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COORDINATIVE INTERACTIONS IN CHELATED COMPLEXES OF SILICON

XII *. MAPPING THE EXPANSION OF COORDINATION OF SILICON FROM 4 TO 5. CRYSTAL STRUCTURE OF 1,2,3,4-TETRAHYDRO-1-TRIMETHYLSILYL-1,10-PHENANTHROLINE

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Summary

Determination of the crystal structure of 1,2,3,4-tetrahydro-1-trimethylsilyl-1,10-phenanthroline has shown that coordination geometry at silicon may be regarded as a strongly distorted trigonal bipyramid or as a distorted tetrahedron, depending on where the boundary between bonded and non-bonded interactions is fixed. An intramolecular Si...N Lewis acid base interaction (2.689(8) Å) is present; the Si...N distance is 54% longer than the Si–N "single bond" (1.746(8) Å) in the molecule. The structural details for the title compound and other pentacoordinated silicon complexes are used as a base for mapping the expansion of coordination at silicon from four to five. The correlation diagrams are interpreted in terms of geometrical transformations along the S_N2 inversion pathway. They provide a possible model for the molecular motions of dynamic rearrangements involving an intermediate alteration of coordination number (5 → 4 → 5) at Si in chelated complexes of pentacoordinate silicon.

Introduction

Experimental studies of detailed structural changes accompanying a chemical transformation may be performed at various levels. The precise crystal structures of starting material and product may give indications of how the structural changes during a chemical reaction might proceed and at least help to reduce the number of possible mechanisms to be discussed [2]. More detailed conclusions can often be

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* For part XI see ref. 1.

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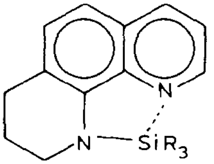
deduced for reactions taking place in the solid state, where the possible molecular motions are rather limited because of the crystal packing (e.g. topochemical solid state polymerization [3], photochemical reactions such as (2 + 2)cyclodimerizations [4], linkage isomerizations [5], solid state racemizations [6], formation of intercalated compounds by diffusion [7]).

For many reactions a number of intermediates are involved along the reaction pathway. These intermediates can sometimes be trapped, crystallized, and investigated by X-ray structure determination, and help to reduce the number of mechanistic possibilities (e.g. studies on intermediates in Wittig [8] and Friedel–Crafts reaction [9], transition metal complexes formed in homogenous catalysis [10]). However, isolable intermediates are often kinetically inactive, stable, and relatively long-lived, and special care is needed to confirm that product formation really does involve these intermediates.

The starting materials as well as the intermediates undergo considerable structural changes on their way to the top of the potential barrier (transition state) separating them from the product states. Such changes may be analysed by using the principle of structural correlation [11–13]. This method is an attempt to derive detailed structural information on a particular reaction pathway from a set of closely related crystal structures. These structures have to be arranged in the right sequence and are regarded as snapshots of frozen-in situations along the reaction pathway.

This paper presents the structure of 1,2,3,4-tetrahydro-1-trimethylsilyl-1,10-phenanthroline (**1a**), in which the Si is found to be intermediate between four- and five-coordination. The results are discussed on the background of crystal structure data for 45 independent molecular fragments containing pentacoordinated silicon. The full set of 46 structures was analysed to obtain information on the geometric changes which occur on going from tetrahedral to trigonal bipyramidal coordination. The results can be interpreted in terms of an S_N2 substitution pathway with inversion of configuration. In addition, a model of molecular motions has been derived to account for the dynamic rearrangements observed by NMR spectroscopy for the chelate complexes (**1a**–**1f**).



(**1a**: $SiR_3 = SiMe_3$;
1b: $SiR_3 = SiMe_2Cl$;
1c: $SiR_3 = SiMeCl_2$;
1d: $SiR_3 = SiCl_3$;
1e: $SiR_3 = SiF_3$;
1f: $SiR_3 = SiClF_2$)

Experimental

Compound **1a** was prepared as described previously [14]. It was initially obtained as an oil, but crystals (m.p. 48°C) were produced from a saturated solution in chloroform at temperatures near the freezing point of the solvent.

Because of their sensitivity to moisture, the crystals were handled under dried argon and sealed in glass capillaries. The space group was determined by film methods to be $P2_1/c$. The lattice parameters were refined from the angular settings of 25 strong reflections on a Philips PW1100 diffractometer and found to be: a 10.369(10), b 11.385(8), c 12.692(7) Å; β 103.91(11); $Z = 4$, V 1454.4(47) Å^3. Data

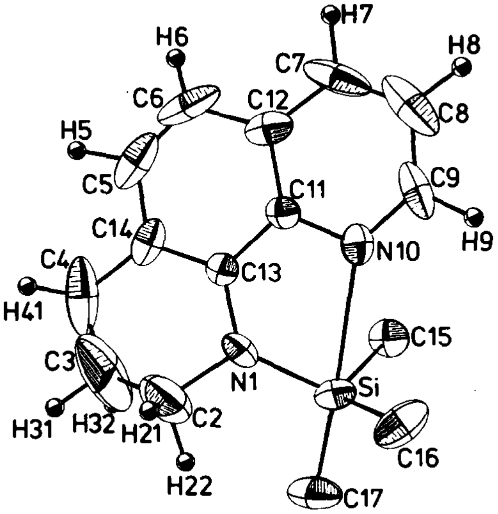


Fig. 1. ORTEP drawing of the molecular structure of **1a**; the thermal ellipsoids are the 20% probability surfaces, H-atoms as spheres, arbitrarily scaled.

