Four independent structures of a pentacoordinate silicon species at different points on the Berry pseudorotation pathway†

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A new pentacoordinate silicon species containing two chelating ligands has been synthesized. The structures of four independent cations of the same compound correspond to different points on the Berry pseudorotation pathway. The percentage of square planar character varies between 19% and 40%.

As a consequence of their structural and dynamic diversity pentacoordinate silicon compounds are of great current interest.[1–7] There are two particularly challenging aspects to the chemistry of pentacoordinate silicon: their use as transition state and intermediate models in the commercially and academically important nucleophilic substitution reactions at tetracoordinate silicon;[8–13] and the study of their stereochemical non-rigidity.[1,7,14,15]

The stereochemical non-rigidity of pentacoordinate compounds and the mechanism of stereomutation can frequently be related to the X-ray crystal structures of a series of closely related compounds. Muetterties and Guggenberger[16] were the first to relate the Berry pseudorotation pathway to the structures of real molecules in a quantitative manner. One Berry pseudorotation with the limiting Berry structures of trigonal bipyramid (TBP) and square pyramid (SP) is shown in Fig. 1.

Holmes,[17,18] with particular reference to a large series of pentacoordinate phosphorus compounds, extended and refined the quantitative approach to the correlation of measured structures with points on the Berry pseudorotation pathway. In particular he demonstrated that for any pentacoordinate species the sums of a set of dihedral angles formed by the normals to adjacent polytopal faces may be used to quantify the extent to which related structures lie on the Berry or turnstile processes.

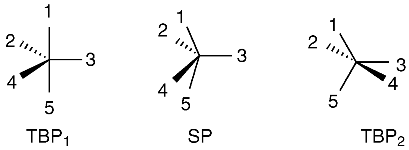

Fig. 1 One Berry pseudorotation of a trigonal pyramidal complex *via* a square pyramid resulting in permutational ligand exchange.

In a landmark paper Corriu *et al.*[19] demonstrated unambiguously that pentacoordinate silicon compounds can undergo stereomutation by pseudorotation. Martin and co-workers[20] were the first to study the pseudorotation of some pentacoordinate siliconates and relate the structures of the anions to positions on the pseudorotation pathway using dihedral angle methods. Most pentacoordinate silicon structures, using one or another dihedral angle method[18] whether neutral,[1a] zwitterionic,[1b] anionic,[1c,7,15,21] or cationic[1a] appear to lie on the TBP–SP continuum. The TBP geometry in silicon compounds is generally very flexible with low energy differences between TBP and SP (or more generally, rectangular pyramid RP) structures.[1a,b,21] There is a small number of cases where a single pentacoordinate silicon species shows two different forms in a single crystal with slightly different geometries[7] as is the case with a pair of siliconates in which all five atoms attached to the silicon atom are carbon atoms. Martin observed two forms of a fluorosiliconate with 23.2% and 31.6% RP character[20] as calculated by the δ_{24} method.[18] The most spectacular difference in structure for independent forms of a pentacoordinate silicon species was reported by Tacke and co-workers[1b,22] and is for a zwitterionic molecule with four forms with distortions of 34.9, 70, 86.2 and 96.3% along the Berry pathway. The first two forms are polymorphs from separate crystals and the second two are found in a third crystal form in which the two crystallographically independent zwitterions in the unit cell are each hydrogen bonded to one water molecule.

Our previous work on mapping nucleophilic substitution reported the use of coordinated pyridones as tuneable ligands in which the electronic environment at silicon can be varied without changing the particular set of atoms in the silicon coordination sphere.[8–10] For example in a series of compounds shown in Fig. 2[10] the percentage O–Si bond formation with the leaving group X = Cl varies from 40 (Y = 3-NO$_2$) to 70%

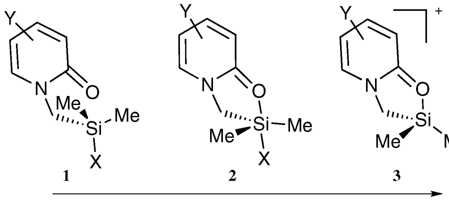

Fig. 2 S$_N$2 profile where the carbonyl O is the nucleophile and X is the nucleofuge.

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† Electronic supplementary information (ESI) available: Synthesis, characterisation and X-ray crystallographic data. CCDC 757287 (**4a**) and 757286 (**4b–d**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000803f

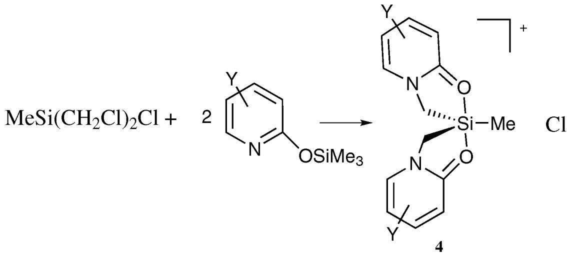

Fig. 3 The synthesis of a new class of pentacoordinate ions containing two pyridone 'responsive ligands'.

