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# Donor-Stabilized Silyl Cations. 3. Ionic Dissociation of Hexacoordinate Silicon Complexes to Pentacoordinate Siliconium Salts Driven by Ion Solvation[1]

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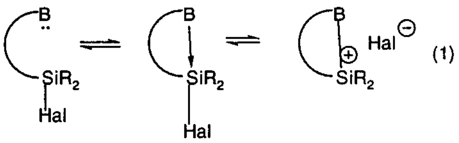
Neutral hexacoordinate silicon complexes **1** undergo an equilibrium dissociation to ionic siliconium chlorides **6** at low temperatures in polar solvents: chloroform, dichloromethane, and fluorodichloromethane. The extent of dissociation increases with decreasing temperature, despite the formation of two ions from each molecule. The reaction enthalpies and entropies for the ionizations are negative, and their absolute values increase with increasing solvent polarity, indicating that solvation of the ions drives the dissociation process. The position of the equilibrium is readily controlled by variation of solvent polarity, temperature, replacement of the chloro ligand by better leaving groups (triflate, bromide, or tetrachloroaluminate), and variation of substituents (R) or ligands (X). The results are supported by crystal structures of the siliconium salts: **8a**,**c**,**d** and **14d**.

## Introduction

The $^{29}$Si NMR chemical shifts in pentacoordinate silicon chelates are known to be temperature and solvent dependent.[3a−c] These changes in chemical shifts were attributed to variations in the extent and intensity of coordination of donor atoms to silicon, representing the progress along a hypothetical nucleophilic substitution ($S_N2$) reaction coordinate (eq 1).[4] However, it is surprising that to date no similar changes in coordination have been reported in hexacoordinate silicon complexes.[3,5]



(1)

It has never been possible to determine clearly whether these chemical shift changes represent equilibrium reactions (as in eq 1) or continuous changes in the strength of coordination, because the components could never be observed individually in the mixture.[3,4] In the present study similar changes in $^{29}$Si chemical shifts in hexacoordinate silicon compounds are reported, resulting from well-defined ionic dissociation equilibria between neutral hexacoordinate and distinct ionic pentacoordinate complexes, in a mechanism best described as an $S_N1$-type substitution reaction.

We have noticed slight changes in the ambient-temperature $^{29}$Si NMR spectra of neutral octahedral silicon complexes (**1**) in different solvents, which might be due to changes in coordination. In addition, two apparently very similar ligand exchange reactions at silicon were reported to yield substantially different products (eq 2): the reaction of trichlorosilanes (**2**) with the isomeric *O*- (**3**) or *N*-trimethlsilylated (**4**) hydrazides led in the former case to neutral, hexacoordinate chelates (**1**),[5,6] but in the latter case to the formation of siliconium chloride salts (**5**).[7] These two observations, the chemical shift dependence upon solvent and the formation of either ionic pentacoordinate or neutral hexacoordinate silicon complexes from very similar

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(1) For number 2 in the series see: Kingston, V.; Gostevskii, B.; Kalikhman, I.; Kost, D. *Chem. Commun.* **2001**, 1272. Ref 7 is considered number 1 in the series.

(2) On leave of absence from the Institute of Chemistry, Russian Academy of Sciences, Siberian Branch, Irkutsk.

(3) For reviews on hypervalent silicon complexes see: (a) Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds;* Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 1339. (c) Voronkov, M. G.; Pestunovich, V. A.; Baukov, Yu. I. *Metalloorg. Khim.* **1991**, *4*, 1210. (d) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17; **1996**, *96*, 927. (e) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester U.K., 1989; p 1241. (f) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, 93, 1371. (g) Chuit, C.; Corriu, R. J. P.; Reyé, C. In *The Chemistry of Hypervalent Compounds*; Kin-ya Akiba, Ed.; Wiley-VCH: Weinheim, Germany, 1999; p 81. (h) Kira, M.; Zhang L. C. In *The Chemistry of Hypervalent Compounds*; Kin-ya Akiba, Ed.; Wiley-VCH: Weinheim, Germany, 1999; p 147. (i) Brook, M. A. *Silicon in Organometallic and Polymer Chemistry*; Wiley: New York, 2000, p 97.

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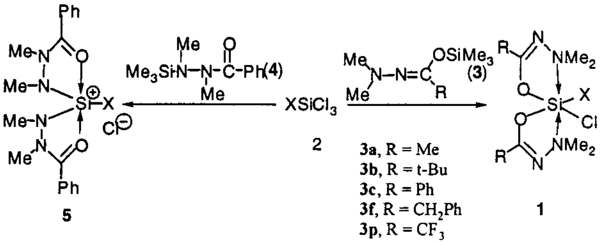
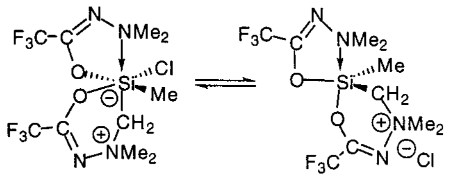
exchange reactions, prompted us to reinvestigate in greater detail the syntheses and structures of compounds **1**, in search for possible formation of siliconium ions.



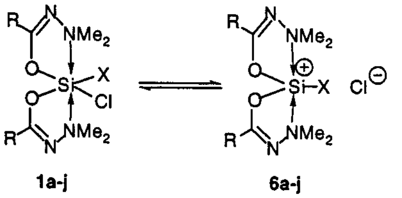
(2)

An early indication that ionic cleavage of the Si–Cl bond takes place has recently been reported (eq 3).[8]



(3)

Compounds **1** had previously been studied, and the evidence (crystal structures, touene-$d_8$ solution NMR) showed that they were neutral, octahedral hexacoordinate complexes.[5,6] The present article describes the solvent-driven reversible ionization of the Si–Cl bond in **1**, resulting in novel siliconium salts (**6** and analogues, eq 4). This is an unusual equilibrium reaction showing *increased dissociation at low temperature*, in contrast to intuitive expectation. Various factors affecting the equilibrium populations of **1** and **6** are analyzed and discussed, including the effect of temperature, solvent, remote substituent R, monodentate ligand X, replacement of the counterion, and steric factors. The only previously reported spontaneous equilibria of similar nature are between neutral and ionic pentacoordinate complexes[9a] and between tetracoordinate silylammonium and pentacoordinate siliconium ions.[9b,c,10] Ionic dissociation of hexacoordinate silicon complexes has not been reported.



**1a-j** **6a-j**

(4)

**a**, R = X = Me
**b**, R = t-Bu, X = Me
**c**, R = Ph, X = Me
**d**, R = Me, X = Ph
**e**, R = t-Bu, X = Ph
**f**, R = CH$_2$Ph, X = Ph
**g**, R = X = Ph
**h**, R = Me, X = CH$_2$Ph
**i**, R = X = CH$_2$Ph
**j**, R = Ph, X = CH$_2$Ph

## Results and Discussion

Two different routes were studied by which species derived from neutral **1** dissociate to form siliconium ion salts: (a) spontaneous dissociation of the Si–Cl bond at low temperature and (b) replacement of the chloro ligand in **1** by other anionic groups (triflate, bromide, and tetrachloroaluminate), generating siliconium salts at room temperature.

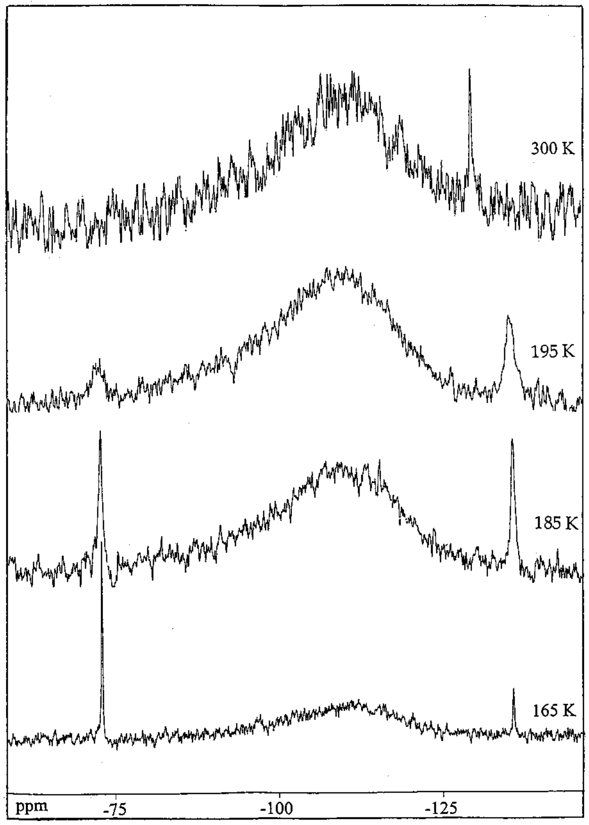


**Figure 1.** $^{29}$Si NMR spectra of **1d** in $CD_2Cl_2$ solution at various temperatures.

**(a) Spontaneous Ionic Dissociation at Low Temperature.** The effects of temperature and solvent on the $^{29}$Si NMR spectra of neutral hexacoordinate silicon complexes **1** have been studied in some detail. For example, upon cooling of a $CD_2Cl_2$ solution of **1d** in an NMR tube, a dramatic change in the $^{29}$Si NMR chemical shift was observed (Figure 1): the initial relatively sharp signal at $\delta$ −131.3 ppm (300 K) shifted gradually toward lower field, accompanied by line broadening. At temperatures below 253 K line broadening caused complete disappearance of the signal into the baseline, until at temperatures below 200 K *two* broad signals emerged, at chemical shifts typical of hexacoordinate and pentacoordinate complexes (−135.6 and −73.0 ppm, respectively). The low-field signal was assigned to the siliconium chloride salt **6d** (eq 4). This is confirmed by exact chemical shift analogy with isolated and well-characterized siliconium triflate and tetrachloroaluminate salts (see below and Table 1), as well as the bromide salt. The high-field signal corresponds to hexacoordinate **1d**, as verified by chemical shift analogy with the temperature-invariant $^{29}$Si NMR spectrum in toluene-$d_8$ solution, in which no ionization takes place (Table 1).[11a]

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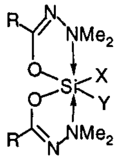
**Table 1. $^{29}$Si Chemical Shifts for the Equilibrium Mixtures of 1 and the Corresponding Siliconium Chlorides 6 at Two Temperatures, Triflates (8), Bromides (11) and Tetrachloroaluminates (14)**

| | | | | **1 ⇄ 6** | **1** | **8** | **11** | **14** |
|---|---|---|---|---|---|---|---|---|
| compd | R | X | *T*, K | $CD_2Cl_2$ | tol-$d_8$ | $CDCl_3$ | $CDCl_3$ | $CDCl_3$ |
| **a** | Me | Me | 300 | −121.3 | −128.6[a] | −61.7 | −61.8 | |
| | | | 165 | −65.0br | −130.0 | | | |
| **b** | *t*-Bu | Me | 300 | −120.3 | −128.8 | | −61.4 | |
| | | | 165 | −65.0br | | | | |
| **c** | Ph | Me | 300 | −121.8 | −127.9 | −60.9 | −61.3 | −62.5 |
| **d** | Me | Ph | 300 | −131.3 | −135.6 | −73.2 | −73.0 | −73.2 |
| | | | 165 | −73.0, −135.6 | | | | |
| **e** | *t*-Bu | Ph | 300 | −132.9 | | −73.6 | | |
| | | | 165 | −73.6, −135.9 | | | | |
| **f** | $PhCH_2$ | Ph | 300 | −133.7 | | −73.4 | | |
| | | | 165 | −73.4, −135.9 | | | | |
| **g** | Ph | Ph | 300 | −133.7 | −136.9[b] | −72.6 | −72.2 | −72.0 |
| | | | 165 | −73.2, −136.9 | | | | |
| **h** | Me | $PhCH_2$ | 300 | −125.4 | | −65.8 | −65.2 | −65.3 |
| | | | 165 | −65.9 | | | | |
| **i** | $PhCH_2$ | $PhCH_2$ | 300 | −128.5 | | −66.1 | | |
| | | | 165 | −66.3, −132.1 | | | | |
| **j** | Ph | $PhCH_2$ | 300 | −127.8 | | −65.1 | −65.0 | |
| | | | 165 | −64.7, −130.3 | | | | |
| **k** | Ph | *t*-Bu | 300 | −61.1 | | | | |
| **l** | *t*-Bu | *t*-Bu | 300 | −61.1 | | | | |
| **m** | Me | *t*-Bu | 300 | −61.6 | | | | |

[a] The corresponding solid state (CP-MAS) value: −128.8 ppm. [b] The corresponding solid state (CP-MAS) value: −136.4 ppm.