were collected at room temperature up to sin θ/λ 0.459 Å^{-1} with graphite-monochromated Cu-K_α radiation in the ω-scan mode, resulting in 3405 reflections. Three standard reflections monitored at regular intervals showed a continuous decrease in intensity due to partial fusion of the crystal. The effect was corrected for by applying a linear scale factor depending on the reflection serial number. Data were not corrected for absorption (μ 11.96 cm^{-1}). After application of background correction (cf. SDP-System [15]) and averaging over symmetry equivalent observations a set of 990 unique reflections remained for structure determination.

A suitable model was found by direct methods using MULTAN [16]. It was refined by least-squares procedures to a final $R(F) = 0.079$, with anisotropic temperature factors for all non-hydrogen atoms. The positional parameters of the H atoms bound to the ring system were calculated and included in the structure model with fixed overall temperature factors. For all refinements the XRAY 76 system of programs was used.

Discussion of the crystal structure of 1a

The fractional coordinates of the atoms in **1a**, the interatomic distances (Å) and bond angles (°) are given in Tables 2, 3 and 4 using the numbering scheme of Fig. 1.

The silicon atom may be regarded as the center of a strongly distorted trigonal bipyramid, provided that the "pyridine" nitrogen situated at a distance of 2.689(8) Å from silicon is included in the inner coordination sphere. If N(10) is excluded the arrangement around Si can be described in terms of a strongly distorted tetrahedron. The Si–N(1), single bond and the three Si–C bonds to the methyl-carbon atoms are only slightly lengthened compared to Si–N or Si–C standard bond lengths for tetrahedral centers [17] (Tab. 1, 3; for estimation of appropriate standard bond lengths see below). The distance between Si and N(10) is more than 50% longer than the Si–N(1) bond or the corresponding reference value of 1.720(5) Å for four-coordinate silicon. The "pure" Van der Waals distance between these atoms was estimated

TABLE 1

STANDARD BOND LENGTHS TO Si (for $CN = 3,4,5,6$) DERIVED BY LEAST-SQUARES ANALYSIS OF EXPERIMENTAL DATA, EMPLOYING THE BOND STRENGTH/BOND LENGTH RELATIONSHIP $n_i/n_0 = \exp(-(d_i - d_{i(0)})/c)$ (a) AND $n_i/n_0 = (d_i/d_{i(0)})^{-N}$ (b)

	$CN = 3$	$CN = 4$	$CN = 5$	$CN = 6$	
Si–C	1.741(1)	1.872(1)	1.973(1)	2.056(1)	(a)
	1.742(1)	1.872(1)	1.979(1)	2.071(1)	(b)
Si–N	1.590(5)	1.721(5)	1.823(5)	1.906(5)	(a)
	1.599(4)	1.718(4)	1.817(4)	1.901(4)	(b)
Si–O	1.479(4)	1.610(4)	1.711(4)	1.794(4)	(b)
	1.502(4)	1.613(4)	1.706(4)	1.785(4)	(b)
Si–F	1.369(6)	1.500(6)	1.602(6)	1.685(6)	(a)
	1.415(5)	1.520(5)	1.607(5)	1.682(5)	(b)
Si–Si	2.260(11)	2.391(11)	2.492(11)	2.576(11)	(a)
	2.226(15)	2.391(15)	2.528(15)	2.645(15)	(b)
Si–Cl	1.895(7)	2.026(7)	2.128(7)	2.211(7)	(a)
	1.881(8)	2.022(8)	2.137(8)	2.236(8)	(b)

by Bondi as 3.65 Å [20] and by Pauling as 3.47 Å [18]. Dräger considered a value of 2.72 Å as "minimal non-bonded approach" between Si and N [21]. Glidewell calculated a value of 2.69 Å as "minimal non-bonded distance" by analysing X...Y distances in non-linear X–M–Y fragments [22]. In the light of this set of numbers, the Si–N(10) distance in **1a** could be considered as being close to the boundary

TABLE 2

FRACTIONAL COORDINATES AND THE ARITHMETIC MEAN OF THE THERMAL ELLIPSOIDS PROJECTED ON THE PRINCIPAL AXIS OF **1a** (estimated standard deviations in parentheses, positions of hydrogens were calculated)

