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Cocrystallising Rotamers of a Pentacoordinate Silicon Complex with a Chiral Aminodiol Ligand

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Crystal structure analysis reveals the cocrystallysation of two turnstyle rotamers of a pentacoordinate silicon complex with a chiral backbone derived from 2-amino-1,1,2-triphenylethanol. The structures of the two epimers are well reproduced by DFT calculations. In addition, the coexistence of

Introduction

Stereomutation at pentavalent centres has been studied most intensively for phosphorus adopting a trigonal-bipyramidal geometry.^[1] Among the different mechanisms that have been postulated in order to rationalise this phenomenon^[2] the Berry pseudorotation,^[3] Ugi's turnstile path^[4] and permutation mechanisms proposed by Muetterties^[5] became valuable concepts. In pentacoordinate silicon complexes,^[6] which have been investigated only to a minor extent, analogous stereomutation processes apply in many cases.^[7] As an alternative path of stereomutation, consecutive fission and formation of a coordinate bond has been taken into account in the case of silicon complexes.^[8] The incorporation of two pseudorotamers in a single crystal was reported in the case of phosphoranes,^[9] but to the be best of our knowledge cocrystallising rotamers of pentacoordinate silicon complexes have not so far been reported.

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two rotamers, which readily interconvert in solution, is confirmed by their solid-state NMR spectroscopic data. Possible mechanisms of their interconversion are discussed, and preference is given to a turnstile-like rotation of three ligands at the silicon atom about 120°.

In this article, the synthesis of a pentacoordinate silicon complex with an amine backbone derived from enantiomerically pure 2-amino-1,1,2-triphenylethanol is described. The crystal structure reveals the first cocrystallisation of rotamers at silicon. For reasons of confirmation, their structures were calculated, and the crystallographic study is supported by solid-state NMR spectroscopic measurements.

Results and Discussion

After penta- and hexacoordinate silicon complexes of O,N,O-ligands with an imine moiety had been described recently,^[10,11] access to the amine counterpart was striven for. Thus, the imine 1, readily available from a condensation of 1-formyl-2-naphthol with (R)-2-amino-1,1,2-triphenylethanol, was reduced with cyanoborohydride to give the aminodiol ligand 2, which was isolated as the hydrochloride.^[12] In order to avoid decomposition, which was observed during storage, the crude product 2 was immediately treated with dichlorodiphenylsilane in the presence of triethylamine to give the silicon complex 3 (Scheme 1), which was obtained as a crystalline trichloromethane solvate. The NMR spectra (¹H, ¹³C, ²⁹Si) measured in CDCl₃ not only at ambient temperature but also at -30 °C point to the existence of a single species. The silicon resonance (δ = -82.7 ppm) indicates pentacoordination.^[10]

The molecular structure, shown in Figure 1, surprisingly revealed the coexistence of two epimers in a 1:1 ratio, both of which feature a distorted trigonal-bipyramidal structure. The *TB*-5-34-*A* configuration (anticlockwise) was assigned to diastereomer **3a**, whereas **3b** adopts a *TB*-5-34-*C* (clockwise) configuration.^[13] The selected bond lengths given in Figure 1, in particular the Si–O and Si–N distances, differ significantly in both epimers. The configuration at the ni-





Scheme 1. Synthesis of the pentacoordinate silicon complex 3. Reagents and conditions: (a) ref.^[12]; (b) Cl_2SiPh_2 , Et_3N , CH_2Cl_2 , -78 to +20 °C, 15 h; 49%.

trogen atom (*S*) that becomes stereogenic in the course of the complexation is identical in both **3a** and **3b**. The geometries of both epimers observed in the crystal structure of **1** were well reproduced by density functional calculations and confirm the structure of a distorted trigonal bipyramid (Figure 1 vs. Figure 2). A comparison of selected experimental and calculated bond parameters is presented in Table 1. According to the calculations, both diastereomers are very close in energy with $\Delta H < 1 \text{ kJ mol}^{-1} [\Delta G(25 \text{ °C})$ $< 2 \text{ kJ mol}^{-1}].$

