

Donor-Stabilized Silyl Cations. 11. Bis-Zwitterionic Penta- and Hexacoordinate Silicon Dichelate Complexes Derived from $(\text{ClCH}_2)_2\text{SiCl}_2$ through Double Internal Displacement of Chloride¹

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The reaction of $(\text{ClCH}_2)_2\text{SiCl}_2$ (**4**) with *O*-Me₃Si-hydrazides (**3**) yields three new types of products: a 1:2 reagent ratio leads to a neutral hexacoordinate dichelate with two six-membered rings each containing an N⁺–N[−] ylide structure, as well as to the corresponding dissociated pentacoordinate dichelate siliconium chloride salt. These products readily undergo partial hydrolysis to form a dinuclear complex: dicationic disiloxane dichloride. All three product types have been characterized by means of single-crystal structure analysis. Nonempirical ab initio calculations were carried out to determine the atomic charges. Natural bond order (NBO) calculations show that there are no significant charge accumulations on either the ammonium or the imidate nitrogen in the ylide moieties and that the net charge on silicon (which could formally be −2) is between +1.8 and +2.1 e in all species, regardless of overall molecular charge.

Introduction

Chloromethyl(dimethyl)chlorosilane ($\text{ClCH}_2\text{SiMe}_2\text{Cl}$, **1**) is known to react in a peculiar manner with *N*-(trimethylsilyl)-amides (**2**, eq 1)² and *O*-(trimethylsilyl)hydrazides (**3**, eq 2),³ forming initially chloromethyl–silicon complexes, which subsequently undergo internal nitrogen alkylation and formation of five- and/or six-membered chelate rings. An apparently fundamental difference exists between the reactions of Me₃Si–derivatives of amides and hydrazides: in silylated hydrazides, the N-alkylation reaction leads to a zwitterionic complex, with a formal positive charge on the tetracoordinate nitrogen and a formal negative charge on the silicon atom.^{3,4} In contrast, the

amide derivatives lead to neutral (O,C)-chelates.² The reaction of bis(chloromethyl)dichlorosilane [$(\text{ClCH}_2)_2\text{SiCl}_2$, **4**] with *N*-Me₃Si-amides has recently been studied and found to produce pentacoordinate siliconium dichelate salts (**5**),⁵ which readily hydrolyze to the corresponding pentacoordinate disiloxane dication salts (**6**)⁶ (eq 3). The ionic **5** could also be converted to a neutral hexacoordinate complex (**7**), by replacement of chloro with fluoro ligands.⁷

In view of the different behavior of Me₃Si-amides and -hydrazides (**2** and **3**, respectively), it was of interest to investigate the transsilylation and subsequent reactions of **4** with *O*-Me₃Si-hydrazides, to find out whether *two* steps of internal displacement and ring formation might take place in the same molecule, leading formally to a *double* negative charge on silicon.

Results

Bis(chloromethyl)dichlorosilane (**4**) was prepared as described previously⁸ and was distilled and collected at 72–75 °C at 30 mmHg. **4** reacts with *O*-Me₃Si-*N,N*-(dimethyl)trifluoroacetylhydrazide (**3a**) in acetonitrile, forming the hexacoordinate dichelate **8a**, as shown in eq 4. **8a** has a characteristically hexacoordinate

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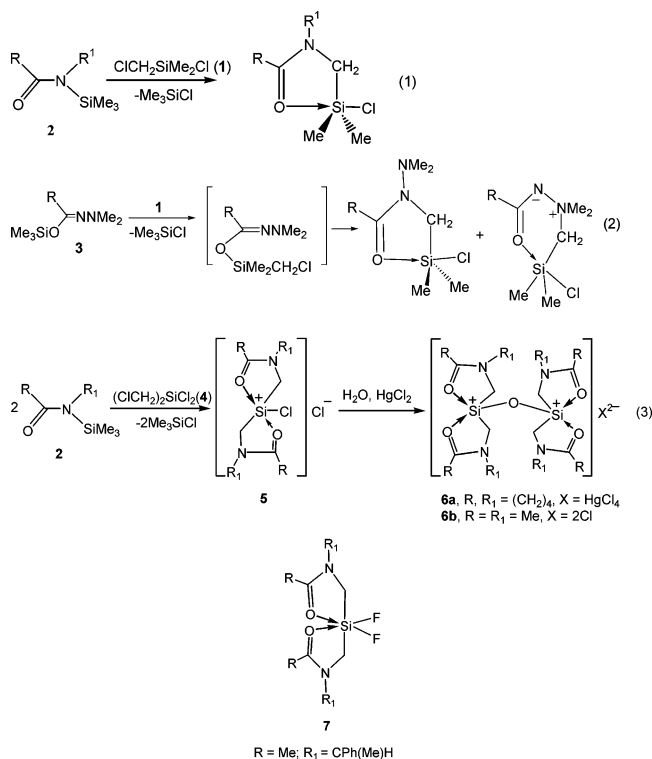
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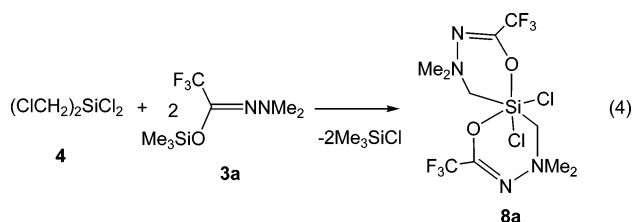
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^{29}Si chemical shift (-166.5 ppm in CDCl_3 solution and -164.9 ppm in CD_3CN solution) and is hence exclusively or predominantly hexacoordinate in these solutions.



A single crystal of **8a** was grown from an acetonitrile solution and was subjected to an X-ray crystallographic analysis. The resulting molecular structure is depicted in Figure 1. Selected bond lengths and angles are listed in Table 1. **8a** adopts an almost exact octahedral geometry: it is a neutral hexacoordinate silicon complex, with the unique feature of two formally zwitterionic six-membered chelate rings.

