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Journal of Organometallic Chemistry 643–644 (2002) 504–507

Journal of Organometallic Chemistry

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Note

# Synthesis and structure of the first pentacoordinate thiasiliranides

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Received 29 June 2001; accepted 31 August 2001

Dedicated to Professor François Mathey on the occasion of his 60th birthday

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## Abstract

Pentacoordinate thiasiliranides, $K^+$, 18-crown-6, $[\{–C_6H_4\text{-}2\text{-}C(CF_3)_2O–\}SiPh\{–CH(CH_2\text{-}t\text{-}Bu)S\text{-}\}]^-$ were synthesized by deprotonation of the corresponding α-mercaptoalkylsilanes, $\{–C_6H_4\text{-}2\text{-}C(CF_3)_2O–\}SiPh\{–CH(CH_2\text{-}t\text{-}Bu)SH\}$ with KH in the presence of 18-crown-6. X-ray crystallographic analysis of *cis*-thiasiliranide showed an exceptionally small Si–C–S angle (87°) as a result of significant intramolecular Si–S interaction. Hydrolysis of the pentacoordinate thiasiliranides gave 2,2-dimethylbutanethiol, while the reaction with HCl afforded the α-mercaptoalkylsilanes. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Brook rearrangement; Pentacoordinate silicon species; Pentacoordinate thiasiliranide; Three-membered ring; X-ray crystallographic analysis

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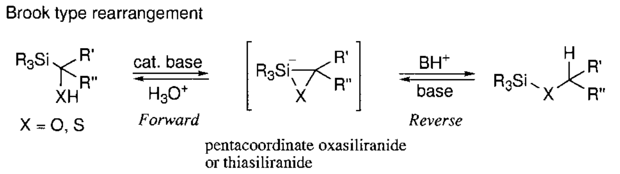
## 1. Introduction

Brook rearrangement is an intramolecular 1,2-migration of silicon from carbon to oxygen (forward Brook rearrangement) or from oxygen to carbon (reverse Brook rearrangement) [1,2], which has been considered to proceed through a three-membered ring compound bearing a pentacoordinate silicon at the position adjacent to an oxygen atom, i.e. a pentacoordinate oxasiliranide (Scheme 1 (X = O)) [1–3]. For the thia-Brook rearrangement (Scheme 1 (X = S)), forward one has been scarcely reported, in contrast to the reverse one which easily proceeds [4]. However, the first example for the forward thia-Brook rearrangement was reported in the reaction using methyllithium as base [5]. Recently, the $FSi(OCH_3)_2(OCH_2)^-$ ion was observed as a minor product in the gas-phase ion/molecule reaction of $Si(OMe)_4$ with $F^-$ and this molecule was suggested to be pentacoordinate oxsilirane species **1a** or **1b** based on its reactivity and theoretical calculation [6]. To the best of our knowledge, three-membered ring compounds containing a pentacoordinate silicon atom whose structures were definitively determined are only **2** and its related compounds [7,8]. Neither isolation nor spectroscopic observation in solution of oxa- or thiasiliranides has been reported [4,9,10].



Scheme 1.

These compounds are also interesting from the viewpoints of their unique structures as pentacoordinate species containing a small membered ring. In the course of our study on four-membered ring compounds containing a pentacoordinate silicon atom [11], we succeeded in the synthesis of pentacoordinate 1,2-oxasiletanides bearing the Martin ligand [12]. High ability of the Martin ligand for the stabilization of such four-membered ring compounds prompted us to investigate on its application to the synthesis of three-membered ring compounds. In this paper, we wish to report the synthesis, structure, and reactions of the first pentacoordinate thiasiliranides.

