ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 611 (2000) 256–263

Journal of Organo metallic Chemistry

Review

Small ring compounds containing highly coordinate Group 14 elements

Takayuki Kawashima *

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received 6 March 2000; accepted 23 March 2000

Abstract

Syntheses, structures, thermolyses of pentacoordinate 1,2-oxasiletanides (**1**), K^+, 18-crown-6, $\{[–C_6H_4–C(CF_3)_2O–]SiPh$-$[–CHRCR^1R^2O–]\}^-$, pentacoordinate1,2-oxastannetanides (**2**), K^+, 18-crown-6, $\{Ph_3Sn[–CH(SPh)CR^1R^2O–]\}^-$, pentacoordinate 1,2-oxagermetanide (**3**), K^+, 18-crown-6, $\{[–C_6H_4–C(CF_3)_2O–]GePh[–CH(CH_2\text{-}t\text{-}Bu)C(CF_3)_2O–]\}^-$, germylalkoxide (**4**), K^+, 18-crown-6, $Ph_3GeCH(CH_2\text{-}t\text{-}Bu)C(CF_3)_2O^-$, pentacoordinate siprobi[1,2-oxasiletanide] (**5**), $DBU{\cdot}H^+$, $\{PhSi[\text{-}CH_2C\text{-}(CF_3)_2O–]_2\}^-$ are summarized. All compounds except for spirobi[1,2-oxasiletanide] **5**, which underwent homo-Brook rearrangement, gave the corresponding olefins upon heating, indicating that they are intermediates of Peterson-type reactions. However, it was found that 1,2-oxasiletanides bearing the Martin ligand, which usually undergo the Peterson reaction, can afford the homo-Brook rearrangement products depending on the substituent at the 3-position and the reaction conditions, demonstrating that the Peterson reaction and homo-Brook rearrangement proceed via a common intermediate, a pentacoordinate 1,2-oxasiletanide. Crystal structures of these compounds are also presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Peterson-type reactions; Homo-Brook rearrangement; Pentacoordinate 1,2-oxasiletanide; Pentacoordinate 1,2-oxastannetanide; Pentacoordinate 1,2-oxagermetanide; Olefin formation; X-ray crystallographic analysis

1. Introduction

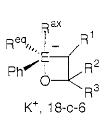
Small (three- and four-membered) ring compounds containing heavier Group 14 elements, which have been usually prepared by cycloaddition or cyclization of highly reactive low-coordinated species such as silenes, disilenes, germenes, digermenes and so on [1], have attracted considerable attention in comparison with their carbon analogs. Therefore, in sharp contrast to compounds with usual valency [1,2], reports on highly coordinate species have been limited [3]. Among these species are oxasiliranide ion **6** proposed as an intermediate in the gas-phase reaction of $(MeO)_4Si$ with fluoride ion [4a,b], a neutral three-membered compound **7** prepared by intramolecular coordination of nitrogen to silicon [4c], fluoro- and allylsilicates **8** [4d,e] by the reaction of the corresponding siletane with anionic species, and pentacoordinate four-membered complexes [5] such as **9a**,**b** [5a,e] by intramolecular or intermolecular donation of a neutral donor. In the course of the author's study on heteracyclobutanes containing a highly coordinate main group element at the position adjacent to the heteroatom [6], his attention was focused on oxetanes containing pentacoordinate Group 14 elements, because they have been considered as transition states or intermediates of the Peterson [7,8] and Peterson-type reactions [9], which are Group 14 element analogs of the Wittig reaction [10]. In this account the author wishes to summarize his study on oxetanes **1**–**5** containing pentacoordinate Si, Ge and Sn.

---

* Tel./fax: +81-3-58006899.

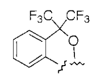
E-mail address: takayuki@chem.s.u-tokyo.ac.jp (T. Kawashima).

0022-328X/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(00)00491-5

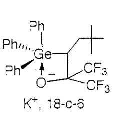


K$^+$, 18-c-6

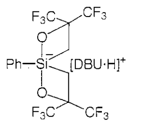
1: E= Si; R^{ax},R^{eq}= ML
2: E= Sn; R^{ax}=R^{eq} = Ph
3: E= Ge; R^{ax},R^{eq}= ML



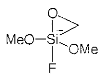
Martin ligand (ML)



