non-hydrogen atoms were refined anisotropically.[15] Final least squares were performed using 452 variables. Final $R_f = 0.054$ and $R_w = 0.074$ with a GOF of 2.00. Selected bond distances and angles are presented in Table V. Complete atomic coordinates and anisotropic thermal factors as well as structure factor tables are included in the supplementary material.

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Registry No. **1a**, 139409-20-4; **1b**, 139409-21-5; **1c**, 139409-22-6; **1d**, 139409-27-1; **1e**, 139409-28-2; **1f**, 139409-29-3; **2** (equatorial isomer), 139409-25-9; **2** (axial isomer), 139492-54-9; **3** (equatorial/equatorial isomer), 139409-26-0; **3** (equatorial/axial isomer 1), 139492-55-0; **3** (equatorial/axial isomer 2), 139492-56-1; **3** (axial/axial isomer), 139492-57-2; **4**, 139409-23-7; **5**, 139409-24-8; Mo, 7439-98-7; $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_4$, 88008-34-8.

Supplementary Material Available: Figures showing two-dimensional COSY ^{31}P NMR spectra of complexes **2** and **3** and tables of atomic coordinates, bond angles and distances, and isotropic and anisotropic thermal parameters for **1d** and **1f** (24 pages); tables of observed and calculated structure factors (148 pages). Ordering information is given on any current masthead page.

Preparation and NMR Studies of Hexacoordinated Fluorosilicates: Nondissociative Fluorine Site Exchange within the Octahedral Complexes in Solution

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Stable 18-crown-6 potassium salts of hexacoordinated tetrafluorosilicates were readily prepared from pentacoordinated trifluorosilanes by reaction with KF/18-crown-6. It also proved possible to perform this transformation even in the absence of 18-crown-6. The crystal structure of the 18-crown-6 potassium salt of (8-(dimethylamino)naphthyl)tetrafluorosilicate was determined and the complex was found to exhibit slightly distorted octahedral geometry. Interestingly, the coordinative Si–N bond is shorter in this hexacoordinated complex (2.213 Å) than in the corresponding pentacoordinated one (2.318 Å). The results of solution NMR studies are consistent with the structure being octahedral. They indicate that intramolecular permutation of fluorine atoms occurs through a regular mechanism, such as the Bailar twist, without cleavage of either the Si–N or Si–F bonds. Similarly, a compound containing two hexacoordinated silicon atoms in the same molecule was prepared. Both silicons were found to be equivalent with fluorine site exchange occurring via a regular mechanism.

Introduction

Both penta- and hexacoordinated silicon compounds have received much attention in recent years. Most of the anionic complexes known have been obtained with exclusively electronegative groups bound directly to silicon,[1] and only a few hexacoordinated neutral or anionic species with more than one carbon–silicon bond have been described.[2] Possible applications for the organopentafluorosilanes are as reagents in organic synthesis,[3,4] and for the silicon tris(catecholates) as intermediates in the direct preparation of silanes from silica.[5]

The hexa- and pentafluorosilicate ions, SiF_6^- and $RSiF_5^-$ (R = alkyl or aryl group) were reported long ago as being air-stable compounds easily isolated in the pure state.[1b,2a] The structure of $2M^+,SiF_6^-$ (M: K^+, Na^+, NH_4^+) has been found to be based on a distorted octahedron.[1a,6]

Recently, Damrauer and Danahey described a general procedure for the preparation of pentacoordinated fluorosilicates in nonpolar solvents using KF solubilized by 18-crown-6.[7] The F^- ion released reacts with neutral tetracoordinated silicon compounds. The method has been applied to the preparation of a wide variety of pentacoordinated fluorosilicates.[8]

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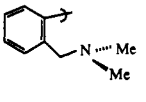
The formation of pentacoordinated silicion derivatives by use of crown ether/alkali-metal salts is a general process and has been extended to the preparation of pentacoordinated alkoxysilicates.[9a] Similar reactions lead to pentacoordinated hydridosilicates.[9b]

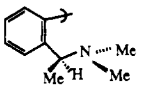
However, under these conditions, even with a large excess of crown ether/alkali-metal salt, the presence of hexacoordinated anions has never been detected in the case of simple alkyl or aryl substituents at silicon.[7,9]

We have previously found[2b] that hexacoordinated silicate salts can be isolated by incorporating two bidentate aromatic amine ligands of the type developed by van Koten[10,11] for stabilization of hypercoordinated species. We now report that pentacoordinated silicate anions containing a single such bidentate amine ligand react with KF/crown ether, or even with KF alone, to give hexacoordinated fluorosilicate anions, the salts of which may be isolated.

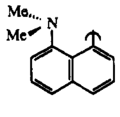
The bidentate amine ligands are of two types: those such as L^1 and L^2 where the nitrogen atom is free to interact or not with the metal[10] and those such as L^3 and L^4 where the nitrogen atom is held by the rigidity of the aromatic ring system in a position for bonding to the central metal atom.[11]



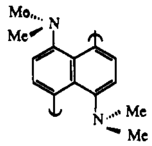
Ligand L^1



Ligand L^2



Ligand L^3



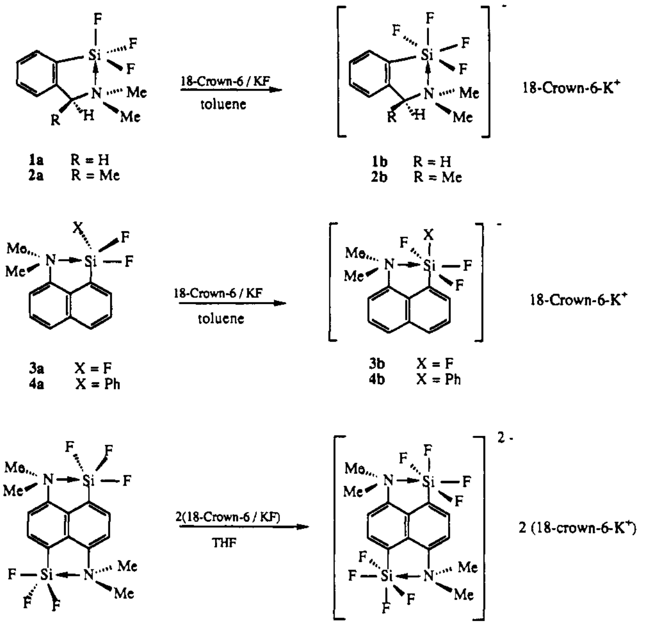
Ligand L^4

Results and Discussion

The preparation of the neutral pentacoordinated trifluorosilanes **1a**–**4a** has been previously described,[12] and we have recently prepared the bis(trifluorosilane) **5a**.[13] The structure of these pentacoordinated trifluorosilanes has been established as being trigonal bipyramidal.[14] Permutational ligand exchange was found to occur in solution via a regular process (pseudorotation) without dissociation of the Si–N dative bond.[15]

Pentacoordinated compounds **1a**–**4a** react with 1 equiv of 18-crown-6/potassium fluoride in toluene to give the corresponding stable hexacoordinated silicates **1b**–**4b** in high yields, as shown in Scheme I. Similarly, the pentacoordinated bis(trifluorosilane) **5a** reacts with 2 equiv of the same reagent in THF to afford the bis(tetrafluorosilicate) **5b** which, to our knowledge, is the first example of a compound containing two hexacoordinated silicon atoms. Compound **5b** was recrystallized from methanol to give colorless crystals containing two molecules of methanol per potassium ion, as shown by both the ^{1}H NMR spectrum and the results of elemental analysis. The hexacoordinate structure in solution is shown by the ^{29}Si and ^{19}F NMR data (see below), and that in the solid state by the results of the X-ray crystal structure determination for **3b**.

