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Hypercoordinate Silicon Complexes Based on Hydrazide Ligands. A Remarkably Flexible Molecular System

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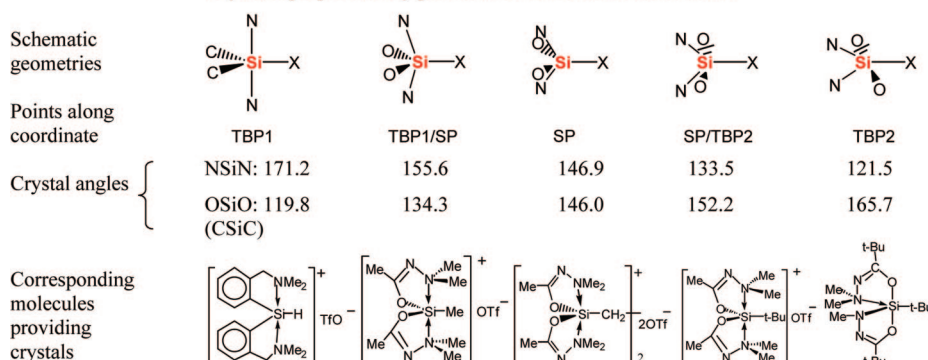# Hypercoordinate Silicon Complexes Based on Hydrazide Ligands. A Remarkably Flexible Molecular System

DANIEL KOST* AND INNA KALIKHMAN

Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva 84105, Israel

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CONSPECTUS

Crystallographic Berry pseudorotation reaction coordinate:

	TBP1	TBP1/SP	SP	SP/TBP2	TBP2
Points along coordinate					
NSiN:	171.2	155.6	146.9	133.5	121.5
OSiO: (CSiC)	119.8	134.3	146.0	152.2	165.7

Though only one row apart on the periodic table, silicon greatly differs from carbon in its ability to readily form five- and six-coordinate complexes, termed "hypercoordinate silicon compounds". The assorted chemistry of these compounds is varied in both structures and reactivity and has generated a flurry of innovative research endeavors in recent years. This Account summarizes the latest work done on a specific class of hypercoordinate silicon compounds, specifically those with two hydrazide-derived chelate rings. This family is especially interesting due to the ability to form multiple penta- and hexacoordinate complexes, the chemical reactivity of pentacoordinate complexes, and the observation of intermolecular ligand crossovers in hexacoordinate complexes.

Pentacoordinate complexes in this family exhibit marked structural flexibility, as demonstrated by the construction of a complete hypothetical Berry-pseudorotation reaction coordinate generated from individual crystallographic molecular structures. Although hexacoordinate complexes generally crystallize as octahedra, with a decrease in the ligand donor strength the complexes can crystallize as bicapped tetrahedra. Hexacoordinate complexes bearing a halogen ligand undergo a solvent-driven equilibrium ionic dissociation, which is controlled by solvent, temperature, counterion, and chelate structure and has been directly demonstrated by conductivity measurements and temperature-dependent ^{29}Si NMR. Hexacoordinate silicon complexes can also undergo reversible neutral nonionic dissociation of the N–Si dative bond.

Ionic pentacoordinate siliconium salts react readily via methyl halide elimination, initiated by their own counterion acting as a base. Pentacoordinate complexes can also undergo intramolecular aldol condensations of imines, which may find potential as a template for organic synthesis. In addition, these complexes are capable of performing an uncatalyzed intramolecular hydrosilylation of imine double bonds.

Perhaps the most striking manifestations of flexibility are the facile and complete intermolecular ligand crossovers. Crossovers have been observed between different hexacoordinate complexes, and between complex molecules and their differently substituted precursors, and take place within minutes. Although the precise mechanisms of these transformations remain elusive, NMR and single-crystal X-ray diffraction measurements have shed light on these interesting phenomena.

A profusion of crystallographic data and careful NMR experimentation has led to an improved understanding of penta- and hexacoordinate hydrazide-based silicon dichelates. The diverse chemical reactivity of these complexes demonstrates both the scope and complexity of silicon chemistry. Future exploration into the structures and chemistry of hypercoordinate silicon will continue to enhance our understanding and appreciation of this unique element.

1. Introduction

Despite expected similarities, carbon and silicon differ substantially by the ease with which carbon, but not silicon, forms low-coordination compounds and, conversely, the ease with which silicon extends its coordination number to 5 and 6. The latter group, referred to as "hypercoordinate silicon compounds", has attracted considerable attention in the last 20−30 years.[1] One particular member of this group is the family of five- and six-coordinated silicon dichelates, based on hydrazide-derived ligands, which are the subject of this Account. The interest in these compounds results from their remarkable flexibility in terms of molecular structure, as well as diverse reactivity. The present Account aims to demonstrate the unique geometrical and reactivity diversity that is characteristic of penta- and hexacoordinate hydrazide-based silicon dichelates.

2. Synthesis by Transsilylation

Hypercoordinate compounds described herein were synthesized using a simple ligand-exchange reaction between two tetracoordinate silicon compounds,[2] a trimethylsilylated hydrazide derivative (**1**) and a polyhalosilane (**2**) (eq 1). The resulting trimethylchlorosilane (**3**) is boiled off in vacuo, leaving essentially pure mono- (**4**) or dichelate (**5**), depending on initial stoichiometry. When a tri- or tetrahalosilane is used (e.g., Y = Cl or X = Y = Cl), the reaction leads directly to the dichelate **5**. R and X can generally be any alkyl, aryl, or halogen residue.
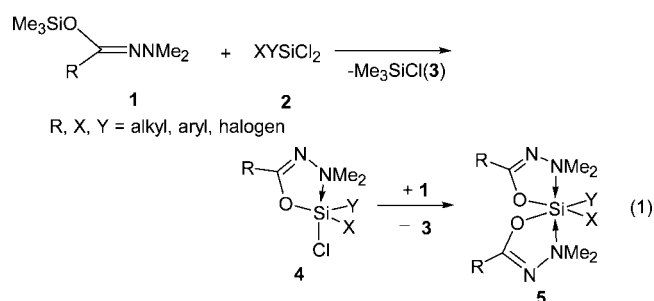
Using **6**, the imino variant of **1**, in this procedure leads to dichelates **7** with the alkylideneimino donor group (eq 2).[3] As will be discussed below, most compounds **7** (when X = alkyl, aryl) ionize to pentacoordinate siliconium chlorides (**7′**) in chloroform solution.

The products **4**, **5**, and **7** are initially characterized by their highly informative ^{29}Si NMR spectra, having essentially separate regions for each coordination number (4, 5, and 6),[1f] followed, whenever possible, by crystal structure analyses.
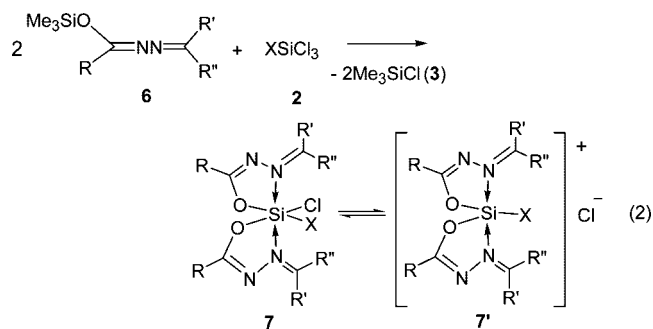
Oxygen−silicon coordination, rather than N→Si, is achieved by two methods shown in eqs 3 and 4. Equation 3 illustrates a transsilylation reaction followed by internal displacement of chloride by the NMe$_2$ group, leading to ring expansion and O→Si coordination:[4]
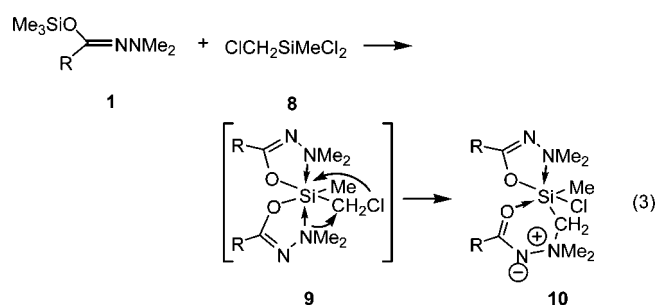
In eq 4 the N-, rather than O-silylated hydrazide (**11**) is used by blocking the imidate (enol) form with an *N*-methyl group, resulting in O→Si coordination.[5] The product **12** is an ionic pentacoordinate siliconium chloride.[6]

