Inorg. Chem. **1999,** *38,* 4163−4167

Neutral Pentacoordinate and Hexacoordinate Germanium(IV) Complexes: Valence Expansion At Gemanium By Transannular Bonding Of Selenium in an Eight-Membered Ring[1]

Thomas Thompson, Stephen D. Pastor,* and Grety Rihs†

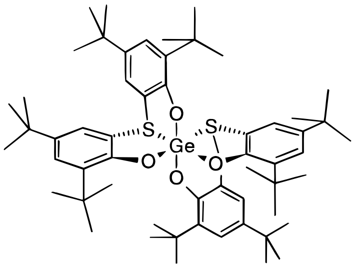
Additives Division Research Department, Ciba Specialty
Chemicals Corporation, 540 White Plains Road,
P.O. Box 2005, Tarrytown, New York 10591

Received April 29, 1999

Introduction

Recently, a significant amount of research has focused on the synthesis, conformational analysis, and elucidation of transannular intramolecular bonding in certain hetero-substituted medium-sized rings,[2] stimulated in part by recent studies on the eight-membered ring containing phosphorus.[3] In particular, 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin derivatives have been shown to provide unique coordination geometries when employed as ligands for transition-metal-catalyzed hydroformylation reactions.[4−6] The observed diequatorial aptitude of certain 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocins incorporated in pentaoxyphosphoranes has important ramifications on literature proposals describing activated states for cyclic adenosine monophosphites where trigonal bipyramidal geometries about phosphorus are invoked.[7] Studies on the conformation of the corresponding silicon containing 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxasilocin ring system have been reported,[8] including a very recent crystallographic study.[9] Quite interestingly, Holmes et al.[10] observed bonding of a transannular sulfur atom to silicon in substituted 12*H*-dibenzo[*d*,*g*][1,3,6,2]dioxathiasilocins, which led to the formation of a hypervalent silicon atom. Holmes and co-workers have observed analogous coordination of sulfur in the corresponding phosphorus containing ring system. Both pentacoordinate and hexacoordinate silicon[11−14] and phosphorus[15−17] compounds serve as models for intermediates or transition states in nucleophilic substitution reactions of the corresponding tetracoordinate state.

Very recently, we reported the first synthesis and characterization of a substituted 12*H*-dibenzo[*d*,*g*][1,3,2]dioxagermocin[18] and a 12*H*-dibenzo[*d*,*g*][1,3,6,2]dioxathiagermocin,[19] for which NMR spectral evidence suggested bonding of sulfur to germanium. Definitive solution and crystallographic evidence was found for transannular bonding of sulfur to germanium in the spirocyclic derivative **1**.[20]



1

Nothing is known about the conformation or bonding in sterically congested eight-membered ring systems containing both selenium and germanium. We report herein the first synthesis of a sterically hindered 12*H*-dibenzo[*d*,*g*][1,3,6,2]-dioxaselenagermocin and definitive solution and solid-state

---

* Author to whom correspondence should be addressed. Tel.: (914) 785 4276. Fax: (914) 785 3681. E-mail: steve.pastor@cibasc.com.

† Present address: Physics Department, Novartis Services AG, Postfach, CH-4002, Basel, Switzerland.

(1) Presented in part at the 216th ACS National Meeting, Boston, MA; August 23−27, 1996; Abstract INOR 253.

(2) For a recent monograph, see: Quin, L. D. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: Weinheim, 1988; pp 181-216.

(3) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; pp 27−39.

(4) (a) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625. (b) van Leeuwen , P. W. N. M.; Buisman, G. J. H.; van Rooy, A.; Kamer, P. C. J. *Recl. Trav. Chim. Pays-Bas.* **1994**, *113*, 61. (c) See also: Jongsma, T.; Fossen, M.; Challa, G.; van Leeuwen, P. W. N. M. *J. Mol. Catal.* **1993**, *83*, 17. (d) van Rooy, A.; Orij, E. N.; A.; Kamer, P. C. J.; van Leeuwen P. W. N. M. *Organometallics* **1995**, *14*, 34. (e) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijk, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719. (f) van Rooy, A.; Kamer, P. C. J.; van Leeuwen , P. W. N. M.; Veldman, N.; Spek, A. L. *J. Organomet. Chem.* **1995**, *494*, C15.

(5) (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. U.S. Patent 4,748,261; *Chem. Abstr.* **1987**, *107*, 7392. See also (b) Babin, J. E.; Whiteker, G. T. U.S. Patent 5,360,938; *Chem. Abstr.* **1995**, *122*, 186609.

