Organometallics **2000,** *19,* 1927−1934 1927

Irreversible Rearrangement in Hexacoordinate Silicon Complexes: From Neutral Bis(N→Si) Chelates to Mono(N→Si) Zwitterionic λ^6-Silicates

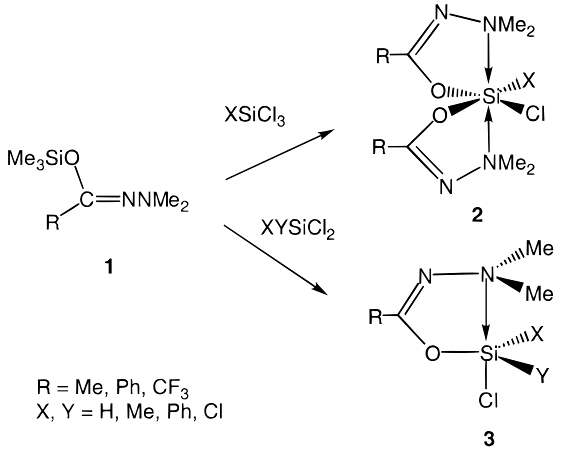
Inna Kalikhman,*,† Olga Girshberg,† Lutz Lameyer,‡ Dietmar Stalke,‡ and Daniel Kost*,†

Department of Chemistry, Ben-Gurion University, Beer-Sheva 84105, Israel, and Institut für Anorganische Chemie, Universität Würzburg, D-97074 Würzburg, Germany

Received December 20, 1999

The reaction of (chloromethyl)trichlorosilane (**7**) with O-trimethylsilylated *N*,*N*-dimethylhydrazides yields initially under kinetic control, in nearly quantitative yields, a neutral hexacoordinate bis(N→Si) chelate, bis(*N*-(dimethylamino)acylimidato-*N*,*O*)chloro(chloromethyl)silicon(IV) (**8a**−**c**). Upon heating, the octahedral complexes **8** are quantitatively and irreversibly converted to the isomeric hexacoordinate chelates zwitterionic λ^6-silicates **9a**−**c**, (*N*-(dimethylamino)acylimidato-*N*,*O*)(1-((1,1-dimethyl-2-acyl)hydrazonium)methyl-*C*,*O*)-dichlorosilicon(IV). This molecular rearrangement is rather unusual, since it involves chelate-ring expansion from the common five-membered ring to a six-membered ring in the thermodynamically favored product **9**. **8b** and **9b** were characterized by X-ray crystal analyses and in solution by their ^{1}H, ^{13}C, and ^{29}Si NMR spectra. The analogous compounds **8a**,**c** and **9a**,**c** were characterized by the respective analogy of their NMR spectra. Both **8b** and **9b** have slightly distorted octahedral geometries around the central silicon atom. Both series of chelates **8** and **9** undergo ligand-site exchange processes, observed by the coalescence of signals due to diastereotopic *N*-methyl and/or CH$_2$ groups. Each compound (of both series) undergoes *two* consecutive rate processes: in **8** this sequence of exchange processes is analogous to previously reported stereomutations through a bicapped-tetrahedral intermediate or transition state; in **9** the first (lower barrier) process is a nitrogen−silicon dissociation−recombination, and the high-barrier process is an inversion of configuration at the silicon center.

We have recently utilized the reaction of *O*-(trimethylsilyl)-*N*,*N*-dimethylhydrazides (**1**) with polyhalosilanes as a convenient method for the synthesis of a variety of different penta- and hexacoordinate silicon complexes with N→Si coordination (eq 1).[1−9] **1** functions as a precursor for five-membered N→Si chelate rings.



(1)

On the other hand, when **1** was allowed to react with (chloromethyl)dimethylchlorosilane (**4**; eq 2), *O*→*Si coordinated* complexes with five- and six-membered chelate cycles (**6** and **5**, respectively) were obtained.[10−13]

---

† Ben-Gurion University.

‡ Universität Würzburg.

[1] (a) Kost, D.; Kalikhman, I.; Raban, M. *J. Am. Chem. Soc.* **1995**, *117*, 11512. (b) Kalikhman, I.; Kost, D.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1253.

[2] Kalikhman, I. D.; Gostevskii, B. A.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *Metalloorg. Khim*. **1989**, *2*, 937; *Chem. Abstr.* **1990**, *112*, 1188926r.

[3] Kalikhman, I. D.; Gostevskii, B. A.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *Metalloorg. Khim*. **1989**, *2*, 205, *Chem. Abstr.* **1990**, *112*, 77291j.

[4] Kost, D.; Krivonos, S.; Kalikhman, I. In *Organosilicon Chemistry III*; Auner, N, Weis, J., Eds.; VCH: Weinheim, Germany, 1997; pp 435−445.

[5] Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D. *Organometallics* **1997**, *16*, 3255. .

[6] Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209.

[7] Mozzhukhin, A. O.; Antipin, M. Yu.; Struchkov, Yu. T.; Gostevskii, B. A.; Kalikhman, I. D.; Pestunovich, V. A.; Voronkov, M. G. *Metalloorg. Khim*. **1992**, *5*, 658. *Chem. Abstr.* **1992,** *117*, 234095w.

[8] Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *15*, 5073.

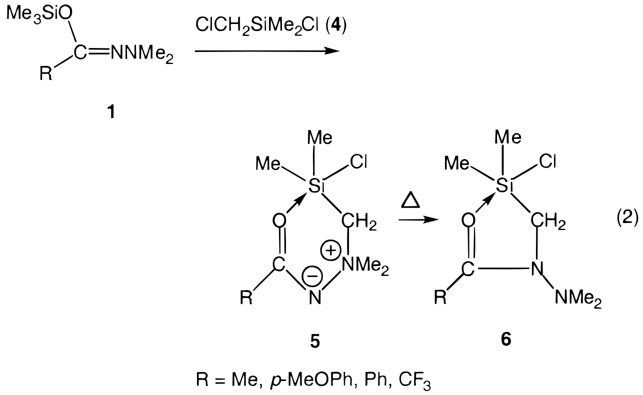
[9] Kalikhman, I.; Kost, D. In *Organosilicon Chemistry III*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1997; p 446.

[10] Kalikhman, I. D.; Bannikova, O. B.; Petuchov, L. P.; Pestunovich, V. A.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1986**, *287*, 870.

[11] Kalikhman, I. D.; Pestunovich, V. A.; Gostevskii, B. A.; Bannikova, O. B.; Voronkov, M. G. *J. Organomet. Chem.* **1988,** *338*, 169.