X = Me, Ph, CH$_2$Cl, CH$_2$Ph
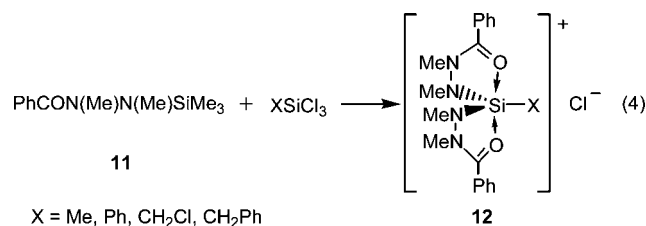
3. Structure

3.1. Hexacoordinate Complexes. Hexacoordinate dichelates **5** generally have distorted octahedral geometries in the solid state. Numerous crystal structures have been reported for **5**: R,X,Y = CF$_3$,Cl,cycloxhexyl;[7a] NMe$_2$,Ph,Ph;[8] *t*-Bu,H,Cl;[9] *t*-Bu,H,Br;[9] CF$_3$,F,F;[10] CF$_3$,H,Cl;[10] CF$_3$,Ph,F;[10] CF$_3$,Ph,Cl;[11] CF$_3$,Cl,Cl;[11] Ph,Me,Cl;[12] Ph,CH$_2$Cl,Cl;[13] Ph,F,F;[3b] Ph,Br,Br;[3a] CF$_3$,Ph,OTf;[14] Ph,OTf,OTf.[14] They all have the N−Si−N *trans* arrangement in the crystal, despite the availability, in principle, of six different diastereomers (five in the case X = Y).[15] This is true as long as at least one of the monodentate ligands (X, Y) is a halogen and changes dramatically when two carbon ligands (X = Y = Ph) are present, as shown below.
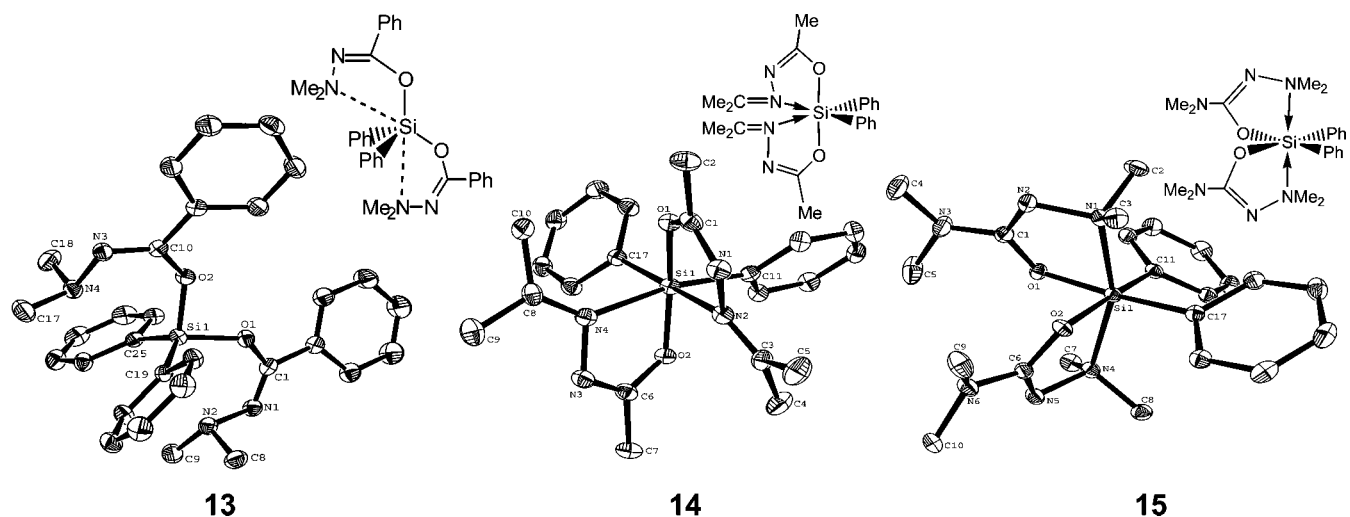
FIGURE 1. Molecular structures of **13**, **14**, and **15** in the crystals.[8]

3.2. Geometrical Modification in the Solid State.

The geometry of **13**, a hexacoordinate complex with two phenyl groups as monodentate ligands, is not the usual octahedron but a bicapped tetrahedron (Figure 1).[8] Modification of the ligand donor group from NMe_2 to the slightly stronger donor $N=CMe_2$ (**14**), results in reversal of the geometry back to essentially octahedral. Likewise, replacement of the remote chelate-substituent R from the electron-withdrawing phenyl groups to the electron-releasing NMe_2 groups (**15**), retaining the original O,O,Ph,Ph,NMe_2,NMe_2 environment about silicon, reversed the geometry back to distorted octahedral (Figure 1). These geometrical changes were attributed to the silicon rehybridization energy, required for its promotion from tetrahedral to octahedral geometry: the energy gained by the formation of two dative $N{\rightarrow}Si$ bonds in **13** is insufficient to provide the necessary rehybridization energy, and consequently silicon retains its ground, tetrahedral configuration, with the two nitrogen ligands directing their electron lone pairs toward silicon from a larger distance (2.724 and 2.868 Å in **13** as opposed to 2.138 and 2.123 Å in **14** and 2.075 and 2.098 Å in **15**).[8] By increasing the donor strength in **14** and **15** (in the latter R = NMe_2 releases electrons through the double bond making the donor NMe_2 group a stronger donor), the energy provided by the two dative bonds becomes sufficient to promote silicon to its octahedral state.