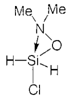
4



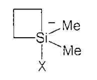
5



6

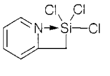


7

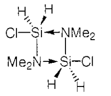


X= F, CH$_2$CH=CH$_2$

8



9a



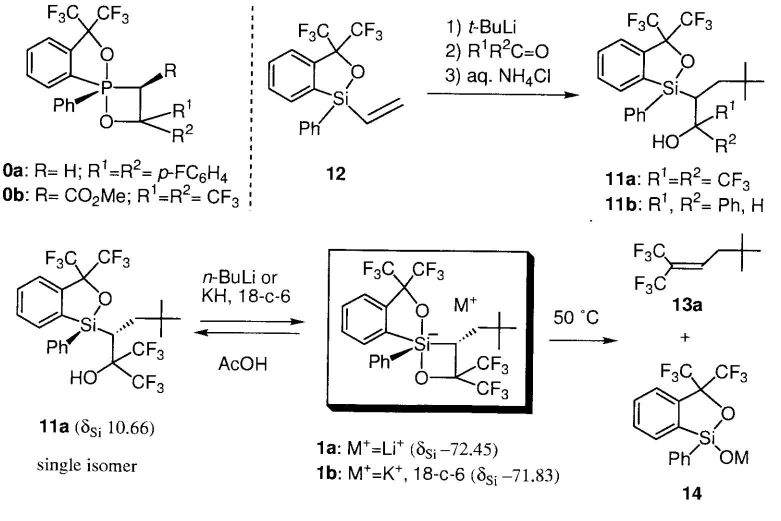
9b

2. Results and discussion

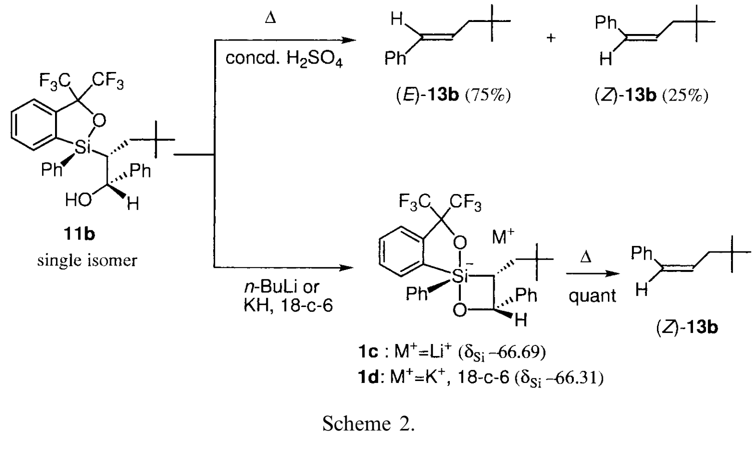
2.1. Pentacoordinate 1,2-oxasiletanides

The Peterson reaction using silyl stabilized carbanions and carbonyl compounds provides an important methodology for the stereospecific formation of (*E*)- and (*Z*)-alkenes from a single diastereomer of β-hydroxyalkylsilanes by changing reaction conditions [7,8]. In contrast to the Wittig reaction, neither isolation nor spectroscopic observation of the reaction intermediate, i.e. pentacoordinate anionic species has been reported. Successful syntheses of pentacoordinate phosphoranes **10** [11] as very stable compounds prompted the author to investigate the synthesis of a pentacoordinate 1,2-oxasiletanide as an isolable compound by taking advantage of stabilizing effect of the Martin ligand [12].

β-Hydroxysilanes **11** bearing the Martin ligand were prepared as a mixture of diastereomers by sequential treatment of vinylsilane **12** with *t*-BuLi, carbonyl compounds and aqueous NH$_4$Cl. A single diastereomer was obtained by passing through silica gel column. Deprotonation of a single diastereomer of **11a** with *n*-BuLi in THF was monitored by ^{19}F- and ^{29}Si-NMR spectroscopy to show the quantitative formation of 1,2-oxasiletanide **1a**. The large upfield shift in δ_{Si} from **11a** (δ_{Si} 10.66) to **1a** (δ_{Si} −72.45) strongly supports the structure of a pentacoordinate silicate. It was found by ^{19}F-NMR spectroscopy that **1a** provided alkene **13a** and lithium silanoxide **14a** in 86% yield together with unreacted **1a** (14%) upon heating (40°C, THF, 24 h), indicating that **1a** is a real intermediate of the Peterson reaction [13]. Treatment of **1a** with acetic acid at room temperature resulted in the quantitative recovery of **11a** (Scheme 1).



Scheme 1.



Scheme 2.

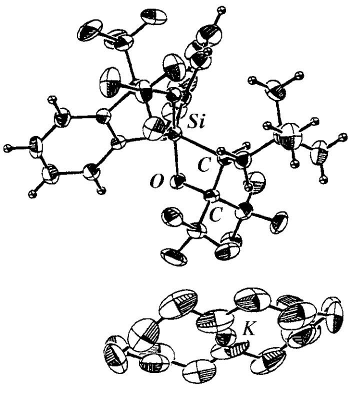


Fig. 1. ORTEP drawing of pentacoordinate 1,2-oxasiletanide **1b** (thermal ellipsoids at 30% probability).

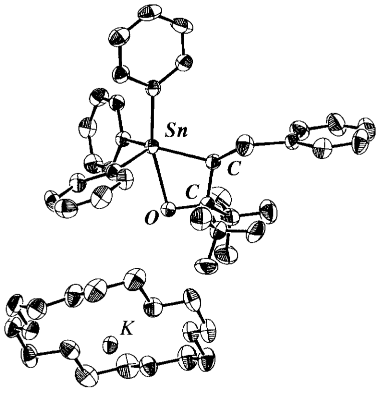


Fig. 2. ORTEP drawing of pentacoordinate 1,2-oxastannetanide **2a** (thermal ellipsoids at 30% probability).