A similar dissociation is observed for other compounds **1** in $CDCl_3$ and $CD_2Cl_2$ solutions (**1a**−**j**) and is evident from the $^{29}$Si NMR spectra (Table 1). This constitutes the first *direct and spontaneous* ionic dissociation of the octahedral chlorocomplexes **1** to the corresponding siliconium chlorides **6**. The dissociation process is completely reversible, and the two species (**1** and **6**) are in equilibrium with each other in solution. It should be noted, however, that not all of the neutral hexacoordinate compounds **1** dissociate spontaneously at low temperature: compounds with electron-withdrawing substituents or ligands (**1n**−**q** and **7a**,**b**) did not show any spectral changes upon cooling.



**1n-q**
**7a,b**

**1n**, R = Ph, X = Y = Cl
**1o**, R = Me, X = Y = Cl
**1p**, R = $CF_3$, X = Me, Y = Cl
**1q**, R = $CF_3$, X = Ph, Y = Cl
**7a**, R = Ph, X = Y = Br
**7b**, R = Me, X = Ph, Y = F

**Temperature Effects on Equilibrium Constant: Negative Reaction Entropy**. The equilibrium constants $K = [\mathbf{6}]/[\mathbf{1}]$ were evaluated directly from the $^{29}$Si NMR spectra below the coalescence temperatures, when the signals for both species were observable and their areas could be measured.[11b] At higher temperatures, at which only a single average signal was observed, the equilibrium populations were calculated from the weighted-average chemical shift and the shifts of each of the components. Using this technique the *K* values for **1d** ⇄ **6d** have been evaluated at several temperatures and used for a ln *K* vs $T^{-1}$ plot (Figure 2). From the linear relation the reaction enthalpy and entropy have been extracted: $\Delta H° = -2.8$ kcal mol$^{-1}$, $\Delta S° = -15$ cal mol$^{-1}$ deg$^{-1}$. The equilibrium constants at selected temperatures and solvents and the thermodynamic data for other members of series **1** have been determined and are listed in Table 2. [11c]

A striking fact with regard to the dissociation process is the observation that it takes place *at low temperature*: one might expect a dissociation process, converting one molecule into two particles, to be favored as the temperature is *increased*. The present observation is at odds with this expectation.[12] The unexpected negative entropies and enthalpies found for all of the equilibrium dissociation reactions suggest that solvent aggregation, associated with the dissociation process, takes place at low temperatures.[13] Solvent aggregation about the chloride anion in **6** may provide the stabilization necessary for ion separation and could account for the negative entropies.

**Solvent Effect on Equilibrium**. The question of possible solvent aggregation was addressed by investigating the solvent effect on the equilibrium reaction

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(10) A case of *photo*isomerization of an azobenzene-derived ligand, leading to interconversion between a pentacoordinate and a hexacoordinate silicate has been reported: Kano, N.; Komatsu, F.; Kawashima, T. *J. Am. Chem. Soc.* **2001**, *123*, 10778.

(11) (a) Previously reported NMR spectra for **1** at low temperatures were measured in toluene-$d_8$ solutions, in which no dissociation took place.[5a] (b) $^{29}$Si NMR was used, despite the potential superiority of $^1$H signal integration, because at low temperatures the two species were well resolved only in the $^{29}$Si spectra, due to the huge chemical shift differences (ca. 6000 Hz!). (c) The fact that reasonable linear correlations were obtained for the ln *K* vs 1/*T* plots, and in particular the fact that points for these plots below and above the coalescence temperature, obtained in different ways, fit well in the same lines, adds confidence to the quantitative data obtained from $^{29}$Si NMR spectra.

(12) A similar phenomenon was found in the ionization of diarylmethyl chlorides in $BCl_3/CH_2Cl_2$: Schneider, R.; Mayr, H.; Plesch, P. H. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1369. We thank Prof. Mayr for bringing this reference to our attention.

(13) This is quite common in aqueous acid solutions, where solvation is a major factor. For examples see: (a) Gelb, R. I.; Alper, J. S. *J. Chem Eng. Data* **1998**, *43*, 1068. (b) Kandegedara, A.; Rorabacher, D. B. *Anal. Chem.* **1999**, *71*, 3140. (c) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; ACS Monograph; Reinhold: New York, 1958; p 667.

**Table 2. Equilibrium Constants at Selected Temperatures, Enthalpies and Entropies for the Reaction 1 ⇄ 6, and Approximate Coalescence Temperatures and Activation Free Energies for the Dissociation**

| | | | | $K$ = [**6**]/[**1**] | | | $\Delta H°$ | $\Delta S°$ | corr | | $T_c$, | $\Delta G^‡$ (±0.5) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | R | X | solvent | 300 K | 180 K | 165 K | kcal mol$^{-1}$ | cal mol$^{-1}$K$^{-1}$ | coeff[a] | n[a] | (±5) K | kcal mol$^{-1}$ |
| **1a** | Me | Me | $CD_2Cl_2$ | 0.10 | 2.1 | | −2.56 | −13.4 | 0.998 | 11 | 170 | 6.5 |
| **1a** | Me | Me | $CDCl_3$ | 0.05 | ∞ | | −3.56 | −18.1 | 0.990 | 8 | | |
| **1a** | Me | Me | $CHFCl_2$ | 0.53[b] | ∞ | | −6.70 | −23.8 | 0.998 | 8 | | |
| **1b** | *t*-Bu | Me | $CD_2Cl_2$ | 0.12 | 3.7 | | −3.08 | −14.6 | 0.993 | 12 | 170 | 6.5 |
| **1c** | Ph | Me | $CD_2Cl_2$ | 0.07 | | | | | | | 170 | 6.5 |
| **1d** | Me | Ph | $CD_2Cl_2$ | 0.08 | 1.38 | 4.0 | −2.84 | −15.0 | 0.992 | 9 | 215 | 8.4 |
| **1d** | Me | Ph | $CDCl_3$ | 0.04 | | | −3.59 | −18.9 | 0.988 | 6 | | |
| **1d** | Me | Ph | $CHFCl_2$ | 2.55[b] | ∞ | | −6.79 | −22.94 | 0.996 | 6 | | |
| **1e** | *t*-Bu | Ph | $CD_2Cl_2$ | 0.05 | 0.85 | 3.3 | −3.94 | −21.8 | 0.990 | 6 | 220 | 8.6 |
| **1f** | $PhCH_2$ | Ph | $CD_2Cl_2$ | 0.14 | 0.69 | 1.2 | −1.94 | −9.4 | 0.996 | 5 | 230 | 9.0 |
| **1g** | Ph | Ph | $CD_2Cl_2$ | 0.05 | 0.13 | | −0.82 | −8.6 | 0.996 | 3 | 220 | 8.6 |
| **1h** | Me | $PhCH_2$ | $CD_2Cl_2$ | 0.04 | | 30.0 | −3.88 | −17.5 | 1.000 | 7 | 195 | 7.5 |
| **1i** | $PhCH_2$ | $PhCH_2$ | $CD_2Cl_2$ | 0.05 | | 0.95 | −1.93 | −12.3 | 0.997 | 9 | 205 | 7.9 |
| **1j** | Ph | $PhCH_2$ | $CD_2Cl_2$ | 0.04 | | 0.5 | −1.78 | −12.2 | 0.997 | 7 | 200 | 7.7 |

[a] Correlation coefficient and number of points in thermodynamic correlation. [b] Measured at 278 K.

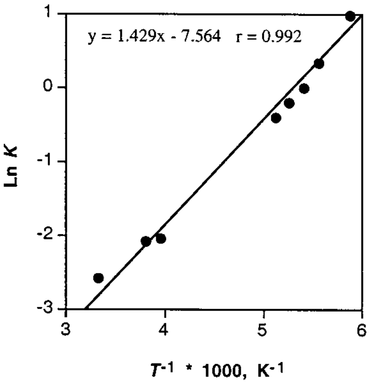

**Figure 2.** Plot of ln $K$ vs $1/T$ for the equilibrium reaction **1d** ⇄ **6d**.

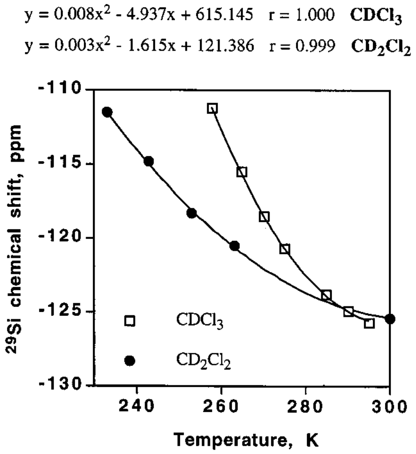

**Figure 3.** Solvent effect on the $^{29}$Si NMR chemical shift of **1h** at various temperatures.

**1d** ⇄ **6d**: the equilibrium constants were obtained from the $^{29}$Si chemical shifts (as described above) in three solvents: $CD_2Cl_2$, $CDCl_3$, and $CHFCl_2$. The resulting $\Delta H°$ and $\Delta S°$ values are listed in Table 2. Examination of these values confirms the strong solvent interaction with the ions: the solvents are listed in order of increasing polarity and hydrogen bond donor ability. Indeed, the more polar the solvent, the more stabilized the ions, and hence the dissociation becomes more exothermic (greater negative enthalpies). However, generation of these stabilized ions is associated with increased solvent–solute ordering, which, in turn, results in greater negative entropies.

This solvent effect can also be viewed from a different viewpoint: the temperature dependence of $^{29}$Si chemical shifts in pentacoordinate silicon complexes has been recognized as a criterion for the extent of coordination.[3c,4] In this study we observe, for the first time, similar intense temperature dependence of the $^{29}$Si chemical shifts in *hexa*coordinate complexes, or actually in the equilibrium reaction between penta and hexacoordinate complexes. Figure 3 shows the temperature dependence of the $^{29}$Si chemical shifts for **1h** in two solvents, at temperatures above the coalescence temperature.[14] It is evident that the first-order temperature dependence of $\delta(^{29}Si)$ is much larger (×3) in chloroform than it is in dichloromethane. This shows that the extent of dissociation of **1h** to **6h** increases much faster upon cooling in the more hydrogen-bonding solvent than it does in dichloromethane, supporting the stronger and more ordered solvent–solute binding in chloroform.

The $^{29}$Si chemical shifts for **1** have also been measured in toluene-$d_8$ solutions, and the corresponding values are listed in Table 1. No trace of dissociation could be detected in this solvent, as judged from the insignificant spectral temperature dependence, and hence no equilibrium constant could be evaluated. The chemical shifts in toluene-$d_8$ equal those in the solid state (Table 1, footnotes a,b), confirming the lack of ionization in this solvent.

