HETEROCYCLES, Vol. 67, No. 2, 2006, pp. 507 - 510. © The Japan Institute of Heterocyclic Chemistry
Received, 28th July, 2005, Accepted, 29th September, 2005, Published online, 30th September, 2005. COM-05-S(T)46

GROUP 14 HETERO- MONO- AND BICYCLOSILANES

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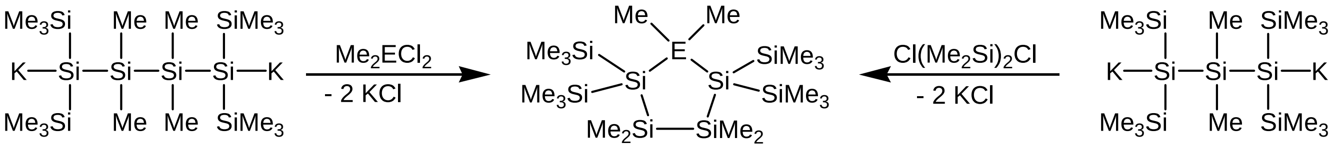
Abstract – Sila-, germa- and stannacyclopentasilanes could be obtained by reaction of a 1,4-dianionic polysilane with the dimethyl dichlorides of silicon, germanium and tin. With potassium *tert*-butoxide the cyclopentasilanes could be transformed into dianions, which were converted to bicyclic compounds by reaction with ethylene glycol ditosylate.

INTRODUCTION

Heterocyclic chemistry by its very definition is concerned with cyclic compounds having as ring member atoms of at least two different elements. Implicitly the notion is used mainly for organic compounds. However, also organoelement chemistry shows a variety of cyclic compounds, where the concept of homo- and heterocyclic compounds is equally applicable. As organosilicon chemistry in general resembles organic chemistry to some extent cyclic polysilanes can be divided into homo- and heterocyclopolysilanes.[1] A common synthetic access to heterocyclic polysilanes is the reaction of linear α,ω-dihalopolysilanes with dinucleophiles.[2] Naturally, this method only works for hetero-elements with nucleophilic properties. Sometimes an inverse approach would be useful to incorporate electropositive elements by reaction with α,ω-polysilyl dianions. As these compounds were easily available only from lithium cleavage of octaphenylcyclotetra- and decaphenylcyclopentasilanes[3] the latter were used for early examples of inverse salt elimination procedure.[4]

RESULTS AND DISCUSSION

Recently, we have introduced a variety of α,ω-dipotassiopolysilanes,[5] which have also been used to obtain heterocyclic silanes.[6] Especially, 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane (**1**) proved to be useful in this respect. Employing this compound, reactions with dimethylsilyl, -germyl, and -stannyl dichlorides gave rise to the formation of cyclopentasilanes (**2**,**3**,**4**) (Scheme 1).[5,7] Compound (**2**) could also be obtained from the reaction of 1,3-dipotassio-1,1,3,3-tetrakis(trimethylsilyl)dimethyltrisilane (**5**) with 1,2-dichlorotetramethyldisilane.



(**1**) E = Si (**2**), Ge (**3**), Sn (**4**) (**5**)

Scheme 1: Synthesis of hetero-2,2,4,4-tetrakis(trimethylsilyl)hexamethylcyclopentasilanes.

Crystal structure analyses of sila- and germacyclopentasilanes (**2**) and (**3**) revealed two isomorphic structures.[8] The rings exhibit half-chair conformations with the bond of the two dimethylsilylene units crossing the plane of the other three ring atoms by some 18 deg (Figure 1). The Si-Si distances in both rings, ranging from 2.348 to 2.375 Å and a Si-Ge distance of 2.408 Å in **3** indicate not much ring strain.

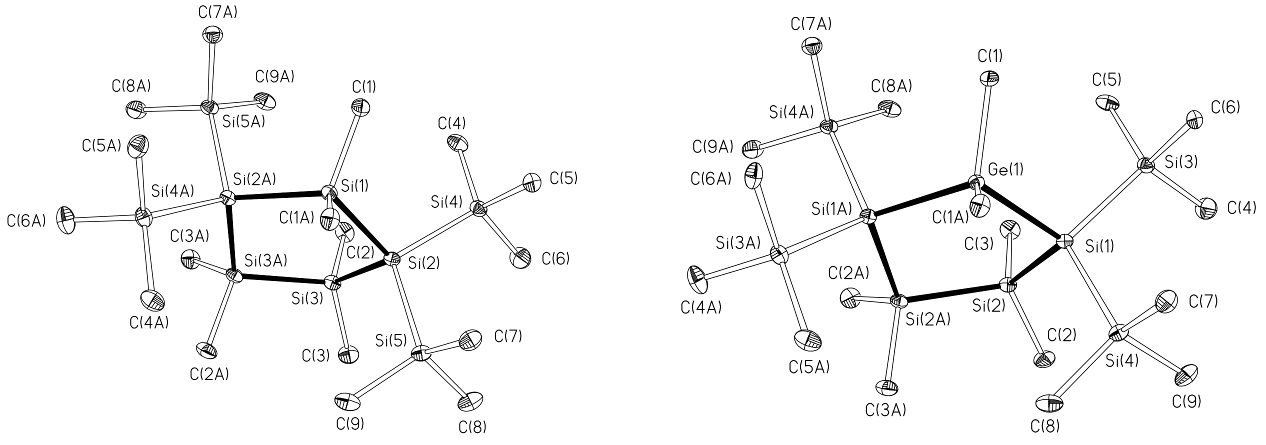
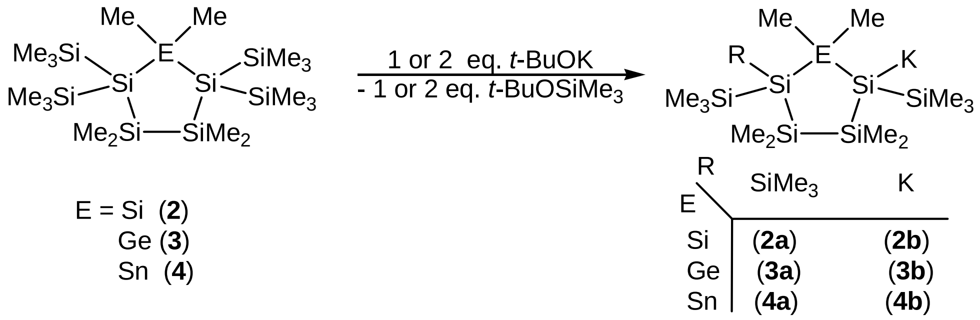