Similarly, a single diastereomer of benzaldehyde adduct **11b** reacted with *n*-BuLi or KH to give **1c** (δ_{Si} − 66.69) or **1d** (δ_{Si} − 66.31), respectively, which decomposed slowly at room temperature and 50°C to afford exclusively (*Z*)-**13b**. Compound **11b** gave mainly (*E*)-**13b** under acidic conditions, showing a typical feature of the Peterson reaction (Scheme 2). These results suggest that the β-hydroxy silane bearing the Martin ligand is not so special as a substrate of the Peterson reaction.

The X-ray crystallographic analysis of K^+, 18-crown-6 salt, **1b** indicated that it has a distorted TBP structure similar to those of pentacoordinate 1,2-oxaphosphetanes **10a** and **10b** (Fig. 1). The phenyl group on silicon is *trans* to the neopentyl group and, as expected, two oxygen and three carbon atoms occupy the apical and equatorial positions, respectively. Thus, the first example for a pentacoordinate 1,2-oxasiletanide was successfully synthesized, although a stable tetracoordinate 1,2-oxasiletane was reported by Brook et al. [14].

2.2. Pentacoordinate 1,2-oxastannetanides

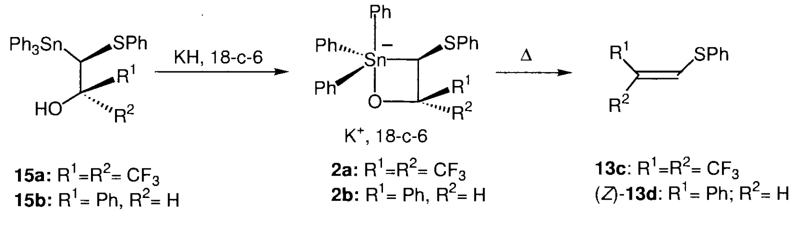
As shown in the case of 1,2-oxasiletanides, multinuclear NMR experiments gave an important information concerning the coordination number of the central atom. So, next, an intermediate of the tin-Peterson reaction was investigated, because of the readiness of measurement of ^{119}Sn-NMR compared with ^{73}Ge-NMR. The synthesis of a β-hydroxy stannane with the Martin ligand was unsuccessful, but fortunately, pentacoordinate 2,2,2-triphenyl-1,2-oxastannetanide **2a** (δ_{Sn} − 229.65) was isolated as a stable compound from **15a** without resort to the Martin ligand as shown in Scheme 3 [15].

The ^{1}H- and ^{13}C-NMR spectra showed only one set of signals for the Sn–Ph, indicating the presence of very fast pseudorotation. The X-ray crystallographic analysis of **2a** revealed a structure close to a square pyramid rather than a TBP in sharp contrast to **1b** (Fig. 2). It was found by ^{19}F-NMR spectroscopy that **2a** provided alkene **13c** (95%) upon heating (70°C, CH_3CN, 36 h), indicating that **2a** has a reactivity similar to that of the silicon compound **1b**. Similar treatment of the benzaldehyde adduct *erythro*-**15b** with KH gave a signal at δ_{Sn} − 239.52 at − 30°C, suggesting the formation of 1,2-oxastannetanide **2b**. When **2b** was heated (50°C, THF, 5 h) without its isolation, (*Z*)-phenyl β-styryl sulfide (*Z*)-**13d** was exclusively obtained, showing that the alkene formation proceeded stereospecifically in the same manner as the reaction starting from *erythro*-**15b** although the reaction conditions were much milder [16].

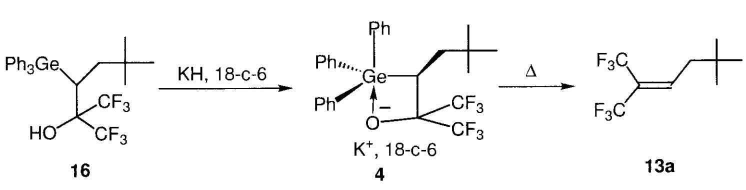
2.3. Pentacoordinate 1,2-oxagermetanides

As oxastannetanide **2a** was successfully synthesized as a stable compound without resort to the Martin ligand, the synthesis of a pentacoordinate 2,2,2-triphenyl-1,2-oxagermetanide was attempted (Scheme 4).

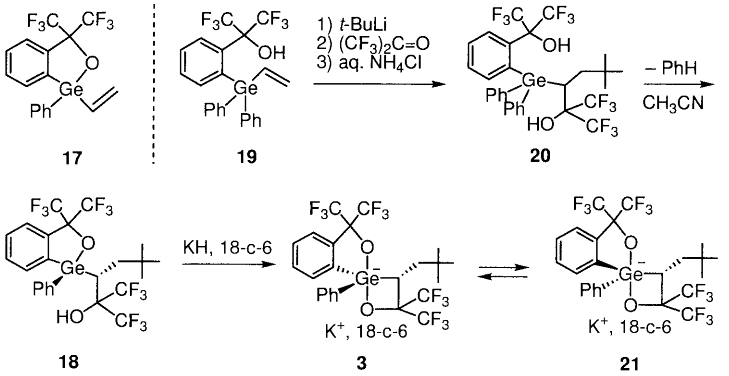
Although triphenyl derivative **4**, which was prepared by deprotonation of β-hydroxy germane **16** with KH, has similar spectral data and reactivity to those of the tin compound **2a** [17], and hence has a structure of



Scheme 3.



Scheme 4.



