

Donor-Stabilized Silyl Cations. 9. Two Dissociation Patterns of Hexacoordinate Silicon Complexes: A Model Nucleophilic Substitution at Pentacoordinate Silicon¹

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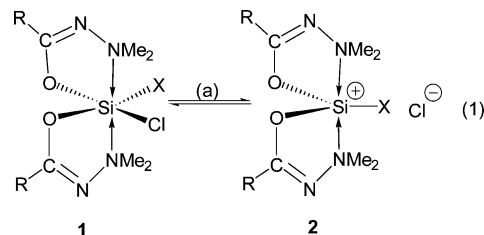
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Hexacoordinate silicon bischelates with bulky monodentate alkyl ligands tend to ionize, while those with electron-withdrawing CF₃ substituents on the chelate rings resist ionization. A hexacoordinate silicon complex with *both* of these structural features was prepared and was found, by its temperature-dependent ²⁹Si NMR spectroscopy, to undergo a reversible neutral dissociation of the N→Si dative bond, which satisfies both tendencies. The results are supported by crystallographic structure analyses and by nonempirical MO calculations of isodesmic reaction energies.

Recent studies on hypercoordinate silicon complexes² demonstrated the unusual reactivity of these compounds: their tendency to reversibly transform between penta- and hexacoordinate compounds, on one hand, and to irreversibly rearrange to more stable complexes, on the other.^{3,4} Thus neutral hexacoordinate bis-chelate complexes (**1**) undergo reversible ionization in solution (eq 1), which has been shown to strongly depend on a variety of factors: temperature (ionization is enhanced at low temperatures), solvent (ionization takes place in hydrogen-bond donor solvents, such as CHCl₃, CH₂Cl₂, and CHFCl₂), the nature of the anion, the monodentate

ligand X, and the remote substituent R.^{4d} A profound steric effect of the ligand X on the equilibrium ionization was found.



X = Me, Ph, PhCH₂
R = Me, Ph, PhCH₂, t-Bu

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(1) Part 8: see ref 4h.

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A closer observation revealed that when R = CF₃, a strongly electron-withdrawing substituent, equilibrium ionization was essentially prevented.^{4d} This was attributed to the decreased donor strength of the dimethylamino ligand in **1**, due to the electron withdrawal of the CF₃ group, resulting in increased partial positive charge on silicon, which tends to suppress formation of a silicon cation.

An opposite effect on ionization was found in complexes with bulky monodentate X ligands (X = cyclohexyl, *tert*-butyl). The proximity of the bulky X group

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Table 1. Selected Bond Lengths and Angles for Complexes **3**,⁵ **6**, **7**, and **9**

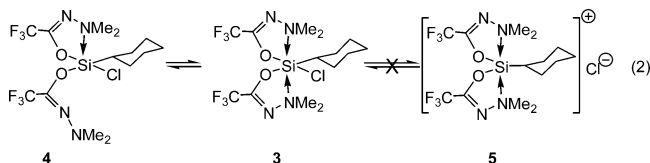
parameter	3	6	7	9
Si–N	2.0968(13)	1.956(3)	1.9683(16)	1.7401(11)
	2.1015(12)	1.963(2)	1.9955(15)	1.9587(11)
Si–O	1.8022(10)	1.7017(19)	1.7196(13)	1.7644(9)
	1.8027(10)	1.706(2)	1.7254(13)	1.8163(10)
Si–C	1.9304(13)	1.867(3)	1.920(3)	1.8721(13)
N–Si–N	158.21(5)	143.93(11)	141.61(6)	124.95(5)
O–Si–O	86.39(5)	143.07(11)	145.64(7)	164.10(5)
O–Si–C	177.81(5)	107.17(11)	107.7(10)	100.32(5)
		109.75(11)	106.6(10)	94.63(5)
O–Si–Cl	171.57(3)			

and the equally bulky dimethylamino groups in the hexacoordinate complexes **1** to the halogeno ligand forced the latter to dissociate preferentially at room temperature.^{4a,d}

In an attempt to understand the different structural effects on the ionization process and, in particular, the outcome of the two opposing effects—resistance to ionization by R = CF₃ group and enhancement of ionization by bulky X ligands—we have studied the various possible transformations of a silicon complex (**3**) containing simultaneously *both* of these structural features. In a preliminary communication we have reported that **3** dissociated in an unexpected manner upon temperature changes; namely, it underwent reversible N→Si dative bond cleavage.⁵ In the present report it is shown how subtle structural changes can profoundly modify the behavior of this class of complexes.