[12] Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *J. Organomet. Chem.* **1988**, *356*, 23.

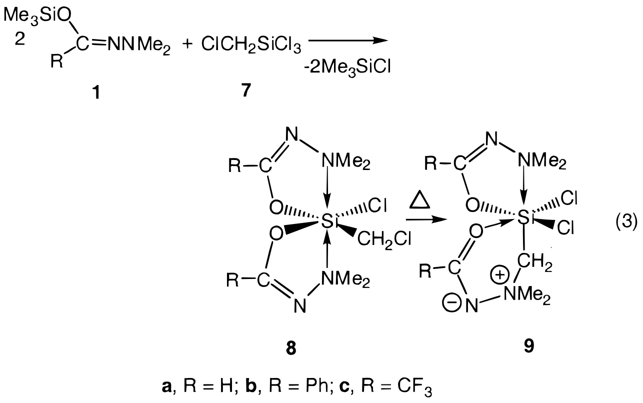
10.1021/om990965v CCC: $19.00



It was of interest to us to investigate how the two separate functionalities (trichlorosilane, on one hand, and chloromethyl ligand, on the other) would react with **1** when placed together in the same molecule ($ClCH_2SiCl_3$ (**7**)). Which of the reactions described in eqs 1 and 2 predominates; i.e., would a bis(N→Si) chelate or a novel, *mixed* (N→Si), (O→Si) dichelate be formed?

Results and Discussion

Molecular Rearrangement. The reaction of **1** with **7** proceeds in two distinct steps (eq 3). When the reagents react at ambient temperature, initially an intermediate (**8**) is formed under conditions of kinetic control. When it is heated or left in solution for several days, **8** is quantitatively converted to the thermodynamically more favorable product **9**. Representatives of both products **8** and **9** have been isolated and characterized by single-crystal X-ray analyses (**8b** and **9b**, Figures 1 and 2).



The initial intermediate **8** is the “normal” bis N→Si coordinated complex, which is obtained in analogy to numerous previously studied neutral hexacoordinate complexes **2** (eq 1), prepared from various trichlorosilanes and substituted O-trimethylsilylated hydrazides.[1-7] The final product **9** is the result of a novel molecular rearrangement, in which a chloride has been displaced by the dimethylamino nitrogen and has migrated from carbon to silicon, accompanied by ring expansion and conversion of the N→Si to O→Si coordination. Thus, the initial expectation that a mixed N→Si, O→Si complex might form has materialized.

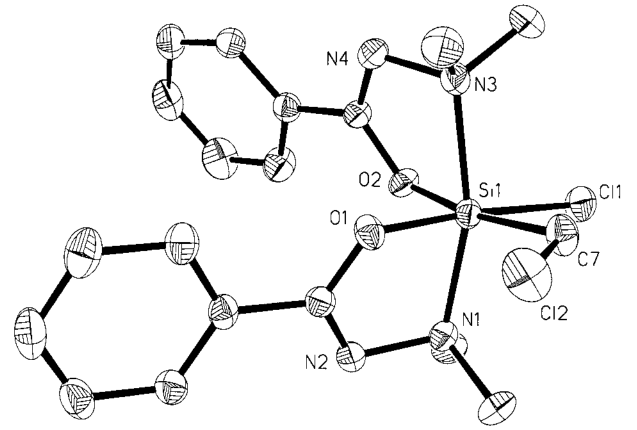


Figure 1. Molecular structure of **8b** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

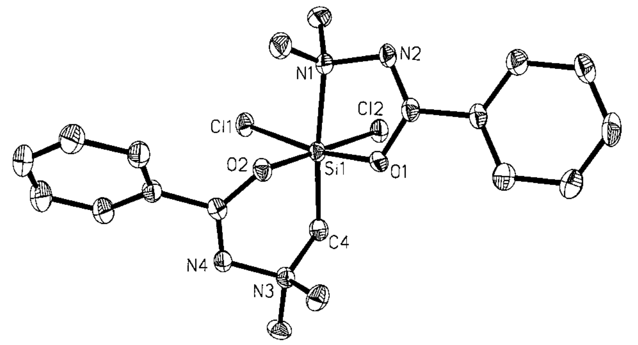


Figure 2. Molecular structure of **9b** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Most of the known hypervalent silicon complexes, whether penta- or hexacoordinate, have five-membered chelate cycles, and it is believed that these are more stable than six-membered chelates.[14-19] In the present study a five-membered chelate ring is initially formed in an exothermic reaction but is further transformed to a six-membered ring, in what appears to be in contrast to the usual chelate ring stability. This apparent conflict is even more puzzling in view of a previous report of a *reverse* rearrangement, from a six- (**5**) to a five-membered (**6**) chelate ring, with similar structures (eq 2), in a Wawzonek[20]-like rearrangement.[11]

One may wonder why the six-membered chelate ring in **9** is more stable than the five-membered ring in **8**. A possible rationale is the accompanying change in the ligand framework around silicon: $\textit{Si}CClN_2O_2$ in **8** and $\textit{Si}CCl_2NO_2$ in **9**. Thus, a Si−N bond in **8** was replaced

---

(13) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Voronkov, M. G.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Pestunovich, V. A. *J. Organomet. Chem.* **1988**, *340*, 23.

(14) 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.

(15) Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99.

(16) 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.

(17) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17; **1996**, *96*, 927.

(18) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(19) Chuit, C.; Corriu, R. J. P.; Reye, C. In *The Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley-VCH: Chichester, U.K., 1999; p 81.

(20) Wawzonek, S.; Yeakey, E. *J. Am. Chem. Soc.* **1960**, *82*, 5718.

