Organometallics **2006,** *25,* 2709−2711

The Surprising Reactions of 1,3-Di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-germa-4-cyclopentene

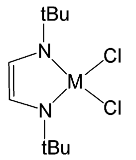
Robert West,*[,†] Daniel F. Moser,[†] Ilia A. Guzei,[§] Gyu-Hwan Lee,[†] Akinobu Naka,[†]
Wenjian Li,[†] Alexander Zabula,[#] Sergei Bukalov,[#] and Larissa Leites[#]

*Organosilicon Research Center, University of Wisconsin, 1101 University Avenue,
Madison, Wisconsin 53706, Molecular Structure Laboratory, University of Wisconsin,
1101 University Avenue, Madison, Wisconsin 53706, and Institute of Organoelement Compounds,
Scientific and Technical Center on Raman Spectroscopy, Russian Academy of Sciences, Vavilova Street 28,
Moscow 119991, Russia*

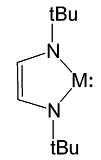
Received October 5, 2005

*Summary: 1,3-Di-tert-butyl-2,2-dichloro-1,3-diaza-2-germa-4-cyclopentene (**1**) was synthesized from N,N-di-tert-butyl-1,2-diiminoethane (NN) and GeCl$_2$. **1** undergoes slow transformation at room temperature to the bicyclic compound **6**. Compound **6** is also produced in the reaction of GeCl$_4$ with N,N′-dilithio-1,4-diaza-2-butene. Treatment of **1** with GeCl$_2$ yields a complex salt, (NN)Ge-Cl$^+$GeCl$_3^-$ (**7**).*

In this paper we describe the synthesis and unexpected chemical transformations of a heterocyclic compound of tetravalent germanium, **1**. The silicon analogue to **1**, compound **2**,[1] is important as an intermediate in the synthesis of the well-known stable silylene **4**.[2,3] The corresponding aromatic germylene, **3**, is obtained by the reaction of GeCl$_2$ with the dianion of *N*,*N*′-di-*tert*-butyl-1,2-diaminoethene,[4,5] so the dichloro derivative **1** is not needed as an intermediate. However, it is curious that the synthesis of **1** has not previously been reported.



M = Ge (**1**), Si (**2**)



M = Ge (**3**), Si (**4**)

Dichlorogermane **1** was obtained from the reaction of *N*,*N*-di-*tert*-butyl-1,2-diiminoethane (**5**) with GeCl$_2$ at 0 °C, as moisture-sensitive orange crystals in 95% yield.[6] Its structure was determined by X-ray crystallography (Figure 1). In the silicon analogue **2**, the five-membered ring is planar,[7,8] but in **1** the ring is nonplanar with the Ge atom 0.229(2) Å out of the plane of the other four atoms. The envelope conformation of the ring in **1** is characterized by a 10.63(3)° folding angle. The Ge−Cl bond length (2.156(5) Å) in **1** is typical for chlorides of tetravalent Ge (Table 1).[9]

The structure of **1** differs significantly from that of the related germylene **3**.[4] The double bond in **3** (1.364 Å) is longer than that in **1** (1.335(3) Å), while the endo C−N bonds in **3** (1.384 Å) are shorter than in **1** (1.416(2) Å). The Raman frequency of the stretching $\nu_{C=C}$ vibration of **1**, 1628 cm^{-1} (an analogous line was found for **2**[3] at 1623 cm^{-1}), is much higher than that of **3**, 1552 cm^{-1}.[5] This comparison provides additional evidence for the aromaticity of **3**.[5]

Surprisingly, **1** is not a stable compound. Upon storage in benzene solution at room temperature, **1** was slowly transformed into the remarkable bicyclic compound **6**. The byproduct, t-BuNH$_2$, was detected in the reaction mixture by ^{1}H NMR.[10] **6** is also the principal (95%) product from the reaction of *N*,*N*′-dilithio-1,4-diazabutene with GeCl$_4$ (Scheme 1).[11]

In the lattice of **6** the molecules occupy crystallographic 2-fold axes, and consequently both five-membered rings in the molecule are planar.[12] The aromatic pyrrole system in this molecule is characterized by a Raman line at 1524 cm^{-1} and an IR band at 1592 cm^{-1}. Vibrations of the GeCl$_2$ fragment (ν^sGeCl at 382 cm^{-1} and ν^{as}GeCl at 425 cm^{-1}) are typical for Ge^{IV} dichlorides.[9] There is no obvious pathway for the formation

---

[*] To whom correspondence should be addressed. E-mail: west@chem.wisc.edu.

