

Tautomeric Equilibrium between Penta- and Hexacoordinate Silicon Chelates. A Chloride Bridge between Two Pentacoordinate Silicons

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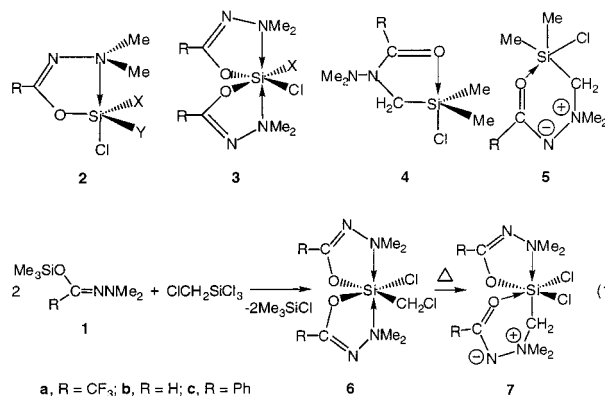
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Abstract: The reaction of *O*-trimethylsilyl-1,1-dimethyl-2-trifluoroacetylhydrazine (**1a**) with chloromethyl(methyl)dichlorosilane affords an unexpected equilibrium mixture, **10a** ⇌ **11a**, between a neutral hexacoordinate silicon chelate with a covalent chloro ligand (**10a**) and an ionic pentacoordinate silicon complex (**11a**). The equilibrium reaction consists formally of a migration of the covalent chloro ligand from silicon to an adjacent ammonium nitrogen, as a chloride anion, and thus constitutes a novel type of tautomeric reaction. Crystallographic and NMR data provide evidence for the reaction. Temperature, solvent, substituent, and counterion effects on the tautomeric equilibrium are discussed: when the temperature of the mixture is raised, the equilibrium ratio **10a/11a** increases. Formation of the mixture in toluene, a nonionizing solvent, shifts the equilibrium completely toward the neutral **10a**. When the initial hydrazide has a phenyl (**11c**) or a hydrogen (**11b**) group as substituent, rather than CF₃, the equilibrium is shifted to the ionic side. Replacement of the chloride counterion by triflate, using trimethylsilyl triflate, shifts the **10a/11a** mixture to the ionic side. Low-temperature NMR monitoring of the stepwise formation of **10/11** was carried out and provided insight into the reaction mechanism. In an attempt to grow crystals of **11c**, the pentacoordinate tautomer analogue, an unprecedented chloride-bridged disiloxane complex, with two pentacoordinate silicons sharing a common axial chloro ligand, crystallized and was characterized and described.

Introduction

In a number of recent studies, the utility of *O*-trimethylsilyl-*N,N*-dimethylhydrazides (**1**) as versatile precursors for the preparation of a variety of hypervalent silicon compounds has been demonstrated.^{1–13} The reaction of **1** with various poly-

halosilanes leads, via exchange of ligands, to the desired chelates which share the common hydrazide chelate skeleton (–O–C–N–N–). Thus, using dichlorosilanes with **1** leads to the formation of neutral pentacoordinate complexes with N → Si coordination (**2**);^{1–3} with trichlorosilanes, two chelate rings are formed, leading to neutral hexacoordinate silicon chelates (**3**).^{4–8} Substitution of a chloromethyl group on the polyhalosilane leads to O → Si coordination: when **1** reacts with chloromethyl(dimethyl)chlorosilane, pentacoordinate complexes **4** and **5** can be obtained.^{9–12} The reaction of **1** with chloromethyltrichlorosilane has recently been shown to lead to a zwitterionic λ⁶ silicate with N → Si coordination, via a stepwise internal displacement reaction (eq 1).¹³



The different courses of this reaction, depending on the number of chloro ligands in the chloromethyl(polychloro)silane, generated interest and led to the present study of the reaction of **1** with chloromethyl(methyl)dichlorosilane (**8**). Indeed, the

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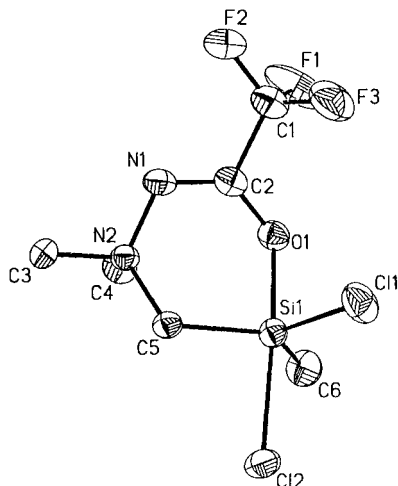
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Table 1. ^1H , ^{13}C , and ^{29}Si NMR Chemical Shifts (δ , ppm) for the Tautomer Mixture **10a** and **11a**, and for Analogous Complexes **7c**, **11b**, and **11c**^{a,b}

	10a	11a	11b	11c ^c	7c ^d
^{29}Si	-134.0	-57.6	-63.53	-61.03	-158.8
^1H					
MeSi	0.59	0.83	0.68	0.88	
CH ₂	3.07d, 3.22d ($J = 13.8$) ^e	3.55d, 6.10d ($J = 15.7$) ^e	3.20d, 5.84d ($J = 15.6$) ^e	3.33d, 5.80d ($J = 15.6$) ^e	3.19d, 3.24d ($J = 13.7$) ^e
NMe ₂	3.32, 3.36	3.70, 3.77	3.61, 3.64	3.81, 3.83	3.22, 3.40
NMe ₂	2.89	2.90, 3.13	2.62, 3.01	2.83, 3.10	2.45, 2.51
^{13}C					
MeSi	15.90	-1.33	-1.24	-1.09	
CH ₂	66.91	52.08	53.18	53.19	67.8
NMe ₂	57.46, 59.40	53.00, 62.65	53.3, 62.28,	53.19, 62.77	56.4, 59.4
NMe ₂	50.12	48.36, 49.11	48.83, 48.94	48.64, 49.18	52.6, 53.0

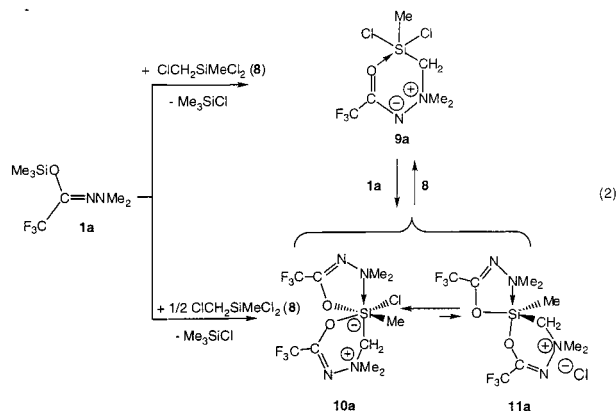
^a Unless stated, spectra were measured in CD_2Cl_2 solution at 253 K. ^b Spectral assignments were verified by H–H and H–C 2D NMR correlations. ^c CDCl_3 solution, 300 K. ^d Toluene-*d*₈ solution, 300 K, ref 13. ^e Coupling constants, Hz.