Atom	x/a	y/b	z/c	U_{eq}
Si	0.3762(2)	0.8374(3)	0.2023(2)	0.083(2)
N(10)	0.1442(7)	0.8470(6)	0.0520(5)	0.082(5)
N(1)	0.2667(7)	0.9313(6)	0.2463(5)	0.083(5)
C(15)	0.3157(9)	0.6806(8)	0.1953(8)	0.097(6)
C(16)	0.4339(10)	0.8895(11)	0.0806(9)	0.127(9)
C(17)	0.5348(9)	0.8322(11)	0.3140(10)	0.146(9)
C(11)	0.0658(8)	0.8812(7)	0.1168(7)	0.067(5)
C(13)	0.1310(8)	0.9261(7)	0.2187(7)	0.063(5)
C(2)	0.315(2)	1.015(2)	0.333(1)	0.18(1)
C(3)	0.251(4)	1.031(3)	0.404(2)	0.31(3)
C(4)	0.119(3)	1.019(1)	0.394(2)	0.17(2)
C(5)	−0.077(2)	0.958(1)	0.252(2)	0.13(1)
C(6)	−0.143(1)	0.915(2)	0.160(2)	0.16(1)
C(7)	−0.122(1)	0.831(9)	−0.024(1)	0.180(9)
C(8)	−0.049(2)	0.798(1)	−0.087(1)	0.20(1)
C(9)	0.084(2)	0.809(1)	−0.0443(9)	0.13(1)
C(12)	−0.0727(8)	0.8754(7)	0.0828(9)	0.098(7)
C(14)	0.058(1)	0.9665(8)	0.2858(8)	0.090(7)

TABLE 3

SELECTED DISTANCES (Å) IN **1a**, e.s.d. IN PARENTHESES

	Distance
Si–N(10)	2.689(8)
Si–N(1)	1.746(8)
Si–C(15)	1.887(10)
Si–C(16)	1.881(13)
Si–C(17)	1.897(10)
N(10)–C(11)	1.345(12)
N(10)–C(9)	1.307(13)
N(1)–C(13)	1.367(11)
N(1)–C(2)	1.44(2)
C(11)–C(13)	1.404(11)
C(11)–C(12)	1.398(11)
C(13)–C(14)	1.347(14)

between bonded and non-bonded interactions (if such a limit can reasonably be defined at all).

In several other crystal structures long coordinative interaction to silicon were observed (Si...O: 2.832 [23], 2.800 [23], 2.613 [24a], 2.92 [24b] Å; Si...N: 2.741 [24c], 2.951 [24d], 3.021 [24e] Å). In all these cases the presence of coordinative interactions can be deduced from the angular distortions in the coordination polyhedra around silicon. In **1a** the arrangement of N(10), Si and C(17) is almost linear. N(10) and C(17) occupy the apical positions of the trigonal bipyramid, while N(1), C(15) and C(16) form the equatorial base plane. Si is shifted by 0.46 Å out of this plane, towards C(17). Its distance from the N(1)–C(15)–C(16) plane is smaller than from the planes through C(15)–C(16)–C(17) (0.69 Å), N(1)–C(16)–C(17) (0.63 Å), and N(1)–C(15)–C(17) (0.68 Å). The angles between Si and N(1), C(15), C(16)

TABLE 4

SELECTED BOND ANGLES IN DEGREES IN **1a**, e.s.d. IN PARENTHESES

Atoms	Angle (°)
N(10)–Si–N(1)	70.3(3)
N(10)–Si–C(15)	76.9(3)
N(10)–Si–C(16)	79.2(4)
N(10)–Si–C(17)	177.0(4)
N(1)–Si–C(15)	111.1(4)
N(1)–Si–C(16)	115.4(5)
N(1)–Si–C(17)	107.1(5)
C(15)–Si–C(16)	115.3(5)
C(15)–Si–C(17)	103.0(5)
C(16)–Si–C(17)	103.5(5)
Si–N(10)–C(9)	142.6(9)
C(11)–N(10)–C(9)	117.(1)
Si–N(1)–C(2)	120.8(8)
Si–N(1)–C(13)	126.9(6)
C(13)–N(1)–C(2)	111.7(9)
N(10)–C(11)–C(13)	116.2(7)
N(1)–C(13)–C(11)	119.3(8)

and C(17) deviate by up to 6° from 109.5°, in a way expected for incipient formation of a trigonal bipyramid.

The closely related halogenosilicon complexes **1b–1e** formed with the same ligand [25] show a nearly ideal trigonal bipyramidal geometry, probably due to a stronger coordinative interaction which results in a shorter Si–N(10) distance. In all halogenated derivatives a linear arrangement of N(10), Si, and halogen is found. The central atom is only slightly shifted out of the trigonal base plane towards the axial halogen atom. The lengthening of the coordinative bond is only 14–15% compared to the internal Si–N(1) "single bond". In **1b–1e** the quinoline ring system, Si and the axial halogen atoms are in a plane, whereas in **1a** Si deviates 0.69 Å from the quinoline plane. The angles and interatomic distances in the ligand skeleton are in the usual range for C–C connections in aromatic ring systems. The intermolecular contacts are in the range of Van der Waals interactions.

Since data collection was performed only 15°C below the melting point, displacement parameters of the atoms are rather high. Their magnitude and directions may be explained in terms of a pronounced libration in the molecular plane about the molecular center of mass (Fig. 1).

Detailed structural studies of the present class of chelated complexes in solution revealed dynamic equilibration processes between the three substituents at Si. They probably result from the lability of the coordinative bond [26]. The positional exchange of substituents at silicon might be achieved through rupture of the Si–N(10) bond, rotation of the intermediate tetra-coordinate silyl group, and reformation of the Si–N(10) bond. The observed energy barrier is comparable to barriers to internal rotation measured for bulky substituents in aromatic systems. The crystal structure of **1a** shows rather high and anisotropic displacement parameters for the carbon atoms in the silyl group; these probably result from several superimposed vibration modes, and it seems difficult to interpret them in terms of a libration about the Si–N(1) bond which might proceed into a rotation of the silyl group in the molten or solution phase (Fig. 2).