**Effect of the Remote Substituent R on the Equilibrium Constant**. Comparison of the temperature dependence of the $^{29}$Si NMR spectra for **1d** (Figure 1) with that of **1g**, in which only the remote substituent R has been replaced (Table 2), reveals a substantial difference: while in **1d** upon cooling the equilibrium shifts from predominance of the hexacoordinate species at 300 K to predominance of the pentacoordinate species at low temperatures (Figure 1), in **1g** the hexacoordinate species *remains the major component* throughout the temperature range. This is reflected in the large change in equilibrium constants observed for **1d**, as opposed to the rather small changes in $K$ for **1g** upon cooling (Table 2). It follows that the remote substituent R has a profound effect on the temperature dependence of $K$,

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[14] The data for $CHFCl_2$ were omitted because ionization was complete at much higher temperatures.

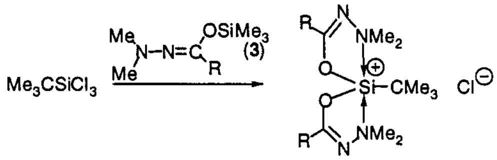
which is manifest in greater negative reaction enthalpy and entropy (Table 2).

To further discuss the effect of the substituent R, we compare the equilibrium reactions for four compounds, which share a common monodentate ligand X = phenyl: **1e** (R = *t*-Bu), **1d** (R = Me), **1f** (R = $PhCH_2$), and **1g** (R = Ph) in $CD_2Cl_2$ solutions. The list is ordered from the most electron-releasing to the least electron-releasing R substituent. Examination of the data for this series in Table 2 shows that both the enthalpies and the corresponding entropies increase (i.e, become less negative) along the series ($\Delta H° = -3.94, -2.84, -1.94, -0.82$ kcal mol$^{-1}$, respectively; $\Delta S° = -21.8, -15.0, -9.4, -8.6$ cal mol$^{-1}$ K$^{-1}$, respectively). This trend can be rationalized as follows: the stronger electron-releasing substituent, R = *tert*-butyl, causes the $Me_2N$ to be a stronger donor group and to bind more strongly to silicon.[15] The stronger coordination of the N-donor groups causes the silicon to have a greater electron density and, hence, to be less susceptible to further donor coordination. This results in an easier dissociation of the chloro ligand, which is translated to a more negative reaction enthalpy (more exothermic reaction).

The greater negative reaction enthalpy is accompanied by a greater negative entropy. This may result from more complete ionization in the exothermic cases and, hence, greater solvent organization about the separate ions. In the less exothermic reactions, in **1f** (R = $PhCH_2$) and **1g** (R = Ph), apparently contact ion pairs are formed, or at least some degree of connected ion pair, so that solvent organization about each ion separately is less intense, and hence the higher entropy.

These results, demonstrated with the series **1** for which X = Ph, is in agreement with the trends in enthalpy and entropy found in the other series, where X = Me (**1a** − **1c**) and X = $PhCH_2$ (**1h**−**j**, see Table 2). The conclusion concerning stronger solvation in the more separated ion pairs is also in agreement with the conclusions regarding solvent and temperature effects, discussed above.

**Effect of Monodentate Ligand X on Equilibrium Constant**. (a) A remarkable effect of the ligand X on the equilibrium constant of the dissociation process has been observed: for one ligand group, X = *tert*-butyl, the synthesis that normally leads to **1** (eq 2) yielded directly the fully dissociated **6k**−**m** (eq 5). This indicates that with this ligand the equilibrium **1** ⇄ **6** is completely shifted to the ionic side already at room temperature. This was evident from the $^{29}$Si NMR spectra which featured temperature-independent chemical shifts clearly at the pentacoordinate resonance range (Table 1). These were the only pentacoordinate siliconium chlorides found to predominate in $CD_2Cl_2$ solution at room temperature, without a sign of equilibrium reaction taking place.



(5)

**6k-m**

**k**, R = Me
**l**, R = CMe3
**m**, R = Ph

**Table 3. $^{29}$Si Chemical Shifts of Hexacoordinate Mono- and Ditriflato (12, 13) Complexes, Their Precursors (1n−q and 7), and the Corresponding Siliconium Tetrachloroaluminates (14, 15)**

| substituent index | R | X | Y | **1n−q** | **12n−q** | **13n,o** | **14n,o** |
|---|---|---|---|---|---|---|---|
| **n** | Ph | Cl | Cl | −145.9 | −150.7 | −161.5 | −80.5 |
| **o** | Me | Cl | Cl | −147.2 | −150.8 | −161.7 | −80.9 |
| **p** | $CF_3$ | Me | Cl | −124.5 | −130.2 | | |
| **q** | $CF_3$ | Ph | Cl | −132.0 | −140.6 | | |
| **7** | Ph | Br | Br | −169.8[a] | | −161.5 | −80.6[b] |

[a] Compound **7** (X = Y = Br). [b] Compound **15** (X = Br).

(b) On the other hand, when both monodentate ligands are electron-withdrawing groups (Cl, Br, as in **1n**,**o**, **7a**) or R is $CF_3$ (**1p**,**q**) or when X = F (**7b**), the equilibrium is shifted completely in the opposite direction: the ambient temperature $^{29}$Si chemical shift, representing the neutral octahedral **1**, is temperature independent down to 170 K; that is, it does not show any sign of dissociation even at low temperature (Table 3). This is attributed to the lower electron density on silicon, as a result of the electron-withdrawing groups, which makes the dissociation and removal of a negatively charged species (chloride anion) more difficult.

The effect described above (b) is clearly an electronic effect; however, the effect of the *tert*-butyl group (a) may either be the other extreme of (b), an electron-releasing ligand pushing the equilibrium to the ionic side, or a steric effect of the *tert*-butyl group forcing the neighboring chloro ligand to depart as a chloride anion already at relatively high temperature, or it may be a combination of both.

**Kinetics of Dissociation: Effect of the Monodentate Ligand X**. After evaluation of the equilibrium data, we turn to the kinetic aspects of the dissociation. Because of the very large chemical-shift differences (ca. 6000 Hz!) between the exchanging species (**1** and **6**), the typical exchange phenomena in the $^{29}$Si NMR spectra take place over a substantial temperature range and are not very well defined. This makes the determination of activation free energies for dissociation (**1** → **6**) inaccurate. The approximate free energy barriers, $\Delta G^‡$ which have been calculated from the chemical shift differences and approximate coalescence temperatures, are listed in Table 2 and are believed to be accurate to within ±0.5 kcal mol$^{-1}$.[16]

While R (in **1**) strongly affects the equilibrium constant *K* and its temperature dependence, the monodentate ligand X appears to have a strong effect on the *activation barrier* for dissociation (Tables 1, 2). For X = phenyl the coalescence temperatures are within an easily measurable range. However, for X = methyl (**1a**−**c**) the coalescence temperature drops, and hence the slow-exchange limit spectrum cannot be observed and the signals of the pure penta- and hexacoordinate

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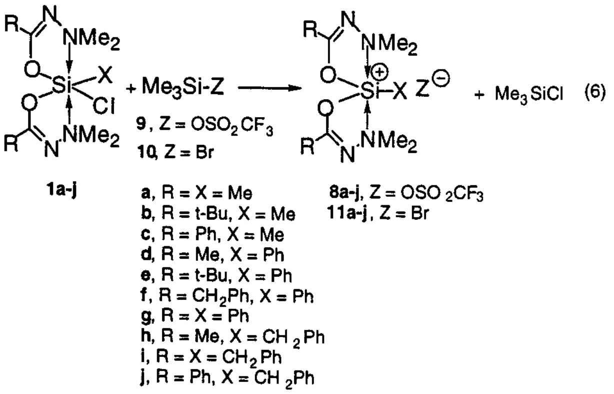
(15) For evidence on the effect of R on the $NMe_2$ donor strength see: Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *15*, 5073.

(16) The major error is due to the uncertainty in temperature. Uncertainty in $\Delta\nu$ between exchanging groups has a negligible effect on the barrier: Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

components are not resolved. The equilibrium constants $K$ can nevertheless be evaluated (Table 2) from the average $^{29}$Si chemical shifts and those of the components, which are obtained from the pure **1a**−**c** in toluene-$d_8$ solution and from the purely ionic triflate salts **8a**−**c** (Table 1). Obviously, the presence of the methyl group as ligand leads to a substantial decrease in the dissociation barrier.

The barriers increase by about 1 kcal mol$^{-1}$ upon changing the ligand from X = Me to X = PhCH$_2$ and again when X is changed from benzyl to phenyl (Table 2). It appears that the barrier increases with increasing electron-withdrawing power of X. It follows that the electron-withdrawing ligand causes silicon to bind more strongly to the chloro ligand and, hence, requires a higher activation energy to break this bond.

**(b) Synthesis of Siliconium Salts by Ligand Substitution: Effect of Counterion. Triflate and Bromide Substitution**. Having demonstrated that neutral compounds **1** dissociate spontaneously at low temperature to siliconium salts **6**, we turned to seek the formation of siliconium-ion salts stable at room temperature, in analogy with the formation of **5**, and to provide evidence for the structural assignment of **6**. In an attempt to shift the equilbrium population at room temperature toward the ionic side, the chloro ligands were replaced by the less nucleophilic triflate group, using trimethylsilyl triflate (**9**)[17] (eq 6). Indeed, this reaction led to complete ionization of **1a**−**j** and formation of the stable siliconium triflates **8a**−**j**, as recognized immediately by the large change in $^{29}$Si chemical shift from high field (−120 to −140 ppm), characteristic of hexacoordinate complexes, to low field (−60 to −74 ppm), typical of pentacoordinate complexes (Table 1).



Crystallization of three of the siliconium triflates (**8a**, **8c**, and **8d**) followed by single-crystal X-ray diffraction analyses (Figures 4−6, Table 4) confirmed the isolation of stable pentacoordinate siliconium salts with well-separated ions, in which the silicon cation is stabilized by coordination with two nitrogen-donor ligands.

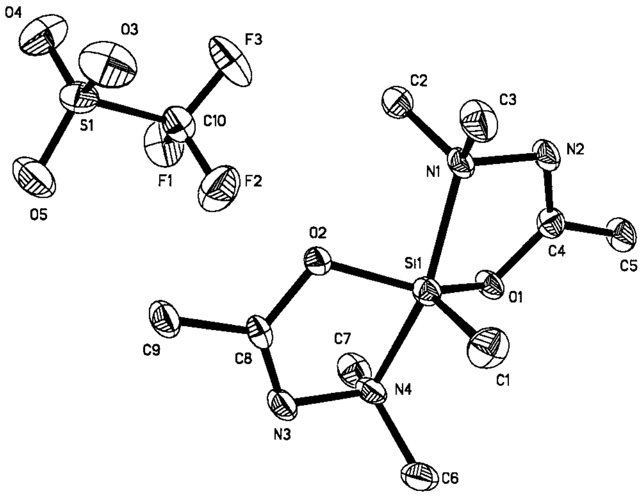


**Figure 4.** Molecular structure in the crystal of **8a**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

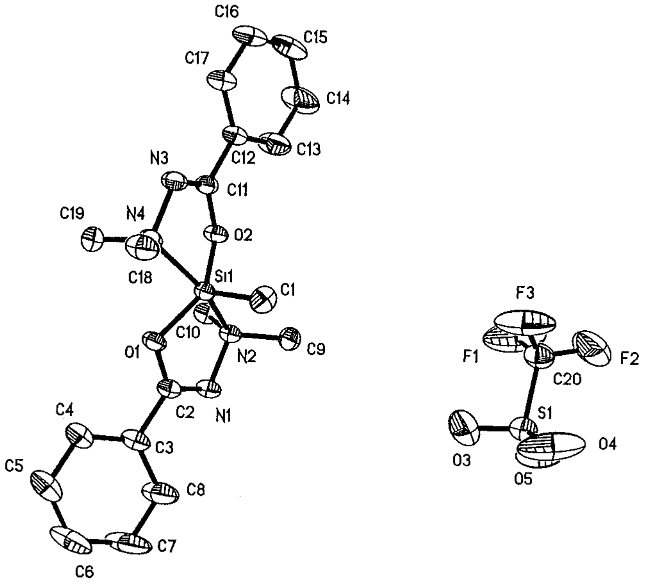


**Figure 5.** Molecular structure in the crystal of **8c**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

A similar ligand exchange reaction, with essentially the same results, was also carried out with trimethylbromosilane (**10**). The chloro ligand was rapidly replaced by a bromine atom, with formation of chlorotrimethylsilane (apparent by its typical $^{29}$Si chemical shift at 31.5 ppm). The $^{29}$Si NMR spectra of the brominated complexes (**11**) indicated complete conversion to ionic siliconium bromides **11a**−**j**, stable at room temperature (Table 1). It is thus evident that the equilibrium population ratio can be effectively controlled by suitable replacement of the monodentate ligands. Perhaps the most convincing evidence of this control is the comparison of the three halogens, F, Cl, and Br, as monodentate ligands: the chloro complexes **1a**−**j** are almost completely hexacoordinate at room temperature, but their equilibrium position shifts to the ionic side upon cooling. On the other hand the bromo complexes (**11a**−**j**) are already completely ionic at room temperature, while the fluoro complex (**7b**) remains neutral and hexacoordinate throughout the entire temperature range.