**Figure 1.** Molecular structure of **9a** in the crystal.

results of this study show that $\text{ClCH}_2\text{Si}(\text{Me})_n\text{Cl}_{3-n}$ reacts with **1** in a different fashion for each of the variants $n = 0-2$. A novel type of tautomeric equilibrium results in the case $n = 1$, and is the subject of the present study.

Results and Discussion

Tautomeric Equilibrium. The reaction described in eq 1 was attempted with **1a** ($\text{R} = \text{CF}_3$) and chloromethyl(methyl)-dichlorosilane (**8**); however, this apparently analogous case resulted in a different reaction pathway, as outlined in eq 2.

**Figure 2.** Variable-temperature ^{29}Si NMR spectra of the equilibrium mixture **10a/11a** in CD_2Cl_2 .

coordinate (**10a**) complex and a pentacoordinate (**11a**) complex (Table 1). The same result is obtained when **9a** is treated with an additional mole equivalent of **1a**. The equilibrium reaction $\text{10a} \rightleftharpoons \text{11a}$ constitutes a novel type of tautomeric equilibrium, in which a chloride ion migrates between silicon and the positively charged ammonium moiety, changing between covalent bonding in a hexacoordinate silicon complex and ionic bonding in a pentacoordinate complex.¹⁴

Evidence for the tautomeric equilibrium is presented in Figure 2: the low-temperature ^{29}Si NMR spectrum of the mixture clearly features two signals, one typical of pentacoordination ($\delta \text{ } ^{29}\text{Si} = -57.6$ ppm, assigned to **11a**) and the other of hexacoordination ($\delta \text{ } ^{29}\text{Si} = -134.0$ ppm, assigned to **10a**). The intensity ratio of these two signals is temperature dependent in a fully reversible fashion, such that at lower temperatures the relative population of the pentacoordinate species (**11a**) increases. A similar temperature dependence was also observed in the ^1H NMR spectra of the mixture, as is listed in Table 2, as well as in a qualitative manner in the ^{13}C NMR spectra.

At 300 K the signal due to **11a** has completely disappeared (Figure 2), due to rapid exchange averaging the small residual

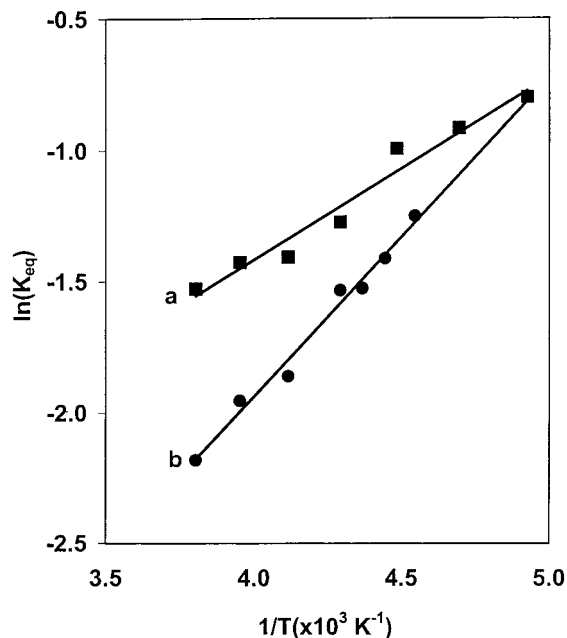
When **1a** reacts with an equivalent amount of **8**, the product (**9a**) is the rearranged O \rightarrow Si-coordinated monochelate (eq 2), analogous to **5**.¹² **9a** has been characterized by its crystal structure analysis, shown in Figure 1.

When 2 mol equiv of **1a** reacted with 1 mol equiv of **8**, an equilibrium mixture of two products was obtained: a hexa-

(14) A different case of equilibrium between a covalent and an ionic chlorosilane has been reported. However, the equilibration is between two pentacoordinate species: Schär, D.; Belzner, J. In *Organosilicon Chemistry III*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1997; p 429.

Table 2. Temperature Dependence of the Tautomer Population Ratio (**11a/10a**) in CD₂Cl₂ and CD₃CN Solutions, Determined by the Corresponding MeSi ¹H Signal Intensity Ratios

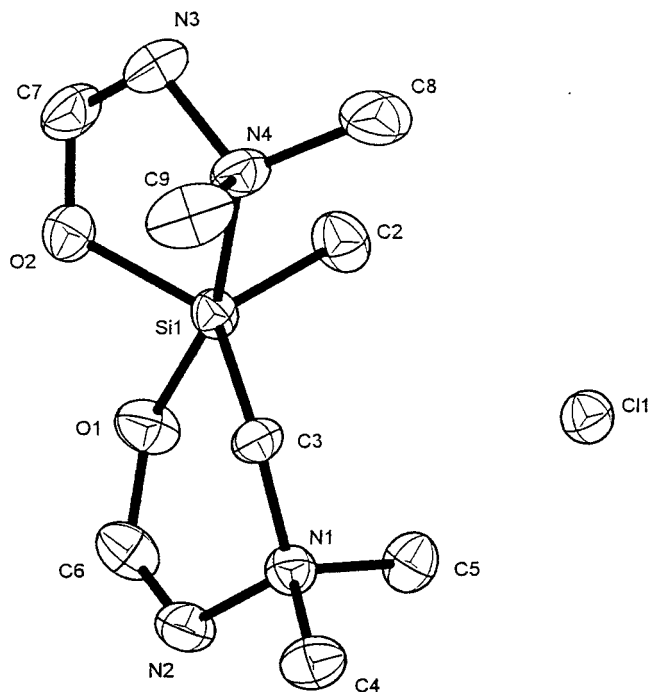
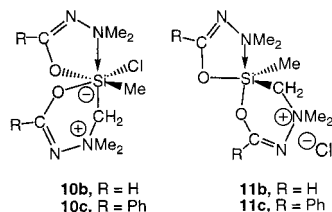
solvent	temp, K									
	263	253	243	233	229	225	223	220	213	203
CD ₂ Cl ₂	0.22	0.24	0.25	0.28			0.37		0.40	0.45
CD ₃ CN	0.11	0.14	0.16	0.22	0.22	0.24		0.29		

**Figure 3.** Plot of $\ln(K)$ vs reciprocal temperature for the equilibrium reaction **10a** \rightleftharpoons **11a**: (a) in CD₂Cl₂ solution and (b) in CD₃CN solution.

signal intensity of **11a** with that of the predominant **10a**. The rapid reversible equilibration allows the extraction of thermodynamic data for the tautomeric process. Plots of $\ln(K)$ vs reciprocal temperature for the equilibrium **10a** \rightleftharpoons **11a** in two solvents (Figure 3) result in two values for the reaction enthalpies, $\Delta H^\circ(\text{CD}_2\text{Cl}_2) = -1.38 \text{ kcal mol}^{-1}$ and $\Delta H^\circ(\text{CD}_3\text{CN}) = -2.41 \text{ kcal mol}^{-1}$, and the respective entropies, $\Delta S^\circ(\text{CD}_2\text{Cl}_2) = -8.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta S^\circ(\text{CD}_3\text{CN}) = -13.5 \text{ cal mol}^{-1} \text{ K}^{-1}$. These data correspond to Gibbs free energies of 0.45 and 0.56 kcal mol⁻¹, respectively, at 220 K, representing a relatively small difference in tautomer stabilities which accounts for the observation of significant concentrations of each one in solution.

