Donor-Stabilized Silyl Cations. 5. Comparison between Mono- and Binuclear Siliconium Chelates[1]

Inna Kalikhman,*,† Vijeyakumar Kingston,† Boris Gostevskii,†,‡
Vadim Pestunovich,‡ Dietmar Stalke,§ Bernhard Walfort,§ and Daniel Kost*,†

*Department of Chemistry, Ben Gurion University, Beer Sheva 84105, Israel,
A. E. Favorsky Irkutsk Institute of Chemistry, Russian Academy of Sciences, Siberian Branch,
664033 Irkutsk, Russia, and Institut für Anorganische Chemie, Universität Würzburg,
D-97074 Würzburg, Germany*

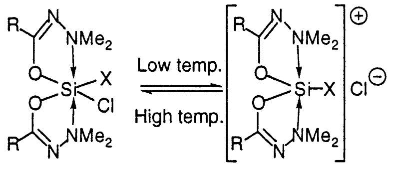
Received May 2, 2002

Binuclear hexacoordinate silicon chelates have been prepared and shown to have octahedral structure by X-ray crystallography. Their ionization in CD_2Cl_2 solution has been studied by ^{29}Si NMR spectroscopy. Only one Si−Cl bond in **5a**−**c** ionizes at low temperature to form the monosiliconium bis-chelates **11a**−**c**. Use of a more acidic solvent, $CHFCl_2$, facilitated the second ionization step to the disiliconium dichloride **12c**. Replacement of the chloro ligands by better leaving groups (triflate, bromide, or iodide) caused complete ionization (**7a**−**c**, **8c**, **9c**) at room temperature. Crystal structure analyses of the binuclear siliconium triflates **7a**,**b** show a square-pyramid geometry around the silicon atoms, with the ethylene bridge at the apex.

Introduction

There has been considerable interest in recent years in the development and study of hypervalent silicon complexes (**1**).[2] Some binuclear[2j,3a−e] and polynuclear[3f−h] silicon chelates have been reported. The present report describes the preparation and properties of binuclear *neutral* hexacoordinate silicon chelates (**5**) and, in particular, their derivation into binuclear donor-stabilized siliconium salts by ligand exchange (**7**−**9**) or by solvent-driven stepwise ionization (**11**, **12**).

Mononuclear silicon bis-chelates (**1**) have recently been shown to undergo ionization via heterolytic cleavage of the Si−Cl bond, to form chloride salts of donor-stabilized pentacoordinate siliconium ions (eq 1).[4] This reversible ionization recombination reaction is driven by solvation of the ions. Its equilibrium constant changed dramatically in response to temperature changes, different substituents (R) and ligands (X), and changes in counterion. Electron-withdrawing R groups (R = CF_3) or X ligands (X = Cl, Br) shifted the equilibrium completely to the hexacoordinate side and essentially prevented ionization. Replacement of the chloro ligand in **1** by better leaving groups (triflate, Br) led to complete ionization to siliconium salts at room temperature.[4]



(1)

1 **2**

In this study the reactions leading from binuclear neutral complexes to formation of binuclear siliconium salts are compared with those studied previously for the mononuclear hexacoordinate complexes (eq 1),[4] and special effects unique to the binuclear chelates are discussed.

Results and Discussion

Synthesis and Structure. Binuclear silicon chelates (**5a**−**d**, eq 2) were prepared from 1,2-bis(trichlorosilyl)ethane (**3**) and *N*-(dimethylamino)-*O*-trimethylsilylimidates (**4a**−**d**) in high yields. The hexacoordination of

---

† Ben Gurion University.

‡ A. E. Favorsky Irkutsk Institute of Chemistry.

§ Universität Würzburg.

(1) For number 4 in the series see: Kalikhman, I.; Gostevskii, B.; Girshberg, O.; Krivonos, S.; Kost, D. *Organometallics* **2002**, *21*, 2551.

(2) For reviews on hypervalent silicon complexes see: (a) Tandura, S. 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. (j) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221.

(3) (a) Ovchinnikov, Yu. E.; Pogozhikh, S. A.; Razumovskaya, I. V.; Shipov, A. G.; Kramarova, E. P.; Bylikin, S. Yu.; Negrebetsky, V. V.; Baukov, Yu. I. *Russ. Chem. Bull.* **1998**, *47*, 967. (b) Kramarova, E. P.; Smirnova, L. S.; Artamkina, A. G.; Shipov, A. G.; Baukov, Yu. I.; Ovchinnikov, Yu. E.; Mozzhukhin, A. O.; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1993**, *63*, 2275. (c) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095. (d) El-Sayed, I.; Hatanaka, Y.; Onozawa, S.-y; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597. (e) Kano, N.; Nakagawa, N.; Kawashima, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3450. (f) Boyer-Elma, K.; Carré, F. H.; Corriu, R. J.-P.; Douglas, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 725. (g) Mucha, F.; Böhme, U.; Roewer, G. *Chem. Commun.* **1998**, 1289. (h) Il Wun Shim; Risen, W. M., Jr. *J. Organomet. Chem.* **1984**, *260*, 171.

