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mechanistic questions raised by these observations.[56]

Summary

(1) The trinuclear cluster $Cp_3Co_3(CO)_3$ (**3**) undergoes a one-electron reduction but the resulting anion is not as stable as proposed in the earlier literature[38] ($t_{1/2}$ = 2.6 s at 298 K). Fragmentation follows, yielding the dinuclear monoanion $[Cp_2Co_2(\mu\text{-}CO)_2]^-$.

(2) The two known isomers of $Cp_3Rh_3(CO)_3$, namely C_s-$Cp_3Rh_3(CO)_3$ (**1**) and C_{3v}-$Cp_3Rh_3(CO)_3$ (**2**) undergo one-electron reduction to a persistent (**1**) or stable (**2**) monoanion. No isomeric interconversion was noted in the monoanions. A second reversible reduction occurs with $\mathbf{2}^-$, whereas $\mathbf{1}^-$ was reduced irreversibly. The order of increasing kinetic stabilities of the monoanions is $[Cp_3Co_3(CO)_3]^- < [C_s\text{-}Cp_3Rh_3(CO)_3]^- < [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-$. The rhodium clusters $\mathbf{1}^-$ and $\mathbf{2}^{2-}$ eventually fragment to apparent dinuclear complexes and other products.

(3) The E^0 value for reduction of the C_{3v} rhodium cluster is 210 mV positive of that of the C_s isomer, consistent with the more facile removal of electron density from the metal core by the additional doubly bridging CO in **2**.

(4) The trirhodium C_s isomer is converted to the C_{3v} isomer in an efficient electron-transfer-catalyzed anodic process. The chain length is about 30 under electrochemical conditions. The thermal isomerization rate is minimally 10^5 higher in the $47e^-$ monocation than in the $48e^-$ neutral complex.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation (Grant Nos. CHE 8303974 and 8603728) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Johnson Matthey Co. for a generous loan of Rh, J. R. Shapley for a gift of **2** which facilitated initial studies, P. H. Rieger for a digital simulation of the isomerization reaction scheme (Gosser, D. K.; Rieger, P. H. *Anal. Chem.* **1988**, *60*, 1159), W. A. Herrmann for a sample of $Cp_2Rh_2(CO)_3$, and C. Amatore and A. Pinhas for helpful discussions.

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Intramolecular Coordination at Silicon. The Small Effect of Equatorial Ligands upon the Stability of Pentacoordinated Organosilanes

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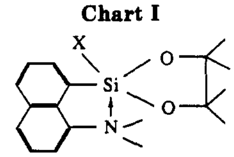
The molecular structure of 2-[8-(dimethylamino)-1-naphthyl]-4,4,5,5-tetramethyl-1,3,2-dioxasilacyclopentane (**1a**, X = H) determined by X-ray diffraction, shows this fused system to adopt a trigonal-bipyramidal geometry with the pinacol ring spanning equatorial–apical positions, the equatorial substituent (X = H) being orthogonal to the apical dimethylamino coordinated ligand. Functional pentacoordinated organosilanes derived from **1** (X = H, F, Cl, OCOR, OPh, Ph) model the trigonal-bipyramidal (tbp) intermediates which have been postulated in nucleophilic substitution with retention at silicon, with X, the leaving group, in the equatorial position of the tbp, and the coordinated nitrogen as the apical incoming nucleophile. ^{1}H NMR dynamic spectroscopy shows the formation of diastereomeric pentacoordinated organosilanes, and the energy barrier for their thermal interconversion is a measure of the intramolecular coordination. Despite the large electronic changes in the equatorial X substituents, the activation energy is only slightly dependent on the nature of this ligand (ΔG^* = 15–20 kcal mol^{-1}). The results confirm kinetic studies and ab initio calculations. The nature of the equatorial ligand has in general little effect on the energy level of the tbp species.

Introduction

The stereochemistry of tetracoordinated silicon compounds containing chiral centers has been extensively studied during the last decade.[1] The results support the formation of pentacoordinated species as intermediates or transition states in nucleophilic displacement reactions (Scheme I).

The reactions which give inversion at the silicon center are believed to occur (process A) through the attack of the nucleophile (Nu) at 180° relative to the leaving group (X) with formation of a trigonal-bipyramidal (tbp) structure, Nu and X being in apical positions. Two possible retention mechanisms (process B or process C) have been discussed in the literature.[2,3] Both involve adjacent attack on the

Chart I



1 (X=H)

(1) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43. Bassindale, A. R.; Taylor, P. G. Reaction Mechanisms of Nucleophilic Attack at Silicon. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds., Wiley: Chichester, 1989; Chapter 13, pp 840–892.

(2) Corriu, R. J. P.; Guérin, C. *J. Organomet. Chem.* **1980**, *198*, 231. Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352.

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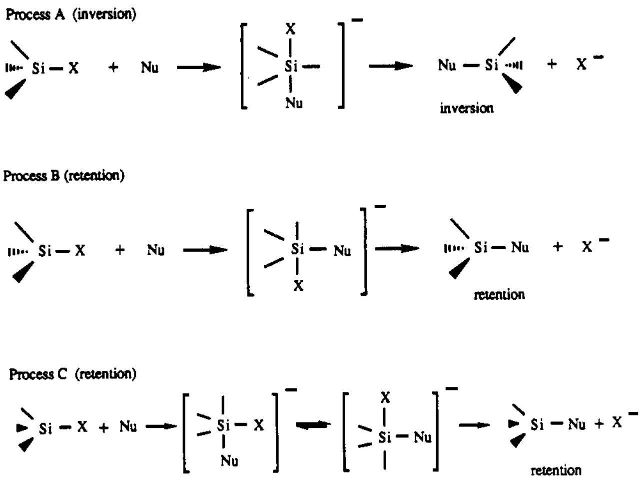
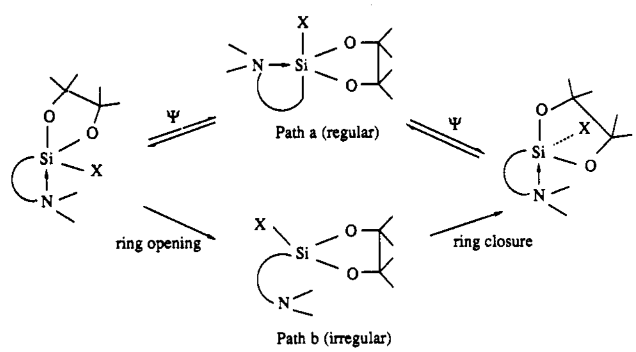
Scheme I



Scheme II



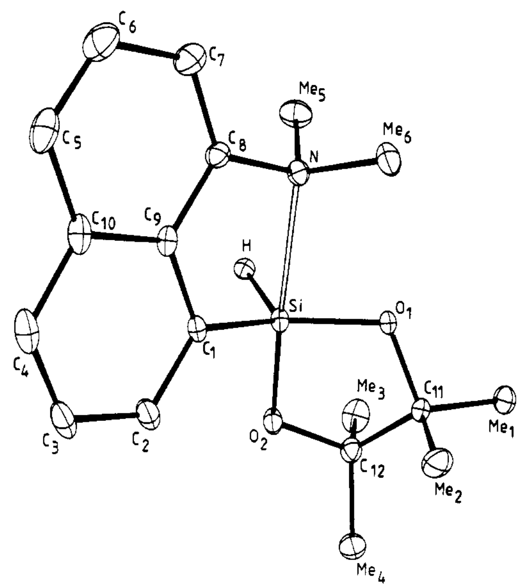
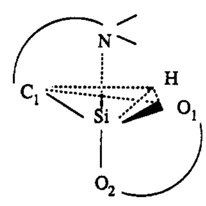


Figure 1. ORTEP diagram of $Ar_NSi(OCMe_2CMe_2O)H$ (**1a**).