(6) Moasser, B.; Gross, C.; Gladfelter, W. L. *J. Organomet. Chem.* **1994**, *471*, 201.

(7) (a) Holmes, R. R.; Dieters, J. A. *Inorg. Chem.* **1994**, *33*, 3235 and references therein. (b) Holmes, R. R. *Acc. Chem. Res.* **1998**, *31*, 535.

(8) (a) Pastor, S. D.; Spivack, J. D.; Rodebaugh, R. K.; Bini, D. *J. Org. Chem.* **1984**, *49*, 1297. (b) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P. *J. Heterocycl. Chem.* **1984**, *21*, 1285. (c) Pastor, S. D.; Denney, D. Z. *Phosphorus Sulfur* **1987**, *32*, 105.

(9) (a) Clarke, F. H.; Fuhrer, H.; Meier, H.-R.; Pastor, S. D.; Rist, G.; Shum, S. P. *Helv. Chim. Acta* **1993**, *76*, 1476. (b) Burke, L. P.; DeBellis, A. D.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rihs, G.; Rodebaugh, R. K.; Shum, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 8313.

(10) (a) Day, R. O.; Prakasha, T. K.; Holmes, R. R. *Organometallics* **1994**, *13*, 1285. (b) Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 10003. (c) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (c) Timosheva, N. V.; Prakasha, T. K.; .; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 3614. (d) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3182. (e) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189. (f) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317.

(11) Holmes, R. R. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1984; Vol. 32, pp 119−235.

(12) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17

(13) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(14) (a) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686. (b) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1692.

(15) (a) For a recent example of a neutral P(V) compound with a thiobisphenol ligand, see: Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 325. (b) For a mixed $P^{III}-P^{V}$ compound having a hexacoordinate phosphorus atom using a phosphinobisphenol, see: Lau, H.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **1998**, *37*, 1098.

(16) Holmes, R. R. *Pentacoordinate Phosphorus: Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I. (b) Holmes, R. R. *Pentacoordinate Phosphorus: Reaction Mechanisms*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; Vol. II. (c) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper & Row: London, 1976.

10.1021/ic990460x CCC: $18.00

crystallographic evidence for transannular bonding of selenium to germanium.

Experimental Section

All melting points were determined in open capillary tubes with a Mettler Toledo FP-900 thermosystem and are uncorrected. ^{1}H NMR (300.08 and 499.84 MHz, respectively) spectra were taken on a Varian model Gemini-300 or Unity-500 spectrometers. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets), atom assignments, coupling constant in Hertz, and number of protons. ^{77}Se{^{1}H} (95.3588 MHz) spectra were taken on a Varian Unity-500 spectrometer. All ^{77}Se chemical shifts are reported relative to dimethyl selenide in $CDCl_3$, where a positive sign is downfield from the standard. Mass spectra were determined on a Finnigan MAT-8200 instrument by using a direct insertion probe/electron impact (DIP/EI) technique. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon.

Synthesis of 2,2′-Se(4,6-di-^{t}BuC$_6$H$_2$OH)$_2$ (3). To a room-temperature solution of 6.7 g (40 mmol) of $SeOCl_2$ in 45 mL of chloroform was added dropwise (slight exotherm) over a 30 min period a solution of 25 g (120 mmol) of 2,4-di-*tert*-butylphenol (**2**) in 70 mL of chloroform. The reaction mixture was stirred for 2 h at room temperature. The resultant mixture was heated at reflux temperature and the evolved HCl gas was removed by a slow sweep of N_2 through the reaction vessel. The volatiles were removed *in vacuo* and the residue recrystallized from a 3:1 mixture of acetonitrile/toluene to give 3.5 g (18%) of a white crystalline product, mp 241 °C. ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 18 H), 1.41 (s, 18), 6.28 (s, OH, 2 H), 7.28 (d, 2 H), 7.30 (d, 2 H); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ 152.3; MS (DIP/EI), the desired molecular ions ($M^{\bullet+}$) were observed in the ratio calculated for the naturally abundant isotope mixture of ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se. Anal. Calcd for $C_{28}H_{42}O_2Se$: C, 68.69; H, 8.65. Found: C, 68.59; H, 8.51.