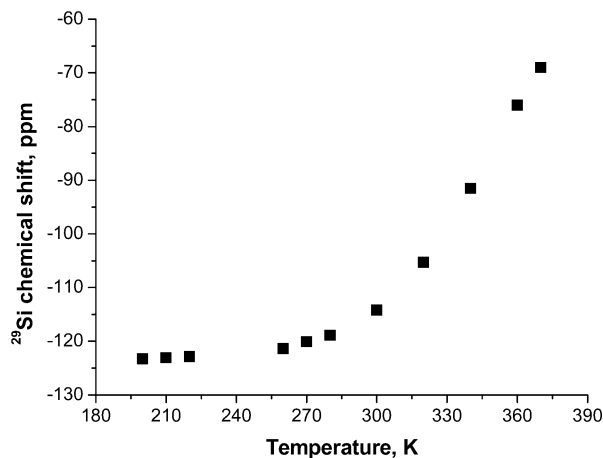
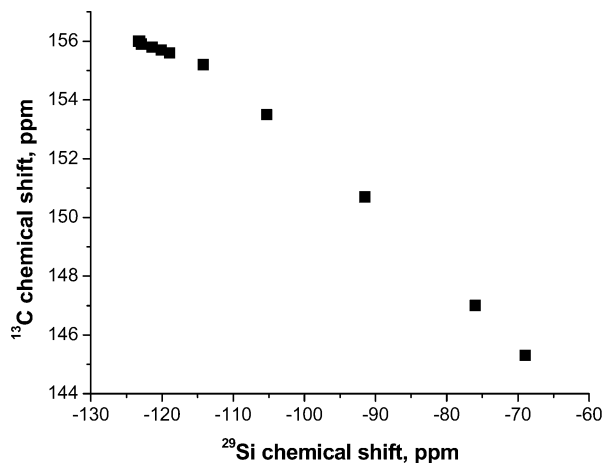
Results and Discussion

3, a neutral hexacoordinate silicon complex (equivalent to **1** with R = CF₃ and X = cyclohexyl), was prepared by transsilylation employing a method described previously,⁶ and its crystal structure was determined (Table 1).⁵ Variable-temperature ²⁹Si NMR spectroscopy of its CD₂Cl₂ solution did not show the expected downfield shift upon cooling, which previous studies had shown to be associated with ionization.^{4d–f} Instead, an *opposite* temperature dependence of the ²⁹Si chemical shift was observed: a downfield shift upon heating (Figure 1). In addition, the ¹³C chemical shift of the ring carbon (C=N) was also found to be temperature dependent and to change simultaneously with the ²⁹Si resonance (Figure 2). This suggested that rather than ionic dissociation, which is enhanced at low temperatures due to solvation, a reversible *neutral* dissociation of the N→Si dative bond had occurred to form the ring-opened **4** (eq 2).



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**Figure 1.** Temperature dependence of the ²⁹Si chemical shift of **3** in toluene-*d*₈ solution.**Figure 2.** Simultaneous variation of ¹³C and ²⁹Si chemical shifts for **3** as a function of temperature.

Since **4** is only predominant in solution at temperatures well above room temperature, and in a mixture with **3**, it could not be isolated and fully characterized. However, support for the structure of **4** is obtained from a comparison of ¹³C chemical shifts at various temperatures: the two dimethylamino groups in **4** give rise to one time-average chemical shift, due to rapid internal nucleophilic displacement (“flip-flop”) which renders all four *N*-methyl groups equivalent.⁷ At 200 K, the common ¹³C=N chemical shift in toluene-*d*₈ solution (156.0 ppm) equals that of a similar, fully hexacoordinate complex (**1**, R = CF₃, X = phenyl, 156.9 ppm^{6a}). In addition, the two dimethylamino groups are diastereotopic and give rise to four signals (49.4, 50.9, 51.8, and 52.6 ppm). It is concluded that at this temperature essentially no dissociation takes place and the compound is predominantly hexacoordinate (**3**). As the temperature is raised, the ¹³C=N resonance shifts to higher field and reaches 147 ppm at 360 K. This chemical shift is almost equal to the mean value of the noncoordinated precursor TMS-hydrazide CF₃C(OSiMe₃)=NNMe₂ (δ C=N 140.0 ppm) and the fully

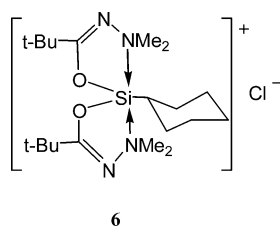
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coordinated compound at 360 K: $(140 + 156)/2 = 148$ ppm. This is in agreement with a fully dissociated Si–N bond, such that the final ^{13}C chemical shift is the average between that of the C=N group in the chelate and in a completely open ring, as in **4**.

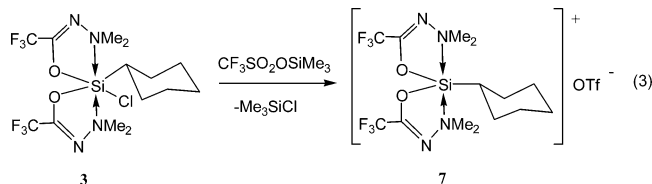
The dissociation of the N→Si bond results from two factors: the strong electron withdrawal by the CF_3 groups, through the C=N double bonds, renders the dimethylamino groups weaker donors, and hence the N→Si bonds more susceptible to cleavage. On the other hand, the bulky cyclohexyl ligand forces one of the adjacent ligands to dissociate, and since ionization is prevented by the CF_3 groups, one of the bulky dimethylamino groups departs, avoiding charge separation.

The weakness of the N→Si bond in **3** is also manifest in its length, 2.1015 Å,⁵ in contrast to other neutral hexacoordinate complexes, in which $d_{\text{N-Si}}$ ranges between 1.98 and 2.04 Å.^{2f} The bond elongation most likely results from both effects: weaker donor and steric congestion.