Chart II



tetrahedral silicon center. In process B, the geometry with the nucleophile equatorial and the leaving group X apical, is directly obtained. In process C, the initial formation of an intermediate with the nucleophile apical and X equatorial is postulated. This intermediate may rearrange by intramolecular isomerization[4] to give the preferred geometry with X in the apical position before departure.

Process C is supported by recent work by Holmes[5] and Martin[6] on isolable pentacoordinated anionic silicon compounds, which have been shown to rearrange via pseudorotation. We have previously detailed the stereodynamical behavior of aminoarylsilicon compounds,[7] containing the *o*-(dimethylamino)methylphenyl ligand.[8] The relative stability of the chelate was found to depend on the ability of the Si–X bond to be stretched rather than on the electronegativity of X. The experimental order RCOO, Cl > F, SR > OR > H parallels the ability of the X group to be substituted with inversion of configuration at silicon.[7]

An analogous model for the process leading to overall retention at silicon[9] would be of interest. We initiated a study of the stereodynamical behavior of trifunctional pentacoordinated organosilanes derived from 1 (Chart I), and containing a pinacoxy group at silicon, for the following reasons: (1) In a previous paper,[10] we showed that in the exchange reaction of pentacoordinated dihydrosilanes with pinacol, cyclic monomers only are formed. There is no rearrangement giving dimers.[11,12]

(2) The compound **1a** presents an interesting topological[13] differentiation of the methyl substituents in both the dimethylamino group and the pinacoxy moiety, which can be exploited in dynamic ^1H NMR studies.

Two mechanisms have been postulated[10] (Scheme II) to explain the equivalence of the methyl groups at higher temperature (one singlet for the dimethylamino group and two singlets for the methyl groups of the pinacoxy moiety).

The first one (path a) is a regular mechanism with two pseudorotations, which "mimics" the S_N2 reaction occurring with retention (as discussed above, process C). The other possibility (path b) involves an irregular mechanism

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

formula	$C_{18}H_{25}NO_2Si$
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	7.961 (1)
b, Å	14.514 (2)
c, Å	15.504 (5)
β, deg	94.45 (2)
vol, $Å^3$	1786.1
mol wt	315.5
Z	4
d_{calcd}, g cm^{-3}	1.173
d_{measd}, g cm^{-3}	1.13 (3)
cryst size, mm^3	0.35 × 0.40 × 0.65
cryst color	colorless
recryst solv	pentane/CH_2Cl_2, 9:1
mp, °C	88.7–90.7
method of data collectn	moving crystal, moving center
radiatn (graphite monochromated)	Mo Kα
μ, cm^{-1}	1.13
2θ limits, deg	4–48
no. of unique rflns	2456
no. of obsd rflns	1356
final no. of variables	91
R	0.0345
R_w	0.0350
residual electron density	0.17

Table II. Fractional Atomic Coordinates (×10⁴) for Compound 1a

atom	x/a	y/b	z/c
Si	5334.2 (11)	1744.1 (6)	1355.4 (6)
C1	4393 (4)	2563 (2)	2111 (2)
C2	4440 (4)	2418 (3)	2994 (2)
C3	3534 (5)	3010 (3)	3524 (2)
C4	2577 (5)	3712 (3)	3180 (2)
C5	1478 (5)	4594 (3)	1884 (3)
C6	1444 (5)	4725 (3)	1017 (3)
C7	2420 (5)	4175 (3)	497 (3)
C8	3382 (4)	3493 (2)	867 (2)
C9	3425 (4)	3307 (2)	1761 (2)
C10	2465 (4)	3881 (2)	2282 (2)
N	4535 (3)	2941 (2)	400 (2)
Me5	3722 (6)	2557 (3)	−410 (2)
Me6	5983 (5)	3530 (2)	209 (3)
O1	7179 (2)	1869 (1)	944 (1)
C11	8508 (4)	1406 (2)	1453 (2)
Me1	9864 (5)	1135 (3)	853 (3)
Me2	9221 (5)	2095 (3)	2131 (3)
O2	6053 (3)	936 (1)	2066 (1)
C12	7651 (4)	570 (2)	1862 (2)
Me3	7319 (6)	−211 (3)	1214 (3)
Me4	8569 (5)	214 (3)	2686 (2)
H	4047 (31)	1268 (17)	798 (15)

with Si←N bond breaking. Our preliminary results with **1a** (X = H) did not allow a choice between the two paths to be made.

The present paper describes a more general study of this system with different functional ligands. Changing H at X to various leaving groups permits an evaluation of the stability of the chelate as a function of the nature of the equatorial ligand in the tbp structure.

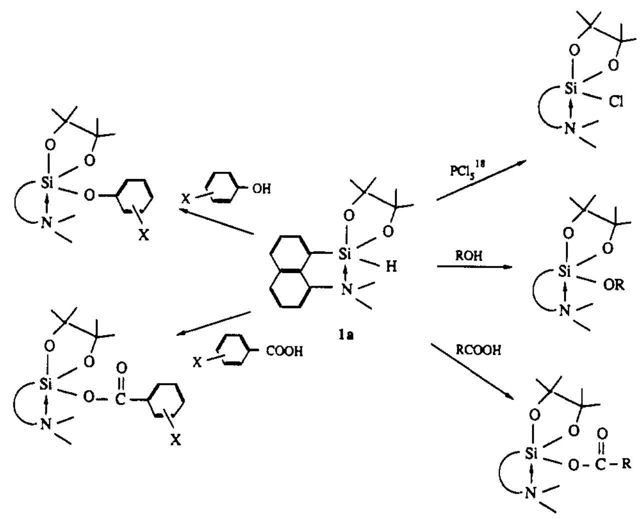
Results

Structure of Compound 1a. The pentacoordinated tbp geometry of compound **1a** has been confirmed by X-ray structure determination under the conditions summarized in Table I. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Structural refinement is described in the Experimental Section; details of the structure determination, including positional parameters and structural

Table III. Bond Lengths (Å) at Silicon and Bond Angles (deg) around Silicon, around Nitrogen, and in the Five-Membered Ring

Si–O1	1.656 (2)	Si–H	1.46 (2)
Si–O2	1.678 (2)	Si···N	2.339 (3)
Si–C1	1.867 (3)		
O1–Si–C1	125.7 (1)	Si···N–C8	104.2 (2)
C1–Si–H	112.0 (9)	C8–N–Me5	112.3 (3)
H–Si–O1	115.2 (9)	C8–N–Me6	108.2 (2)
O2–Si–O1	93.6 (1)	Me5–N–Me6	110.2 (3)
O2–Si–C1	99.6 (1)		
O2–Si–H	104.2 (9)	Si–O1–C11	112.0 (2)
N···Si–O1	83.1 (1)	O1–C11–C12	105.2 (2)
N···Si–C1	79.7 (1)	Si–O2–C12	112.1 (2)
N···Si–H	80.4 (9)	O2–C12–C11	103.1 (3)
N···Si–O2	175.2 (1)		
		Si–C1–C9	118.7 (2)
Si···N–Me5	109.7 (2)	C1–C9–C8	119.8 (3)
Si···N–Me6	112.2 (2)	C9–C8–N	114.6 (3)

Scheme III



factors, are provided as supplementary material. Fractional atomic coordinates are listed in Table II, and relevant bond lengths and angles are listed in Table III. The ORTEP diagram shown in Figure 1 illustrates the nitrogen–silicon interaction of the arylamino ligand.

The geometry at silicon is that of a distorted trigonal bipyramid with the chelated nitrogen in an apical position. The pinacol ring spans equatorial–apical positions. The SiO_2 apical bond (1.678 Å) is somewhat longer than the SiO_1 equatorial bond (1.656 Å), but both of them are slightly elongated relative to similar Si–O bonds[14] in tetravalent silicon compounds (1.640 Å). The silicon atom lies 0.03 Å below the equatorial plane on the side of the apical oxygen atom (Chart II).