The small, but significant, differences in enthalpies and entropies of the equilibration in acetonitrile and dichloromethane suggest that a solvent effect operates. Indeed, in toluene solution the equilibrium is shifted completely toward the covalent side, and only **10a** is observed. In the more polar solvents (CD₂Cl₂, CD₃CN), which better support ions, both tautomers are observed in various population ratios (Table 2).

Substituent effects on the tautomerization equilibrium have been measured by comparison of the three differently substituted analogous systems: **10a/11a** (R = CF₃), **10b/11b** (R = H), and

**Figure 4.** Molecular structure in the crystal for **11b**.

10c/11c (R = Ph). The equilibrium mixture is readily observable only in the first system, **10a/11a** (eq 2). In both **10b/11b** and **10c/11c**, the equilibrium is shifted completely to the five-coordination end, such that only the ionic tautomers, **11b** and **11c**, are observed in the various NMR spectra (Table 1). Attempts to shift the equilibrium toward the six-coordination side, by utilizing the solvent effect established for **10a/11a** and using toluene, did not result in significant spectral changes or in the observation of **10b** or **10c**.

The **10/11** population ratio can also be shifted by varying the counterion. To the mixture of **10a** and **11a** in solution was added trimethylsilyl triflate, resulting in exchange of the chloro ligand by OSO₂CF₃. The CDCl₃ solution of this product consisted entirely of **11a**(OTf), as evident from the ²⁹Si and ¹H NMR spectra (see Experimental Section). It follows that bulkier anions or those which are more stable can shift the equilibrium to the ionic side.

The final characterization of each tautomer was done by comparison of the three substituted systems. The pentacoordinate tautomer **11b** was crystallized, and the molecular structure was obtained from a single-crystal X-ray analysis (Figure 4). Its NMR spectrum was compared with that of the unresolved mixture of tautomers **10a/11a**, in which a complete parallel set of signals could be assigned to **11a**, based on analogy (Table 1 and Figure 5). In particular, an exceptionally large chemical shift difference between the diastereotopic CH₂ protons in **11b** could be found also in the spectra of the **10a/11a** equilibrium mixture and in **11c** (ca. 2.5 ppm). The subspectrum assigned to **11a** by analogy to **11b** in Figure 5 is temperature dependent, such that its intensity decreases upon warming, until it finally disappears at 300 K, in complete agreement with the temperature dependence of the ²⁹Si spectrum (Figure 2). This further confirms the structure assignment to the tautomer **11a**.

The structural assignment of **10a** follows from a spectral comparison with the dichloro analogue λ⁶-silicate **7c**, for which a crystallographic structure has been reported (Figure 6).¹³ Typically, the δ(¹³C) for the CH₂ carbon is unique and almost constant for **7a–c** (67.2, 68.4, and 67.8 ppm, respectively, in toluene-*d*₈ solution);¹³ for **10a** it falls precisely in the same

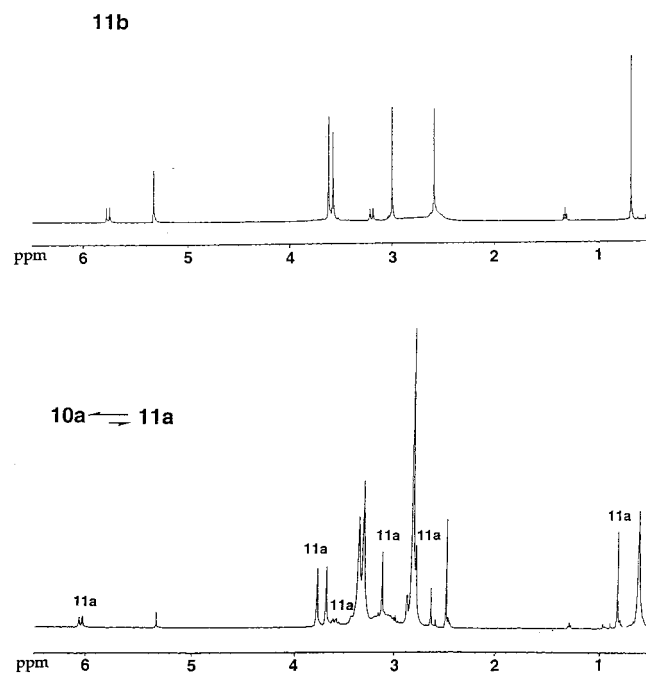


Figure 5. Comparison of ^1H NMR spectra of **11b** and the **10a/11a** equilibrium mixture (233 K, CD_2Cl_2).

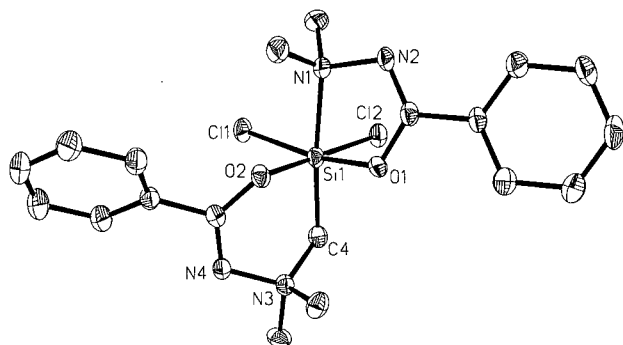


Figure 6. Molecular structure in the crystal for **7c**.¹³

Table 3. Selected Bond Lengths and Angles in **9a**

bond	bond length, Å	angle	bond angle, deg
Si1–O1	1.836 (2)	O1–Si1–Cl2	174.35 (8)
Si1–Cl2	2.3438 (13)	O1–Si1–C6	92.69 (14)
Si1–Cl1	2.0758 (12)	O1–Si1–C5	91.36 (13)
C2–O1	1.296 (4)	C11–Si1–Cl2	89.82 (5)
C2–N1	1.282 (4)	C5–Si1–Cl2	83.60 (11)
Si1–C5	1.892 (3)	C6–Si1–C5	125.1 (2)
Si1–C6	1.847 (3)		

typical range, 66.9 ppm (Table 1), confirming the assignment. In the ^1H NMR spectra, the geminal coupling constants between the CH_2 protons are essentially equal in **10a** and **7c** (13.7–13.8 Hz) and significantly different from those of the tautomers **11a–c** (Table 1).