Table 1. Selected Interatomic Distances and Bond Angles in Complex 8b

Interatomic Distances (Å)			
Si1−O1	1.7606 (11)	C3−O1	1.3252(17)
Si1−O2	1.7625(11)	C3−N2	1.2801(18)
Si1−N1	2.0145(13)	N1−N2	1.4714(17)
Si1−N3	2.0463(13)	C6−O2	1.3201(16)
Si1−Cl1	2.2140(8)	C6−N4	1.2882(18)
Si1−C7	1.9357(15)	N3−N4	1.4731(17)
Bond Angles (deg)			
C7−Si1−O2	170.30(6)	O1−Si1−N1	82.51(5)
O1−Si1−O2	91.02(5)	C7−Si1−N1	100.67(6)
O2−Si1−N1	86.25(5)	O2−Si1−N3	80.53(5)
O1−Si1−N3	87.10(5)	O2−Si1−Cl1	88.54(4)
C7−Si1−N3	93.81(6)	N1−Si1−Cl1	92.13(4)
C7−Si1−Cl1	84.45(5)	N1−Si1−N3	163.03(5)
N3−Si1−Cl1	98.09(4)	O1−Si1−Cl1	174.64(4)
O1−Si1−C7	96.58(6)		

Table 2. Selected Interatomic Distances and Bond Angles in Complex 9b

Interatomic Distances (Å)			
Si1−O1	1.7549(16)	C1−O1	1.321(3)
Si1−O2	1.7726(18)	C1−N2	1.285(3)
Si1−N1	2.048(2)	N1−N2	1.475(2)
Si1−Cl1	2.2352(12)	C5−O2	1.319(3)
Si1−Cl2	2.2591(10)	C5−N4	1.296(3)
Si1−C4	1.911(3)	N3−N4	1.477(3)
Bond Angles (deg)			
O1−Si1−Cl1	170.22(6)	O1−Si1−C4	94.84(10)
O1−Si1−O2	91.22(8)	O1−Si1−N1	81.25(8)
O2−Si1−N1	90.95(9)	O2−Si1−Cl1	88.85(6)
O2−Si1−C4	92.99(10)	N1−Si1−Cl2	89.37(7)
C4−Si1−Cl1	94.93(8)	N1−Si1−Cl1	88.97(7)
O1−Si1−Cl2	89.89(7)	N1−Si1−C4	174.51(9)
C4−Si1−Cl2	86.76(9)	O2−Si1−Cl2	178.88(6)
Cl1−Si1−Cl2	90.09(4)		

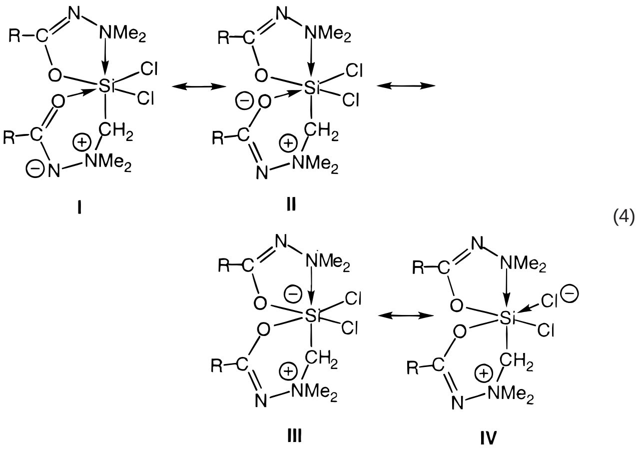
by a second Si−Cl bond in **9**. The additional Si−Cl bond in **9** may be sufficiently more stable than the lost Si−N bond to promote the rearrangement, despite the apparently unfavorable change in chelate ring size.

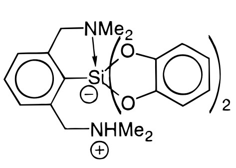
Molecular Structure in the Crystal. Intermediate **8b** has the expected distorted-octahedral geometry, with the N→Si dative bonds *trans* to each other (Figure 1, Table 1). This structure is in agreement with numerous analogous complexes with other R substituents and different monodentate ligands.[5−7]

Complex **9b** (Figure 2, Table 2), has a nearly octahedral geometry, with *cis* bond angles close to 90° and *trans* angles greater than 170°. A chloroform molecule is incorporated in the crystal, forming hydrogen bonds with both chloro ligands.

The molecular and electronic structure of **9** needs further discussion. **9** can be represented by several canonical structures, shown in eq 4. Which of these resonance forms contributes most to the actual molecular structure and where the charges should be located can be assessed on the basis of a comparison of bond lengths of **8b** and **9b** relative to standard bond lengths. Examination of the data in Tables 1 and 2 reveals that all the single Si−O bonds are 0.126−0.144 Å longer than the mean Si−O bond in a tetracoordinate silane (1.629 Å);[21] likewise, the Si−Cl bonds are 0.185−0.209 Å longer than the average Si−Cl bond (2.050 Å)[21] in a silane, as might be expected in a hypervalent complex. Thus, the Si−O and Si−Cl bonds are essentially similar in **8b** and **9b**; i.e., both are covalent. However, the Si−N bonds in **8b** (Table 1) deviate from the standard Si−N bond (1.739 Å)[21] substantially more (ca. 0.3 Å) than normal (covalent) single bonds, as is characteristic of dative bonds. The Si−N distance deviation in **9b** is similar to that in **8b**, confirming the dative nature of this bond in both compounds.

This analysis immediately identifies resonance structure **III** as the best representative (or major contributor) of **9b**. Both the Si−O and the Si−Cl distances in **9b** are well within the range of *single* (covalent) bonds, a situation found only in **III**. It follows that **9b** is best described as a zwitterionic λ^6-silicate, with five covalent bonds and one coordinative bond. The formal charges reside on the ammonium nitrogen and on silicon. This formal charge distribution is similar to that reported by Tacke in a series of *pentacoordinate* silicates.[23] Another example of such coordination to a formally negatively charged silicon in a zwitterionic λ^6-silicate (**10**) was reported by Corriu et al.[24] However, zwitterionic λ^6-silicates with the present ligand framework ($\mathit{Si}CCl_2O_2N$) have not been reported.





10

The amide moiety (O−C−N) of the complexes **8b** and **9b** can be analyzed in a similar fashion: the data in Tables 1 and 2 show that in both complexes the C−O and C−N distances are very close to the standard *imide* bond lengths (O−C=N, average C−O distance 1.330 Å, average C=N distance 1.279 Å[22]), while they deviate substantially from the standard amide (O=C−N) bond lengths (1.234 and 1.325 Å, respectively[22]). It may thus be concluded that in both **8b** and **9b** the amide moiety

---

[21] (a) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 181. (b) Sheldrick, W. S. Willliams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 228.

[22] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[23] Tacke, R.; Pulm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221.

[24] (a) Carre, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *J. Organomet. Chem.* **1993**, *446*, C6. (b) Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Chem. Eur. J.* **1996,** *2*, 342.

Table 3. ^{29}Si and ^{13}C NMR Chemical Shifts (δ, ppm) for Complexes 8a–c and 9a–c in Toluene-d_8 Solutions at 300 K

nucleus	**8a**	**8b**	**8c**	**9a**	**9b**	**9c**
^{29}Si	−139.9	−137.0	−135.3	−162.3	−158.8	−156.8
$N^{13}CH_3$	50.2	50.4	49.7	51.9	52.6	52.1
	50.7	51.0	50.5	52.2	53.0	52.5
	51.9	51.7	51.3	56.0	56.4	57.1
	52.1	52.2	51.5	58.0	59.4	57.8
$^{13}CH_2$	37.7	37.9	37.9	68.4	67.8	67.2
$^{13}C{=}N$	156.9	163.9	156.3	159.9	167.6	157.9
	156.4	163.4	156.8	156.1	163.2	156.3

is predominantly in its enol form, ruling out structure **I** as the major contributor.