The same reaction with the silylated hydrazide **3b** did not produce the hexacoordinate **8b** analogous to **8a**, but led to a different product type, the pentacoordinate chlorosiliconium chloride **9b** (eq 5). This is evident from the ^{29}Si chemical shift in CD_3CN solution, -93.4 ppm, characteristic of pentacoordination, and is further supported by a single-crystal X-ray analysis (Figure 2, Table 1).

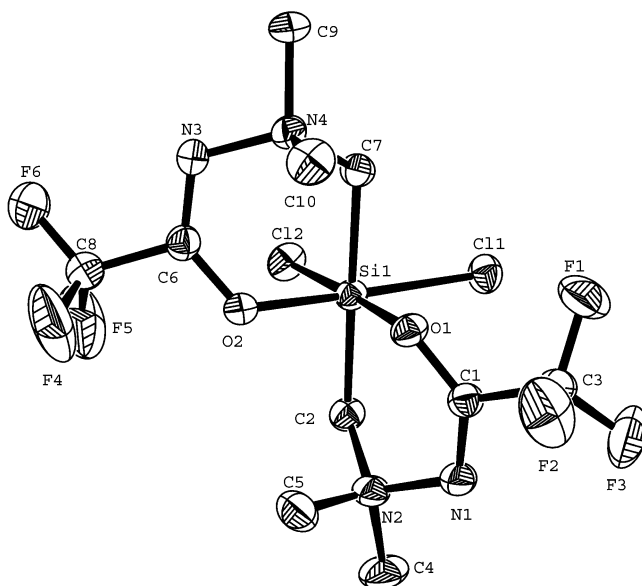
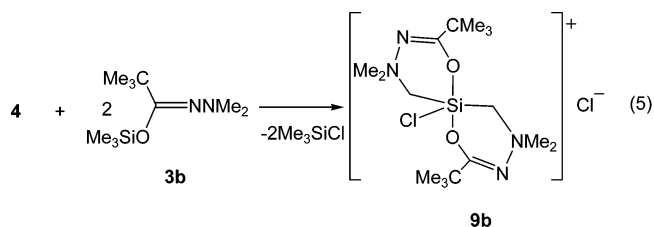


Figure 1. Molecular structure of **8a** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Compounds **8a**, **9a**, and **9b**^a

	8a	9a	9b	5	12
Bond Lengths					
Si—Cl	2.301(1)	2.059(1)	2.106(2)	2.074(1)	2.235(1)
	2.254(1)			4.091(1)	2.259(1)
Si—O	1.839(2)	1.832(1)	1.798(1)	1.847(2)	1.755(2)
	1.838(2)	1.832(1)	1.798(1)	1.847(2)	1.773(2)
Si—C	1.930(3)	1.882(2)	1.893(2)	1.874(3)	1.911(1)
	1.926(3)	1.882(2)	1.893(2)	1.874(3)	
C—O	1.294(3)	1.296(2)	1.311(3)	1.292(2)	1.321(3)
	1.287(3)			1.298(2)	
C=N	1.278(4)	1.281(2)	1.297(3)	1.281(2)	1.285(3)
	1.285(4)			1.275(2)	
Bond Angles					
C—Si—C	177.6(1)	119.59(10)	150.09(16)	128.1(1)	
O—Si—Cl	177.27(8)	90.96(4)	97.37(7)	92.71	170.22(6)
O—Si—Cl	90.70(7)	90.96(4)	97.37(7)		178.88(6)
O—Si—Cl	177.53(8)				
O—Si—Cl	89.25(7)				
C—Si—Cl	91.8(1)	120.21(5)	104.96(8)	116.0(1)	86.76(9)
C—Si—Cl	86.4(1)	120.21(5)	104.96(8)		
C—Si—Cl	86.6(1)				
C—Si—Cl	91.9(1)				
O—Si—O	89.1(1)	178.1(1)	165.3(1)	174.6(1)	91.22(8)
O—Si—C	89.1(1)	86.72(6)	85.39(8)		
O—Si—C	91.5(1)	92.31(6)	90.81(8)		
O—Si—C	90.7(1)				
O—Si—C	90.3(1)				

^a Analogous amide-derived **5**⁵ and hexacoordinate mono-ylide **12**¹¹ are shown for comparison.

The different structures of **8a** and **9b** are in agreement with previous experience⁹ that hexacoordinate silicon complexes tend to ionize to pentacoordinate siliconium-halide salts, as long as the substituents are not strongly electron-withdrawing. However, hexacoordinate complexes with two chloro ligands (**10**) resisted ionization,⁹ while **9b**, in which CH_2 groups have been inserted between nitrogen and silicon, is predominantly pentacoordinate and ionic.

Since the *tert*-butyl-substituted **3b** gave an ionic product (**9b**) upon reaction with **4**, and with CF_3 substitution the analogous

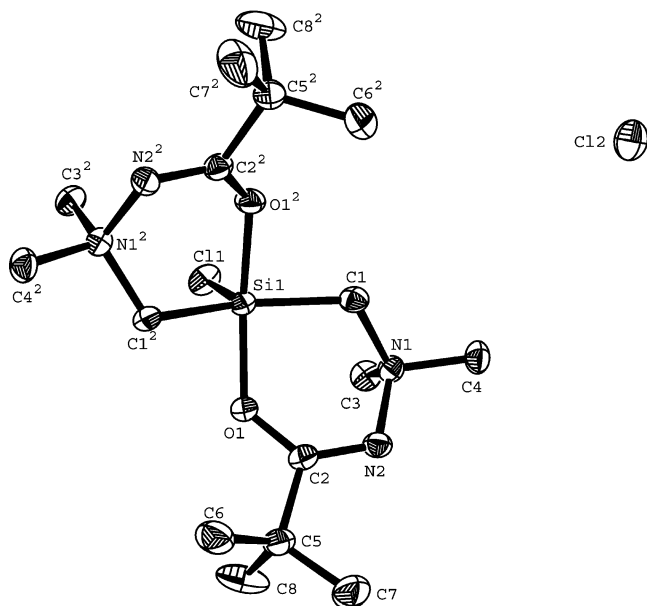


Figure 2. Molecular structure of **9b** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