The ease of ionization caused by the bulky cyclohexyl ligand, observed in the absence of the CF_3 substituent, is demonstrated by the isolation of the ionic siliconium salt **6**: **6** is an analogue of **5**, in which only the CF_3 groups have been replaced by *tert*-butyl groups. It is formed in solution completely ionic already at ambient temperature, as is evident from its solution ^{29}Si chemical shift, -65.7 ppm (CDCl_3), and from its single-crystal X-ray diffraction analysis, shown in Figure 3. Thus the fact that no ionization can be observed in **3** must be attributed to the electron-withdrawing CF_3 groups. Compound **6** is the first hydrazide-based pentacoordinate siliconium chloride fully isolated to date. In other siliconium chlorides the ionization equilibrium lies closer to the nondissociated (hexacoordinate, **1**) form near room temperature and, hence, could not be crystallized.^{4d}



On the other hand, the flexibility of hypercoordinate silicon complexes allows the ionization of a close derivative of **3** (**7**) in which the chloride counterion has been replaced by triflate, through transsilylation (eq 3).



The crystal structure of **7** is depicted in Figure 4, and selected bond lengths and angles are listed in Table 1. The ionic character of **7** is evident from the well-separated independent triflate anion.

In the preliminary report⁵ a model nucleophilic substitution reaction coordinate was suggested, when in eq 2 the CF_3 groups were replaced by alkyl or phenyl

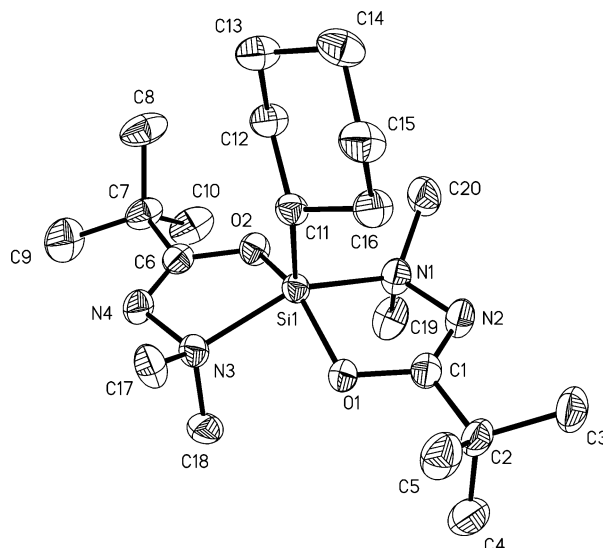


Figure 3. Molecular structure of the siliconium chloride salt **6** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity, as well as the chloride counterion.

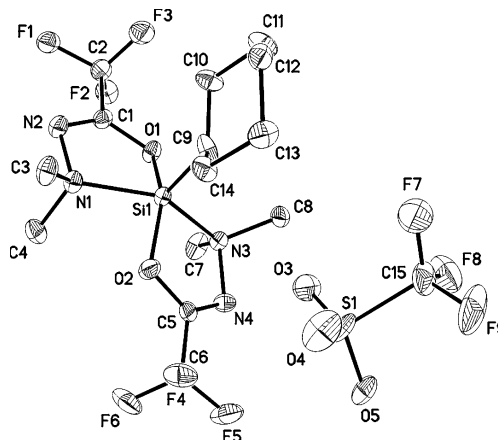


Figure 4. Molecular structure of the siliconium triflate salt **7** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

groups, such as in **6**, resulting in ionic dissociation. The complete sequence of eq 2 models a nucleophilic displacement at pentacoordinate silicon, via the hexacoordinate intermediate **3**. In this report a similar model is presented, whereby ionization is effected merely by replacing the counterion from chloride to triflate (and retaining the CF_3 substituent). Thus, subtle structural changes, either replacement of CF_3 by *tert*-butyl or replacement of the chloride counterion by triflate, completely reverse the dissociation behavior of these complexes and provide a model for a nucleophilic substitution reaction coordinate.

Interestingly, although **7** is formed in high yield, it does not undergo a methyl-triflate elimination reaction (in analogy with methyl-halide elimination found in similar siliconium-halide salts).^{4a} However, in the presence of a more powerful nucleophile, elimination readily takes place: although **3** does not ionize to any noticeable extent in CDCl_3 solution at room temperature, addition of Me_3SiI causes immediate ionization, as is evident from the immediate change in ^{29}Si chemical shift from

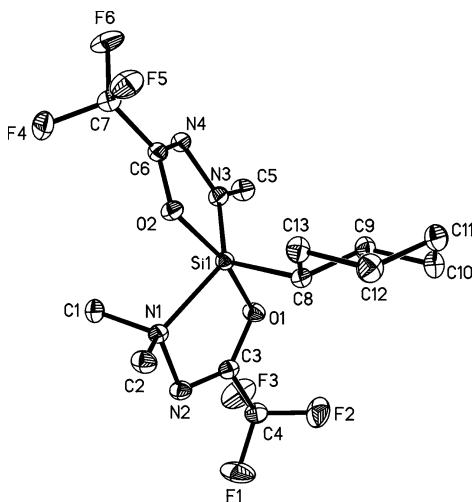
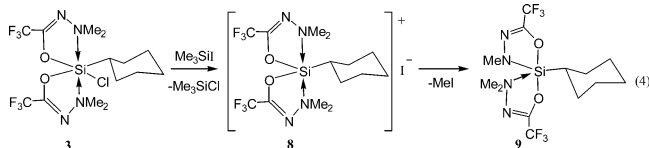


Figure 5. Molecular structure of the methyl-iodide elimination product **9** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

–114.2 to –60.4 ppm, characteristic of pentacoordination (**8**, eq 4). MeI elimination follows after mild heating and affords the neutral pentacoordinate **9**.