Scheme 5.

pentacoordinate 1,2-oxagermetanide in solution, the X-ray crystallographic analysis indicated that **4** is close to a β-germyl alkoxide with a strong interaction between oxygen and germanium atoms rather than a pentacoordinate 1,2-oxagermetanide. So, introduction of the Martin ligand seemed necessary to synthesize an intermediate having a four-membered ring. However, the Michael addition of *t*-BuLi to cyclic vinylgermane **17**, a germanium analog of **12**, was unsuccessful, because the Lewis acidity of the germanium was increased by the Martin ligand [12d]. Very fortunately, β-hydroxy germane **18** could be synthesized by sequential treatment of acyclic vinylgermane **19** instead of cyclic **17** with *t*-BuLi, $(CF_3)_2C{=}O$, and aqueous NH_4Cl, followed by unique cycloelimination of benzene of a resulting acyclic β-hydroxy germane **20** in CH_3CN [18]. Subsequent deprotonation of **18** with KH in the presence of 18-crown-6 gave a pentacoordinate 1,2-oxagermetanide **3**, an intermediate of the germanium-Peterson reaction (Scheme 5) [19]. Formation of a desired four-membered ring was revealed by the X-ray crystallographic analysis (Fig. 3). In sharp contrast to silicon analog, **1b** oxagermetanide **3** is equilibrated with its stereoisomer **21** by a non-dissociative pseudorotation mechanism, before giving the corresponding alkenes [20]. Observation of such isomerization is probably due to increase in activation energy of the olefin formation by the stabilization of the ground states of the oxagermetanides and/or decrease in the pseudorotation barrier.

Selected crystal structural parameters of **1b**, **2a** and **3** are summarized in Table 1 together with those of **10a** and **10b**.

2.4. A pentacoordinate spirobi[1,2-oxasiletanide]

Next the synthesis of spirosilicate **5** with two oxasiletanide rings as silicon analog of **22** [21] was tried, because this compound was expected to generate an oxidosilanone ($RSi(O)O^-$), a Si analog of a carboxylate, with the formation of two molar equivalents of the corresponding alkene. Treatment of bis(β-hydroxyalkyl)silane **23** with trifluoromethanesulfonic acid in $CDCl_3$ afforded the silyl triflate **24** along with benzene [22]. Without further purification **24** was allowed to react with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at low temperature (−40 ∼ −20°C) to form **5** almost quantitatively along with $[DBU{\cdot}H]^+$ triflate (Scheme 6), as monitored by ^1H-, ^{13}C-, ^{19}F- and ^{29}Si-NMR spectroscopy.

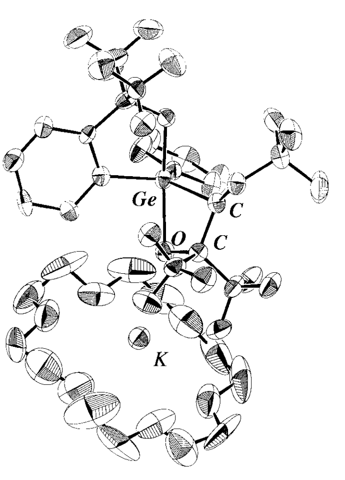
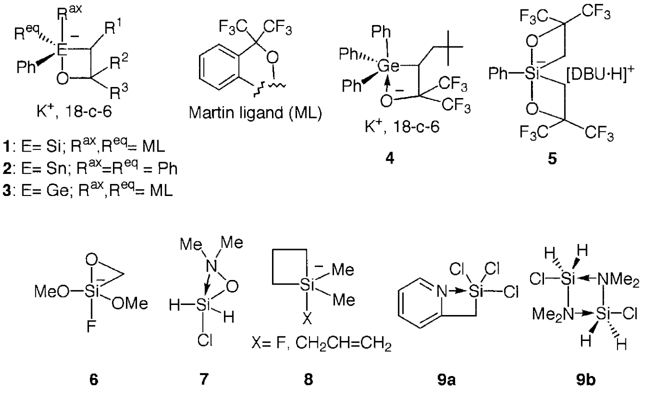


Fig. 3. ORTEP drawing of pentacoordinate 1,2-oxagermetanide **3** (thermal ellipsoids at 30% probability).