Mapping the valence shell expansion at silicon from tetra- to penta-coordination

Single crystal X-ray data of 46 independent molecular fragments containing pentacoordinated silicon were correlated to obtain a detailed description of the

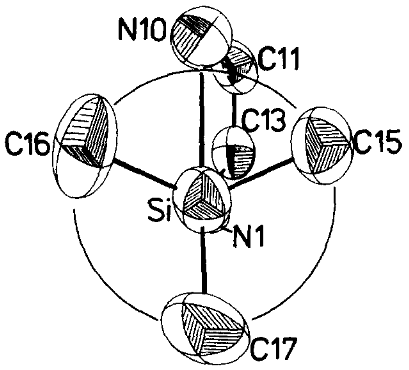


Fig. 2. ORTEP plot of the silyl substituent in **1a** viewed along the normal on the plane through the methyl carbon atoms in the silyl substituent; the thermal ellipsoids are the 50% probability surfaces.

TABLE 5

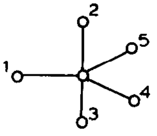
REFERENCE CODES OF THE SILICON COMPOUNDS TAKEN FROM THE CAMBRIDGE STRUCTURAL DATA BASE (CSDB) AND LITERATURE CITATION INDEX OF THE ADDITIONAL STRUCTURES USED IN THE DIAGRAM OF FIG. 3.

CSDB
BABZAF, BABZEJ, BASSET, BAZXEF, BEHVIT, BENHOR, PEPCAA, BIDSIQ, BOJLER, BOMFSI, BOMFSI1, CLMESI, CLSITR, CMSIAT, CMSIST, FMESIA, FMESIB, FSIMPI, IEOXSI, MAPPSI, MNPSIL, MSISTR, NNESIL, PNEOSI, PNEOSI2, PNEOSI11, PNPOSI, XZSIDO, ZEFWOW
Literature reference No. 23, 24a–d, 25a–c, 26, 40, 41, present paper

geometrical transformations which occur during the expansion of valence shell at silicon from tetra- to penta-coordination. Structural data were taken from the Cambridge Structural Data Base and literature (listing of reference codes and literature citation, see Tab. 5) and cast into the form of symmetry displacement coordinates, as described by Murray-Rust, Bürgi and Dunitz [27]. These coordinates are appropriate for comparing various nuclear arrangements of a certain molecular fragment that can be regarded as a distorted version of a more symmetrical structure. In the present case the D_3h-symmetrical trigonal bipyramid was taken as the reference geometry. Displacement coordinates S_1 and S_2 belonging to the irreducible representation A^{II} of D_3h are sufficient to describe the transformation from tetrahedral to trigonal-bipyramidal coordination [28]:

$$S_1 = \frac{1}{\sqrt{2}}(\Delta_2 - \Delta_3) \qquad \Delta_i = d_{\mathrm{obs}\,i} - d_{\mathrm{ref}\,i}$$

$$S_2 = \frac{1}{\sqrt{2}}(\alpha_{12} - \alpha_{13} + \alpha_{24} - \alpha_{34} + \alpha_{25} - \alpha_{35})$$



The two ligand atoms separated by the largest angle (150–180°) were assigned to the axial positions in order to obtain a consistent description of the distorted fragments. The coordinate S_1 reflects the difference between the lengthening of one axial bond and the contraction of the other. In order to compare variations in bond lengths between Si and different types of ligand atoms, standard bond lengths ($d_{\mathrm{ref}\,i}$) were subtracted from the observed distances ($d_{\mathrm{obs}\,i}$) to obtain bond increments Δ_i. The values of such standard bond lengths have a pronounced influence on the scatter in the correlation plots of S_1 versus S_2.

A consistent set of values for $d_{\mathrm{ref}\,i}$ was determined from 189 four-, five-, and six-coordinated Si compounds with as many as three different ligand atoms per compound (C, N, O, F, Si, Cl). Two empirical expressions relating bond strength (n) to bond length (d) were used: $n_i/n_0 = \exp(-(d_{\mathrm{obs}\,i} - d_{\mathrm{ref}\,i})/c)$ [18] and $n_i/n_0 = (d_{\mathrm{obs}\,i}/d_{\mathrm{ref}\,i})^{-N}$ [19]. It was assumed that the bond strengths of the individual bonds around a central atom add up to a constant independent of its coordination state. Values of standard distances $d_{\mathrm{ref}\,i}$ were refined by minimizing the expression

