23)	109.4(4)
C(21)–C(20)–C(23)	107.9(5)	C(22)–C(20)–C(23)	107.1(5)
Si(1)–C(30)–C(31)	111.0(4)	Si(1)–C(30)–C(32)	113.2(4)
C(31)–C(30)–C(32)	108.2(5)	Si(1)–C(30)–C(33)	109.5(4)
C(31)–C(30)–C(33)	105.9(5)	C(32)–C(30)–C(33)	108.8(4)
Si(1)–N(1)–Si(2)	134.5(2)	Si(1)–N(1)–Si(2A)	136.4(3)
Si(2)–N(1)–Si(2A)	88.4(2)	N(1)–Si(2)–F(1)	116.9(2)
N(1)–Si(2)–F(2)	115.4(2)	F(1)–Si(2)–F(2)	102.1(2)
N(1)–Si(2)–N(1A)	91.6(2)	F(1)–Si(2)–N(1A)	114.9(2)
F(2)–Si(2)–N(1A)	116.9(2)	N(1)–Si(2)–Si(2A)	45.9(1)
F(1)–Si(2)–Si(2A)	128.7(2)	F(2)–Si(2)–Si(2A)	129.2(2)
N(1A)–Si(2)–Si(2A)	45.7(2)		

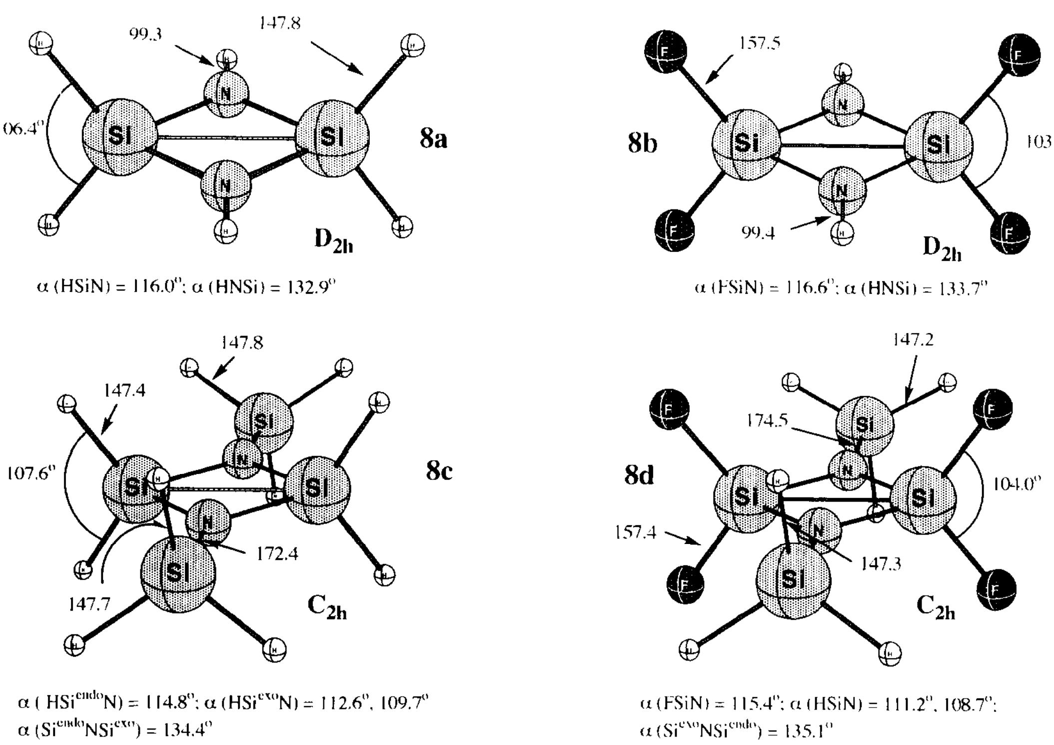


7

R = SiMe(CMe$_3$)$_2$

3. Molecular orbital calculations

Standard molecular orbital ab initio calculations [14] were carried out for several substituted 1,3-cyclodisilazanes, **8a**–**8d**, which serve as close models for the synthesized compounds **4′** and **7** in order to see if they could reproduce the experimental X-ray structures and provide a rationalization for the very short Si · · · Si distances in **4** and **7**. Calculations were carried out for the parent 1,3-cyclodisilazane, **8a**, the tetra-fluoro-substituted **8b**, the N,N-disilyl-substituted 1,3-cyclodisila-



α (HSiN) = 116.0°; α (HNSi) = 132.9°

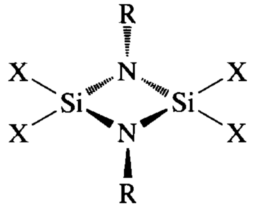
α (FSiN) = 116.6°; α (HNSi) = 133.7°

α (HSi^{endo}N) = 114.8°; α (HSi^{exo}N) = 112.6°, 109.7°
α (Si^{endo}NSi^{exo}) = 134.4°

α (FSiN) = 115.4°; α (HSiN) = 111.2°, 108.7°;
α (Si^{exo}NSi^{endo}) = 135.1°

Fig. 2. Calculated geometries of **8a–8d** at HF/6-31G* (bond lengths in pm, bond angles in degrees). The geometrical parameters of the inner (SiNSiN) ring are given in Table 4.

zane **8c** and the N,N-disilyl-, tetra-fluoro-substituted **8d**, 1,3-cyclodisilazane the latter being the closest model for **4** and **7** that we have considered.