Formation of **9** is further confirmed by crystallographic analysis of its single crystal, shown in Figure 5. Selected bond lengths and angles are listed in Table 1.

Not only are the pentacoordinate silicon complexes discussed here versatile in terms of the mode of dissociation which they undergo, they are also exceptionally flexible in terms of the molecular geometry that they assume. Examination of the crystal structures of the complexes involved (Table 1) reveals some interesting facts. Most of the previously reported siliconium ion salts had distorted trigonal bipyramidal (TBP) geometries with N–Si–N angles about 155° and O–Si–O angles about 135°; that is, the nitrogens were axial-like and the oxygens equatorial-like, in a ~35% distorted TBP (toward square pyramid).^{4a,d} The crystallographic molecular geometries of the highly congested compounds **6**, **7**, and **9** reported here are quite different: in **6** and **7** the N–Si–N and the O–Si–O angles are essentially equal, at ~143°, and the resulting geometry is a nearly pure square pyramid. This must be a result of severe steric crowding near the bulky cyclohexyl group, forcing the equally bulky dimethylamino groups away from the axial positions.

The methyl iodide elimination product **9** is a completely inverted TBP: the originally axial nitrogen ligands now occupy essentially equatorial positions (N–Si–N angle 124.98°), while the oxygens have switched from equatorial to axial positions: O–Si–O = 164.02°. **9** is a rather unusual complex, having the dative bond in an equatorial position. Together with its recent precedent resulting from the same type of elimination

reaction,^{4a} it is the first case, to the best of our knowledge, of a dative N→Si bond in equatorial position.

Computations

To support the experimental results and gain insight into the possible reasons for the different dissociation patterns of **3** and related complexes, ab initio quantum chemical calculations were carried out for representative molecules.⁸ Full geometry optimizations, as well as harmonic frequencies and zero-point vibrational energies, were calculated using restricted density functional theory (DFT) at the B3LYP level^{9a,b} and employing the polarized 6-31G(d)^{9c,d} basis set using the GAUSSIAN-03w software system.¹⁰ All of the reported structures occupy minima on the potential energy hypersurface, as determined by vibrational frequency calculation of each compound. Total energies were also calculated at B3LYP/6-311G(3d)//B3LYP/6-31G(d), as well as the isotropic NMR shielding tensors employing the GIAO methodology.¹¹

Three basic structures were calculated and compared: the neutral hexacoordinate structure **1**, the pentacoordinate siliconium cation **2**, and the neutrally dissociated pentacoordinate complex **10** (generalized analogue of **4**), with different R substituents (R = CF₃, methyl) and X ligands (X = cyclohexyl, methyl, *tert*-butyl). The total calculated energies (including ZPE corrections) and the associated GIAO-calculated ²⁹Si chemical shifts (after subtraction of the calculated TMS chemical shift tensor) are listed in a table in the Supporting Information. The optimized geometry of the open-ring complex **4** is depicted in Figure 6. Interestingly, the dative N occupies an equatorial position in the distorted TBP complex, while O and Cl oppose each other in the axial positions (despite the fact that in the initial geometry the nitrogens occupied axial positions).

The calculated ²⁹Si chemical shifts are generally in good agreement with experiment, where the actual compounds have been prepared and measured (Table 2). Notable exceptions are found for **10**(Me,Me) and for **1**(CF₃,*t*-Bu). In the former, the calculated resonance is shifted *downfield* relative to the corresponding **2**(Me,Me), in contrast to all other similar pairs. This may be because the geometry about the C=N double bond in

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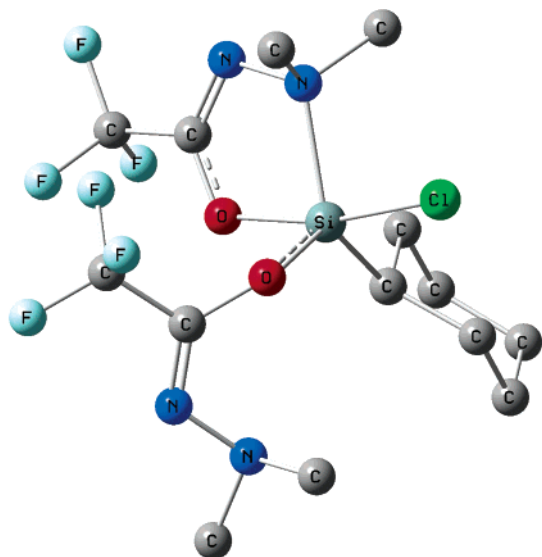


Figure 6. B3LYP/6-31g(d) optimized geometry of the open-ring complex **4**, featuring one chelate ring and one open side chain. The dative N–Si bond occupies an equatorial position.