[†] Organosilicon Research Center, University of Wisconsin.

[§] Molecular Structure Laboratory, University of Wisconsin.

[#] Russian Academy of Sciences.

(1) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

(2) Moser, D. F.; Guzei, I. A.; West, R. *Main Group Met. Chem.* **2001**, *24*, 811.

(3) Leites, L. A.; Bukalov, S. S.; Denk, M.; West, R.; Haaf M. *J. Mol. Struct.* **2000**, *550−551*, 329.

(4) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

(5) Leites, L. A.; Bukalov, S. S.; Zabula, A. V.; Garbuzova, I. A.; Moser, D. F.; West, R. *J. Am. Chem. Soc.* **2004**, *126*, 4114.

(6) Synthesis of **1**. A 100 mL Schlenk flask equipped with a stir bar and addition funnel was charged with 0.592 g of GeCl$_2$·dioxane (2.56 mmol). The flask was immersed in an ice bath, 10 mL of THF was added, and the resulting solution was stirred at 0 °C for 10 min. A solution containing 0.430 g of diimine **5** (2.56 mmol) in 10 mL of THF was then slowly added to the germanium dichloride solution over a period of 10 min. Upon first addition of diimine solution, the reaction mixture turned bright orange. After the addition of all the diimine solution, ^{1}H NMR of an aliquot showed complete conversion of diimine to the cyclic compound. No other products were detected. The solvent was removed in vacuo, and the resulting orange powder was dissolved in a minimal amount of THF (∼5 mL) and refrigerated. Orange crystals were recovered (0.76 g, 95%) and submitted for X-ray analysis. Mp: 133−136 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ (ppm) 1.24 (s, 18H, ^{t}Bu); 5.90 (s, 2H, CH). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 30.6 (s, (CH$_3$)$_3$C); 54.7 (s, (CH$_3$)$_3$$C$); 112.8 (s, CH). MS (EI): *m*/*z* (%) 312.0 (40) (M$^+$), 277.1 (60) (M$^+$ − Cl), 242.4 (70) (M$^+$ − 2Cl). Also found in MS: 406 (M$^+$ for **6**, probably resulting from the heating of **1**). Anal. Calcd (found) for C$_{10}$H$_{20}$N$_2$Cl$_2$Si: C, 38.46 (38.74); H, 6.41 (6.77); N, 8.97 (8.51).

(7) Becker, J. S.; Staples, R. J.; Gordon, R. G. *Cryst. Res. Technol.* **2004**, *39*, 85.

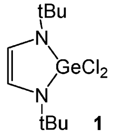
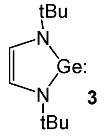
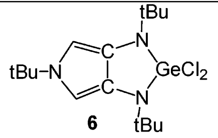
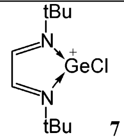
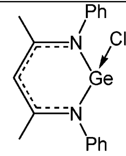
(8) Karsch, H, H.; Schleuter, P. A.; Bienlein, F.; Herker, M.; Witt, E.; Sladek, A.; Heckel, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 295.

(9) Leites, L. A.; Zabula, A. V.; Bukalov, S. S.; Korlyukov, A. A.; Koroteev, P. S.; Maslennikova, O. S.; Egorov M. P., Nefedov, O. M. *J. Mol. Struct.* **2005**, *750*, 116.

(10) A solution of **1**, 0.06 M in deuterobenzene, was 5% transformed into **6** after 5 days at 25 °C. At 55 °C, 25% transformation took place in 2 days. Neither t-BuNH$_2$ nor GeCl$_2$ catalyzed the transformation of **1** to **6** in solution.