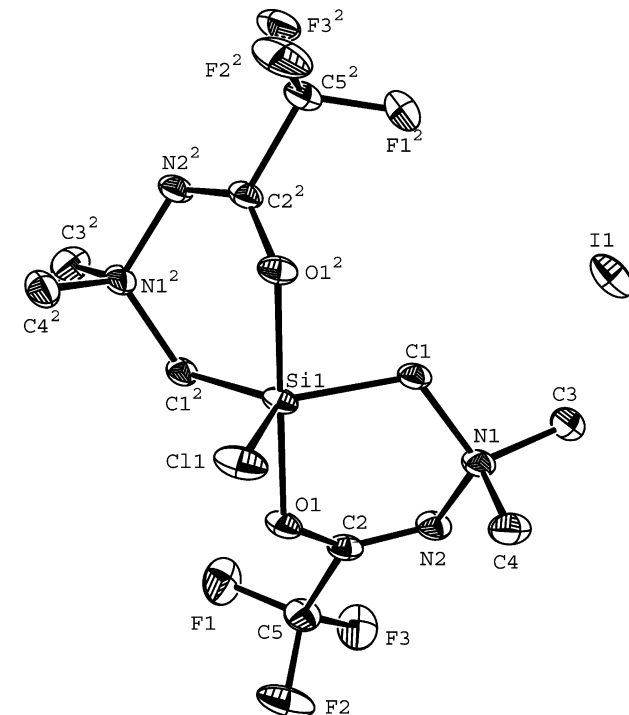
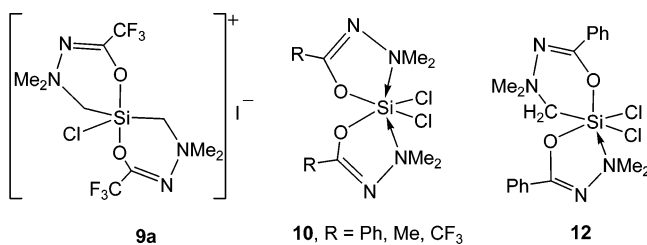


Figure 3. Molecular structure of **9a** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

reaction gave the *neutral* hexacoordinate **8a**, an attempt was made to ionize the latter in analogy with **9b**. This was achieved by replacement of the chloride counterion by iodide, using $\text{Me}_3\text{-SiI}$. The resulting **9a** is indeed a pentacoordinate chlorosiliconium iodide, as evident from its ^{29}Si chemical shift in solution (-87.3 ppm in CD_3CN) and its crystal structure (Figure 3, Table 1).

8 and **9** are extremely sensitive to moisture and upon minimal exposure to air are partly hydrolyzed and converted to the disiloxane dication dichloride salts, **11a,b**.

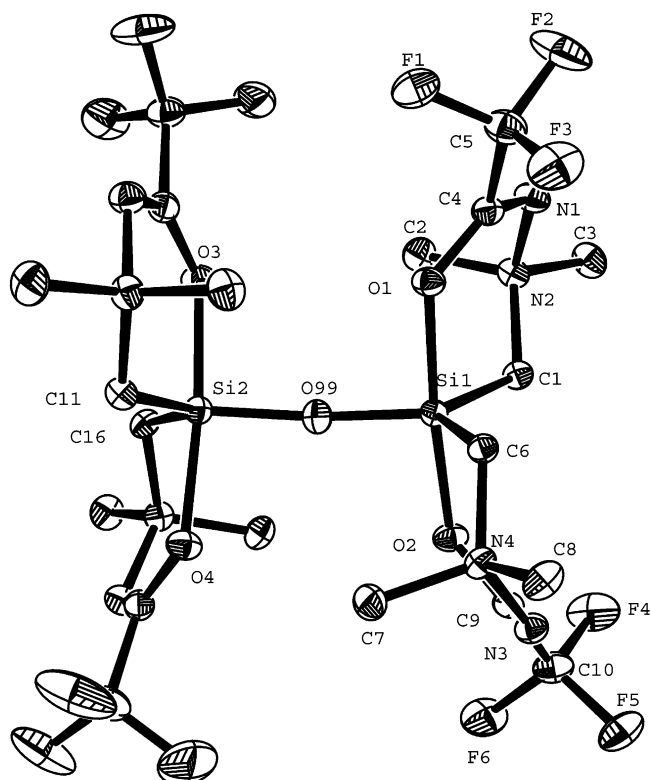
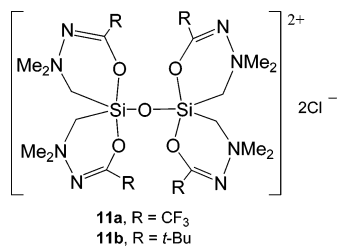


Figure 4. Molecular structure of **11a** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and chloride anions, as well as two acetonitrile molecules, are omitted for clarity.

The X-ray structural analysis of **11a**, depicted in Figure 4, features two trigonal bipyramidal pentacoordinate silicon centers, connected by an oxygen bridge in the equatorial positions of both centers, and with chelate-oxygen atoms in axial positions. **11b**, which is also formed spontaneously, was not isolated and was identified by its analogous and characteristic NMR spectra (see Experimental Section).

Discussion

The new dichelate complexes that have been synthesized from **4** are unique, having two six-membered zwitterionic chelate

rings. Each complex has two (and the disiloxane four) quaternary nitrogen atoms, which are formally positively charged.