Table 2. Experimental and Calculated ^{29}Si Chemical Shifts

compound	^{29}Si chemical shift, ppm	
	experimental	calculated
hexacoordinate (3)	–115.0 (295 K)	–118.67
siliconium ion (5)	–59.5 (7)	–64.65
	–60.3 (8)	
	–69.1 (360 K)	
open chelate (4)		–72.61

Table 3. Relative Calculated Stabilities of the Closed (1**) vs Open (**10**) Silicon Complexes ($\Delta E = E^1 - E^{10}$), at 6-311G(3d) + ZPE**

entry	R	X	ΔE , kcal/mol
1	CF ₃	cyclohexyl	1.44
2	methyl	cyclohexyl	–1.15
3	CF ₃	<i>tert</i> -butyl	9.19
4	methyl	<i>tert</i> -butyl	7.91
5	CF ₃	methyl	–4.91
6	methyl	methyl	–7.22

this compound is *E*, whereas in all other analogues **10** it is *Z*. The second “abnormal” chemical shift is for the hexacoordinate complex **1**(CF₃,*t*-Bu). Indeed this compound could not be synthesized, and the comparison is simply made with other hexacoordinate complexes. The discrepancy of about 20 ppm must be due to a somewhat distorted calculated geometry and elongated Si–N dative bonds (2.220 and 2.275 Å, compared to 2.129 and 2.101 Å in **1**(CF₃,Me)).

For the isomeric molecules **1** and **10**, the closed- and open-ring complexes, respectively, with various R and X groups, a direct energy comparison can be made to evaluate relative stabilities. The results of this comparison are listed in Table 3. Indeed we find that in the presence of a CF₃ substituent and the bulky cyclohexyl (entry 1, comparison of **3** and **4**) the open structure **4** is more stable than the closed **3** by 1.44 kcal/mol. Replacement of the CF₃ substituents by methyl groups (Table 3 entry 2) reverses this order of stability: the methyl groups are substantially less electron withdrawing than the CF₃ groups and, hence, support stronger donor abilities of the dimethylamino groups, causing strength-

ening of the N→Si bonds and consequent stabilization of the hexacoordinate (**1**).

The steric effect on the relative stability of **10** becomes much more dramatic with a *tert*-butyl ligand (entries 3, 4). With X = *tert*-butyl, the open-ring **10** is preferred by 9.19 kcal/mol relative to the hexacoordinate **1** in the presence of CF₃ groups and by 7.91 kcal/mol with methyl groups. This result serves to emphasize the huge difference in steric requirements of a tertiary alkyl relative to a secondary alkyl group. In this example the N→Si bond-weakening effect of the CF₃ groups is evident in the lower preference for **10** in the presence of methyl substituents (entry 4). This difference amounts to ~1.3 kcal/mol, which may be attributed to the electron-withdrawing power of the CF₃ groups.

Upon removal of the steric bulk by replacement of the bulky ligands by a methyl group (Table 3, entries 5, 6), the drive to open the chelate ring and release some of the congestion near the silicon atom no longer operates. This results in reversal of relative stabilities in favor of the hexacoordinate complexes **1**. Indeed, only in the presence of the bulky cyclohexyl ligand was it possible to observe neutral dissociation to **10** experimentally. In these two cases (entries 5, 6) again the electron-withdrawing power of the CF₃ groups is evident by the smaller preference of **1** relative to **10**, compared to entry 6 with methyl substitution.

Direct comparisons of molecular stabilities cannot be used for the ionic and neutral species (**2** and **1**, as well as **2** and **10**), because they are not isomers. For comparisons of nonisomeric structures, we resort to isodesmic reactions. The effects of the remote substituents R and the monodentate ligand X on relative stabilities of the three basic structures (**1**, **2**, and **10**) were studied by means of isodesmic reaction energies. Two isodesmic reactions were formulated (eqs 5 and 6), describing the effect of exchanging substituents R with R¹ between **1** and **2**, and between **2** and **10**, respectively, while keeping the ligand X constant. Analogous reactions were also used to probe the effect of interchanging the monodentate ligands X and X¹ between each pair of nonisomeric complex types (**1** and **2**, and **2** and **10**), while keeping the remote substituent R constant (eqs 7 and 8, respectively). The reaction energies for all four isodesmic reactions were evaluated at both levels of calculation and are listed in Table 4.

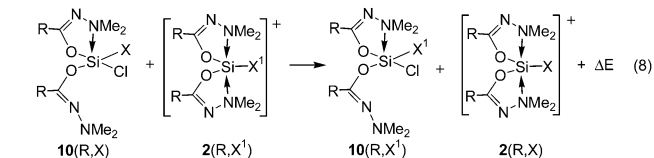
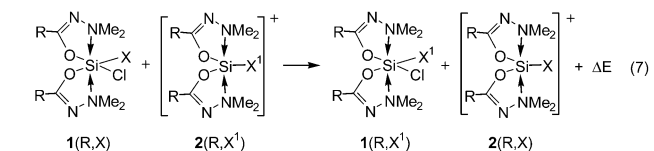
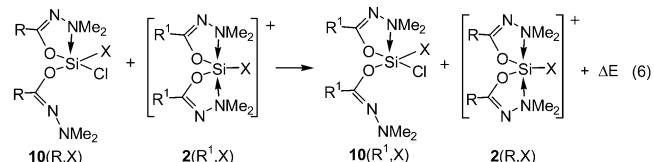
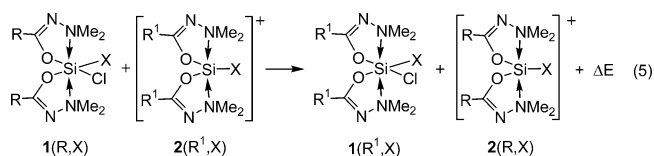
Examination of the data in Table 4 provides a consistent picture of electronic and steric effects on the dissociation patterns of **1**, in full agreement with the experimental observations. First, it should be noted that the results obtained from the two levels of theory [B3LYP/6-31G(d)//B3LYP/6-31G(d) and B3LYP/6-311G(3d)//B3LYP/6-31G(d)] are essentially equivalent. The analysis below relates to the higher level of computation.