The sum of the equatorial angles at silicon is 353°, which is less than the 360° expected for a pure tbp geometry. The angles $NSiC_1$, $NSiO_1$, and NSiH are all less than 90°, respectively, 79.7°, 83.1°, and 80.4°. The N→Si bond length (2.34 Å) is shorter than the value generally observed with this ligand in acyclic penta- or hexacoordinated species[7,15] (2.5–2.6 Å). The tbp preferred geometry with two five-membered rings in apical–equatorial positions and equatorial hydrogen atom[16] enhances the electrophilic character of the silicon center.

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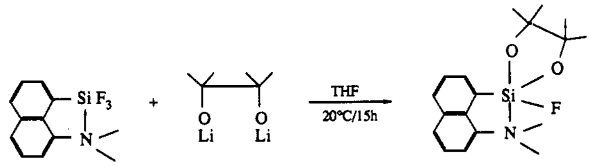
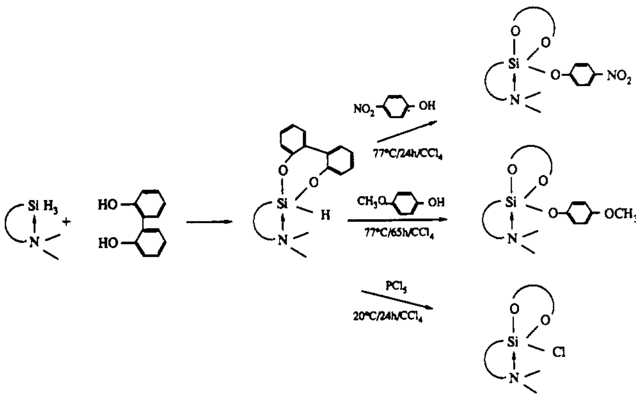
(15) Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, C. *J. Chem. Soc., Dalton Trans.* **1989**, 43.
(16) Brelière, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G. *Organometallics* **1986**, *5*, 388.

Scheme IV



Scheme V



Synthesis of Substituted 1,3,2-Dioxasilacyclopentanes. The increased reactivity[17] of pentacoordinated hydrosilane **1a** allowed the synthesis of functional pentacoordinated silanes via exchange reactions (Scheme III). The fluoro compound has been obtained by reaction of dilithiopinacolate on trifluorosilane (Scheme IV).

Some derivatives of 2,2′-dihydroxybiphenyl were also prepared[19] for comparison (Scheme V). They are highly hygroscopic, and easily converted to siloxanes. Their thermal decomposition prevented variable-temperature ^{1}H NMR studies.

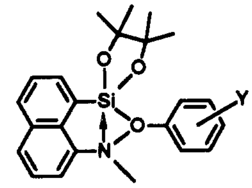
^{1}H NMR Data. (1) Substituted-Phenoxy Derivatives. Two signals are observed at room temperature for the NMe_2 group, and only one singlet above 80 °C. The methyl groups of the pinacoxy moiety are also diastereotopic at room temperature (four signals), giving two signals at higher temperature. The free energies of activation have been evaluated by using the Eyring equation.[20] The same $\Delta G^{\ddagger}$ values are obtained from the two systems, NMe_2 and pinacol, for a given compound.

Compounds containing a variety of substituents on the aromatic ring of the phenoxy moiety have been studied. The $\Delta G^{\ddagger}$ values are reported in Table IV. Only a small range is observed for the free energy of activation, $\Delta(\Delta G^{\ddagger})$ = 0.5 kcal mol^{-1}.

(2) [(Substituted-aroyl)oxy]silanes. The same comparison can be made in the case of more polarizable [(substituted-aroyl)oxy]silanes, for which data are reported in Table V. The $\Delta G^{\ddagger}$ values determined from NMe_2 and $(>CO)_2$ signals are very similar, showing a unique process. Again, we note the very small range with change of the functional group ($17.5 < \Delta G^{\ddagger}$ kcal mol^{-1} < 18.2), with the order

$$p\text{-F} < m\text{-Cl} < o\text{-F} < p\text{-Me} < m\text{-CN} < \text{H} < p\text{-NO}_2$$

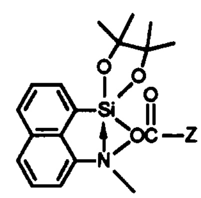
Table IV. ^{1}H NMR Data[a] at Variable Temperature for the Substituted Phenoxy Compounds

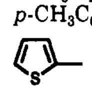
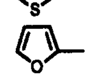
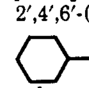


Y	$N(CH_3)_2$ T_c,[b] °C	$\Delta\nu$,[c] Hz	$\Delta G^{\ddagger}$, kcal/mol	$OC(CH_3)_2C(CH_3)_2O$ T_c,[b] °C	$\Delta\nu$,[c] Hz	$\Delta G^{\ddagger}$, kcal/mol
o-OCH_3	76	38	17.4	56	12	17.2
p-OCH_3	75	34	17.5	55	6	17.5
p-CH_3	75	34	17.5	54	6	17.5
H	75	34	17.5	56	7	17.5
p-t-Bu	78	34	17.6	58	8	17.5
3′,5′-$(OCH_3)_2$	80	34	17.7	68	12	17.8
p-Cl	80	34	17.7	62	8	17.7
m-Cl	79	32	17.7	62	8	17.7
o-F	85	44	17.8	70	10	18.0
p-NO_2	85	36	17.9	70	10	18.0
2′,4′,6′-Br_3	66	8	18.0	84	22	18.2
m-CN	89	34	18.2	72	10	18.1
m-NO_2	92	36	18.3	73	10	18.2

[a] Solvent is toluene-d_8. [b] T_c = coalescence temperature. [c] $\Delta\nu$ = chemical shift difference of the methyl signals below the coalescence temperature.

Table V. ^{1}H NMR Data[a] at Variable Temperature for the Substituted Carboxy Compounds



Z	$N(CH_3)_2$ T_c,[b] °C	$\Delta\nu$,[c] Hz	$\Delta G^{\ddagger}$, kcal/mol	$OC(CH_3)_2C(CH_3)_2O$ T_c,[b] °C	$\Delta\nu$,[c] Hz	$\Delta G^{\ddagger}$, kcal/mol
p-FC_6H_4	62	12	17.5	65	14	17.5
m-ClC_6H_4	65	13	17.6	60	7	17.7
o-FC_6H_4	68	14	17.7	60	7	17.7
p-$CH_3C_6H_4$	67	12	17.7	72	14	17.9
	71	18	17.7	68	14	17.7
	74	20	17.8	70	15	17.8
	70	10	18.0	75	15	18.0
m-CNC_6H_4	75	16	18.0	72	14	17.9
p-$NO_2C_6H_4$	79	17	18.2	77	13	18.2
2′,4′,6′-$(CH_3)_3C_6H_2$	87	20	18.5	82	8	18.8
	86	18	18.5	83	16	18.4

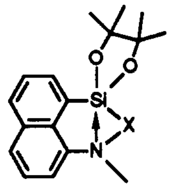
[a] Solvent is toluene-d_8. [b] T_c = coalescence temperature. [c] $\Delta\nu$ = chemical shift difference of the methyl signals below the coalescence temperature.

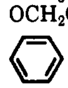
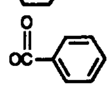
The mesityl group leads to a somewhat higher $\Delta G^{\ddagger}$ value ($\Delta G^{\ddagger}$ = 18.8 kcal mol^{-1}), which is probably associated with steric effects. The other acylsilanes also display comparable values ($\Delta G^{\ddagger}$ = 17.7–18.4 kcal mol^{-1}).