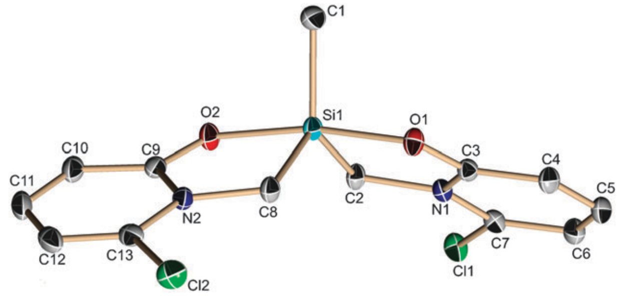

Fig. 4 ORTEP drawing of the cation in crystal structure of **4a** (Y = 6-Cl) with the thermal ellipsoids shown at the 50% probability level. For clarity, one non-coordinating molecule of water and one non-coordinating molecule of ligand, 6-chloropyridone, in the unit cell have been removed from the figure.

(Y = 6-Me), while at the same time the configuration at the silicon atom inverts from a structure on the **1–2** continuum with 80% TBP character through a 100% TBP (**2**) (where Y = H) to a structure on the **2–3** continuum with 81% TBP character. So by varying only the substituent, Y, on the aromatic ring approximately 40% of the S_N2 profile is modelled by a closely related series of compounds. Similarly the X may be varied and a similar S_N2 profile was observed in both the solid state and in solution.[8]

In this work we introduce the use of a related tuneable ligand to examine the effect of electronic changes at a silicon atom with two pyridone ligands. The reaction shown in Fig. 3 could potentially have given either the pentacoordinate ion or the neutral hexacoordinate structure in which there is a covalent Si–Cl bond. Kost and Kalikhman[1] have observed both types of structure in similar, but not identical, series of compounds. They also observed interconversion between the two differently coordinated structures as parameters such as temperature were varied. In all of the examples we have studied only pentacoordinate ions of type **4** have been observed in the solid state and in solution at all available temperatures.

The compound that is the main subject of this communication, the 6-Cl derivative of **4** has a temperature independent ^{29}Si NMR solution shift of $\delta = -48$ ppm in $CDCl_3$ between −70 and +50 °C by contrast with some of the ions reported by Kost and Kalikhman.[1] The lack of silicon chlorine bonding, or indeed interaction, is shown by the Si···Cl distance of 410 pm or more, compared with a typical Si–Cl bonding distance in pentacoordinate silicon compounds of about 191–230 pm. Other compounds of type **4** have been synthesised and the effect of variations in the nature of the substituent Y on their structures and dynamics are currently being evaluated.

The crystal structures of two salts containing cation **4** (Y = 6-Cl) have been determined by single crystal X-ray diffraction.[23] In one crystal there is only one form of **4** (Y = 6-Cl) in the unit cell (**4a**) (Fig. 4) whereas in the other there are three independent structures of **4** (Y = 6-Cl) (**4b–d**) each with widely different geometrical parameters. Strictly, these salts are not polymorphs[24] as the composition of each crystal is slightly different. The crystal with three different structures of the pentacoordinate ion also has in the independent part of the unit cell two H_3O^+ cations, not hydrogen

Table 1 Structural parameters for compounds **4a–d** as determined by X-ray crystallography and calculation of percentage SP for each independent structure. More detailed information, in particular standard deviations for bonds and angles can be found in the ESI†

	TBP (ideal)	**4a** (Y = 6-Cl)	**4b** (Y = 6-Cl)	**4c** (Y = 6-Cl)	**4d** (Y = 6-Cl)	SP (ideal)
Bond lengths/pm						
Si–O		184, 187	185, 187	185, 186	185, 186	
Si–C (endocyclic)		189, 189	189, 189	189, 189	188, 191	
Si–C(Me)		184.7	186.1	185.3	184.2	
Bond angles/°						
O–Si–O/°, θ_{15}	180	169	169.3	167.1	165.7	151
C–Si–C/°, θ_{24}	120	122.7	125.7	128.6	132.7	151
δ_{24}	53.1	43.1	40.8	36.6	32.1	0
%SP	0	19	23	31	40	100
O–Si–C (endocyclic)	90	86.4, 85.3	86.5, 85.6	86.2, 85.9	85.7, 85.2	86
O–Si–C (exocyclic)	90	89.4, 88.3	89.8, 88.4	89.9, 87.0	89.1, 88.5	86
O–Si–Me θ_{13},θ_{35}	90, 90	95.3, 95.4	95.2, 95.4	96.9, 96.0	97.1, 97.2	105, 105
Average (OSiMe)	90	95.35	95.3	96.45	97.15	105
C–Si–Me θ_{32}, θ_{34}	120, 120	119.8, 117.4	117.8, 116.4	119.3, 112	115.0, 112.3	105, 105
Average (CSiMe)	120	118.6	117.1	115.7	113.7	105
ΔAv/°	30	23.25	21.8	19.2	16.5	0
%SP	0	22.5	27.3	35.8	44.8	100
$\sum_i\lvert\delta_i(C) - \delta_i(TBP)\rvert$		41.4	53	76.2	85	
$217.7 - \sum_i \lvert\delta_i(C) - \delta_i(SP)\rvert$		41.4	53	76.2	85	
%SP^a	0	19	24	34.9	40	100