The complex geometry is uniquely determined in the solid state as either octahedral or tetrahedral. However, in solution the two molecular geometries coexist in equilibrium, which was monitored by ^{29}Si and ^1H NMR spectroscopy as a function of temperature (Figure 2).[8] The NMR evidence clearly shows that at ambient temperature in CD_2Cl_2 solution **13** is tetrahedral, while at lower temperatures the resonance for the
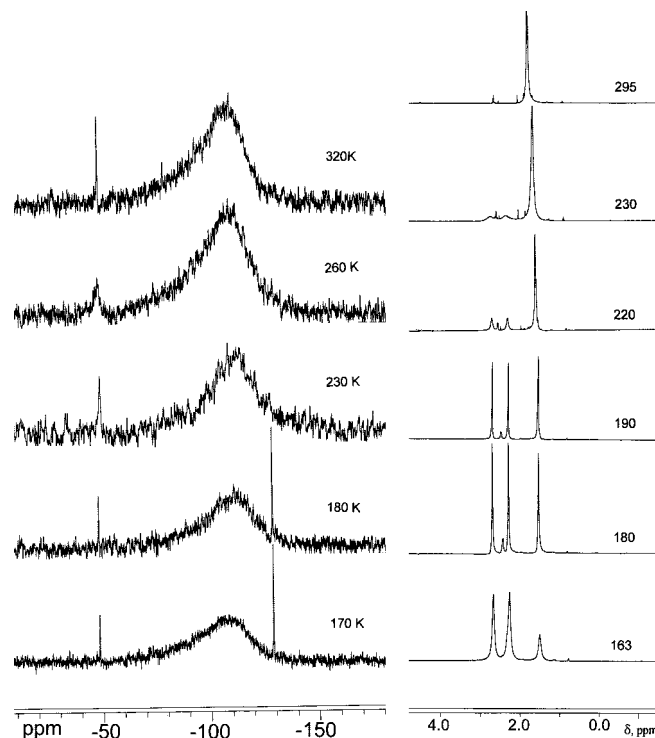

FIGURE 2. Temperature-dependent ^{29}Si (left) and ^1H (right, N-methyl region) NMR spectra of **13** in CD_2Cl_2 solution, showing tetracoordinate (low field) to hexacoordinate (high field, ^{29}Si) and time-averaged C_{2v} (singlet, tetrahedral) to C_2 (two singlets, octahedral) transformation upon decreasing the temperature.[8]

more tightly bound octahedral variant gradually appears and eventually becomes predominant.

3.3. Ionic Dissociation.

Hexacoordinate chloro complexes **5** and **7** undergo a solvent-driven ionic dissociation leading to chloride salts of the corresponding pentacoordinate siliconium ions (**16**), as shown in eq 5 (for **5**)[14] and in eq 2 (for **7**).[3] Thus, hexa- and pentacoordinate dichelates coexist in equilibrium and have comparable free energies in solution. Complexes

with the more powerful oxygen-donor ligands (**12**) are formed directly as ionic species (eq 4).[6] The extent of ionization, determined by ^{29}Si NMR spectroscopy, depends on a variety of factors and can effectively be controlled by their manipulation:[16,17] ionization of **5** takes place in H-bond donor solvents such as chloroform, dichloromethane, and $CHFCl_2$ but not in toluene and other apolar solvents.[14] Ionization is enhanced as the temperature is *decreased*, because it is driven by formation of an anion solvate shell and hence involves negative ionization entropy. Replacement of the chloro ligand in **5** by bromo or iodo, known as better leaving groups, drives the equilibrium entirely to the ionic side, as does its replacement by the poorly nucleophilic triflate or $AlCl_4^-$ group.[14] Several pentacoordinate siliconium salts (**16**) have been characterized by crystallographic analysis and shown to have a distorted trigonal bipyramid (TBP) geometry and well-separated ions (**16**: R,X,Y = Me,Me,TfO;[14] Ph,Me,TfO;[14] Me,Ph,TfO;[14] Me,Ph,AlCl$_4$;[14] Me,t-Bu,TfO;[18] t-Bu,c-C$_6$H$_{11}$,Cl;[7b] CF$_3$,c-C$_6$H$_{11}$,TfO.[7b]).

5   **16**

X = Me, Ph, PhCH$_2$
Y = Cl, Br, I, TfO
R = Me, Ph, PhCH$_2$, t-Bu
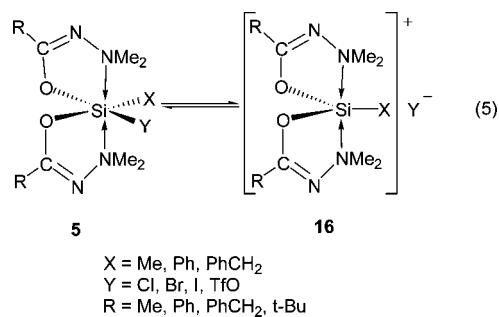
Steric bulk also plays a role in conversion of neutral hexacoordinate **5** to the ionic pentacoordinate **16**. When X = *t*-Bu, complete ionization is observed already at room temperature, presumably due to the strain resulting from the proximity of the *t*-Bu and chloro ligands.[14] When powerful electron-withdrawing groups are attached in **5** (such as both X and Y = Cl or triflate or R = CF$_3$), insufficient donor support for positive charge completely suppresses ionization.[14]

Ionic dissociation depends strongly on the chelate ligand donor group: complexes **5** are predominantly hexacoordinate at room temperature in chloroform solutions and ionize at lower temperatures.[14] In contrast, complexes **7** (R^1 = R^2 = Me), with the more powerful imino-donors, tend to be ionic (**7′**) at room temperature.[3b] With even stronger oxygen donors, in **12** and analogues, ionization is complete and no hexacoordination has been observed.[6]

Even formation of dications has been reported in dinuclear silicon complexes **17** and **18**, where the formal positive charges are separated from each other by only three bonds.

Ionization is facile in the dichloro complex **17**, with oxygen donors,[6] but requires replacement of the chloro ligands by the more effective anions (Br, I, TfO) in **18**, with its Me$_2$N ligands.[19]

17   **18**, R = Ph, Me, t-Bu; Y = TfO, Br, I
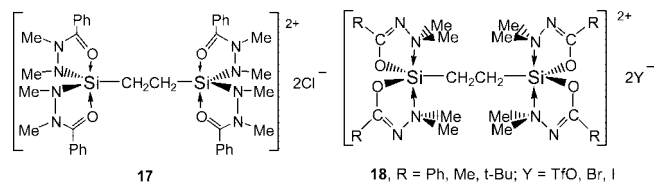
Like in **5**, the presence of two electron-withdrawing ligands in **7** (X = Cl), suppresses ionization.[3b] However, with two *bromo* ligands, which are bulkier and better leaving groups, equilibrium ionic dissociation is observed as a function of temperature in the ^{29}Si NMR spectra; dissociation is followed by a large shift to lower field, characteristic of increasing proportion of penta- to hexacoordination, as the sample temperature is lowered.[3b] Another striking feature of **7** with two halogen or triflate ligands is their geometry in the solid state (Scheme 1):[3b] unlike any of the complexes **5**, in which the monodentate ligands are always cis positioned, the dichloro, dibromo, and ditriflato analogues of **7** have trans (C_{2h}) geometries, while the difluoro complex is cis. This was attributed to steric repulsion between the *cis*-halogen and an isopropylidene methyl group.[3b]

SCHEME 1. : Solid State Geometry of Variants of **7**, *cis*-F$_2$ and *trans*-Cl$_2$, Br$_2$, and Ditriflato[3b]
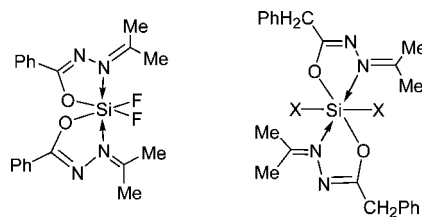
Measurements of the temperature-dependent electric conductivities of several complexes **5** unequivocally demonstrated ionic dissociation to separated ion pairs in CH$_2$Cl$_2$ solution, as well as increasing ion concentration with *decreasing* temperature, as required by the negative entropy solvent-driven dissociation (eq 5).[20]