It is interesting, and perhaps symbolic of hypercoordinate silicon chemistry, that all three product types—neutral hexacoordinate **8a**, ionic pentacoordinate **9a**, and the derived disiloxane

11a—have been isolated and characterized from the same starting materials, **4** and **3a**. Previously studied silicon dichelates (for example, **10**) do not ionize as long as *both* monodentate X-ligands are halogens or the chelate-ring substituent R is the electron-withdrawing CF₃ group.^{9,10} However, in the present case of **8a**, which includes *both* structural features (electron-withdrawing CF₃ substituent as well as two chloro ligands), ionization to **9a** could be realized simply by replacement of one of the chloro ligands by the better leaving group iodide. One wonders why, despite the heavily electron-withdrawing substitution, **8a** is capable of ionization. This is probably due to the different ligand frameworks in the two complex types: SiN₂O₂X₂ in **10**, and SiC₂O₂X₂ in **9a**. The more electronegative atoms attached to silicon in **10** reduce its electron density and prevent the release of an anion, which would increase even more the positive charge on silicon. Since in **8a** the ligand atoms are less electronegative, this effect is reduced, to the extent that ionization can be achieved with a powerful (and bulky) leaving group as iodide, even in the presence of the highly electronegative substituents.

It is even more surprising that **8a** not only ionizes to **9a**, but is so sensitive to hydrolysis and tends to form the dicationic disiloxane **11a**. The facile formation of **11a**, while suggesting greater stability of the siliconium relative to the hexacoordinate complexes, surely also reflects the greater stability of the two new Si—O bonds relative to the hydrolyzed Si—Cl bonds, even at the expense of decreased motional degrees of freedom in **11**.

Disiloxane Complexes. The ease with which **11a,b** are formed parallels the facile formation of similar disiloxanes (**6a,b**) reported previously from amide-derived silicon dichelates.⁶ The two classes of dinuclear complexes differ in their chelate ring sizes, as well as in their formal charge distributions. As a result some notable experimental differences are observed: (1) The ²⁹Si NMR resonances for the hydrazide-derived **11a,b** (from -101 to -107 ppm, see Experimental Section) are shifted approximately 40 ppm upfield relative to those of the amide analogues **6** (-62 to -70 ppm),⁶ despite the equal ligand environment, SiC₂O₃, shared by both series. (2) The Si—O bonds are on average all shorter in **11a** relative to the amide analogues **6a,b** (Table 2): three groups of Si—O bonds are found in both series, two relatively short chelate bonds (~1.81 Å in **11a**, 1.83–5 Å in **6**), two long Si—O bonds (~1.85–6 Å in **11a**, 1.86–9 Å in **6**), and the bridging Si—O bond (~1.61 Å in **11a**, ~1.63 Å in **6**). In each of these groups the Si—O bonds are longer in **6** than in **11a**. (3) A remarkable difference in the Si—O—Si bond angles is found: in the hydrazide the angle is ca. 23° greater than in the amide-derived compounds.

The first of these differences, the upfield shift of the ²⁹Si resonance, was discussed previously and appears to be general.¹¹ For each six-membered chelate ring an upfield shift of approximately 20 ppm was observed, relative to similarly substituted complexes with five-membered chelate rings (**12**¹¹ in comparison with analogous **10**¹²). This was reported for mono-, di-, and trichelates, regardless of the formal charges on silicon, and the present case is in full agreement with these observations: a 40 ppm upfield shift corresponding to two six-membered chelate rings in **8a**.¹¹

Table 2. Comparison of Crystallographic Bond Lengths (Å) and Angles (deg) in Disiloxane Dication Complexes Derived from Hydrazide (11a**) and Amides (**6a,b**)⁶**

	11a	6a	6b
Bond Lengths			
Si—O	1.818(1)	1.885(6)	1.850(5)
	1.852(1)	1.849(6)	1.864(5)
	1.815(1)	1.870(6)	1.832(4)
	1.855(1)	1.842(6)	1.883(5)
Si—C	1.880(2)	1.865(8)	1.870(7)
	1.887(2)	1.887(9)	1.873(7)
	1.882(2)	1.878(9)	1.883(6)
	1.886(2)	1.879(9)	1.895(7)
Si—O' ^a	1.609(1)	1.625(6)	1.634(5)
	1.613(1)	1.628(6)	1.634(5)
C—O	1.292(2)	1.286(10)	1.296(9)
	1.298(2)	1.300(10)	1.301(8)
	1.290(2)		
C=N	1.292(2)		
	1.281(2)	1.301(11)	1.313(9)
	1.275(2)	1.307(12)	1.314(9)
	1.279(2)		
	1.282(2)		
Bond Angles			
O'—Si—O ^a	92.20(5)	93.2(3)	93.1(2)
	92.71(5)	93.6(3)	94.1(2)
	93.39(6)		
	92.49(5)		
O1—Si—O2	175.05(5)	172.3(3)	174.1(2)
	174.12(6)	172.2(3)	
O'—Si—C ^a	119.55(6)	115.6(4)	117.8(3)
	120.42(6)	120.2(4)	122.6(3)
	118.43(6)		
	115.32(6)		
Si1—O'—Si2 ^a	167.22(8)	144.8(4)	144.4(3)

^a O' refers to the central oxygen atom.

The second listed difference, that the Si—O distances are shorter in the hydrazide-based complexes, may provide an explanation for the large difference in ²⁹Si chemical shifts: the shorter Si—O distances in **11a** indicate that coordination is stronger in these chelates relative to that in **6**, resulting in further upfield shifts of their ²⁹Si resonances relative to the amide analogues.^{1c}

The remarkable difference in the central Si—O—Si bond angles between the two series suggests that in **11a**, in which the chelate rings are six-membered, steric congestion is substantial, causing further spread of the two chelate units from each other by an increase of the central angle.