Crystal Structure Analysis. (a) 9a. The molecular structure of **9a** in the crystal is depicted in Figure 1, and selected bond lengths and angles are shown in Table 3. The overall geometry is a slightly distorted trigonal bipyramid (TBP), with oxygen and chlorine occupying the apical positions. This structure is similar to previously reported structures of analogous systems (**5a**, $\text{R} = \text{CF}_3$;¹² **5d**, $\text{R} = 4\text{-MeOC}_6\text{H}_4$ ¹¹), which are the only previously reported complexes with $\text{Cl}^- \rightarrow \text{Si}$ coordination. **9a** is another rare case of $\text{Cl}^- \rightarrow \text{Si}$ coordination: like in the analogues, the Si–O distance in **9a** (Table 3) is relatively short, and the Si–Cl distance is relatively long for a coordination bond,

Table 4. Selected Bond Lengths and Angles for **11b**

bond	bond length, Å	angle	bond angle, deg
Si1–O1	1.753(4)	O1–Si1–N4	163.6(2)
Si1–O2	1.711(4)	O2–Si1–C3	125.9(2)
Si1–N4	2.162(5)	O2–Si1–C2	112.3(3)
Si1–C2	1.843(6)	C2–Si1–C3	120.8(3)
Si1–C3	1.876(5)	O2–Si1–O1	88.1(2)
C6–N2	1.277(9)	C2–Si1–O1	99.6(3)
C7–N3	1.271(9)	O1–Si1–C3	92.8(2)
C6–O1	1.314(8)	O2–Si1–N4	78.4(2)
C7–O2	1.324(8)	C2–Si1–N4	94.2(3)
N1–C3	1.519(7)	C3–Si1–N4	87.7(2)

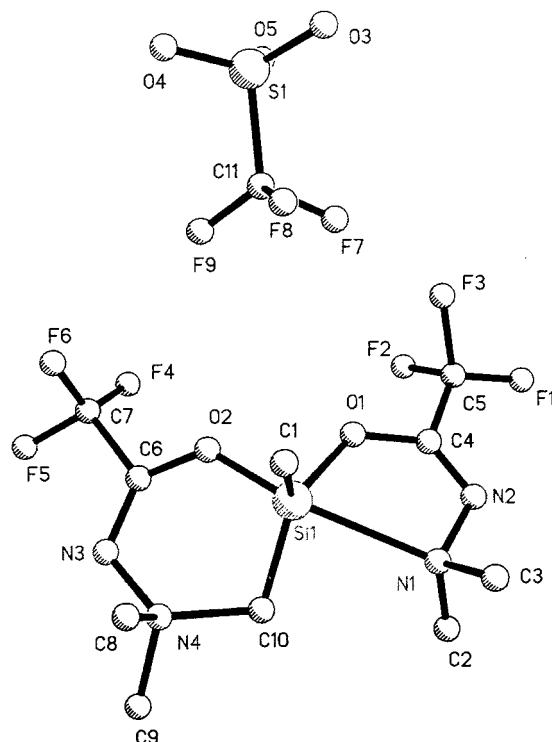


Figure 7. Crystal structure of **11a(OTf)**. Low crystal quality did not permit sufficient refinement.

especially in comparison to the equatorial Si–Cl distance in the same molecule. In all three complexes (**9a**, **5a**, and **5d**), the silicon atom deviates from the plane defined by the equatorial ligands toward the axial oxygen atom, in agreement with a $\text{Cl}^- \rightarrow \text{Si}$ coordination bond.

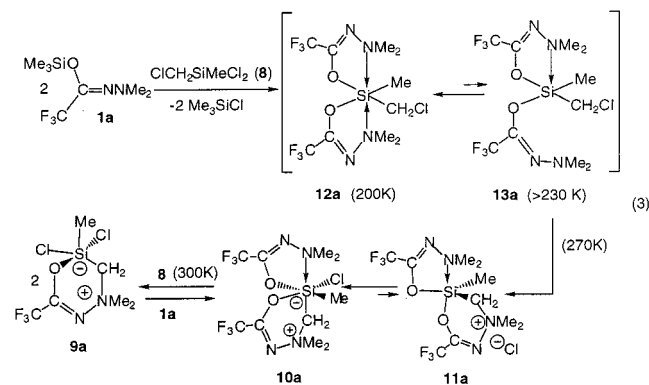
(b) 11b. The molecular structure of **11b** in the crystal is shown in Figure 4, and selected geometrical data are presented in Table 4. The geometry is a distorted TBP, with the dative $\text{N} \rightarrow \text{Si}$ bond occupying the apical position, opposite the oxygen atom of the six-membered chelate ring. The chloro ligand, which was attached to silicon in the analogue **10a**, has dissociated to form a chloride anion adjacent to the ammonium cation present in the six-membered chelate ring. Thus, the molecular structure of **11b** supports the pentacoordinate silicon and cationic ammonium features assigned to the tautomer **11a**.

(c) 11a(OTf). Support for the structure of **11a** comes from a crystallographic study of **11a(OTf)**, for which a limited refinement (13%) was achieved (Figure 7): the general molecular shape is consistent with the structural assignment for **11a**, although exact geometrical parameters could not be obtained due to the low quality of the crystal.¹⁵

(15) Further attempts to obtain adequate crystals for a single-crystal structure determination of **11a(OTf)** are underway.

Complex Formation Mechanism by NMR Monitoring. The different results obtained in the reaction of **1a** with **8** (eq 2) relative to those from the reaction of **1b** and **1c** with **8**, and in particular the isolation of a stable intermediate, **9a**, in the case of **1a**, prompted us to study the formation mechanism in more detail. This was accomplished by low-temperature monitoring of the NMR spectra (^1H , ^{13}C , and ^{29}Si) of the reaction mixtures during product formation. CD_2Cl_2 solutions of the reagents for each reaction (**1a–c** and **8**) were placed in a 5-mm NMR tube at liquid nitrogen temperature and immediately transferred to the precooled (200 K) NMR spectrometer probe. After the initial mixture had dissolved, spectral changes were recorded as a function of temperature changes.

(a) The Reaction of 1a with 8. Equation 3 summarizes the reaction pathway of **1a** with **8** as deduced from the low-temperature NMR monitoring. The initial spectrum after dis-



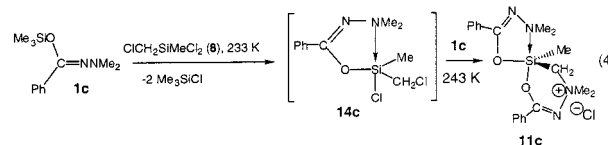
solution of the reagents at 200 K is that of the hexacoordinate intermediate **12a**, along with unreacted starting materials **1a** and **8**. From the ^{29}Si chemical shift ($\delta = -124.6$ ppm), it is evident that the intermediate is an essentially octahedral^{4,16} hexacoordinate silicon complex. The ^1H and ^{13}C spectra further prove its structure: there are four *N*-methyl signals, as required by the two chelated NMe_2 groups. The CH_2Cl carbon resonance is very typical at 35.7 ppm, by sharp contrast to its shifts in **9a**, **10a**, and **11a**, 67.8, 66.9, and 52.1 ppm, respectively (Table 1). Intermediate **12a** belongs to a large group of neutral hexacoordinate silicon complexes which have been studied extensively.^{4–7} These complexes generally show a characteristic stereochemical nonrigidity, with two consecutive ligand-exchange processes observable by variable-temperature NMR spectroscopy.^{4–6} Indeed, in **12a** the *N*-methyl signals show typical line broadening and coalescence phenomena between 190 and 230 K, providing further confidence in the structural assignment, in the absence of a complete characterization of this unstable intermediate.