(4) (a) Kingston, V.; Gostevskii, B.; Kalikhman, I.; Kost, D. *Chem. Commun.* **2001**, 1272. (b) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

10.1021/om020339p CCC: $22.00

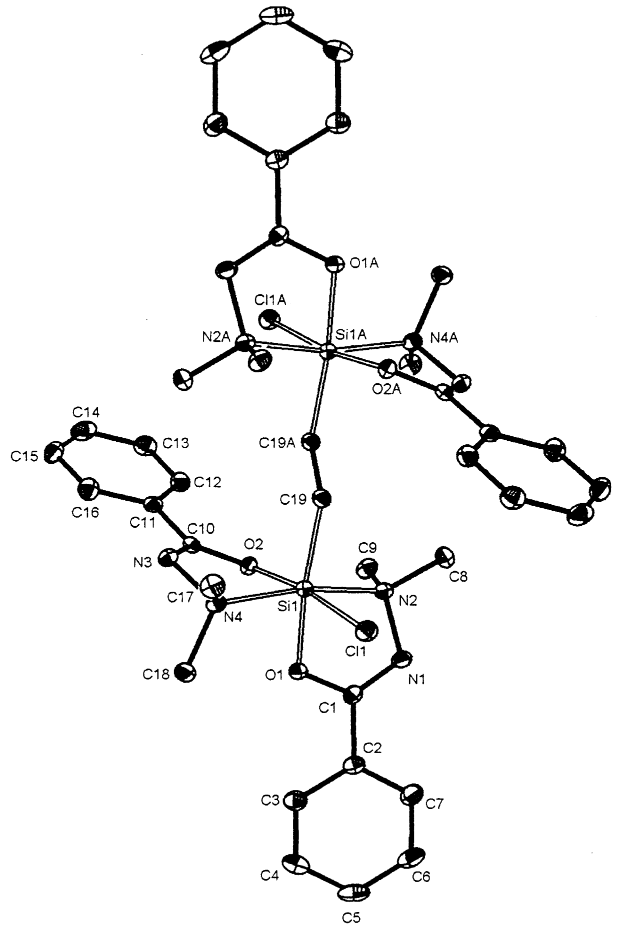
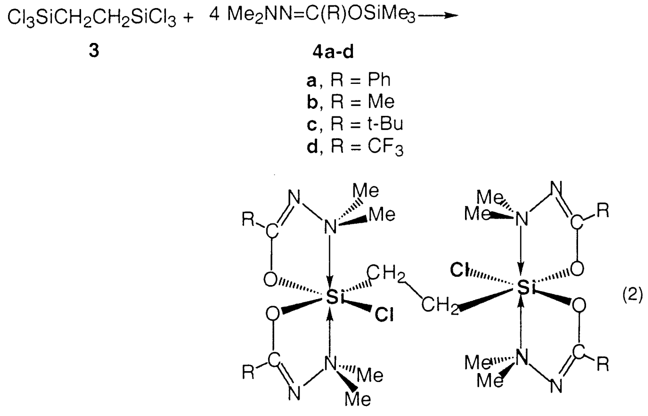


Figure 1. Molecular structure of *meso*-**5a** in the crystal. The thermal ellipsoids (at 50% probability) are small due to the low measurement temperature (Table 4).

these complexes is evident from a crystal structure analysis obtained for **5a** (Figure 1, Table 1), as well as from their ^{29}Si NMR chemical shifts (Table 2), which fall within the typical range of hexacoordinate complexes.[2] This is in contrast to the structure of previously reported isomeric binuclear O→Si chelates **6**, which were formed and observed only as pentacoordinate binuclear disiliconium salts.[5]



$$Cl_3SiCH_2CH_2SiCl_3 + 4\ Me_2NN{=}C(R)OSiMe_3 \longrightarrow$$

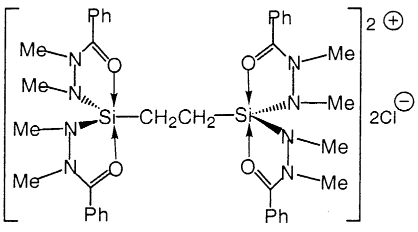
3 **4a-d**

a, R = Ph
b, R = Me
c, R = t-Bu
d, R = CF_3

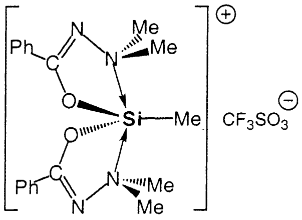
5a-d (2)

The geometrical data for the crystal of **5a** are compared with those obtained previously for the mononuclear analogue **1a** (R = Ph, X = Me)[6] and **1e** (R = Ph, X = CH_2Cl)[7] in Table 1. As expected, in both compound types the basic geometry is a distorted octahedron, with N–Si–N, O–Si–Cl, and O–Si–C angles close to 180°. Further examination of Table 1 shows that, with the exception of the Si–C bonds, all of the bonds to silicon are longer in **5a** than in its mononuclear analogue **1**.

Compounds **5a–c** are quantitatively transformed to ionic compounds through substitution of the chloro ligands by triflate, a better leaving group: *both* chloro ligands are readily replaced at ambient temperature, resulting in the *dicationic* binuclear triflate salts **7a–c** (eq 3). Likewise, the reaction of **5c** with Me_3SiBr or Me_3SiI resulted in the dicationic dibromide (**8c**) and diiodide (**9c**). Single-crystal X-ray analyses for **7a**,**b** (Figure 2, Table 1) confirm the bis-siliconium structure, with two pentacoordinate silicon moieties in each molecule. Both of the crystals have a molecular inversion center and, hence, are the *meso* forms. In solution, for each compound *both* of the diastereomers can be observed in the NMR spectra (Table 2).

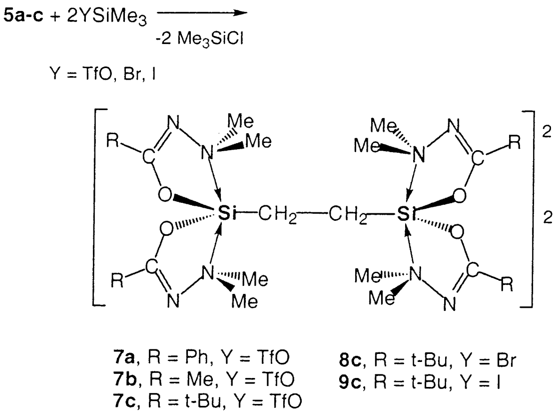


6



10

Interestingly, the geometry around the silicon atoms in both of the binuclear crystals is almost exactly a square pyramid (SP), with nearly equal N–Si–N and O–Si–O angles, in contrast to the mononuclear **10**, in which the angles were N–Si–N ≈ 155°, O–Si–O ≈ 136°, corresponding to 62–69% progress along the TBP → SP coordinate.[4b]



$$\text{5a-c} + 2YSiMe_3 \xrightarrow[-2\ Me_3SiCl]{}$$

Y = TfO, Br, I

(3)

7a, R = Ph, Y = TfO
7b, R = Me, Y = TfO
7c, R = t-Bu, Y = TfO
8c, R = t-Bu, Y = Br
9c, R = t-Bu, Y = I

---

(5) Kalikhman, I.; Krivonos. S.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2001**, *20*, 1053.