Scheme I



All the salts are crystalline, and they are remarkably stable toward hydrolysis, as previously observed for both hexa-[16] and pentacoordinated[7] fluorosilicon compounds. For instance, **3b** and **5b** could be recovered unchanged, as confirmed by the ^{1}H and ^{19}F NMR spectra, after being stirred in aqueous methanol for several hours at room temperature.

The pentacoordinated fluorosilanes are more reactive than are the tetracoordinated analogues toward KF. This is shown by the fact that **3a** reacts with KF in the absence of crown ether to give a very stable salt which is only slightly soluble in organic solvents, and which has identical spectroscopic characteristics to those of the crowned salt, **3b**. In contrast, the presence of crown ether is necessary for the reaction of tetracoordinated trifluorosilanes with KF giving the corresponding pentacoordinated tetrafluorosilicates.[8b]

Also, we have observed that whereas F^- coordination takes place with pentacoordinated di- and trifluorosilanes to give the corresponding hexacoordinated tri- and tetrafluorosilicates, the pentacoordinated monofluorosilicates do not react. For instance, **6** is recovered unchanged after treatment with excess KF/crown ether.

Attempts to obtain heptacoordinated silicates from the hexacoordinated species were unsuccessful. Thus, **7** was recovered quantitatively after treatment with KF/crown ether, even in the case of excess reagent. Treatment of the bis(benzylamine) derivative $(L^1)_2SiF_2$ with KF/crown ether

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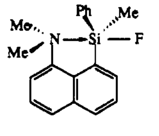

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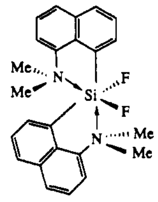

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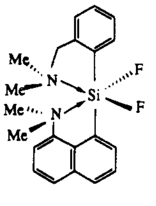

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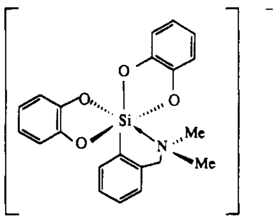

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resulted in cleavage of one Si–C bond and loss of one of the two L^1 chelate ligands with quantitative formation of $[L^1SiF_4]^-$.

Structure in the Solid State. The X-ray crystal structure determination shows that **3b** adopts a C_1 structure in a slightly distorted octahedral framework (Figure 1). One molecule of acetone of crystallization is present. The following are the main structural features:

(i) The four Si–F bonds are approximately equivalent (1.653–1.682 Å). The slight variations in Si–F bond lengths can be explained by crystal-packing factors, and in particular by the unequal interactions between three of the fluorines and the potassium cation,[17] the shortest K···F interaction (K···F^4, 2.679 (5) Å) corresponding to the longest SiF bond (Si–F^4, 1.682 (5) Å)[18] (Table I).

There are marked differences with respect to the corresponding pentacoordinated compound **3a**. The Si–F bonds in the hexacoordinated compound **3b** are longer than those in **3a** (1.612 Å axial; 1.568 and 1.574 Å equatorial).[19] This elongation may be the result of more extensive delocalization of the negative charge owing to the presence of the additional fluoride ligand. The Si–F bond lengths for **3b** lie in the same range as those for SiF_6^{2-} complexes.[1a,6] It should be noted that the Si–F^2 bond (Figure 1) opposite to the Si–N coordinative bond is the shortest in spite of some F···K interaction.

(ii) The Si–N distance in **3b** (2.213 (6) Å) is very short compared to the previously reported values (2.59 (1)–2.81 (1) Å) for the neutral hexacoordinated difluorosilane **8**.[2b] In order to explain this, one can consider **3b** as being formed by nucleophilic attack of the nitrogen on the anionic pentacoordinated species $ArSiF_4^-$ whereas **8** can be considered as being the result of nucleophilic attack by both nitrogens on the neutral species Ar_2SiF_2. The Si–N bond in **3b** is therefore shorter than those in **8**, consistent with the greater reactivity of anionic pentacoordinated silicon than of neutral tetracoordinated silicon toward nucleophiles. Likewise, **3b** possesses almost perfect octahedral symmetry whereas the structure of **8** is based on a bicapped Ar_2SiF_2 tetrahedron resulting from neutral tetracoordinate silicon undergoing 2-fold nucleophilic coordination.[2b]

(iii) The Si–N bond in the anionic hexacoordinated complex **3b** is shorter (2.213 Å) than that in the neutral pentacoordinated starting material **3a** (2.318 Å). In this case, **3a** can be considered as resulting from nucleophilic attack by nitrogen on the neutral tetracoordinate species $ArSiF_3$, thus explaining the longer bond (vide supra).

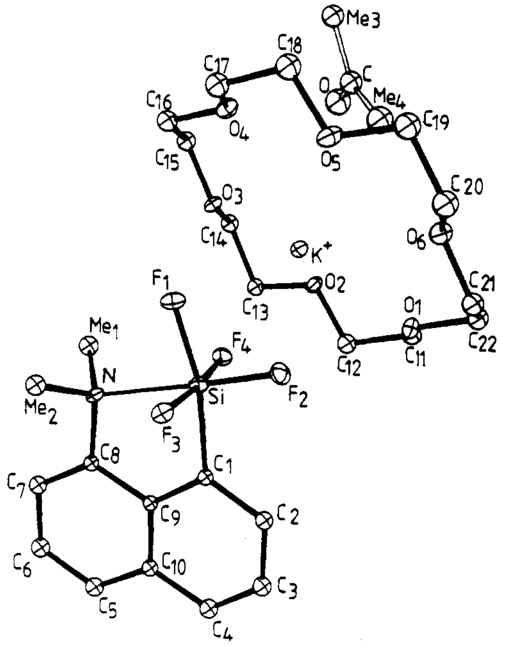

Figure 1. ORTEP drawing of the molecular structure of salt **3b** including one molecule of acetone. The ellipsoids and spheres enclose 10% of the electron density.