2,2′-Se(4,6-di-^{t}BuC$_6$H$_2$O)$_2$GeMe$_2$ (4): Synthesis. To a room-temperature solution of 0.53 g (3.1 mmol) of dimethylgermanium dichloride in 8 mL of toluene was added dropwise over a 15 minute period a solution of 1.50 g (3.1 mmol) of **3** and 0.60 g (6 mmol) of triethylamine in 15 mL of toluene. The reaction mixture was stirred overnight at room temperature and then the resultant precipitate of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo* and the residue was recrystallized from a 2:1 mixture of acetonitrile/toluene to give 0.40 g (22%) of a white crystalline solid, mp 237 °C. ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.30 (s, 18 H), 1.38 (s, 18 H), 7.32 (d, 2 H), 7.63 (d, 2 H); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ 207.5; MS (DIP/EI), the desired molecular ions ($M^{\bullet+}$) were observed in the ratio calculated for the naturally abundant isotope mixture of ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se, ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. Anal. Calcd for $C_{30}H_{46}O_2SeGe$: C, 61.05; H, 7.86. Found: C, 60.91; H, 7.65.

X-ray Structural Analysis. Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile vapor in a dichloromethane solution of **4**. Crystal data: $C_{30}H_{46}O_2GeSe$; formula weight (g mol^{-1}) = 590.22; system is monoclinic; cell parameters, $a = 26.065(5)$ Å, $b = 6.336(2)$ Å, $c = 37.974(6)$ Å, $\beta = 93.54(1)°$; $V = 6259$ (3) Å^3; space group = $C2/c$; $d_{calc} = 1.253$ Mg m^{-3}; $Z = 8$; θ range from data collection = 3 to 24.2°; intensity variation = ±1%; $\mu = 1.850$ mm^{-1}; Philips PW 1100 diffractometer; Mo Kα ($\lambda = 0.709\,26$ Å) radiation; highly oriented graphite crystal monochromator; number of variables 285; number of reflections measured 4514; number of reflections in least squares 4183; $R = 0.033$; largest diff. peak/hole 0.651/−0.278; solution, direct methods; structure solved by direct methods (Siemens SHELXS-86 (VMS) system and parameters refined by full-matrix least-squares calculations (SHELXS-92) with anisotropic displacement parameters for all non-H atoms. The difference Fourier map showed 33 of 40 hydrogen atoms, with the positions of the remaining ones where calculated assuming normal geometry (H atom parameters idealized and not refined).

[2,2′-Se(4,6-di-^{t}BuC$_6$H$_2$O)$_2$]$_2$Ge (5): Synthesis. To a room-temperature solution of 0.32 g (1.5 mmol) of germanium(IV) tetrachloride in 3 mL of toluene was added dropwise over a 30 minute period a solution of 1.50 g (3.1 mmol) of **3** and 1.25 g (12.4 mmol) of triethylamine in 6 mL of toluene. The reaction mixture was heated at 60 °C overnight, and then the resultant heterogeneous reaction mixture was allowed to cool to room temperature. The precipitate of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo*, and the residue was recrystallized from a mixture of acetonitrile and toluene to give 0.48 g (31%) of a white crystalline solid, mp 312 °C. ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 18 H), 1.27 (s, 18 H), 1.29 (s, 18 H), 1.53 (s, 18 H), 7.30 (d, 2 H), 7.40 (d, 2 H), 7.42 (d, 2 H), 7.48 (d, 2 H); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ 88.6; MS (DIP/EI), the desired molecular ions ($M^{\bullet+}$) were observed in the ratio calculated for the naturally abundant isotope mixture of ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se, ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge.

X-ray Structural Analysis. Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile vapor in a toluene solution of **5**. Crystal data: $C_{56}H_{80}O_4GeSe_2$; formula weight (g mol^{-1}) = 1047.71; crystal size 0.81 × 0.59 × 0.54 mm; system is orthorhombic; cell parameters, $a = 15.427(2)$ Å, $b = 19.279(2)$ Å, $c = 19.218(2)$ Å; $V = 5714$ (1) Å^3; space group = $Pccn$; $d_{calc} = 1.218$ Mg m^{-3}; molecular symmetry C_2; $Z = 4$; data collection, θ range from data collection = 3 to 24.2°; intensity variation = ±2%; $\mu = 2.164$ mm^{-1}; Philips PW 1100 diffractometer; Mo Kα ($\lambda = 0.709\,26$ Å) radiation; highly oriented graphite crystal monochromator; number of variables 307; number of reflections measured 5080; number of reflections in least squares 4674; $R = 0.047$; largest diff. peak/hole 0.979/−0.777; solution: direct methods; structure solved by direct methods (Siemens SHELXS-86 (VMS) system and parameters refined by full-matrix least-squares calculations (SHELXS-92) with anisotropic displacement parameters for all non-H atoms. The difference Fourier map showed 34 of 46 hydrogen atoms, with the positions of the remaining ones where calculated assuming normal geometry (H atom parameters idealized and not refined).

