Silicon rehybridization and molecular rearrangements in hypercoordinate silicon dichelates*

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Abstract: Hydrazide-based hypercoordinate silicon dichelates are remarkably flexible in terms of geometry and reactivity: this paper demonstrates how rather subtle constitutional changes result in dramatic geometrical and reactivity changes. A change of ligand-donor group from NMe_2 to $N=CMe_2$ changes the solid-state geometry from bicapped tetrahedral to octahedral. These two geometries are shown to coexist in solution in dynamic equilibrium. Hexacoordinate complexes are shown to dissociate to pentacoordinate compounds in two distinct ways: ionic or neutral, depending on substitution. Hexacoordinate dichelates with imino-donor groups undergo a skeletal rearrangement (intramolecular aldol-type condensation of imines), catalyzed by their dissociated halide counterions. However, even in the absence of counterions, silacyclobutane dichelates undergo a similar rearrangement.

Keywords: silicon; pentacoordinate; hexacoordinate; rehybridization; molecular rearrangement; bicapped-tetrahedral.

INTRODUCTION

Penta- and hexacoordinate silicon complexes have received considerable attention recently, owing to their versatile and interesting structure and reactivity [1]. On the one hand, silicon complexes have been reported to readily change their coordination numbers between 5 and 6 [2,3], and on the other, they undergo several unique reactions [4,5]. The present paper further illustrates and emphasizes the remarkable flexibility of hydrazide-based silicon dichelates, enabling dramatic geometrical and structural modifications as a result of subtle changes in constitution or reaction conditions.

Silicon dichelates (**1**) are readily prepared by trans-silylation, the exchange of ligands between two silicon compounds, as shown in eq. 1 [1r,3]. This clean synthetic method produces a single volatile byproduct, Me_3SiCl, which is distilled off under vacuum, leaving a nearly pure product and avoiding tedious separations.

$$\text{(1)}$$

R = alkyl, aryl, Me$_2$N   X = alkyl, aryl, halogen

1

Dichelates **1** and their analogous complexes undergo various transformations, which may be divided into two groups: reversible and irreversible processes.

REVERSIBLE TRANSFORMATIONS

Dissociation

Neutral hexacoordinate silicon dichelates undergo *two* different reversible bond dissociations, leading to pentacoordinate complexes. The first of these is a solvent-driven ionic dissociation, resulting in a pentacoordinate siliconium salt (**2**, eq. 2). It takes place only in hydrogen-bond donor solvents, such as CHCl$_3$ and CH$_2$Cl$_2$ [3a]. The ionization is enhanced at low temperatures, owing to the relatively ordered anion-solvent shell, in what may be viewed as a counterintuitive process. Indeed, the reaction entropies, evaluated from the temperature-dependent equilibrium population ratios as determined by NMR, are negative [3a]. The ionization strongly depends on several factors. (a) The solvent: chloroform is more effective than dichloromethane, and less effective than CHFCl$_2$. (b) The counterion: the better leaving group stabilizes the ionized form. Thus, Y = I > Br > Cl listed in order of decreasing ionization constant. (c) Steric bulk: the bulkier the monodentate X ligand, the more ionized the complex at a given temperature. (d) The remote substituent R: electron-withdrawing substituents cause the ligand to be a weaker donor, resulting in a less stabilized siliconium ion, and hence shifting the equilibrium position to the left (hexacoordinate) side.