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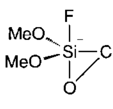
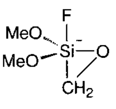
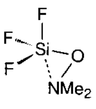


**1a**



**1b**

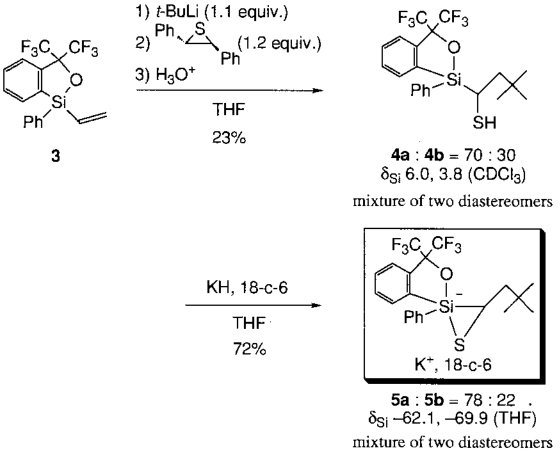


**2**

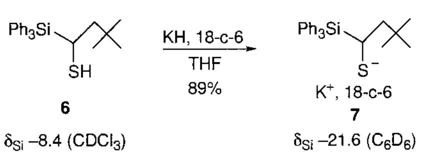
## 2. Results and discussion

Sequential treatment of vinylsilane **3** bearing the Martin ligand with *t*-butyllithium, *trans*-stilbene sulfide as a sulfur source, and aq. $NH_4Cl$ gave a mixture of two diastereomers **4a** and **4b** in a low yield (Scheme 2) [13]. It was difficult to separate two diastereomers **4a** and **4b** by silica gel chromatography or gel permeation liquid chromatography (GPLC). Therefore, these compounds were used in the next reaction as a mixture of diastereomers. The stereochemistry of **4a** and **4b** could not be determined.

The reaction of **4** with potassium hydride in the presence of 18-crown-6 was monitored by $^{29}$Si-NMR spectroscopy to show largely upfield-shifted (about 70 ppm) signals compared with those of the starting materials. The $^{19}$F-NMR spectrum showed two sets of double quartets due to two diastereomers (78:22). Such an upfield shift in $^{29}$Si NMR chemical shifts is a characteristic feature of the formation of pentacoordinate silicon compounds from tetracoordinate species, strongly suggesting the formation of pentacoordinate thiasiliranides **5** (Scheme 2) [14]. On the other hand, thiolate anion **7** generated from α-mercaptoalkylsilane **6** without the Martin ligand showed a slightly upfield shifted signal in $^{29}$Si NMR compared to that due to **6** (Scheme 3), supporting also the formation of pentacoordinate thiasiliranides in the former case.



Scheme 2.



Scheme 3.

X-ray crystallographic analysis of one isomer of pentacoordinate thiasiliranides **5a**,**b** indicated that the phenyl group on the silicon is *cis* to the neopentyl group and that it has a very distorted trigonal bipyramidal (TBP) structure with oxygen and sulfur atoms at apical positions and three carbon atoms at equatorial positions (Fig. 1) [15]. This is the first example of X-ray crystallographic analysis of a pentacoordinate thiasiliranide, and moreover, the first example of a pentacoordinate anionic silicate containing a three-membered ring. The bond length of Si–S (2.57 Å) is substantially longer than those observed in bis(triphenylsilyl) sulfide (2.152(2) Å) [16] and tetracoordinate thiasilirane [$-Me_2CC_6H_4CMe_2-$]Si[$-SSiMes_2-$] (2.093 Å) [17] as well as the sum of the covalent radii (2.20 Å). However, taking it into consideration that the Si–S bond is an apical bond and that in pentacoordinate silicates an apical bond is generally ca. 10% longer than the same bond in tetracoordinate silicon compounds, the Si–S bond length of *cis*-**5** (2.57 Å) seems to be a reasonable value. The Si1–C1–S1 bond angle is 87.4°, which is significantly smaller than the tetrahedral angle (109.5°), supporting the existence of Si–S interaction. This striking feature was also observed in (*N*,*N*-dimethylaminoxy)trifluorosilane **2** having β-donor interaction [7a].