**Dissociation-Resistant Hexacoordinate Complexes 1**. Formation of the cations by means of the reaction with **9** (eq 6) succeeds only for those complexes bearing relatively electron releasing substituents R and ligands X. In the case of **1n**−**q**, in which either both of

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(17) For a similar use of TMS triflate see: (a) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840. (b) Berlekamp, U.-H.; Jutzi, P.; Mix, A.; Neumann, B.; Stammler, H.-G.; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 2048.

**Table 4. Selected Bond Lengths and Angles from Crystal Structures of Silicon Complexes and Calculated Percent TBP→SP for Siliconium Complexes**

| | bond lengths (Å) | | | angles (deg) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| complex | Si−O | Si−N | Si−C | O−Si−O | N−Si−N | O−Si−C | N−Si−C | O−Si−N | %TBP→SP[a] | %TBP→SP[b] |
| **8a** | 1.683(3)<br>1.680(3) | 1.959(3)<br>1.954(3) | 1.831(4) | 134.33(13) | 155.62(14) | 113.34(17)<br>112.33(17) | 101.75(18)<br>102.61(18) | 83.44(13)<br>86.23(14) | 65 | 71 |
| **8c** | 1.6844(15)<br>1.6964(14) | 1.9665(17)<br>1.9681(19) | 1.835(2) | 136.27(8) | 154.78(8) | 113.54(10)<br>110.16(10) | 101.05(10)<br>104.14(9) | 83.94(7)<br>87.18(7) | 69 | 75 |
| **8d** | 1.6833(11)<br>1.6911(11) | 1.9645(13)<br>1.9747(13) | 1.8453(15) | 137.05(6) | 157.24(6) | 112.09(6)<br>110.86(6) | 100.55(6)<br>102.21(6) | 83.70(6)<br>87.54(5) | 66 | 71 |
| **14d** | 1.6806(15)<br>1.6822(15) | 1.9855(17)<br>1.9699(18) | 1.838(2) | 135.19(8) | 157.89(8) | 112.96(8)<br>111.83(9) | 100.37(8)<br>101.74(8) | 83.52(8)<br>87.48(7) | 62 | 67 |
| **1c**[c] | 1.771(6)<br>1.780(6) | 2.036(6)<br>2.015(7) | 2.089(8) | 86.7(3) | 170.7(3) | 172.8(3)<br>88.5(3) | | 90.7(3)<br>93.3(3) | | |
| **12q** | 1.775(4)<br>1.782(4)<br>1.828(4) | 2.029(4)<br>2.037(4) | 1.916(5) | 87.92(18)<br>86.32(17)<br>172.09(18) | 168.5(2) | 175.52(18)<br>95.56(19)<br>90.5(2) | | 83.07(16)<br>88.93(18)<br>95.74(17)<br>88.44 (17) | | |
| **13n** | 1.731(3)<br>1.724(3)<br>1.793(3)<br>1.796(3) | 1.967(3)<br>1.989(3) | | 94.76(14)<br>89.95(13)<br>173.60(13)<br>173.62(14)<br>89.09(13)<br>86.62(13) | 172.34(14) | 106.0(2)<br>97.7(2) | | 94.98(14)<br>83.37(13)<br>84.29(13)<br>89.08(13)<br>90.51(14)<br>91.91(13) | | |

[a] Calculated by comparison of the NSiN and OSiO angles, see text. [b] Calculated by the "dihedral angle method" (ref 18). [c] From ref 6, listed here for comparison.

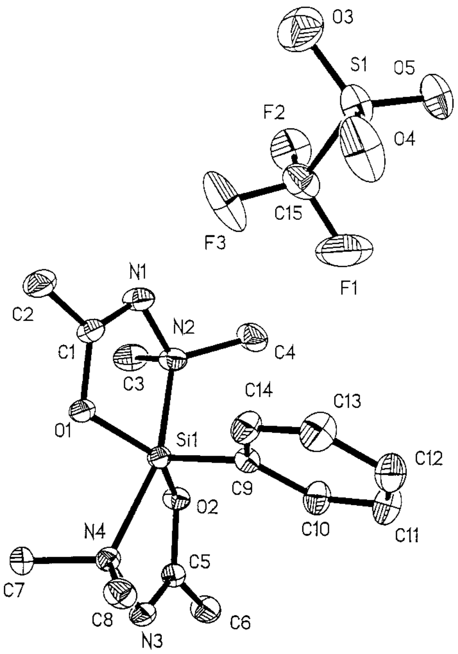


**Figure 6.** Molecular structure in the crystal of **8d**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

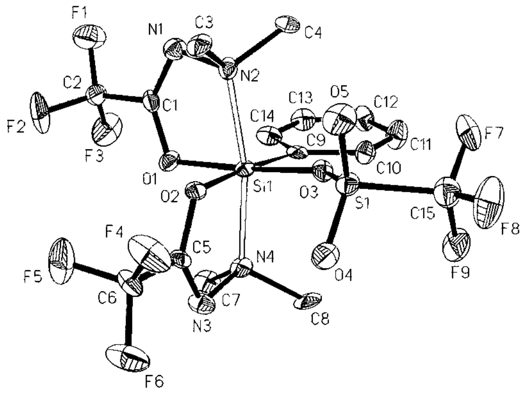
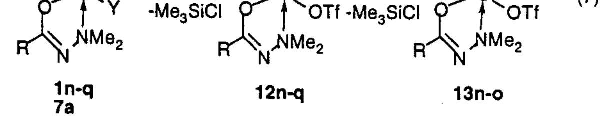


**Figure 7.** Molecular structure in the crystal of the monotriflato complex **12q**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

the monodentate ligands are Cl (or Br, in **7a**) or R = $CF_3$ (these are the same complexes that resisted dissociation at low temperature), exchange of the halogen ligand with triflate does not cause dissociation to the corresponding ionic **8**. Instead, in the case of **1n**, the $^{29}$Si chemical shift indicates that the two chloro ligands are substituted *stepwise* by triflate groups, which remain covalently attached to silicon and form the chlorotriflato (**12n**) and ditriflato (**13n**) complexes (eq 7). In molecules in which only one halogen ligand is present, obviously the replacement by triflate stops after the first step at the monotriflato product **12**. The $^{29}$Si chemical shifts of **12** and **13** are given in Table 3.



(7)

**1n-q**
**7a**

**12n-q**

**13n-o**

**1n**, R = Ph, X = Y = Cl
**1o**, R = Me, X = Y = Cl
**1p**, R = $CF_3$, X = Me, Y = Cl
**1q**, R = $CF_3$, X = Ph, Y = Cl
**7a**, R = Ph, X = Z = Br

**12n**, R = Ph, X = Cl
**12o**, R = Me, X = Cl
**12p**, R = $CF_3$, X = Me
**12q**, R = $CF_3$, X = Ph

**13n**, R = Ph
**13o**, R = Me

The molecular structures of representatives of these two series, **12** and **13**, were analyzed by X-ray crystallography (Figure 7, 8, Table 4), confirming the replacement of chloro ligands by triflato ligands, while keeping the essentially octahedral geometry and the hexacoordination unchanged. The dibromo complex **7** reacted in a similar manner, but without isolation or observation of the monotriflate, which reacted further directly to produce the identical ditriflato complex **13n**.

**Ionization by Aluminum Chloride.** It is evident that the triflate and bromide substitutions are still insufficient to effect dissociation of the complexes **1n**−**q** and **7**, bearing electron-withdrawing substituents R or

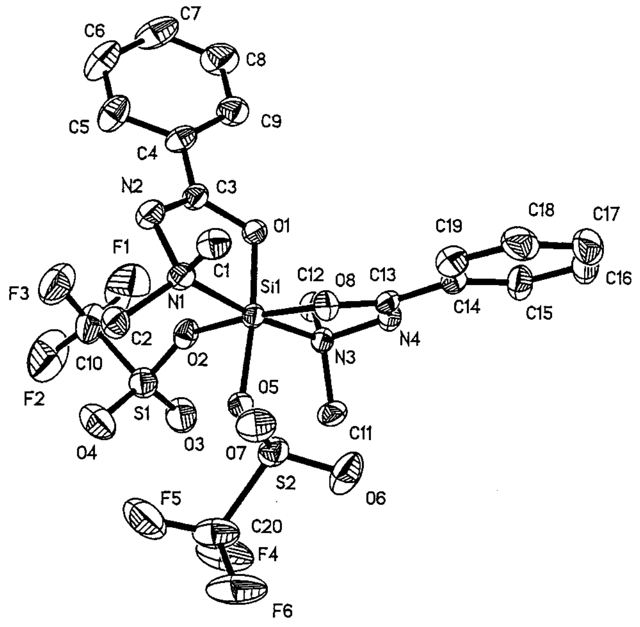
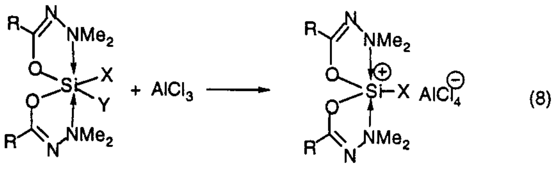


**Figure 8.** Molecular structure in the crystal of the ditriflato complex **13n**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

ligands X. However, using a more powerful ionizing agent, $AlCl_3$, which renders the chloro ligand a better leaving group and a poor nucleophile, led to the desired siliconium salts. The reaction of $AlCl_3$ with **1n**,**o** and **7a** resulted in the siliconium tetrachloroaluminates, **14n**,**o** and **15**, respectively (eq 8, Table 3). This reagent was also used for the ionization of other hexacoordinate complexes **1**, and the corresponding $^{29}$Si chemical shifts (Table 1) were almost exactly equal to those for the triflates (**8**) and bromides (**11**). Under these conditions, however, the $CF_3$-substituted complexes **1p**,**q** did not dissociate.



**1c,d,g,h,n,o**
**7a**

**14c**, R = Ph, X = Me
**14d**, R = Me, X = Ph
**14g**, R = Ph, X = Ph
**14h**, R = Me, X = $CH_2Ph$
**14n**, R = Ph, X = Cl
**14o**, R = Me, X = Cl
**15**, R = Ph, X =Br

One of the tetrachloroaluminate complexes, **14d**, prepared from **1d** and $AlCl_3$, crystallized to a single crystal suitable for X-ray analysis, and its crystal structure was determined (Figure 9, Table 4).