Results and Discussion

Synthesis. Korcek et al. reported the synthesis of a selenobisphenol by the reaction of a substituted phenol with selenium oxychloride ($SeOCl_2$).[21] The selenobisphenol **3** was prepared by the analogous reaction of the hindered phenol **2** with $SeOCl_2$ in chloroform. Korcek suggested a triarylselenonium ion intermediate in this reaction. Quite recently, Guziec presented convincing evidence that triarylselenonium ions are indeed intermediates in the reaction of phenol with $SeOCl_2$ to give diaryl selenides[22] (Scheme 1).

The dimethyl-substituted dibenzo[*d*,*g*][1,3,6,2]dioxaselenagermocin **4** was prepared by the reaction of **3** with dimeth-

---

(17) (a) Sherlock, D. J.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 93. (b) Chandrasekaran, A.; Sood, P.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 459. (c) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3747. (d) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3862. (e) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 6329.

(18) Pastor, S. D.; Smith, A. R.; Rihs, G. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *115*, 169.

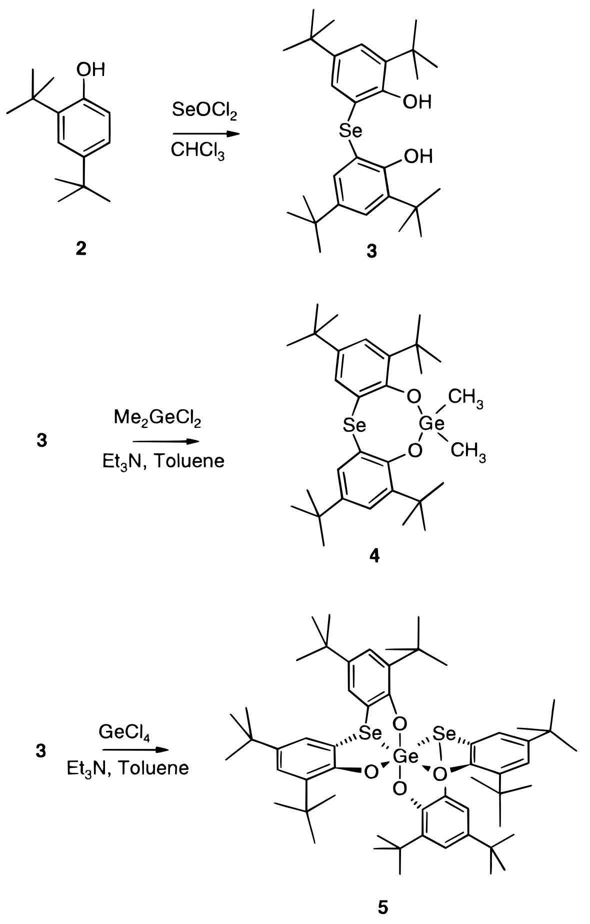
(19) Pastor, S. D.; Huang, V.; NabiRahni, D. . *Phosphorus, Sulfur, Silicon Relat. Elem.* **1998**, *139*, 87.

(20) Pastor, S. D.; Huang, V.; NabiRahni, D.; Koch, S. A.; Hsu, H.-F. *Inorg. Chem.* **1997**, *36*, 5966.

(21) (a) Korcek, Š.; Holotík, Š.; Leško, J.; Vesely, V. *Chem. Zvesti* **1969**, *23*, 281. (b) For the reaction of selenium dioxide and HCl with phenols, see: Funk, H.; Papenroth, W. *J. Prakt. Chem.* **1960**, *11*, 191.

(22) Grant, J. R.; Youens, K. E.; Guziec, L. J.; Guziec, F. S. 215th ACS National Meeting, Dallas, TX, March 29−April 2, 1998; Abstract ORGN 304.

Scheme 1



ylgermanium(IV) dichloride using triethylamine as an acid acceptor. In an analogous manner, the spirocyclic derivative **5** was obtained by the reaction of **3** with germanium(IV) chloride. Both derivatives were obtained as white crystalline solids. In the MS of both **4** and **5**, the molecular ions ($M^{\bullet+}$) were observed in the ratio calculated for the naturally abundant isotope mixture of ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se, ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge.

