Possibility of Heptacoordination at Silicon: Synthesis and X-ray Crystal Structures of Tris[8-(dimethylamino)naphthyl]silane and Tris[2-((dimethylamino)methyl)phenyl]fluorosilane

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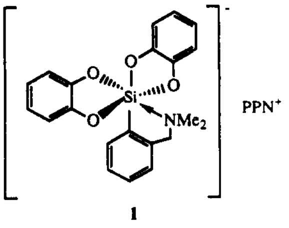
The title compounds exhibit an imperfect C_3 geometry: in addition to the four σ-bonds (Si–H or Si–F and three Si–C), three weak donating Si $\leftarrow$ N interactions ranging from 2.87 to 3.47(1) Å are also observed. The overall tetrahedral environment of the silicon (or germanium) atom is retained, and the structure can be described as a "tricapped tetrahedron". In most cases, and despite the large distances encountered, the nitrogen lone pair is directed toward the silicon atom opposite to an aryl–silicon bond. In the case of the fluorosilane no dative bonding opposite to the fluorine atom is observed, and the approach of the three amino groups occurs exclusively on the frontal faces of the Si–F bond. Steric hindrance appears as the critical factor preventing closer approach of the three nitrogen lone pairs to the silicon atom.

Introduction

In the course of our studies concerning hypercoordinated derivatives of silicon, we have observed that both penta- and hexacoordinated complexes display unusual reactivity toward nucleophilic reagents.[1] In the case of nucleophilic reactions at pentacoordinated silicon, intermediates (or transition states) containing a hexacoordinated silicon atom have been suggested.[1-3]

The interest in nucleophilic attack on pentacoordinated silicon species has been stimulated recently by the X-ray crystallographic determination of the structure of hexacoordinated silanes[4] and the case of the anionic complex **1**[5] is of particular interest. Following Dunitz's ideas,[6] the structure of this compound can be considered as a model of a nucleophilic attack at the pentacoordinated silicon.



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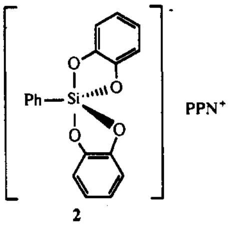

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Its short Si–N bond (2.16 Å) is in agreement with the reactivity observed for the reaction of the analogous pentacoordinated silicon anion **2** with nucleophiles.[7]

Hexacoordinated silicon compounds in neutral[8] and anionic[9] state have been described to react with nucleophilic reagents with a different reactivity from those observed for tetra- and pentacoordinated compounds.[3,10]

The nucleophilic attack at silicon atom in the case of compounds for which hexacoordination has been demonstrated in solution[9] could imply a heptacoordinated intermediate (or transition state). We have synthesized and examined the X-ray structure of compounds in which the central atom could become heptacoordinated by intramolecular donation from three chelating ligands bound to tetravalent metal (Si or Ge).

Results and Discussion

As in our previous work with penta- and hexacoordination at germanium and silicon[11] (M), the chosen

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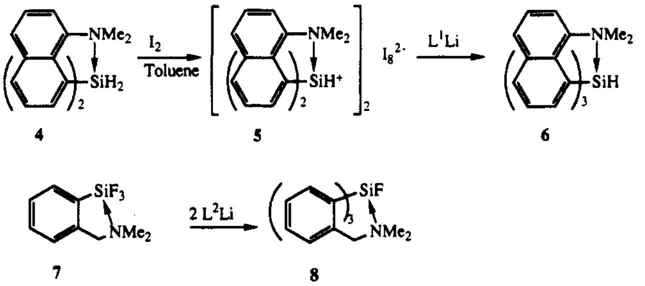
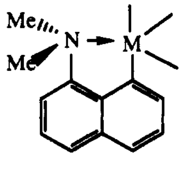
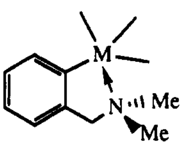
Scheme 1



bidentate amino ligands are of two types: (i) L^1, where the nitrogen is held by the rigidity of the aromatic ring system in a position for bonding to the central metal atom,[12] and (ii) L^2, where the nitrogen atom is free to interact or not with the metal.[13]



Ligand L^1



Ligand L^2

The syntheses of germane **3a**, $(L^2)_3GeH$, and silane **3b**, $(L^2)_3SiH$, have been previously described.[14] In addition we present here the syntheses and the X-ray structures of compounds **6** and **8**, bearing three L^1 and L^2 ligands (Scheme 1). These potentially heptacoordinated structures may be regarded as possible models for a further nucleophilic attack at a hexacoordinated silicon center.

As illustrated in Scheme 1, the hexacoordinated silane **4** treated by iodine in toluene gives salt **5**[15] which reacts with 1 equiv of [8-(dimethylamino)naphthyl]lithium to give the silane, $(L^1)_3SiH$, **6**. On the other hand, the trifluorosilane **7**[11] reacts with 2 equiv of [2-((dimethylamino)methyl)phenyl]lithium (L^2Li) to lead to the fluorosilane, $(L^2)_3SiF$, **8**.

All the spectroscopic data and the elemental analyses agree with the proposed structures in both solid state and solution.

Detailed Description of the Structure of Compounds $(L^2)_3GeH$ (3a) and $(L^2)_3SiH$ (3b). A preliminary account of the structures of the title compounds was given.[14] The X-ray crystal structure of the germane **3a** was first determined (Figure 1), but a careful examination of our silane **3b** sample failed to discover any crystal fitting both conditions of correct quality and size needed for a data collection. However, compounds **3a** and **3b** were shown to display almost the same unit cells and to have identical molecular shapes in the crystalline state. This isomorphism was readily established by two independent experiments:

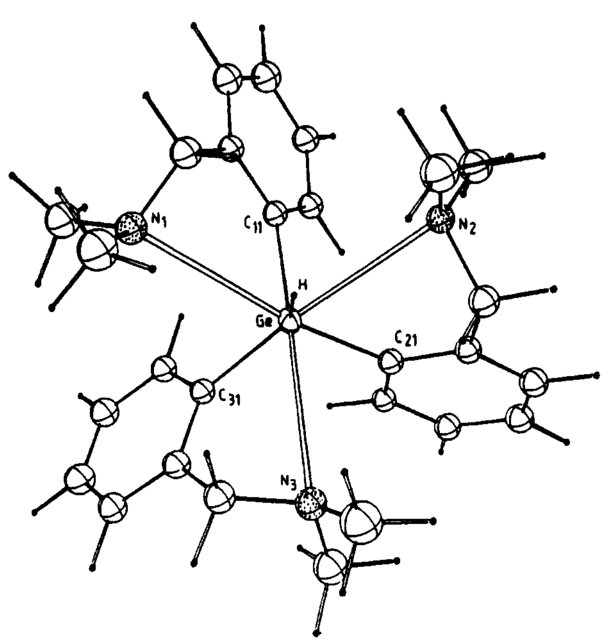


Figure 1. ORTEP drawing of germane **3a**, $(L^2)_3GeH$. The spheres are at the 20% probability level and the hydrogen atoms at an arbitrary size. Important bond distances (Å): average N···Ge = 3.05(1), av Ge–C(Ph) = 1.959(8), and Ge–H = 1.58(6). Angle mean values (deg): Ar–Ge–Ar = 107.3(3), H–Ge–Ar = 111(2), and N···Ge–H = 68(2). Typical angle values: C11–Ge–N3 = 176.8(3), C11–Ge–N2 = 77.7(3), and C11–Ge–N1 = 68.7(3).

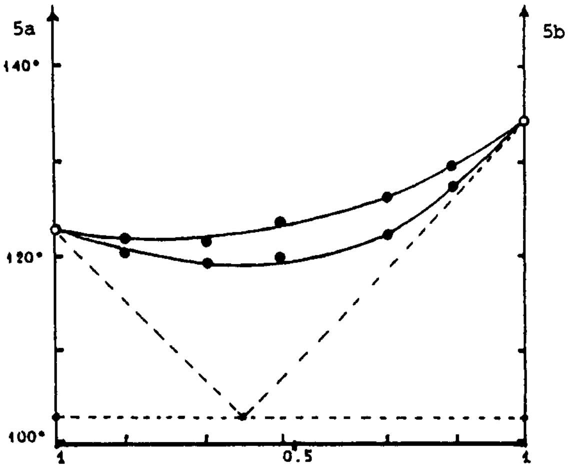


Figure 2. Phase diagram of compounds **3a** and **3b**. Microcalorimetric measurements (reference lithium metal) are as follows: **3a**, mp = 123.4 °C, $D(H_M)$ = 9029.6 cal·mol^{-1}; **3b**, mp = 134.4 °C, $D(H_M)$ = 10258 cal·mol^{-1}. Calculated eutectic: T = 103 °C. Molar fraction of **3b** in the mixture: 0.407.

(i) The thermal analysis diagrams of the mixtures of the two hydrides (**3a**, mp 123.4 °C; **3b**, mp 134.4 °C) using the Fregda method[16a] show a single solid solution (Figure 2) instead of the calculated eutectic (molar ratio of **3b** in the eutectic mixture, 40.7%; T = 103 °C).[16b] This result leaves no doubt about the structural identity of these two compounds since cocrystallization of isosteric silicon and germanium compounds of nearly the same molecular size is well known, the best example being the cocrystallization

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[15] The X-ray determination of the structure of compound **5** reveals an ionic structure with the bipyramidal pentacoordinated silyl cation associated with the anionic part I_8^{2-}. Brelière, C.; Carré, F.; Corriu, R. J. P.; Wong Chi Man, M., manuscript in preparation.

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of +α-NpMePhSiH and +α-NpMePhGeH studied by Brook.[16c]

(ii) The X-ray powder diagrams were examined, and an approximate unit cell could be determined in each case. The similarity between the two unit cell shapes is striking.[14] Very recently, an accurate determination of the unit cell of compound **3b** using a monocrystal gave us a good comparison: $(L^2)_3GeH$ (**3a**) parameters are 35.046(5), 16.787(1), 8.907(2) Å, β = 90.26(2)° and $(L^2)_3SiH$ (**3b**) parameters are 34.760(8), 16.742(4), 8.869(3) Å, β = 90.41(3)°, respectively.

The X-ray crystal structure of the germane **3a** has been fully determined; the observed isomorphism leads to the same crystal packing laws, and then we may assume the overall geometry of the silane **3b** is very close to that of compound **3a**. Only weak local modifications could arise from the slightly shorter Si–C(Ar) interatomic distance (1.872(7) Å),[17] compared to the Ge–Ph mean bond distance (1.959(8) Å). The remaining bond distances and angles values observed for compound **3a** are very likely to fit the structure of the silane **3b** with a good degree of accuracy.

The main structural feature of germane **3a**[14,18] is an approximate C_3 geometry (Figure 1). The basic tetrahedral geometry of the germane Ar_3GeH is retained with angles H–Ge–Ar ranging from 102° to 118(2)° (mean 112°) and Ar–Ge–Ar angles from 104.5° to 108.5(5)° (mean 106.7°), similar to the average of 106.3(5)° reported for tri-*o*-tolylgermane.[19] The Ar–Ge–N angle varies from 172.5° to 176.8(3)° (mean 174.0°). This angle is comparable to other angles measured in various penta-[11a,20] or hexacoordinated silicon species[4,5,21] and depends partially on the strain in the five-membered rings, e.g., Ge–C11–C16–C17–N1.

The approach of each dimethylamino ligand occurs opposite to an Ar–Ge bond. In other words, the observed geometry of germane **3a** results from three coordinations of the nitrogen atoms on the frontal faces of the Ge–H bond. The nitrogen–germanium distance varies slightly from 3.013 to 3.076(8) Å (mean 3.05 Å). The germanium van der Waals radius, as extrapolated from Bondi's work,[22] has a probable value between 2.1 and 2.2 Å. Then the N···Ge distances are 0.6–0.7 Å shorter than the sum of the van der Waals radii. These data are to be compared with the slightly stronger N···Si interactions reported for hexacoordinated species $(L^1)_2SiHF$ and $(L^1)_2SiH_2$,[4] 2.68(1) and 2.61(1) Å, respectively, and therefore are 0.97 and 1.04 Å shorter than the addition (2.10 + 1.55) of the corresponding van der Waals radii. We think this approach of the three dimethylamino ligands to germanium is largely restricted due to the bulkiness of the "axial" methyl groups, e.g., Me2, Me3, and Me5. This steric hindrance is probably less sensitive for the hexacoordinated silicon species. We will discuss that particular point through comparative description (*vide infra*, Table 1) of compounds **6** and **8** and of a related phosphine, $(L^1)_3P$ [23] (Figure 6).