8a: R = H; X = H
8b: R = H; X = F
8c: R = SiH_3, X = H
8d: R = SiH_3, X = F

3.1. Method

The ab initio molecular orbital calculations were carried out with the GAUSSIAN 92 series of programs [15]. The geometries of **8a–8d** were fully optimized with both the split-valence and the polarized 6-31G* basis-set [16] using gradient techniques [15]. Minima were characterized as such by their Hessian matrixes [14,15]. The HF/6-31G* optimized geometries of **8a–8d** are given in Fig. 2 and the important geometrical parameters of the 1,3-disilazane ring are summerized in Table 4.

The calculated total energies using the various basis sets as well as the zero point vibrational energies, calculated at HF/6-31G*, (scaled by a factor of 0.89 [17,18]) are reported in Table 5.

3.2. Substituent effects on the thermodynamic stability

The effect of the substituents attached to the (SiNSiN) cycle on the thermodynamic stability of 1,3-cyclodi-

Table 4
Important calculated geometrical parameters of **8a–8d**, (bond lengths in pm, bond angles in deg.)

Compound	Method	Si–Si	N–N	Si–N	Si–N–Si	N–Si(exo) [a]	Si–F
8a	HF/6-31G*	254.2	236.2	173.5	94.2	–	–
8b	HF/6-31G*	247.6	236.2	171.1	92.7	–	157.5
	HF/6-311 + G**	247.0	235.4	170.6	92.7	–	157.5
	MP2(fu)/6-31G*	247.7	238.6	172.0	92.2	–	160.0
8c	HF/6-31G*	249.7	244.3	174.6	91.3	172.4	–
8d	HF/6-31G*	242.5	243.4	171.8	89.8	174.5	157.4
4	X-ray	237.6	244.2	170.1	88.4	178.3	155.0–156.7
8d [b]	HF/6-31G*	237.6	245.0	170.6	88.3	174.5	157.5

[a] Exocyclic N–Si bond length.
[b] Partially optimized structure keeping the Si ··· Si distance at the experimentally determined distance in **4** of 237.6 pm.

Table 5
Calculated absolute energies (Hartree) and zero-point energies (ZPE [a], in kcal mol^{-1}) of **8a**–**8d** and of other molecules used in eqns. 5–11

Compound	Point group	Energy [b]	ZPE [a]
8a	D_{2h}	−690.29898	44.8
8b	D_{2h}	−1086.04997 [c]	31.4
8c	C_{2h}	−1270.51697	66.5
8d	C_{2h}	−1666.26491	52.6
SiH_4	T_d	−291.22513	21.0
H_3SiF	C_{3v}	−390.14840	18.6
H_2SiF_2	C_{2v}	−489.08180	15.7
NH_3	C_{3v}	−56.18436	23.2
H_3SiNH_2	C_s	−346.28395	33.8
$FSiH_2NH_2$	C_s	−445.21986	31.1
$(H_3Si)_2NH$	C_1	−636.38767	44.6
$H_2Si(NH_2)_2$	C_{2v}	−401.34970	46.2
$H_2NSiH_2NHSiH_3$	C_1	−691.45523	57.3

[a] Zero point energies scaled by a factor of 0.89.
[b] Structures were fully optimized at HF/6-31G* within the constraints of the given point group.
[c] Geometry optimized at HF/6-311+G*: −1086.23375; MP2(fu)/6-31G*: −1087.26430.

silazane can be evaluated by the isodesmic Eqs. 5–8 [14] and the results are reported in Table 6.

$$\mathbf{8b} + 2\,SiH_4 \longrightarrow \mathbf{8a} + 2\,F_2SiH_2 \qquad (5)$$

$$\mathbf{8c} + 2\,H_3N \longrightarrow \mathbf{8a} + 2\,H_2NSiH_3 \qquad (6)$$

$$\mathbf{8d} + 2\,SiH_4 \longrightarrow \mathbf{8c} + 2\,F_2SiH_2 \qquad (7)$$

$$\mathbf{8d} + 2\,H_3N \longrightarrow \mathbf{8b} + 2\,H_2NSiH_3 \qquad (8)$$

Replacement of all the hydrogens bonded to silicon by fluorine atoms leads to a very large stabilization of 26.4 kcal mol^{-1} at HF/6-31G* in **8b** (Eq. 5) and 25.0 kcal mol^{-1} in **8d** (Eq. 7). Replacement of the amino hydrogens by silyl groups, either in the parent **8a** (Eq. 6) or in the tetrafluoro-derivative **8b** (Eq. 8), results in a smaller but still significant stabilization of the 1,3-cyclodisilazane skeleton by 11.3 kcal mol^{-1} and 9.9 kcal mol^{-1}, respectively. The overall effect of the four fluorines and the two silyl substituents in **8d** is very large, **8d** being more stable than the parent **8a** by 36.3 kcal mol^{-1}.