(3) Functional Silanes. Table VI gives data for a series of different compounds with various functional groups attached directly to the silicon center. Different coalescence temperatures are observed for the dimethylamino and the pinacoxy moieties, but the $\Delta G^{\ddagger}$ values

(17) Boyer, J.; Brelière, C.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *311*, C39.
(18) Corriu, R. J. P.; Poirier, M.; Royo, G. *C. R. Acad. Sci. Paris Sér. 2* **1990**, *310*, 1337.
(19) Preliminary experiments performed by K. D. Gupta, with $Ar_NSi(2,2'\text{-}OC_6H_4C_6H_4O)H$[10] and $Ar_NPhSi(2,2'\text{-}OC_6H_4C_6H_4O)$[10] showed these compounds to rearrange through pseudorotation, with a low activation energy ($\Delta G^{\ddagger}$ = 10–12 kcal mol^{-1}).
(20) Gunther, H. *NMR Spectroscopy*; Wiley: New York, 1980; pp 240–244.

Table VI. ¹H NMR Data[a] at Variable Temperature for the Substituted Compounds



	N(CH$_3$)$_2$			OC(CH$_3$)$_2$C(CH$_3$)$_2$O		
X	T_c,[b] °C	$\Delta\nu$,[c] Hz	ΔG^*, kcal/mol	T_c,[b] °C	$\Delta\nu$,[c] Hz	ΔG^*, kcal/mol
H	18	13	15.0	20	16	15.0
F	54	26	16.5	45	13	16.5
	75	34	17.5	56	7	17.5
OCH$_3$	75	28	17.6	64	11	17.6
OCH$_2$CH$_3$	79	28	17.8	57	4	17.9
	90	60	17.8	63	8	17.8
	70	10	18.0	75	15	18.0
Cl	100	46	18.5	80	12	18.5
OCH$_2$CF$_3$	110	36	19.3			
OCH$_2$CCl$_3$	>120	50	>20	119	8	20.9

[a] Solvent is toluene-d_8. [b] T_c = coalescence temperature. [c] $\Delta\nu$ = chemical shift difference of the methyl signals below the coalescence temperature.

calculated from the Eyring equation correlate well, showing that only one process is occurring to make the methyl signals become equivalent (Table VI).

The lowest values are obtained with X = H, F (ΔG^* = 15–16 kcal mol^{-1}), and slightly higher values are noted with better leaving groups at silicon, X = Cl or X = OC(O)R, but the change is not large. A particular behavior occurs with the halogenoalkoxy substituents, X = OCH$_2$CF$_3$ (ΔG^* = 19.3 kcal mol^{-1}) and X = OCH$_2$CCl$_3$ (ΔG^* = 20.9 kcal mol^{-1}), which exhibit free energies of activation higher than expected, by reference to the scale previously[21] obtained.

Discussion

The obvious result which must be emphasized, before discussing the stereodynamical behavior of the pentacoordinated bicyclic functional organosilanes studied here, is the observation that the nature of *the equatorial substituent has relatively little effect on the free activation energy of the rearrangement process.* Whatever the equatorial group, the ΔG^* values are always in the range 15–20 kcal mol^{-1}. Some variations exist, depending either on the steric or electronic properties of the substituents, but the changes are small.

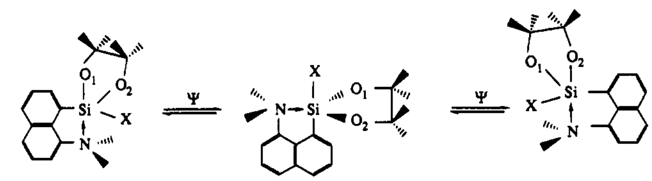
The ¹H NMR equivalence of the methyl signals of NMe$_2$ groups occurring with the same ΔG^* values as the equivalence (four to two) of the methyl groups of the pinacoxy moiety implies a symmetrical geometry, at least in the transition state. The question is to know how this geometry can be reached.

"A priori" two pathways must be considered: path a (regular) or path b (irregular) (Scheme VI).

(1) Path a. Pseudorotation of the tbp (Regular). Pseudorotation about any one of the three equatorial ligands as pivot is possible, but only one, which maintains O$_2$ equatorial as the pivot gives the geometry the degree

Scheme VI

a) Pseudorotation (regular)



b) Opening/closure (irregular)

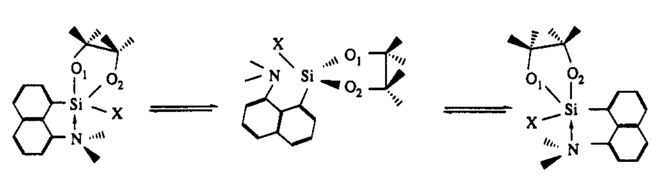
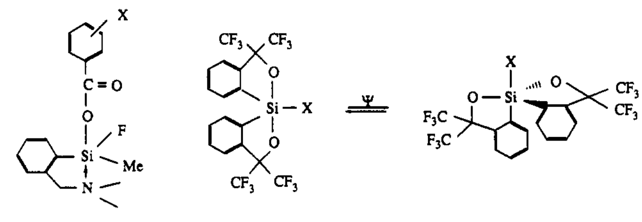


Chart III



(A) (B) (B')

of symmetry required for the equivalence of the methyl groups. In this conformation, the nitrogen is in an equatorial position, X is apical (which can be favorable), but the pinacoxy moiety is in the highly unfavorable[22] diequatorial position.

(2) Path b. Opening and Reclosure of the Dative Amino Bond (Irregular). This process supposes the Si←N bond breaking, followed by rotation around the C$_1$Si bond. Then, nitrogen ring closure is possible, opposite the other oxygen atom.

Precedents for both of these processes have been already described at silicon.[23] ¹⁹F NMR studies have shown[24] that the chemical shifts of equatorial fluorine atoms in tbp geometries are relatively constant, while the shifts of apical fluorine atoms are highly dependent on the electronic nature of the other substituents, and the environment around the silicon center.

X-ray structural data have shown that bonds to apical ligands in a tbp are generally longer than those of the same ligands in an equatorial position.[9,14,22] This is well illustrated in the case of pentacoordinated chlorosilane in which the Si–Cl bond can be elongated by more than 16%.[25,26]

Kinetic studies of S$_N$2 reactions at silicon showed that for reactions occurring with retention of configuration, the rates are similar[27] with only a small dependence on the

(21) Corriu, R. J. P.; Mazhar, M.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *306*, C5.

(22) Holmes, R. R. *Pentacoordinated Phosphorus*; American Chemical Society: Washington, DC, 1980; Vols. I, II.

(23) Corriu, R. J. P.; Kpoton, A., Poirier, M.; Royo, G.; Corey, J. Y. *J. Organomet. Chem.* **1984**, *277*, C25.

(24) Corriu, R. J. P.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1982**, *233*, 165.

(25) Klebe, G.; Nix, M.; Hensen, K. *Chem. Ber.* **1984**, *117*, 797. Klebe, G.; Hensen, K.; Fuess, H. *Chem. Ber.* **1983**, *116*, 3125. Klebe, G.; Bats, J. W.; Hensen, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1.

(26) Machardshvili, A. A.; Shklover, V. E.; Struchkov, Y. T.; Voronkov, M. G.; Gostevsky, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Pestunovich, V. A. *J. Organomet. Chem.* **1988**, *340*, 23.

nature of the leaving groups Si–X (X = F, Cl, OMe), for a given nucleophile.

Ab initio calculations have been performed[3,28] for H_3SiX (X = F, Cl) with H^- as the nucleophile attacking, simulating the retention pathway. The equatorial Si–X bonds are only slightly stretched under the influence of the incoming apical nucleophile.

These observations suggest that ligands in equatorial sites of trigonal bipyramidal silicon are relatively insensitive to the molecular environment, and particularly to the nature of apical ligands. The apicophilicity of aroyloxy substituents[24] versus F in *o*-$(Me_2NCH_2)C_6H_4SiFOC(O)C_6H_4$-*p*-X (A, Chart III) varies in the order *p*-NO_2 > H > *p*-MeO, with a relative ratio respectively 84/14,73/27,64/36. The relative stability of the topomers is highly sensitive to the substituents on the benzoyloxy ligand.