$$\sum_{j=1}^{189}\left(CN_0 - \sum_{i=1}^{CN} n_i\right)^2$$

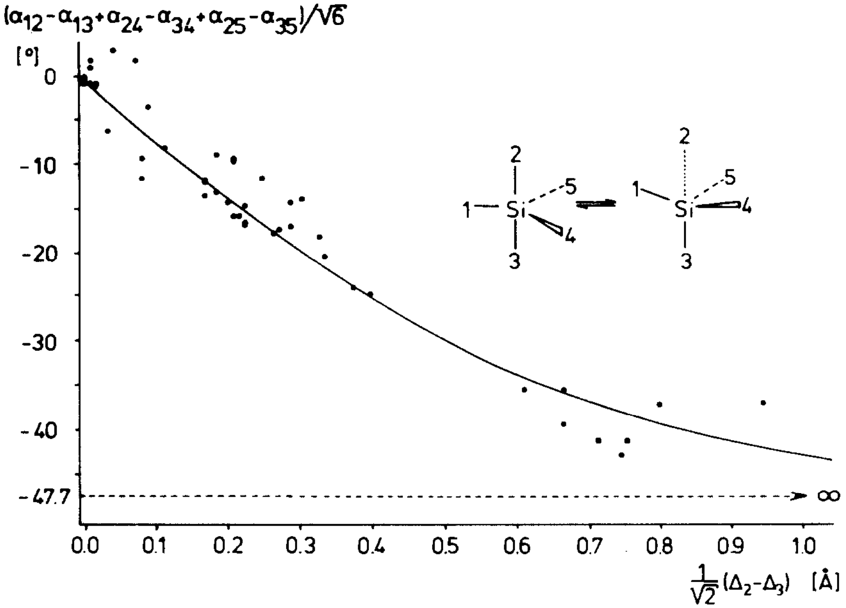


Fig. 3. Correlation of the symmetry displacement coordinates S_1 and S_2 to A_2'' of D_3h mapping the expansion of coordination state at silicon from four to five.

CN_0 is an arbitrary coordination number, CN the actual coordination number of each fragment in the data set; n_0 is taken as 1 and $d_{\text{ref}\,i}$ are the reference distances applicable to the reference coordination number CN_0 (taken as 4 in the present investigation). Reference distances for other coordination states CN are obtained from $n_i = CN/CN_0$ and the above equations (see Tab. 1).

The scatter of experimental data from the calculated regression curve in the correlation diagram (Fig. 3) is smaller if the standard bond distances (Tab. 1) are used than if other reference values, e.g. the sum of the covalent radii proposed by Pauling [18] are used.

The smooth regression curve in Fig. 3 is:

$$S_1 = \frac{c}{\sqrt{2}}\left[\ln\left(\left(3\cos\left(\frac{S_2}{\sqrt{6}}+90\right)+1\right)/2 - \ln\left(\left(-3\cos\left(\frac{S_2}{\sqrt{6}}+90\right)+1\right)/2\right)\right)\right]$$

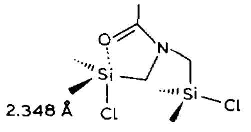
It is based on relationships given by Bürgi [28] and Dunitz [12]. A least-squares determination of the parameter c results in a value which agrees to within 3σ with that derived together with standard bond lengths to Si [17].

Correlation to the S_N2 pathway

The structural data shown in Fig. 3 represent the structural changes on going from four- to five-coordinate silicon; there is a direct analogy to the geometrical changes that occur during S_N2 displacement proceeding with inversion of configuration at tetrahedral centers. The bimolecular substitution is assumed to proceed through a trigonal-bipyramidal arrangement, with nucleophile and leaving group in axial positions.

Partial correlations for a small set of structural data on pentacoordinated silicon complexes [30–32] have been used previously to derive a relationship between the bond distances of the axial ligand and the distortions from tetrahedral geometry at Si along a substitution pathway. The results seen in Fig. 3, are analogous to those obtained by Bürgi [28], who showed that in a series of pentacoordinated Cd complexes the variations in bond lengths to the apical ligands and the angles around Cd could be related to successive situations along the pathway of nucleophilic displacement. Dunitz and Britton [29] extended these correlations to tin compounds in various crystal environments.

The fundamental assumption of the structure correlation model of Bürgi and Dunitz is to use a particular arrangement of a certain fragment found in various crystal structures which display molecular geometries at equilibrium as illustration of non-equilibrium configurations on the way to the transition state along the reaction coordinate (e.g. S_N2 reaction). Dewar and Healy [33] have presented MNDO calculations for the S_N2 reaction pathway; for carbon (alkyl halide + halide anion) the results show that the "intermediate" in the S_N2 reaction is a transition state at a saddle point and not a stable intermediate at a minimum of the potential energy surface, but in the case of silicon ($R_3SiX + X^-$; X = halide, R = H, alkyl) (without taking 3*d* AO into account) there is an exothermic addition to silicon and the nucleophilic displacement has to be assumed to proceed through a stable reaction intermediate. The authors explain the differences between C and Si in terms of the different sizes of the two elements. The calculations are consistent with the fact that five-coordination has so far been found (e.g. in the crystal) only at silicon and not at carbon. The bond length to chlorine calculated for the intermediates in the bimolecular substitution of silicon halides compares reasonably well with the axial Si–Cl distances in the pentacoordinated **1b**–**1e** and **2** [34].



(2)

To elucidate the electron distribution around the pentacoordinated Si we performed a deformation density study on **1d** [35]. A section through the linear arrangement of the incoming "pyridine"-nitrogen, the central atom Si, and the leaving group chlorine is shown in Fig. 4. It gives an idea of the electronic distribution between the substrate, the nucleophilic center, and the atom being displaced. The "attack" of the basic center might be described by the "lone" pair of the "pyridine"-nitrogen, which is heavily deformed by the central atom.