What is the origin of these large substituent effects? According to the isodesmic eqn. 9 the stabilization of a silane by geminal amino and fluorine substituents is 8.2 kcal mol^{-1} (HF/6-31G* + ZPE, 7.9 kcal mol^{-1} without ZPE [19a]). The geminal FSiN subunit appears several times in the 1,3-cyclodisilazanes **8b** and **8d**, and this cumulative effect is the major contributor to the very large stabilization of the (SiNSiN) cycle by the four fluorine substituents. The relatively large geminal interaction in H_2NSiH_2F has been ascribed to the operation of an anomeric effect at silicon, or in other words to negative hyperconjugative interaction between the lone pair on nitrogen and the empty σ^*_{SiF} orbital [19]. The anomeric effect at silicon, although substantial in this case, is significantly smaller than when carbon is the central atom, as has been pointed out elsewhere [19]. For example the isodesmic equation for H_2NCH_2F analogous to Eq. 9 is exothermic by 14.8 kcal mol^{-1} at HF/6-31G*.

Table 6
Calculated energies (ΔE, kcal mol^{-1}) at HF/6-31G* of eqns. 5–11

Equation	ΔE	ΔE(ZPE) [a]
5	23.6	26.4
6	11.8	11.3
7	21.7	25.0
8	9.9	9.9
9	7.9	8.2
10	2.6	2.4
11	3.7	3.2

[a] Included corrections for ZPEs.

Table 7
Occupancies and second-order pertubation energies, ΔE_{ij}, derived from NBO analysis for **8a** and **8b** (HF/6-31G*)

	8a	**8b**
Occupancy of n_N	1.9033	1.8890
Occupancy of σ^*_{SiX}	0.0511	0.0862
Occupancy of σ^*_{SiN}	0.0187	0.0579
$\Delta E_{ij}\{n_N \rightarrow \sigma^*_{SiX}\}$	8.5	11.0
$\Delta E_{ij}\{\sigma_{SiX} \rightarrow \sigma^*_{SiN}\}$	4.1	1.8
$\Delta E_{ij}\{n_F \rightarrow \sigma^*_{SiN}\}$	–	8.9; 3.2 [a]

[a] The two values refer to the different oriented lone pairs of the fluorines.

$$H_2NSiH_2F + SiH_4 \rightarrow H_3SiNH_2 + FSiH_3 \qquad (9)$$

The occurrence of significant hyperconjugative interactions in 1,3-cyclodisilazanes is supported by NBO analysis [20] (Table 7) of the Hartree Fock wave functions of **8a** and **8b**. The occupancy of the lone pair at the nitrogen (1.889 electrons) in **8b** is significantly depleted with respect to the ideal value of 2.0 electrons or to its value in **8a** (1.903), and the occupancy of the σ^*_{SiF} orbital in **8b** of 0.086 electrons is significantly larger than the occupancy of the σ^*_{SiH} orbital (0.051 electrons) in **8a**. Thus, the $n_N \rightarrow \sigma^*_{SiX}$ delocalization is more pronounced in the fluorinated **8b** than in the parent **8a**. The second-order perturbative energy term ΔE_{ij} [20a,21] of the $n_N \rightarrow \sigma^*_{SiX}$ interaction is 11.0 kcal mol^{-1} in **8b**, by 2.5 kcal mol^{-1} larger than in **8a** (Table 7). In addition to the $n_N \rightarrow \sigma^*_{SiX}$ interaction in **8b** the fluorine lone pairs interacts with the empty σ^*_{SiN} orbital. This interaction has no equivalent in the non-substituted **8a**. This $n_F \rightarrow \sigma^*_{SiN}$ interaction depopulates slightly the fluorine lone pairs (1.959, 1.954 electrons) relative to the reference compound H_2SiF_2 (1.966, 1.955 electrons). Despite the small electronic change the second-order perturbative energy terms for these interactions, δE_{ij}, are substantial: 8.9 kcal mol^{-1} and 3.2 kcal mol^{-1}, for the two differently oriented fluorine lone pairs, respectively. Thus, according to NBO analysis the stronger $n_N \rightarrow \sigma^*_{SiX}$ interaction in **8b** vs. **8a** and the additional $n_F \rightarrow \sigma^*_{SiN}$ delocalization in **8b** both contribute to the calculated large thermodynamic stabilization of **8b** relative to **8a**.