**Structure Assignment by $^{29}$Si NMR Analogy.** Table 1 compares the $^{29}$Si chemical shifts of isolated siliconium triflates **8**, bromides **11**, and tetrachloroaluminates **14** in solution with those obtained at low temperatures for the siliconium chlorides **6**. It is evident from the table that the various anions have a very small effect on the $^{29}$Si chemical shifts of the siliconium cations, within the range of experimental accuracy and possible concentration effects. This leads to two conclusions: (a) that the cations are well separated from the counteranions in solution, and hence that ionization is essentially complete, and (b) that the chemical shift analogy provides the necessary support for the assignment of the $^{29}$Si signals to the siliconium chlorides **6**. Complexes **6** could not be isolated and characterized directly because they are in rapid equilibrium with the corresponding **1** (which had been reported previously)[5a] and predominate only at low temperatures.

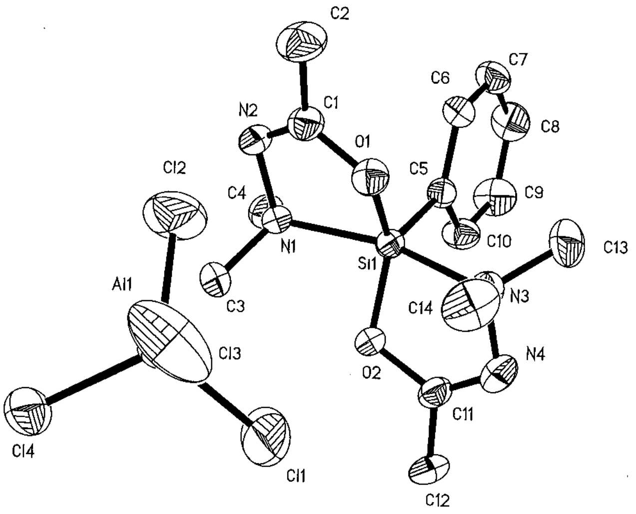


**Figure 9.** Molecular structure in the crystal of the siliconium tetrachloroaluminate **14d**. The ellipsoids correspond to a 50% probability level. Hydrogen atoms have been omitted for clarity.

The first one of these conclusions is fully confirmed by the X-ray crystal structures of **8a**,**c**,**d** and **14d** (Figures 4−6, 9), in all of which the anions are well separated from the siliconium cations. One may well assume that if ion separation is so complete in the solid state, it is likely to be predominant also in solution.

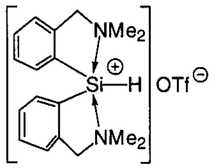
Indirect support for the ionic structure of **6** in solution comes from the observation of a distinct concentration effect on the $^{29}$Si chemical shifts: the average signal for the mixture $\mathbf{1} \rightleftarrows \mathbf{6}$ above the coalescence temperature shifts significantly to lower field when the solution is diluted, as noticed for most of the series **1**. For example, the $^{29}$Si chemical shift for **1a** at 180 K in $CD_2Cl_2$ solution shifted from −91.1 through −88.1 to −85.3 ppm upon dilution, due to a relative increase in the population of ionic **6a** (56, 60, and 65%, respectively). This is in accord with a dissociation−recombination equilibrium, in which dilution shifts the equilibrium toward increased dissociation.

**Molecular Structure in the Crystal.** The crystal structures shown in Figures 4−6 clearly confirm the ionic nature of **8a**,**c**,**d**, with their well-separated ions. It is thus shown that bis-(N→Si)-coordinated siliconium cations can be formed, in analogy with the previously reported bis-(O→Si)-siliconium salts **5**,[7] both in solution and in the solid state.

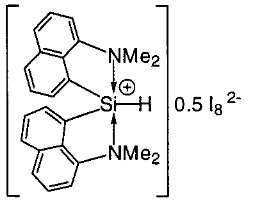
The crystal structures of the siliconium triflate complexes **8a**,**c**,**d** and the tetrachloroaluminate **14d** show that the geometry about the silicon atom in each complex is a distorted trigonal bipyramid (TBP). It is interesting to note that the deviation from TBP is almost the same in all four complexes: the O−Si−O angles range between 134° and 137°, and the N−Si−N angles between 155 and 157° (Table 4). The percentage of progress along the TBP → SP (square pyramid) coordinate has been evaluated by two methods: the dihedral angle method[18] and from the difference between the N−Si−N and O−Si−O angles (eq 9). In all four siliconium complexes the structures are closer to SP than to TBP (Table 4).

$$\%\mathrm{TBP} = \frac{\mathrm{NSiN} - \mathrm{OSiO}}{60°} \times 100 \qquad (9)$$

The close resemblance of molecular geometry among the four crystals may seem surprising, in view of large variation found in the geometries of other pentacoordinate complexes: in the two previous crystal structures measured for siliconium complexes (**16**[17a] and **17**[19]) the geometries were nearly exact TBP. On the other hand, a compilation of crystal structures for pentacoordinate silicates sharing the common $SiO_4C$ framework showed great variation in geometry, ranging between 25 and 97% progress along the TBP → SP coordinate.[18]



**16**



**17**

Another structural feature that emerges from the crystal data (Table 4) is the very short N→Si bond: these bonds in siliconium salts **8** and **14** are shorter than in any of the previously reported N→Si coordinated siliconium complexes (intra-[17a,19] and intermolecular[20]), as well as in neutral pentacoordinate complexes.[15] The N→Si bonds (as well as other bonds around the silicon atoms) are also short in comparison with the hexacoordinate precursors **1** (**1c**, see Table 4), which are typically about 2.00−2.05 Å.[5b,c,6]

The significant shortening of the N→Si coordination bond that accompanies the dissociation process of compounds **1** as the temperature is lowered is similar to the observation of coordination changes in eq 1, associated with cooling. It may appear that the common driving force for the reactions described here and by Kummer[4e] is an intrinsic temperature dependence of the N→Si (or O→Si) coordination bond, which becomes shorter and stronger upon cooling. However, in both cases these phenomena occur simultaneously with the formation of ions. In view of the temperature and solvent effects described above, it seems most likely that solvent organization about the ions at low temperature is the major driving force in both cases and that the shortening of the coordination bond is the result of this effect and not its driving force.

In the introduction to this article the progress along a hypothetical $S_N2$ reaction coordinate was mentioned in connection with ligand exchange in pentacoordinate silicon complexes. The dissociation−recombination reaction investigated in the present study constitutes ligand exchange in neutral hexacoordinate complexes, in a mechanism closely related to the $S_N1$ type mechanism in carbon compounds.

## Experimental Section

**General Procedures.** All the reactions were carried out under dry nitrogen or argon, using solvents dried and purified by standard methods. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.130, 125.758, and 99.362 MHz, respectively, for $^1$H, $^{13}$C, and $^{29}$Si spectra, and are reported in $\delta$ (ppm) relative to tetramethylsilane (TMS), as determined from standard residual solvent-proton (or carbon) signals. The variable-temperature $^{29}$Si NMR spectra for the determination of population ratios were run using 35° pulses, without $^1$H decoupling, and with 5−10 s delay times between pulses. The reproducibility of peak-intensity ratios was found essentially invariant within this delay range. The peak-intensity ratios are believed to be accurate within ±10%. NMR measurements in $CHFCl_2$ solutions were carried out below 9 °C, and the solvent was condensed directly into preevacuated sample tubes. Melting points were measured in sealed capillaries using a Buchi melting point instrument. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Single-crystal X-ray diffraction patterns were measured at 173(2) K on a Bruker Smart CCD 1000 diffractometer [$\lambda$(Mo K$\alpha$) = 0.71073 Å, graphite monochromator, a scan width of 0.3° in $\omega$ and exposure time of 10 s frame$^{-1}$, detector−crystal distance = 4.95 cm]. Data for compound **12q** were measured at 130(2) K on a Bruker Smart Apex CCD diffractometer (scan width 0.3°, exposure time 5 s, detector distance 6 cm). **12q** crystallized as a nonmerohedral twin. Only nonoverlapped reflections of the main domain were used for solution and refinement. Experimental data are presented in Table 5. The complete crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-178863 (**8a**), CCDC-178864 (**8c**), CCDC-157088 (**8d**),[1] CCDC-178865 (**12q**), CCDC-157089 (**13n**),[1] and CCDC-178866 (**14d**). 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].

**Synthesis**: **1a, 1c, 1d, 1f, 1g**, **1n, 1o, 1p, 1q**, **3a**, **3c**, **3f**, and **3p** were prepared as described previously.[5a]

***O*-Trimethylsilylated 1,1-Dimethyl-2-pivaloylhydrazine (3b)**. A solution of 4.81 g (80.0 mmol) of 1,1-dimethylhydrazine and 16.90 g (167.0 mmol) of triethylamine in 80 mL of dry $Et_2O$ was cooled to −20 °C. A pivaloyl chloride (9.65 g, 80.0 mmol) solution in 50 mL of dry $Et_2O$ was added dropwise with stirring. The mixture was stirred for 1 h at ambient temperature and then refluxed for 2 h. Chlorotrimethylsilane (8.69 g, 80.0 mmol) was added dropwise, followed by 8 h of reflux. The mixture was cooled and filtered under argon, and the filtrate was distilled under reduced pressure. The product was collected at 61−62 °C (11 mmHg), 12.6 g (72.8% yield). $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.16 (s, 9H, $SiMe_3$), 1.06 (s, 9H, $CMe_3$), 2.25 (s, 6H, $NMe_2$). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 0.85 ($SiMe_3$), 27.51 ($C(CH_3)_3$), 36.42 ($CMe_3$), 46.52 ($NMe_2$), 165.86 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ 14.92. Anal. Calcd for $C_{10}H_{24}N_2OSi$: C, 55.50; H, 11.18; N, 12.95. Found: C, 55.72; H, 10.99; N, 13.05.

**Chlorobis[*N*-(dimethylamino)pivaloimidato-*N*,*O*]methylsilicon(IV) (1b)**. To a stirred solution of **3b** (0.603 g, 2.78 mmol) in 10 mL of dry $CHCl_3$ was added $MeSiCl_3$ (0.217 g, 1.45 mmol) at room temperature under dry argon. The mixture

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**Table 5. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 8a, 8c, 8d, 12q, 13n, and 14d**