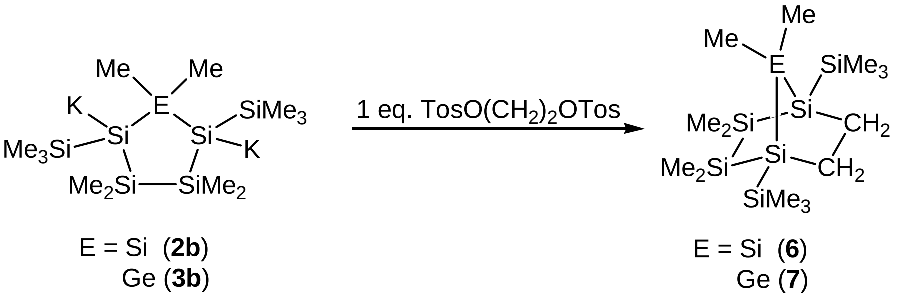
Figure 1: Molecular structures of the isostructural cyclopentasilanes (**2**) and (**3**) (with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity).

Reactions of the heterocyclopentasilanes with one or two equivalents of potassium *tert*-butoxide in the presence of crown ether therefore promoted the formation of the respective mono- or di-potassium compounds (Scheme 2) and no ring-opening was observed.



Scheme 2: Formation of hetero-2,2,4,4-tetrakis(trimethylsilyl)hexamethylcyclopentasilanylanions

Reactions of the dianions with ethylene glycol ditosylate was attempted to obtain heterobicyclo[2.2.1]-heptanes. While these proceeded smoothly for the cases of the sila- and germacyclopentasilanyldianions (**6**, **7**)[9] (Scheme 3) the reaction of the respective tin (**4b**) compound failed.



Scheme 3: 1,4-Bis(trimethylsilyl)-1,2,3,4-tetrasila-7-hetero-2,2,3,3,7,7-hexamethylbicyclo[2.2.1]heptanes

Applications of the obtained hetero-bicyclosilanes as precursors for the synthesis of higher hetero-polysilanes or for the generation of nano-wires are currently under investigation.

ACKNOWLEDGEMENTS

Financial support by the *Fonds zur Förderung der wissenschaftlichen Forschung in Österreich* (START-project Y-120 *Chiral polysilanes*) is gratefully acknowledged. The *Wacker Chemie GmbH*, Burghausen kindly provided various organosilanes as starting materials.

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7. Synthesis of **3**: **1** (0.49 mmol) in toluene (4 mL) was added dropwise to a solution of dimethylgermanium dichloride (85 mg, 0.49 mmol). The reaction was stirred for 2 h after which the solution was poured into 5 % aqueous sulfuric acid and extracted with ether. The organic phase was dried over sodium sulfate and the solvent was removed in vacuo. Yellow crystals (250 mg, 90 %) were obtained in pentane at room temperature. NMR (δ in ppm): ^{1}H (C_6D_6): 0.69 (s, 6H); 0.38 (s, 12H); 0.30 (s, 36H). ^{13}C (C_6D_6): 3.7; 3.3; -2.0. ^{29}Si (C_6D_6): -7.4; -24.5; -122.2. Anal. Calcd for $C_{18}H_{54}GeSi_8$: C 38.07, H 9.58. Found C 38.12, H 9.47.
8. For crystallographic details see the supplementary information. All data have been deposited at the Cambridge Crystallographic Deposition Centre: CCDC 278678 (**2**), CCDC 278677 (**3**).
9. Synthesis of **7**: To **3** (142 mg, 0.25 mmol) in toluene (3 mL) were added potassium *tert*-butoxide (55 mg, 0.49 mmol) and 18-crown-6 (130 mg, 0.49 mmol). After 30 min ethylene glycol ditosylate (91 mg, 0.25 mmol) was added to the brown-red solution. After completion of the reaction the mixture was subjected to aqueous work-up (5 % sulfuric acid/ ether), dried over sodium sulfate and the solvent removed in vacuo to leave **7** (90 mg, 80 %) as a colorless oil. NMR (δ in ppm): ^{1}H (C_6D_6): 1.13 (m, 2H); 1.13 (m, 2H); 0.61 (s, 3H); 0.58 (s, 3H); 0.33 (s, 6H); 0.30 (s, 6H); 0.27 (s, 18H). ^{13}C (C_6D_6): 3.7; 1.3; -4.1; -4.9; -5.2; -5.7. ^{29}Si (C_6D_6): -10.7; -36.8; -66.2. Anal. Calcd for $C_{14}H_{40}GeSi_6$: C 37.40, H 8.97. Found C 37.02, H 9.09.