$$\text{(2)}$$

1   **2**

The second type of dissociation of hexacoordinate to pentacoordinate dichelates is demonstrated by the reaction in eq. 3. This dissociation constitutes a *neutral*, nonionic dissociation of the silicon–nitrogen dative bond [3c,d]. It takes place when R, the chelate-ring substituent, is a strong electron-withdrawing group, such as CF$_3$. Under these conditions, the expected ionic structure is destabilized, as mentioned above, and on the other hand, the N→Si dative bond is weaker and more susceptible to cleavage. This dissociation is not affected significantly by the solvent, since no charge separation is involved, and is readily distinguished from the ionic dissociation by examining the temperature dependence of their respective ^{29}Si NMR spectra (Fig. 1) [3c].
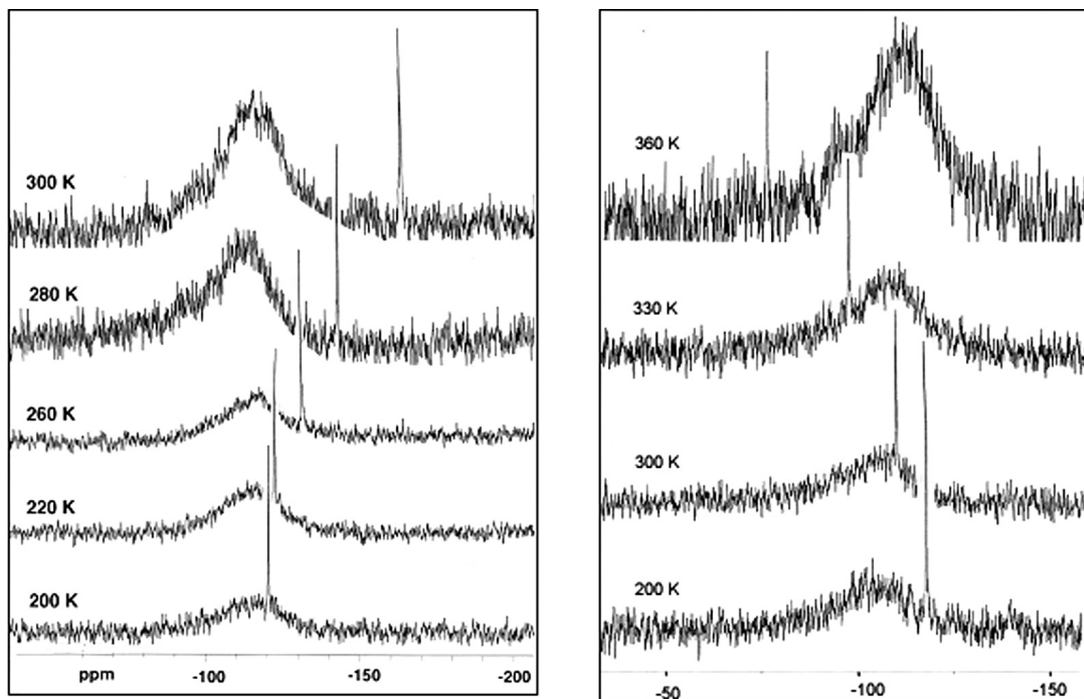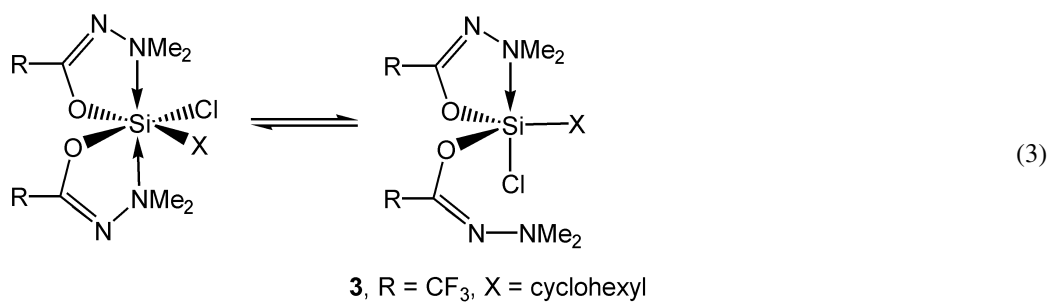
$$(3)$$

3, R = CF$_3$, X = cyclohexyl

Fig. 1 Temperature-dependent ^{29}Si NMR spectra of silicon complexes: left, **3** in CD$_2$Cl$_2$ solution; right, **4** in toluene-d$_8$ solution.

The opposite temperature-dependencies found in Fig. 1 for the two dissociation types character-ize each process: while the ionic dissociation (eq. 2) of the dibromo compound **4** is enhanced at low temperature [6], as evident by the shift of the ^{29}Si resonance to lower field, the neutral dissociation is enhanced as the temperature is *increased*, as one might expect intuitively.