3.4. Nonionic Dissociation. Investigation of the factors affecting ionic dissociation (eq 5) led to discovery of conflicting effects: while electron-withdrawing ring substituents R in **5** suppressed ionization, bulky X ligands forced ionization.[14] Competition between these two factors in **19** was attempted by incorporation of both steric bulk (cyclohexyl ligand) and electron-withdrawing substituent (CF$_3$ groups, eq 6).[7] Rather than the expected predominance of either **19** or **19a**, depend-
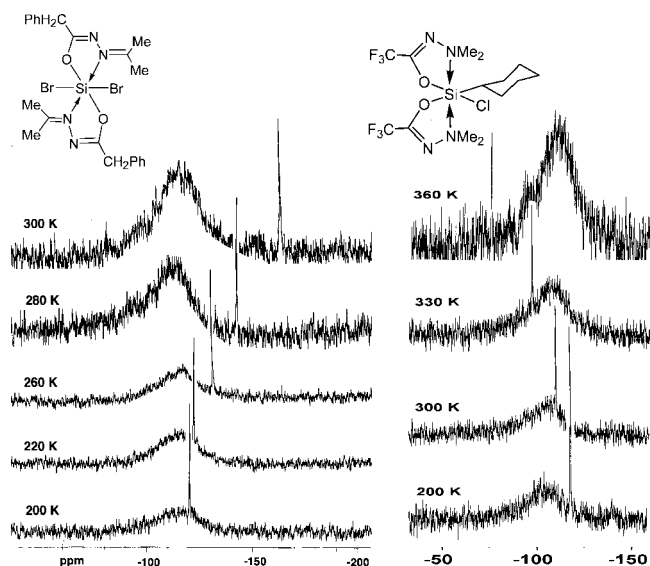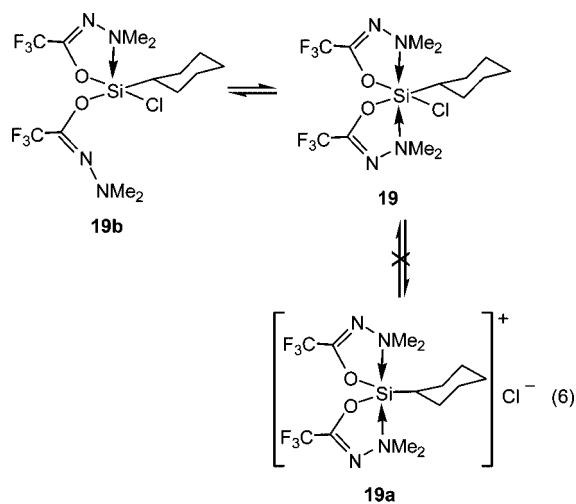
FIGURE 3. Temperature-dependent ^{29}Si NMR spectra featuring ionic (left, dibromo **7**) and neutral (right, **19**) dissociation.[7]

ing on which is the prevailing effect, the competition resulted in a different, neutral dissociation of the N–Si dative bond (**19b**, eq 6), which satisfies both factors: development of positive charge is avoided by the neutral dissociation, while a bulky ligand (dimethylamino, rather than a chloro group) dissociates to avoid steric congestion.


This second type of dissociation, leading reversibly from hexa- (**19**) to pentacoordinate (**19b**), is characterized by its *opposite* ^{29}Si NMR temperature dependence relative to that of ionic dissociation (**19 → 19a**), as shown in Figure 3: neutral dissociation is essentially solvent independent and proceeds in the "intuitive" direction, that is, the higher the temperature, the more dissociated (pentacoordinate, low-field ^{29}Si-resonance) the mixture.[7] Conversely, solvent-assisted ionic dissociation is *enhanced* as the temperature is decreased.[14] The stability of **19b** relative to **19** and **19a** was verified by ab initio calculations. Compound **19b** was shown by direct compar-

ison to be 1.44 kcal mol^{-1} lower in energy than its isomer **19**, and isodesmic reaction energies were used for comparison of the energies with that of **19a**, in agreement with experiment.[7]

3.5. Pentacoordinate Complexes: Crystallographic Pseudorotation Reaction Coordinate. In sections 3.1–3.3, the structures of hexacoordinate dichelates are described, along with their ability to equilibrate with ionic or neutral pentacoordinate species. The present section is about the structural flexibility of purely pentacoordinate silicon dichelates.

Pentacoordinate silicon complexes are known to undergo facile nondissociative intramolecular ligand exchange by the Berry or Turnstile mechanisms.[21–23] This process has been demonstrated *in the solid state*, in the sense that various molecules crystallize in geometries corresponding to points along the pseudorotation reaction coordinate.[18] Figure 4 depicts the molecular formulas and lists the corresponding N–Si–N and O–Si–O bond angles, which define the positions on the pseudorotation coordinate in the Bürgi–Dunitz sense.[24]

3.6. Formal Negative Charge on Silicon. Zwitterionic pentacoordinate silicon complexes bearing a formal *negative* charge[1e] and with hydrazide ligands[25] have also been studied; these (**20**, **21**) are complexes with an ammonium nitrogen in the β position and a formal negative charge on silicon. In addition to the apparent charge flexibility (five-coordinate silicon compounds with negative, neutral, and positive charges have been described), **21** also demonstrates significant geometrical flexibility; in contrast to most previously reported complexes with the SiCN$_2$O$_2$ skeleton, which have nitrogen atoms in axial positions, in **21** the nitrogens occupy equatorial and the oxygens axial positions in the solid state. Furthermore, the NMR spectra indicate that in solution a minor diastereomer of **21** is found, in which one nitrogen and one oxygen are equatorial and one of each axial.[25] Neither of these geometries is common in analogous neutral or cationic dichelates.

20, R = Me, *i*-Pr, *t*-Bu   **21**
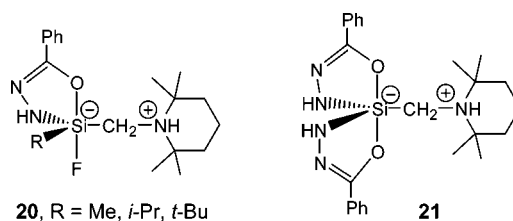
4. Reactivity

4.1. Elimination of Methyl Halide from NMe$_2$-Coordinated Complexes. When ionized complexes **16** bear bulky monodentate X-ligands, they readily undergo a methyl halide elimination, as shown in eq 7.[18] The steric bulk first causes complete ionization,[14] followed by nucleophilic attack of the

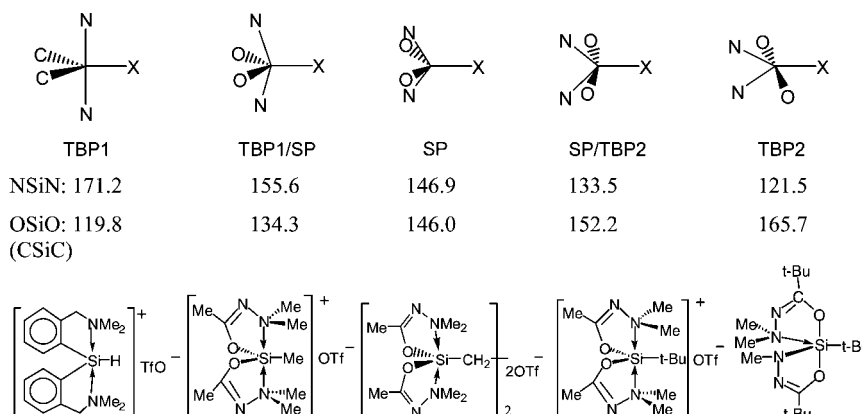| TBP1	TBP1/SP	SP	SP/TBP2	TBP2
NSiN: 171.2	155.6	146.9	133.5	121.5
OSiO: 119.8 (CSiC)	134.3	146.0	152.2	165.7

FIGURE 4. Crystallographic pseudorotation. Schematic geometries of points along the reaction coordinate, corresponding experimental N–Si–N and O–Si–O angles (C–Si–C in first molecule),[18] and corresponding molecules for which geometries are given.