Correlation to dynamic rearrangements in solution

As noted earlier, NMR studies in solution provide evidence for positional exchange of substituents R at silicon in **1a**–**1f** [26] through a low energy barrier (< 10 kcal/mol). This equilibration of nuclei can be performed by regular (cf. Berry pseudorotation, turnstile rotation, Fig. 5 pathway a, b) or irregular rearrangements (Fig. 5, pathway c). The two regular processes occur with conservation of pentacoordination in all steps of the isomerization. The third pathway which is most likely for the compounds under consideration, is made possible by the lability of the

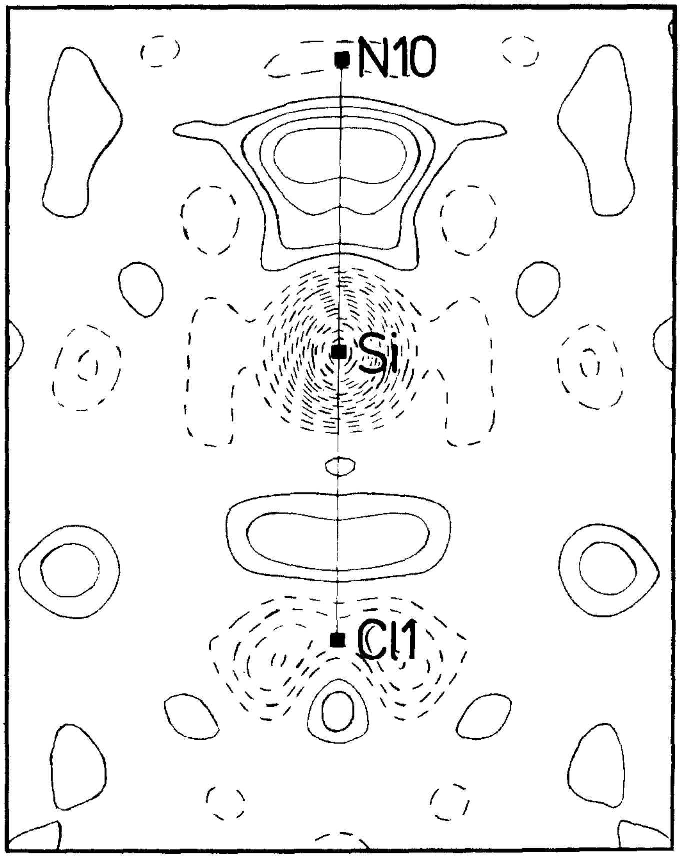
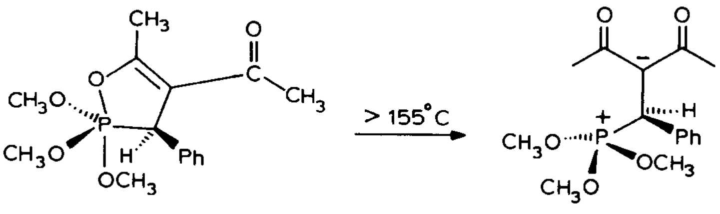


Fig. 4. Deformation density distribution in a section through the substrate (N(10)–central atom (Si)–leaving group (Cl(1)) arrangement of the trigonal bipyramidal complex **1d**. The contour interval is 0.1 e/Å^{-3}, zero contour omitted, negative contours broken.

coordinative bond. The following mechanism, which is consistent with NMR experiments [26,36] for the SiF_3 compound **1e**, can be proposed. As a first step the coordination state at silicon changes from five to four. The reaction coordinate in Fig. 3 gives an idea of how this transformation might proceed. This change of coordination is presumably followed by, or combined with, an internal jump rotation of the intermediate tetravalent SiR_3 group around the Si–N(1) bond axis. In a final step pentacoordination at Si is reestablished along a pathway which is the reverse of the initial step.

Assuming that the equilibration in solution is a first order process, line shape analysis of the NMR resonances of the exchanging nuclei gives information on the stability of an intermediate with respect to time. The DNMR properties of the monocyclic oxyphosphorane **3** [37] underlines the concurrence between irregular and regular exchanging mechanisms. In the temperature range between −70°C and room temperature the coalescence of the methoxy group indicates intramolecular isomerization, presumably through pseudorotation.



(3)

Above 155°C the NMR signals of the methyl groups α to the C–O groups also coalesce. This result is consistent with an opening and closing mechanism of the five-membered ring through a zwitterionic intermediate which rearranges through bond rotations. The choice of isomerization pathway depends on the stability of the various bonds around the central atom. Phosphorus is able to form five "stable" bonds in an uncharged complex and bond rupture occurs at temperatures well above room temperature. In the neutral silicon complexes under consideration (**1a–1f**), one