The isodesmic reaction energies show which side of each equation is more stable: the products are more stable when $\Delta E < 0$, and the reactants when $\Delta E > 0$. Examination of eq 5 (Table 4, entries 1–3) shows that in all cases the reactants are substantially more stable than the products. This suggests that the ionic **2** is more stable with a methyl than with a CF₃ substituent, in accord with experiment.^{4d} However, the possibility that the positive reaction energy is dominated by a greater

Table 4. Calculated Isodesmic Reaction Energies at B3LYP/6-31G(d) and at B3LYP/6-311G(3d)^a

entry	equation	R	R ¹	X	X ¹	ΔE , kcal/mol 6-31G(d)	ΔE , kcal/mol 6-311G(3d)
1	5	CF ₃	Me	cyclohexyl	cyclohexyl	13.65	14.19
2	5	CF ₃	Me	Me	Me	14.08	14.56
3	5	CF ₃	Me	<i>tert</i> -butyl	<i>tert</i> -butyl	14.23	14.78
4	6	CF ₃	Me	cyclohexyl	cyclohexyl	16.92	16.78
5	6	CF ₃	Me	Me	Me	16.83	16.88
6	6	CF ₃	Me	<i>tert</i> -butyl	<i>tert</i> -butyl	16.40	16.05
7	7	CF ₃	CF ₃	cyclohexyl	Me	-4.90	-5.16
8	7	Me	Me	cyclohexyl	Me	-4.47	-4.80
9	7	CF ₃	CF ₃	<i>tert</i> -butyl	Me	-4.50	-4.55
10	7	Me	Me	<i>tert</i> -butyl	Me	-4.65	-4.77
11	8	CF ₃	CF ₃	cyclohexyl	Me	1.14	1.17
12	8	Me	Me	cyclohexyl	Me	1.05	1.26
13	8	CF ₃	CF ₃	<i>tert</i> -butyl	Me	9.62	9.53
14	8	Me	Me	<i>tert</i> -butyl	Me	10.05	10.36

^a Calculated total energies and zero point vibrational corrections, as well as ²⁹Si NMR chemical shifts for all of the molecules are given in the Supporting Information.



stability of the hexacoordinate **1**(CF₃) relative to **1**(Me) cannot be ruled out completely.

Regardless of the ligand X, in all three entries for eq 5 (entries 1–3) the reaction energies are essentially the same; that is, the electronic influence of the substituent R is practically independent of the steric bulk of ligand X. This general observation remains true also for the other data in Table 4, relating to eqs 6–8. It is concluded that the electronic and steric effects probed by eqs 5–8 are mutually independent.

Even greater isodesmic reaction energies are found in entries 4–6, relating to eq 6, which probes the ionic vs the open-ring pentacoordinate complex stabilities. These also indicate that the ionic form is preferred in the presence of the methyl- over the CF₃-substituted species. In this case, *both* **2** and **10** favor the reactant relative to the product substitution, resulting in the greatest reaction energies in the entire series.

The remaining isodesmic equations, 7 and 8, probe the effect of changing steric bulk of the ligands X. Like in eqs 5 and 6, the reaction energies are independent of the remote substituent R. For entries 7 and 8 in Table 4, the reaction energy corresponds to greater stability of the products relative to the reactants. This can easily

be understood, since the cation (**2**) with the bulky cyclohexyl is more stable than that with a methyl ligand, and the hexacoordinate **1** is *less* stable with a cyclohexyl than with a methyl ligand. Strangely, the isodesmic energies for entries 9 and 10 are the same as those for 7 and 8, indicating that replacement of a methyl by a cyclohexyl or by a *tert*-butyl ligand is essentially equivalent.

The reaction energies for eq 8 (entries 11, 12) show a small preference for the reactants relative to products. The open-ring complex **10** is more stable with the cyclohexyl relative to a methyl ligand, while the cation **2** is apparently also more stable with cyclohexyl relative to methyl, thus reducing the overall effect of exchanging X ligands. This result is different for X = *tert*-butyl (entries 13, 14): in this case the reactants are favored by ~10 kcal/mol. Apparently, both parts of the reaction favor the reactants: the *tert*-butyl is more stable in the **10** geometry, while the methyl is more stable in the ionic (**2**) form. The components of eq 8 are all pentacoordinate; that is, the steric relief by removal of one of the ligands has already occurred. One can speculate as to why the reaction energies are so different in entries 11 and 12 relative to entries 13 and 14. Perhaps the less sterically demanding cyclohexyl group is equally stabilizing for **10** as it is for **2**, while the bulkier *tert*-butyl group prefers **10**, in which the bulky NMe₂ group has been moved out of the way, over **2**, in which the less bulky chloro ligand has dissociated.

The calculations provide additional evidence that the open-ring complex **4**, which was seen only by NMR and could not be isolated, is a stable species relative to **3** and **5** and, hence, is a reasonable intermediate. Furthermore, its calculated ²⁹Si chemical shift is in good agreement with observation. Attempts to prepare **4** with a *tert*-butyl ligand (which should be stable according to calculations) failed. The effects of the R substituent and the X ligand have been demonstrated, in agreement with NMR experiments, namely, that an electron-withdrawing R group destabilizes the ionic form and stabilizes the open-ring structure, while bulky ligands promote both the ionic and the open-ring geometries, at the expense of the destabilized hexacoordinate **3**.