Furthermore, in the same series, we have never observed[29] a regular mechanism involving a five-membered ring becoming diequatorial: the $\Delta G^{\ddagger}$ for the irregular process was always found to be lower than the $\Delta G^{\ddagger}$ for the complete pseudorotation.

Similarly, but on a different system, Martin has observed that the energy barrier to inversion of 10-Si 5-substituted silicates (B) lies in the range 16–30 kcal mol^{-1} depending on the nature of X in the equatorial position.[6] The conformation B′ is expected to be at or near the maximum of the energy barrier to inversion. Such an intermediate would be more stable, the more apicophilic is the group X. The lower values are observed with electron-withdrawing ligands, with an excellent linear correlation between the energy barrier $\Delta G^{\ddagger}$ to inversion at silicon and Taft σ^* inductive parameters (slope = −3.37 kcal mol^{-1}).

Such a correlation is not observed with our compounds. Even if the equatorial ligands are as different as H, F, OPh, Ph, Cl, and OC(O)R, the $\Delta G^{\ddagger}$ varies only from 15 to 20 kcal mol^{-1}, much smaller than the large range 16–30 kcal mol^{-1} obtained by Martin. Obviously, the results are better interpreted by the irregular pathway. We must note that the lower energy observed in the case of the fluoro and hydrosilanes parallels the ability of R_3SiX (X = H, F) to be substituted with retention. Moreover, with monofunctional pentacoordinated organosilanes, the barrier ascribed to a dissociative mechanism[21] is also in the range $\Delta G^{\ddagger}$ = 19–22 kcal mol^{-1}.

In fact, all the data are consistent with the hypothesis of an irregular process at silicon with the rigid system 1. The regular pseudorotation pathway is prevented, because of the high energy of the configuration having the dioxygenated ring in diequatorial position.[22]

Conclusion

The rigid system with a pinacoxy moiety allowed a study of the stereodynamical behavior of trifunctional pentacoordinated (aminoaryl)silanes as a function of the equatorial ligands, orthogonal to the coordinated apical amino groups. The energy barriers to invert the tbp structures are not very different ($\Delta G^{\ddagger}$ = 15–19 kcal mol^{-1}) despite the very different electronic properties of the equatorial substituents (H, F, OPh, Ph, Cl, OC(O)R...). The results can be interpreted by an irregular process corresponding to Si←N bond breaking and reclosure, which "mimics" the S_N2 retention pathway at silicon. The absence of effect observed here with the equatorial substituents confirms S_N2(Si) kinetic data[27] and ab initio calculations.[3,28]

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen, with use of dry and degassed solvents. ^{1}H NMR spectra were obtained with a Varian EM 360 or a Bruker AW 60, with reference TMS. Variable-temperature ^{1}H NMR were recorded in the same conditions, on a Varian HA 100 spectrometer, in toluene-d_8, with hexamethyldisiloxane used as internal standard. Mass spectra were recorded on a JEOL JMS-DX 300 spectrometer (electronic impact mode at 70 eV). The preparation of $Ar_NSi(OCMe_2CMe_2O)H$ (**1a**) has previously been described[10] (Ar_N is 8-(dimethylamino)-1-naphthyl).

Preparation of $(Ar_N)(PhO)Si(OCMe_2CMe_2O)$. PhOH (0.29 g, 3.1 mmol) in 3 mL of CCl_4 was added to a solution of $(Ar_N)Si(OCMe_2CMe_2O)H$ (1.0 g, 3.1 mmol) in 3 mL of CCl_4. The mixture was refluxed for 48 h. Pentane (3 mL) was added. The solvents were concentrated in vacuo. The product separated as an oil: yield, 77%. ^{1}H NMR ($CDCl_3$): δ 1.15, 1.18, 1.32, 1.35 (4 s, 12 H, $OCMe_2CMe_2O$), 2.70, 2.98 (2 s, 6 H, NMe_2), 6.47, 8.44 (m, 11 H, ArH). Anal. Calcd for $C_{24}H_{29}NO_3Si$: C, 70.76; H, 7.13. Found: C, 70.43; H, 6.92.

The following compounds were similarly prepared. After usual workup, the products were separated, and characterized.

(Ar_N)(*p*-$CH_3C_6H_4O)Si(OCMe_2CMe_2O)$. Yellow oil. Yield, 97%. ^{1}H NMR ($CDCl_3$): δ 1.12, 1.32 (2s, 12 H, $OCMe_2CMe_2O$), 2.06 (s, 3 H, *p*-$CH_3C_6H_4O$), 2.62, 2.92 (2s, 6 H, NMe_2), 6.24, 8.30 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{31}NO_3Si$: C, 71.26; H, 7.36. Found: C, 71.42, H, 7.53.

(Ar_N)(*p*-*t*-$BuC_6H_4O)Si(OCMe_2CMe_2O)$. The reaction has been performed in refluxing CH_2Cl_2, for 40 h, giving an oil. Yield, 94%. ^{1}H NMR ($CDCl_3$): δ 1.15, 1.20, 1.29, 1.38 (4s, 21 H, $OCMe_2CMe_2O$, $C(Me)_3$), 2.62, 2.97 (2s, 6 H, NMe_2), 6.25, 6.97 (4s, 4 H, *p*-*t*-BuC_6H_4O), 7.12, 8.22 (m, 6 H, ArH). Anal. Calcd for $C_{28}H_{37}NO_3Si$: C, 72.57; H, 7.99. Found: C, 72.41; H, 8.11.

(Ar_N)(*p*-$OCH_3C_6H_4O)Si(OCMe_2CMe_2O)$. Yellow oil. Yield, 57%. ^{1}H NMR ($CDCl_3$): δ 1.10, 1.16, 1.24, 1.30 (2s, 12 H, $OCMe_2CMe_2O$), 2.60, 2.92 (2s, 6 H, NMe_2), 3.46 (s, 3 H, OCH_3), 6.32 (s, 4 H, *p*-$OCH_3C_6H_4O$), 7.12, 8.22 (m, 6 H, ArH). Anal. Calcd for $C_{25}H_{31}NO_4Si$: C, 68.65; H, 7.09. Found: C, 68.45; H, 6.91.

(Ar_N)(*o*-$OCH_3C_6H_4O)Si(OCMe_2CMe_2O)$. The reaction has been performed in refluxing CH_2Cl_2 for 48 h, giving an oil. Yield, 61%. ^{1}H NMR (toluene-d_8): δ 0.96, 1.01, 1.08, 1.12 (4s, 12 H, $OCMe_2CMe_2O$), 2.39 (s, 3 H, OCH_3), 2.58, 2.96 (2s, 6 H, NMe_2), 6.18, 8.35 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{31}NO_4Si$: C, 68.65; H, 7.09. Found: C, 68.35; H, 7.24.

(Ar_N)(*p*-$ClC_6H_4O)Si(OCMe_2CMe_2O)$. Pure compound as a yellow oil. Yield, 92%. ^{1}H NMR ($CDCl_3$): δ 1.11, 1.19, 1.27 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.62, 2.94 (2s, 6 H, NMe_2), 6.27, 6.90 (m, 4 H, *p*-ClC_6H_4O), 7.24, 8.32 (m, 10 H, ArH). EI-MS: *m/e* 441 (M^+), 426 ($M^+ - CH_3$), 383 ($M^+ - (CH_3)_2CO$), 314 ($M^+ - ClC_6H_4O$, 100). Anal. Calcd for $C_{24}H_{28}NO_3SiCl$: C, 65.20; H, 6.34. Found: C, 65.09, H, 6.39.