Table 1
Selected crystal structural parameters

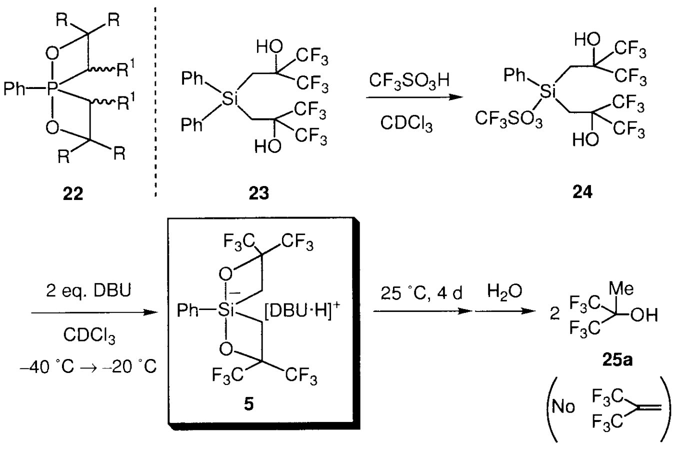


Compound[a]	Bond lengths (Å)			Angles (°)				%TBP
	X–O	X–R^{ax}	X–Cl	∠O–X–O	∠C1–X–O	Σ	Φ	
1b	1.844(4)	1.798(4)	1.913(5)	166.3(2)	73.9(2)	359.2	11.4(3)	29.4
2a	2.401(5)	2.188(8)	2.200(7)	165.1(2)	61.3(2)	347.7	12.5(7)	37.4
3	2.150(5)	1.928(6)	1.972(8)	165.5(2)	69.1(3)	358.6	16.9(6)	84.0
4	2.832(8)[b]	2.00(1)	2.04(1)	162.6(5)	54.1(4)	337.8	33(1)	–
10a	1.728(2)	1.754(3)	1.808(4)	163.6(1)	77.4(1)	359.9	9.7(2)	44.5
10b	1.781(6)	1.716(6)	1.823(9)	165.9(3)	75.5(3)	359.5	4.7(6)	26.2

[a] R^{ax}–R^{eq} means the Martin ligand except for **2a** and **4**, see their formulae in the text.
[b] Bond distance between X and O.

Compound **5** was stable below 25°C, but it gradually decomposed at 25°C to give alcohol **25a** almost quantitatively instead of the corresponding alkene after treatment with water (Scheme 6). Methanolysis of **5** also gave alcohol **25a**, while thermolysis of **1b** in the presence of methanol in CD_3CN afforded a complicated mixture including alkene **13a**.

Protodesilylation-type alcohol formation from a β-hydroxyalkylsilane under basic conditions in the presence of a proton source is known as homo-Brook rearrangement [23]. Hudrlik et al. proposed a plausible mechanism of this reaction which involves a pentacoordinate 1,2-oxasiletanide [24]. In this sense, pentacoordinate silicate **5** can be regarded as the first example of the detectable intermediate of homo-Brook rearrangement.

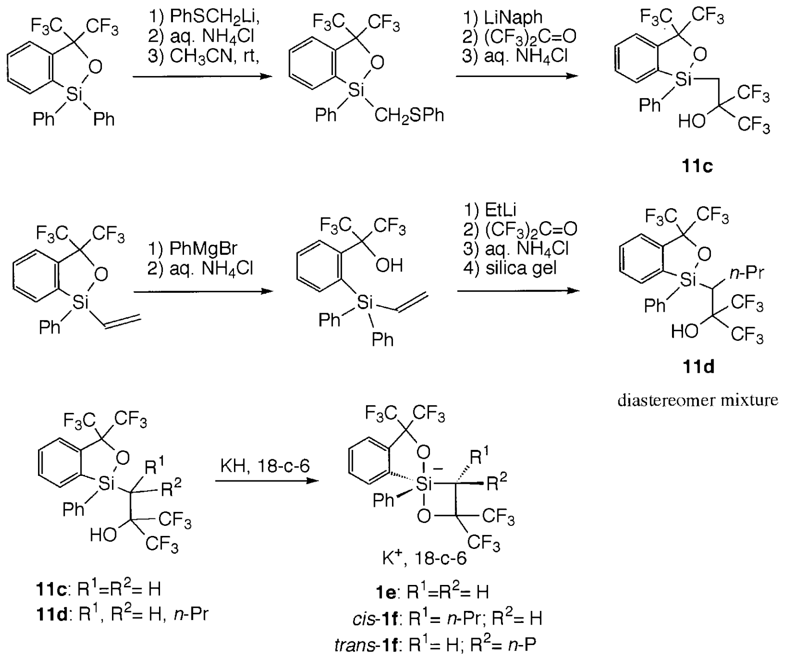


Scheme 6.

2.5. Control factors of two reaction modes of pentacoordinate 1,2-oxasiletanides, the Peterson reaction and homo-Brook rearrangement

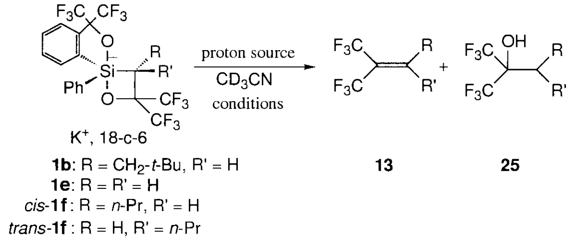
It is very interesting that the pentacoordinate 1,2-oxasiletanide bearing the Martin ligand and spirobi[1,2-oxasiletanide] indicated the different reactivity, whereas they have the same partial structure. There are differences between them both in the substituent at the 3-position of the 1,2-oxasiletanide ring and in the ring system. Therefore, it is necessary to compare the reactivity between the compounds which have different substituents only at the 3-position of 1,2-oxasiletane ring. Since deriverization of 1,2-oxasiletanides with the Martin ligand is considered to be much easier than that of spirobi[1,2-oxasiletanide] because of their high stability, we decided to use the former ring system for the purpose of elucidating control factors of two reaction modes, the Peterson reaction and homo-Brook rearrangement.

3-Unsubstituted derivative **1e** [25a] and 3-propyl derivatives **1f** [25b] were prepared from the correspond-



Scheme 7.