Table I. Interatomic Distances (Å) for Compound 3b with Esd's in Parentheses

Si–F(1)	1.669 (5)	K···O(3)	2.906 (6)
Si–F(2)	1.653 (5)	K···O(4)	3.030 (6)
Si–F(3)	1.669 (5)	K···O(5)	2.900 (6)
Si–F(4)	1.682 (5)	K···O(6)	2.874 (6)
Si–C(1)	1.893 (8)		
Si···N	2.213 (6)	O(1)–C(11)	1.41 (1)
		C(11)–C(12)	1.48 (1)
N–C(8)	1.463 (9)	C(12)–O(2)	1.45 (1)
N–Me(1)	1.483 (11)	O(2)–C(13)	1.42 (1)
N–Me(2)	1.475 (10)	C(13)–C(14)	1.49 (1)
C(1)–C(2)	1.42 (1)	C(14)–O(3)	1.41 (1)
C(2)–C(3)	1.41 (1)	O(3)–C(15)	1.41 (1)
C(3)–C(4)	1.32 (1)	C(15)–C(16)	1.46 (1)
C(4)–C(10)	1.44 (1)	C(16)–O(4)	1.42 (1)
C(10)–C(5)	1.40 (1)	O(4)–C(17)	1.41 (1)
C(5)–C(6)	1.37 (1)	C(17)–C(18)	1.45 (2)
C(6)–C(7)	1.42 (1)	C(18)–O(5)	1.45 (1)
C(7)–C(8)	1.36 (1)	O(5)–C(19)	1.42 (1)
C(8)–C(9)	1.42 (1)	C(19)–C(20)	1.51 (2)
C(9)–C(1)	1.38 (1)	C(20)–O(6)	1.40 (1)
C(9)–C(10)	1.44 (1)	O(6)–C(21)	1.45 (1)
		C(21)–C(22)	1.47 (1)
K···F(1)	2.899 (5)	C(22)–O(1)	1.43 (1)
K···F(2)	2.825 (5)		
K···F(4)	2.679 (5)	C–O	1.22 (2)
K···O(1)	2.900 (6)	C–Me(3)	1.48 (2)
K···O(2)	2.931 (6)	C–Me(4)	1.43 (2)

(iv) The structure of **3b** is very similar to that of the catecholate complex **9**, the latter also having slightly distorted octahedral geometry with a very short Si–N bond (2.157 Å).[20a]

In both cases, the geometry can be described in terms of a square bipyramid with the silicon atom slightly displaced in the direction away from the nitrogen, out of the

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[18] The potassium is displaced toward the silicon by ca. 0.84 Å from the mean plane defined by the six oxygens belonging to the crown ether.

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Table II. Bond Angles (deg) for Compound 3b

F(1)–Si–C(1)	165.0 (3)	C(5)–C(6)–C(7)	119.5 (8)
F(2)–Si···N	178.1 (3)	C(6)–C(7)–C(8)	119.5 (8)
F(3)–Si–F(4)	173.0 (3)	C(7)–C(8)–N	123.6 (7)
F(2)–Si–F(3)	94.5 (3)	C(7)–C(8)–C(9)	122.8 (7)
F(2)–Si–F(1)	94.4 (3)	C(9)–C(8)–N	113.5 (6)
F(2)–Si–F(4)	92.1 (2)	C(8)–C(9)–C(1)	119.2 (7)
F(2)–Si–C(1)	100.4 (3)	C(1)–C(9)–C(10)	123.7 (7)
N···Si–F(3)	86.6 (2)	C(8)–C(9)–C(10)	117.2 (6)
N···Si–F(1)	84.1 (2)		
N···Si–F(4)	86.7 (2)	C(22)–O(1)–C(11)	113.0 (7)
N···Si–C(1)	81.1 (3)	O(1)–C(11)–C(12)	108.3 (7)
C(1)–Si–F(3)	91.5 (3)	C(11)–C(12)–O(2)	106.7 (7)
F(3)–Si–F(1)	89.7 (3)	C(12)–O(2)–C(13)	111.9 (6)
F(1)–Si–F(4)	87.4 (3)	O(2)–C(13)–C(14)	107.8 (7)
F(4)–Si–C(1)	89.7 (3)	C(13)–C(14)–O(3)	108.2 (7)
Me(1)–N–Me(2)	109.3 (6)	C(14)–O(3)–C(15)	112.3 (6)
Me(1)–N–C(8)	108.8 (6)	O(3)–C(15)–C(16)	108.7 (7)
Me(2)–N–C(8)	109.4 (6)	C(15)–C(16)–O(4)	109.4 (7)
Me(1)–N···Si	110.2 (5)	C(16)–O(4)–C(17)	115.4 (7)
Me(2)–N···Si	111.4 (5)	O(4)–C(17)–C(18)	109.8 (8)
C(8)–N···Si	107.7 (4)	C(17)–C(18)–O(5)	108.4 (8)
Si–C(1)–C(9)	118.5 (6)	C(18)–O(5)–C(19)	113.8 (8)
Si–C(1)–C(2)	124.5 (6)	O(5)–C(19)–C(20)	109.5 (9)
C(9)–C(1)–C(2)	117.1 (7)	C(19)–C(20)–O(6)	108.5 (9)
C(1)–C(2)–C(3)	119.9 (7)	C(20)–O(6)–C(21)	110.7 (7)
C(2)–C(3)–C(4)	122.8 (8)	O(6)–C(21)–C(22)	107.4 (8)
C(3)–C(4)–C(10)	120.3 (8)	C(21)–C(22)–O(1)	108.2 (8)
C(4)–C(10)–C(9)	116.2 (7)		
C(4)–C(10)–C(5)	124.9 (7)	Me(3)–C–O	117 (1)
C(9)–C(10)–C(5)	119.0 (7)	Me(4)–C–O	125 (1)
C(10)–C(5)–C(6)	122.1 (8)	Me(3)–C–Me(4)	118 (1)

Table III. ^{29}Si NMR Data of Hexacoordinated Anionic Silicates Compared to Pentacoordinated Neutral Compounds[a]

compd	temp, °C	δ, ppm	J_{SiF}, Hz
1a L^1SiF_3	+25	−102.3 (q)	233.4
1b $L^1SiF_4^-$	+25	−160.1 (quint)	197.1
	−60	−161.6 (ddt)	218.4 (SiX_2), 186.7 (SiY), and 147.6 (SiZ)
2a L^2SiF_3	+25	−103.2 (q)	231.5
2b $L^2SiF_4^-$	+25	−159.9 (quint)	193.1
	−40	−161.1 (dt)	219.0 (SiX_2), 184.0 (SiY), and 146.3 (SiZ)
3a L^3SiF_3	+25	−96 (q)	234
3b $L^3SiF_4^{-\,b}$	+25	−156.3 (ddt)	223 (SiX_2), 181.2 (SiY), and 149.8 (SiZ)
4a L^3SiPhF_2	+25	−51.9	267.2
4b $L^3SiPhF_3^{-\,b}$	+25	−137.0 (dt)	246.2 (SiX_2) and 196.7 (SiY)
5a $L^4(SiF_3)_2$	+25	−94.3 (q)	236.5
5b $L^4(SiF_4)_2^{2-}$	+25	−154.5 (ddt)	225.3 (SiX_2), 184.0 (SiY), and 117.6 (SiZ)