The structure of **12a** is surprising in that both of the monodentate ligands are carbon ligands, by contrast to numerous analogues with electronegative ligands.^{4–7} This suggests that **12a** should be relatively unstable, and indeed a further increase in temperature leads to dissociation of **12a** to form the pentacoordinate monochelate **13a**. This transformation is reversible, as shown in eq 3: at 200 K, only **12a** can be detected, while at temperatures between 230 and 250 K, both isomers are observed, with the relative population of **13a** increasing with temperature up to $\sim 4:1$ (**12a** to **13a**). The evidence for this equilibrium reaction is as follows: (a) The appearance of a typical five-coordination signal in the ^{29}Si NMR spectrum, and

particularly its temperature dependence, is highly characteristic of pentacoordinate complexes [δ ^{29}Si ppm (*T*): -8.3 (230 K), -6.9 (240 K), -5.7 (250 K), -4.8 (260 K)]. (b) In addition, two of the *N*-methyl signals are equivalent, while the other two are diastereotopic and anisochronous (in the ^1H and ^{13}C spectra), consistent with one chelated dimethylamino group and one open-chain dimethylamino group. (c) The methylene protons are diastereotopic, giving rise to an AB quartet centered at 3.15 ppm ($J_{\text{AB}} = 16.0$ Hz), proving that the silicon is chiral. The CH_2 chemical shift is, however, substantially different from that in **12a**, $\delta = 2.85$ ppm, $J_{\text{AB}} = 16.5$ Hz.

Only at temperatures as high as 260 K, an irreversible transformation of the mixture **12a/13a** to the tautomeric mixture **10a/11a** takes place. The latter equilibration reaction and spectra have been discussed above. This equilibrium reaction, in turn, responds to excess **8** by dissociation to the monochelate **9a**. Excess **1a** shifts this reaction back to the mixture **10a/11a**.

(b) The Reaction of 1c with 8. Interestingly, the reactions of the benzhydrazide and formhydrazide derivatives **1c** and **1b** with **8** are substantially different from that of **1a**. No initial hexacoordinate complex could be detected at any temperature down to 190 K. The initial intermediate at 200 K is the



pentacoordinate complex **14c** (eq 4), as assigned on the basis of the ^{29}Si , ^1H , and ^{13}C NMR spectra: (a) the temperature-dependent ^{29}Si chemical shift [-44.1 ppm (206 K), 42.9 ppm (233 K), -39.3 ppm (253 K)]; (b) diastereotopicity and nonequivalence of the *N*-methyl groups (2.67 and 2.80 ppm) and the methylene protons (3.27, 3.28 ppm, $J_{\text{AB}} = 14.0$ Hz), and (c) a ^{13}C chemical shift for the CH_2 carbon (33.6 ppm) typical of the SiCH_2Cl group. As the temperature of the solution is raised above 220 K, the *N*-methyl singlets broaden and coalesce ($T_c = 223$ K, corresponding to $\Delta G^* = 10.7$ kcal mol^{-1}), while the CH_2 protons remain diastereotopic, in what must be a ring-opening process, again in accord with the behavior of a previously studied similar pentacoordinate complex.²

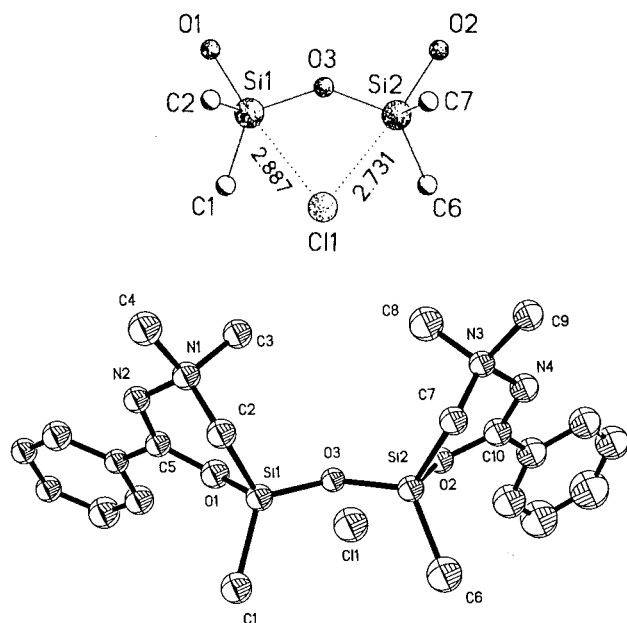
A further increase in temperature, beginning at about 233 K, brings about the irreversible transformation of **14c** to **11c**. For this reaction to occur, at least *two* processes must take place: trans-silylation, substituting the chloro ligand for a hydrazide moiety, and an internal displacement of a chloride by the dimethylamino group accompanied by chelate ring expansion. A similar behavior was observed for the reaction of **1b** with **8**.

In summary, NMR monitoring of these reactions shows that the trifluoromethyl derivative **1a** consistently behaves in a different manner than **1b** and **1c**, the corresponding formyl and phenyl derivatives. Only in the reaction of **1a** was a hexacoordinate intermediate (**12a**) observed at low temperature; likewise, it is only **10a/11a** in which tautomerization is observed, favoring the hexacoordinate tautomer **10a**. In the analogues **11b** and **11c**, only the pentacoordinate species can be detected. These observations lead to the conclusion that the trifluoromethyl substituent destabilizes pentacoordinate complexes and favors hexacoordination. This is in agreement with a previous observation that in pentacoordinate complexes **2**, the trifluoromethyl derivatives (**2**, $\text{R} = \text{CF}_3$) form weaker chelates than when $\text{R} = \text{H}$, Ph : this was manifest in both a lower field ^{29}Si chemical shift for **2**, $\text{R} = \text{CF}_3$, and a substantially lower barrier for $\text{Si}-\text{N}$

(16) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp 1339–1445.

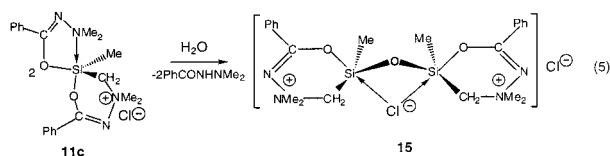
Table 5. Selected Bond Lengths and Angles for **15**

bond	bond length, Å	angle	bond angle, deg	angle	bond angle, deg
Si1–O1	1.716(3)	O1–Si1–Cl1	173.08(12)	O2–Si2–Cl1	173.45(12)
Si1–O3	1.621(3)	O1–Si1–C1	102.1(2)	O2–Si2–C6	100.8(2)
Si1–C1	1.838(5)	O1–Si1–C2	97.4(2)	O2–Si2–C7	96.2(2)
Si1–C2	1.872(4)	O1–Si1–O3	99.3(2)	O2–Si2–O3	95.4(2)
Si1–Cl1	2.887(2)	C1–Si1–O3	117.2(2)	C6–Si2–O3	116.9(2)
Si2–O3	1.632(3)	C2–Si1–O3	115.4(2)	C7–Si2–O3	118.4(2)
Si2–O2	1.731(3)	C1–Si1–Cl1	84.7(2)	C6–Si2–Cl1	85.7(2)
Si2–C6	1.828(5)	C2–Si1–Cl1	80.06(14)	C7–Si2–Cl1	80.75(13)
Si2–C7	1.882(4)	O3–Si1–Cl1	76.30(11)	O3–Si2–Cl1	81.09(11)
Si2–Cl1	2.731(2)				

**Figure 8.** Molecular structure of **15** in the crystal (lower part). Expansion of the bridge area, showing the critical Si–Cl distances and the TBP geometry around each silicon (upper part).

dissociation and ring opening.² The reason for this preference of the CF₃ hydrazide chelates is probably the electron-withdrawing nature of CF₃, which makes the NMe₂ group a weaker donor, and hence leaves the silicon acceptor susceptible to coordination to additional donor atoms, making a hexacoordinate product more likely and more stable.