The stabilizing effect of the exocyclic silyl substituents in **8c** and **8d** of 9.9–11.3 kcal mol^{-1} (Eq. 6 and Eq. 8, respectively), on the average 5.3 kcal mol^{-1} per silyl group, is also substantial. Only part of this stabilization can be attributed to a geminal interaction of silyl groups which are bonded to a nitrogen center. According to Eq. 10 disilylamine is stabilized relative to silylamine by only 2.4 kcal mol^{-1} (HF/6-31G* + ZPE, Table 6). In the non-cyclic $H_2NSiH_2NHSiH_3$, a closer model to the 1,3-cyclodisilazane, the silyl effect is larger, 3.2 kcal mol^{-1} (Eq. 11, HF/6-31G* + ZPE, Table 6), but still smaller than in **8c** or **8d**. We attribute the larger silyl stabilization of 5.3 kcal mol^{-1} per exo-silyl group in the (SiNSiN) cycle to the presence of a cyclic $\underbrace{Si^1–N^2–Si^3–N^4}$ unit.

$$HN(SiH_3)_2 + NH_3 \rightarrow 2\ H_3SiNH_2 \qquad (10)$$

$$H_2NSiH_2NHSiH_3 + NH_3 \rightarrow H_3SiNH_2 + (H_2N)_2SiH_2 \qquad (11)$$

3.3. Molecular structure

The calculations reveal the following substituent effects on the geometry of the parent 1,3-cyclodisilazane, **8a**.

(1) Substitution of the silicon atoms in **8a** or in **8c** with four fluorine atoms results in a significant shortening of the Si · · · Si distance by 6.6 pm in **8b** and by 7.2 pm in **8d**. The Si–N bonds are also shortened although to a smaller extent, i.e. by 2.4 pm in **8b** and by 2.8 pm in **8d**. The N...N distance in **8b** remains unchanged relative to that in **8a**, but it is slightly shorter (by 0.9 pm) in **8d** than **8c**.

(2) Substitution of the hydrogens on the nitrogen atoms in **8a** or in **8b** by silyl groups also shortens significantly the Si · · · Si distance in **8c** or **8d**, i.e. by ca. 4.5 pm and 5.1 pm, respectively. The Si–N bonds are slightly elongated (i.e. by 1.1 pm in **8c** and 0.7 pm in **8d**).

(3) The combined effects of the four fluorines at silicon and of the two silyl groups on the nitrogen atoms, lead to an overall shortening of the endocyclic Si · · · Si distance in **8d** by 11.7 pm relative to **8a**.

Although the geometrical effects of both the fluorine and the silyl substituents are very large the calculated Si · · · Si distance in **8d** is still considerably longer (by 4.9 pm) than the experimentally measured Si · · · Si separations in **4** and in **7**. The Si–N bonds are also slightly shorter (by 1.7 pm) in **4** or **7** than calculated for **8d**.

The effect of the basis-set size and of electron correlation on the calculated geometries were evaluated for **8b**. The structure of **8b** was also optimized with the triply split and polarized 6-311 + G* basis-set [22] and with the Møller-Plesset second-order perturbation theory (MP2) [23] using the 6-31G* basis-set. These calculations showed that in **8b** both larger basis sets and electron correlation have relatively small effects on the geometry (Table 4), indicating that the calculated geometry of **8d** at HF/6-31G* is computationally reliable. On the basis of the computational results with **8b**, it is reasonable to conclude that expansion of the basis beyond 6-31G* may lead only to a small further shortening by ca. 1 pm of the Si · · · Si distance in **8d**, but the remaining difference of ca. 4 pm between the calculated geometry of **8d** and the experimental geometry of **4** (or **7**), is clearly too large to be attributed to deficiencies in the computational methods.

What is the reason for this relatively large difference between the calculated and the experimental structures? Partial optimization of the geometry of **8d** (in C_{2h} symmetry) with the Si · · · Si distance "frozen" at the experimentally determined value of 237.6 pm leads to a striking result. The partially optimized structure of **8d** constrained to have the experimental Si · · · Si distance is calculated to be only 0.6 kcal mol^{-1} (at HF/6-31G*) higher in energy than the fully optimized structure. Furthermore, the differences in the other structural parameters between the fully optimized and the partially constrained structures are small (Table 4, last entry). Additional calculations in which the Si · · · Si distance in **8a** and in **8d** were fixed at specific values, while optimizing all other geometrical parameters, revealed that the 1,3-disilazane cycle is extremly flexible with respect to bending of the NSiN angle (see Table 8 and Fig. 3). Elongation or shortening of the Si · · · Si distance in the non-substituted **8a** up to ± 10 pm leads to a rise in energy of only 2.4 kcal mol^{-1}! Elongation of the Si · · · Si distance leads to a small increase in the Si–N bond distance and inevitably to a decrease in the N · · · N distance. This unusual flexibility of the (SiNSiN) cycle, revealed by the parent **8a**, seems to be a general feature of 1,3-cyclodisilazanes regardless of the substitution pattern on the ring atoms. As can be seen in Fig. 3, the behavior of the parent **8a** and of the fully substituted **8d** is very similar. In particular, the dependence of the calculated relative energies on the degree of distortion from the equilibrium Si · · · Si distance (Δd) are nearly the same for the two compounds (Fig. 3).