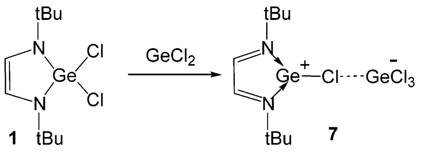
10.1021/om050860u CCC: $33.50

Table 1. Experimental Interatomic Distances (Å)

Bond	 1	 3	 6	 7	 8
Ge-N	Av. 1.8022(17)	1.856	1.809(3)	Av. 2.073(3)	1.955/1.965
Endo C-N	Av. 1.416(2)	1.384	1.424(4)	Av. 1.265(5)	1.337/1.338
C-C	1.335(3)	1.364	1.432(8)	1.470(4)	1.390
Ge-Cl	Av. 2.156(2)	-	2.1492(13)	2.2696(8)	2.340

of **6** from **1**. However it is reasonable to suppose that **1** is in equilibrium with **5** and $GeCl_2$. A crucial step in the transformation may be formation of a carbon−carbon bond from two molecules of **5**, perhaps coordinated to $GeCl_2$.

When **1** is kept at −8 °C in an ampule sealed in vacuo for several weeks, it decomposes to a mixture, containing **1**, **6**, and yellow crystals of the complex salt **7**. Identification of the compounds in the mixture was possible using a micro-Raman method.[13] When viewed under the microscope (magnification 100 ×), the mixture appeared heterogeneous, containing blocklike orange crystals of **1** and needlelike yellow crystals of **7**, identified by their Raman spectra. Compound **7**, a stable crystalline solid, was also produced in high yield when **1** was treated with 1 equiv of $GeCl_2$ (eq 1).

 (1)

The X-ray structure of **7** is shown in Figure 2. The diimine moiety is evidenced by double C═N bonds of 1.265(5) Å and an ordinary C5−C6 bond of 1.470(4) Å (Table 1). The coordinate character of the Ge···N bonds follows from long interatomic distances, 2.073 Å, much longer than the ordinary covalent Ge−N bonds in molecules **1** and **6** (1.80 Å). The Ge−Cl bond in the germylene cation is 2.2696(8) Å and that in the anion $GeCl_3^-$ is 2.31(3) Å (av), values typical for Ge^{II} chlorides (cf. 2.281 Å in the Cl_2Ge^{II} complex with dioxane[9] and 2.31 Å in the salt $RbGe^{II}Cl_3$[14]). The interionic distance Ge···Cl is only 3.37 Å, indicating a moderately strong Ge···Cl interaction. The vibrational spectrum is in accord with structure **7**, exhibiting intense Raman lines at 1595 cm^{-1} ($\nu_{C=N}$) and 311 cm^{-1} (ν_{Ge-Cl}). The latter low-frequency value is similar to that observed

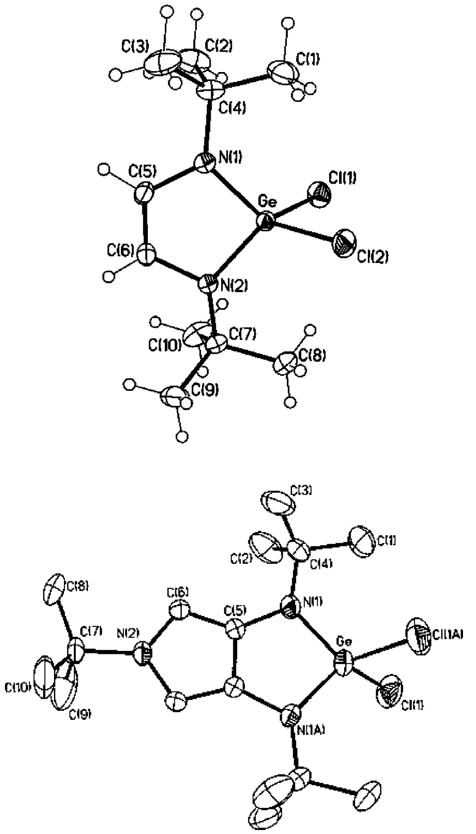
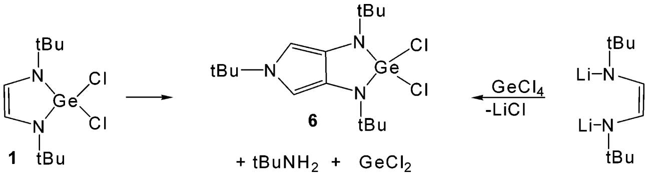


Figure 1. Molecular drawing of **1** (top) and **6** (bottom) shown with 30% thermal probability ellipsoids.