Table 1. Comparison of Selected Crystal Data for Mononuclear and Binuclear Hexa- and Pentacoordinate Complexes (bonds in Å, angles in deg)

	neutral, hexacoordinate complexes			ionic, pentacoordinate complexes			
bond or angle	**5a**	**1e**[a]	**1a**[b]	**7a**	**7b**	**6**[c]	**10**[d]
Si1−O1	1.7892(15)	1.7606(11)	1.780(6)	1.7134(19)	1.7070(16)	1.802(2)	1.6844(15)
Si1−O2	1.7768(15)	1.7625(11)	1.771(6)	1.7216(19)	1.7073(16)	1.807(2)	1.6964(14)
Si1−N1	2.0578(17)	2.0463(13)	2.036(6)	1.931(2)	1.931(2)	1.755(3)	1.9665(17)
Si1−N2	2.0441(17)	2.0145(13)	2.015(7)	1.931(2)	1.936(2)	1.770(3)	1.9681(19)
Si1−Cl1	2.2410(7)	2.2140(8)	2.197(4)				
Si1−C	1.925(2)	1.9357(15)	2.089(8)	1.864(3)	1.855(2)	1.878(3)	1.835(2)
N4−Si1−N2	168.20(7)	163.03(5)	170.7(3)	144.14(11)	146.93(10)	127.20(14)	154.78(8)
O1−Si1−O2	87.76(7)		86.7(3)	149.62(10)	146.01(9)	168.80(12)	136.27(8)
O1−Si1−C1	173.70(8)	170.30(6)	172.8(3)	107.13(11)	108.82(9)	113.54(10)	110.16(10)
O2−Si1−Cl1	171.01(5)	174.64(4)	170.2(2)				

[a] From ref 7. [b] From ref 6. [c] From ref 5. [d] From ref 4.

Table 2. ^{29}Si Chemical Shifts for Binuclear Complexes 5a−d ⇄ 11a−d (CD_2Cl_2, 180 and 300 K), Mononuclear 1 (CD_2Cl_2, 300 K), and 7a−c, 8c, 9c (300 K)

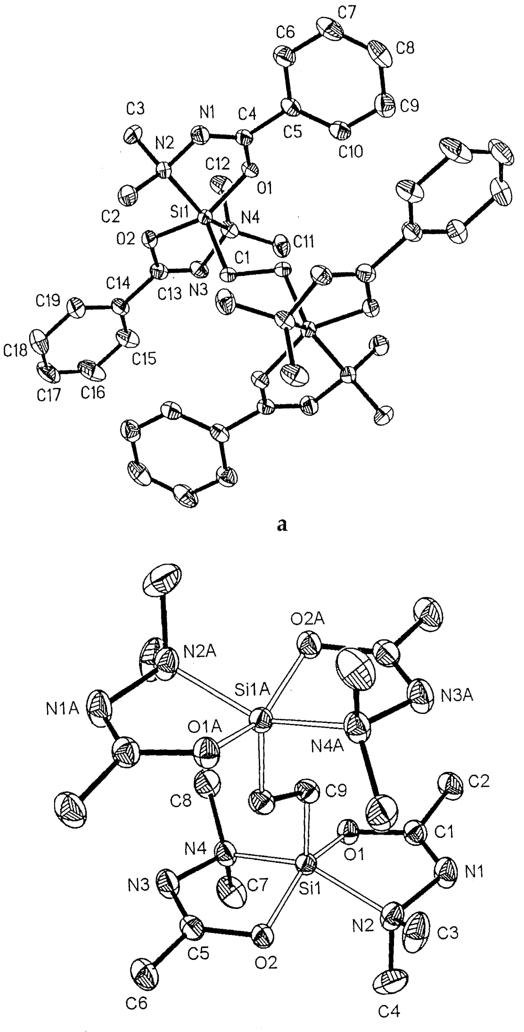
compd index	R	**5a−d ⇄ 11a−d** 300 K	**5a−d ⇄ 11a−d** 180 K	**1a−d**[a] (X = Me)	**7a−c**, (**8c**), [**9c**]
a	Ph	−116.6	−61.8; −130.8	−121.8	−63.3; −63,7[b,c]
b	Me	−110.3	−63.3; −132.3	−121.3	−64.7[d]
c	t-Bu	−103.1; −104.4[b]	−62.6; −131.6	−120.3	−65.0[e] (−66.4; −66.7)[b,c] [−65.0][e]
d	CF_3	−121.7	−123.6	−123.3	

[a] From ref 4. [b] Two diastereomers. [c] $CDCl_3$ solution. [d] CD_3CN solution. [e] CD_2Cl_2 solution.

One may wonder why the two apparently very similar chelate types (**10** and **7**) adopt so different geometries. The reason is probably the steric repulsion in **7** between the two bridged silicon chelates, particularly between the opposing *N*-methyl pairs, which forces the silicon ligands to be as far away from the methylene bridge as possible. The geometry that provides optimum distances is the SP, with methylene at the apex position. This view is supported by the observation that the structure of the oxygen-coordinated analogues **6** is a slightly distorted TBP (Table 1):[5] in the absence of the repulsive *N*-methyl interactions, **6** is free to adopt a TBP geometry, which is avoided in **7**.