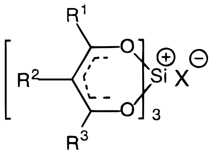
These results compare well with the monocyclic analogue **5** (eq 2), with R = 4-methoxyphenyl.[12] The six-membered chelate rings in **5** and in **9b** are nearly equal, in the sense that the bond lengths in **5** (C–O = 1.321 Å, C(O)–N = 1.289 Å, O–Si = 1.788 Å) almost equal the corresponding bond lengths in **9b** (Table 2). The striking difference between these two chelates is in the Si–Cl bond lengths (Si–Cl = 2.624 Å in **5**), which is ~0.3 Å longer in **5** than in **9b**.[25] It may be concluded that while in **5** the Si–Cl bond is essentially dative (as implied by structure **IV**), it is mostly covalent in **9b**, in accord with structure **III**.

The type of coordination in **9** may seem strange, since a formally negatively charged silicon coordinates as an electron acceptor with a nitrogen donor. One explanation may be that the negative charge is in fact distributed among the surrounding electronegative atoms, to the extent that the silicon remains electron deficient and capable of further coordination with a donor. This is supported by the hydrogen bonds between the chloro ligands and the chloroform molecule found in the crystal, suggesting that substantial negative charges reside on the chloro ligands. This is also in agreement with a report by Gordon et al.,[26] who had concluded, on the basis of SCF-MO calculations, that the positive charge on silicon *increases* as the number of ligands attached increases, even when the total molecular charge becomes more negative.

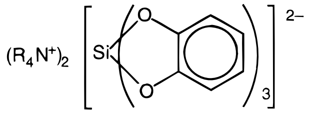
NMR. Comparison of the ^{29}Si chemical shifts (Table 3) shows a dramatic upfield shift from complexes **8** to **9** (ca. 22 ppm for similarly substituted complexes). This may result, in part, from the change in ligand framework from **8** to **9** ($SiCClN_2O_2$ and $SiCCl_2NO_2$, respectively), whereby a nitrogen was replaced by a chloro ligand. However, comparison with a complex with an overall *more* electronegative ligand environment, $SiCl_2N_2O_2$ (**2**, X = Cl, eq 1; δ(^{29}Si) −147 ppm),[1] shows that even relative to this complex **9** has a substantially upfield ^{29}Si chemical shift.

This comparison leads to the conclusion that the variation in ^{29}Si chemical shifts is associated primarily with the change in chelate-ring size: the presence of a six-membered ring in **9** causes the upfield shift, apparently due to relief of ring strain of the five-membered chelate ring. This conclusion is supported by various previous reports, relating chelate ring size to ^{29}Si chemical shifts. In a review by Williams[27] a compilation of ^{29}Si chemical shifts of tetracoordinate silanes was reported, from which it was concluded that replacement of a five-membered chelate by a similar six-membered chelate causes an upfield shift of ca. 20 ppm.

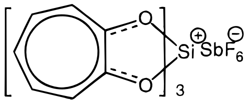
In a similar comparison of a series of hexacoordinate silicon complexes with tris bidentate ligand coordination (SiO_6 ligand framework), an average 60 ppm upfield shift was observed for six-membered chelate rings, *regardless of formal charge on silicon* (acetylacetonates **11**; δ(^{29}Si) ≅ −193 ppm), relative to the corresponding complexes with five-membered rings (catecholates **12** and tropolonates **13**; δ(^{29}Si) ≅ −135 ppm).[28] This is in perfect agreement with the present observation of an average upfield shift of 20 ppm per chelate ring.



11



12



13

Examination of the ^{13}C NMR data in Table 3 shows characteristic differences between the five- and six-membered chelate ring signals. The two $C{=}N$ signals in complexes **8** have essentially equal chemical shifts, the same as in the five-membered chelates of compounds **9**. However, in the six-membered chelate rings of **9a–c** the $C{=}N$ signals are shifted 2–4 ppm to higher field, providing a means for distinction between the five- and six-membered rings in compounds **9**. The $N{-}CH_3$ signals are characteristic in a similar way: in all the five-membered chelate rings these have essentially equal chemical shifts, regardless of the compound, **8** or **9**; however, a substantial upfield shift (ca. 4–6 ppm) is observed in the corresponding *N*-methyl groups of the six-membered chelate rings in **9**.

Dynamic NMR and Stereomutation. Compounds **8**, with two similar five-membered chelate rings in each, undergo two consecutive ligand-exchange processes observable by the coalescence of diastereotopic signals of the *N*-methyl and CH_2 groups. This behavior is fully analogous to the spectral changes observed and discussed previously in a large series of compounds (**2**) with essentially similar structure.[1,6] The resulting barriers for stereomutation are listed in Table 4. The barrier evaluation for **8a**,**c** suffers from relatively large error ranges, resulting from several factors. (a) The two consecutive barriers do not differ substantially in free energy, and hence are insufficiently resolved from each other. (b) The chemical shift differences (particularly in **8a**,**c**) between signal pairs of diastereotopic groups are

---

(25) Substantially long Si–Cl bonds (2.598 Å) in pentacoordinate silanes have also been reported by Kummer et al.: Kummer, D.; Chaudhry, S. C.; Seifert, J.; Deppisch, B.; Mattern, G. *J. Organomet. Chem.* **1990**, *382*, 345.

(26) Gordon, M. S.; Carrol, M. T.; Davis, L. P.; Burggraf, L. W. *J. Phys. Chem.* **1990**, *94*, 8125.

(27) Willliams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 511, Table 17.

(28) Evans, D. F.; Wong, C. Y. *Polyhedron* **1991,** 1131.

Table 4. Variable-Temperature NMR Data for *N*-Methyl Exchange for Complexes 8 in $CDCl_3$ Solutions

compd	nucleus	$\Delta\nu$, Hz[a]	coalescence temp, T_c, K	$\Delta G^{\ddagger}$, kcal mol^{-1}
8a	^1H	45	315	15.6 ± 0.5
	^1H	15	290	14.9 ± 0.5
	^{13}C	174	330	15.5 ± 0.5
8b	^1H	10	235	12.5 ± 0.5
	^1H	40	260	12.8 ± 0.5
	^1H	80	>333	18.0 ± 0.8[b]
8c	^1H	24	325	16.5 ± 0.5
	^1H	27	315	15.7 ± 0.5

[a] Chemical shift difference in Hz between signals of exchanging groups at the slow exchange limit temperature. [b] In this solvent extensive line broadening is observed but full coalescence cannot be reached.