[a] Solvent: CD_2Cl_2: δ is relative to $CFCl_3$. [b] Solvent: DMSO-d_6.

mean plane defined by the four ligand atoms constituting the pyramid base. In **3b**, the silicon is displaced 0.16 Å from the $C^1F^4F^1F^3$ mean plane, and in the case of **9** the displacement is 0.10 Å from the mean plane defined by three of the catecholate oxygens and the aromatic carbon.[20b]

Structure in Solution. The ^{29}Si and ^{19}F NMR results are consistent with a symmetrical hexacoordinated octahedral structure similar to the geometry observed in the solid state for **3b**.

The ^{29}Si NMR chemical shifts for **1b–5b** lie in the range expected for hexacoordinated silicon compounds,[21a] the resonances occurring ca. 50 ppm (85 ppm in the case of **4b**) upfield of those for the corresponding pentacoordinated starting materials. The ^{29}Si–^{19}F coupling constants for the hexacoordinated compounds are smaller than those for the corresponding pentacoordinated starting materials (Table III). Coupling constants between silicon and ligands have been previously observed to decrease with increased coordination number, as a result of reduced s character in the Si–ligand bonds.[21b]

Table IV. ^{19}F NMR Data of Hexacoordinated Anionic Silicates[a]

compd	temp, °C	δ, ppm	$^2J_{\mathrm{FF}}$, Hz
1b $L^1SiF_4^-$	+50	−123.2 (s)	
	+25[b]	no signal	
	−70[b]	−118.8 (d, 2 F)	20
		−131.8 (d, 1 F)	10
		−139.8 (dt, 1 F)	20 and 10
2b $L^2SiF_4^-$	+25[b]	no signal	
	−60[b]	−109.1 (dd, 1 F)	15
		−128.1 (dd, 1 F)	19
		−132.1 (dd, 1 F)	10
		−140.0 (ddd, 1 F)	19, 15, and 10
3b $L^3SiF_4^-$	+25	−108 (d, 2 F)	21
		−139 (d, 1 F)	14
		−144 (dt, 1 F)	21 and 14
4b $L^3SiPhF_3^-$	+25	−105.2 (s, 2 F)	
		−119.3 (s, 1 F)	
	+90	no signal	
5b $L^4(SiF_4)_2^{2-}$	+25	−108.4 (dd, 2 F)	22 and 6
		−137.8 (dt, 1 F)	13 and 6
		−142.0 (dt, 1 F)	22 and 13

[a] Solvent: DMSO-d_6; δ is relative to $CFCl_3$. [b] Solvent: CD_2Cl_2; at 25 °C (coalescence temperature) no signal appeared, but in DMSO we observed a broad singlet.

Table V. Free Energies of Activation, $\Delta G_F^{\ddagger}$, for Equivalence of $-SiF_4$ and $-SiF_3$ Groups in Fluorosilicates[a]

compd	$\Delta G_F^{\ddagger}$, kcal·mol^{-1}	temp, °C
1b $L^1SiF_4^-$	11	+10
2b $L^2SiF_4^{-\,b}$	11	+20
3b $L^3SiF_4^{-\,c}$	15	+90
4b $L^3SiPhF_3^{-\,c}$	15	+80

[a] Solvent: CD_2Cl_2. $\Delta G_F^{\ddagger}$ was calculated at the temperature just before the disappearance of the ^{19}F NMR signals. [b] In this particular case, an additional free energy of activation, $\Delta G_H^{\ddagger}$, with a value of 14 kcal·mol^{-1} could be obtained from the coalescence temperature (+17 °C) in the ^{1}H NMR spectrum. [c] Solvent: DMSO.

For all the compounds **1b–5b**, ^{29}Si–^{19}F coupling persists throughout the temperature range studied, and therefore intermolecular fluoride exchange, which has been proposed as occurring in the case of pentacoordinated silicates,[1c,23] can be ruled out. However, intramolecular fluoride site exchange does occur since all the fluorines become equivalent as the temperature is raised. The ^{19}F NMR coalescence temperatures can be used in the Eyring equation to calculate the values of the free energy of activation ($\Delta G_F^{\ddagger}$) for this permutational site-exchange process.[21c,d] As can be seen in Table V, the $\Delta G_F^{\ddagger}$ values lie in the range 11–15 kcal mol^{-1}. Although the F$^-$ site-exchange process does not involve Si–F bond breaking since the ^{29}Si–^{19}F coupling is always present, rupture of the Si–N bond can be envisaged leading to scrambling of the F$^-$ sites. However, this dissociative mechanism can be eliminated since, as discussed below, for the benzylamine derivative

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(21) (a) Marsmann, H. *NMR Basic Princ. Prog.* **1981**, *17*, 65. (b) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *368*, C25. (c) Gunther, H. *NMR Spectroscopy*; Wiley: Chichester, U.K., 1980; p 243. (d) The term $\Delta G_F^{\ddagger}$ denotes the free energy of activation measured using ^{19}F NMR spectroscopy and $\Delta G_H^{\ddagger}$ that measured using ^{1}H NMR spectroscopy.

(22) Kleboth, K.; Rode, B. M. *Monatsh. Chem.* **1974**, *105*, 815.