(Ar_N)(*m*-$ClC_6H_4O)Si(OCMe_2CMe_2O)$. Oily residue. ^{1}H NMR ($CDCl_3$): δ 1.14, 1.18, 1.22 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.68, 2.86 (2s, 6 H, NMe_2), 6.35, 8.37 (m, 10 H, ArH). Anal. Calcd for $C_{24}H_{28}NO_3SiCl$: C, 65.20; H, 6.34. Found: C, 65.19; H, 6.44.

(Ar_N)(*p*-$NO_2C_6H_4O)Si(OCMe_2CMe_2O)$. Oil. Yield, 93%. ^{1}H NMR ($CDCl_3$) δ 1.05, 1.22, 1.30 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.32, 2.72 (2s, 6 H, NMe_2), 6.26, 6.45 (4s, 4 H, *p*-$NO_2C_6H_4O$), 6.85, 8.37 (m, 6 H, ArH). Anal. Calcd for $C_{24}H_{28}N_2O_5Si$: C, 63.72; H, 6.19. Found: C, 64.09; H, 6.45.

(Ar_N)(*m*-$NO_2C_6H_4O)Si(OCMe_2CMe_2O)$. Viscous residue. Yield, 87%. ^{1}H NMR ($CDCl_3$): δ 1.06, 1.08, 1.10 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.64, 3.00 (2s, 6 H, NMe_2), 6.84, 8.36 (m, 10 H, ArH). Anal. Calcd for $C_{24}H_{28}N_2O_5Si$: C, 63.72; H, 6.19. Found: C, 63.68; H, 6.01.

(Ar_N)(*o*-$FC_6H_4O)Si(OCMe_2CMe_2O)$. The reaction has been

(27) Corriu, R. J. P.; Henner, B. J. L. *J. Organomet. Chem.* **1975**, *102*, 407.
(28) Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103. Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889.
(29) Unpublished data from this laboratory.

performed in refluxing CH_2Cl_2 for 60 h, giving an oil. Yield, 89%. ^1H NMR (toluene-d_8): δ 0.93, 1.03 (2s, 12 H, $OCMe_2CMe_2O$), 2.32, 2.76 (2s, 6 H, NMe_2), 6.30, 8.68 (m, 10 H, ArH). Anal. Calcd for $C_{24}H_{28}NO_3SiF$: C, 67.76; H, 6.59. Found: C, 67.16; H, 6.52.

$(Ar_N)(m\text{-}CNC_6H_4O)Si(OCMe_2CMe_2O)$. Oily residue. ^1H NMR (toluene-d_8): δ 1.00, 1.04, 1.10, 1.14 (4s, 12 H, $OCMe_2CMe_2O$), 2.30, 2.64 (2s, 6 H, NMe_2), 6.42, 8.34 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{28}N_2O_3Si$: C, 69.44; H, 6.48. Found: C, 68.86; H, 5.96.

$(Ar_N)(3',5'\text{-}(OCH_3)_2C_6H_3O)Si(OCMe_2CMe_2O)$. Yellow oil. Yield, 92%. ^1H NMR ($CDCl_3$): δ 1.53, 1.59 (2s, 12 H, $OCMe_2CMe_2O$), 2.88, 3.18 (2s, 6 H, NMe_2), 3.62 (s, 6 H, OCH_3), 5.80, 583 (2s, 3 H, $3',5'\text{-}(OCH_3)_2C_6H_3$), 7.40, 8.54 (m, 6 H, Ar-H). Anal. Calcd for $C_{26}H_{33}NO_5Si$: C, 66.81; H, 7.07. Found: C, 67.14; H, 6.89.

$(Ar_N)(2',4',6'\text{-}Br_3C_6H_2O)Si(OCMe_2CMe_2O)$. Red oil. Yield, 63%. ^1H NMR ($CDCl_3$): δ 0.80, 0.86, 1.08, 1.14 (4s, 12 H, $OCMe_2CMe_2O$), 2.66, 2.80 (2s, 6 H, NMe_2), 6.89, 7.78 (m, 8 H, ArH). Anal. Calcd for $C_{24}H_{26}NO_3SiBr_3$: C, 44.72; H, 4.04. Found: C, 45.28; H, 4.39.

Preparation of $(Ar_N)(PhCOO)Si(OCMe_2CMe_2O)$. **1a** (1.0 g, 3.1 mmol) and 0.37 g (3.1 mmol) of PhCOOH were stirred in 5 mL of CCl_4 for 48 h at 77 °C. After 5 mL of pentane was added, the mixture was concentrated in vacuo. The product separated as an oil. Yield, 76%. ^1H NMR ($CDCl_3$): δ 1.18, 1.28, 1.38 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.70, 2.80, (2s, 6 H, NMe_2), 7.18, 8.42 (m, 11 H, ArH). EI-MS: m/e 435 (M^+, 10), 420 ($M^+ - CH_3$, 12), 377 ($M^+ - (CH_3)_2CO$, 47), 362 ($M^+ - (CH_3)_2CO\text{-}CH_3$, 75), 170 ($C_{12}H_{12}N^+$, 3), 55 (100). Anal. Calcd for $C_{25}H_{29}NO_4Si$: C, 68.97; H, 6.67. Found: C, 68.05; H, 6.78.

The following compounds were similarly prepared. Evaporation of the solvents gave the pure products as yellow oils.

$(Ar_N)(p\text{-}NO_2C_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 79%. ^1H NMR ($CDCl_3$) δ 1.30, 1.38 (2s, 12 H, $OCMe_2CMe_2O$), 2.70, 2.82 (2s, 6 H, NMe_2), 7.30, 8.44 (m, 10 H, ArH). EI-MS: m/e 481 [$(M + H)^+$, 14], 408 [$(M + H)^+ - (CH_3)_2CO - CH_3$, 100], 365 [$(M + H)^+ - C_6H_{12}O_2$, 92], 170 ($C_{12}H_{12}N^+$, 58%). Anal. Calcd for $C_{25}H_{28}N_2O_6Si$: C, 62.50; H, 5.83. Found: C, 62.32; H, 5.54.

$(Ar_N)(p\text{-}OCH_3C_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 90%. ^1H NMR (CCl_4) δ 1.12, 1.18, 1.24 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.58, 2.70 (2s, 6 H, NMe_2), 3.52 (s, 3 H, OCH_3), 6.43, 8.34 (m, 10 H, ArH). Anal. Calcd for $C_{26}H_{31}NO_5Si$: C, 67.10; H, 6.67. Found: C, 66.81; H, 6.43.

$(Ar_N)(p\text{-}FC_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 97%. ^1H NMR (CCl_4) δ 1.10, 1.22, 1.25, 1.38 (4s, 12 H, $OCMe_2CMe_2O$), 2.70, 2.80 (2s, 6 H, NMe_2), 6.72, 8.40 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{28}NO_4SiF$: C, 66.23; H, 6.18. Found: C, 66.48; H, 6.34.

$(Ar_N)(o\text{-}FC_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 85%. ^1H NMR ($CCCl_4$) δ 1.20, 1.30, 1.40 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.75, 2.80 (2s, 6 H, NMe_2), 6.80, 8.40 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{28}NO_4SiF$: C, 66.23; H, 6.18. Found: C, 66.04; H, 5.75.

$(Ar_N)(p\text{-}ClC_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 81%. ^1H NMR ($CDCl_3$) δ 1.18, 1.27, 1.36 (3s, (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.70, 2.75 (2s, 6 H, NMe_2), 7.10, 8.40 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{28}NO_4SiCl$: C, 63.90; H, 5.96. Found: C, 64.28; H, 6.24.

$(Ar_N)(m\text{-}ClC_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 75%. ^1H NMR ($CDCl_3$): δ 1.00, 1.13, 1.26 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.68, 2.98 (2s, 6 H, NMe_2), 6.80, 8.34 (m, 10 H, ArH). Anal. Calcd for $C_{25}H_{28}NO_4SiCl$: C, 63.90; H, 5.96. Found: C, 64.32; H, 6.17.