Table 5. Variable-Temperature NMR Data for Exchange of *N*-Methyl Groups in Complexes 9

compd	nucleus[a]	solvent	$\Delta\nu$, Hz	T_c, K	$\Delta G^{\ddagger}$, kcal mol^{-1}
9a	^1H	$C_6D_5CD_3$	30	332	16.7 ± 0.3
	^1H	$C_6D_5CD_3$	160	335	15.8 ± 0.3
	^{13}C	$C_6D_5CD_3$	261	363	16.8 ± 0.3
	^{13}C	$C_6D_5CD_3$	34	318	15.9 ± 0.3
	^1H	$CDCl_3$	12	263	13.6 ± 0.3
	^1H	$CDCl_3$	75	310	15.0 ± 0.3
	^{13}C	$CDCl_3$	10	263	13.7 ± 0.3
	^{13}C	$CDCl_3$	435	335	15.1 ± 0.3
9	^1H	$C_6D_5CD_3$	89	360	17.4 ± 0.3
	^1H	$C_6D_5CD_3$	33	373	18.8 ± 0.3
	^{13}C	$C_6D_5CD_3$	40	348	17.4 ± 0.3
	^{13}C	$C_6D_5CD_3$	200	385	18.1 ± 0.3
9c	^1H	$C_6D_5CD_3$	133	350	16.6 ± 0.3
	^1H	$C_6D_5CD_3$	145	>370	21.2 ± 0.2[b]
	^{13}C	$C_6D_5CD_3$	50	335	16.5 ± 0.3
	^{13}C	$C_6D_5CD_3$	80	>370	>20
	^1H	$C_6D_5NO_2$	103	350	16.8 ± 0.3
	^1H	$C_6D_5NO_2$	40	>370	>20
	^{13}C	$C_6D_5NO_2$	34	335	16.8 ± 0.3
	^{13}C	$C_6D_5NO_2$	13	>370	>20

[a] The two entries for each nucleus correspond to the two pairs of exchanging *N*-methyl groups in each compound, with different $\Delta\nu$, T_c, and barrier values. [b] Measured by selective inversion recovery (Figure 4).

relatively small, reducing the accuracy of measurement. (c) At the temperatures necessary for observation of the two rate processes the rate of the third process, the irreversible rearrangement (**8** → **9**), becomes significant and severely interferes with the barrier measurement.

Compounds of type **9** have not been described previously, and their stereochemical nonrigidity and ligand exchange mechanisms are of interest. In **9** also, as in **2**[1,6] (and **8**), two exchange processes are observed by dynamic NMR spectroscopy (Table 5). However, the evidence shows that, in contrast to **2**, in which the two processes were assigned to nondissociative adjacent ligand (O,O and X,Cl) interchange,[1,6] the first (lower) barrier in **9** is due to chelate ring opening and reclosure, via dissociation of the dative N→Si bond in the five-membered chelate. This is shown in Figure 3 for **9c**, in which the first line broadening and coalescence observed upon heating involves two of the four *N*-methyl signals, while the second pair of *N*-methyl signals, as well as the AB quartet due to the diastereotopic CH_2 protons, remain unchanged. It follows that this process does not effect inversion of configuration at silicon, and hence, *N*-methyl exchange must be due to dissociation–recombination of the N→Si bond.

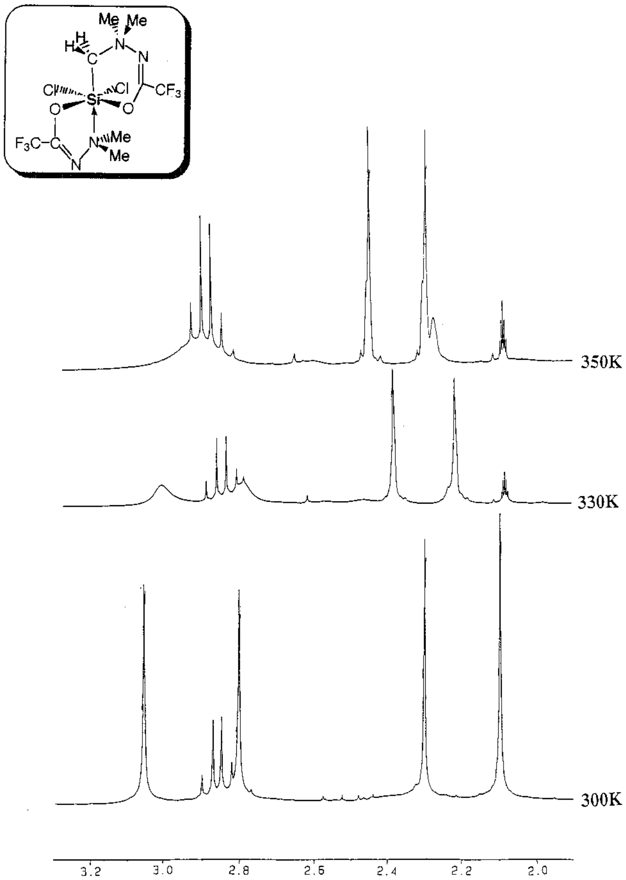


Figure 3. Variable-temperature ^1H NMR spectra of **9c** in toluene-d_8 solution.

When the temperature of a sample of **9c** is raised further, a second rate process takes place. This barrier could not be fully monitored by variable-temperature ^1H NMR spectroscopy, due to the high temperature necessary, and was measured utilizing the selective inversion recovery (SIR) NMR method (Figure 4).[29] This method is superior for monitoring and measurement of relatively high barriers, because it is carried out at temperatures approximately 50 °C lower than the coalescence temperature. From the intensities of the signals of the exchanging *N*-methyl groups at various time intervals τ between the selective inversion and the $\pi/2$ observation pulses, a linear correlation can be obtained using eq 5. In eq 5 I_A and I_B are the intensities

$$\ln\left(1 - \frac{I_A + I_B}{I_A^{\infty} + I_B^{\infty}}\right) - \ln\frac{I_B - I_A}{I_B^{0} - I_A^{0}} = 2k\tau \qquad (5)$$

of the corresponding signals in arbitrary units, and I_A^0, I_B^0, I_A^{∞}, and I_B^{∞} are the corresponding intensities at τ delay times zero and infinity (in practice: 0.001 and 10 s, respectively). From the slope of this function the first-order rate constant for exchange at the experiment temperature is calculated. The corresponding first-order rate constant and free energy barrier for exchange in **9c** are 0.96 s^{-1} and 21.2 kcal mol^{-1}, respectively, at 360 K.