As expected, all the bonds to silicon in the dicationic **7a**,**b** are significantly shorter than in the neutral precursor **5a**,**b**. Perhaps more interesting is the comparison of bond lengths in **7a**,**b** with those of the mononuclear siliconium triflate **10**: while the Si−O bonds in **7a**,**b** are longer than in **10**, the Si−N bonds are significantly shorter. This indicates that N→Si coordination in **7** is stronger than in **10** and may explain the more facile ionization of the binuclear complexes **5** relative to **1**. Examination of the geometrical environment about the silicon explains the different effects on O−Si and N−Si bond lengths in **7**: because the ligand arrangement in **7** is SP, while in **10** it is a distorted TBP, the semiaxial N−Si bonds in the latter are longer than in **7**, and the semiequatorial O−Si bonds are shorter.

Ionization in Solution. The ^{29}Si NMR spectra of **5a**−**c** have been measured in CD_2Cl_2 solutions (Table 2). In comparison to the mononuclear analogues (**1**), **5a**−**c** have relatively low-field ^{29}Si chemical shifts. In view of previous results with the mononuclear complexes (**1**),[4] the ambient-temperature low-field shifts indicated that **5a**−**c** might be equilibrium mixtures of neutral and ionic species. Indeed, the ^{29}Si NMR spectra in CD_2Cl_2 solutions of **5a**−**c** were strongly temperature dependent and upon cooling split into two resonances typical of penta- and hexacoordination (Table 2, Figure 3). The spectral features were fully reversible with respect to temperature.



a

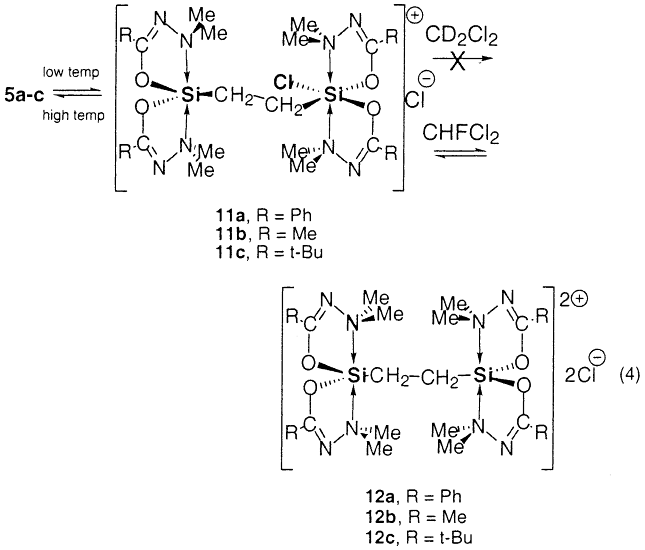
b

Figure 2. X-ray crystal structures of *meso*-**7a** (a) and *meso*-**7b** (b).

The ^{29}Si chemical shift of **5d** in CD_2Cl_2 solution is almost equal to that found in the mononuclear **1a**−**d**, suggesting that no detectable ionization takes place in

5d. This is confirmed by the lack of any significant temperature dependence of the ^{29}Si NMR spectra of **5d** and, hence, the absence of ionization in this complex. This is in accord with the mononuclear analogue **1d**, in which no ionization was observed at any temperature.[4]

Ionization and possible dissociation of **5a**–**c** may proceed stepwise and result either in mixed pentahexacoordinate monocations (**11a**–**c**) or in dications (**12a**–**c**, eq 4). The ^{29}Si NMR spectral changes with temperature provide evidence to answer this question (Figure 3). At temperatures just below room temperature the average signal shifts to low field as the temperature decreases, as a result of ionization, leading to increased population of the ionic form (**11** or **12** or both). However, at lower temperatures (below the coalescence temperature) the two signals for the penta- and hexacoordinate species reach equal intensities, which no longer change upon further cooling. This proves that the ionization produces the monoionic **11a**–**c** and stops at this stage without further ionization to the dicationic **12**.



11a, R = Ph
11b, R = Me
11c, R = t-Bu

12a, R = Ph
12b, R = Me
12c, R = t-Bu

(4)

This observation, that the dichloro chelates **5** ionize at low temperature only to the single-ion stage, while the triflate salts **7** are fully ionized already at room temperature, seems puzzling. This shows that the chloro ligand acts as a poorer leaving group in this system than the triflate group, supporting previous observations in the mononuclear **1**.[4] The ^{29}Si chemical shifts of the chloride (**11a**–**c**) and triflate (**7a**–**c**) salts differ by about 2–2.5 ppm (Table 2), indicating that different silicon species (mono- and dications) are involved.

Apparently, the presence of one positive charge on a silicon atom in **11** is sufficient to avoid formation of a second charge in the molecule, even though the effect must be transmitted through three bonds, a distance generally considered beyond the range of inductive effects. The possibility of a chloride-bridged monocation cannot be completely ruled out; however, only a *non-symmetrical* bridged cation can be considered, with a substantial barrier for exchange between penta- and hexacoordinate silicon atoms, since at low temperatures individual signals for each silicon are observed (Figure 3), at temperatures comparable to those for the ionization of **1**.

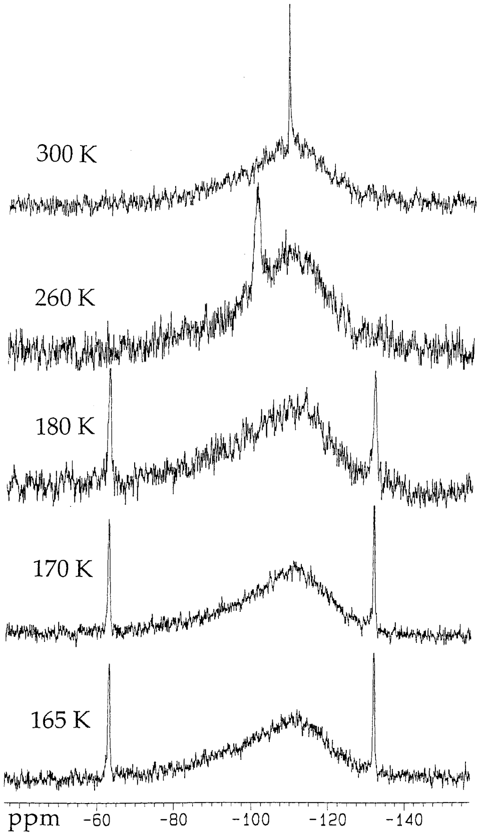


Figure 3. ^{29}Si NMR spectra of **5b** in CD_2Cl_2 solution at various temperatures.