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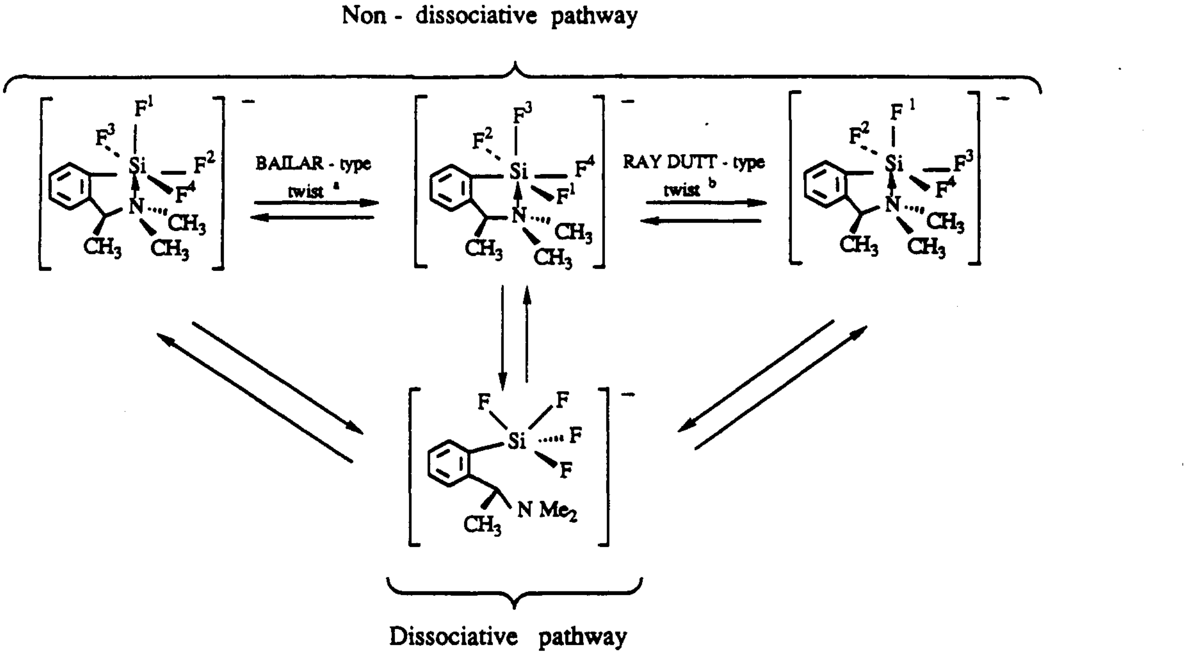
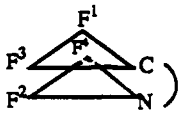
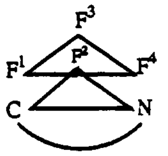
(24) Brelière, C.; Corriu, R. J. P.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1834.

(25) (a) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165. (b) Ray, P.; Dutt, N. K. *J. Ind. Chem. Soc.* **1943**, *20*, 81. (c) Rodger, A.; Johnson, B. F. G. *Inorg. Chem.* **1988**, *27*, 3061.

Scheme II. Possible Mechanisms for Intramolecular F^- Site Interchange in 2b



[a] 120° Rotation of ligands in N F^4 F^2 face via  intermediate.

[b] 120° Rotation of ligands in F^1 F^3 F^4 face via  intermediate.

2b the barrier to rotation/inversion at N is found by ^1H NMR spectroscopy to be greater than the barrier to F^- site exchange. Hence this must also be so for the naphthylamine derivatives since in this case the Si–N bond is imposed by the ligand geometry. Si–N bond rupture is therefore not implicated in site exchange which must instead occur via regular, nondissociative mechanisms such as Bailar- and Ray–Dutt-type twists, as illustrated in Scheme II, or other possible processes.[26] Similar F^- site-exchange phenomena have been observed for cyclic and acyclic trifluorosilicates[8a,c] ($\Delta G_F^{\ddagger}$ for the cyclic compound has the very low value of 10 kcal mol^{-1}) and also for neutral hexacoordinated systems (e.g. 7[24]). Although the Bailar twist[25a] and Ray–Dutt twist[25b] were originally applied to isomerization of tris chelate complexes, the analogous processes can also be envisaged in the case of octahedral compounds such as those studied in the present work, with a single chelating ligand and four monodentate ligands. The intermediates in both processes are similar.[25c] In the case of the Bailar-type twist, the chelate connects the two triangular faces rotating with respect to each other, whereas in the Ray–Dutt-type twist the chelate is contained in one of the two faces, as shown in Scheme II.

Benzylamine Derivatives 1b and 2b. For compound **2b**, in addition to $\Delta G_F^{\ddagger}$ derived from the ^{19}F NMR coalescence temperature for the process of F^- site exchange as observed for all the complexes **1b**–**5b**, a different free energy of activation, $\Delta G_H^{\ddagger}$,[21d] can be obtained from the ^1H NMR coalescence temperature for the protons belonging to the two methyl groups which are diastereotopic because of chirality at the α-carbon. $\Delta G_H^{\ddagger}$ corresponds to the process of rotation/inversion at N, and is hence related to rupture of the Si–N coordinative bond. Its value was found to be 14 kcal mol^{-1} for **2b** (Table V), which if anything is slightly higher than that observed (13 kcal mol^{-1}) for the corresponding pentacoordinated silane **2a**.[15a] The greater electrophilicity of pentacoordinated with respect to tetracoordinated silicon might be expected to result in the Si–N bond being stronger in hexacoordinated than in pentacoordinated complexes. The $\Delta G_F^{\ddagger}$ measured from the ^{19}F NMR spectrum is lower (11 kcal mol^{-1}) for both **1b** and **2b**. It can therefore be concluded that the fluxionality at silicon occurs via a regular mechanism which does not involve rupture of the Si–N bond.

The ^{19}F NMR spectrum of **1b** exhibits three distinct coupled signals at −70 °C corresponding to an X_2YZ coupled system. In the case of **2b**, there are four coupled signals characteristic of an XX′YZ system. Unfortunately, it was not possible to determine all the coupling constants with our experimental procedure. No trans coupling is observed between the two trans fluorines, and one of the two other fluorines does not couple with the trans fluorines. Of the four signals, one is a doublet of doublets of doublets, the other three being doublets with coupling constants of 15, 19, and 10 Hz (Table IV).

At room temperature, the ^{19}F NMR spectra of **1b** and **2b** disappear because of line broadening, but at 50 °C a single resonance from the four magnetically equivalent fluorines is observed.

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(26) (a) Pignolet, L. H. *Top. Curr. Chem.* **1975**, *56*, 91 and references therein. (b) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

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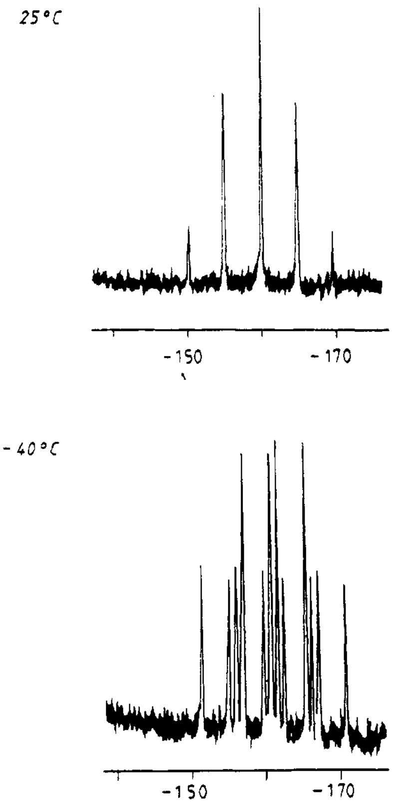

Figure 2. Variable-temperature ^{29}Si NMR spectra for **2b** (in CD_2Cl_2/TMS).