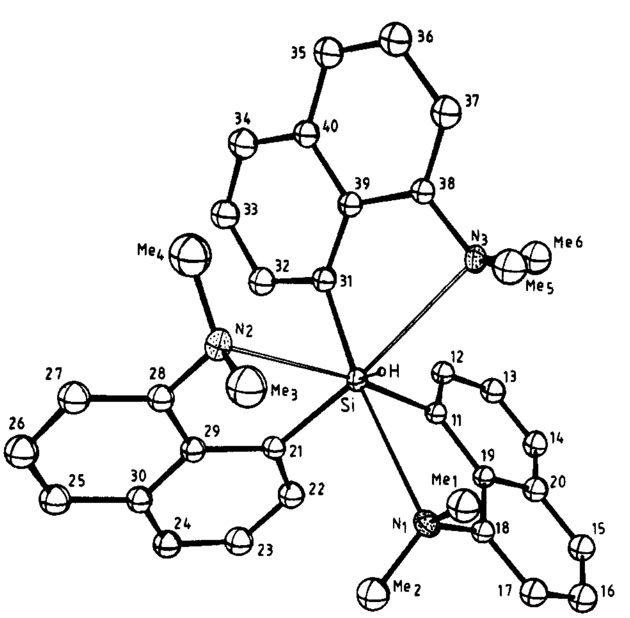

Figure 3. ORTEP drawing of silane **6**, $(L^1)_3SiH$. The spheres enclose 20% of the electron density. Interesting features are as follows: average N···Si = 2.895(7), av Si–C(Ar) = 1.900(8), and Si–H = 1.42(6) Å; mean angle values (deg): Ar–Si–Ar = 105.7(4), H–Si–Ar = 113(2), N···Si–H = 64(2), and Ar–Si···N = 172.7(3).

On the whole, the germanium atoms[18] largely maintain the basic tetrahedral geometry in spite of the approach of three nitrogen atoms; it could be described as a "tricapped tetrahedron" by analogy to the bicapped tetrahedron defined by Hoffman *et al.*[24]

Description of the Structure of Compound $(L^1)_3$SiH (6). Compound **6** exhibits the same imperfect C_3 axis (Figure 3) with Ar–Si–Ar, Ar–Si···N, and Ar–Si–H mean angles values comparable to those reported above for $(L^2)_3GeH$, **3a** (Table 5). Taking into account a covalent radius difference of ca. 0.08–0.09 Å between silicon and germanium,[17,25,26] we can put forward that the observed range of N···Si distances (Table 4) is close to the value one would expect for silane **3b**, i.e., 2.94 Å. Deformations of the angles around the C(1)–naphthyl ring atoms are observed (see Table 5): the mean Si–C(1)–C(9) angle is 127.0(6)°. In addition, the ability of the ligand to enlarge the Si···N separation is also due to an overall twisting of the naphthalene nucleus: the dihedral angles between the Si–C(1)–C(2)–C(9) and the N–C(7)–C(8)–C(9) least-squares mean planes are 2.7°, 6.3°, and 20.0° for each naphthyl ring; this last value yields the longest N···Si distance, i.e., 2.928(7) Å. Other twisted naphthalenes have been previously described,[27] especially in Tamao's group

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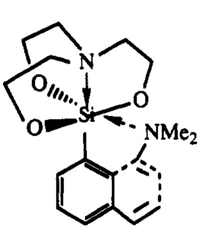
Table 1. van der Waals Contacts (Å) in Compounds L_3MX (M = Si, Ge; X = H, F) and L_3P

	M···N	H···N or F···N	H···Me[a] or F···Me	Me···Me	ref
sum of van der Waals radii	Si, N 3.65 Ge, N 3.70 P, N 3.35	H, N 2.75 F, N 3.02	H, Me 3.20 F, Me 3.47	Me, Me 4.0	22
3a $(L^2)_3GeH$					
(molecule 1)	3.055(8)[b]	2.89(6)[b]	3.20(6)[b]	5.31(2)[b]	14
(molecule 2)	3.042(8)[b]	2.82(6)[b]	3.12(6)[b]	5.11(2)[b]	
$(L^1)_3P$	2.834(6)	-	-	3.90 3.91 3.97(1)	23
6 $(L^1)_3SiH$	2.895(7)[b]	2.57 2.60 2.65(6)	2.67 2.71 2.74(6)	3.86 3.87 4.67(2)	this work
8 $(L^2)_3SiF$	3.267(5)[b]	2.80 2.98 3.16(1)	3.25 3.46 3.55(1)	5.47 5.49 6.09(1)	this work

[a] The methyl groups referred to here are all in the axial position. [b] Average of three values.

with organosilicon compounds.[28a] As an illustration, the silatrane **9** bearing the aminonaphthyl ligand L^1 as aromatic group on silicon was studied in our group.[28b]



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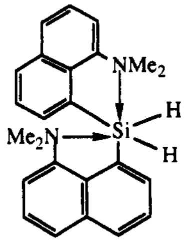

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The X-ray structure determination of **9** established that the silatrane cage is slightly deformed, and only a weak interaction (Si···N: 2.952(7) Å) is occurring between the Si atom and the NMe_2 moiety. The dihedral angle value calculated as above between the Si–C(1)–C(2)–C(9) and the N–C(7)–C(8)–C(9) least-squares planes is 23.3°. It appears that the dimethylaminonaphthyl ligand is slightly more efficient at participating in a heptacoordinated structure rather than changing a stable pentacoordinated silatrane to a hexacoordinated species.

The most repulsive interactions within the molecule of **6** are probably the H···Me contacts (see Table 1), lying in the range 2.64–2.74(6) Å (an average 0.5 Å less than the calculated sum of vdW radii).

From the molecular structure of silane **6** it is worth emphasizing that none of the NMe_2 groups has approached the silicon atom in the direction opposite to the Si–H bond, contrary to the case of **4**, $(L^1)_2SiH_2$[4], in which two types of dimethylamino bondings are observed.

Description of the Structure of Compound $(L^2)_3SiF$ (8). The Si–F bond is known to be substituted in most cases with inversion of the configuration at silicon,[3] and we have observed that intramolecular coordination always takes place opposite to the Si–F bond.[20,21,29] Hence, we thought it to be of interest to prepare and study fluorosilane $(L^2)_3SiF$, **8**, in which at least one of the NMe_2 ligands could be coordinated opposite to the Si–F bond.

We have found that the overall propeller shape of **8** is similar to that of **3a** and **3b** with the three NMe_2 ligands in the vicinity of the Si–F bond (Figures 4 and 5). However, the molecule deviates markedly from a rigorous C_3 symmetry: the N1···Si–C31 angle value is only 152.8(2)°, compared to N2···Si–C11 and N3···Si–C31, with a mean of 175.3(2)°.