Computational Chemistry. The most intriguing question in connection with the new silicon complexes is the nature of bonding and the related charge density distribution.¹³ Thus, formally the two ammonium nitrogen atoms in **8a** bear two positive charges, and the silicon is left (formally) with two negative charges. This excess negative charge on silicon is released by the dissociation of an anion (chloride, or iodide in **9a**), but even a single negative charge seems unlikely on the generally electropositive silicon atom.¹³ Alternatively, the pair of adjacent nitrogen atoms in each chelate ring forms an independent ylide structure, with a positive charge on the quaternary ammonium nitrogen and a negative charge on the imidate nitrogen. This option is supported by the fact that many stable similar "imineimide" ylide structures, without silicon, have been reported.¹⁴ If this is the case, the silicon atom is positively charged in the pentacoordinate **9** and **11**. To answer

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Table 3. Calculated Selected Optimized Bond Lengths (Å) and Angles (deg) for **8a,b** and **9a,b** (B3LYP/6-31G(d)), ^{29}Si Chemical Shifts at B3LYP/6-311G(3d)//B3LYP/6-31G(d), and Experimental Data^a

	8a	9a	8b	9b
Bond Lengths				
Si1–Cl32	2.240	2.082	2.284	2.098
Si1–O8	1.916	1.834	1.888	1.821
Si1–C26	1.955	1.927	1.948	1.924
C7–O9	1.289	1.307	1.306	1.322
C7=N5	1.294	1.289	1.303	1.300
N3–N5	1.468	1.473	1.473	1.478
Bond Angles				
C26–Si1–C29	177.60	136.73	178.98	136.84
O9–Si1–Cl33	90.15	95.11	90.31	94.57
O9–Si1–Cl32	174.31		176.00	
C29–Si1–Cl33	93.49	111.64	92.36	111.58
C29–Si1–Cl32	88.13		86.93	
O8–Si1–O9	84.47	169.78	86.59	170.86
$\delta(^{29}\text{Si})$, ppm calcd ^b	–165.4	–86.6		–93.1
exptl (CD ₃ CN)	–164.9	–87.3		–93.4

^a Atom numbering is shown in Figure 5. All calculated models have C_2 symmetry. ^b GIAO NMR calculation for **8b** failed to converge.

these questions, ab initio nonempirical quantum chemical calculations were conducted on the relevant molecules, **8a**, **9a** (excluding the counterion), **9b**, and the hypothetical (unattainable) **8b**, the hexacoordinate analogue of **8a** with a *tert*-butyl ring substituent.

The four molecular structures were fully optimized with respect to minimum energy, at the density functional theory (DFT) level, using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP),^{15,16} and employing the 6-31G(d) basis set, within the GAUSSIAN 03w program system.¹⁷ All optimized structures reached ground-state potential energy minima, verified by calculation of vibrational harmonic frequencies. Final energies and NBO charges were also calculated at the second-order perturbation MP2/6-31G(d) level.¹⁸ Selected calculated bond lengths and angles are listed in Table 3, and they agree quite well with the geometries obtained from crystallographic analysis (**8a**, **9a**, and **9b**). All four calculated molecules adopt C_2 symmetry, the hexacoordinate complexes (**8a**, **8b**) being essentially octahedral with carbon atoms *trans* and oxygen and chloro ligand pairs in *cis* positions, while pentacoordinate **9a** and **9b** have the oxygen atoms *trans*-diaxial and carbon and chloro ligands in equatorial positions. These calculated ligand arrangements are in accord with the crystallographically determined molecular geometries of **8a**, **9a**, and **9b**. NMR chemical shifts (relative to TMS) were calculated using the GIAO method and employing a larger basis set, B3LYP/6-311G(3d), at the geometries optimized at B3LYP/6-31G(d). The resulting ^{29}Si shifts for **8a**, **9a**, and **9b**, which are listed in Table 3, are in

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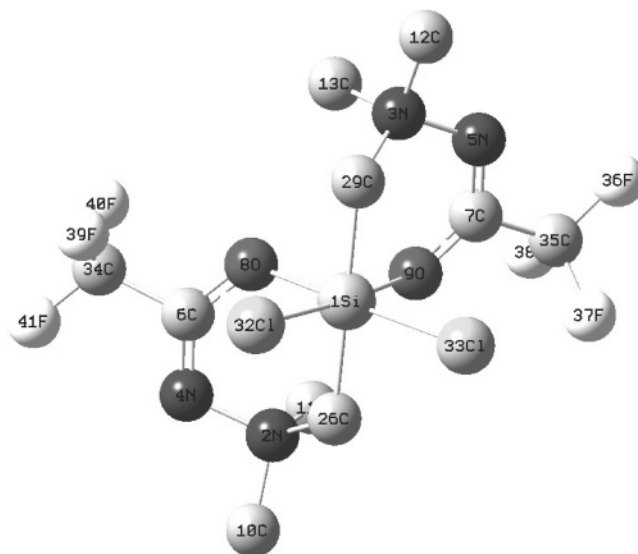


Figure 5. Atom-numbering system used for calculations (Tables 2 and 4). **8a** is shown, but numbers are the same for the *tert*-butyl carbons in **8b** and **9b**.

excellent agreement with experiment. Atomic charges were evaluated by calculation of natural bond orders (NBO)¹⁹ and are listed in Table 4.