It is evident that the epimers **3a** and **3b** originate from a stereomutation at silicon. This interconversion may proceed, as depicted in Figure 2, by means of a 120° cyclic permutation, thus following one of the mechanisms postulated by Muetterties.^[5] In the course of this cyclic permutation, one axial and one equatorial position are kept fixed, whereas the remaining three substituents rotate about 120°.^[14] An alternative isomerisation pathway is composed of two consecutive Berry pseudorotations as shown in Scheme S1 in the Supporting Information. This isomerisation sequence would result in a trigonal bipyramid with both oxygen atoms in axial positions and the nitrogen atom in an equatorial position as intermediate between epimer 3a and 3b. Furthermore, a dissociative mechanism from temporary cleavage of the Si-N bond, a reorientation of the backbones and a reclosure of the Si-N bond could be considered. Differentiation between these different isomerisation pathways based on the results of the experimental structural data is not possible. One should take into account, however, that both the consecutive Berry pseudorotations and the dissociative pathway require severe reorientation of the backbones and will probably encounter considerable steric hindrance and repulsion. We therefore prefer, as a rationale for the interconversion of epimers 3a and **3b**, the 120° cyclic permutation as shown in Figure 2, particularly since more recent calculations have revealed the turnstile rotation^[15] as "the most viable alternative"^[14] to the Berry pseudorotation.



Figure 1. Molecular structure of complex 3a (a)/3b (b) in the crystal; displacement ellipsoids are drawn at the 25% probability level; H atoms are drawn with an arbitrary radius. Only one orientation of the disordered phenyl group containing atoms C81 to C86 is shown.

In contrast to the NMR spectra in solution, two signals are present in the solid-state ²⁹Si and ¹⁵N NMR spectra (Table 2), which is in excellent agreement with the crystal structure analysis that shows the presence of two epimers. The δ (²⁹Si) and δ (¹⁵N) values that were obtained from the study in solution are in between those from the solid-state spectra. Furthermore, the experimental chemical shifts are in good agreement with calculated δ (²⁹Si) and δ (¹⁵N) values, which enabled the assignment of both epimers **3a** and **3b**. In the solid-state ¹³C NMR spectrum, for some of the sig-





Figure 2. Possible isomerisation pathway of epimer 3a to result in epimer 3b by a 120° cyclic permutation (highlighted by red arrows) and calculated structures of both epimers [B3LYP/6-31++G(d)].

Table 1.	Comparison	of selected	experimental	and	calculated	bond	lengths	[Å]	and	angles	[°]	of	epimers	3a an	d 3b.[a]
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Parameter	Epimer 3a			Epimer 3b		
		Exptl. ^[b]	Calcd.	•	Exptl. ^[b]	Calcd.
Si–N	Si(1)–N(1)	2.105(4)	2.259	Si(2)–N(2)	2.321(4)	2.438
Si-O	Si(1)–O(2)	1.674(4)	1.701	Si(2)–O(4)	1.634(4)	1.684
Si-O2	Si(1) - O(1)	1.678(4)	1.715	Si(2)–O(3)	1.648(5)	1.691
Si-C1 _{Ph}	Si(1)–C(38)	1.837(6)	1.910	Si(2)–C(75)	1.842(6)	1.895
Si-C2 _{Ph}	Si(1)–C(32)	1.870(5)	1.890	Si(2)–C(81)	1.903(5)	1.903
(N-Si-C _{Ph.trans})ax	N(1)-Si(1)-C(38)	162.4(2)	161.0	N(2)-Si(2)-C(81)	173.7(3)	172.2
$(O1-Si-O2)_{eq}$	O(1)-Si(1)-O(2)	132.6(2)	129.6	O(3)-Si(2)-O(4)	115.7(2)	116.5
(O1-Si-C _{Ph}) _{eq}	O(2)-Si(1)-C(32)	113.6(3)	113.5	O(4)-Si(2)-C(75)	126.2(3)	123.8
(O2-Si-C _{Ph}) _{eq}	O(1)–Si(1)–C(32)	111.1(2)	111.0	O(3)-Si(2)-C(75)	110.2(3)	110.4

[a] Calculated at the B3LYP/6-31++G(d) level of theory. [b] Labelling used for the X-ray structure analysis (Figure 1).

nals, two sets are found as well. In contrast to the X-ray diffraction study that indicates equal amounts of both rotamers, in the solid state the relative intensities of the signals in the NMR spectra, which are only rough estimates because of the cross-polarisation applied during acquisition, indicate a slightly higher ratio for epimer **3a**.