The main feature to point out is the presence of the three unequal N···Si interactions. The N2···Si interatomic

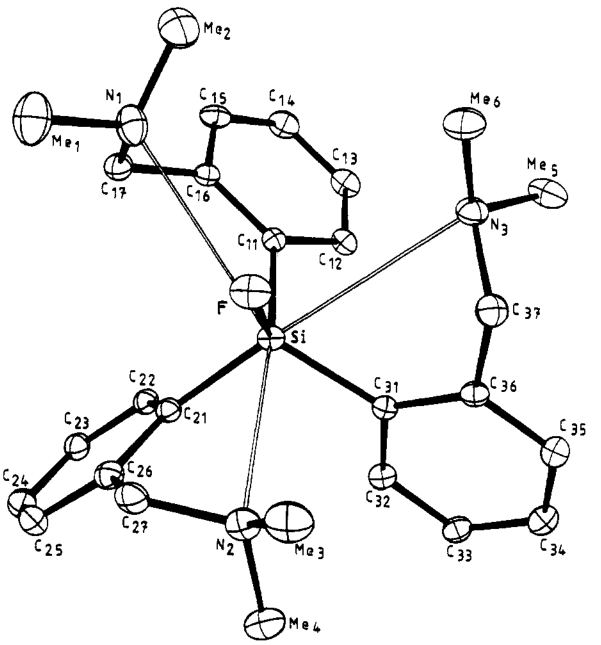

Figure 4. ORTEP drawing of fluorosilane **8**, $(L^2)_3SiF$. The ellipsoids are at the 10% probability level. Important bond distances (Å): Si–F = 1.627(3) and av Si–C(Ar) = 1.877(5). Angle mean values (deg): Ar–Si–Ar = 108.2(2), F–Si–Ar = 110.6(2), and N···Si–F = 65.3(2). The Si···N separations range is 3.004–3.489(6) Å.

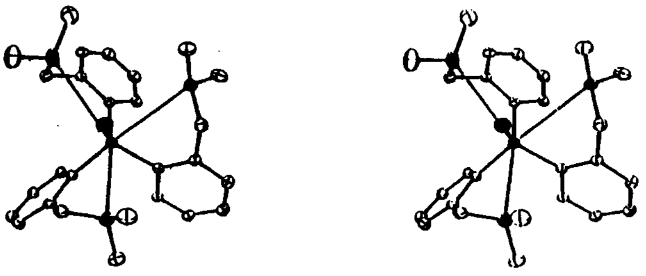

Figure 5. Stereoscopic view of fluorosilane **8**. Silicon, fluorine, and nitrogen atoms are plain black ellipsoids. Notice the particular shape of the five-membered-ring Si–C11–C16–C17–N1 with carbon atom C17 below the ring mean plane.

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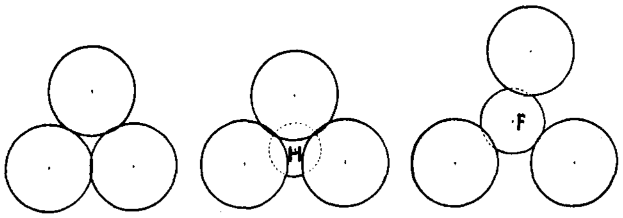
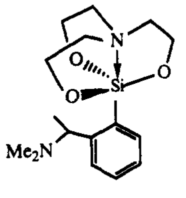


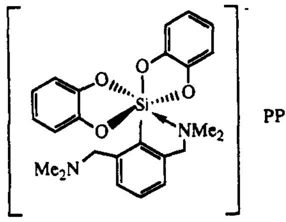
Figure 6. Diagram showing the van der Waals spheres of the axial methyl groups in compounds $(L^1)_3P$, $(L^1)_3SiH$ (6), and $(L^2)_3SiF$ (8). The molecules are viewed along their approximate C_3 axis.

distance, 3.004(4) Å, is in the range of the values observed for compounds **3a** and **6**. The N3···Si and N1···Si separations, 3.307(4) and 3.489(6) Å, fall just below the sum of the N and Si van der Waals radii (3.65 Å). The particular value of the N2···Si distance might suggest that compound **8** displays only pentacoordinate instead of heptacoordinate geometry. However, the overall shape of **8** differs from commonly known trigonal bipyramidal geometry of pentacoordinated silicon compounds[1c] since the nearest NMe_2 group to Si is *not* trans to the fluorine atom but actually to an aryl group. By analogy with compounds **3b** and **6**, in which the tetrahedral configuration owing to the four covalent σ bonds around Si is also preserved, we think that all three N···Si long-distance interactions are incipient dative bondings which cannot perform a more efficient coordination because of considerable hindrance around the silicon atom. In view of the electronegativity of the fluorine atom, and compared with compounds **3a** and **6**, one might expect the silicon atom of the $(L^2)_3SiF$ molecule to give rise to stronger attractive interactions with the nucleophilic amino groups. However, this fact is not observed due to the repulsive contacts between NMe_2 groups and the fluorine atom: the methyl to fluorine mean distance is also less than the sum of the van der Waals radii (cf. Table 1). These F···N and F···Me contacts prevent any closer approach between the silicon atom and any of the nitrogen atoms. This induces long distances between the axial Me groups (5.47–6.09 Å, see Figure 6).

Despite their very weak interactions, it is worth noting that all three dimethylamino ligands are still confined to the proximity of the silicon atom. We think this is unusual. It is probably due to the overall flexible character of the molecule. Indeed with **10**[28b] and **11**,[30] which both exhibit a rigid geometry, the NMe_2 group lies apart from the silicon atom. Compound **11**[30] was prepared from the bis-ortho chelating diamine aryl ligand extensively used in the transition metal chemistry.[31]



10



11

In both cases an extra coordination would have obviously produced important angle modifications at silicon.

Geometry in Solution. The NMR spectra are consistent with heptacoordination even in solution: (i) In the case of silane **6**, both ^1H and ^{13}C NMR spectra exhibit two diastereotopic NMe_2 resonances in agreement of the C_3 axis and the propeller shape observed in the crystal. The ^{29}Si spectrum shows an upfield doublet (δ = −25.86 ppm, $^1J_{SiH}$ = 284 Hz). This upfield shift although not large is in agreement with the previous results obtained for the analogous hypervalent (dimethylamino)naphthyl derivatives.[11a] (ii) In the case of [(dimethylamino)methyl]phenyl derivatives, both ^1H and ^{13}C spectra display only a singlet for the NMe_2 groups. This is due to the supplementary degree of freedom for the benzylic ligand for which an equilibrium exists between the coordinated and uncoordinated NMe_2. Thus the ^{29}Si NMR signal is shifted upfield, though not as much as might be expected.