| | **8a** | **8c** | **8d** | **12q** | **13n** | **14d** |
|---|---|---|---|---|---|---|
| empirical formula | $C_{10}H_{21}F_3N_4O_5SSi$ | $C_{20}H_{25}F_3N_4O_5SSi$ | $C_{15}H_{23}F_3N_4O_5SSi$ | $C_{15}H_{17}F_9N_4O_5SSi$ | $C_{20}H_{22}F_6N_4O_8S_2Si$ | $C_{14}H_{23}AlCl_4N_4O_2Si$ |
| formula mass, g mol$^{-1}$ | 394.46 | 518.59 | 456.52 | 564.48 | 652.63 | 476.23 |
| collection $T$, K | 173 | 173 | 173 | 130 | 173 | 173 |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | triclinic | monoclinic | triclinic | monoclinic | monoclinic | triclinic |
| space group | P-1 | $C2/c$ | $P\bar{1}$ | $P2(1)/\bar{c}$ | $P2(1)/\bar{n}$ | $P\bar{1}$ |
| $a$, Å | 7.900 (5) | 28.606 (4) | 8.4678(15) | 8.1265(6) | 16.466(5) | 8.5697(11) |
| $b$, Å | 9.956 (5) | 12.2959(16) | 11.032(2) | 17.6498(12) | 8.193(3) | 11.8936(16) |
| $c$, Å | 11.399(7) | 18.410(3) | 11.517(2) | 16.1947(11) | 20.861(7) | 11.9049(15) |
| $\alpha$, deg | 81.211(13) | 90 | 89.784(5) | 90 | 90 | 94.449(3) |
| $\beta$, deg | 76.092(13) | 129.768(6) | 84.087(5) | 98.676(2) | 102.427(7) | 107.249(3) |
| $\gamma$, deg | 79.078(9) | 90 | 75.050(5) | 90 | 90 | 96.720(3) |
| $V$, Å$^3$ | 849.1(9) | 4977.3(12) | 1033.7(3) | 2296.2(3) | 2748.3(15) | 1142.8(3) |
| Z | 2 | 8 | 2 | 4 | 4 | 2 |
| $\rho_{\text{calc,}}$ Mg/m$^3$ | 1.543 | 1.384 | 1.467 | 1.633 | 1.577 | 1.384 |
| $F$(000) | 412 | 2160 | 476 | 1144 | 1336 | 492 |
| $\theta$ range, deg | 1.85−28.56 | 1.85−28.31 | 1.78−28.30 | 13.81−26.39 | 2.53−23.26 | 1.74−28.29 |
| no. of coll reflns | 8132 | 21 494 | 12 650 | 12 188 | 26 602 | 10 229 |
| no. of indep reflns | 4255 | 6179 | 5128 | 4598 | 3920 | 5665 |
| $R_{\text{int}}$ | 0.0616 | 0.0293 | 0.0241 | 0.0975 | 0.0500 | 0.0158 |
| no. of reflns used | 4255 | 6179 | 5128 | 2856 | 3920 | 5665 |
| no. params | 217 | 312 | 268 | 320 | 374 | 241 |
| Goof | 1.003 | 1.074 | 1.028 | 1.025 | 1.086 | 1.047 |
| R1[a] wR2[b] [$I > 2\sigma(I)$] | 0.0828 0.2234 | 0.0573 0.1609 | 0.0365 0.0941 | 0.0738 0.1723 | 0.0506 0.1202 | 0.0476 0.1248 |
| R1[a] wR2[b] (all data) | 0.1121 0.2435 | 0.0706 0.1732 | 0.0520 0.1016 | 0.1099 0.1970 | 0.0642 0.1258 | 0.0612 0.1340 |
| max./min. res electron dens (e Å$^3$) | 1.487/−0.665 | +0.997/−0.818 | +0.403/−0.523 | +0.502/−0.5379 | +0.372/−0.424 | +0.840/−0.788 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

was stirred for 1 h. Removal of the volatiles under vacuum (0.05 mmHg) resulted in a colorless crystalline solid (0.500 g, 98.3% yield), **1b**, mp 107−107.5 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.47 (s, 3H, SiMe), 1.02 (s, 18H, *t*-Bu), 2.82 (s, 6H, $NMe_2$), 2.86 (s, 6H, $NMe_2$). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 11.74 (SiMe), 26.96 (C($C$H$_3$)$_3$), 34.98 ($C$Me$_3$), 51.06 ($NMe_2$), 173.23 (C═N). $^{29}$Si NMR $\delta$ ($CDCl_3$, 300 K): −123.7. Anal. Calcd for $C_{15}H_{33}ClN_4O_2Si$: C, 49.36; H, 9.11; N, 15.35. Found: C, 49.39; H, 8.99; N, 14.96.

**Chlorobis[*N*-(dimethylamino)pivaloimidato-*N,O*]-phenylsilicon(IV) (1e)**. **1e** was prepared from **3b** (0.584 g, 2.70 mmol) and $PhSiCl_3$ (0.274 g, 1.29 mmol) as described for **1b**, colorless crystalline solid (0.534 g, 96.8% yield), mp 119−120.5 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 1.17 (s, 18H, *t*-Bu), 2.32 (s, 6H, $NMe_2$), 2.86 (s, 6H, $NMe_2$), 7.23−8.08 (m, 5H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 27.19 (C($C$H$_3$)$_3$), 35.36 ($C$Me$_3$), 51.36 ($NMe_2$), 127.36, 128.29, 137.08, 144.15 (Ph), 173.19 (C═N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −131.20. Anal. Calcd for $C_{20}H_{35}ClN_4O_2Si$: C, 56.25; H, 8.26; N, 13.12. Found: C, 55.99; H, 8.33; N, 12.96.

**Benzylchlorobis[*N*-(dimethylamino)acetimidato-*N,O*]-silicon(IV) (1h)**. **1h** was prepared from $PhCH_2SiCl_3$ (0.201 g, 0.89 mmol) and **3a** (0.325 g, 1.87 mmol) as described for **1b**. The residual oily mass was crystallized by successive triturations with hexane (3 × 5 mL), yielding a white semisolid (0.257 g, 81% yield). $^1$H NMR ($CD_2Cl_2$, 300 K): $\delta$ 1.70 (s, 6H, CMe), 2.79 (br s, 2H, $CH_2$), 2.97 (br s, 12H, $NMe_2$), 7.07−7.22 (m, 5H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 17.27 (C$C$H$_3$), 35.74 ($CH_2$), 51.61 ($NMe_2$), 124.25, 127.84, 129.25, 142.33 (Ph), 165.85 (C═N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −125.97.

**Benzylchlorobis[*N*-(dimethylamino)phenylacetimidato-*N,O*]silicon(IV) (1i)**. **1i** was prepared directly in the NMR tube from **3f** and $PhCH_2SiCl_3$ and characterized by analogy of the NMR spectra to other compounds in the series. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 2.66 (br s, 6H, $NMe_2$), 2.92 (br s, 8H, $NMe_2$, $CH_2$), 3.16 (s, 4H, $CH_2$), 7.20−7.93 (m, 15H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 36.54 (Si$C$H$_2$), 37.46 (C$C$H$_2$), 51.43 ($NMe_2$), 124.00, 126.53, 127.63, 128.07, 128.88, 129.30, 134.73, 142.27 (Ph), 166.54 (C═N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −128.37.

**Benzylchlorobis[*N*-(dimethylamino)benzimidato-*N,O*]-silicon(IV) (1j)**. To a solution of $PhCH_2SiCl_3$ (0.389 g, 1.73 mmol) in 5 mL of dry $CHCl_3$ was added **3c** (0.820 g, 3.47 mmol). The mixture was kept at 60 °C for 1 h, followed by removal of volatiles under vacuum. The product was obtained as an oily mass (0.799 g, 96% yield). $^1$H NMR ($CD_2Cl_2$, 300 K): $\delta$ 2.90 (br s, 2H, $CH_2$), 3.25 (br s, 12H, $NMe_2$), 7.04−7.79 (m, 15H, Ph). $^{13}$C NMR ($CD_2Cl_2$, 300 K): $\delta$ 36.87 ($CH_2$), 52.51 ($NMe_2$), 124.41, 127.73, 128.14, 128.77, 129.92, 130.91, 131.54, 143.06 (Ph), 163.75 (C═N). $^{29}$Si NMR ($CD_2Cl_2$, 293 K): $\delta$ −127.82.

***tert*-Butylbis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Chloride (6k)**. A mixture of *t*-$BuSiCl_3$ (0.205 g, 1.07 mmol) in 5 mL of dry $CHCl_3$ and **3a** (0.390 g, 2.24 mmol) was allowed to reflux for 2 days. Evaporation of the volatiles under reduced pressure resulted in an oily mass, 0.312 g, 90% yield, identified as **6k** by spectral analogy. $^1$H NMR ($CDCl_3$, 273 K): $\delta$ 1.05 (s, 9H, *t*-Bu), 2.10 (br s, 6H, CMe), 3.10 (s, 6H, NMe), 3.22 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 273 K): $\delta$ 17.23 (C$C$H$_3$), 22.70 (Si$C$Me$_3$), 29.43 (SiC($C$H$_3$)$_3$), 49.44 (NMe), 52.04 (NMe), 168.72 (C═N). $^{29}$Si NMR ($CDCl_3$, 273 K): $\delta$ −61.54.

***tert*-Butylbis[*N*-(dimethylamino)pivaloimidato-*N,O*]-siliconium Chloride (6l)**. **6l** was prepared directly in the NMR sample tube and characterized by spectral analogy. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.90 (s, 9H, *t*-Bu), 0.99 (s, 18H, C*t*-Bu), 2.90 (s, 6H, NMe), 2.99 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 26.44 (CC($C$H$_3$)$_3$), 26.56 (Si$C$Me$_3$), 29.77, (SiC($C$H$_3$)$_3$), 35.25 (C$C$Me$_3$), 50.01 (NMe), 52.65 (NMe), 175.66 (C═N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −61.33.

***tert*-Butylbis[*N*-(dimethylamino)benzoimidato-*N,O*]-siliconium Chloride (6m)**. A mixture of *t*-$BuSiCl_3$ (0.205 g, 1.07 mmol) in 5 mL of dry $CHCl_3$ and **3c** (0.529 g, 2.24 mmol) was heated in an oil bath at 80 °C for 4 days. Evaporation of the volatiles under reduced pressure resulted in a brown semisolid (0.460 g, 89% yield), which could not be recrystallized. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.99 (s, 9H, *t*-Bu), 3.24 (br s, 6H, NMe), 3.37 (br s, 6H, NMe), 7.11−7.79 (m, 10H, Ph). $^{13}$C NMR ($CDCl_3$, 273 K): $\delta$ 23.09 (Si$C$Me$_3$), 29.33 (SiC($C$H$_3$)$_3$), 50.10 (NMe), 52.24 (NMe), 123.70−133.57 (Ph), 165.13 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −61.13.

**Dibromobis[*N*-(dimethylamino)benzimidato-*N,O*]silicon(IV) (7a)**. A mixture of SiBr$_4$ (0.465 g, 1.31 mmol) in 5 mL of dry CHCl$_3$ and **3c** (0.611 g, 2.59 mmol) was allowed to stand at ambient temperature for 1 h. Evaporation of the volatiles under reduced pressure resulted in a solid, which was washed with hexane to give a white powder (0.592 g, 89% yield). $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 3.34 (br s, 6H, NMe$_2$), 3.50 (br s, 6H, NMe$_2$), 7.37−7.87 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 52.21 (NMe$_2$), 53.73 (NMe$_2$), 126.99, 128.36, 129.29, 131.97, (Ph), 162.70 (C=N). $^{29}$Si NMR (CD$_2$Cl$_2$, 293 K): $\delta$ −170.02. Anal. Calcd for C$_{18}$H$_{22}$Br$_2$N$_4$O$_2$Si: C, 42.04; H, 4.31; N, 10.89; Br, 31.04. Found: C, 41.92; H, 4.41; N, 10.68; Br, 30.89.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]fluoro(phenyl)silicon(IV) (7b)**. **7b** was prepared directly in the NMR sample tube and characterized by spectral analogy. $^1$H NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 1.83 (s, 3H, CMe), 1.94 (s, 3H, CMe), 2.06 (s, 3H, NMe), 2.43 (s, 3H, NMe), 2.44 (s, 3H, NMe), 2.92 (s, 3H, NMe), 7.26−8.00 (m, 5H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 17.28 (Me), 49.38 (NMe$_2$), 50.03 (NMe), 52.49(NMe), 127.30, 128.16, 136.52, 137.80, 146.06, 145,72 (Ph), 166.65 (C=N), 166.92 (C=N). $^{29}$Si NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −148.72 (d, $^1J_{\mathrm{FSi}}$ = 268.3 Hz).

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]methylsiliconium Triflate (8a)**. To a stirred solution of **1a** (0.120 g, 0.43 mmol) in 3 mL of dry CHCl$_3$ was added 0.160 g (0.72 mmol) of trimethylsilyl triflate at room temperature. After 15 min, concentration under 0.1 mmHg afforded 0.33 g (82% yield) of a colorless powder, **8a**, mp 235 °C (dec). $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 0.58 (s, 3H, SiMe), 2.08 (s, 6H, CMe), 2.88 (s, 6H, NMe), 2.90 (s, 6H, NMe). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ −7.82 (SiMe), 16.74 (CMe), 48.43 (NMe), 49.33 (NMe), 120.0 (q, $^1J_{\mathrm{FC}}$ = 320 Hz, CF$_3$), 167.39 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −61.72. Anal. Calcd for C$_{10}$H$_{21}$F$_3$N$_4$O$_5$SSi: C, 30.45; H, 5.37; N, 14.20. Found: C, 30.13; H, 5.58; N, 14.10.