$(Ar_N)(m\text{-}CNC_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 86%. ^1H NMR (CCl_4): δ 1.20, 1.29, 1.33, 1.42 (4s, 12 H, $OCMe_2CMe_2O$), 2.75, 2.88 (2s, 6 H, NMe_2), 7.30, 8.40 (m, 10 H, ArH). Anal. Calcd for $C_{26}H_{28}N_2O_4Si$: C, 67.83; H, 6.09. Found: C, 67.50; H, 6.14.

$(Ar_N)(p\text{-}CH_3C_6H_4COO)Si(OCMe_2CMe_2O)$. Yield, 86%. ^1H NMR ($CDCl_3$): δ 1.10, 1.24, 1.38 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.30 (s, 3 H, CH_3), 2.70, 2.90 (2s, 6 H, NMe_2), 7.00, 8.50 (m, 10 H, ArH). Anal. Calcd for $C_{26}H_{31}NO_4Si$: C, 69.49; H, 6.90. Found: C, 68.92; H, 6.72.

$(Ar_N)(2',4',6'\text{-}Me_3C_6H_2COO)Si(OCMe_2CMe_2O)$. ^1H NMR (toluene-d_8): δ 1.22, 1.28, 1.34 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 1.82 (s, 9 H, CH_3), 2.26, 2.46 (2s, 6 H, NMe_2), 6.28, 8.44 (m, 8 H, ArH). Anal. Calcd for $C_{28}H_{35}NO_4Si$: C, 70.44; H, 7.34. Found: C, 70.59; H, 7.96.

$(Ar_N)(CF_3COO)Si(OCMe_2CMe_2O)$. ^1H NMR ($CDCl_3$): δ 1.15, 1.27, 1.40 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.72, 2.95 (2s, 6 H, NMe_2), 7.15, 8.38 (m, 6 H, ArH). Anal. Calcd for $C_{20}H_{24}NO_4SiF_3$: C, 56.21; H, 5.62. Found: C, 56.57; H, 5.55.

$(Ar_N)(CH_3COO)Si(OCMe_2CMe_2O)$. Yield, 69%. ^1H NMR (toluene-d_8): δ 1.02, 1.09, 1.18, 1.27 (4s, 12 H, $OCMe_2CMe_2O$), 1.44 (s, 3 H, CH_3COO), 2.31, 2.54 (2s, 6 H, NMe_2), 6.82, 8.42 (m, 6 H, ArH). Anal. Calcd for $C_{20}H_{27}NO_4Si$: C, 64.34; H, 7.24. Found: C, 63.91; H, 7.42.

$(Ar_N)(2'\text{-}C_4H_3SCOO)Si(OCMe_2CMe_2O)$. Yield, 82%. ^1H NMR (CCl_4): δ 1.12, 1.21, 1.30 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.70, 2.80 (2s, 6 H, NMe_2), 7.70, 8.40 (m, 9 H, C_4H_3S, ArH). Anal. Calcd for $C_{23}H_{27}NO_4SiS$: C, 62.59; H, 6.12. Found: C, 62.24; H, 6.08.

$(Ar_N)(2'\text{-}C_4H_3OCOO)Si(OCMe_2CMe_2O)$. Yield, 85%. ^1H NMR ($CDCl_3$): δ 1.20, 1.30, 1.40 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.70, 2.94 (2s, 6 H, NMe_2), 6.28, 8.46 (m, 9 H, C_4H_3O, ArH). Anal. Calcd for $C_{23}H_{27}NO_5Si$: C, 64.94; H, 6.35. Found: C, 65.08; H, 6.24.

$(Ar_N)(C_6H_{11}COO)Si(OCMe_2CMe_2O)$. Yield, 78%. ^1H NMR (toluene-d_8): δ 1.06, 1.11, (2s, 11 H, $C_6H_{11}COO$), 1.17, 1.22, 1.33, 1.38 (4s, 12 H, $OCMe_2CMe_2O$), 2.37, 2.55 (2s, 6 H, NMe_2), 6.87, 8.46 (m, 6 H, ArH). Anal. Calcd for $C_{25}H_{35}NO_4Si$: C, 68.03; H, 7.94. Found: C, 67.52; H, 7.61.

Preparation of $(Ar_N)(CCl_3CH_2O)Si(OCMe_2CMe_2O)$. CCl_3CH_2OH (0.33 g, 2.2 mmol) in 3 mL of CCl_4 was added to a solution of **1a** (0.69 g, 2.2 mmol) in 3 mL of CCl_4. The mixture was refluxed for 24 h with stirring. Pentane (3 mL) was added. The solvents were concentrated in vacuo. The product separated as an oil. Yield, 69%. ^1H NMR (CCl_4): δ 1.20, 1.28, 1.32 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.60, 2.98 (2s, 6 H, NMe_2), 3.72, 4.28 (2d, 2 H, OCH_2CCl_3), 7.18, 8.20 (m, 6 H, ArH). Anal. Calcd for $C_{20}H_{26}NO_3SiCl_3$: C, 51.89; H, 5.62. Found: C, 51.51; H, 5.37.

Preparation of $(Ar_N)Si(OCH_2CF_3)H_2$. CF_3CH_2OH (1.6 mL, 20 mmol) was added to a solution of $(Ar_N)SiH_3$[10] (1.0 g, 4.98 mmol) in CCl_4 (5 mL). The mixture was stirred for 13 h at room temperature. The solvent and the excess alcohol were evaporated in vacuo, oil. Yield, 91%. ^1H NMR ($CDCl_3$) δ 3.08 (s, 6 H, NMe_2), 3.83, 4.29 (q, 2 H, CF_3CH_2O), 4.83 (s, 2 H, SiH_2), 7.39, 8.13 (m, 6 H, ArH). EI-MS: m/e 299 $(M)^+$.

Preparation of $(Ar_N)(CF_3CH_2O)Si(OCMe_2CMe_2O)$. $(Ar_N)Si(OCH_2CF_3)H_2$ (1.0 g, 3.34 mmol) and 0.4 g (3.4 mmol) of $HOCMe_2CMe_2OH$ were stirred together in 5 mL of anhydrous benzene for 24 h at 70 °C. The solvent was evaporated in vacuo, the residue was precipitated out of hexane. Yield, 78%, mp 85–87 °C. ^1H NMR ($CDCl_3$): δ 1.10, 1.18, 1.22, 1.30 (4s, 12 H, $OCMe_2CMe_2O$), 2.50, 2.70 (2s, 6 H, NMe_2), 3.70 (m, 2 H, CF_3CH_2O), 7.00, 8.00 (m, 6 H, ArH). EI-MS: m/e 413 $(M)^+$. Anal. Calcd for $C_{20}H_{26}NO_3SiF_3$: C, 58.11; H, 6.30. Found: C, 57.95; H, 6.10.

Preparation of $(Ar_N)(CH_3O)Si(OCMe_2CMe_2O)$. $(Ar_N)Si(OCH_3)_3$[15] (1.0 g, 3.4 mmol) and $HOCMe_2CMe_2OH$ (0.40 g, 3.4 mmol) were dissolved in toluene (5 mL). The mixture was refluxed for 48 h. The solvent was removed, the residue was recrystallized from pentane to afford pale green crystals: yield, 85%; mp 78 °C. ^1H NMR ($CDCl_3$): δ 1.18, 1.29, 1.40 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.56, 2.85 (2s, 6 H, NMe_2), 3.25 (s, 3 H, OCH_3), 7.31, 8.29 (m, 6 H, ArH). EI-MS: m/e 345 (M^+, 58), 330 ($M^+ - CH_3$, 18), 287 ($M^+ - (CH_3)_2CO$, 100), 272 ($M^+ - (CH_3)_2CO - CH_3$, 43), 229 ($M^+ - C_6H_{12}O_2$, 55), 170 ($C_{12}H_{12}N^+$, 47). Anal. Calcd for $C_{19}H_{27}NO_3Si$: C, 66.09; H, 7.83. Found: C, 66.18; H, 8.02.