---

(29) (a) Blanca, B.-D. M.; Maimon, E.; Kost, D. *Angew. Chem.* **1997**, *109*, 2294; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2216. (b) Orrell, K. G.; Sik, V. *Annu. Rep. NMR Spectrosc.* **1993**, *27*, 103.

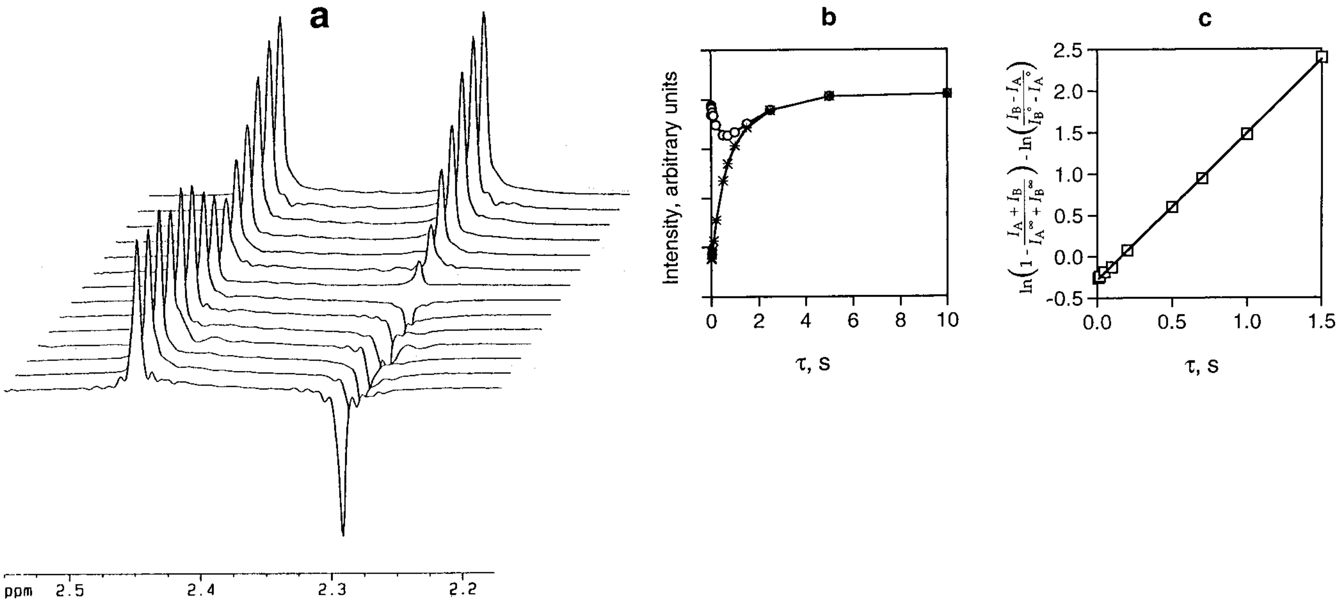


Figure 4. Selective inversion recovery measurement of the barrier for inversion of configuration at silicon in **9c** in toluene-d_8 solution at 360 K: (a) Stack plot of inversion recovery ^{1}H NMR spectra; (b) plot of signal intensities as a function of the variable delay τ; (c) linear correlation of data according to eq 5.

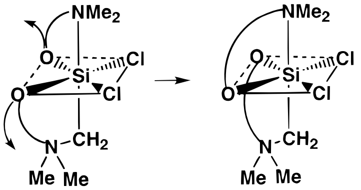


Figure 5. Schematic representation of inversion of configuration at silicon in compounds **9** by an O,O-exchange reaction, changing the helicity of the chelate-ring sequence.

This unusually high barrier for inversion of configuration at the chiral silicon atom in **9c** is probably due to O,O exchange (Figure 5), in analogy to silicon inversion in compounds **2**.[1,6] Addition of excess pyridine-d_5 to the sample lowered the first activation barrier by 0.6 kcal mol^{-1}, while leaving the higher barrier essentially unchanged. This may support the N−Si dissociation mechanism, assuming that pyridine effectively competes with the dimethylamino group in binding to silicon, and hence the dative bond is weakened and its dissociation barrier lowered.

In the analogous complexes **9a**,**b** the two consecutive dynamic processes are also observed (Table 5), but in this case the difference in free energy between the two processes (in each compound) is much smaller than in **9c**, resulting in lower resolution between the two processes. In these compounds, the higher of the two barriers is sufficiently low to permit coalescence measurement, without having to use the SIR method.

By analogy to **9c**, it is concluded that in **9a**,**b** the same two kinetic processes take place, N−Si dissociation at the five-membered chelate ring and inversion of configuration at silicon, possibly by O,O exchange.

Experimental Section

General Considerations. All the reactions were carried out under dry nitrogen or argon. NMR spectra were recorded on a Bruker 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 δ (ppm) relative to internal tetramethylsilane (TMS). Selective inversion recovery (SIR) spectra were carried out using a modified T_1 measurement pulse sequence, in which the π-pulse was replaced by the sequence $\pi/2-1/(2\Delta\nu)-\pi/2$, and the pulses were on-resonance of one of the exchanging signals ($\Delta\nu$ is the chemical shift difference between the exchanging groups, expressed in Hz). For the linear fitting of eq 5 (Figure 4c) no data points beyond τ = 1.5 s were included, because no kinetic information is available after the two intensity curves (Figure 4b) have merged. All the reactions were nearly quantitative, as determined by complete conversion of the real-time NMR spectra.

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

X-ray Structures of 8b and 9b. The crystal data for **8b** and **9b** are presented in Tables 1 and 2. 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.[30] Data were collected on a STOE IPDS diffractometer. The structures were solved using direct methods (SHELXS-97[31]) and refined to convergence by full-matrix least-squares iterations against F^2 (SHELXL-97[32]), minimizing the function $w(F_o^2 - F_c^2)$ ($w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = {}^1/_3[\max(F_o^2,0) + 2F_c^2]$). 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 1.2 times the U_{eq} value of their parent atom (1.5 times U_{eq} in the case of methyl groups). Experimental parameters are listed 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 Publication Nos. CCDC-134721 (**8b**) and CCDC-134722 (**9b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) + 44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk).