4

5a, R = Ph
5b, R = NMe$_2$

6
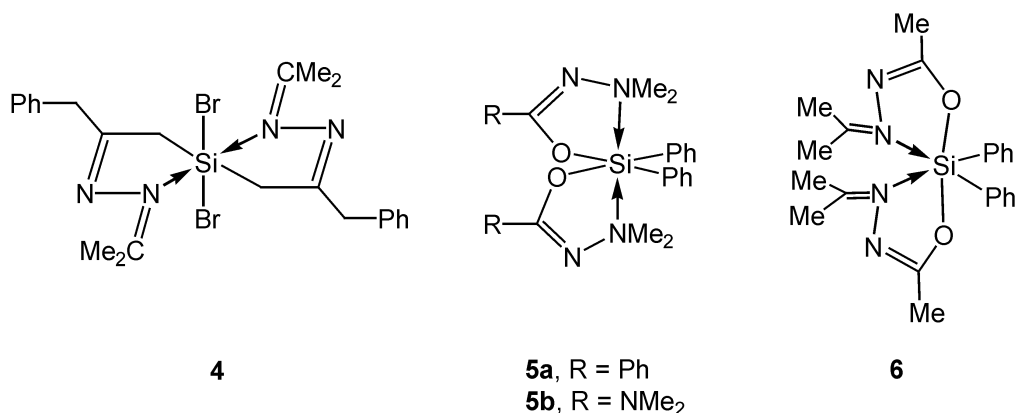
Silicon rehybridization in the solid state

The hexacoordinate silicon complexes **5–6** were prepared by trans-silylation from dichlorodiphenylsilane in analogy with eq. 1, using large excess of the corresponding *O*-trimethylsilylhydrazides. These are the first reported members of the hydrazide-derived hexacoordinate silicon complex family containing *two* monodentate carbon ligands [7].

Complexes **5a** and **6** were crystallized, and their crystal structures were determined by X-ray crystallographic analysis. The resulting molecular structures are depicted in Fig. 2. Despite the substantial constitutional similarity of **5a** and **6**, a striking geometrical difference is found in these two crystal structures. Complex **6** features, as expected for a hexacoordinate molecule, a distorted octahedral geometry. In contrast, **5a** is essentially a *tetrahedron*, with the nitrogen ligands pointing their electron lone pairs toward silicon from a great distance, "capping" two of the tetrahedral faces. This molecular shape in silicon compounds was previously reported by Corriu [8a–d] and by others [8e–h] and was termed "bicapped tetrahedron".
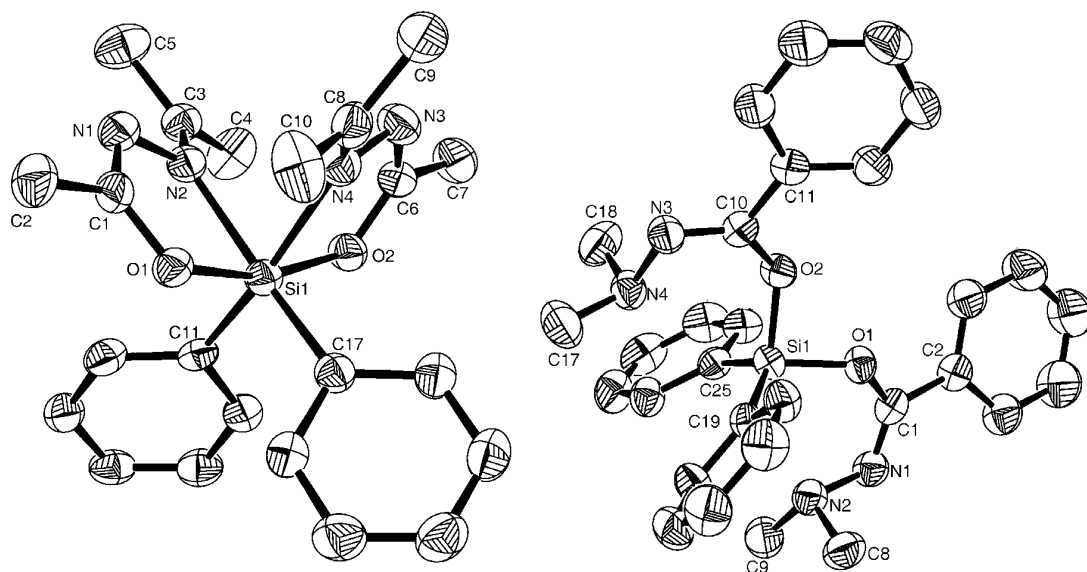
Fig. 2 Molecular structures of **5a** (right) and **6** (left) in the crystal, depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Complexes **5a** and **6** share the same coordination skeleton: $SiC_2N_2O_2$. They differ only in the ligand-donor group: Me_2N- in **5a**, and the corresponding acetone-imine (isopropylideneimino group) in **6**. It is known from previous work [6] that the latter group acts as a stronger donor in silicon complexes, relative to the former. Thus, the dramatic geometrical change can be accounted for by the relatively small change in strength of complexation. In **6**, the two dative N→Si bonds provide sufficient energy to promote the silicon atom from its ground, tetrahedral, to the higher, octahedral, configuration. This is not the case in **5a**; here, the N→Si bonds do *not* provide sufficient energy to promote silicon, and hence the silicon atom remains at its ground, tetrahedral geometry, at the expense of losing the binding energies of the two N→Si bonds. This is immediately evident from a comparison of the N→Si distances in the compounds: 2.12, 2.14 Å in **6**, as opposed to 2.72, 2.86 Å in **5a** [7]. Clearly, the very long N–Si distances in **5a** reflect much weaker coordination than the corresponding bonds in **6**. Thus, by a relatively small change in donor strength it has been possible to place the silicon promotion energy between an upper and a lower limit: the sum of two isopropylideneimino-Si and two dimethylamino-Si dative-bond energies, respectively.

