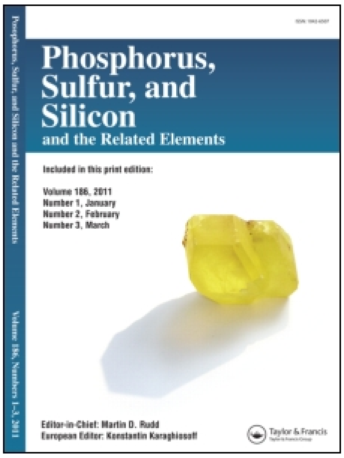


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis, Structures and Reactions of Polychalcogenadisilabicyclo[l.m.n]alkanes and Their Germanium Analogues

Nami Choi; Kumiko Asano; Sakura Watanabe; Wataru Ando

To cite this Article Choi, Nami , Asano, Kumiko , Watanabe, Sakura and Ando, Wataru(1997) 'Synthesis, Structures and Reactions of Polychalcogenadisilabicyclo[l.m.n]alkanes and Their Germanium Analogues', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 379 — 380

To link to this Article: DOI: 10.1080/10426509708545557

URL: http://dx.doi.org/10.1080/10426509708545557

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 379–380
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis, Structures and Reactions of Polychalcogenadisilabicyclo[l.m.n]alkanes and Their Germanium Analogues

Nami Choi, Kumiko Asano, Sakura Watanabe, and Wataru Ando*
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

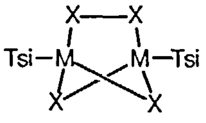
1,3-Bis[tris(trimethylsilyl)methyl]-2,4,5-trichalcogena-1,3-disilabicyclo[1.1.1]pentanes display unusual short bridgehead Si---Si distances despite the absence of formal Si—Si bonds, and chalcogen---chalcogen interactions are observed by nmr, X-ray analysis and electronic spectroscopy.

INTRODUCTION

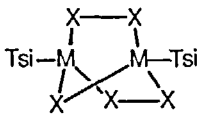
Over the past decade, the chemistry of cyclic polychalcogenides has been of great interest and widely explored from the standpoints of not only their unique structures and reactivities but also their biological activities.[1] However, there are few examples of bicyclic polychalcogenides containing group 14 elements. Recently, we disclosed very efficient routes to polychalcogenadisilabicyclo[l.m.n]alkanes and their germanium analogues by taking advantage of a bulky protecting group, tris(trimethylsilyl)methyl (denoted as Tsi).[2] Herein, we report the synthesis and structural features of polychalcogenadisilabicyclo[l.m.n]alkanes **1-M-XL** (M= Si, Ge, X= S, Se; L = l+m+n, L = 4~7) and their germanium analogues as well as their reactivities.

RESULTS AND DISCUSSION

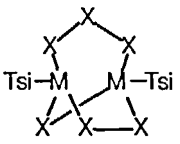
Polychalcogenadisilabicyclo[l.m.n]alkanes and their germanium analogues were synthesized by the reaction of trihydrosilane or germane bearing Tsi group with elemental sulfur or selenium. The structures of these compounds were determined by single crystal X-ray structure analysis.



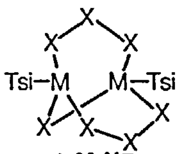
1-M-X4



1-M-X5



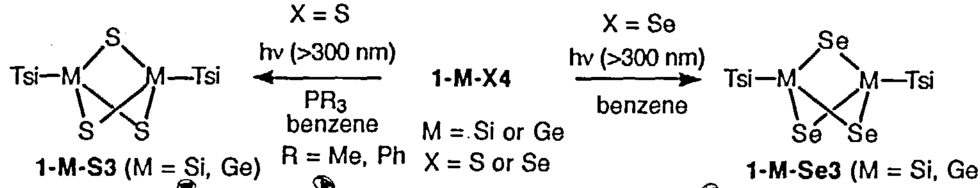
1-M-X6



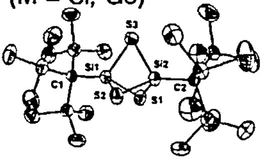
1-M-X7

Tsi = $C(SiMe_3)_3$; M = Si or Ge, X = S or Se

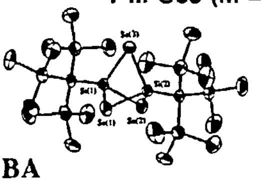
Moreover, we have achieved the synthesis of trichalcogenadisilabicyclo-[1.1.1]pentanes **1-Si-X3** (X=S or Se) and these germanium analogues **1-Ge-X3** which were obtained by dechalcogenation of the corresponding tetrachalcogenides **1-M-X4**. The structures of **1-M-X3** determined by single crystal X-ray diffraction studies indicated that trichalcogenadisila- or digerma-bicyclo[1.1.1]pentanes have dramatically short distances between bridgehead atoms and between peripheral atoms (Si---Si; 2.406 Å; S---S; 3.15 Å in **1-Si-S3**[2a], Si---Si; 2.515 Å; Se---Se; 3.38 Å in **1-Si-Se3**[2b], and Ge---Ge; 2.672 Å; Se---Se; 3.47 Å in **1-Ge-Se3**[2c]). These extremely short M---M distances are arising due to a tug-of-war between the three M-X-M and six X-M-X angles. The atomic distances between the peripheral atoms are within the sum of van der Waals radii of chalcogen atoms (S---S; 3.70 Å, Se---Se; 4.0 Å). The interaction between peripheral selenium atoms were observed by ^{77}Se nmr spectroscopy (M=Si; 830 ppm, Ge; 995 ppm), and these values could be explained by stereo compression effect, and were supported by the electronic spectrum (M=Si; 366 nm (ε 33), Ge; 365 nm (100)).



1-Si-S3

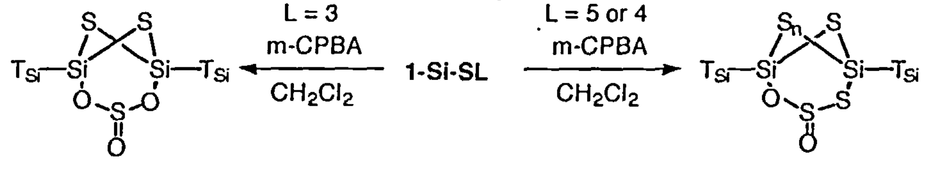


1-Si-Se3



Oxidation of 1-Si-SL (L=5, 4, and 3) by m-CPBA

The oxidation of **1-Si-SL** (L = 5, 4, and 3) by 2 equiv. of m-CPBA led to the formation of oxygenated ring expansion products **2** (83% yield), **3** (80%) and **4** (62%). In cases where 1 equiv. of m-CPBA was used, products **2**, **3**, and **4** were obtained in 68%, 33%; and 27% yields along with the remaining corresponding starting materials.



4

n=1; **2**
n=2; **3**

REFERENCES

1. Davidson, B. S.; Molinski, T. F.; Barrows, L. R.; Ireland, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 4709, and references cited therein.
2. (a) Choi, N.; Asano, K.; Ando, W. *Organometallics* **1995**, *14*, 3146. (b) Yoshida, H.; Takahara, Y.; Erata, T.; Ando, W. *J. Am. Chem. Soc.* **1992**, *114*, 1098. (c) Ando, W.; Watanabe, S.; Choi, N. *J. Chem. Soc., Chem. Commun.* **1995**, 1683.