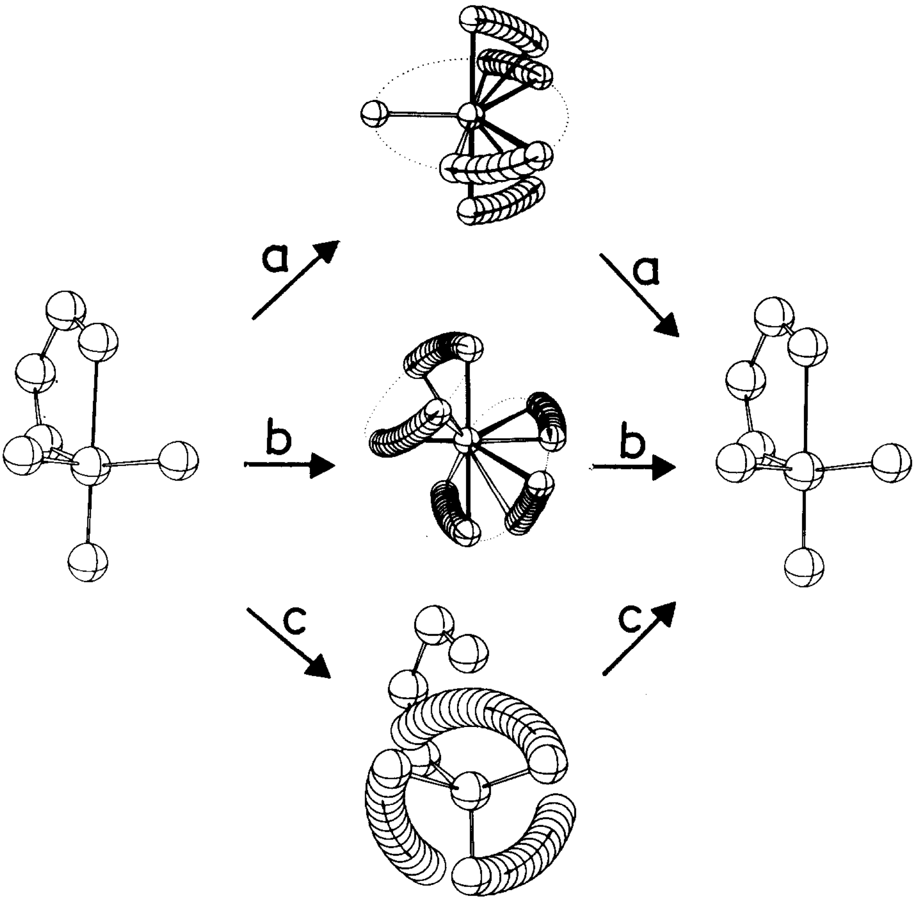
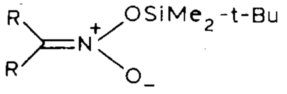


Fig. 5. Positional exchange of substituents at the trigonal bipyramid through: (a) Berry pseudorotation, (b) turnstile rotation, and (c) bond fission/bond reformation in a chelate complex.

of the five bonds, namely the "coordinative bond", is sufficiently weak so that an irregular isomerization mechanism may compete with the regular ones even at low temperatures. In anionic pentacoordinate silicon complexes with five relatively short bonds (cf. P) positional exchange of substituents was explained in several cases in terms of pseudorotation [38,39].

Colvin et al. [23] compared the dynamic behavior of trialkylsilylnitronates (**4**) in solution with the molecular structure in the crystalline state. The DNMR data provide evidence for rapid bond switching of the silyl group between the two vicinal O atoms. The energy barrier of the process, assumed to be intramolecular, is estimated to be ~ 10 kcal/mol. In the crystalline state silicon is found to be bonded to one of the two oxygens, but an interaction with the second vicinal oxygen can be deduced from marked perturbations in the coordination geometry around Si (cf. **1a**). The tetrahedral arrangement is distorted by the "incoming" oxygen towards a trigonal bipyramid (cf. S_N2 pathway with retention of configuration). The coordinative interaction is longer (2.831, 2.800 Å) than in **1a** and the deviation of the angle (153.7, 150.4°) to the two "axial" substituents from linearity is more pronounced.



(**4a**: R = Ph;
4b: R = Me)

(**4**)

The arrangement of **4a, b** can be associated with an incipient situation on the migration pathway of the silyl group. The bond switching of $SiMe_2$-t-Bu between the two vicinal O atoms is presumably performed through a pentavalent transition state. In contrast to the isomerization pathway of the chelate complexes **1b**–**1f**, which proceeds through a lower coordinated transition state, the bond switching in the silyl nitronates occurs with expansion of the coordination number at silicon (4 → 5 → 4).

Supplementary material available

Lists of anisotropic temperature factors and the observed and calculated structure factors are available from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, under the deposit number CSD-51500, together with the journal reference.

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References

1 Part XI: G. Klebe and D. Tranqui, Inorg. Chim. Acta, 81 (1984) 1.
2 K.P.C. Vollhardt and T.W. Weidman, J. Am. Chem. Soc., 105 (1983) 1676.
3 (a) R.B. Wilson, Y.S. Chen, I.C. Paul and D.Y. Curtin, J. Am. Chem. Soc., 105 (1983) 1672; (b) D. Kobelt and E.F. Paulus, Acta Cryst. B, 30 (1974) 232.

4 (a) M. Cohen, Angew. Chem., 87 (1975) 439; (b) G.M.J. Schmidt et al., D. Ginsburg (Ed.), Solid State Photochemistry, Monographs in Mod. Chem., Vol. 8, Verlag Chemie, 1976; (c) J. Trotter, Acta Cryst. B, 39 (1983) 373.