A further change in complex structure reverses the bicapped-tetrahedral back to the octahedral geometry: without any change in the immediate coordination environment around silicon, by changing only the remote substituent R from phenyl in **5a** to dimethylamino in **5b**, the reversal back to distorted octahedral geometry is realized. This is evident from the crystal structure of **5b**, shown in Fig. 3 [7]. The remote substituent R = Me_2N is an effective π-electron donor which, through the double bond, pushes electrons to the ligand Me_2N group, making it a stronger electron donor. As a result, the two dative N→Si bonds are now sufficiently stronger to overcome the silicon promotion energy and generate the distorted octahedral molecular geometry found in Fig. 3.
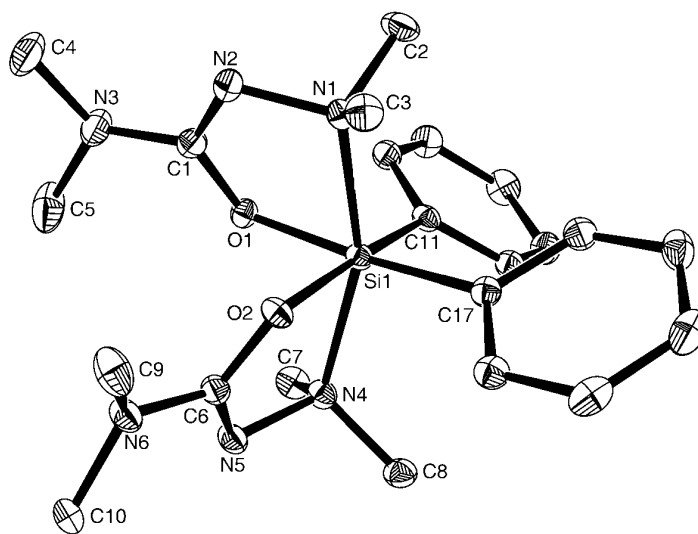

Fig. 3 Molecular structure of **5b** in the crystal, depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Silicon rehybridization in solution