halide counterion on an N-methyl carbon and methyl halide elimination, presumably thereby releasing steric congestion. The counterion is involved in the rate process, as evident from the reaction rate order I[-] > Br^{-} > Cl^{-}, the order of halide nucleophilicity. The less nucleophilic triflate is unreactive under similar conditions.[18]

$$R = Me, \ t\text{-Bu}, \ Ph \qquad Y = Cl, \ Br, \ I$$
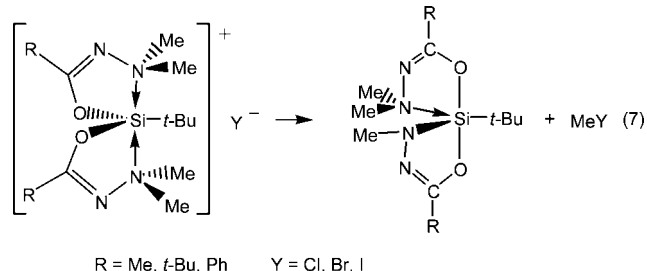
Interestingly, in the elimination product both nitrogen atoms occupy *equatorial* positions in the slightly distorted TBP complex, whereas in all previously studied N→Si coordinated complexes the nitrogens occupied axial positions.[1]

4.2. Intramolecular Aldol-Type Condensation of Imines in Imino-Silicon Complexes. Dichelate complexes **7′** also undergo a facile transformation upon mild heating, namely, a rearrangement consisting of an intramolecular aldol-type condensation of the imine groups on the two chelate rings (eq 8).[26a] The reaction results in formation of a new carbon–carbon bond to form a third chelate ring. It is general and was observed in numerous complexes with imines of cyclic ketones and aldehydes, as well as different R and X groups. It is presumably initiated by the halide counterion acting as a base and abstracting an allylic proton, as indicated by the order of reactivity, that is *opposite* to that in the previous section, Cl^{-} > Br^{-} > I[-], and follows the order of basicity of the halides toward proton. The carbanion formed by proton abstraction, which is stabilized by the allylic position and electron-withdrawal by the nitrogen, which donates electrons to

silicon, eventually attacks the electrophilic imino-carbon at the adjacent chelate ring to form **24**.

$$R = X = Me;$$
$$R = Ph, \ X = c\text{-}C_6H_{11};$$
$$R = CF_3, \ X = Me$$
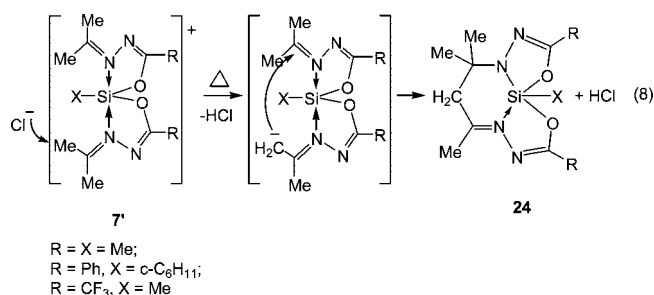
Somewhat similar condensation was observed in transition metal compounds,[26b] but this is the first report in main group compounds.

4.3. Uncatalyzed Internal Condensation in Imino-Silacyclobutane Complexes. An interesting variant of the condensation described in the previous section is observed in silacyclobutane analogues of **7** (**25**).[27] Compounds **25** were prepared by transsilylation from dichlorosilacyclobutane and **6** in analogy with eq 2. Since **25** lacks a halogen ligand, it is strictly hexacoordinate and does not undergo ionic dissociation. Yet warming in chloroform solution transforms **25** to a tricyclic complex (**26**, eq 9) remarkably similar to **24**, *but in the absence of a counterion*. In addition, the rearrangement is accompanied by opening of the four-membered ring and formation of an *n*-propyl group.
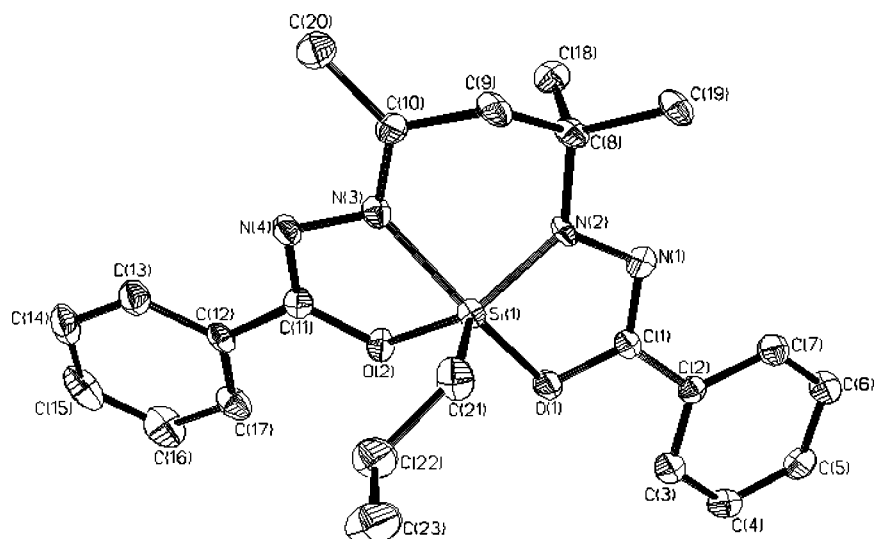

26	**25**	**27**
R[1], R[2] = Me,Me; H,Me; (CH₂)ₙ		R[1],R[2] = H,Ph
R = Me, Ph, CF₃		R = Me, CF₃
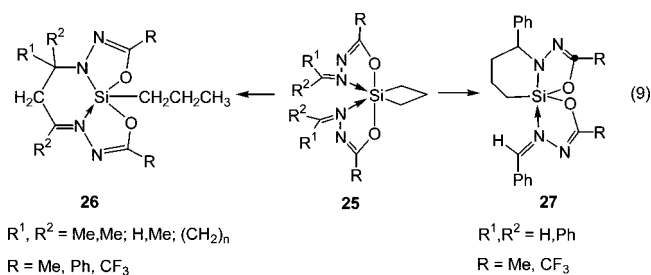
FIGURE 5. Molecular structure of **26** ($R^1 = R^2 = $ Me, R = Ph) in the solid state.

To form the *n*-propyl chain, as evident from the crystal structure of one of the rearrangement products **26** (Figure 5), a proton must have been abstracted by the ring-opened chain residue. This, and the similarity of the reaction to the halide-initiated aldol condensation, suggests that the four-membered ring opens spontaneously to form a primary carbanion or radical, which immediately (possibly simultaneously) abstracts an adjacent allylic proton from one of the imino groups, followed by the condensation described above. This is the only course of reaction observed in the presence of allylic hydrogens; however, in the absence of allylic hydrogens, the transient carbanion or radical adds directly to the electrophilic imino-carbon, forming a different third chelate ring (**27**, eq 9).[27]

In both of these reaction pathways, a carbon−silicon bond is replaced by a stronger carbon−carbon bond and one of the two dative N→Si bonds (recognized by its greater length) is converted to a covalent bond.