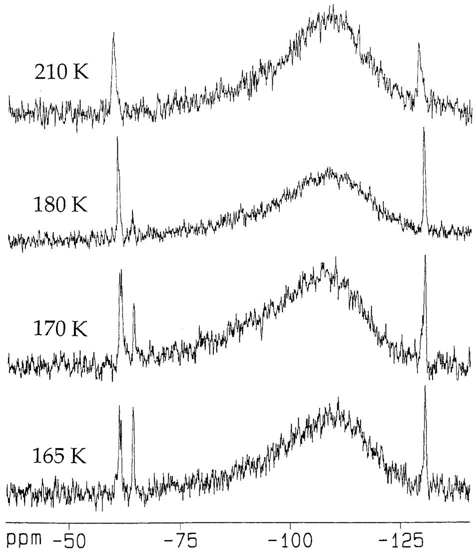


Figure 4. ^{29}Si NMR spectra of **5c** $\rightleftarrows$ **11c**, **12c** in $CHFCl_2$ solution at low temperatures. Second ionization (**11c** → **12c**) is evident from the emergence of a new signal at −64.9 ppm below 180 K. The doubling of signals at −61 ppm appears to be due to the diastereomeric **11c** complexes.

In the mononuclear **1** ionization was strongly dependent upon solvation and was greatly enhanced by hydrogen-bonding solvents.[4] Measurement of the low-temperature ^{29}Si NMR spectra of **5c** in $CHFCl_2$ solution indicated that indeed chloride ionization was enhanced to the extent that now the second ionization step was observed at low temperature, as is evident from the spectra presented in Figure 4: a second ^{29}Si resonance (−64.9 ppm) appears at low temperature, due to forma-

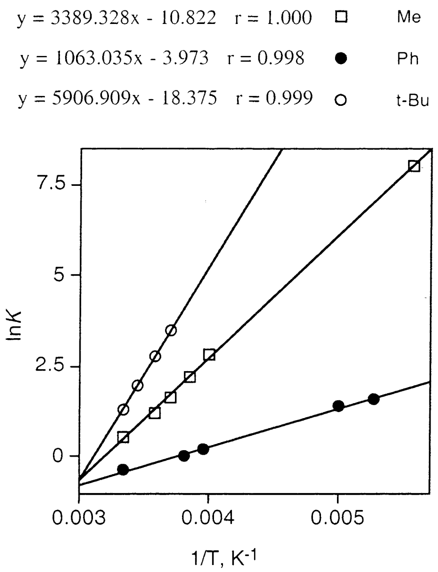


Figure 5. ln *K* vs T^{-1} plots for the equilibrium reactions of **5a**−**c** ⇄ **11a**−**c**.

Table 3. Equilibrium Population Ratios[a] and Reaction Enthalpies and Entropies for 5a−d ⇄ 11a−d in CD_2Cl_2 Solution

reaction	R	K_{eq} 300 K	K_{eq} 250 K	$\Delta H°$,[b] kcal mol^{-1}	$\Delta S°$,[b] cal mol^{-1} K^{-1}	n[c]	r[c]
5a ⇄ **11a**	Ph	0.7	1.2	−2.1	−8	5	0.998
5b ⇄ **11b**	Me	1.8	17.2	−6.7	−22	6	1.000
5c ⇄ **11ac**	t-Bu	3.8	32.3[d]	−11.7	−37	4	0.999

[a] See ref 8. [b] Obtained from the linear correlation ln *K* vs T^{-1}. [c] Number of points used and correlation coefficient. [d] At 270 K.

tion of **12c**, which has the same ^{29}Si chemical shift as the analogous ditriflate salt **7c** (Table 2).

The equilibrium constants at various temperatures and the resulting enthalpies and entropies for the reaction **5a**−**c** ⇄ **11a**−**c** (Figure 5) have been determined and are listed in Table 3.[8] The data in Table 3 confirm previously reported results obtained for **1**, that the thermodynamic parameters are strongly affected by the remote substituent R.[4] In both series (**1** and **5**) the enthalpies and entropies of the ionization process are negative, and their absolute magnitudes increase with increasing electron-releasing power of R. The trends in enthalpies and entropies are similar for both series, although the effects are larger in the binuclear chelates **5**.

Comparison of equilibrium constants for the ionization (Table 3) shows that in **5a**−**c** they are more than an order of magnitude greater than in the monomeric analogues, with the same R groups (**1**, R = Ph, X = $PhCH_2$: $K = 0.04$; R = Me, X = $PhCH_2$: $K = 0.04$).[4] This is evidence for the greater tendency of binuclear complexes to ionize relative to the mononuclear complexes. Since the electronic requirements of the alkyl ligand in both systems are similar, one may conclude that the steric bulk of the binuclear complex is responsible for the greater tendency to ionize. This result, that steric bulk in **5** is responsible for its better ionization relative to **1**, is in agreement with the preceding discussion of the change in molecular geometry in the crystals of **7** and **10**: the steric bulk, which forces an SP geometry for the binuclear silicon environments in **7a**,**b**, is also responsible for the facile ionization of their precursors **5a**,**b**.

This is also in agreement with the previous observation that compounds **2** (X = t-Bu, various R), with the bulky *tert*-butyl group adjacent to silicon, were completely ionic at room temperature.[4] It is concluded that also in that case, in which either steric or electronic factors could have been responsible for the shift of equilibrium, it was the steric factor that predominated.