**Bis[*N*-(dimethylamino)pivaloimidato-*N,O*]methylsiliconium Triflate (8b)**. The preparation was the same as that for **8a**. **8b** was obtained in 98% yield as a white powder, mp 245 °C (dec). $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 0.49 (s, 3H, SiMe), 1.17 (s, 18H, *t*-Bu), 2.90 (s, 6H, NMe), 2.91 (s, 6H, NMe). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ −7.60 (SiMe), 26.21 (C(*C*H$_3$)$_3$), 35.52 (*C*(CH$_3$)$_3$), 48.48 (NMe), 49.04 (NMe), 122.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 175.07 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −61.35. Anal. Calcd for C$_{16}$H$_{33}$F$_3$N$_4$O$_5$SSi: C, 40.15; H, 6.95; N, 11.71. Found: C, 39.89; H, 6.92; N, 11.48.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]methylsiliconium Triflate (8c)**. The preparation was the same as that for **8a**. **8c** was obtained as a white powder, mp 175−180 °C (dec), in 75% yield. $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 0.68 (s, 3H, SiMe), 3.18 (s, 6H, NMe), 3.20 (s, 6H, NMe), 7.33−7.93 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ −7.82 (SiMe), 49.18 (NMe), 49.72 (NMe), 120.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 125.71, 127.97, 128.68, 133.86 (Ph), 164.33 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −60.94. Anal. Calcd for C$_{20}$H$_{25}$F$_3$N$_4$O$_5$SSi: C, 46.32; H, 4.86; N, 10.80. Found: C, 46.44; H,4.90; N, 10.82.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]phenylsiliconium Triflate (8d)**. The preparation was the same as that for **8a**. **8d** was obtained in 81% yield as a colorless powder, mp 182−184 °C. $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 2.24 (s, 6H, CMe), 2.37 (s, 6H, NMe), 2.98 (s, 6H, NMe), 7.32−7.57 (m, 5H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 16.71 (CMe), 49.30 (NMe), 49.66 (NMe), 120.01 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 122.01, 129.74, 133.17, 133.40 (Ph), 167.22 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −73.19. Anal. Calcd for C$_{15}$H$_{23}$F$_3$N$_4$O$_5$SSi: C, 39.47; H, 5.08; N, 12.27. Found: C, 38.98; H, 4.98; N, 11.91.

**Bis[*N*-(dimethylamino)pivaloimidato-*N,O*]phenylsiliconium Triflate (8e)**. The preparation was the same as that for **8a**. The yield of colorless **8e** was 94%, mp 255 °C (dec). $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 0.68 (s, 3H, SiMe), 3.18 (s, 6H, NMe), 3.20 (s, 6H, NMe), 7.33−7.93 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ −7.82 (SiMe), 49.18 (NMe), 49.72 (NMe), 120.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 125.71, 127.97, 128.68, 133.86 (Ph), 164.33 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −60.94. Anal. Calcd for C$_{21}$H$_{35}$F$_3$N$_4$O$_5$SSi: C, 46.65; H, 6.52; N, 10.36. Found: C, 46.34; H, 6.57; N, 10.18.

**Bis[*N*-(dimethylamino)phenylacetimidato-*N,O*]phenylsiliconium Triflate (8f)**. The preparation was the same as that for **8a**. The yield of colorless **8f** was 85%, mp 180−190 °C (dec). $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 2.26 (s, 6H, NMe), 3.00 (s, 6H, NMe), 3.76, 3.87 (ABq, $^2J_{\mathrm{AB}}$ = 14.4 Hz, 4H, CH$_2$), 6.34−7.33 (m, 15H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 37.60 (CH$_2$), 49.62 (NMe), 50.09 (NMe), 120.80 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 128.12, 129.02, 129.21, 129.65, 132.72, 132.83, 133.48 (Ph), 168.28 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −73.36. Anal. Calcd for C$_{27}$H$_{31}$F$_3$N$_4$O$_5$SSi: C, 53.28; H, 5.13; N, 9.20. Found: C, 52.79; H, 4.99; N, 8.88.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]phenylsiliconium Triflate (8g)**. The preparation was the same as that for **8a**. The yield of colorless **8f** was 96%, mp 180−182 °C. $^1$H NMR (CDCl$_3$, 300 K): $\delta$ 2.70 (s, 6H, NMe), 3.25 (s, 6H, NMe), 7.35−8.06 (m, 15H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 49.99 (NMe), 50.11 (NMe), 120.60 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 125.68, 127.86, 129.22, 129.81, 133.70, 133.90 (Ph), 164.30 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −72.3. Anal. Calcd for C$_{25}$H$_{27}$F$_3$N$_4$O$_5$SSi: C, 51.71; H, 4.69; N, 9.65. Found: C, 50.84; H, 4.58; N, 9.34.

**Benzylbis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Triflate (8h)**. The preparation was the same as that for **8a**. The yield of colorless **8h** was 48%, mp 132−3 °C. $^1$H NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 1.91 (s, 6H, CMe), 2.62, 2.65 (ABq, $^2J_{\mathrm{AB}}$ = 16.5 Hz, 2H, CH$_2$), 2.96 (s, 6H, NMe), 3.12 (s, 6H, NMe), 7.10−7.32 (m, 5H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 16.87 (C*C*H$_3$), 17.57 (SiCH$_2$), 48.76 (NMe), 49.99 (NMe), 121.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 126.73, 129.44, 133.36 (Ph), 168.53 (C=N). $^{29}$Si NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −65.30. Anal. Calcd for C$_{16}$H$_{25}$F$_3$N$_4$O$_5$SSi: C, 40.84; H, 5.36; N, 11.91. Found: C, 40.52; H, 5.58; N, 11.24.

**Benzylbis[*N*-(dimethylamino)phenylacetimidato-*N,O*]siliconium Triflate (8i)**. **8i** was prepared directly in the NMR sample tube and identified by spectral analogy. $^1$H NMR (CD$_2$Cl$_2$, 300 K): 2.14, 2.44 (ABq, $^2J_{\mathrm{AB}}$ = 16.4 Hz, 2H, CH$_2$), 2.77 (s, 6H, NMe), 2.87 (s, 6H, NMe), 3.63 (s, 4H, CH$_2$), 6.90−7.33 (m, 5H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 17.49 (Si*C*H$_2$), 37.22 (C*C*H$_2$), 48.70 (NMe), 49.89 (NMe), 121.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 126.90, 128.17, 129.25, 129.63, 133.15 (Ph) 169.62 (C=N). $^{29}$Si NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −66.10.

**Benzylbis[*N*-(dimethylamino)benzimidato-*N,O*]siliconium Triflate (8j)**. The preparation was the same as that for **8a.** The yield of colorless **8j** was 65%, mp 189−191 °C. $^1$H NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 2.70, 2.78 (ABq, $^2J_{\mathrm{AB}}$ = 16.4 Hz, 2H, CH$_2$), 3.20 (s, 6H, NMe), 3.39 (s, 6H, NMe), 6.90−7.90 (m, 5H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 17.67 (SiCH$_2$), 49.57 (NMe), 50.40 (NMe), 121.00 (q, $^1J_{\mathrm{CF}}$ = 320 Hz, CF$_3$), 126.24, 128.44, 129.27, 129.63, 132.54, 134.05 (Ph), 165.29 (C=N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −65.13. Anal. Calcd for C$_{26}$H$_{29}$F$_3$N$_4$O$_5$SSi: C, 52.51; H, 4.92; N, 9.42. Found: C, 52.14; H, 5.06; N, 9.32.

Of the series **11** the following compounds were fully characterized: **11c**, **11h**, **11j**, and **11k**, (see below). Other members in this series were prepared directly in NMR sample tubes by dissolving the corresponding **1** in CDCl$_3$ and adding excess Me$_3$SiBr and were identified by NMR spectral analogy with the corresponding siliconium triflate complexes (**8**).

**Benzylbis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Bromide (11h)**. **1h** was first prepared (see above) from PhCH$_2$SiCl$_3$ (0.201 g, 0.89 mmol) and **3a** (0.325 g, 1.87 mmol) to give a white solid, which was redissolved in 5 mL of dry CHCl$_3$ and to which trimethylbromosilane (0.115 g, 0.75 mmol) was added. After a few minutes the volatiles were removed under vacuum and the residual white solid was washed with dry hexane (3 × 5 mL) and dried under vacuum to yield 0.250

g (86% yield) of **11h**, mp 138−140 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 1.91 (s, 6H, $CH_3$), 2.61 (s, 2H, $CH_2$), 2.98 (s, 6H, NMe), 3.10 (s, 6H, NMe), 6.86−7.03 (m, 6H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 16.64 ($CH_3$), 17.19 ($SiCH_2$), 48.42 (NMe), 49.81 (NMe), 125.45, 128.97, 129.14, 132.78 (Ph), 168.13 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −65.37. Anal. Calcd for $C_{15}H_{25}BrN_4O_2Si$: C, 44.89; H, 6.28; N, 13.96. Found: C, 44.44; H, 6.19; N 13.80.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]methylsiliconium Bromide (11c).** **11c** was prepared as described for **11h**, from $MeSiCl_3$ (0.608 g, 4.06 mmol) and **3c** (1.920 g, 8.14 mmol) and excess $Me_3SiBr$. The yield of colorless **11c** was 1.186 g (65% yield), mp 205 °C (dec). $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.77 (s, 3H, SiMe), 3.17 (s, 6H, NMe), 3.26 (s, 6H, NMe), 7.24−7.93 (m, 12H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ −7.28 (SiMe), 49.79 (NMe), 50.38 (NMe), 125.43−133.49 (Ph), 164.20 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −61.89. Anal. Calcd for $C_{19}H_{25}BrN_4O_2Si$: C, 50.78; H, 5.61. Found: C, 50.19; H, 5.85.

**Benzylbis[*N*-(dimethylamino)benzimidato-*N,O*]siliconium Bromide (11j).** Freshly prepared crude **1j** made of 0.389 g (1.73 mmol) of $PhCH_2SiCl_3$ and 0.820 g (3.47 mmol) of **3c** as described above was redissolved in 3 mL of $CHCl_3$ and 5 mL of hexane. Then 0.263 g (1.72 mmol) of $Me_3SiBr$ was added to the solution, resulting in immediate precipitation of a white powdery solid. After filtration the solid was washed by three 5 mL portions of hexane and dried under vacuum. The yield of **11j** was 0.83 g (91%), mp 170−172 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 2.58, 2.65 (ABq, $^2J_{AB}$ = 16.5 Hz, 2H, $CH_2$), 3.18 (s, 6H, NMe), 3.13 (s, 6H, NMe), 6.72−7.75 (m, 15H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 17.22 ($SiCH_2$), 49.35 (NMe), 50.49 (NMe), 125.35, 125.78, 127.48, 128.31, 128.49, 128.58, 131.74 133.31 (Ph), 164.44 (C=N). $^{29}$Si NMR: $\delta$ −65.02. Anal. Calcd for $C_{25}H_{29}BrN_4O_2Si$: C, 57.14; H, 5.56; N, 10.66. Found: C, 57.05; H, 5.66; N, 10.61.

***tert*-Butylbis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Bromide (11k).** **11k** was prepared as described for **11j**, from crude **6k** made of *t*-$BuSiCl_3$ (0.205 g, 1.07 mmol) and **3a** (0.390 g, 2.24 mmol), and from 0.160 g (1.05 mmol) of $Me_3SiBr$. The white powdery **11k** (0.323 g, 90% yield) had mp 130−133 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 1.09 (s, 9H, *t*-Bu), 2.12 (s, 6H, CMe), 3.11 (s, 6H, NMe), 3.19 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 17.26 ($C\mathit{C}H_3$), 22.93 ($Si\mathit{C}CH_3$), 29.61 ($SiC(\mathit{C}H_3)_3$), 49.72 (NMe), 52.60 (NMe), 168.85 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −61.45. Anal. Calcd for $C_{12}H_{27}BrN_4O_2Si$: C, 39.23; H, 7.41; N, 15.25. Found: C, 38.83; H, 7.31; N, 15.04.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]methylsiliconium Bromide (11a).** $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.47 (s, 3H, SiMe), 1.93 (s, 6H, $CCH_3$), 2.74 (s, 12H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ −7.46 (SiMe), 16.81 ($C\mathit{C}H_3$), 48.33 (NMe), 49.42 (NMe), 166.79 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −61.75.