Examination of Table 4 reveals some striking figures that are common to all four molecules, at both levels of theory: (a) the quaternary ammonium nitrogen atom, which has a formal positive charge, is actually *negatively* charged in all four molecules, including the cations of **9a,b**. The NBO atomic charge of that nitrogen atom is -0.20 ± 0.1 e, in each of the molecules. (b) The charges on the adjacent imidate nitrogen atoms are also negative, as expected, but the NBO atomic charge is only twice as large as that on the “ammonium” nitrogen, at -0.45 ± 0.03 e. (c) No negative charge is found on silicon, in any of the molecules, in agreement with the experimental charge density determination of difluorobis[*N*-(dimethylamino)phenylacetimidato-*N,O*]silicon.¹³ In fact, the NBO charges on silicon, in all four species, are very close to +2 electronic charges, with negligible variation from neutral (**8**) to ionic (**9**) species.

We first address the problem of the charges on the ammonium nitrogens. The formal positive charge on nitrogen is more than neutralized by the electron release from eight neighboring hydrogen atoms in geminal positions relative to N. This is evident from examination of the NBO charges on these hydrogen atoms, which are all within the range 0.2–0.3 e. Summation of the positive charges on the hydrogen atoms leads to well over a unit positive charge and accounts for the absence of the expected positive charge on the ammonium nitrogen. To demonstrate that the absence of positive charge on the ammonium nitrogen is not a unique and peculiar property of the silicon compounds at hand, we have calculated for comparison the trimethylammonium ion, Me_3NH^+ , at the B3LYP/6-31G(d) level. The resulting NBO charge on the nitrogen atom is -0.502 e, while the charge on each of the nine methyl hydrogens is $+0.250 \pm 0.005$, and that on the amino-hydrogen atom is $+0.475$ units. This clearly shows that ammonium nitrogen atoms in general are stabilized by charge distribution to the hydrogen atoms on adjacent carbon atoms, and the ammonium nitrogen atoms in the present compounds **8** and **9** are no exception.

The formal double negative charge on silicon, implied by the silicate structure **8a** with six covalent bonds (eq 6), is

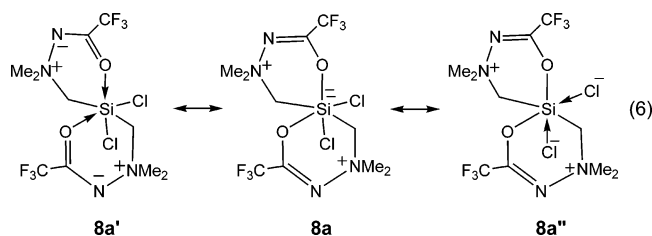
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Table 4. Calculated NBO Atomic Charges for **8a**, **8b**, **9a** and **9b** at MP2/and B3LYP/6-31G(d) Levels, Geometries Optimized at B3LYP/6-31G(d)^a

atom	8a		9a		8b		9b	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
Si1	1.991	1.803	2.111	1.933	2.039	1.849	2.145	1.960
Cl32	-0.551	-0.506	-0.414	-0.370	-0.580	-0.533	-0.442	-0.395
C26	-0.749	-0.767	-0.764	-0.783	-0.751	-0.770	-0.763	-0.782
H27	0.257	0.268	0.264	0.276	0.256	0.269	0.274	0.269
H28	0.251	0.263	0.282	0.294	0.242	0.255	0.256	0.287
N2	-0.194	-0.140	-0.201	-0.146	-0.193	-0.138	-0.200	-0.144
C10	-0.390	-0.452	-0.393	-0.456	-0.389	-0.451	-0.391	-0.454
H14	0.228	0.242	0.258	0.270	0.223	0.237	0.253	0.266
H15	0.252	0.264	0.236	0.250	0.250	0.262	0.229	0.244
H16	0.229	0.252	0.259	0.271	0.234	0.247	0.254	0.267
C11	-0.403	-0.464	-0.406	-0.468	-0.401	-0.463	-0.404	-0.466
H17	0.231	0.245	0.262	0.253	0.221	0.237	0.231	0.246
H18	0.234	0.247	0.239	0.273	0.229	0.242	0.256	0.268
H19	0.265	0.273	0.241	0.255	0.263	0.272	0.238	0.252
N4	-0.464	-0.398	-0.422	-0.359	-0.514	-0.439	-0.482	-0.409
C6	0.675	0.535	0.664	0.532	0.811	0.665	0.805	0.664
C34	1.251	1.092	1.259	1.099	-0.108	-0.104	-0.116	-0.110
O8	-0.907	-0.798	-0.936	-0.828	-0.942	-0.834	-0.967	-0.857
X39 ^b	-0.402	-0.346	-0.394	-0.337	-0.631	-0.671	-0.634	-0.671
X40 ^b	-0.419	-0.364	-0.402	-0.345	-0.631	-0.668	-0.632	-0.668
X41 ^b	-0.401	-0.347	-0.389	-0.334	-0.627	-0.663	-0.635	-0.675
H(t-Bu)					0.22–0.25	0.23–0.25	0.22–0.24	0.23–0.25

^a Atom labels are as shown in Figure 5. ^b X represents F for **8a** and **9a**, and C for **8b** and **9b**.

effectively distributed to the adjacent oxygen atoms, as well as to the nitrogen atoms adjacent to the ammonium nitrogens (Table 4). This indicates that **8a** has at least a substantial contribution of **8a'**, the diylide structure, in which silicon is formally neutral.



The average charge on silicon resulting from admixture of the three canonical forms **8a**, **8a'**, and **8a''** should still be negative. The calculated positive charge on silicon is further accounted for by the significant partial negative charges on the adjacent oxygen, carbon, and chlorine atoms directly connected to it. The substantial negative charges on the chloro ligands are borne out also by the calculated (Table 3) and experimental (Table 1) exceptionally long Si–Cl bonds, suggesting coordination between chloride anions and silicon, as shown in **8a''**.

The remarkably small difference in charges on the silicon atom in neutral **8a** and ionic **9a** (very near +2 in both cases) indicates a very efficient charge distribution mechanism. The only substantial change in atomic charge is found on the chloro atom, which loses, upon ionization (**8a** → **9a**), 25–40% of its negative charge (depending on the method of calculation). On all other atoms the changes in atomic charges associated with ionization are much smaller, and thus the extra positive charge in **9a** is fairly evenly dispersed over the entire molecule.