Experimental Section

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 500.13, 125.76, and 99.36 MHz, respectively, for ^{1}H, ^{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. 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 and was also tested and found invariant up to 40 s relaxation-delay times. The peak-intensity ratios are believed to be accurate within ± 10%. Most of the equilibrium constants were evaluated from weighted-average ^{29}Si chemical shifts *above* the coalescence temperature, and these were tested at a wide range of relaxation delays (3−80 s) and were found to be totally stable and independent of the delay time.

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 on a Bruker Smart Apex CCD diffractometer at low temperature using oil-coated shock-cooled crystals[9] using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS 97.[10] The structures were refined by full-matrix least-squares procedures on F^2, using SHELXL 97.[11] All non hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The denoted *R* values are defined as follows: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\{\sigma^2(F_o^2) + (g_1P)^2 + g_2P\}$; $P = (F_o^2 + 2F_c^2)/3$. Experimental data are presented in Table 4. Other crystallographic data (excluding structure factors) for the crystal structures of **5a**, **7a**, and **7b** can be found in the Supporting Information and have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-183831 (**5a**), CCDC-183832 (**7a**), and CCDC-183833 (**7b**). Copies of the data can be

---

(6) 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.

(7) Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2000**, *19*, 1927.

(8) The equilibrium constant is taken as the population ratio: *K* = [**11**]/[**5**]. This is only valid if ionization proceeds to contact ion pairs that do not significantly dissociate to free ions. This is confirmed by the absence of a noticeable common-ion effect on the population ratio upon addition of up to a 7-fold molar excess of tetrabutylammonium chloride to the methylene chloride solution of **5c**, at temperatures between 170 and 300 K.

(9) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465. (c) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.

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

(11) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.

Table 4. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 5a, 7a, and 7b

	5a	**7a**	**7b**
empirical formula	$C_{42}H_{58}Cl_2N_8O_5Si_2$	$C_{42}H_{50}Cl_6F_6N_8O_{10}S_2Si_2$	$C_{20}H_{40}F_6N_8O_{10}S_2Si_2$
formula mass, g mol^{-1}	882.04	1273.92	786.90
collection T, K	100(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2(1)/c$
a, Å	11.2198 (4)	10.399 (2)	8.5079(8)
b, Å	18.5407 (6)	11.416(2)	13.5290(13)
c, Å	21.2626(7)	12.320(2)	15.8713(15)
α, deg	90	85.318(5)	90
β, deg	100.9370(10)	74.439(5)	92.908(2)
γ, deg	90	87.077(5)	90
V, Å^3	4342.8(3)	1403.6(5)	1824.5(3)
Z	4	1	2
$\rho_{calc,}$ Mg/m^3	1.349	1.510	1.432
F(000)	1872	656	820
θ range, deg	1.95−26.38	1.72−28.32	1.98−27.15
no. of coll reflns	17531	12311	10745
no. of indep reflns	4435	6940	3964
R_{int}	0.0393	0.0413	0.0355
no. of reflns used	4435	6940	3964
no. params	280	343	231
Goof	1.092	0.992	1.086
R1,[a] wR2[b] $[I > 2\sigma(I)]$	0.0460, 0.1056	0.0685, 0.1849	0.0569, 0.1267
R1,[a] wR2[b] (all data)	0.0530, 0.1102	0.0973, 0.2052	0.0715, 0.1344
max./min. res electron dens (e Å^{-3})	0.637/−0.237	0.948/−0.710	0.552/−0.249

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

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].

Determination of Equilibrium Constants, Enthalpies, and Entropies. The equilibrium population ratios for **5a**−**c** $\rightleftarrows$ **11a**−**c** cannot be derived directly from the corresponding signal intensity ratios in the ^{29}Si NMR spectra,[8] as for the reaction **1** $\rightleftarrows$ **2**,[4] because the contribution of the hexacoordinate silicon atom of **11** to the overall intensity of the high-field signal must be considered. Above the coalescence temperature, the observed ^{29}Si NMR chemical shift (δ_{obs}) is the weighted average of the three hexacoordinate silicon shifts (δ_6, two in **5** and one in **11**) and the pentacoordinate shift (δ_5) and is given by eq 5 (this assumes equal shifts for all three hexacoordinate silicons, as has been observed):

$$\delta_{obs} = 1/2[(\delta_5 + \delta_6)x + 2(1 - x)\delta_6] \qquad (5)$$

where x is the mole fraction of **11**. The resulting expression for the equilibrium constant K is given in eq 6:

$$K = x/(1 - x) = \frac{2(\delta_{obs} - \delta_6)}{\delta_5 + \delta_6 - 2\delta_{obs}} \qquad (6)$$

Below the coalescence temperature the observed intensities of the penta- and hexacoordinate resonances (I_5 and I_6, respectively) are related to the equilibrium constant K as follows:

$$K = 2I_5/(I_6 - I_5) \qquad (7)$$

The equilibrium constants for the ionization reaction **5** $\rightleftarrows$ **11** have been determined at several temperatures using eqs 5 and 6 and used further for ln K vs 1/T plots (Figure 5), from which the reaction enthalpies and entropies were evaluated (Table 3).

Syntheses. Bis-1,2-{chlorobis[*N*-(dimethylamino)benzimidato-*N*,*O*]silyl(IV)}ethane (5a). A 0.740 g (3.13 mmol) sample of **4a**[12] was added in one portion to a stirred solution of 0.220 g (0.74 mmol) of **3** in 15 mL of $CHCl_3$. The mixture was stirred at ambient temperature for 1 h. The volatiles were removed under reduced pressure (0.2 mmHg), leaving a white solid, which was recrystallized from hexane to yield 0.561 g (91%) of **5a**, mp 198−199 °C. A single crystal for X-ray analysis was grown from a $CHCl_3$, CH_2Cl_2, ether (25:50:25) solution. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.20 (s, 4H, CH_2), 2.97 (s, 24H, NMe), 7.29−7.79 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 23.76 (CH_2), 51.5 (NMe), 127.4, 128.2, 130.0, 131.5 (Ph) 163.8 (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −117.1. Anal. Calcd for $C_{38}H_{48}Cl_2N_8O_4Si_2$: C, 56.49; H, 5.99; N, 13.87. Found: C, 56.20; H, 6.35; N, 13.51.