Heptacoordinated Geometry. Although these N···Si attractive interactions are quite weak, especially in the case of the fluorosilane **8**, we have to underline that the preferred conformation we observed in each case is an imperfect "tricapped tetrahedron" involving the participation of *three* dimethylamino ligands and leading to a formally heptacoordinated species, in which the three nitrogen atoms are bound to silicon *trans* to the *ipso* carbons of the aromatic rings. This means also that each dimethylamino ligand, which "mimics" a nucleophilic attack at silicon, approaches this atom on the side of the Si–H or Si–F bond in a similar manner as in some cases of nucleophilic substitutions leading to retention of configuration.[10] However, one cannot completely rule out the possibility that the NMe_2 groups approach faces of the tetrahedron common to the Si–H (**6**) or Si–F (**8**) bonds, which might be due to the best packing in the crystal lattice. To sum up the above crystallographic results, three points of interest must be underlined here:

(i) Despite the dual possibility of the 2-[(dimethylamino)methyl]phenyl moiety to bring the nitrogen lone pair near silicon or to hold it apart, the coordination takes place without ambiguity. Although the link is probably weak, the direction of the extra bonding is essentially collinear with respect to the opposite Si–Ar bond. In each case the formally heptacoordinated molecular structure is observed in spite of severe steric hindrances limiting the flank access of the Si–H or Si–F bond.

(ii) Normally, fluorosilanes achieve penta-[20c,29] or hexacoordination[4,21b] with the additional ligand(s) bonded opposite to the fluorine(s). However, in the present case there is exclusive frontal coordination at the Si–F bond by the three equivalent amino groups.

(iii) The steric hindrance appears as a critical factor preventing a better access of the nitrogen lone pairs to the silicon atom. Figure 6 shows schematically the positions of the three "axial" methyl groups above the central atom: (a) The overall geometry of the molecules results from a close packing of the NMe_2 groups around the central atom. In fact, the length of the Si–N bond is controlled by the steric interactions taking place between the NMe_2 groups and the substituent X bound to Si (or Ge). Methyl groups and also the nitrogen atoms are located at distances from X which are close to the sum of the van der Waals radii. (b) Figure 6 shows the interactions observed for the phosphine $(L^1)_3P$, for silane **6**, and for fluorosilane **8**. In the case of the phosphine (lone pair at the central atom),

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[30] Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Réyé, C., to be published.

[31] Van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.

Table 2. Summary of Crystal Data, Intensity Measurements, and Refinement

	6 ($C_{36}H_{37}N_3Si$)	8 ($C_{27}H_{36}FN_3Si$)
cryst system	monoclinic	monoclinic
space group	$P2_1/a$	$C2/c$
a, Å	18.854(3)	28.094(11)
b, Å	16.319(3)	11.013(2)
c, Å	9.644(2)	17.629(3)
β, deg	100.82(2)	104.76(3)
vol, Å^3	2914.5	5274
mol wt	539.8	449.7
Z	4	8
d_{calcd}, g cm^{-3}	1.230	1.132
d_{measd}, g cm^{-3}	1.23(2)	1.11 (2)
cryst size, mm^3	0.20 × 0.25 × 0.60	0.35 × 0.40 × 0.65
cryst color	colorless	colorless
recryst solv	toluene[a]	hexane
mp, °C	296–296.5	108–109.5
method of data collectn	ω/θ	ω/θ
radiatn (graphite monochromated)	Mo Kα	Mo Kα
μ, cm^{-1}	1.05	1.07
2θ limits, deg	4–50	4–42
no. of unique reflectns	4087	2457
no. of obsd reflectns	1417	1294
final no. of variables	205	130
R	0.058	0.041
R_w	0.062	0.045
residual electron density	0.29	0.18

[a] Crystals with the composition $C_{36}H_{37}N_3Si$,2THF were obtained first by crystallization in tetrahydrofuran. Efflorescence occurred rapidly when these crystals were removed from the solvent.

Table 3. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) for 6

atom	x/a	y/b	z/c	U_{iso}, Å^2
Si	1973(1)	6280(2)	2477(2)	*a*
H	2377(31)	6849(36)	3427(65)	37(19)
C11	1676(4)	5366(5)	3446(8)	34(2)
C12	1801(4)	4608(5)	2905(9)	46(2)
C13	1597(4)	3860(6)	3506(9)	55(3)
C14	1287(4)	3881(5)	4640(9)	53(3)
C15	794(4)	4631(6)	6426(10)	59(3)
C16	617(5)	5340(6)	6986(11)	69(3)
C17	772(4)	6089(6)	6412(10)	60(3)
C18	1112(4)	6111(5)	5251(9)	40(2)
C19	1315(4)	5385(5)	4631(8)	38(2)
C20	1137(4)	4628(5)	5242(9)	47(2)
C21	1119(4)	6645(5)	1263(8)	38(2)
C22	518(4)	6150(5)	1238(9)	52(2)
C23	−156(5)	6293(6)	309(10)	65(3)
C24	−216(5)	6943(6)	−587(10)	59(3)
C25	303(5)	8113(6)	−1639(10)	60(3)
C26	855(5)	8598(6)	−1705(10)	68(3)
C27	1520(5)	8501(5)	−799(9)	59(3)
C28	1605(4)	7873(5)	178(9)	46(2)
C29	1040(4)	7330(5)	290(8)	41(2)
C30	362(4)	7448(5)	−655(9)	45(2)
C31	2570(4)	5881(5)	1243(9)	40(2)
C32	2240(4)	5777(5)	−163(9)	54(3)
C33	2645(5)	5631(5)	−1234(11)	63(3)
C34	3367(5)	5635(5)	−952(10)	63(3)
C35	4505(5)	5742(5)	766(10)	57(3)
C36	4863(5)	5792(6)	2101(10)	65(3)
C37	4486(5)	5806(5)	3242(10)	58(3)
C38	3744(4)	5800(5)	2969(9)	39(2)
C39	3338(4)	5806(5)	1562(9)	40(2)
C40	3747(4)	5735(5)	457(9)	47(2)
N1	1266(3)	6885(4)	4676(7)	*a*
Me1	1807(5)	7348(6)	5661(11)	71(3)
Me2	614(5)	7373(6)	4194(11)	72(3)
N2	2278(4)	7785(4)	1152(8)	*a*
Me3	2302(6)	8355(7)	2337(12)	92(4)
Me4	2915(6)	7840(7)	540(13)	96(4)
N3	3365(3)	5763(4)	4132(7)	*a*
Me5	3609(5)	6360(7)	5213(11)	78(3)
Me6	3405(5)	4938(6)	4727(11)	70(3)