Methanol in excess (1 mL) was added to a solution of **1a** (1.0 g, 3.1 mmol) in 3 mL of CCl_4. The mixture was refluxed for 48 h. After usual workup, the product crystallized in pentane: yield 35%; mp 77–78 °C.

Preparation of $(Ar_N)(CH_3CH_2O)Si(OCMe_2CMe_2O)$. The experimental procedure was identical with that described for the preparation of $(Ar_N)(CH_3O)Si(OCMe_2CMe_2O)$. Yield, 80%. ^1H NMR (toluene-d_8): δ 0.67 (t, 3 H, OCH_2CH_3), 1.09, 1.13, 1.24, 1.28

(4s, 12 H, $OCMe_2CMe_2O$), 2.38, 2.66 (2s, 6 H, NMe_2), 3.50 (q, 2 H, OCH_2CH_3), 6.91, 8.37 (m, 6 H, ArH). Anal. Calcd for $C_{20}H_{29}NO_3Si$: C, 66.85; H, 8.08. Found: C, 67.2; H, 8.14.

Preparation of $(Ar_N)\overline{Si(OCMe_2CMe_2O})Cl$. $(Ar_N)Si(OCMe_2CMe_2O)H$ (1.0 g, 3.2 mmol) and PCl_5[18] (0.67 g, 3.2 mmol) were stirred together in CCl_4 (5 mL) for 15 h at room temperature. The mixture was concentrated. The product separated as a pale yellow powder: yield, 92%; mp 43–47 °C dec. ^1H NMR ($CDCl_3$): δ 1.29, 1.39 (2s, 12 H, $OCMe_2CMe_2O$), 2.60, 2.82 (2s, 6 H, NMe_2), 7.27, 8.32 (m, 6 H, ArH). Anal. Calcd for $C_{18}H_{24}NO_2SiCl$: C, 61.80; H, 6.87. Found: C, 62.14; H, 6.52.

Preparation of $(Ar_N)\overline{Si(OCMe_2CMe_2O})F$. *n*-BuLi (25 mmol, 2.5 M in hexane) was added dropwise to a solution $HOCMe_2CMe_2OH$ (1.4 g, 12 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature. After 4 h, a solution of $(Ar_N)SiF_3$[15] (3.0 g, 12 mmol) in THF (5 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 15 h at room temperature, then concentrated in vacuo. The product separated as an oil. Yield, 41%. ^1H NMR ($CDCl_3$): δ 1.30, 1.38, 1.46 (3s (1:2:1), 12 H, $OCMe_2CMe_2O$), 2.70, 2.95 (2s, 6 H, NMe_2), 7.34, 8.38 (m, 6 H, ArH). ^{19}F NMR ($CDCl_3$) δ 24.4 (C_6F_6). Anal. Calcd for $C_{18}H_{24}NO_2SiF$: C, 64.86; H, 7.21. Found: C, 64.73; H, 7.28.

Preparation of $(Ar_N)(p\text{-}NO_2C_6H_4O)\overline{Si(2,2'\text{-}OC_6H_4C_6H_4O})$. $p\text{-}NO_2C_6H_4OH$ (0.42 g, 3 mmol) in 2 mL of CCl_4 was added to a solution of $Ar_NSi(2,2'\text{-}OC_6H_4C_6H_4O)H$[10] (1.2 g, 3 mmol) in 3 mL of CCl_4. The mixture was refluxed for 48 h, and then concentrated in vacuo giving an oil. ^1H NMR (CCl_4): δ 3.04 (s, 6 H, NMe_2), 6.52, 8.34 (m, 18 H, ArH). Anal. Calcd for $C_{30}H_{24}N_2O_5Si$: C, 69.23; H, 4.62. Found: C, 69.10; H, 4.54.

Preparation of $(Ar_N)(p\text{-}OCH_3C_6H_4O)\overline{Si(2,2'\text{-}OC_6H_4C_6H_4O})$. The preparation of this compound was carried out as described above. ^1H NMR (CCl_4): δ 2.30, 2.65 (2s, 6 H, NMe_2), 3.40 (s, 3 H, OCH_3), 6.41, 8.23 (m, 18 H, ArH). Anal. Calcd for $C_{31}H_{27}NO_4Si$: C, 73.66; H, 5.35. Found: C, 73.72; H, 5.46.

Preparation of $(Ar_N)\overline{Si(2,2'\text{-}OC_6H_4C_6H_4O})Cl$. $(Ar_N)Si(2,2'\text{-}OC_6H_4C_6H_4O)H$ (1.0 g, 2.6 mmol) and PCl_5[18] (5.5 g, 2.6 mmol) were stirred together in CH_2Cl_2 (5 mL) for 24 h at room temperature. The solvent was evaporated in vacuo, the product separating as a powder: yield, 84%; mp 153–156 °C dec. ^1H NMR ($CDCl_3$): δ 2.64 (s, 6 H, NMe_2), 6.80–8.39 (m, 14 H, Ar). The compound is insoluble in toluene. Anal. Calcd for $C_{24}H_{20}NO_2SiCl$: C, 68.98; H, 5.75. Found: C, 69.10; H, 5.73.

Variable-Temperature ^1H NMR Studies. Standard solutions of compounds 1 (ca. 0.1 M) in freshly distilled toluene-d_8 were carefully transferred through a cannula into 2-mm NMR tubes, flushing with argon. Variable-temperature ^1H NMR spectra were all recorded on a Varian HA 100 spectrometer (100 MHz). Probe temperatures were measured from the ^1H chemical shift difference of an ethylene glycol sample. As an example, the ^1H NMR spectrum of **1a** (X = H) in toluene-d_8 at 20 °C, showed broad signals, centered at 1.09, 1.20, and 2.35 ppm (relative to hexamethyldisiloxane). At +60 °C, the signals became sharp (integration 6/6/6 compared to the Si–H proton signal at 5.2 ppm). At −50 °C, the two pinacoxy methyl signals were splitted into four singlets, respectively at 1.01, 1.12, 1.18, 1.28; two signals of the same intensity (3 H for each) appeared at 2.29 and 2.42 for the NMe_2 group. The coalescence temperatures (T_c ±2 °C) were estimated from at least three registered spectra; from T_c and the $\Delta\nu$ values of the splitted signals, the activation energies were calculated by means of the Eyring equation.[20]

Crystal Structure Determination of 1a. Elongated colorless crystals of compound **1a** were obtained by recrystallization at −18 °C of a saturated solution in pentane and dichloromethane (9:1). Preliminary Weissenberg photographs established a monoclinic unit cell with space group $P2_1/n$ (No 14). A small parallelepiped was sealed inside a Lindeman glass capillary with the [101] direction parallel to the ϕ axis of the diffractometer.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.17069 Å). Lattice constants (Table I) came from a least-square refinement of 23 reflections obtained in the range $18 \leq 2\theta < 25°$. The intensities of three standard reflections were monitored after intervals of 60 min; no significant change occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $F > 3\sigma(F)$ were considered to be observed. No absorption corrections were made.

Structure Determination and Refinement. The structure was solved by use of a 1980 version of the MULTAN program. The silicon atom, the two oxygen atoms, and the nitrogen atom were used to phase a Fourier map which revealed the remainder of the molecule. The atomic scattering factors were taken.[30] After four cycles of least-squares refinement with isotropic thermal parameters to all atoms, the hydrogen atoms were positioned by calculation (SHELX 76 program). Refinement was resumed with anisotropic thermal parameters to the non-hydrogen atoms and converged to the final R value of 0.035, the anisotropic thermal parameters being fixed during the last three cycles of refinement.

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Supplementary Material Available: Tables of interatomic distances, bond angles, anisotropic thermal parameters, and calculated atomic coordinates for the H atoms (4 pages); a listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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