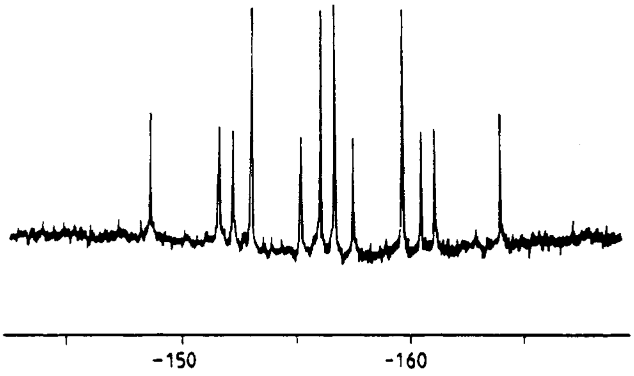

Figure 3. ^{29}Si NMR spectrum of complex **3b** (in DMSO-d_6, relative to TMS).

The ^{29}Si NMR spectrum for **1b** at −60 °C shows a doublet of doublets of triplets corresponding to an SiX_2YZ coupled system containing four fluorines of which two are equivalent. In the case **2b** (Figure 2), an SiX_2YZ pattern is also observed in spite of the benzylic chiral center which might have been expected to give rise to an SiXX′YZ system. Presumably, two of the J_{SiF} coupling constants have the same value.

At room temperature, the ^{29}Si NMR spectra for both **1b** and **2b** (Figure 2) show a quintet due to coupling of the silicon atom with four equivalent fluorines undergoing site exchange via a nondissociative mechanism as discussed above (Scheme II).

Naphthylamine Derivatives 3b–5b. The ^{29}Si NMR spectra of both **3b** (Figure 3) and **5b** show a doublet of doublets of triplets arising from coupling with the four fluorine ligands, only two of which (F^3 and F^4 in Figure 1) are magnetically equivalent. Three coupling constants can be measured (Table III). Both silicon groupings in **5b** are equivalent. In the case of **4b**, a doublet of triplets is observed arising from coupling of silicon with three fluorine atoms, two of them being equivalent.

It can be noted that, for each complex, all the $^1J_{SiF}$ values are very different: for instance 223, 181.2, and 149.8 Hz are observed for **3b**. These values are smaller than those observed for the neutral pentacoordinated starting materials (267.2–233.4 Hz). The highest values are observed for the two magnetically equivalent fluorine atoms, and there is no relationship between the coupling constants and the observed Si–F bond lengths in compound **3b**.[1a,22]

The room-temperature ^{19}F NMR spectrum (Table IV) for complex **5b** exhibits three fluorine signals due to the symmetrical structure and corresponding to an X_2YZ pattern for the fluorine resonances (Figure 4) with three unequal cis F–F coupling constants (22, 13, and 6 Hz). Similarly, complex **3b** also exhibits three resonances but only two couplings are observed. It was not possible to measure all the couplings because lines are too broad and coupling constants are very weak as expected.[7,8] In the case of **4b** two resonances are observed.

At higher temperature ($T > 90$ °C), ^{19}F NMR spectra of **3b** and **4b** show only a single resonance characteristic of four and three equivalent fluorine atoms, respectively. The coalescence temperatures correspond to a value of 15 kcal mol^{-1} for the $\Delta G_F{}^{*}$ of this process (Table V).

Unfortunately, in the case of **5b** a temperature-dependent ^{19}F NMR study was not possible because the compound is thermally unstable above 90 °C. The ^{1}H NMR spectra for compounds **3b–5b** (see Experimental Section) are as expected. It may therefore be concluded that the compounds with naphthylamine bidentate groups are hexacoordinated and that, as observed by ^{19}F NMR spectroscopy at 235.192 MHz, site exchange of the fluorine atoms occurs at temperatures in excess of ca. 90 °C, the $\Delta G_F{}^{*}$ for this process being on the order of 15 kcal mol^{-1}. This $\Delta G_F{}^{*}$ value is lower than that for the $\Delta G_H{}^{*}$ we have

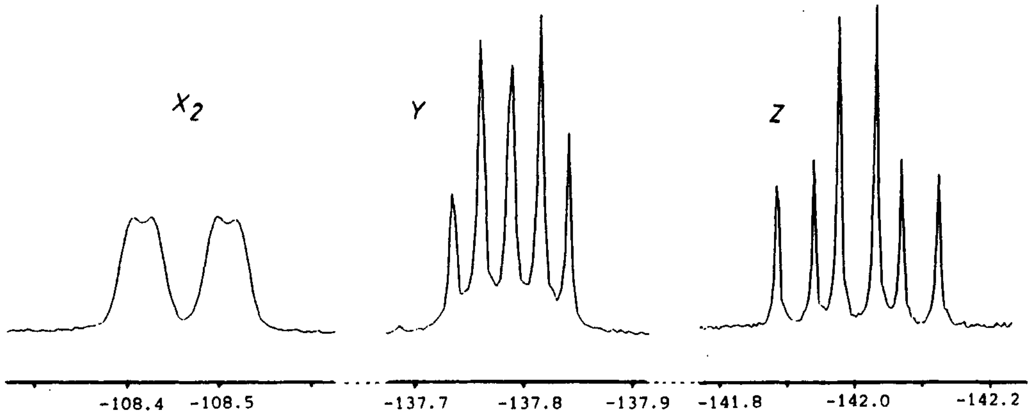

Figure 4. ^{19}F NMR spectrum (X_2YZ system) for **5b** (in CD_2Cl_2, relative to TMS).

Table VI. Summary of Crystal Data, Intensity Measurements, and Refinement for Complex 3b

formula	$C_{27}H_{42}F_4KNO_7Si$
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.515 (7)
b, Å	14.193 (3)
c, Å	23.644 (6)
β, deg	99.76 (6)
Vol, Å^3	3146.8
mol wt	635.8
Z	4
d_{calcd}, g cm^{-3}	1.342
d_{measd}, g cm^{-3}	1.34 (2)
cryst size, mm^3	0.65 × 0.50 × 0.25
cryst color	colorless
recrystallizing solvent	acetone
mp, °C	172
method of data collectn	moving crystal, moving counter
radiatn (graphite monochromated)	Mo Kα
μ, cm^{-1}	2.67
2θ limits, deg	4–44
no. of unique reflectns	3423
no. of obsd reflectns	1957
final no. of variables	246
R	0.062
R_w	0.068
residual electron dens, e Å^{-3}	0.48

previously ascribed as arising from rupture of the Si–N bond in the corresponding pentacoordinate complexes.[15] Therefore, in this case as in that of the benzylamine derivatives, F^- site exchange occurs without rupture of the Si–N bond via a nondissociative route of the same type as shown in Scheme II for **2b**.