In conclusion, calculation of NBO atomic charges further substantiates the findings of experimental charge density investigations,¹³ that charges accumulate on atoms primarily due to atomic electronegativities and only marginally due to formal charges implied by Lewis type formulas. Neither the ylide structure nor the positive ionic charge on silicon in **9a** is actually found in the calculated charges. The adjacent positive and

negative charges in the N–N ylide moiety are essentially dispersed over neighboring hydrogen atoms and the N–C=O group, respectively, in both **8a** and **9a**; likewise, the extra positive charge on silicon, which should be expected in **9a** relative to **11a**, is completely dispersed over neighboring atoms, so that the actual calculated charge difference on silicon amounts to only 0.1–0.2 e.

Experimental Section

The reactions were carried out under dry argon using Schlenk techniques. Solvents were 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 ¹H, ¹³C, and ²⁹Si spectra. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent–proton (or carbon) signals for ¹H and ¹³C and directly from TMS for ²⁹Si. Melting points were measured in sealed capillaries using a Büchi melting point instrument and are uncorrected. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Single-crystal X-ray diffraction measurements were performed on a Nonius Kappa-CCD diffractometer (**8a**, **9b**), on a Bruker Smart 1000 CCD diffractometer (**9a**), and on a Bruker Smart Apex D8-goniometer (**11a**). The data were collected from oil-coated shock-cooled crystals. The diffractometers are equipped with a low-temperature device using graphite-monochromated Mo Kα radiation, λ = 71.073 pm.²⁰ The data were integrated with SAINT,²¹ and an empirical absorption correction (SADABS) was applied.²² The structures were solved by direct methods (SHELXS-97)²³ and refined by full-matrix least-squares methods against F² (SHELXL-97).²⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp² carbon atoms were assigned ideal positions and refined using a riding model

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Table 5. Crystal Data and Experimental Parameters for the Structure Analyses of **8a**, **9a**, **9b**, and **11a**

	8a	9a	9b	11a
CCDC number	612079	612080	612081	612078
Empirical formula	C ₁₀ H ₁₆ Cl ₂ F ₆ N ₄ O ₂ Si	C ₁₀ H ₁₆ ClF ₆ IN ₄ O ₂ Si	C ₁₆ H ₃₄ Cl ₂ N ₄ O ₂ Si	C ₂₄ H ₃₈ Cl ₂ F ₁₂ N ₁₀ O ₅ Si ₂
form mass, g mol ⁻¹	437.26	528.71	413.46	901.72
collection T, K	240(1)	120(2)	240(1)	100(2)
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>Ab</i> a2	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	10.251(2)	10.059(2)	8.994(2)	10.438(1)
<i>b</i> , Å	11.918(2)	10.375(2)	21.354(4)	18.379(1)
<i>c</i> , Å	16.501(3)	18.348(3)	11.089(4)	20.784(1)
α, deg	90	90	90	90
β, deg	117.47(3)	101.543(5)	90	95.229(1)
γ, deg	90	90	90	90
<i>V</i> , Å ³	1788.7(6)	1876.1(6)	2130(1)	3970.5(4)
<i>Z</i>	4	4	4	4
ρ _{calc} , Mg/m ³	1.624	1.872	1.289	1.508
<i>F</i> (000)	888	1032	888	1848
θ range, deg	2.20–25.36	2.27–30.00	2.96–25.36	1.48–25.50
no. of coll reflns	11 376	7791	3389	39 662
no. of indep reflns	3257	2710	1765	7388
<i>R</i> _{int}	0.0510	0.0195	0.0222	0.0207
no. of reflns used	3257	2710	1765	7388
no. of params	226	117	115	506
goodness-of-fit	1.048	1.056	0.782	1.056
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0463 0.1093	0.0234 0.0596	0.0311 0.0897	0.0317 0.0841
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0743 0.1195	0.0252 0.0604	0.0380 0.0964	0.0344 0.0861
max./min. res electron dens, e Å ⁻³	0.588/−0.492	1.152/−0.903	0.190/−0.308	0.708/−0.521

with *U*_{iso} constrained to 1.2 times the *U*_{eq} value of the parent atom. Experimental details are listed in Table 5, and full data tables are included in the Supporting Information. Crystallographic data for **8a**, **9a**, **9b**, and **11a** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 5. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

Bis(*N,N*-dimethyl-*N*-trifluoroacetimidatoammoniomethyl-*C*-*O*)dichlorosilicon(IV) (8a**).** To 1.222 g (5.35 mmol) of *O*-(trimethylsilyl)-1,1-dimethyl-2-trifluoroacetylhydrazine (**3a**)²⁵ were added by vacuum condensation 5 mL of THF and 0.524 g (2.66 mmol) of (ClCH₂)₂SiCl₂ (**4**). The mixture was allowed to warm to room temperature and was stirred for 4 h, followed by 1 h at 80 °C. The volatiles were removed under reduced pressure (0.05 mmHg), leaving a white solid residue, which was recrystallized from 5 mL of CH₃CN. Pure crystals of **8a** (0.399 g, 34%) were obtained, mp 186 °C. ¹H NMR (CD₃CN, 295 K): δ 3.17, 3.44 (ABq, ²*J*_{AB} = 13.3 Hz, 4H, CH₂), 3.30, 3.31 (2s, 12H, NMe). ¹³C NMR (CD₃CN, 295 K): δ 55.7, 62.4 (NMe), 71.8 (CH₂), 117.1 (q, ¹*J*_{CF} = 376.6 Hz, CF₃), 159.2 (q, ²*J*_{CF} = 37.3 Hz, N=CCF₃). ²⁹Si NMR (CD₃CN, 295 K): δ −164.9. Anal. Calcd for C₁₀H₁₆Cl₂F₆N₄O₂Si: C, 27.47; H, 3.69; N, 12.81. Found: C, 27.52; H, 3.80; N, 12.95.