Moreover, the sum of three equatorial angles is 350°, which is closer to that of ideal TBP structure (360°)

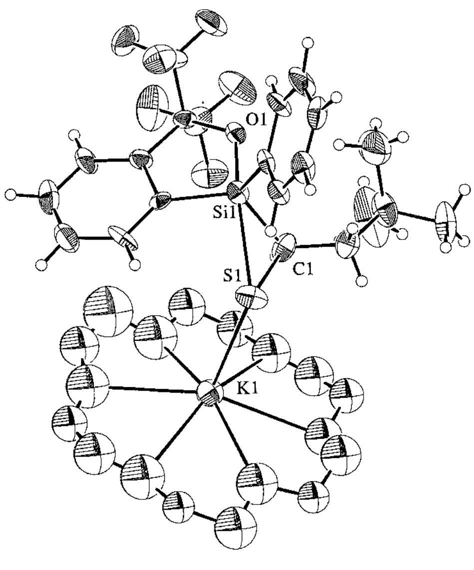
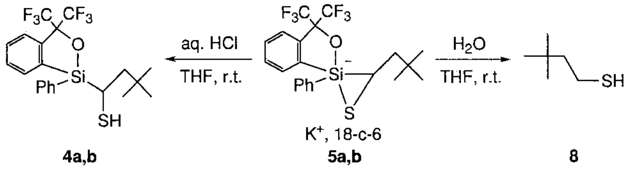


Fig. 1. ORTEP drawing of *cis*-**5** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°): Si(1)–S(1), 2.569(9); Si(1)–C(1), 1.85(2); S(1)–C(1), 1.86(2); Si(1)–O(1), 1.745(14); S(1)–K(1), 3.116(9); Si(1)–C(1)–S(1), 87.4(10); O(1)–Si(1)–C(1), 112.3(9).

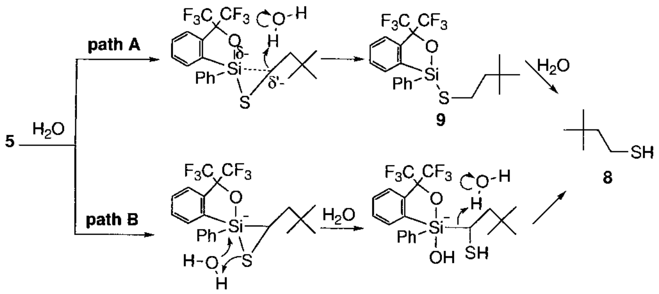
than that of ideal tetrahedral structure (328°). The distance (3.12 Å) between K and S is shorter than the sum (4.55 Å) of the van der Waals radii of K and S, indicating the significant interaction between K and S in the solid state. However, *cis*-**5** is thought to retain a pentacoordinate structure judging from the above discussion on the bond angles.

Pentacoordinate thiasiliranides **5a** and **5b** are unstable against moisture. When a mixture of **5a** and **5b** was treated with an excess amount of water in THF solution, **5a** and **5b** were decomposed immediately, and 3,3-dimethylbutanethiol (**8**) was detected by GC-MS. On the other hand, the reaction of **5** with an excess amount of hydrochloric acid gave a mixture of two diastereomers of α-mercaptoalkylsilanes **4** (Scheme 4).

Two reaction mechanisms can be proposed for the formation of thiol **8**, that is, the C-protonation mechanism (path A) and the S-protonation mechanism (path B) (Scheme 5). In path A, at first the protonation takes place on negatively charged carbon, which would be generated by elongation of the Si–C bond in the thiasilirane ring. Hydrolysis of alkylthiosilane **9** thus obtained gave thiol **8**. In this case, compound **5** shows reactivity as an intermediate of Brook rearrangement type reaction. On the other hand, the protonation to the sulfur atom is assumed to occur at first in path B. Simultaneously, a nucleophilic attack of $HO^-$ to the silicon center occurs to give a pentacoordinate silicate. Further hydrolysis of this compound is considered to give thiol **8**. The fact that **4a**,**b** were obtained by the reaction of **5a**,**b** with hydrochloric acid strongly suggests that the first protonation occurs on the sulfur atom of pentacoordinate thiasiliranides, although further investigation is necessary to determine the reaction pathway.