4.4. Addition of a Cyano Group to the Imino Double Bond. The selectivity order described above (preference for aldol condensation over addition to imino carbon) is completely reversed in the following reactions involving the cyanide group. Attempts to replace chloride by cyanide in a silicon complex (**28 → 29**) via transsilylation, using Me₃SiCN (eq 10), resulted in spontaneous addition of the cyano group to the imino carbon of one of the chelate rings (**30**), despite the availability of 12 α-protons.[28] Thus, when instead of the presumed initial alkyl carbanion in eq 9 a cyanide ion (also a carbon base) is present in the reaction, addition to the imino carbon becomes the overwhelmingly preferred reaction. This has been attributed to the softness of cyanide as a base, relative to chloride, which causes it to prefer addition to the soft

carbon electrophile over abstraction of a hard proton to initiate the aldol condensation.[28]
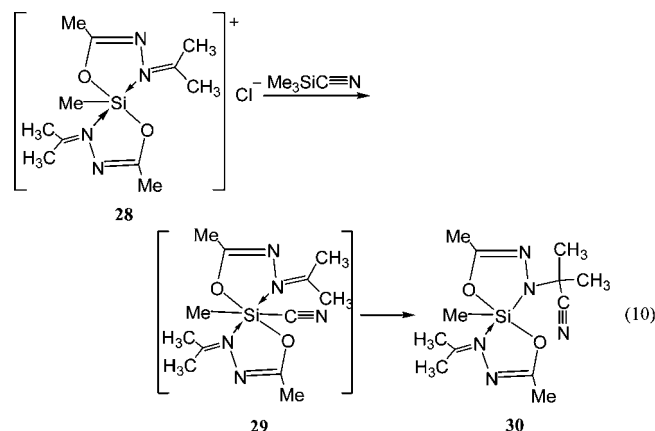
4.5. Rearrangement of Hydrido Ligand. A reactivity pattern similar to that described for the cyano ligand was observed for the hydrido group.[29] A hydrazide precursor (**6**) reacts with MeHSiCl₂ to give initially the pentacoordinate monochelate **31**, in which H is connected to silicon (eq 11). With a second mole equivalent of **6** the dichelate **32** is obtained, in which the hydride has shifted from silicon to the imino carbon, in analogy with the cyano reaction.

Strangely, even **32** rearranges upon heating to a tricyclic product (**33**), analogous to **24** and **26**, although no halide is present, and the reaction proceeds with loss of hydrogen, suggesting that hydride anion may have abstracted an allylic proton to initiate the aldol condensation.

The reaction proceeds with various ketone or aldehyde imino complexes, such as cycloalkanone imines, through *both* of the steps to form the tricyclic complexes analogous to **33**. Of course in the absence of α-(allylic) protons, the condensa-

31

(11)

32   **33**
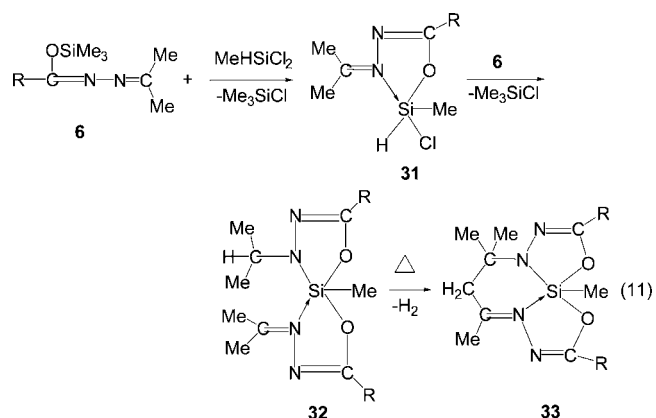
tion step cannot take place, and the final product is the analogue of **32**. This was the case with benzylideneimino complexes (**34**), in which one of the initial imino groups was converted to a benzylamino group through a hydride shift.[30]

34, R =Me,CH$_2$Ph,*t*-Bu,CF$_3$
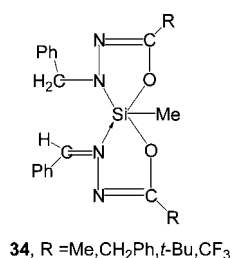
4.6. Complete Intermolecular Ligand Crossover. Perhaps the most impressive manifestation of silicon complex flexibility is the ability of the complexes to rapidly exchange mono- and bidentate ligands between different complexes and between complex and various precursors.

4.6.1. Ligand Exchange between Complex and Trichlorosilane. The monodentate ligand X is *formally* replaced by Z when **5** is mixed with ZSiCl$_3$ in solution (eq 12).[31] The reaction proceeds by exchange of chelating ligands, and not by cleavage of the Si–X or Si–Z bonds.

(12)

5   **5'**
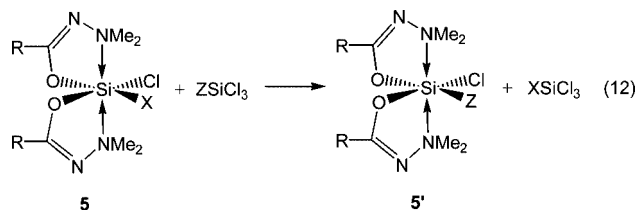
The exchange is selective and irreversible; a ligand Z *quantitatively* replaces all of the X ligands placed after it in the following "ligand priority list": Cl > H > vinyl > Ph > Me > Et > *i*-Bu > cyclohexyl, essentially in order of decreasing ligand electron-withdrawing power.

4.6.2. Bidentate Ligand Exchange between Complex and Hydrazide Precursor. Equation 13 shows another type of intermolecular ligand exchange, crossover of *bidentate*

ligands between **5** and the precursor (**1**) of a differently substituted (R^2) complex. Like the exchange described in section 4.6.1, this reaction is controlled by priority rules. However, the priority order is in the *opposite* sense relative to that in section 4.6.1: electron-withdrawing R substituents are driven out by *less* electron-withdrawing groups. This seems to be controlled, as in section 4.6.1, by overall complex stabilities: the electron-withdrawing R^1 = CF$_3$, through the double bond, withdraws electron density from the nitrogen donor atom and hence reduces the overall complex stability. As a result, CF$_3$ is readily and quantitatively replaced by any one of the other groups R^2, while the reverse chelate replacement is not observed.[31]

5, R^1 = Me,*t*-Bu,Ph,CF$_3$ **1**, R^2 = Me,*t*-Bu,Ph

R^1 ≠ R^2

(13)

5'   **1'**
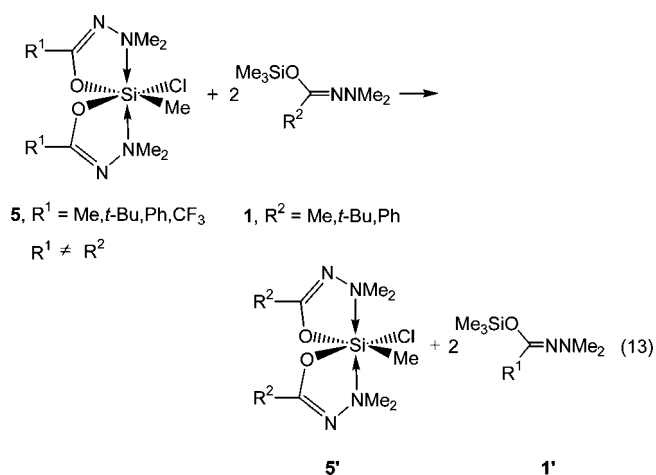
The selectivity in this exchange is not as total as in the previous case, when R^1 = Me and R^2 = Ph, or in the opposite case, approximately 1:1 mixtures of **5** and **5'** are observed. R^2 = *t*-Bu is the most "powerful" substituent and replaces all other three from their complexes. Mixed dichelates have not been found in this reaction.