Bis(*N,N*-dimethyl-*N*-trifluoroacetimidatoammoniomethyl-*C*-*O*)chlorosiliconium Iodide (9a**).** To a CH₃CN solution (20 mL) of crude **8a**, prepared as described above from 1.101 g (4.32 mmol) of **3a** and 0.473 g (2.40 mmol) of **4**, was added 0.984 g (4.92 mmol) of trimethyliodosilane. The mixture was heated for 1 h in an oil bath at 110 °C. After several days at room temperature **9a** crystallized out. The liquid was decanted off, leaving (after vacuum-drying) pure **9a**, 0.329 g (26%), mp 201–202 °C. ¹H NMR (CD₃CN, 295 K): δ 3.41 (br s, 12H, NMe), 3.77 (br s, 4H, CH₂). ¹³C NMR (CD₃CN, 295 K): δ 59.6 (CH₂), 56.2 (NMe), 117.8 (q, ¹*J*_{CF} = 389 Hz, CF₃), 156.4 (q, ²*J*_{CF} = 37.4 Hz, N=CCF₃). ²⁹Si NMR (CD₃CN, 295 K): δ −87.3. Anal. Calcd for C₁₀H₁₆ClF₆IN₄O₂Si: C, 22.72; H, 3.05; N, 10.60. Found: C, 22.81; H, 3.10; N, 10.48.

Bis(*N,N*-dimethyl-*N*-pivaloimidatoammoniomethyl-*C*-*O*)chlorosiliconium Chloride (9b**).** **9b** was prepared as described for **8a**,

from 1.103 g (5.10 mmol) of **3b**⁹ and 0.507 g (2.57 mmol) of **4**. Crystalline **9b** (0.719 g, 68%) was obtained, mp 229–231 °C. ¹H NMR (CD₃CN, 300 K): δ 1.25 (s, 18H, *t*-Bu), 3.40 (br s, 12H, NMe), 3.54 (br s, 4H, CH₂). ¹³C NMR (CD₃CN, 300 K): δ 27.9 (C(CH₃)₃), 39.3 (C(CH₃)₃), 56.2 (CH₂), 59.0 (NCH₃), 177.1 (C=N). ²⁹Si NMR (CD₃CN, 300 K): δ −93.4. Anal. Calcd for C₁₆H₃₄Cl₂N₄O₂Si: C, 46.48; H, 8.29; N, 13.55. Found: C, 46.40; H, 8.18; N, 13.57.

Di(bis(*N,N*-dimethyl-*N*-trifluoroacetimidatoammoniomethyl-*C*-*O*)disiloxanedications Dichloride (11a**).** To a 25 mL dry, round-bottom flask were added by vacuum condensation at liquid N₂ temperature 1.141 g (5.00 mmol) of **3a**, 5 mL of chloroform, and 0.414 g (2.10 mmol) of **4**. The mixture was allowed to warm to ambient temperature, and 10 min after thawing a precipitate separated. The product was recrystallized from a CHCl₃–CH₃CN mixture, to yield 0.990 g (48%) of **11a**, mp 157–159 °C. **11a** is composed of two nearly equally populated diastereomers, observed in the NMR spectra. ¹H NMR (CD₃CN, 295 K): δ 3.39, 3.43, 3.51, 3.62 (4s, 24H, NMe), 3.64, 3.86 (ABq, ²*J*_{HaHb} = 16.4 Hz, 8H, CH₂). ¹³C NMR (CD₃CN, 295 K): δ 55.0, 55.3, 55.6, 55.7 (NMe), 62.9, 63.1 (CH₂), 117.1 (q, ¹*J*_{CF} = 377 Hz, CF₃), 156.7 (q, ²*J*_{CF} = 37 Hz, N=CCF₃). ²⁹Si NMR (CD₃CN, 295 K): δ −104.8, −105.9. Anal. Calcd for C₂₀H₃₂Cl₂F₁₂N₈O₅Si₂: C, 29.20; H, 3.90; N, 13.65. Found: C, 28.80; H, 3.83; N, 13.67.

Di(bis(*N,N*-dimethyl-*N*-pivaloimidatoammoniomethyl-*C*-*O*)disiloxanedications Dichloride (11b**).** **11b** was obtained from **9b** in the NMR tube by dissolution in semidry DMSO-*d*₆ and was not isolated. It is composed of two nearly equally populated diastereomers, observed in the NMR spectra. ¹H NMR (CD₃CN + DMSO-*d*₆, 295 K): δ 1.59, 1.60 (s, 36H, *t*-Bu), 3.72, 3.74, 3.75, 3.81 (4s, 24H, NMe), 3.27, 3.40 (ABq, ²*J*_{HaHb} = 15 Hz, 8H, CH₂). ¹³C NMR (CD₃CN + DMSO-*d*₆, 295 K): δ 27.0, 27.2 (C(CH₃)₃), 38.0, 38.1 (C(CH₃)₃), 55.5, 55.7 (CH₂), 53.6, 53.8, 61.0, 61.4 (NMe), 175.8, 176.1 (N=C). ²⁹Si NMR (CD₃CN + DMSO-*d*₆, 295 K): δ −101.7, −106.6.

Acknowledgment. This work was supported by the Israel Science Foundation, grant ISF-139/05; by INTAS, project 03-51-4164; and by the Deutsche Forschungsgemeinschaft, Priority Program 1178.

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Supporting Information Available: Crystal data tables for **8a**, **9a**, **9b**, and **11a**, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters in WORD and cif-

file formats are available free of charge via the Internet at <http://pubs.acs.org>.
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