[a] The anisotropic thermal parameters ($U_{11,22,33,23,13,12}$) for these atoms are as follows. Si: 0.036(1), 0.047(1), 0.027(1), 0.004(1), 0.003(1), 0.000(1). N1: 0.043(4), 0.059(5), 0.047(5), 0.000(4), 0.001(4), 0.009(4). N2: 0.060(5), 0.065(6), 0.050(5), 0.014(5), 0.014(4), 0.002(4). N3: 0.051(4), 0.051(5), 0.033(4), 0.003(4), 0.006(4), 0.004(4).

the three NMe_2 "axial" methyl groups lie in close contact with a distance of 3.92 Å which is a little bit less than the sum of the van der Waals radii. In the case of silane **6**, two methyl groups are adjacent to the third one with a distance of 3.86 Å while they are separated themselves by 4.67 Å. Finally with the fluorosilane **8**, the stronger interaction between nitrogen and fluorine atoms induces a longer separation of the NMe_2 groups (5.47, 5.49 and 6.09 Å; see Table 1).

The above results are not the demonstration that the reactions which have been previously described between hexacoordinated silicon complexes and nucleophiles are taking place through heptacoordinated intermediates (or transition state). However, from these results, we can conclude, whatever is geometry, that a heptacoordinated intermediate (or transition state) is a possibility which cannot be *a priori* excluded for explaining the mechanism of these reactions since we have shown the existence of a "tricapped tetrahedron" in which a silicon atom is subjected to three nucleophilic interactions.

Experimental Section

All the reactions were carried out under dry nitrogen in Schlenk tubes. ^1H, ^{19}F, and ^{29}Si NMR spectra were obtained using a Bruker 200-SY or a Bruker 250 AC spectrometer. ^1H and ^{29}Si chemical shifts are reported relative to Me_4Si and ^{19}F chemical shifts relative to $CFCl_3$. Mass spectra were obtained with a Jeol JMSD-100 instrument. Elemental analyses were performed by the Centre de Microanalyse du CNRS.

[8-(Dimethylamino)naphthyl]lithium,[12] [2-((dimethylamino)-methyl)phenyl]lithium,[13] bis[8-(dimethylamino)naphthyl]iodosilane,[15] and [2-((dimethylamino)methyl)phenyl]trifluorosilane[11a] were prepared by methods previously described.

Tris[2-((dimethylamino)methyl)phenyl]germane (3a) and Tris[2-((dimethylamino)methyl)phenyl]silane (3b). See ref 14.

Tris[8-(dimethylamino)naphthyl]silane (6). To bis[8-(dimethylamino)naphthyl]iodosilane, **5** (0.982 g, 2 mmol), in 5 cm^3 of dry THF was added dropwise a solution of [8-(dimethylamino)naphthyl]lithium in 20 cm^3 of dry THF at −60 °C. After complete addition, the solution was stirred at room temperature overnight. Hexane (5 cm^3) was then added, and the resulting solution was filtered, concentrated to about 15 cm^3, and cooled at −20 °C overnight. White crystals of tris[8-(dimethylamino)-naphthyl]silane (**6**) were obtained (0.744 g, 69%) from THF, mp 296–296.5 °C. Anal. Calcd for $C_{36}H_{37}N_3Si$: C, 80.10; H, 6.91; N, 7.78. Found: C, 80.65; H, 6.94; N, 7.92. Mass: 539 (38.7%, M$^+$). IR ($CHCl_3$): ν_{SiH} 2290 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.58 (9H, s, NMe_2), 2.66 (9H, s, NMe_2), 6.61 (1H, s, SiH), 7.0–7.75 ppm (12H, m, aromatic). ^{13}C NMR ($CDCl_3$): 46.7 and 49.6 (NCH_3), 119.8, 125.4, 125.8, 126.8, 128.8, 135.5, 136.5, 138.95, 138.0, 154.4 (aromatic). ^{29}Si NMR ($CDCl_3$, $\delta_{TMS} = 0$): δ −25.86 ppm, $^1J_{SiH}$ = 284 Hz.

Tris[2-((dimethylamino)methyl)phenyl]fluorosilane (8). To [2-((dimethylamino)methyl)phenyl]lithium (5 g, 3.5 10^{-2} M) in suspension in dry ether (50 cm^3) a solution of [2-((dimethylamino)methyl)phenyl]trifluorosilane (**7**) (4.4 g, 1.75 10^{-2} M) in ether (50 cm^3) was added dropwise at room temperature. After stirring overnight, the solution was filtered and the solvent removed in vacuo leading to colorless crystals (60%), after recrystallization from hexane–benzene (1:1), mp 111–111.5 °C. Anal. Calcd for $C_{27}H_{36}FN_3Si$: C, 72.12; H, 8.07; N, 9.34. Found: C, 71.97; H, 8.24; N, 9.21. Mass 449 (31%, M$^+$). ^1H NMR ($CDCl_3$): δ 2.40 (18H, s, NMe_2), 3.6 (6H, s, CH_2N), 7.2–7.7 (12H, m, aromatic). ^{19}F NMR ($CDCl_3$, $\delta(CFCl_3) = 0$): δ −170 ppm. ^{13}C

Table 4. Interatomic Distances (Å) in Compound $(L^1)_3Si-H$ (6)

Si–H	1.42(6)	C25–C26	1.32(1)
Si–C11	1.899(8)	C26–C27	1.40(1)
Si–C21	1.900(8)	C27–C28	1.38(1)
Si–C31	1.900(8)	C28–C29	1.41(1)
Si···N1	2.882(7)	C29–C21	1.45(1)
Si···N2	2.876(8)	C29–C30	1.44(1)
Si···N3	2.928(7)	N2–C28	1.44(1)
C11–C12	1.38(1)	N2–Me3	1.47(1)
C12–C13	1.43(1)	N2–Me4	1.44(1)
C13–C14	1.33(1)	C31–C32	1.39(1)
C14–C20	1.40(1)	C32–C33	1.42(1)
C20–C15	1.41(1)	C33–C34	1.34(1)
C15–C16	1.35(1)	C35–C40	1.42(1)
C16–C17	1.40(1)	C40–C35	1.40(1)
C17–C18	1.39(1)	C35–C36	1.34(1)
C18–C19	1.41(1)	C36–C37	1.42(1)
C19–C11	1.44(1)	C37–C38	1.38(1)
C19–C20	1.44(1)	C38–C39	1.43(1)
N1–C18	1.43(1)	C39–C31	1.43(1)
N1–Me1	1.47(1)	C39–C40	1.43(1)
N1–Me2	1.47(1)	N3–C38	1.44(1)
C21–C22	1.39(1)	N3–Me5	1.44(1)
C22–C23	1.43(1)	N3–Me6	1.46(1)
C23–C24	1.36(1)	H···Me(mean)	2.70(6)
C24–C30	1.38(1)	H···N(mean)	2.61(6)
C30–C25	1.43(1)	N···Si(mean)	2.895(7)