**Bis[*N*-(dimethylamino)pivaloimidato-*N,O*]methylsiliconium Bromide (11b).** $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 0.39 (s, 3H, SiMe), 1.06 (s, 18H, *t*-Bu), 2.81 (s, 6H, NMe), 2.84 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ −7.69 (SiMe), 26.26 ($\mathit{C}(CH_3)_3$), 35.30 ($C(\mathit{C}H_3)_3$), 48.90 (NMe), 49.54 (NMe), 174.75 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −61.49.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]phenylsiliconium Bromide (11d).** $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 2.16 (s, 6H, CMe), 2.26 (s, 6H, NMe), 2.99 (s, 6H, NMe), 7.25−7.42 (m, 5H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 17.17 (CMe), 49.33 (NMe), 50.37 (NMe), 121.88, 129.55, 132.86, 133.34 (Ph) 166.93 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −72.99.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]phenylsiliconium Bromide (11g).** $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 2.82 (s, 6H, NMe), 3.47 (s, 6H, NMe), 7.36−8.18 (m, 15H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 49.95 (NMe), 50.59 (NMe), 121.47−133.89 (Ph) 164.00 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −72.15.

**Bis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*]methyl(triflato)silicon(IV) (12p).** To a solution of **1p** (0.215 g, 0.55 mmol), prepared as described previously, in 5 mL $CHCl_3$ was added trimethylsilyl trifluoromethanesulfonate (TMS-triflate), 0.154 g (0.69 mmol). Removal of volatiles under reduced pressure resulted in a white crystalline solid, which was washed with three portions of 5 mL of hexane and dried under vacuum, to yield 0.180 g (65% yield) of **12p**, mp 140−143 °C. $^1$H NMR ($CDCl_3$, 300 K): 0.54 (s, 3H, SiMe), 2.97 (s, 6H, NMe), 3.04 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): 6.05 (SiMe), 49.94 (NMe), 50.43 (NMe), 116.85 (q, $^1J_{CF}$ = 277 Hz, $CF_3$), 119.50 (q, $^1J_{CF}$ = 274 Hz, $CF_3$), 156.51 (q, $^3J_{CF}$ = 39 Hz, C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −130.20. Anal. Calcd for $C_{10}H_{15}F_9N_4O_5SSi$: C, 23.91; H, 3.01; N, 11.15. Found: C, 23.01; H, 2.95; N, 11.36.

**Chlorobis[*N*-(dimethylamino)benzimidato-*N,O*]triflatosilicon(IV) (12n).** **12n** was prepared directly in the NMR sample tube from **1n** and a small excess of TMS triflate and was characterized by NMR spectral analogy with **12p**. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 3.29 (s, 6H, NMe), 3.34 (s, 6H, NMe), 7.25−7.90 (m, 10H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 50.14 (NMe), 52.62 (NMe), 118.65 ($CF_3$), 127.60, 129.44, 132.33 (Ph) 163.97 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −150.65.

**Chlorobis[*N*-(dimethylamino)acetimidato-*N,O*]triflatosilicon(IV) (12o).** **12o** was prepared directly in the NMR sample tube from **1o** and a small excess of TMS triflate and was characterized by NMR spectral analogy with **12p**. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 1.91 (s 6H, CMe), 2.98 (s, 6H, NMe), 3.17 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 17.06 (CMe), 50.16 (NMe), 51.78 (NMe), 118.65 ($CF_3$), 166.12 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −151.04.

**Bis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*)-phenyl(triflato)silicon(IV) (12q).** **12q** was prepared as described for **12p**, from 0.810 g (1.80 mmol) of **1q** and 0.453 g (2.03 mmol) of TMS triflate. The white solid product weighed 0.961 g (90% yield) and had mp 110−112 °C. $^1$H NMR ($CD_2Cl_2$, 300 K): $\delta$ 2.55 (s, 6H, NMe), 2.96 (s, 6H, NMe), 7.40−7.66 (m, 10H, Ph). $^{13}$C NMR ($CD_2Cl_2$, 300 K): $\delta$ 50.01 (NMe), 51.68 (NMe), 116.85 (q, $^1J_{CF}$ = 277 Hz, $CF_3$), 119.50 (q, $^1J_{CF}$ = 274 Hz, $CF_3$), 156.23 (q, $^3J_{CF}$ = 39 Hz, C=N). $^{29}$Si NMR: $\delta$-140.61. Anal. Calcd for $C_{15}H_{17}F_9N_4O_5SSi$: C, 31.92; H, 3.04; N, 9.93. Found: C, 32.03; H, 3.16; N, 9.80.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]ditriflatosilicon(IV) (13n).** **7a** (0.515 g, 1.00 mmol) and TMS triflate (0.466 g, 2.10 mmol) were dissolved in 5 mL of $CHCl_3$ under dry argon. The solution was heated to 70 °C for 24 h followed by removal of the volatiles under vacuum. The resulting mass was washed with hexane (3 × 5 mL), filtered, and dried under vacuum, yielding 0.517 g (79% yield) of **13n** as a white solid, mp 193−195 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 3.31 (s, 6H, NMe), 3.35 (s, 6H, NMe), 7.25−7.90 (m, 10H, Ph). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 50.87 (NMe), 52.40 (NMe), 118.7 (q, $^1J_{CF}$ = 318 Hz, $CF_3$), 127.6, 128.7, 132.3 (Ph), 164.0 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −161.7. Anal. Calcd for $C_{20}H_{22}F_6N_4O_8S_2Si$: C, 36.81; H, 3.40; N, 8.59. Found: C, 36.43; H, 3.39; N, 8.57.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]ditriflatosilicon(IV) (13o).** A solution of **1o** (0.759 g, 2.52 mmol) and TMS triflate (0.623 g, 5.06 mmol) in 5 mL of $CHCl_3$ was kept at 70 °C for 4 h under argon. The volatiles were removed under reduced pressure, and the resulting solid washed with dry hexane (3 × 5 mL) and dried under vacuum, yielding 1.239 g (93% yield) of **13o**, mp 195−197 °C. $^1$H NMR ($CDCl_3$, 300 K): $\delta$ 1.95 (s, 6H, CMe), 3.00 (s, 6H, NMe), 3.04 (s, 6H, NMe). $^{13}$C NMR ($CDCl_3$, 300 K): $\delta$ 16.80 (CMe), 49.44 (NMe), 52.13 (NMe), 118.65 (q, $^1J_{CF}$ = 318 Hz, $CF_3$), 165.97 (C=N). $^{29}$Si NMR ($CDCl_3$, 300 K): $\delta$ −161.97.

**Bis[*N*-(dimethylamino)acetimidato-*N,O*]phenylsiliconium Tetrachloroaluminate (14d).** To a solution of **1d** (0.518 g, 1.40 mmol) in 10 mL of $CHCl_3$ was added in small portions anhydrous $AlCl_3$ (0.196 g, 1.47 mmol) at room temperature. The mixture was filtered off, and the filtrate was concentrated to half the volume under reduced pressure. A white crystalline solid precipitated upon cooling and was filtered and dried (0.610 g, 85% yield), mp 222−224 °C. $^{1}$H NMR (CDCl$_3$, 300 K): $\delta$ 2.30 (s, 6H, CMe), 2.40 (s, 6H, NMe), 3.00 (s, 6H, NMe), 7.34−7.62 (m, 5H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 17.15 (CMe), 49.48 (NMe), 50.00 (NMe), 121.68, 129.99, 133.43 (Ph), 167.25 (C═N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −72.06. Anal. Calcd for $C_{14}H_{23}AlCl_4N_4O_2Si$: C, 35.31; H, 4.87; N, 11.76. Found: C, 35.30; H, 4.96; N, 11.79.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]methylsiliconium Tetrachloroaluminate (14c)**. **14c** was prepared directly in the NMR sample tube from **1c** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 0.70 (s, 3H, SiMe), 3.16 (s, 6H, NMe), 3.21 (s, 6H, NMe), 7.54−8.00 (m, 10H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −7.40 (SiMe), 49.62 (NMe), 50.22 (NMe), 126.24, 128.14, 129.41, 130.05, 134.30 (Ph), 164.76 (C═N). $^{29}$Si NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −62.47.

**Bis[*N*-(dimethylamino)benzimidato-*N,O*]phenylsiliconium Tetrachloroaluminate (14g)**. **14g** was prepared directly in the NMR sample tube from **1g** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 2.76 (s, 6H, NMe), 3.30 (s, 6H, NMe), 7.40−8.14 (m, 15H, Ph). $^{13}$C NMR (CD$_2$Cl$_2$, 300 K): $\delta$ 50.38 (NMe), 50.48 (NMe), 121.50−136.20 (Ph), 164.71 (C═N). $^{29}$Si NMR (CD$_2$Cl$_2$, 300 K): $\delta$ −71.96.

**Benzylbis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Tetrachloroaluminate (14h)**. **14h** was prepared directly in the NMR sample tube from **1h** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CDCl$_3$, 300 K): $\delta$ 1.93 (s, 6H, CMe), 2.60, 2.68 (ABq, $^{2}J_{AB}$ = 16.5 Hz, 2H, CH$_2$), 2.94 (s, 6H, NMe), 3.13 (s, 6H, NMe), 7.05−7.29 (m, 5H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 16.67 (CCH$_3$), 16.96 (CH$_2$), 48.30 (NMe), 49.56 (NMe), 126.22, 128.81, 129.94, 132.26 (Ph), 167.90 (C═N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −65.27.

**Chlorobis[*N*-(dimethylamino)benzimidato-*N,O*]siliconium Tetrachloroaluminate (14n)**. **14n** was prepared directly in the NMR sample tube from **1n** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CDCl$_3$, 300 K): $\delta$ 3.30 (s, 6H, NMe), 3.36 (s, 6H, NMe), 7.24−7.95 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 50.17 (NMe), 50.90 (NMe), 124.67, 127.80, 128.98, 134.29 (Ph), 163.80 (C═N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −80.47.

**Chlorobis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium Tetrachloroaluminate (14o)**. **14o** was prepared directly in the NMR sample tube from **1o** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CDCl$_3$, 300 K): $\delta$ 2.34 (s. 6H, CMe), 3.20 (s, 12H, NMe). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 17.14 (CMe), 49.61 (NMe), 50.76 (NMe), 167.11 (C═N). $^{29}$Si NMR (CDCl$_3$, 300 K): $\delta$ −81.41.

**Bromobis[*N*-(dimethylamino)benzimidato-*N,O*]siliconium Bromotrichloroaluminate (15h)**. **15h** was prepared directly in the NMR sample tube from **7a** and excess AlCl$_3$ and characterized by NMR spectral analogy. $^{1}$H NMR (CDCl$_3$, 300 K): $\delta$ 3.35 (s, 6H, NMe), 3.38 (s, 6H, NMe). $^{13}$C NMR (CDCl$_3$, 300 K): $\delta$ 50.29 (NMe), 51.00 (NMe), 124.54, 127.93, 129.31, 130.44, 134.71 (Ph), 164.33 (C═N). $^{29}$Si NMR: $\delta$ −80.64.

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**Supporting Information Available:** Tables of crystallographic data for **8a**, **8c**, **8d**, **12g**, **13n** and **14d** are given in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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