Δ [°], the difference between angles θ_{15} and θ_{24} (for ligand numbering see Fig. 1: ligand 3, Me, is the pivot ligand); that is 60° for an ideal TBP and 0° in an ideal SP. ΔAv [°], the difference between average angles θ_{32}, θ_{34} and θ_{13}, θ_{35} that is 30° for an ideal TBP and 0° for an ideal SP. [a] Muetterties/Holmes method (ref. 16 and 17).

bonded to the cation, and a free pyridone ligand, together with five chloride anions. The crystal with only one ion, **4a** has one water molecule, one neutral pyridone ligand and one chloride ion in the unit cell. The results are discussed below.

The important structural parameters for **4a–d** are shown in Table 1. The bond lengths in **4a–d** are almost invariant from one to another structure. There are a number of bond angles and dihedral angles associated with the change from TBP to SP along the Berry pseudorotation profile. The bond angles θ_{15} and θ_{24} are the angles O1–Si–O5 and C2–Si–C4 respectively (see Fig. 1 for ligand numbering; the pivot ligand, Me, is labelled 3). The angle θ_{15} is the angle between axial ligands in the trigonal bipyramid form, where it is 180° and 151° in a square pyramid. The angle θ_{24} is the angle between the non-pivot equatorial ligands in the trigonal bipyramid form where it is 120° and again it is 151° in a square pyramid. For structures on the Berry pseudorotation pathway the angle will be intermediate between the two limiting values. Measuring the value of the difference between θ_{15} and θ_{24} allows the estimation of the percentage SP character for each structure.[17] As calculated by this method, the percentage SP character varies between 22.5% for **4a** and 44.8% for **4d**. A similar set of values was obtained by measuring the differences between the average values of θ_{32} and θ_{34} and θ_{13} and θ_{35}. The Holmes dihedral angle method gives values varying between 19% for **4a** and 40% for **4d** (Table 1).

Holmes reported that the definitive method for determining whether a series of related molecular structures, C, lie on the Berry pathway is to compare each dihedral angle, δ_i, for a particular structure, with those of the corresponding TBP and SP structures. The dihedral angle is that formed between normals to the TBP faces sharing a common edge. If the quantities $\sum_i |\delta_i(\mathrm{C}) - \delta_i(\mathrm{TBP})|$ and $217.7 - \sum_i |\delta_i(\mathrm{C}) - \delta_i(\mathrm{SP})|$ are found to be the same then the various structures are on the TBP–SP Berry pseudorotation pathway.[16–18] These two quantities are identical for each of the structures **4a–d** (Table 1) showing that the four independent structures represent different points on an evolving Berry pseudorotation. The percentages SP for each structure using this extended dihedral angle method are 19, 24, 35 and 40%, respectively, for **4a**, **4b**, **4c** and **4d**. The more comprehensive dihedral angle methods give slightly lower values for the extent of SP formation than the bond angle methods.[17] However, the degree of agreement between all of the various methods for estimating TBP/SP character is exceptionally good.

There is no obvious reason beyond crystal packing forces why in one unit cell there should be three independent structures of the same molecule. It has been recognised for some time that pentacoordinate structures are particularly easily deformed.[1b,21] The four structures described here are outstanding in illustrating that, when put under even the small physical constraints involved in efficiently packing a molecule in a crystal, pentacoordinate silicon compounds deform along the lowest energy pathway—the Berry pseudorotation pathway.

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23 Crystal data for **4a**. Crystals of $C_{18}H_{19}Cl_4N_3O_4Si$ are monoclinic, space group $P2_1/n$, a = 7.6414(8) Å, b = 21.915(2) Å, c = 12.8697(14) Å, β = 96.267(2)° V = 2142.3(4) Å^3, Z = 4, M = 511.25. 26 805 reflections were measured at 100 K, 6212 independent reflections were used (R_{int} = 0.0325). The refinement converged to wR_2 = 0.0958 and GOF = 1.014 for all independent reflections [R_1 = 0.0374 for 5481 observed reflections with $I > 2\sigma(I)$]. CCDC number: 757287. Crystal data for **4b–d**. Crystals of $C_{44}H_{49}Cl_{12}N_7O_9$-$Si_3$ are triclinic, space group $P\bar{1}$, a = 13.549(5) Å, b = 15.753(6) Å, c = 16.005(7) Å, α = 67.998(8)°, β = 74.146(9)°, γ = 66.783(7)°, V = 2879(2) Å^3, Z = 6 (Z' = 2), M = 1329.57. 12 463 reflections were measured at 100 K, 12 355 independent reflections were used (R_{int} = 0.01). The refinement converged to wR_2 = 0.1408 and GOF = 1.003 for all independent reflections [R_1 = 0.0536 for 9987 observed reflections with $I > 2\sigma(I)$]. CCDC number: 757286.

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