Bis-1,2-{chlorobis[*N*-(dimethylamino)acetimidato-*N*,*O*]silyl(IV)}ethane (5b). **5b** was prepared as described for **5a**, from 0.582 g (3.33 mmol) of **4b**[13] and 0.221 g (0.74 mmol) of **3** to yield 0.379 g (91%). Mp: 174−175 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.07 (s, 4H, CH_2), 1.90 (s, 12H, CMe) 2.90 (s, 24H, NMe). ^{13}C NMR ($CDCl_3$, 300 K): δ 17.1 (CMe), 18.6 (CH_2), 50.5 (NMe), 166.5 (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −106.5. Anal. Calcd for $C_{18}H_{40}Cl_2N_8O_4Si_2$: C, 38.63; H, 7.20; N, 20.02; Cl, 12.67. Found: C, 38.83; H, 7.60; N, 19.60; Cl, 13.08.

Bis-1,2-{chlorobis[*N*-(dimethylamino)pivaloimidato-*N*,*O*]silyl(IV)}ethane (5c).[14] **5c** was prepared as described for **5a**, from 0.815 g (3.77 mmol) of **4c**[4] and 0.256 g (0.86 mmol) of **3**, yielding 0.567 g (83%) of **5c**, mp 196−197 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.09 (s, 36H, t-Bu), 1.16 (s, 4H, CH_2), 2.88, 2.92 (2s, 24H, NMe). ^{13}C NMR ($CDCl_3$, 300 K): δ 26.9 (CH_3C), 27.2 (CH_2), 35.3 (CH_3C), 49.8, 49.9, 51.3 (NMe), 174.3 (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −102.4, −100.9. Anal. Calcd for

---

[12] Kalikhman, I. D.; Bannikova, O. B.; Volkova, L. I.; Gostevskii, B. A.; Yushmanova, T. I.; Lopyrev, V. A.; Voronkov, M. G. *Bull. Akad. Nauk SSSR* **1988**, 460; *Chem. Abstr.* **1989**, *110*, 75608c.

[13] Kalinin, A. V.; Apasov, E. T.; Bugaeva, S. V.; Ioffe, S. L.; Tartakovskii, V. A. *Bull. Akad. Nauk SSSR*, **1983**, 1413; *Chem. Abstr.* **1983**, *99*, 175871f.

[14] The ^{1}H, ^{13}C, and ^{29}Si NMR spectra for **5c** feature exchange phenomena, resulting in splitting of the ^{1}H *N*-methyl signals upon cooling initially to two, and at 265 K to four singlets. Similar phenomena are found in the ^{13}C and ^{29}Si NMR spectra. The likely reason for the doubling of spectra is the slowing down of exchange between diastereomers: $\Lambda\Lambda \rightleftarrows \Delta\Lambda$ (and their respective enantiomers). In **5a**,**b** a single species is observed at room temperature and the ^{1}H *N*-methyl signals split upon cooling (265 K) only to two signals. This could be the result either of rapid exchange of diastereomers or of a very large equilibrium population ratio in **5a**,**b**. The presence of diastereomers in **5c** and their absence (or lack of resolution) in **5b** are reflected also in Figures 3 and 4.

$C_{30}H_{64}Cl_2N_8O_4Si_2$: C, 49.50; H, 8.86; N, 15.39. Found: C, 49.38; H, 8.94; N, 15.16.

Bis-1,2-{chlorobis[*N*-(dimethylamino)trifluoroacetimidato-*N,O*]silyl(IV)}ethane (5d). 5d was prepared as described for **5a**, from 0.761 g (3.33 mmol) of **4d**[15] and 0.232 g (0.77 mmol) of **3**. The yield was 0.530 g (88%), mp 164−165 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.33 (s, 4H, CH_2), 2.99 (s, 24H, NMe). ^{13}C NMR (CD_2Cl_2, 300 K): δ 25.9 (CH_2), 51.6 (NMe), 117.5 (q, $^1J_{CF} = 277$ Hz, CF_3), 156.4 (q, $^2J_{CF} = 38$ Hz, C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −121.7. Anal. Calcd for $C_{18}H_{28}Cl_2F_{12}N_8O_4Si_2$: C, 27.88; H, 3.64; N, 14.45. Found: C, 27.18; H, 3.46; N, 14.52.

Bis-1,2-{bis[*N*-(dimethylamino)benzimidato-*N,O*]siliconium}ethane ditriflate (7a). To a stirred solution of **5a** (0.673 g, 0.83 mmol) in 10 mL of $CHCl_3$ was added 0.552 g (2.48 mmol) of *O*-trimethylsilyl triflate. After 15 min at ambient temperature the mixture was concentrated under reduced pressure, followed by crystallization from hexane, yielding 0.78 g, 90% of **7a**. Mp: 230 °C (dec). A single crystal for X-ray analysis was grown from CH_3CN. ^{1}H NMR ($CDCl_3$, 300 K): for two diastereomers (4:1) δ 0.68−1.40 (m, 4H, CH_2), 3.00, 3.19 (major) 3.02, 3.60 (minor) (4s, 24H, NMe), 7.26−7.77 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 0.9 (major), 1.8 (minor) (CH_2), 49.3, 49.4 (major) 49.1, 49.7 (minor) (NMe), 120.6 (q, $^1J_{CF} = 320.2$ Hz, CF_3), 124.9−133.6 (Ph), 165.2 (major), 164.9 (minor) (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −63.3 (major), −63,7 (minor). Anal. Calcd for **7a**·$2CHCl_3$ $C_{42}H_{50}Cl_6F_6N_8O_{10}S_2Si_2$: C, 39.60; H, 3.96; N, 8.80. Found: C, 40.02; H, 3.70; N, 9.21.