Conformation in the Solid-State and Solution Dimethylgermanium Derivative. The commonly accepted nomenclature to describe the conformation of eight-membered rings is used herein; namely the boat−chair (C_S symmetry), boat−boat (C_S symmetry), twist-boat (C_1 symmetry), and Twist (C_2 symmetry), which are abbreviated BC, BB, TB, and T, respectively.[23−25] Arshinova has noted that the boat conformer (C_1 symmetry; abbreviated B) should also be considered as it is commonly found in the solid state (Figure 1).[26] The B conformation represents a highly distorted TB geometry about halfway between the symmetric C_2 T and BB geometry.[23] The B conformation is characterized by a $C_{\mathrm{Aromatic}}{-}O{-}P{-}O$ torsion angle of 0°.[26a]

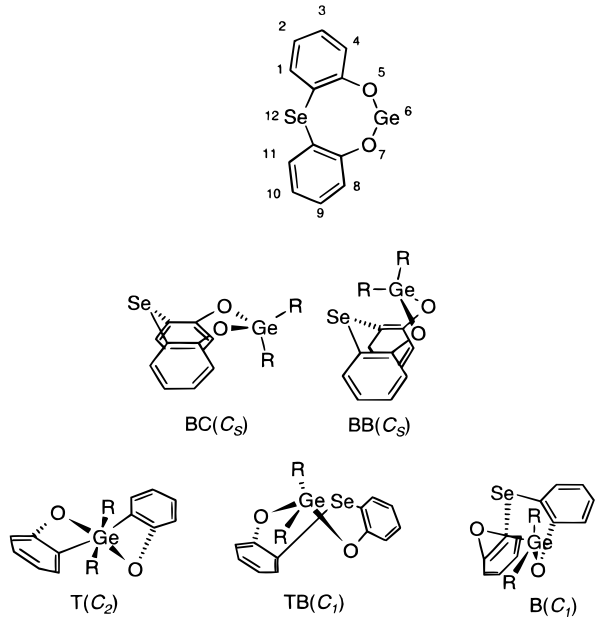


Figure 1. Chemical Abstracts Service numbering system and conformations of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaselenagermocin ring system. The TB boat structure represents only one member of a family of flexible TB forms.

In the ^{1}H NMR spectrum (500 MHz; $CDCl_3$) of **4** at 27 °C, a singlet was observed at δ 1.04 whose peak area integrated to six protons, which was assigned to the protons of two equivalent methyl groups bonded to germanium. In the VT ^{1}H NMR spectrum (500 MHz; CD_2Cl_2) of **4** below −60 °C, the coalescence temperature (T_C), two singlets were observed at δ 0.85 and δ 1.12 whose peak area integrated to three protons each, which were assigned to the protons of two anisochronous methyl groups bonded to germanium. The free energy of activation ($\Delta G^\ddagger$) required to render the methyl group protons equivalent is 9.9 kcal/mol, which is significantly lower than previously observed for methylene and sulfur bridged silocins and germocins.[8,9,18,19] The VT ^{1}H NMR spectrum of **4** below the T_C showed the presence of two pairs of equivalent *tert*-butyl groups as well as two pairs of equivalent aromatic protons. A singlet was observed at δ 207.5 in the ^{77}Se{^{1}H} NMR ($CDCl_3$) of **4**.[27]

The VT ^{1}H NMR spectrum of **4** below the T_C requires that the ring conformation possess a σ plane of symmetry passing through the germanium and the bridging selenium atom. This must be the case in order to explain the observation of anisochronous methyl groups bonded to germanium as well as two pairs of equivalent *tert*-butyl groups. The symmetry requirements are satisfied by either the BC or BB conformer, although TB conformers that rapidly pass through the required symmetry plane below the T_C cannot be excluded. Previously in our studies of related eight-membered silocins and germanocins, large anisotropic shifts were observed for anisochronous methyl group protons bonded to either silicon or germanium the BC conformer.[8,9,18,19] In the TB and BB conformations of the related silocins and germanocins, the anisotropic shielding of the methyl groups is reduced.[9b,10a,b,19] The BB conformer has only been observed in solution when transannular bonding of a bridging heteroatom to phosphorus,

---

(23) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6986.