Partial Hydrolysis of 11c: A Chloride Bridging Two Pentacoordinate Silicons. Attempts to crystallize **11c** and isolate a single crystal for X-ray analysis resulted in partial hydrolysis and formation of the unexpected crystalline chloride-bridged disiloxane **15** (eq 5). The molecular structure of **15** was



studied by X-ray crystal analysis and is shown in Figure 8, accompanied by the crystal packing in Figure 9. The bridging chloride clearly occupies the axial positions of *both* silicon atoms, which each have a distorted TBP geometry. Selected bond lengths and angles for **15** are listed in Table 5. To the best of our knowledge, this is the first reported case of a chloride bridge between two silicon atoms. A number of *fluorine*-bridged complexes have been described previously.^{17–19}

(17) Tamao, T.; Hayashi, K.; Ito, Y. *Organometallics* **1992**, *11*, 2099.

Each of the two silicon atoms of **15** deviates from the central plane (defined by the corresponding equatorial ligands) toward the axial oxygen atom, indicating that the bridging chloride (Cl1 in Figure 8) forms a dative bond to each of the silicon centers. This is fully confirmed by reference to the Si–Cl1 distances, 2.887 and 2.731 Å, respectively, which are both substantially longer than normal covalent Si–Cl bonds (2.05 ± 0.03 Å)²⁰ and yet significantly shorter than the sum of the corresponding van der Waals radii (3.97 Å).^{20,21}

In terms of the progress along a hypothetical S_N2 reaction coordinate, this structure may be viewed either as an early stage of a chloride anion displacing the axial oxygen leaving group, or as an almost complete displacement of a chloride by an oxygen nucleophile. This may be expressed semiquantitatively by referring to the geometry about the silicons in terms of the percentage TBP geometry (along a tetrahedron (TH) → TBP reaction coordinate), following Tamao's definitions.¹⁷

percent pentacoordination (% TBP_a) =

$$\frac{109.5^\circ - \frac{1}{3}(\sum_{n=1}^3 \theta_n)}{109.5^\circ - 90^\circ} \times 100 \quad (6)$$

percent pentacoordination (% TBP_e) =

$$\frac{120^\circ - \frac{1}{3}(\sum_{n=1}^3 \phi_n)}{120^\circ - 109.5^\circ} \times 100 \quad (7)$$

(where θ_n is the angle O_{ax}–Si–L_{eq}, and ϕ_n are the angles L_{eq}–Si–L_{eq}).

According to the equatorial angle definition (eq 7), the percentage TBP of Si1 and Si2 in the crystal is 73 and 84%, respectively. The alternative definition (eq 6) yields the TBP percentages 51 and 62%, respectively. The discrepancy between the TBP characters obtained by the two alternative methods is due to the assumption that both silicon structures lie somewhere along the TH → TBP reaction coordinate; however, this pathway requires that the O_{ax}–Si–Cl angle be 180° at all times, a requirement that is clearly not met by the present system.

The observation of **15** in the solid state raises the question of whether the bridged molecule is also stable in solution. To answer this question, **15** was generated in solution by slowly

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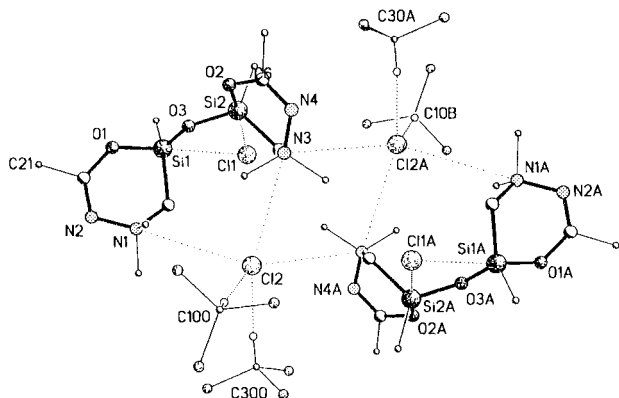


Figure 9. Crystal packing of **15**, featuring the centrosymmetric unit with two bridging chlorides, and two additional chloride anions located each between two ammonium nitrogens, and supported by hydrogen bonding to two chloroform molecules. The four phenyl rings have been omitted for clarity.

bubbling air through a CDCl_3 solution of **11c** in an NMR tube. The formation of **15** was monitored by the gradual disappearance of the ^{29}Si signal at -61.03 ppm (**11c**), and the accompanying evolution of a new signal at -39.6 ppm, at 300 K. The latter chemical shift is typical of pentacoordinate silicon, and hence is evidence that the hydrolysis product in solution is a pentacoordinate complex (if Cl^- did not coordinate to silicon in this product, a ^{29}Si chemical shift near -2.5 ppm,²² as in the analogous silane $\text{Me}_2\text{Si}(\text{OMe})_2$, would be expected).

The pentacoordinate character of the hydrolysis product in solution is further confirmed by observation of the highly characteristic temperature dependence of the ^{29}Si chemical shift of **15** in solution, as follows [δ , ppm (T , K)]: -41.4 (330), -39.6 (300), -37.2 (275), -35.6 (243). The inverse linear relationship is evidence for the coordination of the chloride to silicon, rather than $\text{O} \rightarrow \text{Si}$ coordination (which was reported to have a regular linear dependence of $\delta(^{29}\text{Si})$ on temperature).¹⁰ However, the present results do not permit a bridged complex in solution to be distinguished from one in which a chloride is attached to each silicon.

The two silicon atoms in **15** are chiral, and hence should give rise to two diastereomers. The crystal structure of **15** represents one of these diastereomers, possessing the *meso* geometry. Formation of the bridged **15** in solution should also result in two diastereomers, and hence in two sets of overlapping NMR spectra. This is indeed observed in the ^1H and ^{29}Si NMR spectra (see Experimental Section). The population ratio of diastereomers in CDCl_3 at 300 K is ca. 10:1. Judging from the *meso* structure of the crystal of **15**, which was the sole product obtained in the solid state, one may speculate that the major isomer in solution represents the *meso* geometry, while the minor isomer is the racemic *d,l*.