Bis-1,2-{bis[*N*-(dimethylamino)acetimidato-*N,O*]siliconium}ethane ditriflate (7b). 7b was prepared as described for **7a** from 0.231 g (0.41 mmol) of **5b** and 0.352 g (1.57 mmol) of *O*-trimethylsilyl triflate to yield 0.294 g (90%) of **7b**. Recrystallization from a $CHCl_3/CH_3CN$ mixture afforded a single crystal for X-ray analysis. Mp: 195−197 °C (dec). ^{1}H NMR (CD_3CN, 300 K): 0.7−1.3 (m, 4H, CH_2), 2.09 (s, 12H, CMe), 2.89, 2.96 (2s, 24H, NMe). ^{13}C NMR (CD_3CN, 300 K): δ 1.2 (CH_2), 16.4 (CMe), 48.2, 49.4 (NMe), 120.6 (q, $^1J_{CF} = 320.2$ Hz, CF_3), 168.7 (C=N). ^{29}Si NMR (CD_3CN, 300 K): δ −64.7. Anal. Calcd for $C_{20}H_{40}F_6N_8O_{10}S_2Si_2$: C, 30.53; H, 5.12; N, 14.24. Found: C, 30.48; H, 5.29; N, 14.12.

Bis-1,2-{bis[*N*-(dimethylamino)pivaloimidato-*N,O*]siliconium}ethane ditriflate (7c). 7c was prepared directly in the NMR sample tube from **5c** and *O*-trimethylsilyl triflate in CD_2Cl_2 solution and was identified by spectral analogy with **7a**,**b**. ^{1}H NMR (CD_2Cl_2, 300 K): for two diastereomers (10:9) δ 0.68−1.40 (m, 4H, CH_2), 1.24 (s, 36H, t-Bu), 2.93, 3.09 (major) 2.94, 3.08 (minor) (4s, 24H, NMe). ^{13}C NMR (CD_2Cl_2, 300 K): δ 2.0 (major) 2.3 (minor) (CH_2), 26.2 (major) 26.1(minor) (C*C*H3), 35.6 (*C*CH_3), 48.7, 49.8 (major) 48.5, 49.8 (minor) (NMe), 120.6 (q, $^1J_{CF} = 320.2$ Hz, CF_3), 175.8 (major), 175.6 (minor) (C=N). ^{29}Si NMR (CD_2Cl_2, 300 K): δ −65.0.

Bis-1,2-{bis[*N*-(dimethylamino)pivaloimidato-*N,O*]siliconium}ethane dibromide (8c). 5c was obtained as described above from 0.824 g (3.81 mmol) of **4c** and 0.268 g (0.90 mmol) of **3** and was used further without isolation after removal of volatiles. A 5 mL portion of $CHCl_3$ was added followed by addition of 0.363 g (2.36 mmol) of Me_3SiBr. The mixture was allowed to react with stirring at ambient temperature for 1 h, after which the volatiles were removed under vacuum (0.2 mmHg). The resulting white solid was washed by hexane and then dried under vacuum to yield 0.722 g (92%) of **8c**, mp 183−185 °C. ^{1}H NMR ($CDCl_3$, 300 K): for two diastereomers (3:1) δ 0.68−1.40 (m, 4H, CH_2), 1.20 (major) 1.17 (minor) (2s, 36H, t-Bu), 2.92, 3.21 (major) 2.98, 3.13 (minor) (4s, 24H, NMe). ^{13}C NMR ($CDCl_3$, 300 K): δ 2.0 (CH_2), 26.8 (major) 26.7 (minor) (C*C*H3), 35.7 (*C*CH_3), 50.2, 50.3 (major) 49.6, 50.7 (minor) (NMe), 175.5 (major), 175.2 (minor) (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −66.4, −66,7. Anal. Calcd for $C_{30}H_{64}Br_2N_8O_4Si_2$: C, 44.11; H, 7.90; N, 13.72. Found: C, 43.86 H, 8.23; N, 12.76.

Bis-1,2-{bis[*N*-(dimethylamino)pivaloimidato-*N,O*]siliconium}ethane diiodide (9c). 9c was prepared as described for **8c** from 0.829 g (3.83 mmol) of **4c**, 0.270 g (0.91 mmol) of **3**, and 0.383 g (1.91 mmol) of Me_3SiI. The yield was 0.813 g (98%), mp 181−183 °C. ^{1}H NMR (CD_2Cl_2, 300 K): for two diastereomers (1:1.1 ratio) δ 0.68−1.50 (m, 4H, CH_2), 1.26 (s, 36H, t-Bu), 2.99, 3.20 (major) 3.00, 3.19 (minor) (4s, 24H, NMe). ^{13}C NMR (CD_2Cl_2, 300 K): δ 1.9 (major), 1.5 (minor) (CH_2), 26.6 (major) 26.5 (minor) (C*C*H_3), 35.7 (*C*CH_3), 50.4, 50.6 (major) 49.8, 50.9 (minor) (NMe), 175.6 (major), 175.4 (minor) (C=N). ^{29}Si NMR (CD_2Cl_2, 300 K): δ −65.0. Anal. Calcd for $C_{30}H_{64}N_8O_4I_2Si_2$: C, 39.56; H, 7.08; N, 12.30. Found: C, 38.98; H, 7.18; N, 12.30.

Acknowledgment. Financial support from the German Israeli Foundation for Scientific Research and Development (GIF), grant I-628-58.5/1999, and from the Russian Foundation for Basic Research (RFBR), grant number 01-03-33034, is gratefully acknowledged.

Supporting Information Available: Tables with X-ray crystal data for **5a**, **7a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020339P

---

[15] Kalikhman, I. D.; Medvedeva, E. N.; Bannikova, O. B.; Fabina, N. G.; Larin, M. F.; Lopyrev, V. A.; Voronkov, M. G. *Zh. Obshch. Khim.* **1984**, *54*, 477; *Chem. Abstr.* **1984**, *101*, 55158s.