(24) Fraser, R. R.; Raza, M. A.; Renaud, R. N.; Layton, R. B. *Can. J. Chem.* **1975**, *53*, 167.

(25) Moore, J. A.; Anet, F. A. L. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon: Oxford, 1984; Vol. 7, pp 653−707.

(26) (a) Arshinova, R. P.; Danilova, O. I.; Arbusov, B. A. *Phosphorus Sulfur Silicon Relat. Elem.* **1987**, *34*, 1. (b) Arshinova, R. P. *Russian Chem. Rev.* **1988**, *57*, 1142. (c) Arshinova, R. P.; Plyamovatyi, A. Ch.; Kadyrov, R. A.; Gnevashev, S. G.; Arbusov, B. A. *Phosphorus Sulfur Silicon Relat. Elem.* **1989**, *41*, 449. (d) Arshinova, R. P. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *68*, 155.

(27) For a review on ^{77}Se NMR spectroscopy, see: Luthra, N. P.; Odom, J. D. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chapter 6.

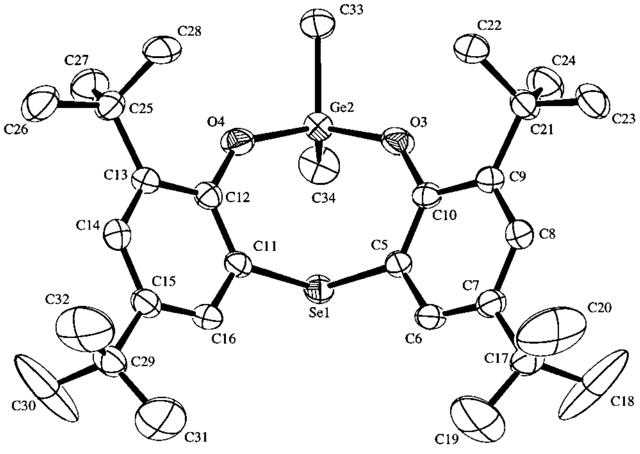


Figure 2. Molecular structure of **4** showing the crystallographic numbering scheme.

silicon or germanium is present. In the absence of transannular bonding, the BB conformer is calculated to be a transition state for the interconversion of enantiomeric TB conformations.[28] The degree of nonequivalence observed for the anisotropic methyl groups bonded to germanium in **4** suggests that the eight-membered ring adopts a BB conformation with transannular bonding of selenium to germanium.

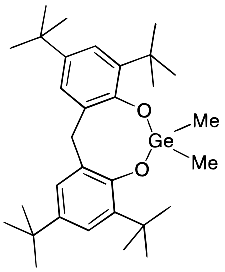
Care must be exercised in comparing the $\Delta G^{\ddagger}$ of processes in different molecules because a significant temperature-dependent entropy term could be misleading. However, the structural similarity of **4** with previously reported silocins and germocins suggests that the $\Delta G^{\ddagger}$ for the process rendering the methyl-group protons on Ge equivalent would be similar. Prior studies have shown that this process is inversion of the eight-membered ring.[8,9,18,19] The observed $\Delta G^{\ddagger}$ for **4** (9.9 kcal/mol) is significantly lower than those previously measured for other silocin and germocin analogues (12−14 kcal/mol).[8,9,18,19] The large reduction of the $\Delta G^{\ddagger}$ required for rendering the anisotropic methyl groups bonded to germanium of **4** equivalent suggests that ring inversion may not be the process involved, but rather a pseudorotational process in which the Se−Ge bond remains intact is operative.[29,30] Corriu and co-workers suggested the involvement of hexacoordinated germanium in the racemization of enantiomerically pure chlorogermanes.[29,30] Further work is required to distinguish between these two possible mechanistic pathways.

Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile vapors into a solution of **4** in dicloromethane (Figure 2, Table 1). In the solid-state the eight-membered ring adopts a BB conformation with transannular bonding of selenium to germanium. The Ge−Se bond length is 3.10 Å, which is 31% longer than the sum of the covalent radii of Se and Ge (2.36 Å) but significantly shorter than the sum of the van der Waals radii (3.85 Å).[31] The O(3), O(4), and C(34) ligands comprise the equatorial plane with the sum of the appropriate bond angles about Ge equal to 344.1°.