Experimental Section

General Procedures. The reactions were carried out under dry argon using Schlenk techniques. Solvents were dried and

Table 5. Crystal Data and Experimental Parameters for the Structure Analyses of 6, 7 and 9

	6	7	9
CCDC number	225180	261966	261965
empirical formula	C ₂₃ H ₄₄ Cl ₁₀ N ₄ O ₂ Si	C ₁₅ H ₂₃ F ₉ N ₄ O ₅ SSi	C ₁₃ H ₂₀ F ₆ N ₄ O ₂ Si
formula mass, g mol ⁻¹	791.21	570.52	406.42
collection <i>T</i> , K	173(2)	100(2)	100(2)
cryst syst	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pca</i> 2 ₁	<i>P</i> 1
<i>a</i> , Å	18.6709(11)	18.726(3)	8.0658(16)
<i>b</i> , Å	10.0493(6)	8.0215(13)	9.4973(19)
<i>c</i> , Å	20.2826(12)	15.525(3)	12.373(3)
α, deg	90	90	81.993(3)
β, deg	100.5080(10)	90	73.243(3)
γ, deg	90	90	83.597(3)
<i>V</i> , Å ³	3741.8(4)	2332.0(7)	896.2
<i>Z</i>	4	4	2
ρ _{calc} , Mg/m ³	1.405	1.625	1.506
<i>F</i> (000)	1640	1168	420
θ range, deg	2.14–25.35	2.54–26.33	2.17–26.44
no. of coll reflns	58 765	42 991	18 909
no. of indep reflns	6858	4743	3673
<i>R</i> _{int}	0.0236	0.0376	0.0233
no. of reflns used	6858	4743	3673
no. params	443	422	238
Goof	1.036	1.085	1.053
<i>R</i> 1, ^a <i>wR</i> 2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0529, 0.1400	0.0307, 0.0767	0.0308, 0.0806
<i>R</i> 1, ^a <i>wR</i> 2 ^b (all data)	0.0579, 0.1450	0.0315, 0.0772	0.0324, 0.0816
max./min. res electron dens (e Å ⁻³)	+1.258/−0.586	+0.419/−0.191	+0.464/−0.241

purified by standard methods. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13, 125.76, and 99.36 MHz, respectively, for ¹H, ¹³C, and ²⁹Si spectra. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent-proton (or carbon) signals for ¹H and ¹³C and directly from TMS for ²⁹Si. Melting points were measured in sealed capillaries using a Buchi melting point instrument. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

X-ray Measurements. The data sets for all compounds were collected from oil-coated shock-cooled crystals on a Bruker SMART-APEX diffractometer with a D8 goniometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) equipped with a low-temperature device in omega-scan mode (see Table 5)^{12–14} The data were integrated with SAINT,¹⁵ and an empirical absorption correction was applied.¹⁶ The structures were solved by direct methods (SHELXS-97)¹⁷ and refined by full-matrix least-squares methods against *F*² (SHELXL-97).¹⁸ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp² (sp³) carbon atoms were assigned ideal positions and refined using a riding model with *U*_{iso} constrained to 1.2 (1.5) times the *U*_{eq} value of the parent atom. Disordered moieties were refined using bond lengths and similarity restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 5. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

Chlorobis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*]-cyclohexylsilicon(IV) (3). To a stirred solution of *O*-trimethylsilylated 1,1-dimethyl-2-(trifluoroacetyl)hydrazine¹⁹ (0.511 g,

2.24 mmol) in 5 mL of dry CHCl₃ was added C₆H₁₁SiCl₃ (0.243 g, 1.12 mmol) at room temperature under dry argon. The mixture was stirred for 12 h at 90 °C. Removal of the volatiles under vacuum (0.02 mmHg) resulted in a colorless crystalline solid (0.502 g, 98% yield), **3**, mp 65 °C. ¹H NMR (CDCl₃, 300 K): δ 1.12–2.01 (m, 11H, C₆H₁₁), 2.98 (s, 12H, NMe₂). ¹³C NMR (CDCl₃, 300 K): δ 26.8, 28.8, 31.3, 31.4, 39.6, 40.0 (C₆H₁₁), 50.7 (NMe₂), 118.0 (q, ¹*J*_{CF} = 276 Hz, CF₃), 155.1 (q, ²*J*_{CF} = 37.8 Hz, C=N). ²⁹Si NMR (CDCl₃, 300 K): δ −113.2. Anal. Calcd for C₁₄H₂₃ClF₆N₄O₂Si: C, 36.80; H, 5.07; N, 12.26. Found: C, 36.86; H, 5.10; N, 12.30.