Table 2
Thermolysis of pentacoordinate 1,2-oxasiletanides in the presence of a proton source



Entry	Compound	Proton source	Conditions	Yield [d]	
				13	**25**
1	**1b**	CH_3OH [b]	60°C, 15 h	– [e]	–
2	**1b**	CF_3CH_2OH [b]	60°C, 24 h	– [e]	–
3	**1b**	CH_3COOH [c]	60°C, 5 h; 80°C, 4 h	Quant. [f]	–
4	**1e**	CH_3OH [b]	70°C, 16 h	– [e]	–
5	**1e**	CF_3CH_2OH [b]	60°C, 8 h	2%	98%
6	**1e**	CH_3COOH [c]	R.t., 27 h	–	Quant.
7	**1f** [a]	CH_3OH [b]	60°C, 6 h; 80°C, 35 h	– [e]	–
8	**1f** [a]	CF_3CH_2OH [b]	60°C, 40 h	– [e]	–
9	**1f** [a]	CH_3COOH [c]	60°C, 20 h; 80°C, 20 h	94% [f]	6%

[a] *cis*-**1f**:*trans*-**1f** = 56:44.

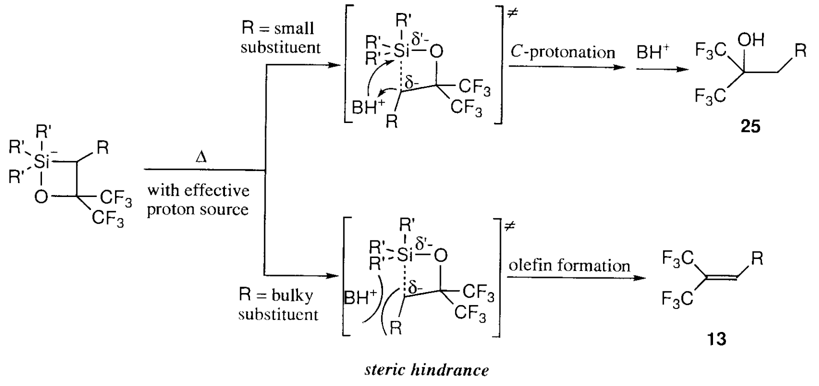
[b] 50 equivalents of proton source was used.

[c] 10 equivalents of proton source was used.

[d] Estimated by ^{19}F-NMR spectroscopy.

ing β-hydroxy silanes **11c** and **11d** as shown in Scheme 7. 3-Propyl derivatives were obtained as a mixture of two diastereomers *cis*-**1f** and *trans*-**1f**, in which the phenyl group on Si and the propyl group are *cis* and *trans*, respectively. Since several efforts to separate these diastereomers were unsuccessful, 3-propyl derivatives were used as a mixture.

Thermolyses of **1b**, **1e**, and **1f** were carried out in the presence of proton sources such as methanol, 2,2,2-trifluoroethanol, and acetic acid. The results are summa-



Scheme 8.

rized in Table 2 [25]. As shown in entries 1–3, **1b** gave the corresponding alkene, and the alcohol was not obtained at all [26]. In the cases of **1e** and **1f**, the ratio of the alkene to the alcohol significantly depended on the acidity of the proton source. In the presence of acetic acid, thermolysis of propyl derivative **1f** gave small amount of the alcohol (entry 9), while that of **1e** predominantly afforded the alcohol even in the presence of 2,2,2-trifluoroethanol (entry 5).

Considering these results, the selectivity of two reaction modes (olefin formation versus alcohol formation) seems to be determined as follows. Alcohol **25** was only formed in the reaction of pentacoordinate 1,2-oxasiletanides, which have a small substituent at the 3-position in the four membered ring in the presence of a proton source that has relatively high acidity. If a bulky group exists at this position, olefin **13** was formed because the protonation of the negatively charged carbon, which would be generated by elongation of the Si–C bond in the oxasiletanide ring, was encumbered by the bulky group (Scheme 8). A possibility that electronic effects of the substituents at the 3-position determined the selectivity can be excluded by the comparison between entries 3 and 9 in Table 2. Propyl and neopentyl groups are considered to have a similar electronic character. However, the reaction of pentacoordinate 1,2-oxasiletanide **1f** afforded the alcohol in the presence of acetic acid, while thermolysis of **1b** gave only olefin under the same conditions. Therefore, the steric factor is important for the determination of the reaction modes. It was demonstrated that pentacoordinate 1,2-oxasiletanides undergo two reactions, the Peterson reaction and homo-Brook rearrangement.

Finally, in the course of study on three-membered ring compounds containing two heteroatoms including a highly coordinate main group element, a pentacoordinate thiasiliranide, which is a sulfur analog of an oxasiliranide proposed as an intermediate of Brook rearrangement [27], has been successfully synthesized [28]. Further investigations are in progress.

Acknowledgements

This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas, the Chemistry of Inter-element Linkage, from the Ministry of Education, Science, Sports and Culture, Japan. The author thanks Professor R. Okazaki of Japan Women's University for his valuable discussions and Professor N. Tokitoh of Kyushu University for the determination of the X-ray structures. He is also grateful to N. Iwama, Y. Nishiwaki and K. Naganuma for their experimental works. The author thanks Central Glass, Tosoh Akzo Co. Ltd., and Shin-etsu Chemicals for gifts of chemicals.