Conclusion

A novel tautomeric equilibrium reaction has been described, in which a neutral hexacoordinate silicon chelate transforms to an ionic pentacoordinate complex, through a reversible migration of a chloro ligand from silicon to an ammonium nitrogen. The equilibrium is facilitated by the trifluoromethyl ligand, which destabilizes pentacoordination and promotes hexacoordination. Temperature, solvent, substituent, and counterion effects on the equilibrium have been studied.

An unusual chloride-bridged disiloxane, **15**, was obtained by partial hydrolysis of the pentacoordinate tautomer **11b**. It has

two pentacoordinate silicon moieties sharing a common axial chloride ligand.

Experimental Section

General. All the reactions were carried out under dry nitrogen or argon, using solvents that were dried and purified by standard methods. NMR spectra were recorded on a Bruker DMX-500 spectrometer operating at 500.130, 125.758, and 99.362 MHz, respectively, for ^1H , ^{13}C , and ^{29}Si spectra and are reported in δ (ppm) relative to tetramethylsilane (TMS), as determined from standard residual solvent proton (or carbon) signals.

Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

X-ray Structures of 9a, 11b, and 15. Crystals coated by a drop of perfluorinated polyether were mounted on the tip of a glass fiber and shock frozen in the cold nitrogen stream of the low-temperature device of the diffractometer.²³ Data were collected on a STOE IPDS diffractometer (**9a** and **15**) and a Bruker AXS Smart 1000 CCD diffractometer (**11b**). The structures were solved using direct methods (SHELXS-97²⁴) and refined to convergence by full-matrix least-squares iterations against F^2 (SHELXL-97²⁵), minimizing the function $\omega(F_o^2 - F_c^2)$ ($\omega = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^2$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.2 times the U_{eq} of their parent atom (1.5 times U_{eq} in the case of methyl groups). Experimental parameters are given in Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-159128 (**9a**), CCDC-159130 (**11b**), and CCDC-159129 (**15**). 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].

1a–c were prepared as described previously.¹³ **8** and trimethylsilyl-trifluoromethanesulfonate (trimethylsilyl triflate) were obtained commercially (Sigma-Aldrich) and used without purification.

(1-((1,1-Dimethyl-2-trifluoroacetyl)hydrazonium)methyl-C,O)-methylchlorosilicon(IV) (9a). To a solution of 0.20 g (0.87 mmol) of **1a** in 2 mL of chloroform was added 0.20 g (1.2 mmol) of $\text{ClCH}_2\text{-SiMeCl}_2$ in one portion. After 5 min at room temperature, the NMR spectra indicated quantitative conversion. About a quarter of the solvent was removed under reduced pressure. The mixture was kept at 4 °C for two weeks, until crystals had separated. The liquid was decanted off and the solid dried under vacuum. The yield was 75%. Mp: 88–90 °C. Anal. Calcd for $\text{C}_6\text{H}_{11}\text{Cl}_2\text{F}_3\text{N}_2\text{OSi}$: C, 25.40; H, 3.87; N, 9.86. Found: C, 25.43; H, 3.95; N, 9.81. ^1H NMR (CD_2Cl_2 , 300 K): δ 1.02 (s, 3H, SiCH_3), 3.43 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.63 (s, 2H, CH_2). ^1H NMR (CD_2Cl_2 , 190 K): δ 0.96 (s, 3H, SiCH_3), 3.37 (s, 3H, NCH_3), 3.45 (s, 3H, NCH_3), 3.73 (br s, 2H, CH_2). ^{13}C NMR (CDCl_3): δ 12.7 (s, SiCH_3), 57.6 (s, $\text{N}(\text{CH}_3)_2$), 61.1 (s, CH_2), 158.8 (q, $^2J_{\text{CF}} = 37.9$, C=N), 118.6 (q, $^1J_{\text{CF}} = 280.7$, CF_3). ^{29}Si NMR (CDCl_3 , 297 K): δ -63.1 .

Equilibrium Mixture of (N-(Dimethylamino)trifluoroacetimidato-N,O)(1-((1,1-dimethyl-2-trifluoroacetyl)hydrazonium)methyl-C,O)-methylchlorosilicon(IV) (10a) and (N-(Dimethylamino)trifluoroacetimidato-N,O)(1-((1,1-dimethyl-2-trifluoroacetyl)hydrazonium)methyl-C,O)methylsilicon(IV) Chloride (11a). To a solution of 0.32 g (1.42 mmol) of **1a** in 3 mL of toluene was added 0.10 g (0.61 mmol) of $\text{ClCH}_2\text{SiMeCl}_2$ in one portion. Colorless solid precipitated after 2 days at room temperature. The liquid was decanted off and the solid dried under vacuum. The yield was 95%. Mp: 120–121 °C. Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{ClF}_6\text{N}_4\text{O}_2\text{Si}$: C, 29.82; H, 4.25; N, 13.91; Cl, 8.80. Found: C, 29.90; H, 4.35; N, 13.85; Cl, 8.78. ^1H NMR (CD_2Cl_2 , 297 K): δ 0.64 (s, 3H, SiCH_3), 2.87 (br s, 6H, $\text{N}(\text{CH}_3)_2$), 3.28 (br s, 2H, CH_2), 3.45 (br s, 6H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (CD_2Cl_2 , 297 K): δ 15.98 (SiCH_3), 50.0 ($\text{N}(\text{CH}_3)_2$), 58.7 ($\text{N}(\text{CH}_3)_2$), 67.4 (CH_2), 155.4 (q, $^2J_{\text{CF}} =$

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Table 6. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of **9a**, **11b** and **15**

	9a	11b	15
empirical formula	C ₆ H ₁₁ Cl ₂ F ₃ N ₂ O ₅ Si	C ₉ H ₂₀ Cl ₄ N ₄ O ₂ Si	C _{24.50} H _{34.50} Cl _{9.50} N ₄ O ₃ Si ₂
formula mass, g mol ⁻¹	283.16	386.18	826.02
collection <i>T</i> , K	173	173	173
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2(1)	<i>P</i> 2 ₁ / <i>n</i> ⁻
<i>a</i> , Å	12.487(2)	6.1313(11)	11.311(2)
<i>b</i> , Å	7.1123(6)	21.369(4)	17.410(4)
<i>c</i> , Å	13.738(2)	6.7900(12)	19.369(4)
α, deg	90	90	90
β, deg	98.68(8)	98.496(4)	95.20(3)
γ, deg	90	90	90
<i>V</i> , Å ³	1206.1(3)	879.9(3)	3798.7
<i>Z</i>	4	2	4
ρ _{calc} , Mg/m ³	1.559	1.458	1.444
<i>F</i> (000)	576	400	1692
θ range, deg	3.00–24.99	1.91–28.30	2.47–22.50
no. of collected reflns	2304	12228	20472
no. of indep reflns	2126	4113	4939
<i>R</i> _{int}	0.0189	0.0253	0
no. of reflns used	2126	4113	4939
no. parameters	140	186	440
<i>Goof</i>	1.162	1.074	0.870
<i>R</i> 1 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0391	0.0863	0.0405
<i>wR</i> 2 ^b (all data)	0.1248	0.2364	0.0948
<i>g</i> ₁	0.0486	0.0904	0.0788
<i>g</i> ₂	0	0	0
max/min res electron density (e Å ⁻³)	+0.482/–0.521	+2.527/–0.568	+0.412/–0.337

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

37.9, C=N), 157.7 (q, ²J_{CF} = 37.9, C=N), 117.7 (q, ¹J_{CF} = 274.4, CF₃). ²⁹Si NMR (CD₂Cl₂, 297 K): δ –131.7.