Cyclohexylbis[*N*-(dimethylamino)pivaloimidato-*N,O*]-siliconium Chloride (6). To a stirred solution of *t*-BuC(OTMS)=NNMe₂^{4d} (0.732 g, 3.38 mmol) in 10 mL of dry CHCl₃ was added C₆H₁₁SiCl₃ (0.381 g, 1.75 mmol) at room temperature under dry argon. The mixture was stirred for 10 min. Removal of the volatiles under vacuum (0.02 mmHg) resulted in a colorless crystalline solid. It was washed with 10 mL of hexane and dried. The yield was 91% (0.669 g) **5**, mp 90–92 °C. ¹H NMR (CDCl₃, 300 K): δ 0.85–1.75 (m, 11H, C₆H₁₁), 1.08 (s, 18H, *t*-Bu), 2.91 (s, 12H, NMe₂). ¹³C NMR (CDCl₃, 300 K): δ 26.2 (C(CH₃)₃), 35.1 (CMe₃), 23.2, 25.3, 26.8, 27.2, 27.6 (C₆H₁₁), 48.6, 50.6 (NMe₂), 175.1 (C=N). ²⁹Si NMR (CDCl₃, 300 K): δ −65.7. Anal. Calcd for C₂₀H₄₁ClN₄O₂Si: C, 55.46; H, 9.54; N, 12.94. Found: C, 55.10; H, 9.60; N, 12.81.

Cyclohexylbis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*]-siliconium Triflate (7). To a frozen solution of crude **3** [prepared from CF₃C(OTMS)=NNMe₂ (0.706 g, 3.09 mmol) and C₆H₁₁SiCl₃ (0.310 g, 1.43 mmol)] in 5 mL of dry CHCl₃ was added by vacuum condensation 0.345 g (1.55 mmol) of trimethylsilyl triflate. The mixture was allowed to warm and after 1 h at ambient temperature was concentrated under 0.1 mmHg and washed twice with hexane, to yield 0.777 g (96%) of a colorless powder, **6**. Mp: 145–147 °C. ¹H NMR (CD₃CN, 270 K): δ 1.25–1.74 (m, 11H, C₆H₁₁), 3.09 (s, 6H, NMe), 3.26 (s, 6H, NMe). ¹³C NMR (CD₃CN, 270 K): δ 23.0, 26.0, 26.4, 27.5, 27.9, 28.2 (C₆H₁₁), 50.4 (NMe), 50.8 (NMe), 127.3 (q, ¹*J*_{FC} = 320 Hz, CF₃), 121.5 (q, ¹*J*_{FC} = 280 Hz, CF₃), 158.0 (q, ²*J*_{FC} = 41 Hz, C=N). ²⁹Si NMR (CD₃CN, 270 K): δ −59.5. Anal. Calcd

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for $C_{15}H_{23}F_9N_4O_5SSi$: C, 31.58; H, 4.06; N, 9.82. Found: C, 31.63; H, 4.15; N, 9.71.

Cyclohexylbis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*]siliconium Iodide (8). **8** was prepared as described for **7**, from crude **3** [made from $C_6H_{11}SiCl_3$ (0.349 g, 1.60 mmol) and $CF_3C(OTMS)=NNMe_2$ (0.765 g, 3.35 mmol)] and 0.857 g (1.56 mmol) of Me_3SiI . The solid residue **8** was washed with hexane and dried (0.452 g, 71% yield), mp 101–103 °C. 1H NMR ($CDCl_3$, 280 K): δ 0.85–1.68 (m, 11H, C_6H_{11}), 3.18 (s, 6H, NMe), 3.20 (s, 6H, NMe). ^{13}C NMR ($CDCl_3$, 280 K): δ 22.2, 24.9, 25.8, 26.2, 26.5, 26.8 (C_6H_{11}), 50.0 (NMe), 51.6 (NMe), 115.4 (q, $^1J_{FC} = 278$ Hz, CF_3), 156.6 (q, $^2J_{FC} = 42$ Hz, C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ -60.3. Anal. Calcd for $C_{14}H_{23}F_6IN_4O_2Si$: C, 30.67; H, 4.23; N, 10.22. Found: C, 30.66; H, 4.31; N, 10.26.

Cyclohexyl[*N*-(dimethylamino)trifluoroacetimidato-*N,O*][*N*-(methylamino)trifluoroacetimidato-*N,O*]silicon-(IV)** (9).** A solution of **8** (0.857 g, 1.57 mmol) in 5 mL of $CHCl_3$ was heated and kept for 3 h at 70 °C under reduced pressure, followed by removal of the volatiles under vacuum. The slightly yellow solid residue was recrystallized from hexane to give **9** (0.452 g, 71% yield), mp 92–93 °C. 1H NMR ($CDCl_3$, 270 K): δ 1.00–1.68 (m, 11H, C_6H_{11}), 2.65 (s, 3H, NMe), 3.03 (s, 3H,

NMe), 3.13 (s, 3H, NMe). ^{13}C NMR ($CDCl_3$, 270 K): δ 26.4, 27.5, 27.6, 27.8 (C_6H_{11}), 37.2 (NMe), 47.6 (NMe), 48.0 (NMe), 118.8 (q, $^1J_{FC} = 278$ Hz, CF_3), 120.0 (q, $^1J_{FC} = 278$ Hz, CF_3), 142.9 (q, $^2J_{FC} = 42$ Hz, C=N), 149.6 (q, $^2J_{FC} = 42$ Hz, C=N). ^{29}Si NMR ($CDCl_3$, 270 K): δ -69.4. Anal. Calcd for $C_{13}H_{20}F_6N_4O_2Si$: C, 38.42; H, 4.96; N, 13.79. Found: C, 38.35; H, 5.01; N, 13.69.

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Supporting Information Available: Tables of crystallographic data for compounds **6**, **7**, and **9**. Calculated optimum-geometry coordinates for all of the differently substituted **1**, **2**, and **10**, in Gaussian Archive format, and a table of final calculated energies and ^{29}Si NMR chemical shifts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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