References

[1] For three-membered rings with one Si, Ge, Sn, or Pb, see: E. Roskamp, C. Roskamp, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, Vol. 1A, Pergamon, Oxford, 1996, pp. 305–331. For three-membered rings with two heteroatoms including Se or Te, see: N. Tokitoh, N. Choi, W. Ando, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, Vol. 1A, Pergamon, Oxford, 1996, pp. 457–468. For four-membered rings with one Si, Ge, Sn, or Pb, see: E. Lukevics, O. Pudova, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, Vol. 1B, Pergamon, Oxford, 1996, pp. 867–886. For four-membered rings with two heteroatoms including Si to Pb, see: R.T. Conlin, T.P. Meagher, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, Vol. 1B, Pergamon, Oxford, 1996, pp. 1175–1187.

[2] For cyclotrisilenes, see: (a) T. Iwamoto, C. Kabuto, M. Kira, J. Am. Chem. Soc. 121 (1999) 886. (b) M. Ichinohe, T. Matsuno, A. Sekiguchi, Angew. Chem. Int. Ed. 38 (1999) 2194. For cyclotrigermenes, see: A. Sekiguchi, N. Fukaya, M. Ichinohe, N. Takagi, S. Nagase, J. Am. Chem. Soc. 121 (1999) 11587. For cyclotetrasilene, see: M. Kira, T. Iwamoto, C. Kabuto, J. Am. Chem. Soc. 118 (1996) 10303.

[3] For hypercoordinate silicon species, see: C. Chuit, R.J.P. Corriu, C. Reyé, in: K.-y. Akiba (Ed.), Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999 (Chapter 4).

[4] (a) M.L.P. Silva, J.M. Riveros, J. Mass Spectrom. 30 (1995) 733. (b) N.H. Morgon, A.B. Argenton, M.L.P. Silva, J.M. Riveros, J.

Am. Chem. Soc. 119 (1997) 1708. (c) N.W. Mitzel, U. Losenhand, J. Am. Chem. Soc. 120 (1998) 7320, and references cited therein. (d) R. Damrauer, J.A. Hankin, J. Organomet. Chem. 521 (1996) 93. (e) S.A. Sullivan, C.H. DuPuy, R. Damrauer, J. Am. Chem. Soc. 103 (1981) 480.

[5] For intramolecular donation, see: (a) T. van den Ancker, B.S. Jolly, M.F. Lappert, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc., Chem. Commun. (1990) 1006. (b) L.M. Englehardt, P.C. Junk, W.C. Patalinghug, R.E. Sue, C.L. Rasto, A.H. White, J. Chem. Soc., Chem. Commun. (1991) 930. (c) H.H. Karsch, F. Bienlein, A. Sladek, M. Heckel, K. Burger, J. Am. Chem. Soc. 117 (1995) 5160. For intermolecular donation, see: (d) W.S. Sheldrick, W. Wolfsberger, Z. Naturforsch. Teil B 32 (1977) 22. (e) D.G. Anderson, A.J. Blake, S. Cradock, E.A.V. Ebsworth, D.W.H. Rankin, A.J. Welch, Angew. Chem. Int. Ed. Engl. 25 (1986) 107.

[6] (a) T. Kawashima, R. Okazaki, Synlett (1996) 600. (b) T. Kawashima, in: K.-y. Akiba (Ed.), Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999 (Chapter 6). (c) T. Kawashima, R. Okazaki, in: B. Halton (Ed.), Advances in Strained and Interesting Organic Molecules, Vol. 7, JAI Press, Stamford, 1999, pp. 1–41.

[7] (a) E.W. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981, pp. 141–152. (b) W.P. Weber, Silicon Reagents for Organic Synthesis, Springer-Verlag, New York, 1983, pp. 58–73. (c) D.J. Ager, Synthesis, (1984) 384. (d) D.J. Ager, Org. React. (N.Y.) 38 (1990) 1.

[8] (a) P.F. Hudrlik, D. Peterson, J. Am. Chem. Soc. 97 (1975) 1464. (b) P.F. Hudrlik, D. Peterson, R.J. Rona, J. Org. Chem. 40 (1975) 2263. (c) P.F. Hudrlik, E.L.O. Agwaramgbo, A.M. Hudrlik, J. Org. Chem. 54 (1989) 5613.

[9] (a) T. Kauffmann, Top. Curr. Chem. 92 (1980) 109. (b) T. Kauffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 410. (c) M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987, pp. 176–177.

[10] For reviews, see: (a) A. Maercker, Org. React. (N.Y.) 14 (1965) 270. (b) D.J.H. Smith, in: D.H.R. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, Vol. 2, Pergamon, Oxford, 1979, pp. 1316–1329. (c) I. Gosney, A.G. Rowley, in: J.I.G. Cadogan (Ed.), Organophosphorus Reagents in Organic Synthesis, Academic Press, New York, 1979, pp. 17–153;. (d) B.E. Maryanoff, A.B. Reitz, Phosphorus Sulfur Silicon 27 (1986) 167. (e) B.E. Maryanoff, A.B. Reitz, Chem. Rev. 89 (1989) 863. (f) E. Vedejs, M.J. Peterson, Top. Stereochem. 21 (1994) 1.