These calculations suggest that the discrepancy of 5 pm in the endocyclic Si · · · Si distance found experimentally in **4** and **7** and calculated for the model **8d** is related to the very flat bending potential of the central angle in the 1,3-disilazane cycle. Because the potential energy surface of the 1,3-disilazane cycle is so flat, even small steric effects of the substituents or crystal lattice forces may influence strongly the Si · · · Si distance. In **4** and **7** the very bulky substituents at the nitrogens (R = $(Me_3C)_2PhSi$) and $(Me_3C)_2MeSi$, respectively) are probably responsible for the additional shortening of ca. 5 pm in the Si · · · Si separation in **4** and **7**.

Table 8
Selected geometrical parameters and relative energies (kcal mol^{-1}) at HF/6-31G* of partially optimized structures of **8a** and **8d** as a function of the Si · · · Si distance (bond lengths in pm, bond angles in deg.)[a]

	r(SiSi)	Δd[b]	r(NN)	r(NSi)	α(SiNSi)	α(NSiN)	ΔE[c]
8a							
	220	−34.2	249.1	166.2	82.91	97.09	29.2
	225	−29.2	247.0	167.0	84.67	95.33	20.9
	230	−24.2	244.2	168.0	86.39	93.61	14.1
	232	−22.2	244.2	168.4	87.07	92.93	11.7
	234	−20.2	243.4	168.8	87.75	92.25	9.7
	236	−18.2	242.6	169.2	88.42	91.58	7.8
	238	−16.2	241.8	169.7	89.08	90.92	6.1
	240	−14.2	241.1	170.1	89.74	90.26	4.7
	242	−12.2	240.4	170.6	90.38	89.62	3.4
	244	−10.2	239.6	171.0	91.04	88.96	2.4
	248	−6.2	238.3	172.0	92.30	87.70	0.9
	250	−4.2	237.6	172.4	92.92	87.08	0.4
eq.[d]	**254.2**	**0**	**236.2**	**173.4**	**94.20**	**85.80**	**0**
	258	3.8	235.0	174.5	95.33	84.67	0.3
	260	5.8	234.5	175.1	95.91	84.09	0.7
	264	9.8	233.4	176.2	97.05	82.95	2.0
	266	11.8	232.8	176.8	97.61	82.39	2.9
	268	13.8	232.3	177.3	98.16	81.84	4.0
	270	15.8	231.8	177.9	98.70	81.30	5.2
	272	17.8	231.4	178.5	99.23	80.77	6.6
	274	19.8	230.9	179.2	99.76	80.24	8.1
	276	21.8	230.5	179.8	100.27	79.73	9.7
	278	23.8	230.1	180.4	100.78	79.22	11.5
	280	25.8	229.7	181.1	101.28	78.72	13.4
	285	30.8	228.8	182.7	102.48	77.52	18.8
	300	45.8	226.9	188.1	105.79	74.21	39.5
8d							
	215	−27.5	253.2	166.1	80.68	99.32	20.4
	220	−22.5	251.2	167.0	82.42	97.58	13.3
	225	−17.5	249.3	167.9	84.12	95.88	7.9
	228	−14.5	248.2	168.5	85.13	94.87	5.3
	230	−12.5	247.5	169.0	85.79	94.21	3.9
	232	−10.5	246.8	169.4	86.40	93.60	2.7
	235	−7.5	245.8	170.0	87.40	92.60	1.4
X-ray	**237.6**	**−4.9**	**245.0**	**170.6**	**88.25**	**91.75**	**0.6**
	240	−2.5	244.2	171.2	89.01	90.99	0.2
eq.[d]	**242.5**	**0**	**243.4**	**171.8**	**89.80**	**90.20**	**0**
	243	1	243.1	172.0	90.10	89.90	0.02
	246	3.5	242.3	172.6	90.86	89.14	0.3
	255	12.5	239.9	175.0	93.50	86.50	3.5
	260	17.5	238.6	176.4	94.90	85.10	6.8
	265	22.5	237.5	177.9	96.26	83.74	11.0
	270	27.5	236.5	179.5	97.56	82.44	16.1
	280	37.5	234.9	182.7	100.01	79.99	28.9

[a] Geometry optimizations were performed within the constraints of C_{2h} symmetry.
[b] $\Delta d = r(\mathrm{SiSi})^{\mathrm{fix}} - r(\mathrm{SiSi})^{\mathrm{eq}}$.
[c] $\Delta E = E^{\mathrm{fix}} - E^{\mathrm{eq}}$.
[d] Fully optimized equilibrium geometry.
[e] Calculations carried out at the experimentally determined Si · · · Si distance in **4**.