Table 1. Selected Bond Distances and Bond Angles for **4**

bond lengths (Å)		bond angles (deg)	
Ge(2)−C(33)	1.912(5)	C(33)−Ge(2)−C(34)	112.1(2)
Ge(2)−C(34)	1.923(4)	O(3)−Ge(2)−O(4)	112.2(2)
Ge(2)−O(3)	1.782(3)	C(10)−O(3)−Ge(2)	137.3(3)
O(3)−C(10)	1.352(5)	O(3)−Ge(2)−C(34)	115.9(2)
Ge(2)−Se(1)	3.099(2)	O(4)−Ge(2)−C(34)	116.0(2)
Se(1)−C(5)	1.908(4)	C(5)−Se(1)−C(11)	101.9(2)
Se(1)−C(11)	1.912(4)	O(3)−Ge(2)−C(33)	99.2(2)
Ge(2)−O(4)	1.786(3)	O(4)−Ge(2)−C(33)	98.9(2)
O(4)−C(12)	1.352(5)	C(12)−O(4)−Ge(2)	137.7(3)

The C(33)−Ge−O(3), C(33)−Ge−O(4), and C(33)−Ge−C(34) bond angles are 99.2°, 98.9°, and 112.1°), respectively. The Ge−C(33) and Ge−C(34) bond lengths are 1.91 and 1.92 Å, respectively, and are in the range typically found for a Ge−C single bond.[33] Although the Ge−C bonds found in **6** in which no donor atoms are present were found to be 1.92 Å,[18] the corresponding geminal Me−Ge−Me bond angle is 122.2° in **6** compared to 112.1° in **4**. Following the procedure of Holmes[10a,b] based upon donor−acceptor atom bond distance, the geometry at Ge is displaced 50.3% from tetrahedral to trigonal bipyramidal geometry. A similar value of 49.5% displacement from tetrahedral to trigonal bipyramidal geometry at Ge can be obtained by comparing the sum of the equatorial bond angles about Ge (344.1°) found in **4** with that expected for tetrahedral geometry (328.5°) and trigonal bipyramidal geometry (360°).



6

Spirocyclic Germanium Derivative. Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile vapors into a solution of **5** in dicloromethane. In the solid state X-ray structure of **5**, a distorted octahedral geometry about Ge is observed. In addition to the expected bonding of the four oxygen ligands to Ge, bonding of the two transannular Se atoms to Ge is observed (Figure 3, Table 2).

The conformation (BB conformer) as well as bonding parameters of both eight-membered rings are identical with the molecule possessing C_2 symmetry. The Se atoms lie in a plane with one oxygen atom of each eight-membered ring and are cis to one another. The O(3)−Ge(2)−O(3*), O(3*)−Ge(2)−Se(1*), O(3)−Ge(2)−Se(1), and Se(1*)−Ge(2)−Se(1) bond angles are 89.9°, 87.2°, 87.2°, and 96.0°, respectively. The sum of the appropriate bond angles in the plane is 360.3°. The remaining two oxygen atoms are perpendicular to the plane passing through the O(3), O(3*), Se(1), and Se(1*) atoms and are trans to one another. The trans oxygen atoms are bent toward one another [O(4)−Ge(2)−O(4*) = 164.9°]. Quite interestingly, the observed cis relationship of the Se atoms in **5** is similar to

---

(28) See ref 9b and references therein.

(29) (a) Carre, F. H.; Corriu, R. J. P.; Thomassin, R. B. *J. Chem. Soc., Chem. Commun.* **1968**, 560. (b) Carre, F.; Corriu, R. J. P.; Leard, M. *J. Organomet. Chem.* **1970**, *24*, 101.

(30) (a) For a recent review on the stereochemistry of organogermanium compounds, see: Marshall, J. A.; Jablonowski, J. A. In *The Chemistry of Organic Germanium, Tin, and Lead Compounds*; Patai, S., Ed; Wiley: New York, 1995; pp 195−211. (b) For a review on stereochemistry, see: Mackay, K. M. In *The Chemistry of Organic Germanium, Tin, and Lead Compounds*; Patai, S., Ed; Wiley: New York, 1995; pp 97−187.

(31) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(32) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: Special Publication No. 11, 1958, and Supplement; Special Publication No. 18, 1965; London, UK.

(33) (a) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690. (b) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1994**, *33*, 93.