[11] (a) T. Kawashima, K. Kato, R. Okazaki, J. Am. Chem. Soc. 114 (1992) 4008. (b) T. Kawashima, K. Kato, R. Okazaki, Angew. Chem. Int. Ed. Engl. 32 (1993) 869.

[12] For the bidentate ligand which is very effective in stabilizing the higher coordination states of nonmetallic elements, see: (a) E.F. Perozzi, R.S. Michalak, G.D. Figuly, W.H. Stevenson III, D.B. Dess, M.R. Ross, J.C. Martin, J. Org. Chem. 46 (1981) 1049. For sulfurane oxides, see: (b) J.C. Martin, E.F. Perozzi, Science 191 (1976) 154. For organo-nonmetallic species, see: (c) J.C. Martin, Science 221 (1983) 509. For 10-Ge-5, see: (d) S.E. Denmark, R.T. Jacobs, G. Dai-Ho, S. Wilson, Organometallics 9 (1990) 3015. For 10-Si-5, see: (e) W.H. Stevenson III, S. Wilson, J.C. Martin, W.B. Farnham, J. Am. Chem. Soc. 107 (1985) 6340.

[13] T. Kawashima, N. Iwama, R. Okazaki, J. Am. Chem. Soc. 114 (1992) 7598.

[14] A.G. Brook, W.J. Chatterton, J.F. Sawyer, D.W. Hughes, K. Vorspohl, Organometallics 6 (1987) 1246.

[15] T. Kawashima, N. Iwama, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 2507.

[16] T. Kauffmann, R. Kriesgesmann, A. Hamsen, Chem. Ber. 115 (1982) 1818.

[17] T. Kawashima, N. Iwama, N. Tokitoh, R. Okazaki, J. Org. Chem. 59 (1994) 491.

[18] A similar reaction was reported for silicon compounds: Y. Yamamoto, Y. Takeda, K.-y. Akiba, Tetrahedron Lett. 30 (1989) 725.

[19] T. Kawashima, Y. Nishiwaki, R. Okazaki, J. Organomet. Chem. 499 (1995) 143.

[20] A similar isomerization was observed in tetracoordinate 1,2-oxathietanes, see: T. Kawashima, F. Ohno, R. Okazaki, Angew. Chem. Int. Ed. Engl. 33 (1994) 2094.

[21] (a) T. Kawashima, H. Takami, R. Okazaki, J. Am. Chem. Soc. 116 (1994) 4509. (b) T. Kawashima, R. Okazaki, R. Okazaki, Angew. Chem. Int. Ed. Engl. 36 (1997) 2500.

[22] T. Kawashima, K. Naganuma, R. Okazaki, Organometallics 17 (1998) 367.

[23] For silyl group migration from carbon to oxygen, see: (a) K. Yamamoto, Y. Tomo, Tetrahedron Lett. 24 (1983) 1997. (b) F. Sato, Y. Tanaka, M. Sato, J. Chem. Soc. Chem. Commun. (1983) 165. (c) S.R. Wilson, G.M. Georgiadis, J. Org. Chem. 48 (1983) 4143. (d) K. Yamamoto, T. Kimura, Y. Tomo, Tetrahedron Lett. 26 (1985) 4505. (e) H. Shinokubo, K. Miura, K. Oshima, K. Utimoto, Tetrahedron Lett. 34 (1993) 1951. (f) H. Shinokubo, K. Oshima, K. Utimoto, Chem. Lett. (1995) 461.

[24] (a) P.F. Hudrlik, G.A. Nagendrappa, K. Kulkarni, A.M. Hudrlik, Tetrahedron Lett. (1979) 2237. (b) P.F. Hudrlik, A.M. Hudrlik, A.K. Kulkarni, J. Am. Chem. Soc. 104 (1982) 6809.

[25] (a) K. Naganuma, T. Kawashima, R. Okazaki, Chem. Lett. (1999) 1139. (b) K. Naganuma, D. Sci. Thesis, the University of Tokyo, Tokyo, Japan (2000). Although the correct structure of *trans*-**1e** is an enantiomer of the structure as shown in Scheme 7, the structure was used conveniently in order to fix the configuration of the silicon center.

[26] No reaction took place when **1b** was treated with acetic acid at room temperature in sharp contrast to **1a** (see text).

[27] For Brook rearrangement, see; A.G. Brook, Acc. Chem. Res. 7 (1974) 77. For reverse Brook rearrangement, see: R. West, R. Lowe, H.F. Stewart, A. Wright, J. Am. Chem. Soc. 93 (1971) 282; A. Wright, R. West, J. Am. Chem. Soc. 96 (1974) 3214; A. Wright, R. West, J. Am. Chem. Soc. 96 (1974) 3227; R.J. Linderman, A. Ghannam, J. Org. Chem. 53 (1988) 2878; R.J. Linderman, A. Ghannam, J. Am. Chem. Soc. 112 (1990) 2392.

[28] K. Naganuma, T. Kawashima, The 12th International Symposium on Organosilicon Chemistry, Sendai, May, 1999, Abstracts, p. 173.