O-trimethylsilylated 1,1-dimethyl-2-acylhydrazines (**1b**,**c**) were prepared as described previously[1,33] and distilled under reduced pressure. The boiling points were as follows: **1b**, 80−82 °C (0.8 mmHg), lit.[33a] bp 110−112 °C (2 mmHg); **1c**, 70−73 °C (30 mmHg), lit.[33b] bp 41 °C (10 mmHg).

---

(30) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.

(31) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(32) Sheldrick, G. M. Program for crystal structure refinement; University of Göttingen, Göttingen, Germany, 1997.

Table 6. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 8b and 9b

	8b	9b
empirical formula	$C_{19}H_{24}Cl_2N_4O_2Si$	$C_{20}H_{25}Cl_5N_4O_2Si$
formula mass, g mol^{-1}	439.41	558.78
collecn T, K	173	173
λ(Mo Kα), Å	0.710 73	0.710 73
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	8.9893(18)	10.2555(17)
b, Å	13.593(3)	11.2707(19)
c, Å	17.610(4)	13.378(3)
α, deg	90	106.51(2)
β, deg	102.64(3)	100.52(2)
γ, deg	90	113.858(19)
V, Å^3	2099.6	1275.5(4)
Z	4	2
ρ_{calcd}, Mg/m^3	1.390	1.455
$F(000)$	920	576
θ range, deg	2.76−29.15	2.31−25.00
no. of coll rflns	19 749	10 093
no. of indep rflns	5627	4209
R_{int}	0.0425	0.0503
no. of rflns used	5627	4209
no. of params	257	293
GOF	0.974	0.907
R1[a] ($I > 2\sigma(I)$)	0.0331	0.0348
wR2[b] (all data)	0.0847	0.0878
g_1	0.0498	0.0523
g_2	0	0
max/min res electron dens, e Å^{-3}	+0.307/−0.305	+0.285/−0.379

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

(Trimethylsilyl)-1,1-dimethyl-2-formylhydrazine (1a) was prepared by the same method, reaction of Me_3SiCl (16 mL, 14 g, 0.13 mol) with *N*,*N*-dimethylformhydrazide (6 g, 0.068 mol).[34] The product (3.22 g, 30%) was a colorless liquid, bp 35−36 °C (11 mmHg). The NMR spectra feature an equilibrium mixture of the O- and N-trimethylsilylated hydrazide isomers with a 1.2:1 population ratio at room temperature. ^{1}H NMR ($CDCl_3$): δ 0.82 (s, Me_3Si, 9H), 3.04, 3.37 (2 s, NMe_2, 6H), 8.20, 8.72 (2 s, HC═N, 1H). ^{13}C NMR ($CDCl_3$): δ −0.3, −1.4 (Me_3Si), 44.3, 47.4 (NMe_2), 150.9, 163.8 (C═N). ^{29}Si NMR ($CDCl_3$): δ 9.0, 23.0. Anal. Calcd for $C_6H_{16}N_2OSi$: C, 44.96; H, 10.06; N, 17.48. Found: C, 45.11; H, 10.04; N, 17.46.

Bis(*N*-(dimethylamino)formimidato-*N*,*O*)chloro(chloromethyl)silicon(IV) (8a). To a solution of 0.25 g (1.55 mmol) of **1a** in 2 mL of chloroform under dry argon was added 0.25 mL (2 mmol) of $ClCH_2SiCl_3$ (**7**) in one portion. After 5 min at room temperature, the NMR spectra indicated quantitative conversion. About half of the solvent was removed under reduced pressure, until a white solid had precipitated. The solution was decanted and the solid washed with 2 mL of chloroform, followed by drying under vacuum. The residue of pure **8a** weighed 0.197 g, (89%). Mp: 87 °C dec. ^{1}H NMR ($CDCl_3$, 262 K[35]): δ 2.91, 2.92, 2.94, 3.00 (4 s, NMe_2, 12H), 3.13, 3.29 (AB q, J = 15.8 Hz, CH_2, 2H), 7.01, 7.07 (2 s, HC═N, 2H). ^{13}C NMR ($CDCl_3$, 297 K): δ 50.2, 50.7, 51.9, 52.1 (NMe_2), 37.1 (CH_2Cl), 156.4, 156.9 (C═N). ^{29}Si NMR ($CDCl_3$, 297 K): δ −139.9. Anal. Calcd for $C_7H_{16}Cl_2N_4O_2Si$: C, 29.27; H, 5.61; N, 19.51; Cl, 24.69. Found: C, 28.62; H, 5.89; N, 19.27; Cl, 24.28.

Bis(*N*-(dimethylamino)benzimidato-*N*,*O*)chloro(chloromethyl)silicon(IV) (8b). The procedure was the same as for **8a**, using 0.25 g (1 mmol) of **1b** and 0.25 mL (2 mmol) of **7**. **8b** precipitated after half of the chloroform solution had evaporated, followed by adding 1 mL of hexane and cooling to −15 °C for 1 week. The solvent was decanted and the residue vacuum-dried to yield 0.218 g (99%) of a white solid, mp 122 °C dec (with complete conversion to **9b**, as determined by ^{1}H NMR after cooling). ^{1}H NMR ($CDCl_3$, 220 K[35]): δ 3.07, 3.09, 3.23, 3.31 (4 s, NMe_2, 12H), 3.19, 3.48 (AB q, J = 15.8 Hz, CH_2, 2H), 7.30−7.82 (m, Ph, 10H). ^{13}C NMR ($CDCl_3$, 230 K[33]): δ 50.2, 50.7, 51.9, 52.1 (NMe_2), 37.1 (CH_2Cl), 163.8, 164.1 (C═N), 127.4, 127.5, 128.9, 129.6, 129.8, 131.7 (Ph). ^{29}Si NMR ($CDCl_3$, 297 K): δ −136.7. Anal. Calcd for $C_{19}H_{24}Cl_2N_4O_2Si$: C, 51.93; H, 5.51; N, 12.75; Cl, 16.14. Found: C, 51.74; H, 5.54; N, 12.68; Cl, 16.28.