(*N*-(Dimethylamino)formimidato-*N,O*)-(1-((1,1-dimethyl-2-formylhydrazonium)methyl-*C,O*)methylsilicon(IV) Chloride (11b). To a solution of 0.26 g (1.6 mmol) of **1b** in 4 mL of chloroform was added 0.14 g (0.86 mmol) of ClCH₂SiMeCl₂ in one portion. About a quarter of the solvent was removed under reduced pressure. After 2 days at room temperature, crystals had separated. The liquid was decanted off and the solid dried under vacuum. The yield was 81%. Mp: 64–65 °C. Anal. Calcd for C₈H₁₉ClN₄O₂Si•0.5CHCl₃: C, 31.27; H, 6.02; N, 17.16; Cl, 27.15. Found: C, 30.32; H, 5.82; N, 16.81; Cl, 27.02. ¹H NMR (CD₂Cl₂, 297 K): δ 0.68 (s, 3H, SiCH₃), 2.77 (br s, 6H, N(CH₃)₂), 3.20, 5.84 (ABq, ²J = 15.6 Hz, 2H, CH₂), 3.63 (s, 6H, N(CH₃)₂), 7.24 (s, 1H, CH=N), 7.29 (s, 1H, CH=N). ¹³C NMR (CD₂Cl₂, 297 K): δ –1.3 (SiCH₃), 48.9 (N(CH₃)₂), 54.1 (NCH₃), 54.1 (CH₂), 62.3 (NCH₃), 155.8 (HC=N), 157.8 (HC=N). ²⁹Si NMR (CD₂Cl₂, 297 K): δ –62.3.

(*N*-(Dimethylamino)benzimidato-*N,O*)-(1-((1,1-dimethyl-2-benzoylhydrazonium)methyl-*C,O*)methylsilicon(IV) Chloride (11c). To a solution of 0.20 g (0.84 mmol) of **1c** in 2 mL of chloroform was added 0.20 g (1.2 mmol) of ClCH₂SiMeCl₂ in one portion. About one-third of the solvent was removed under reduced pressure, and 0.5 mL of *n*-hexane was added until the solution turned turbid. The mixture was kept at room temperature for a week, after which a solid had separated. The liquid was decanted off and dried under vacuum. The yield was 99%. Mp: 122–123 °C. Anal. Calcd for C₂₀H₂₇ClN₄O₂Si•CHCl₃: C, 46.89; H, 5.25; N, 10.42; Cl, 26.36. Found: C, 46.58; H, 5.03; N, 9.97; Cl, 25.02. ¹H NMR (CDCl₃, 297 K): δ 0.83 (s, 3H, SiCH₃), 2.74 (s, 3H, NCH₃), 3.08 (s, 3H, NCH₃), 3.73 (s, 3H, NCH₃), 3.75 (s, 3H, NCH₃), 3.25, 5.76 (ABq, ²J = 15.6 Hz, 2H, CH₂), 7.37–7.59 (m, 6H, ArH), 7.85 (d, ³J = 7.2 Hz, 2H, *o*-ArH), 8.06 (d, ³J = 7.2 Hz, 2H, *o*-ArH). ¹³C NMR (CDCl₃, 297 K): δ –1.1 (SiCH₃), 48.3 (NCH₃), 48.9 (NCH₃), 52.8 (NCH₃), 63.4 (NCH₃), 52.8 (CH₂), 127.3–132.7 (Ar), 162.8 (C=N), 164.9 (C=N). ²⁹Si NMR (CD₂Cl₂, 297 K): δ –61.0.

(*N*-(Dimethylamino)trifluoroacetimidato-*N,O*)-(1-((1,1-dimethyl-2-trifluoroacetyl)hydrazonium)methyl-*C,O*)methylsilicon(IV) Triflate (11a(OTf)). To a solution of 0.25 g (1.10 mmol) of **1a** in 4 mL

of chloroform was added 0.09 g (0.55 mmol) of ClCH₂SiMeCl₂ in one portion. After 5 min, 0.14 g (0.63 mmol) of MeSiOTf was added. Crystals precipitated after 1 h at room temperature. The liquid was decanted off and the solid dried under vacuum. The yield was 85%. Mp: 130 °C (dec). Anal. Calcd for C₁₁H₁₇F₉N₄O₅SSi: C, 25.58; H, 3.32; N, 10.85; F, 33.11. Found: C, 25.95; H, 3.48; N, 10.05; F, 31.00. ¹H NMR (CDCl₃, 333 K): δ 0.82 (s, 3H, SiCH₃), 2.92 (br s, 6H, N(CH₃)₂), 3.56 (s, 3H, NCH₃), 3.68 (s, 3H, NCH₃), 4.45, 3.56 (ABq, ²J = 16.3 Hz, CH₂). ¹³C NMR (CDCl₃, 333 K): δ –1.2 (SiCH₃), 49.0 (N(CH₃)₂), 53.0 (NCH₃), 55.2 (CH₂), 62.8 (NCH₃), 116.1 (q, ¹J_{CF} = 278 Hz, CF₃), 118.9 (q, ¹J_{CF} = 318 Hz, CF₃), 157.0 (C=N). ²⁹Si NMR (CDCl₃, 333 K): δ –56.7.

Bis[1-((1,1-dimethyl-2-benzoylhydrazonium)methyl-*C,O*)methyl]-disiloxane Dichloride (15). Crystallization of a chloroform solution of **11c** resulted in the partly hydrolyzed **15**. Two diastereomers were observed in the NMR spectra. *Major diastereomer.* ¹H NMR (CDCl₃, 300 K): δ 0.85 (s, 6H, SiCH₃), 3.54 (s, 6H, NCH₃), 3.69 (s, 6H, NCH₃), 3.55, 4.60 (ABq, ²J = 16.5 Hz, 4H, CH₂), 7.23–7.98 (m, 10H, Ph). ¹³C NMR (CDCl₃, 300 K): δ 5.4 (SiCH₃), 57.7, 59.3 (NCH₃), 58.6 (CH₂), 127.3–132.7 (Ph), 161.1 (C=N). ²⁹Si NMR (CDCl₃, 300 K): δ –39.6. *Minor diastereomer.* ¹H NMR (CDCl₃, 300 K): δ 0.80 (s, 6H, SiCH₃), 3.60 (s, 6H, NCH₃), 3.70 (s, 6H, NCH₃), 3.82, 4.18 (ABq, ²J = 16.5 Hz, 4H, CH₂), 7.23–7.98 (m, 10H, 2Ph). ²⁹Si NMR (CDCl₃, 300 K): δ –39.9.

Acknowledgment. We thank Dr. Arkady Ellern for the crystallographic analyses of **11a(OTf)** and **11b**. Financial support from the Israel Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of crystal data for **9a**, **11b**, and **15** (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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