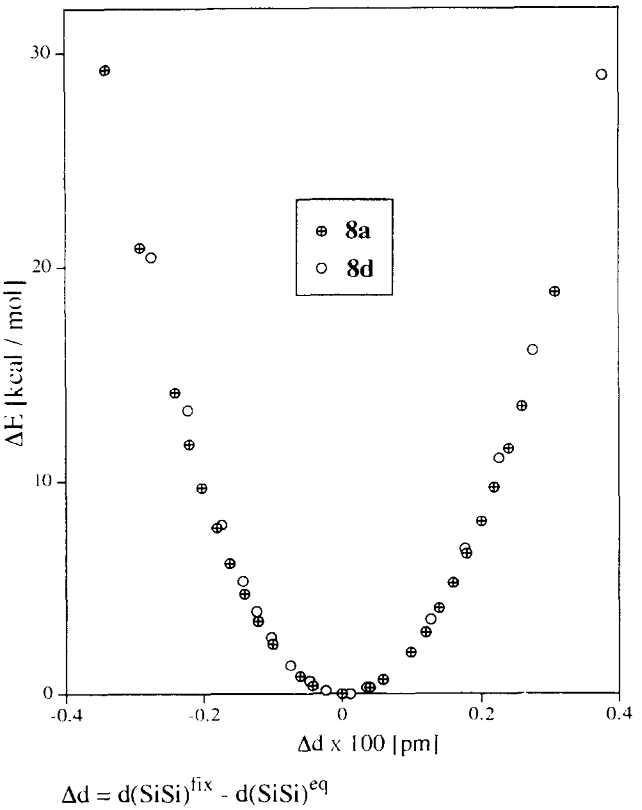


Fig. 3. Calculated energy (ΔE) as a function of the deviation, Δd, from the equilibrium Si · · · Si distances in **8a** and **8b** (HF/6-31G*).

3.4. Bonding

The bonding characteristics and the structure of the parent 1,3-cyclodisilazanes have been discussed in detail previously [24]. The major conclusion was that despite the relatively short Si · · · Si separations found in this type of molecule there is no significant bonding between the two silicon atoms. The same applies also to **4** and **7**, in which the Si · · · Si distance is shorter by 12 pm than in the parent 1,3-cyclodisilazane **8a**. Thus, NBO analysis [20] of the HF/6-31G* wave function reveals that in **8d** the Wiberg bond index [25] between the two silicon atoms is very small (0.0262, Table 9). Substitution of the four hydrogen atoms in **8a** or **8c** by four fluorine atoms increases the calculated Si · · · Si Wiberg bond index in **8b** and **8d** only slightly (Table 9). These Wiberg bond indexes calculated for **8a**–**8d** may be compared with the calculated Si–Si Wiberg bond index for disilane of 0.9851. The calculated bond length of disilane is 235.2 pm, only 2.4 pm shorter than the Si · · · Si separation in **4** (HF/6-31G*). The comparison indicates that in the 1,3-cyclodisilazanes **8** and in the experimentally studied **4** and **7** there is essentially no bonding interaction between the silicon atoms. Fi-

Table 9
Wiberg bond indexes for bonds between the ring atoms in the 1,3-cyclodisilazanes **8a**–**8d** (HF/6-31G*)

	8a	**8b**	**8c**	**8d**	**8d** [a]
Si···Si	0.0178	0.0230	0.0223	0.0262	0.0275
N···N	0.0282	0.0299	0.0229	0.0255	0.0259
Si–N	0.6432	0.6174	0.5875	0.5722	0.5746

[a] Partially optimized structure keeping the Si···Si distance at the experimentally determined distance in **4** of 237.6 pm.

nally we note that in all four compounds the ring nitrogen atoms are planar (Fig. 2). This is expected as each of the nitrogen atoms is bonded to at least two silicon atoms, substituents which are known to induce planarity at nitrogen, e.g. $(H_3Si)_2NH$, is planar [26].

The ^{29}Si NMR resonance of the SiF_2 group in **4** (−72.88 ppm) shows a significant upfield shift relative to that for H_2SiF_2 (−28.50 ppm [27]), Me_2SiF_2 (+4.4 ppm [28]), and for other known silicon-containing four-membered ring species such as $(R_2SiN)_2$ where R = Me (−2 to +6 ppm [9,10]), $(R_2SiO)_2$ (2–3 ppm [12,13]), or (SiNSiO) (−2.5 to +15 ppm [29,30]). The strong hyperconjugative interactions present in the $(F_2SiNR)_2$ cycle (see above) may be responsible for the strongly shielded ^{29}Si NMR signal of the ring silicon atom of **4**.

4. Conclusions

The following main conclusions can be drawn from this combined experimental and theoretical study regarding the structures of 1,3-cyclodisilazanes.