Table 2. Comparison of selected experimental and calculated ²⁹ Si, ¹⁵ N and ¹⁵ C chemical	shifts of e	epimers 3a and	3b. [a,b]
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Parameter	Solution in CDCl ₃	Solid state	[c]		Calculation	n
	-	3a	3b	Ratio ^[d]	3a	3b
δ ⁽²⁹ Si)	-82.7	-88.1	-72.0	2.3:1.0	-83.0	-68.9
$\delta(^{15}N)$	n.o. ^[e]	-313.1	-326.3	1.7:1.0	-290.9	-306.2
$\delta(^{13}C)$ C-11	42.6	43.6	40.8	1.3:1.0	47.9	42.3
$\delta(^{13}C)$ C-12	67.8	83.9	78.8	1.3:1.0	74.3	74.8
$\delta(^{13}C)$ C-2	153.6	154.8	153.4	1.2:1.0	163.4	163.1

[a] Chemical shifts in ppm. [b] Calculated at the B3LYP/6-311++G(2d,p)//B3LYP/6-31++G(d) level of theory. [c] ²⁹Si VACP/MAS NMR (79.5 MHz); ¹⁵N VACP/MAS NMR (40.6 MHz); ¹³C VACP/MAS NMR (100.6 MHz); additional ¹³C NMR signals that were not assigned to either epimer: $\delta = 66.6$, 70.4, 125.0–135.7, 138.4, 143.9, 146.1, 149.0 ppm; in the²⁹Si NMR spectrum a third weak signal can be found at $\delta = -68.6$ ppm. [d] The ratio is a rough approximation, since cross-polarisation was employed during acquisition. [e] n.o. = not observed.



Conclusions

For the first time the turnstile rotamers of a pentacoordinate silicon complex have been demonstrated to cocrystallise as shown not only by a crystal structure analysis but also by a solid-state NMR spectroscopic study. Experimental and calculated data for the rotamers, which readily interconvert in solution, are in excellent agreement. A 120° turnstile rotation is assumed as the preferred path of the observed stereomutation.

Experimental Section

Synthesis

 $(R_{\rm C},S_{\rm N})$ -3,4,4,6,6-Pentaphenyl-1,2,3,4-tetrahydronaphtho[1,2-*h*]-[1,3,6,2]dioxazasilonin-Trichloromethane (3a and 3b): A 250 mL two-necked flask equipped with a magnetic stirrer and a connection to a combined nitrogen/vacuum line was charged with the amine hydrochloride 2 (482 mg, 1.00 mmol) and closed with a septum. The air in the flask was replaced by nitrogen, and dry dichloromethane (75 mL) was injected by syringe through the septum in order to dissolve the solid. The solution was cooled to -78 °C, and dichlorodiphenylsilane (0.21 mL, 1.0 mmol) and triethylamine (0.28 mL, 2.0 mmol) were added in succession by syringe. After stirring at -78 °C for 10 min, the solution was allowed to reach room temperature over 12 h and poured into water. The organic layer was separated, and the aqueous phase was extracted three times with dichloromethane (30 mL each). The combined organic layers were dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was submitted to column chromatography (silica gel; chloroform). The fractions containing the product, as indicated by TLC control, were combined and concentrated by using a rotary evaporator, while the water bath was kept at 40 °C. In the course of this, the crystalline silicon complex **3a/3b** formed, which was collected and dried. Yield: 305 mg (49%). $R_{\rm f} = 0.73$ (chloroform). M.p. 138 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.0 (br. s, 1 H), 3.70 (dd, J = 14.6, J = 6 Hz, 1 H), 3.88 (d, J = 14.2 Hz, 1 H), 4.69 (d, J = 11.9 Hz, 1 H), 6.47 (d, J = 7.4 Hz), 7.01 (t, J = 7.4 Hz, 2 H), 7.06 (d, J = 8.7 Hz, 1 H), 7.10–7.25 (m, 16 H), 7.35 (d, J = 8.9 Hz, 1 H), 7.47 (d, J = 6.9 Hz, 2 H), 7.56 (d, J = 7.2 Hz, 2 H), 7.69 (d, J = 8.5 Hz, 2 H), 7.22 (d, J = 7.2 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 42.6, 67.8, 83.2, 113.4, 121.1, 123.2, 123.5–134.3, 127.7, 129.1, 131.8, 142.3, 146.4, 153.6 ppm. MS (ESI): m/z (%) = 626 (15) [M + H]⁺, 471 (100). HRMS: calcd. for C₄₃H₃₆SiNO₂ 626.2506; found 626.2509.

Quantum Chemical Calculations: DFT calculations^[16] were carried out by using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP)^[17–19] with the Gaussian 03 program suite.^[20] Geometries were optimised, and energies were calculated with the 6-31++G(d) basis set. All structures represent true minima on the respective hypersurface (no imaginary frequency). DFT-GIAO^[21] NMR shielding constants were calculated at the B3LYP/6-311++G(2d,p) level of theory by using the geometries derived at the B3LYP/6-31++G(d) level of theory. The ¹³C and ²⁹Si NMR shielding constants were calibrated to the respective chemical shift scale by using predictions for Me₄Si with a chemical shifts of $\delta = 0$ ppm, and for the calibration of the ¹⁵N NMR shielding constants a prediction for liquid ammonia of $\delta =$ -380.3 ppm was used.