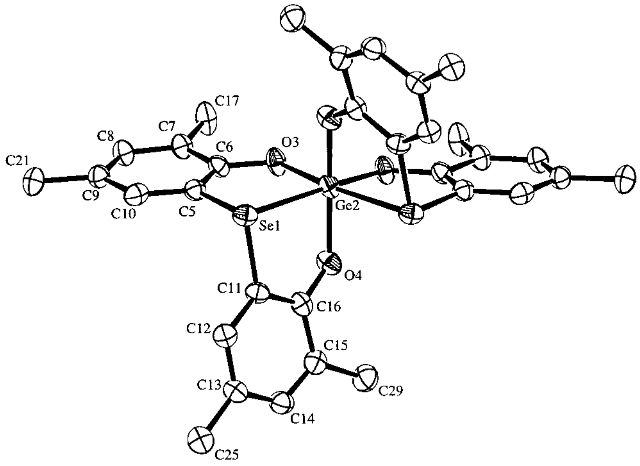


Figure 3. Molecular structure of **5** showing the crystallographic numbering scheme (*tert*-butyl methyl carbons deleted for clarity).

Table 2. Selected bond distances and bond angles for **5**

bond lengths (Å)		bond angles (deg)	
Ge(2)−Se(1)	2.5959(6)	O(4)−Ge−O(4*)	164.88(14)
Ge(2)−O(3)	1.792(2)	O(3)−Ge(2)−O(4)	92.35(11)
O(3)−C(6)	1.349(4)	O(3)−Ge(2)−Se(1)	87.19(7)
C(6)−C(5)	1.390(5)	O(3)−Ge(2)−O(3*)	89.9(2)
Se(1)−C(5)	1.915(3)	O(3*)−Ge(2)−Se(1*)	87.19(7)
Se(1)−C(11)	1.897(4)	C(5)−Se(1)−C(11)	101.89(14)
C(11)−C(16)	1.393(5)	Se(1)−Ge(2)−Se(1*)	96.00(2)
O(4)−C(16)	1.337(4)	O(3)−Ge(2)−Se(1*)	175.00(8)
Ge(2)−O(4)	1.849(2)	O(4)−Ge(2)−Se(1)	85.83(8)

that observed for the corresponding sulfur atoms in **1**[20] and opposite to the observed trans relationship observed in hexacoordinated phosphorus compounds studied by Holmes et al.[33] The five-membered rings, [comprising Se(1), Ge(2), O(3), C(5), C(6) and Se(1), Ge(2), O(4), C(16), C(11)], are planar within 0.09 Å, and the dihedral angle between the two five membered rings is 78°.

The Se−Ge bond lengths in **5** (2.60 Å) is significantly shorter than the sum of the van der Waals radii of Ge and Se (3.85 Å) but only 10% longer than the sum of the covalent radii (2.36 Å). Following the procedure of Holmes[10a,b] based upon donor-acceptor atom bond distance, the geometry at Ge is displaced 83.9% from tetrahedral to octahedral geometry. The O−Ge bond lengths (1.84 Å) trans to an oxygen atom are longer than the Ge−O bond lengths (1.79 Å) trans to a selenium atom.

In the ^{1}H NMR spectrum of **5** in chloroform-*d*, four singlets were observed that were assigned to the protons of four nonequivalent pairs of *tert*-butyl substituents. Similarly, four doublets were observed that were assigned to the protons of four nonequivalent pairs of aromatic protons. The ^{1}H NMR spectrum observed is that expected if the bonding of selenium to germanium observed in solid state is maintained in solution. Furthermore, the observation of four pairs of both nonequivalent *tert*-butyl substituents and aromatic protons strongly suggests that ligand permutation by psuedorotational processes, which are often observed for ligands of hypervalent phosphorus species,[17,18] are either absent or slow on the NMR time scale.

Conclusions

This report constitutes the first crystallographic evidence for selenium-induced hexacoordination in a neutral germanium complex. The ^{1}H NMR spectral data suggests that the observed selenium-induced penta- and hexacoordination of germanium in **4** and **5**, respectively, in the solid state is maintained in solution. The observed solid-state Se−Ge bond distance was significantly shorter in **5** than in **4**. A reasonable explanation for this difference is the greater electron acceptor properties of the Ge atom in **5** with four electronegative oxygen ligands rather than the Ge atom in **4** with only two oxygen ligands.

Acknowledgment. The authors thank Ciba Specialty Chemicals Corporation for support and permission to publish this work. The authors thank Dr. R. K. Rodebaugh for ^{77}Se NMR spectra.

Supporting Information Available: Data from X-ray crystallographic analysis of **4** and **5**, including crystal data, bond angles, bond lengths, and atomic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990460X