4.6.3. Complete Chelate Crossover between Complexes. Even in the case of admixture of two different complexes, where there is no apparent thermodynamic incentive for ligand exchange, chelate scrambling is observed within minutes (eq 14).[31]

(14)

5x   **5y**   **5xy**   **5yx**

R^1, R^2 = Ph, *t*-Bu, Me, CF$_3$

R^1 ≠ R^2
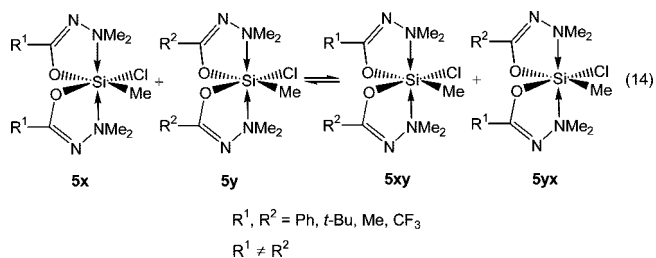
Complete scrambling requires that exchange of both mono- and bidentate ligands take place. To this end, two complexes with different R groups and monodentate ligands (R^1 = CF$_3$,

ligand = Me; R^2 = Ph, ligand = *i*-Bu) were boiled for 5 min in CDCl$_3$ solution, after which the ^{29}Si NMR spectrum featured at least six signals, corresponding to different complexes and providing evidence for the exchange of individual chelate rings between silicon centers and hence complete scrambling.[31]

The exact mechanism of exchange remains uncertain. It appears likely that the first step is cleavage of one of the N→Si bonds, followed by attack of the N-donor on the silicon of an adjacent molecule.

4.6.4. Ligand crossover in silacyclobutane complexes. Similar exchange experiments were carried out with silacyclobutane complexes, in an attempt to understand the exchange mechanism: in the latter compounds no ionic dissociation is possible, and hence the role of chloride in the exchange can be tested.[32] The finding that **35** undergoes chelate exchange as easily as other dichelates (eq 15) is evidence that chloride involvement is not essential.
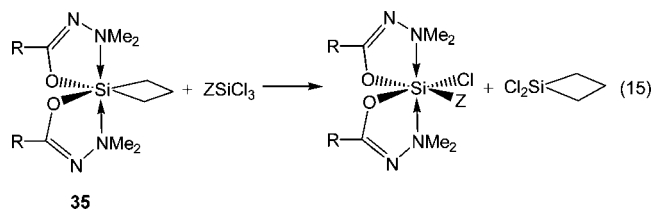
The four-membered ring took the *lowest* priority, and was replaced by any Z ligand, regardless of the ring substituent R. This is not surprising in view of the fact that a chloro ligand, which was shown previously to have the highest priority,[31] replaces a carbon ligand in eq 15 in all cases.

The observation that the exchange produces dichlorosilacyclobutane is regarded as evidence that at no point during the exchange sequence a silicon−carbon bond is cleaved: it is unlikely that after Si−C cleavage the open chain would quantitatively close back to a four-membered ring, suggesting that in none of the reactions described above (sections 4.6.1−4.6.4) such cleavage takes place.[32]

4.7. Chloromethyl Ligand Rearrangement and Ring Expansion. The rearrangement of chloromethyl-silicon complexes (mentioned earlier in eq 3) deserves a separate discussion.

The transsilylation reactions of three chloromethylsilanes were studied: ClCH$_2$SiMe$_2$Cl (**36**),[33] ClCH$_2$SiMeCl$_2$ (**37**),[4] and ClCH$_2$SiCl$_3$ (**38**).[13] Compound **36** reacted with silylated hydrazides (**1**) to form only *mono*chelates with internal displacement of chloride by one of the nitrogen atoms (**39**, **40**, eq 16). Depending on the stereochemistry about the imidate double bond, chloride is displaced by either one of the two
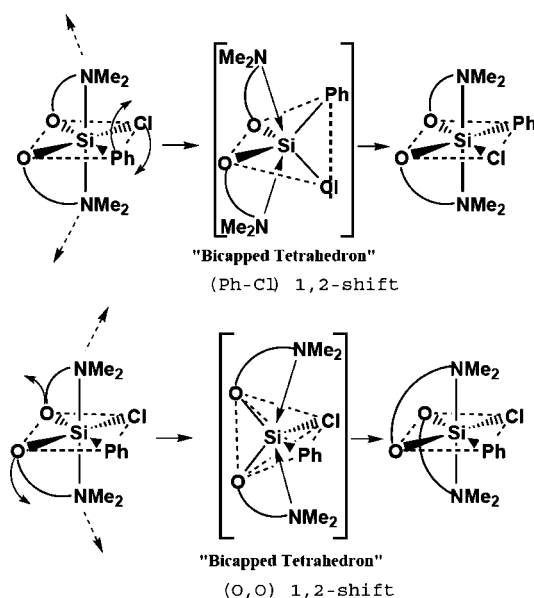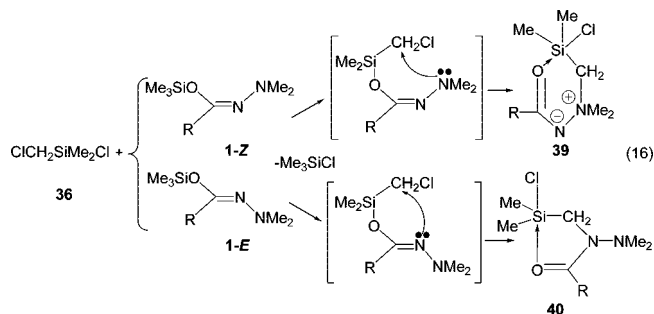
FIGURE 6. Schematic nondissociative ligand-exchange processes in hexacoordinate complexes **5** via bicapped tetrahedron: upper part, topomerization by Ph,Cl exchange; lower part, silicon epimerization by O,O exchange.[15]

nitrogen atoms.[33] Compound **39** is converted to **40** by a Wawzonek[34] rearrangement.[33]

Analogous rearranged *di*chelates are formed from **37** and **1** (eq 17), in this case *without* the stereochemical selectivity observed in eq 16.[4] Interestingly, dichelates **41a** and **41b** are *ionic* in CHCl$_3$ solution (**42**), and do not associate to hexacoordination even in apolar toluene solution, in contrast to complexes **5**, which dissociate only at lower temperatures and certain conditions. This is probably because the positive charge resides on the ammonium nitrogen of the chelate ring.

In contrast, the CF$_3$-substituted **41c** is in tautomeric equilibrium with ionic **42c** in solution, with chloride presumably migrating between the ammonium nitrogen and silicon (eq 17). The CF$_3$ group withdraws electron density from silicon, thus making it difficult for silicon to release chloride and become partly positively charged.[4] The equilibrium **41c** ⇌ **42c** is affected by temperature, solvent, and counterion in much the same way as that of symmetric dichelates discussed above (eq 5), despite obvious differences in charge distribu-

$$(17)$$

41   **a, R = H**   **42**
   **b, R = Ph**
         c, R = CF₃
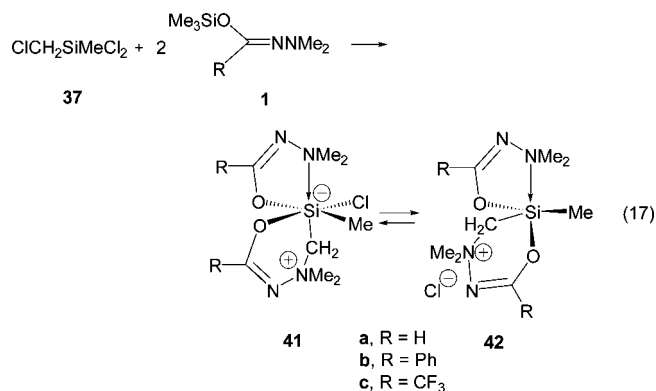
tions: in **42** the quaternary nitrogen permanently carries a positive charge, while the negative charge can either be on the dissociated chloride or be distributed along the Si−O−C−N sequence in the six-membered chelate in **41**.