Table 5. Selected Bond Angles (deg) in Compound 6

C11–Si–C21	104.8(3)	C31–Si···N3	70.6(3)
C21–Si–C31	104.8(4)	C11–Si···N3	79.8(3)
C31–Si–C11	107.6(4)	C21–Si···N1	83.7(3)
H–Si–C11	112(2)	C31–Si···N2	79.8(3)
H–Si–C21	119(2)	H–Si···N1	64(2)
H–Si–C31	109(2)	H–Si···N2	67(2)
C11–Si···N2	172.4(3)	H–Si···N3	61(2)
C21–Si···N3	174.5(3)	N1···Si···N2	101.2(2)
C31–Si···N1	171.2(3)	N2···Si···N3	104.8(2)
C11–Si···N1	71.8(3)	N3···Si···N1	100.9(2)
C21–Si···N2	71.1(3)		
Si–C11–C12	115.6(6)	C29–C28–N2	118.4(7)
Si–C11–C19	127.0(6)	C27–C28–N2	119.7(7)
C19–C11–C12	117.4(7)	C27–C28–C29	121.8(8)
C11–C19–C18	124.2(7)	C28–N2···Si	98.7(5)
C19–C18–N1	119.0(7)		
C17–C18–N1	119.5(7)	Si–C31–C32	116.3(6)
C17–C18–C19	121.5(8)	Si–C31–C39	126.2(6)
C18–N1···Si	98.0(5)	C39–C31–C32	116.7(7)
		C31–C39–C38	123.1(7)
Si–C21–C22	115.0(6)	C39–C38–N3	119.1(6)
Si–C21–C29	127.8(5)	C37–C38–N3	119.1(7)
C29–C21–C22	117.0(7)	C37–C38–C39	121.8(8)
C21–C29–C28	123.3(7)	C38–N3···Si	95.1(4)

NMR ($CDCl_3$): 45.1 (NCH_3), 64.4 (CH_2N) 126.6, 129.7, 129.9, 136.9, 137.7, 145.4 (aromatic). ^{29}Si NMR ($CDCl_3$, $\delta_{TMS} = 0$): δ −9.86 ppm.

Crystal Structure of Tris[8-(dimethylamino)naphthyl]silane (6). Crystals of compound 6 were first isolated by cooling a saturated THF solution. Efflorescence occurred rapidly when these crystals were removed from the solvent. A further recrystallization from toluene gave a few stable colorless elongated prisms. Preliminary Weissenberg photographs established a monoclinic unit cell with the nonstandard space group $P2_1/a$ (No. 14) with general positions $\pm(x, y, z; {}^1/_2-x, {}^1/_2+y, -z)$. A small block was cut from a needle and sealed inside a Lindemann glass capillary with the [001] direction parallel to the ϕ axis of the diffractometer.

1. **X-ray Data Collection.** Data were collected at 22 °C on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). Lattice constants (Table 2) came from a least-squares refinement of 25 reflections obtained in the range $8.8° < 2\theta < 37.8°$. The intensities of three standard reflections were monitored after intervals of 60 min; no significant change in these intensities occurred. The structure amplitudes were obtained after the usual Lorentz and polarization reductions. Only the reflections having $\sigma(F)/F < 0.4$ were considered to be observed. No absorption corrections were made.

Table 8. Fractional Atomic Coordinates (×10⁴) for Compound 8, $(L^2)_3Si-F$

atom	*x/a*	*y/b*	*z/c*
Si	8698.4(5)	1967.4(13)	933.7(9)
F	9265(1)	1663(3)	1395(2)
C(11)	8300(2)	599(4)	995(3)
C(12)	7858(2)	808(5)	1219(3)
C(13)	7536(2)	−153(6)	1245(3)
C(14)	7644(2)	−1299(6)	1047(4)
C(15)	8074(2)	−1531(5)	822(3)
C(16)	8398(2)	−577(5)	786(3)
C(17)	8854(2)	−875(5)	511(3)
N(1)	9298(2)	−834(5)	1130(3)
Me(1)	9723(2)	−1111(9)	830(5)
Me(2)	9308(2)	−1592(7)	1787(4)
C(21)	8649(2)	2155(4)	−137(3)
C(22)	8234(2)	1695(4)	−682(3)
C(23)	8182(2)	1773(5)	−1483(3)
C(24)	8541(3)	2291(6)	−1765(4)
C(25)	8956(2)	2745(6)	−1260(4)
C(26)	9014(2)	2709(5)	−454(3)
C(27)	9456(2)	3265(5)	97(3)
N(2)	9313(1)	4068(4)	649(3)
Me(3)	9719(2)	4366(7)	1320(4)
Me(4)	9079(2)	5168(5)	271(4)
C(31)	8447(2)	3323(4)	1335(3)
C(32)	8087(2)	4001(4)	806(3)
C(33)	7874(2)	5032(5)	1034(3)
C(34)	8010(2)	5408(5)	1798(4)
C(35)	8363(2)	4741(5)	2339(3)
C(36)	8582(2)	3716(4)	2115(3)
C(37)	8955(2)	3038(5)	2728(3)
N(3)	8790(2)	1797(4)	2839(2)
Me(5)	8384(2)	1820(7)	3201(4)
Me(6)	9196(2)	1075(6)	3291(4)

2. **Structure Determination and Refinement.** Direct methods (SHELXS-86 program[32]) were used to solve the structure. The whole set of non-hydrogen atoms was obtained through a single calculation. After five cycles of least-squares refinement with isotopic thermal parameters to all atoms, the hydrogen atoms were positioned by calculation (SHELX-76 program),[33] and two isotropic thermal parameters were attributed to these hydrogen atoms according to the groups to which they were attached (methyl or naphthyl). Two more least-squares cycles followed by a difference Fourier synthesis gave the position of the hydrogen atom on silicon in the expected direction with the bond distance of 1.32 Å. Refinement was resumed with anisotropic thermal parameters for the silicon and nitrogen atoms, including the coordinates and isotropic thermal parameter of the $H_{(Si)}$ atom. At this stage, 1326 reflections having $\sigma(F)/F < 0.36$ were used, and the conventional R factor was 0.056. However, since convergence was difficult to achieve more data were included in the calculation (see Table 2), resulting in the decrease of all the shift over error ratios. Refinement converged to the final R value of 0.058.