(1) The major shortening (ca. 12 pm out of ca. 17 pm) of the Si···Si distance in **4** and **7** compared to that in the parent **8a**, is a result of the combined substituent effects of the four fluorine and the two silyl substituents.

(2) The remaining ca. 5 pm shortening between the experimentally measured endocyclic Si···Si distance in **4** and **7** and the calculated Si···Si distance in the close model **8d** can be attributed to the very flat bending potential of the central angle in the 1,3-disilazane cycle. Because the potential energy surface of the 1,3-disilazane cycle is so flat, even small steric effects of the substituents or crystal lattice forces may influence strongly the Si···Si distance. In **4** and **7** the very bulky substituents at the nitrogens (R = $(Me_3C)_2PhSi$) and $(Me_3C)_2MeSi$, respectively) are probably responsible for this additional shortening.

(3) The flexibility of the (SiNSiN) cycle is not connected with the electronic properties of the substituents. The non-substituted **8a** and the fully substituted **8d** show nearly the same energy dependence on the distortion of the Si···Si distance.

(4) Despite the very short endocyclic Si···Si distance in **4** and **7** there are no bonding interactions between the ring silicon atoms.

5. Experimental details

All experiments have been carried out by exclusion of moisture. NMR spectra (20% solution in $CDCl_3$ or C_6D_6, TMS) were recorded on a Bruker AM 250 instrument.

5.1. Compounds 1 and 2

A solution of *n*-BuLi (0.1 mol) in hexane (100 ml) was treated with di-tert-butylphenylsilylamine (0.1 mol) and the mixture was refluxed for 2 h. When the lithiation was complete the solution was cooled to −75°C and either 0.05 mol of SiF_4 for **1** or 0.1 mol of SiF_4 for **2** was introduced. During 14 h the mixture was allowed to warm up, and the hexane was then distilled off. The products were separated from the LiF and fractionally distilled.

5.1.1. Bis[(di-tertbutylphenylsilyl)amino]difluorosilane (1)

$C_{28}H_{48}F_2N_2Si_3$ (534.9), Yield: 54%, bp: 200°C/0.01 mbar. MS (EI): m/z (%) = 477 (43) $[M-CMe_3]^+$. ^{1}H NMR: $\delta = 1.05$ ($SiC(CH_3)_3$, 36H), 7.30–7.40 (Ph–$H_{3/4/5}$, 6H), 7.70 (Ph–$H_{2/6}$, 4H). ^{13}C NMR: $\delta = 20.29$ ($SiCC_3$), 28.51 ($SiC\mathit{C}_3$), 127.33–135.27 (Ph–C). ^{19}F NMR: $\delta = 36.25$. ^{29}Si NMR: $\delta = -58.79$ (t, $^1J_{SiF2} = 216.5$ Hz), 1.60 ($SiC(CH_3)_3$).

5.1.2. (Di-tertbutylphenylsilyl)(trifluorosilyl)amine (2)

$C_{14}H_{24}F_3NSi_2$ (319.5), Yield: 47%, bp: 79°C/0.01 mbar. MS (EI): m/z (%) = 262 (14) $[M-CMe_3]^+$; (FI): m/z (%) = 319 (44) $[M^+]$. ^{1}H NMR: $\delta = 0.62$ (NH, 1H), 1.03 ($SiC(CH_3)_3$, 18H), 7.32–7.37 (Ph–$H_{3/4/5}$, 3H), 7.68 (Ph–$H_{2/6}$, 2H). ^{13}C NMR: $\delta = 20.32$ (q, $^4J_{CF} = 0.3$ Hz, $SiCC_3$), 28.46 (q, $^5J_{CF} = 0.5$ Hz, $SiC\mathit{C}_3$), 127.34–135.53 (Ph–C). ^{19}F NMR: $\delta = 18.60$. ^{15}N NMR: $\delta = -376.11$ (q, $^2J_{NF} = 4.7$ Hz, NH). ^{29}Si NMR: $\delta = -82.23$ (q, $^1J_{SiF} = 204.0$ Hz), 3.05 ($SiC(CH_3)_3$).

5.2. N,N′-dilithium-bis[(di-tert.-butylphenylsilyl)amino] difluorosilane (3)

A solution of (**1**) (0.01 mol) in *n*-hexane (50 ml) was lithiated at 0°C with *t*-BuLi (0.02 mol). After 1 h THF (20 ml) was added.

NMR spectra-solution: (C_6D_6, THF, hexane, TMS). $C_{28}H_{46}F_2Li_2N_2Si_3$ (684.6), Yield: 95%. ^{19}F NMR: $\delta = 45.00$. ^{7}Li NMR: $\delta = -0.89$. ^{29}Si NMR: $\delta = -60.68$ (t, $^1J_{SiF} = 225.2$ Hz), 0.02 ($SiC(CH_3)_3$).