Compound **41b** readily hydrolyzes to the unusual chloride-bridged **43**, consisting of two pentacoordinate trigonal bipyramidal silicon complexes sharing a common chloride axially coordinated to *both* (eq 18).[4]

$$(18)$$

43
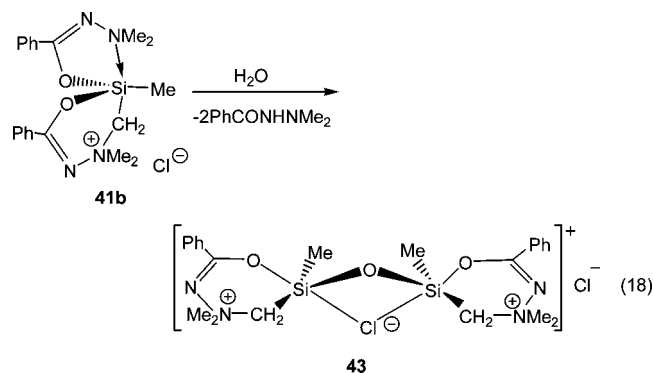
Only when *tri*chloro **38** reacts with **1** can the initial product of transsilylation (**44**) be isolated and characterized without further rearrangement (eq 19). Upon heating, it rearranges quantitatively to **45**.[13] The two chloro ligands in **45** have been utilized to bind a third chelate, forming a complex with three different chelate rings (**46**).[35]


$$(19)$$

44   **45**

46
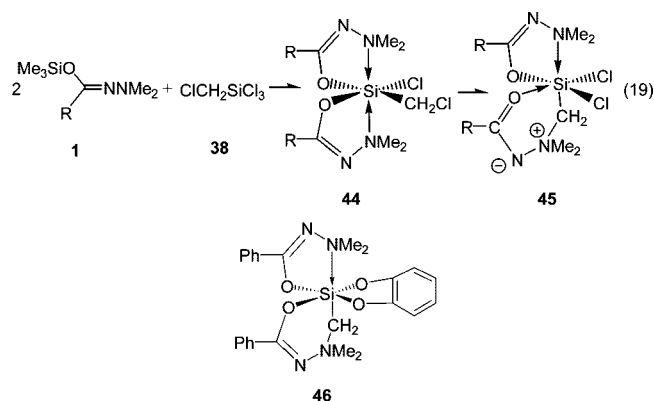
Finally, the reactions of *di*(chloromethyl)dichlorosilane (**47**) were investigated.[36] A *double* ring expansion takes place when **47** reacts with **1** (R = CF₃), forming a neutral hexacoordinate dichelate with two of the less common six-membered chelate rings (**48**, eq 20). Charge distribution in **48** is peculiar, suggesting that silicon carries formally *two* negative charges. Replacement of a chloro by an iodo ligand gave the *dissociated* pentacoordinate chlorosiliconium iodide (**49**). Compounds **48** and **49** readily hydrolyze to the dinuclear disiloxane **50**. The three different products **48**−**50**, derived from the same initial reactants, have been characterized by crystal structures.[36]

$$(20)$$

47   **48**   **49**

50
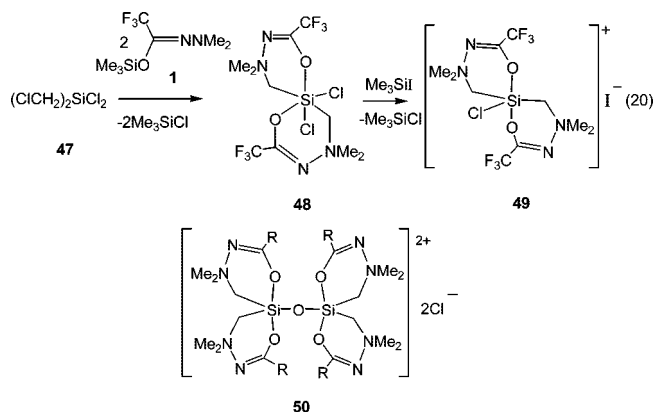
5. Stereodynamics

Many of the molecules described above are associated with rapid conformational or other changes compatible with the "NMR time scale", that have been monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. These are collectively termed "stereodynamics". Several examples were mentioned above, and one additional case is described below.

5.1. Assignment of Two Rapid Ligand-Exchange Reactions in Hexacoordinate Complexes. Complexes **5** undergo *two* consecutive intramolecular ligand-exchange (i.e., conformational) processes in toluene solution, observed by temperature dependence of their NMR spectra.[11,15] The two processes were monitored by observing spectral changes in the N-methyl region of the ¹H and ¹³C NMR spectra of **5a**. It was shown that the four N-methyl singlets (C_1 molecular symmetry) first coalesced to *two* singlets for a C_2 time-average symmetric molecule, due to rapid exchange of the monodentate ligands. At higher temperature further coalescence of the remaining N-methyl signals to a singlet was observed, when time-average C_{2v} symmetry was achieved. A simple exchange of adjacent ligands (X,Cl and O,O) via a bicapped tetrahedron transition state or intermediate was postulated, based on these observations (Figure 6).

5a   **5b**, *R*Δ*R* + *R*Λ*R*
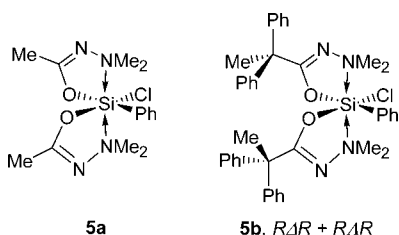
To assign each of these processes to either of the observed NMR rate processes two identical and enantiopure chiral carbon centers were introduced in **5b**.[11] The three stereogenic units generate two diastereomers: *R*Δ*R* and *R*Λ*R*, which in toluene-d_8 solution at 250 K gave rise to eight *N*-methyl signals, four for each diastereomer, in a 4:3 intensity ratio. The first (lower barrier) *N*-methyl exchange was within the N-methyl groups of each diastereomer: no interchange of diastereomers took place, evidence that this process corresponded to a *topomerization*, exchange of diastereotopic groups within the same molecule, that is, (Ph,Cl)-exchange, which does not effect inversion of configuration at silicon. If (O,O)-exchange, which *does* invert the silicon configuration, were the lower of the two barriers, one would observe exchange between diastereomers, manifest in coalescence of corresponding signals of different intensities.

Based on this analysis, it was concluded that **5b** underwent first (at lower temperature) a nondissociative exchange of Ph and Cl, followed by exchange of the chelate rings (O,O exchange), accompanied by inversion of configuration at silicon.[11]

BIOGRAPHICAL INFORMATION

Daniel Kost received his B.Sc. and M.Sc. degrees in chemistry at the Hebrew University of Jerusalem and his Ph.D. at Tel Aviv University. After postdoctoral training with M. Raban at Wayne State University, Detroit, he joined Ben Gurion University where he is now Chemistry Professor. He is interested in aspects of physical organic chemistry, NMR spectroscopy, stereochemistry, and organo-silicon chemistry.

Inna Kalikhman received her M.Sc. degree in physics from Moscow University and Ph.D. and D.Sc. degrees from Irkutsk Institute of Organic Chemistry. She joined the Chemistry Department at Ben-Gurion University after immigration to Israel in 1993. Her interests are in hypecrcoordinate main group compounds and NMR spectroscopy.

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