5 (a) I. Grenthe and E. Nordin, Inorg. Chem., 18 (1979) 1109; (b) I. Grenthe and E. Nordin, Inorg. Chem., 18 (1979) 1869.

6 T. Kurihara, Y. Ohashi, Y. Sasada and Y. Ohgo, Acta Cryst. B, 39 (1983) 243.

7 (a) C. Riekel, Prog. Solid State Chem., 13 (1980) 89; (b) C. Riekel and E.O. Fischer, J. Solid State Chem., 29 (1979) 181.

8 G. Chioccola and J.J. Galy, J. Chem. Soc. A, (1968) 568.

9 S.E. Rasmussen and N.C. Broch, J. Chem. Soc., Chem. Comm., (1965) 298.

10 (a) O.S. Mills and G. Robinson, Proc. Chem. Soc., 187 (1964); (b) K. Miki, Y. Kai, N. Kasai and H. Kurosawa, J. Am. Chem. Soc., 105 (1983) 2482.

11 H.B. Bürgi, Angew. Chem., 87 (1975) 461.

12 J.D. Dunitz X-ray Analysis and the Structure of Organic Molecules, Cornell University Press, Ithaca, N.Y., 1979.

13 H.B. Bürgi and J.D. Dunitz, Acc. Chem. Res., 16 (1983) 153.

14 Part I: K. Hensen and G. Klebe, J. Organomet. Chem., 209 (1981) 17.

15 Structure-Determination-Package, Enraf–Nonius, Delft, The Netherlands.

16 P. Main, L. Lessinger, M.M. Woolfson, G. Germain and J.P. Declercq, MULTAN, a Computer Program for the Automatic Solution of Crystal Structures, Version 1977 and 1980, Univ. York.

17 G. Klebe and H.B. Bürgi, Abstract to the IUCr-Meeting, 1984, Hamburg.

18 L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, N.Y. 1960.

19 (a) G. Donnay and R. Allmann, Amer. Mineral., 55 (1970) 1003; (b) I.D. Brown and R.D. Shannon, Acta Cryst A, 29 (1973) 266.

20 A. Bondi, J. Phys. Chem., 68 (1964) 441.

21 M. Dräger, Z. Anorg. Allg. Chem., 423 (1976) 53.

22 C. Glidewell, Inorg. Chim. Acta, 12 (1975) 219.

23 E.W. Colvin, A.K. Beck, B. Bastani, D. Seebach, Y. Kai and J.D. Dunitz, Helv. Chim. Acta, 63 (1980) 697.

24 (a) F.P. Boer and F.P. Remoortere, J. Am. Chem. Soc., 92 (1970) 801; (b) U. Schubert and M. Wiener, F.H. Köhler, Chem. Ber., 112 (1979) 708; (c) M. Veith, Acta Cryst. B, 31 (1975) 678; (d) W.F. Paton, E.R. Corey, J.Y. Corey and M.D. Glick, Acta Cryst. B, 33 (1977) 3322; (e) W.F. Paton, E.R. Corey, J.Y. Corey and M.D. Glick, Acta Cryst. B, 33 (1977) 226.

25 (a) Part III: G. Klebe, J.W. Bats and K. Hensen, Z. Naturforsch. B, 38 (1983) 825; (b) Part IV: G. Klebe, K. Hensen and H. Fuess, Chem. Ber., 116 (1983) 3125; (c) Part V: G. Klebe, J.W. Bats and K. Hensen, J. Chem. Soc., Dalton Trans., (1985) 1.

26 Part IX: G. Klebe, M. Nix and K. Hensen, Chem. Ber., 117 (1984) 797.

27 P. Murray-Rust, H.B. Bürgi and J.D. Dunitz, Acta Cryst. A, 35 (1979) 703.

28 H.B. Bürgi, Inorg. Chem., 12 (1973) 2321.

29 D. Britton and J.D. Dunitz, J. Am. Chem. Soc., 103 (1981) 2971.

30 M.J. Barrow, E.A.V. Ebsworth and M.M. Harding, J. Chem. Soc., Dalton Trans., 1838 (1980).

31 V.A. Pestunovich, V.F. Sidorkin, O.B. Dogaev and M.G. Voronkov, Dokl. Akad. Nauk SSR, 251 (1980) 1440.

32 F. Liebau, Inorg. Chim. Acta, in press.

33 M.J.S. Dewar and E. Healy, Organometallics 1 (1982) 1705.

34 K.D. Onan, A.T. McPhail, C.H. Yoder and R.W. Hillyard, J. Chem. Soc., Chem. Comm., 209 (1978).

35 G. Klebe, J.W. Bats and H. Fuess, J. Am. Chem. Soc., 106 (1984) 5202.

36 G. Klebe and K. Hensen, J. Chem. Soc., Dalton Trans., (1984) 5.

37 R.R. Holmes, Pentacoordinated Phosphorus, Univ. Mass., Am. Chem. Soc., Wash. D.C., 1980.

38 W.B. Farnham and R.L. Harlow, J. Am. Chem. Soc., 103 (1981) 4608.

39 F. Klangberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.

40 P. Bird, J.F. Harrod and K.A. Than, J. Am. Chem. Soc., 96 (1974) 1222.

41 A.J. Blake, E.A.V. Ebsworth, A.J. Welch, Acta Cryst. C, 40 (1984) 895.