5.3. *1,3-Bis(di-tertbutylphenylsilyl)-2.2.4.4-tetrafluoro-cycodisilazane (**4**)*

A solution of **3** (0.01 mol) in 50 ml of *n*-hexane was cooled to 0°C and treated with 0.01 mol of SiF_4. The mixture was stirred for 1 h, warmed to room temperature, and then refluxed until reaction was complete. The product was separated from the LiF and purified by recrystallization from hexane.

$C_{28}H_{46}F_4N_2Si_4$ (599.0), Yield: 41%, mp: 213°C. MS (EI): m/z (%) = 541 (18) [M-CMe_3]. ^1H NMR: $\delta =$ 1.13 ($SiC(CH_3)_3$, 36H), 7.31–7.40 (Ph–$H_{3/4/5}$, 6H), 7.71 (Ph–$H_{2/6}$, 4H). ^{13}C NMR: $\delta = 20.28$ ($SiCC_3$), 28.57 (q, $^5J_{CF} = 0.9$ Hz, $SiCC_3$), 127.50–135.42 (Ph–C). ^{19}F NMR: $\delta = 33.98$. ^{29}Si NMR: $\delta = -72.88$ (tt, $^1J_{SiF} = 254.2$ Hz, $^3J_{SiF} = 9.9$ Hz), 1.49 (q, $^3J_{SiF} = 1.0$ Hz, $SiC(CH_3)_3$).

5.4. *1,3-Bis(di-tert.-butylphenylsilyl)-2.4.4-trifluoro-1,3-diaza-2-phospha-4-sila-cyclobutane (**5**)*

A solution of **1** (0.01 mol) in 75 ml of *n*-hexane was cooled to 0°C and treated with 0.02 mol of *t*-BuLi. After 2.5 h the solution was cooled to −78°C and PF_3 was introduced. The solution was allowed to warm-up during 14 h and was then refluxed for 3 h. The product was separated from LiF and sublimed.

$C_{28}H_{46}F_3N_2PSi_3$ (582.9), Yield: 39%, mp: 162°C. MS (EI): m/z (%) = 525 (100) [M-CMe_3]$^+$. ^1H NMR: $\delta = 1.20$ (d, $^5J_{HP} = 8.9$ Hz, $SiC(CH_3)_3$, 36H), 7.17–7.22 (Ph–$H_{3/4/5}$, 6H), 7.86–7.88 (Ph–$H_{2/6}$, 4H). ^{19}F NMR: $\delta = 42.97$ (dd, $^2J_{FF} = 106.6$ Hz, $^3J_{FP} = 7.9$ Hz), 58.14 (ddd, $^2J_{FF} = 106.6$ Hz, $^4J_{FF} = 10.3$ Hz, $^3J_{FP} = 4.9$ Hz), 123.65 (dd, $^1J_{FP} = 1187.0$ Hz, $^4J_{FF} = 10.2$ Hz). ^{31}P NMR: $\delta = 134.50$ (d, $^1J_{PF} = 1187.0$ Hz). ^{29}Si NMR: $\delta = 2.36$ (dddd, $^2J_{SiP} = 3.1$ Hz, $^3J_{SiF} = 1.5$ Hz, $^3J_{SiF} =$ 0.9 Hz, $SiC(CH_3)_3$).

5.5. *Compounds **1** and **6***

A solution of either di-*tert*-butylmethylsilylamine (0.01 mol) or di-*tert*-butylphenylsilylamine (0.01 mol) in 30 ml of *n*-hexane was treated with 0.01 mol of *n*-BuLi. The mixture was refluxed for 1 h. The lithium reagent thus prepared was added to a solution of 2 (0.01 mol) in 25 ml of *n*-hexane cooled to 0°C. The solution was allowed to warm to room temperature during 1 h and was then refluxed for 3 h. The solid LiF was filtered off and the product, **1** or **6** was isolated by distillation.

5.5.1. *Bis[(di-tert-butylmethylsilyl)amino-(di-tert-butylphenylsilyl)amino]difluorosilane (**6**)*

$C_{26}H_{46}F_2N_2Si_3$ (472.88), Yield: 33%, mp: 65°C. MS (EI): m/z (%) = 415 (6) [M-CMe_3]$^+$. ^1H NMR: $\delta = 0.12$ ($SiCH_3$, 3H), 0.87 ($SiCH_3C(CH_3)_3$, 18H), 1.09 ($SiPhC(CH_3)_3$, 18H), 7.30–7.40 (Ph–$H_{3/4/5}$, 3H), 7.73 (Ph–$H_{2/6}$, 2H). ^{13}C NMR: $\delta = -8.11$ (CH_3), 19.88 ($SiCH_3CC_3$), 20.29 ($SiPhCC_3$), 27.68 ($SiCH_3CC_3$), 28.64 ($SiPhCC_3$), 127.19–135.04 (Ph–C). ^{19}F–NMR: $\delta = 33.17$ (dd, $^3J_{FH} = 2.5$ Hz; = 1.3 Hz).

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