Small constitutional changes have determined the exclusive molecular geometry of **5a** and **6** in the solid state to be *either* octahedral *or* bicapped tetrahedral. It was of interest to determine the situation in solution: whether these two molecular forms are also exclusive in solution, or if they interchange and coexist simultaneously. The answer is provided by the temperature-dependent ^{29}Si and ^1H NMR spectra

shown in Figs. 4 and 5, respectively [7]. The initial ^{29}Si resonance found at 320 K in Fig. 4 is assigned to the bicapped tetrahedral geometry. As the temperature is decreased, the signal broadens and eventually an additional, high-field signal appears, corresponding to the hexacoordinate, octahedral geometry. Thus, the two geometries coexist in dynamic equilibrium in solution, with the more tightly bound, compact octahedral geometry prevailing at low temperature.

The ^{1}H NMR spectra shown in Fig. 5 support and strengthen this conclusion: at room temperature only a single resonance is found in the N-methyl region, corresponding to the C_{2v}-symmetric bicapped tetrahedron structure, in which all four N-methyl groups are equivalent. As the temperature is decreased, a pair of lower-field signals appears, owing to the emergence of the C_2-symmetric octahedral species, in accord with the results of the ^{29}Si NMR spectra. However, in addition, the ^{1}H NMR spectra also strongly suggest that the equilibrium involves *only* the tetra- and hexacoordinate species, without the involvement of a pentacoordinate intermediate to any detectable level. This conclusion is based on the observation that the high-field signal in Fig. 5 remains a sharp singlet down to the lowest attainable temperature, 163 K. Had there been a pentacoordinate silicon complex intermediate, with one NMe$_2$ group bound to silicon and the other one loose, there would have been at least *two* corresponding N-methyl signals. The persistent singlet at all temperatures indicates that the C_{2v}-symmetry is never broken, and at this low temperature also rapid exchange and coalescence of N-methyl groups between different geometries ("flip-flop" mechanism) seems highly unlikely [9].
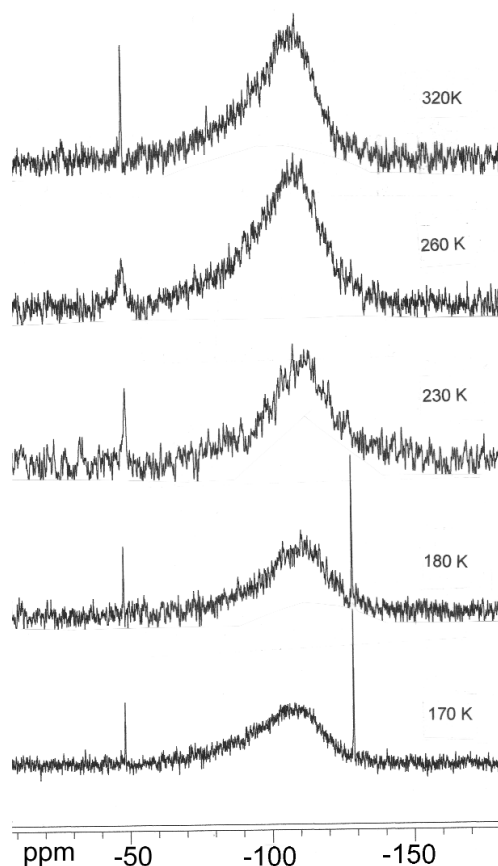