The final atomic coordinates with the associated thermal parameters are listed in Table 3. The labeling scheme is given in Figure 3. Individual bond lengths are listed in Table 4 and important bond angles in Table 5. A full list of the bond angles (Table 6) and the list of calculated hydrogen atoms coordinates (Table 7) are available as supplementary material.

Crystal Structure of Tris[2-((dimethylamino)methyl)phenyl]fluorosilane (8). The fluorosilane 8 was crystallized by slow evaporation of a hexane solution. Large white polycrystalline aggregates were produced from which a small colorless block was detached and sealed inside a capillary. Preliminary

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[32] SHELXS-86, a program for crystal structure solution, G. M. Sheldrick, Institut für Anorganische Chemie der Universitat, Tammanstrasse 4, D3400 Göttingen, Germany.

[33] SHELX-76, a program for a crystal structure determination, G. M. Sheldrick, University of Cambridge, England, 1976.

Weissenberg photographs established a side-centered monoclinic unit cell with space group *Cc* or *C*2/*c* (from the systematic absences). The [001] direction was set parallel to the ϕ axis of the diffractometer.

1. **X-ray Data Collection.** Lattice constants (Table 2) came from the refinement of 25 reflections obtained in the range 14.3° $< 2\theta < 37.6°$. Data were collected in the manner described above. Only the reflections having $\sigma(F)/F < 0.42$ were considered to be observed. No absorption corrections were made.

2. **Structure Determination and Refinement.** The space group *C*2/*c* was chosen and its correctness confirmed by the successful refinement. Direct methods (MULTAN-80 program[34]) succeeded to solve the structure: the silicon and fluorine atoms, along with 11 phenyl ring carbon atoms were clearly revealed. A Fourier map phased on these atoms provided the remainder of the molecule, apart from the dimethylamino moiety $N1(Me)_2$ which was finally revealed by a subsequent difference Fourier synthesis. After four cycles of least-squares refinement with anisotropic thermal parameters to the silicon and fluorine atoms and isotropic parameters to the others, the hydrogen atoms were positioned by calculation (SHELX-76 program). Four more cycles gave a *R* value of 0.067. All atomic coordinates were then kept fixed while all the non-hydrogen atoms were given anisotropic thermal parameters. After three more cycles, the anisotropic thermal parameters for Si and F and the coordinates of all non-hydrogen atoms were again free to adjust. Refinement was resumed and converged to the final *R* value of 0.041, the anisotropic thermal parameters for N and C atoms being fixed during the last five cycles of refinement.

The final atomic coordinates are listed in Table 8. The labeling scheme is given in Figure 4. A stereoview is provided by Figure 5. Bond lengths and angles around the silicon atom are listed in Table 9. Bond lengths and angles in the sila five-membered rings are given in Table 10. The remaining interatomic distances and angles in the molecules (Table 11), the list of the anisotropic thermal parameters (Table 12), and the list of the calculated hydrogen atom coordinates (Table 13) are available as supplementary material.

Table 9. Interatomic Distances (Å) and Bond Angles (deg) around the Si Atom in Compound 8

Si–F	1.627(3)	Si···N(1)	3.489(6)
Si–C(11)	1.897(5)	Si···N(2)	3.004(4)
Si–C(21)	1.868(5)	Si···N(3)	3.307(4)
Si–C(31)	1.867(5)	Si···N(mean)	3.267
F–Si–C(11)	108.9(2)	N(1)···Si···N(2)	114.5(1)
F–Si–C(21)	109.9(2)	N(2)···Si···N(3)	108.3(1)
F–Si–C(31)	113.1(2)	N(3)···Si···N(1)	86.5(1)
F–Si···N(1)	51.9(2)	N(1)···Si–C(11)	64.5(2)
F–Si···N(2)	73.3(2)	N(2)···Si–C(21)	69.1(2)
F–Si···N(3)	70.6(2)	N(3)···Si–C(31)	66.4(2)
C(11)–Si–C(21)	104.6(2)	N(1)···Si–C(31)	152.8(2)
C(21)–Si–C(31)	110.9(2)	N(2)···Si–C(11)	173.7(2)
C(31)–Si–C(11)	109.1(2)	N(3)···Si–C(21)	176.9(2)
N(1)···Si–C(21)	96.2(2)		
N(2)···Si–C(31)	74.7(2)		
N(3)···Si–C(11)	77.9(2)		

Table 10. Important Bond Distances (Å) and Bond Angles (deg) in the Three Sila Five-Membered Rings for Compound 8

Si–C(11)–C(16)	124.3(3)	C(11)–C(16)	1.394(7)
C(11)–C(16)–C(17)	121.8(4)	C(16)–C(17)	1.517(7)
C(16)–C(17)–N(1)	113.0(4)	C(17)–N(1)	1.433(7)
C(17)–N(1)–Si	69.4(3)		
Si–C(21)–C(26)	124.6(4)	C(21)–C(26)	1.426(7)
C(21)–C(26)–C(27)	118.7(5)	C(26)–C(27)	1.498(8)
C(26)–C(27)–N(2)	111.1(4)	C(27)–N(2)	1.447(7)
C(27)–N(2)–Si	85.0(3)		
Si–C(31)–C(36)	125.9(4)	C(31)–C(36)	1.399(7)
C(31)–C(36)–C(37)	121.3(4)	C(36)–C(37)	1.500(7)
C(36)–C(37)–N(3)	111.8(4)	C(37)–N(3)	1.473(7)
C(37)–N(3)–Si	76.0(3)		

Supplementary Material Available: A full list of the bond angles for compound 6 (Table 6) along with a list of calculated hydrogen atoms coordinates (Table 7), interatomic distances and angles in the molecules of compound 8 (Table 11), a list of the anisotropic thermal parameters (Table 12), and a list of the calculated hydrogen atom coordinates (Table 13) (6 pages). Ordering information is given on any current masthead page.

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[34] MULTAN-80, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, P. Main, G. Germain and M. M. Woolfson, Universities of York, England and Louvain, Belgium, 1980.