Bis(*N*-(dimethylamino)trifluoroacetimidato-*N*,*O*)chloro(chloromethyl)silicon(IV) (8c). The same procedure was used as for **8b**. The product crystallized after half of the chloroform solvent had been removed under reduced pressure, followed by 1 week at −15 °C. Mp: 130 °C dec (with complete conversion to **9c**, as determined by ^{1}H NMR after cooling). ^{1}H NMR ($CDCl_3$, 297 K): δ 3.02, 3.06, 3.08, 3.11 (4 s, NMe_2, 12H), 3.32, 3.09 (AB q, J = 16.8 Hz, CH_2, 2H). ^{13}C NMR ($CDCl_3$, 297 K): δ 36.3 (CH_2Cl), 50.1, 50.9, 51.9, 52.0 (NMe_2), 117.0 (q, ^1J(FC) = 277 Hz, CF_3), 156.0, 156.5 (2 q, ^2J(FC) = 38 Hz, C═N). ^{29}Si NMR ($CDCl_3$, 297 K): δ −135.3. Anal. Calcd for $C_9H_{14}Cl_2F_6N_4O_2Si$: C, 25.54; H, 3.33. Found: C, 25.33; H, 3.23.

(*N*-(Dimethylamino)formimidato-*N*,*O*)(1-((1,1-dimethyl-2-formyl)hydrazonium)methyl-*C*,*O*)dichlorosilicon(IV) (9a). The same reagents and quantities as in the preparation of **8a** were dissolved in 2 mL of dry chloroform. The solution was refluxed for 2 h and then cooled to room temperature. After vacuum removal of ca. half of the solvent, the mixture was kept at 4 °C for several days, until crystals had separated. The liquid was decanted off, and the crystals were washed with 2 mL of chloroform followed by vacuum-drying. The remaining white solid weighed 0.202 g (64%, based on a solid containing one chloroform molecule per product molecule).[36] Mp: 125 °C dec. ^{1}H NMR ($C_6D_5CD_3$, 300 K): δ 2.56, 2.62, 2.82, 3.13 (4 s, NMe_2, 12H), 3.11, 3.07 (AB q, J = 13.6 Hz, CH_2, 2H), 6.78, 6.90 (2 s, HC═N, 2H). ^{13}C NMR ($C_6D_5CD_3$, 300 K): δ 51.9, 52.2, 56.0, 58.0 (NMe_2), 68.4 (CH_2Cl), 156.1, 159.9 (C═N). ^{29}Si NMR ($C_6D_5CD_3$, 300 K): δ −162.3. Anal. Calcd for $C_7H_{10}Cl_2N_4O_2Si$: C, 29.27; H, 5.61. Found: C, 28.89; H, 5.85.

(*N*-(Dimethylamino)benzimidato-*N*,*O*)(1-((1,1-dimethyl-2-benzoyl)hydrazonium)methyl-*C*,*O*)dichlorosilicon(IV) (9b). The same reagents and quantities as in the preparation of **8b** were used; the reagents were dissolved in 2 mL of dry chloroform and refluxed for 5 h. The product (0.224 g, 80% based on a solid containing one chloroform molecule per product molecule)[36] crystallized after 1 mL of *n*-hexane had been added and the solution placed in a freezer. Mp: 113 °C dec. ^{1}H NMR ($C_6D_5CD_3$, 300 K): δ 2.45, 2.52, 3.22, 3.40 (4 s, NMe_2, 12H), 3.19, 3.24 (AB q, J = 13.7 Hz, CH_2, 2H), 6.8−8.1 (m, Ph, 10H). ^{13}C NMR ($C_6D_5CD_3$, 300 K): δ 52.6, 53.0, 56.4, 59.4 (NMe_2), 67.8 (CH_2Cl), 163.2, 167.1 (C═N). ^{29}Si NMR ($C_6D_5CD_3$, 300 K): δ −158.8. Anal. Calcd for **9b**·$CHCl_3$ ($C_{20}H_{25}Cl_5N_4O_2Si$): C, 42.99; H, 4.51; N, 10.03. Found: C, 42.29; H, 4.56; N, 9.55.

(*N*-(Dimethylamino)trifluoroacetimidato-*N*,*O*)(1-((1,1-dimethyl-2-trifluoroacetyl)hydrazonium)methyl-*C*,*O*)dichlorosilicon(IV) (9c). The same procedure was used as for the preparation of **9b**. The yield was 0.238 g (79%, based on a solid containing one chloroform molecule per product

---

[33] (a) Kalikhman, I. D.; Bannikova, O. B.; Volkova, L. I.; Gostevskii, B. A.; Yushmanova, T. I.; Lopirev, V. A.; Voronkov, M. G. *Bull. Akad. Nauk SSSR* **1988**, 460; *Chem. Abstr.* **1989**, *110*, 75608c. (b) Kalikhman, I. D.; Medvedeva, E. N.; Bannikova, O. B.; Fabina, N. G.; Larin, M. F.; Lopirev, V. A.; Voronkov, M. G. *J. Obshch. Khim.* **1984,** *54*, 477; *Chem. Abstr.* **1984**, *101*, 55158s.

[34] (a) Beltrami, R. T.; Bissel, E. R. *J. Am. Chem. Soc.* **1958**, *80*, 1895. (b) Hinman, R. L.; Fulton, D. *J. Am. Chem. Soc.* **1956**, *78*, 2467.

[35] At room temperature extensive line broadening due to chemical exchange was observed.

[36] The crystal structure of **9b** and the fact that **9a**−**c** decompose upon melting with evolution of gas bubbles suggest that the solids contain chloroform. The yields have been calculated accordingly.

molecule).[36] Mp: 95 °C dec. ^{1}H NMR ($C_6D_5CD_3$, 300 K): δ 2.24, 2.48, 2.95, 3.20 (4 s, NMe_2, 12H), 2.94, 3.04, (AB q, J = 14.1 Hz, CH_2, 2H). ^{13}C NMR ($C_6D_5CD_3$, 300 K): δ 52.1, 52.5, 57.1, 57.8 (NMe_2), 67.2 (CH_2Cl), 117.3 (q, ^1J(FC) = 280 Hz, CF_3), 118.0 (q, ^1J(FC) = 277 Hz, CF_3), 156.3 (q, ^2J(FC) = 38 Hz, C=N), 157.9 (q, ^2J(FC) = 37 Hz, C=N). ^{29}Si NMR ($C_6D_5CD_3$, 300 K): δ −156.8. Anal. Calcd for $C_9H_{14}Cl_2F_6N_4O_2Si$: C, 25.54; H, 3.33; Cl, 16.75; N, 13.24. Found: C, 24.95; H, 3.02; Cl, 17.45; N, 13.03.

Acknowledgment. We thank the Israel Science Foundation for financial support and the Israel Ministry of Sciences and Arts for a grant toward the purchase of the 500 MHz NMR spectrometer.

Supporting Information Available: Tables of additional crystallographic data for **8b** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990965V