Fig. 4 Temperature dependence of the ^{29}Si NMR spectra of **5a** in CD$_2$Cl$_2$ solution.
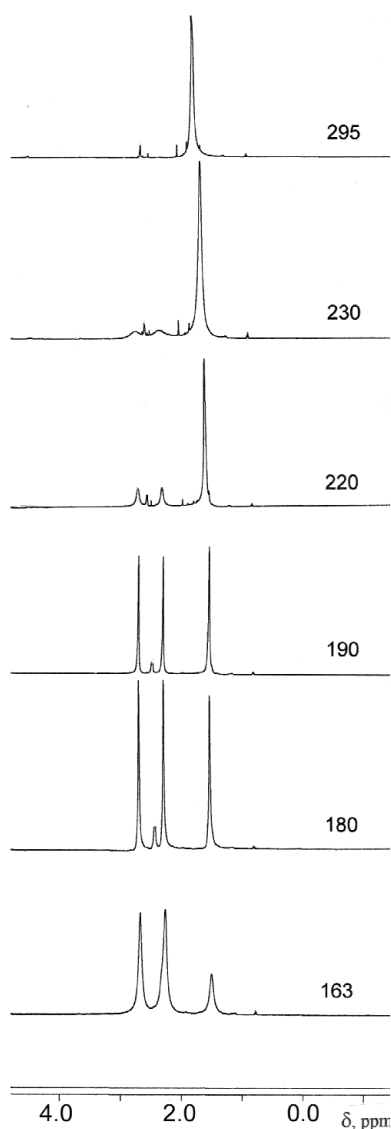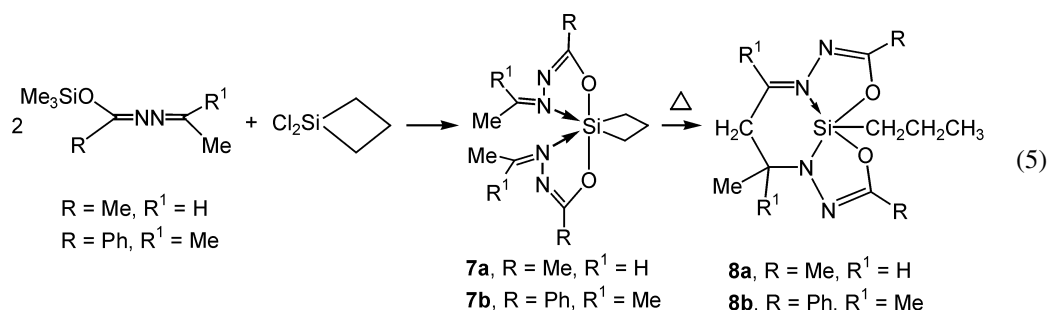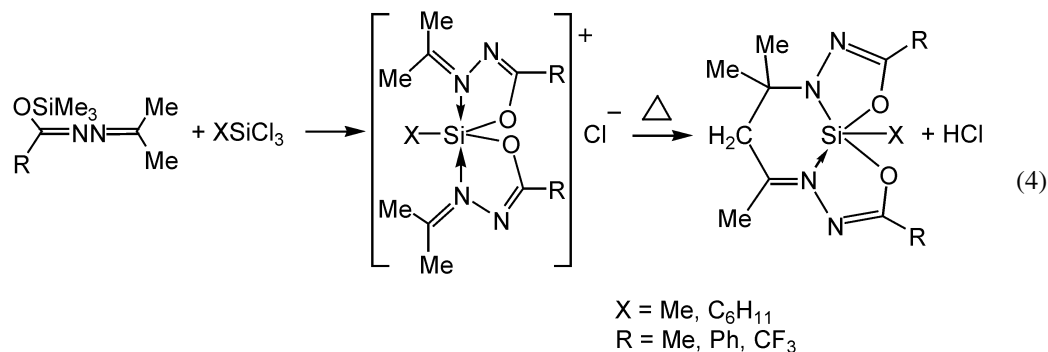
Fig. 5 Temperature dependence of the *N*-methyl region of the ^{1}H NMR spectra of **5a** in CD$_2$Cl$_2$ solution.

IRREVERSIBLE TRANSFORMATIONS

Molecular rearrangement

We have previously reported on the facile skeletal rearrangement which certain pentacoordinate siliconium halides undergo (eq. 4) [5]. Only imino-coordinated complexes with a halide counterion have shown this reactivity, which constitutes an intramolecular, inter-chelate aldol-type condensation of imines, catalyzed by their own halide counterion. More recently, silacyclobutane dichelate complexes (**7**) have been prepared by trans-silylation (eq. 5), bearing no halogen ligand, and hence incapable of ionization [10]. Yet, surprisingly, under mild heating (refluxing chloroform) **7** undergoes a skeletal rearrangement to form the tricyclic **8**, which is very similar to the siliconium-ion rearrangement (eq. 5). However, no anionic catalysis is present in this case! Therefore, it must be concluded that the strained

four-membered ring cleaves upon heating, either heterolytically to form an ion-pair, which subsequently abstracts an α-proton and rearranges in analogy with the siliconium ions (eq. 4), or homolytically, to form a diradical, which reacts in much the same way to abstract an α-hydrogen atom followed by the internal condensation.