As regards **5b**, we have observed no difference in behavior between the two hexacoordinate silicons (except by mass spectrometry (vide infra)). The same identity of behavior has been observed for the two pentacoordinated silicons in **5a**: both exhibit pseudorotation with the same energy ($\Delta G_F^{\ddagger}$ = 12 kcal mol^{-1}).[13]

The mass spectrum of **5b** in the FAB negative mode exhibits a peak corresponding to the reaction of only one silicon center with the glycerol matrix (see Experimental Section).[28]

Conclusion

The F^- site-exchange process for the hexacoordinated silicates **1b**–**5b** described here occurs via a regular mechanism without either Si–F or Si–N bond breaking. The same phenomenon has been observed for neutral hexacoordinated silicon compounds[24] and the hexacoordinated silicon catecholate **9**.[20a]

The $\Delta G_F^{\ddagger}$ values for F^- site exchange are higher in the case of the hexacoordinated naphthylamine derivatives **3b** and **4b** (15 kcal mol^{-1}) than for the hexacoordinated benzylamine derivatives **1b** and **2b** (11 kcal mol^{-1}). This is to be compared to the case for the corresponding pentacoordinated silicates **1a**–**4a** for which the $\Delta G_F^{\ddagger}$ values are all close to 12 kcal mol^{-1} for both naphthylamine and benzylamine derivatives.[12,15,19]

Experimental Section

All the reactions were carried out under dry nitrogen in Schlenk tubes. ^{19}F and ^{29}Si NMR data are given in Tables III and IV; ^{19}F, ^{29}Si, and ^1H NMR spectra were obtained using a Bruker 200 SY or a Bruker 250 AC spectrometer. ^1H and ^{29}Si NMR chemical shifts are reported relative to Me_4Si, and ^{19}F NMR 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. The pentacoordinated fluorosilanes **1a**–**5a** were prepared by published methods.[8,10]

Table VII. Fractional Atomic Parameters (×10^4) and Isotropic Thermal Parameters (×10^3) for Compound 3b with Esd's in Parentheses

atom	x/a	y/b	z/c	U(iso), Å^2
Si	3145 (2)	2244 (2)	9107 (1)	*a*
F(1)	1567 (5)	1973 (3)	9283 (3)	*a*
F(2)	4057 (5)	1538 (3)	9591 (2)	*a*
F(3)	2888 (5)	1426 (3)	8593 (2)	*a*
F(4)	3232 (5)	3138 (3)	9579 (2)	*a*
N	1875 (6)	3199 (4)	8479 (3)	*a*
Me(1)	1094 (10)	3891 (6)	8779 (4)	62 (3)
Me(2)	849 (9)	2671 (6)	8058 (4)	59 (3)
C(1)	4649 (8)	2795 (5)	8790 (3)	38 (2)
C(2)	6109 (9)	2565 (6)	8958 (3)	50 (2)
C(3)	7148 (9)	3007 (6)	8686 (3)	58 (2)
C(4)	6826 (9)	3653 (6)	8282 (3)	57 (2)
C(5)	4908 (10)	4601 (6)	7667 (4)	58 (2)
C(6)	3496 (10)	4827 (6)	7502 (4)	62 (3)
C(7)	2450 (9)	4360 (6)	7763 (3)	52 (2)
C(8)	2866 (8)	3708 (5)	8179 (3)	37 (2)
C(9)	4318 (8)	3462 (5)	8367 (3)	35 (2)
C(10)	5364 (8)	3929 (5)	8094 (3)	44 (2)
K	2699 (2)	2176 (1)	10494 (1)	*a*
O(1)	5643 (6)	2511 (4)	11013 (2)	*a*
O(2)	3762 (5)	4045 (4)	10884 (2)	*a*
O(3)	835 (5)	3806 (4)	10455 (2)	*a*
O(4)	−397 (6)	2032 (4)	10639 (2)	*a*
O(5)	1407 (7)	437 (4)	10797 (3)	*a*
O(6)	4318 (7)	799 (4)	11222 (3)	*a*
C(11)	6026 (10)	3415 (6)	11230 (4)	65 (3)
C(12)	5252 (10)	4119 (7)	10833 (4)	67 (3)
C(13)	2918 (9)	4730 (6)	10548 (4)	54 (2)
C(14)	1440 (9)	4665 (6)	10680 (4)	59 (3)
C(15)	−567 (10)	3679 (6)	10560 (4)	63 (3)
C(16)	−1109 (10)	2781 (7)	10313 (4)	68 (3)
C(17)	−821 (11)	1121 (7)	10447 (4)	79 (3)
C(18)	−92 (11)	425 (8)	10841 (5)	87 (3)
C(19)	2266 (11)	−142 (8)	11208 (5)	89 (3)
C(20)	3792 (12)	−113 (8)	11109 (5)	88 (3)
C(21)	5774 (10)	867 (7)	11125 (4)	70 (3)
C(22)	6344 (11)	1772 (7)	11364 (4)	72 (3)
O	1249 (10)	4499 (7)	12270 (4)	131 (3)
C	1103 (13)	3646 (9)	12229 (5)	94 (4)
Me(3)	−263 (11)	3247 (8)	12334 (5)	88 (3)
Me(4)	2120 (14)	3013 (10)	12052 (6)	126 (5)

[a] Corresponding atom was refined anisotropically. Anisotropic thermal parameters are given in the supplementary material.

General Method for the Synthesis of the 18-Crown-6 Potassium Salts of the Fluorosilicates. To a dispersion of dry potassium fluoride (2.35 mmol) in dry toluene (10 mL) was added 18-crown-6 ether (2.35 mmol) followed by a solution of fluorosilane (2.35 mmol) in 5 mL of toluene. The mixture was vigorously stirred at room temperature for 15 h. The white precipitate obtained was filtered out, washed with diethyl ether, crystallized from acetone, and dried in air.

18-Crown-6 Potassium Salt of (2-((Dimethylamino)methyl)phenyl)tetrafluorosilicate (1b): colorless crystals (85%); mp 164–166 °C. Anal. Calc for $C_{21}H_{36}F_4NO_6SiK$: C, 46.58; H, 6.61; N, 2.59. Found: C, 46.49; H, 6.66; N, 2.58. MS (FAB neg, glycerol): m/z 238 (A^-), 515 ($A^-\cdots K^+\cdots A^-$).

18-Crown-6 Potassium Salt of (2-((Dimethylamino)ethyl)phenyl)tetrafluorosilicate (2b): colorless crystals (90%); mp 180 °C. Anal. Calc for $C_{22}H_{38}F_4NO_6SiK$: C, 47.57; H, 6.85. Found: C, 47.96; H, 7.10. MS (FAB neg, glycerol): m/z 252 (A^-), 543 ($A^-\cdots K^+\cdots A^-$). ^1H NMR (CD_2Cl_2): δ 1.40 (d, 3 H, CH*Me*, J_{HH} 6.9 Hz), 2.32 (s, 6 H, NMe_2), 3.6 (s, 24 H, OCH_2), 4.06 (q, 1 H, C*H*Me, J_{HH} 6.9 Hz), 7.04–7.57 (m, 4 H, aromatic).