NMR Spectroscopy: 1 H, 13 C and 29 Si NMR spectra were recorded at 25 °C in CDCl₃ with a Bruker Avance DRX-500 spectrometer

operating at 500.13, 125.76, or 99.48 MHz for ¹H, ¹³C and ²⁹Si nuclei, respectively. The NMR signals were referenced against TMS (1H, 13C, 29Si) as internal standard. Solid-state 13C, 15N and 29Si VACP/MAS-NMR spectra were recorded at 22 °C with a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter 7 mm) containing approximately 100-150 mg of sample (13C, 100.15 MHz; 15N, 40.55 MHz; 29Si, 79.50 MHz). The measurements were conducted with a spinning rate of 6-7 kHz, a contact time of 2 ms (13 C), 4 ms (15 N) or 5 ms (29 Si), a 90° 1 H transmitter pulse length of 3.6 µs and a repetition time of 10 s for ²⁹Si and ¹⁵N and 6 s for ¹³C. All chemical shifts were calibrated by setting the ¹³C low-field signal of adamantane to δ = 38.48 ppm according to the IUPAC recommendations^[22] resulting in chemical shifts of $\delta = 0$ ppm for $\delta(^{13}C)$ and $\delta(^{29}Si)$ for TMS. For $\delta(^{15}N)$ glycine was applied as a secondary reference with $\delta = -342.0$ ppm with respect to MeNO₂ ($\delta = 0$ ppm).

Crystal Structure Determination for Compound 3-CHCl3: Only relatively weakly diffracting crystals of limited quality were available. Some were selected by means of a polarisation microscope and investigated with a Stoe Imaging Plate Diffraction System by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Unitcell parameters were determined by a least-squares refinement on the positions of 5968 reflections, distributed equally in reciprocal space. Metric and systematic absences were consistent with monoclinic space group types $P2_1/m$ and $P2_1$. The latter was confirmed in the course of the structure refinement. Crystal data and further details: $C_{44}H_{36}Cl_3NO_2Si$, $M_r = 745.18$, a = 18.2894(16) Å, b =11.8876(5) Å, c = 19.4153(16) Å, $\beta = 112.928(9)^\circ$, V = 3887.7(6) Å³, $Z = 4, \rho = 1.273 \text{ g cm}^{-3}, \mu = 0.304 \text{ mm}^{-1}, T = 291 \text{ K}, \text{ crystal dimen-}$ sions: $0.19 \text{ mm} \times 0.19 \text{ mm} \times 0.20 \text{ mm}$, 21362 measured, 12812 unique and 4770 observed reflections with $I > 2\sigma(I)$, $\theta_{\text{max}} = 25.00^{\circ}$, LP correction, direct methods^[23] and ΔF syntheses,^[24] minimisation of $\Sigma w (F_o^2 - F_c^2)^2$, 920 refined parameters, $(\Delta/\sigma)_{\text{max}} = 0.002$, $R_1 [F_o^2]$ $> 2\sigma(F_o^2)$] = 0.054, wR_2 = 0.085 (all data), $w = 1/\sigma^2(F_o^2)$, S = 0.854, $\Delta \rho_{max} / \Delta \rho_{min}$ +0.217 eÅ⁻³ and -0.289 e/Å³. Refined parameters include anisotropic displacement parameters for all non-hydrogen atoms with the exception of those of the disordered phenyl group including atom C81 and C81A, respectively. With idealised bonds lengths and angles assumed for all the NH, CH and CH₂ groups, the riding model was applied for the corresponding H atoms, and their isotropic displacement parameters were constrained to 120% of the equivalent isotropic displacement parameters of the parent nitrogen and carbon atoms. The disordered trichloromethane solvate molecules were treated as rigid with idealised geometries. Appropriate anisotropic displacement restraints had to be applied for their chlorine and carbon atoms, as well as for selected atoms of the silicon complexes. The absolute structure parameter^[25] [x = 0.09(9)] indicates the choice of the correct enantiomorphic structure model. CCDC-901493 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Alternative isomerization pathway of epimer 3a to epimer 3b by two consecutive Berry pseudorotations; geometries and energies of epimer 3a and epimer 3b calculated at the B3LYP/6-31++G(d) level of theory.

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