$$X = Me, C_6H_{11}$$
$$R = Me, Ph, CF_3$$

(4)

$$R = Me, R^1 = H$$
$$R = Ph, R^1 = Me$$

7a, R = Me, R^1 = H   **8a**, R = Me, R^1 = H
7b, R = Ph, R^1 = Me   **8b**, R = Ph, R^1 = Me

(5)

The evidence for such a mechanism is first of all in the product structure (Fig. 6), where clearly the silacyclobutane ring has opened and transformed to an *n*-propyl group, after abstraction of a hydrogen cation or radical.
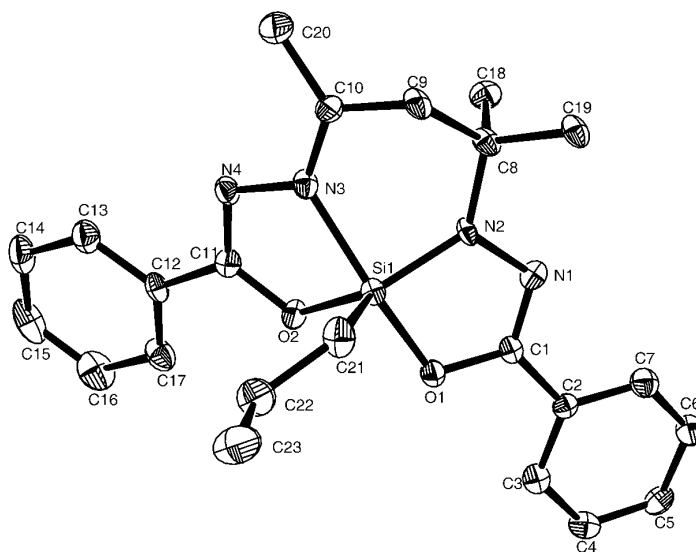

Fig. 6 Molecular structure of **10a** in the crystal, depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

This reaction can be avoided in the absence of α-protons. Indeed, it takes an entirely different path when the benzaldehyde-imine silacyclobutane complexes **9a** and **9b** are heated in boiling chloroform: in the absence of the essential α-protons, the carbanion presumably formed initially (or radical) adds directly to the imino double bond, with formation of a new chelate ring (**10**, eq. 6) [10].
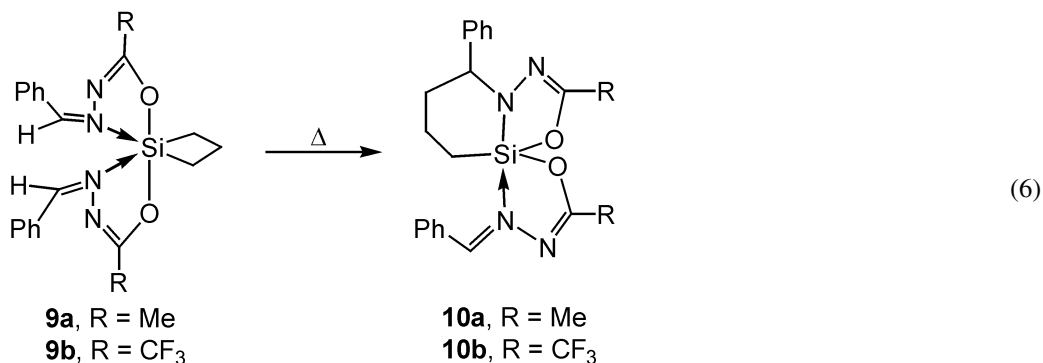
(6)

9a, R = Me
9b, R = CF$_3$

10a, R = Me
10b, R = CF$_3$

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