Scheme 4.



Scheme 5.

## 3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 166131 for compound *cis*-**5**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[13] Spectroscopic data of major isomer **4a**: $^{1}$H-NMR (500 MHz, $CDCl_3$) $\delta$ 0.98 (s, 9H, *t*-Bu), 1.44 (d, $^{3}J = 11.3$ Hz, 1H, S*H*), 1.59 (dd, $^{2}J = 14.7$ Hz, $^{3}J = 8.8$ Hz, 1H, C*H*H′-*t*-Bu), 2.15 (dd, $^{2}J = 14.7$ Hz, $^{3}J = 2.9$ Hz, 1H, CH*H*′-*t*-Bu), 2.27 (ddd, $^{3}J = 11.3$ Hz, $^{3}J = 8.8$ Hz, $^{3}J = 2.9$ Hz, 1H, SiC*H*), 7.40 (t, $^{3}J = 7.4$ Hz, 2H, *meta*), 7.48 (tt, $^{3}J = 7.5$ Hz, $^{4}J = 1.5$ Hz, 1H, *para*), 7.57–7.63 (m, 2H), 7.68–7.73 (m, 1H), 7.64 (dd, $^{3}J = 6.8$ Hz, $^{4}J = 1.5$ Hz, 2H, *ortho*), 8.08 (dd, $^{3}J = 6.0$ Hz, $^{4}J = 2.6$ Hz, 1H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 18.65 (s, Si*C*SH), 29.56 (s, C($C$H$_3$)$_3$), 32.49 (s, $C$(CH$_3$)$_3$), 47.52 (s, $C$H$_2$-*t*-Bu), 84.42 (sept, $^{2}J_{CF} = 31.0$ Hz, $C$(CF$_3$)$_2$), 122.42 (q, $^{1}J_{CF} = 286.6$ Hz, $C$F$_3$), 122.53 (q, $^{1}J_{CF} = 286.2$ Hz, $C$F$_3$), 125.02 (s), 128.13 (s), 129.45 (s), 130.46 (s), 131.08 (s), 131.31 (s), 134.04 (s), 134.31 (s), 135.09 (s), 140.24 (s); $^{19}$F-NMR (254 MHz, $CDCl_3$) $\delta$ $-76.15$ to $-75.95$ (m, 6F); $^{29}$Si NMR (54 MHz, $CDCl_3$) $\delta$ 3.81 (s).

[14] Selected spectroscopic data of **5a** and **5b**: **5a**: $^{19}$F-NMR (254 MHz, THF) $\delta$ $-76.53$ (q, $^{4}J_{FF} = 9.4$ Hz, 3F), $-75.28$ (q, $^{4}J_{FF} = 9.4$ Hz, 3F); $^{29}$Si NMR (99 MHz, THF) $\delta$ $-61.18$ (s). **5b**: $^{19}$F-NMR (254 MHz, THF) $\delta$ $-75.75$ (q, $^{4}J_{FF} = 9.6$ Hz, 3F), $-75.15$ (q, $^{4}J_{FF} = 9.6$ Hz, 3F); $^{29}$Si NMR (99 MHz, THF) $\delta$ $-69.88$ (s).

[15] Crystal data for *cis*-**5**: $C_{33}H_{45}F_6KO_7SSi$, monoclinic, $P2_1/n$ (no. 14), $a = 15.268(5)$, $b = 11.894(3)$, $c = 21.024(7)$ Å, $\beta = 89.47(3)°$, $Z = 4$, $\mu = 2.97$ cm$^{-1}$, $D_{calc} = 1.334$ g cm$^{-3}$, $V = 3818(2)$ Å$^3$, $R = 0.103$, $R_w = 0.080$. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). The structure was solved by direct-methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1499 observed reflections ($I > 3.00\sigma(I)$) and 352 variable parameters.

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