18-Crown-6 Potassium Salt of (8-(Dimethylamino)naphthyl)tetrafluorosilicate (3b): colorless crystals (90%); mp 173–175 °C. Anal. Calc for $C_{24}H_{36}F_4NO_6SiK$: C, 49.9; H, 6.24. Found: C, 49.86; H, 6.20. MS (FAB neg, glycerol): m/z 274 (A^-), 404 ($A^-\cdots K^+\cdots$glycerol), 587 ($A^-\cdots K^+\cdots A^-$). ^1H NMR

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Organometallics 1992, 11, 1593–1597

(CD_2Cl_2): δ 2.98 (s, 6 H, NMe_2), 3.67 (s, 24 H, OCH_2), 7.56–7.93 (m, 6 H, aromatic).

18-Crown-6 Potassium Salt of (8-(Dimethylamino)-naphthyl)phenyltrifluorosilicate (4b): colorless crystals (94%); mp >280 °C. Anal. Calc for $C_{30}H_{41}F_3NO_6SiK$: C, 56.59; H, 6.45; N, 2.20. Found: C, 56.87; H, 6.53; N, 2.43. ^1H NMR (CD_2Cl_2): δ 2.91 (s, 6 H, NMe_2), 3.37 (s, 24 H, OCH_2), 6.9–7.98 (m, 11 H, aromatic).

18-Crown-6 Potassium Salt of 1,5-Bis(tetrafluorosilicato)-4,8-bis(dimethylamino)naphthalene–Tetrakis(methanol) (5b). In this particular case, the reaction was performed in THF, and the compound was recrystallized from methanol giving colorless crystals containing two molecules of methanol per potassium ion (81%): mp 260 °C dec. Anal. Calc for $C_{42}H_{80}F_8N_2O_{16}Si_2K_2$: C, 43.66; H, 6.98; N, 2.42. Found: C, 43.44; H, 6.38; N, 2.50. MS (FAB neg): m/z 419 ($A^{2-}\cdots K^+$), 841 ($A^{2-}\cdots K^+\cdots A^{2-}$). ^1H NMR (CD_2Cl_2): δ 2.84 (s, 12 H, NMe_2), 3.31 (12 H, CH_3OH), 3.55 (s, 48 H, OCH_2), 4.71 (4 H, MeOH), 7.24 (d, 2 H, J_{HH} 7 Hz), 7.54 (d, 2 H, J_{HH} 7 Hz).

Crystal Structure of the 18-Crown-6 Potassium Salt of (8-(Dimethylamino)naphthyl)tetrafluorosilicate (3b). Crystals of the title complex **3b** were grown by cooling a saturated acetone solution in a nitrogen atmosphere. Elongated colorless plates were obtained. Preliminary Weissenberg photographs established a monoclinic unit cell with space group $P2_1/n$ (No. 14). A small plate was sealed inside a Lindemann glass capillary with the [100] direction parallel to the ϕ axis of the diffractometer. Effluorescence occurred to some extent at the crystal surface.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Lattice constants (Table VI) came from a least-squares refinement of 25 reflections obtained in the range 11.4 < 2θ < 35.0°. 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 $\sigma(F)/F < 0.33$ were considered to be observed. No absorption corrections were made.

Structure Determination and Refinement. Direct methods (1980 version of the MULTAN program) were used to solve the structure and to give the positions of the silicon atom and three of the fluorine atoms, which were used to phase a Fourier map. This Fourier map gave the coordinates of the potassium atom, and two subsequent Fourier syntheses revealed all the non-hydrogem atoms of the complex along with the four atoms of the trapped acetone molecule. The atomic scattering factors were taken from ref 27. After three cycles of least-squares refinement with isotropic thermal parameters to all atoms, the silicon, potassium, fluorine, oxygen, and nitrogen atoms were refined anisotropically. At this stage the conventional R factor was 0.086. The hydrogen atoms were positioned by calculation (SHELX-76 program), and refinement converged to the final R value of 0.062.

The final atomic coordinates are listed in Table VII. Individual bond lengths are listed in Table I and bond angles in Table II. Table VIII, anisotropic thermal parameters, and Table IX, calculated hydrogen atom coordinates, and a list of observed and calculated structure factors are available as supplementary material.

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Registry No. **1a** (coordination compound (CC) entry), 77773-10-5; **1a** (silane entry), 87996-42-7; **1b**, 139312-46-2; **2a** (CC entry), 139404-51-6; **2a** (silane entry), 139312-41-7; **2b**, 139346-59-1; **3a** (CC entry), 108034-64-6; **3a** (silane entry), 121497-40-3; **3b**, 139312-48-4; **4a** (CC entry), 108022-89-5; **4a** (silane entry), 139312-42-8; **4b**, 139312-50-8; **5a** (CC entry), 139312-44-0; **5a** (silane entry), 139312-43-9; **5b**, 139404-53-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates (2 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Photolysis of Organopolysilanes. Photochemical 1,2-Silyl Migration of 2-(2-Phenylethenyl)- and 2-(2,2-Diphenylethenyl)-Substituted Trisilanes

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The photochemical behavior of 2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1a**), 2-(2,2-diphenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1b**), and 2-(2,2-diphenylethenyl)-2-phenylhexamethyltrisilane (**1c**) has been studied. Irradiation of (*E*)-**1a** with a low-pressure mercury lamp initially resulted in cis–trans isomerization and then afforded (*E*)-2-phenyl(trimethylsilyl)ethene ((*E*)-**2a**) and (*Z*)-2-phenyl(trimethylsilyl)ethene ((*Z*)-**2a**) in addition to (*E*)-**1a** and (*Z*)-**1a**. Irradiation of **1b** afforded 2,2-diphenyl(trimethylsilyl)ethene (**2b**) and 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silaindene (**3b**), while **1c** afforded **2b**, 1,3-diphenyl-1,2-bis(trimethylsilyl)-1-silaindene (**3c**), and 1,3-diphenyl-1-(trimethylsilyl)-1-silaindene (**4c**). A possible mechanism leading to the observed products is described.

Introduction

We have demonstrated that permethylpolysilane oligomers and π-electron-system-substituted polysilanes are photoactive, and the fate of photochemically excited polysilanes highly depends on the structure and the substituents attached to silicon atoms. For example, irradiation of permethylcyclohexasilane with a low-pressure mercury lamp results in ring contraction with simultaneous extrusion of dimethylsilylene.[1] In contrast to this, irradiation of the disilanes bearing a π-electron system on a silicon atom leads to isomerization involving migration of

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(1) (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1970**, 612. (b) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1971**, 489.

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