Scheme 1. Syntheses of the Bicyclic Germanium Compound



---

(11) Synthesis of **6**. To a 100 mL Schlenk flask was added diimine **5** (0.164 g, 0.975 mmol) followed by 10 mL of THF. This was stirred at room temperature, and 0.140 g of Li metal (2.04 mmol) was added to the flask. The reaction mixture became a dark red and was stirred for 24 h at room temperature. After stirring, any excess lithium was removed from the mixture and the reaction flask was immersed in a −78 °C dry ice/acetone bath. Then a solution of $GeCl_4$ (0.439 g, 2.04 mmol) in 5 mL of hexane was added dropwise. The mixture was stirred for 6 h, and ^1H NMR revealed formation of **6** and a small amount of **1** (95/5 by NMR). All solvent was removed in vacuo, and the resulting crude solid was extracted with 25 mL of hexane and was filtered to remove any LiCl. The resulting orange solution was concentrated in vacuo and refrigerated for 24 h. Orange-red blocklike crystals were isolated in several fractions to give an overall yield of 0.126 g (63.6%) of **6** based on the amount of diimine used. Mp: 193−194 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.19 (s, ^{t}Bu, 9H); 1.48 (s, ^{t}Bu, 18H); 6.12 (s, CH, 2H). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 29.4 (s, $(CH_3)_3C$); 30.3 (s, $(CH_3)_3C$); 55.4 (s, $(CH_3)_3C$); 55.6 (s, $(CH_3)_3C$); 97.9 (s, CH); 124.1 (s). MS (EI) *m/z* (%): 407.0 (100) (M^+), 372.0 (35) (M^+ − Cl), 351.0 (42) (M^+ − ^{t}Bu). UV spectrum of the solid **6** as a Nujol mull: λ_{max} −266 and 355 nm. Anal. Calcd (found) for $C_{16}H_{29}N_3Cl_2Ge$: C, 47.22 (46.75); H, 7.18 (7.31); N, 10.33 (10.10).

(12) Interestingly, compound **6** crystallizes in a monoclinic unit cell at RT but in a triclinic unit cell at 173 K. Data here and in Table 1 refer to the monoclinic lattice. The C═C bonds in the aromatic C_4N ring are 1.362 Å and the C−N bonds 1.378 Å.

(13) The solid samples of **1**, **5**, **6**, and **7** sealed in capillaries were studied by the micro-Raman method with use of Jobin-Yvon LabRAM and T-64000 laser Raman spectrometers equipped with microscopes. The spectra were excited by 632.8 and 514.5 nm lines of He−Ne and Ar^+ lasers. The UV and IR absorption spectra were obtained using computerized Carl Zeiss M-40 and M-82 spectrophotometers.

(14) Messer, D. *Z. Naturforsch.* **1978**, *33B*, 366.

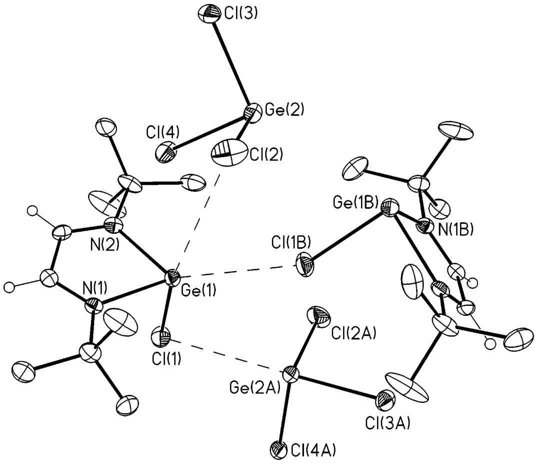
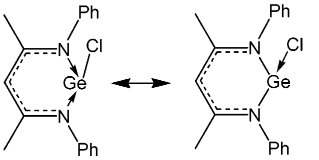


Figure 2. Molecular drawing of **7** showing two symmetry-related ion-pairs drawn with 50% thermal probability ellipsoids. Distal interactions between Ge and Cl atoms are shown as dashed lines.

recently[9] for the complex Cl_2Ge^{II}·dioxane, in which intermolecular Ge···Cl coordination also plays a prominent role.

Several earlier examples of GeX^+ complexes with cyclophane[15] (r_{GeCl} = 2.224 Å) and various bidentate nitrogen-containing donor ligands are known.[16−18] In particular, the three-coordinate divalent germanium L^2GeX derivatives analogous to **7** but with the β-diketiminato ligand PhNCMeCHCMeNPh (L^2) have been described.[16] For X = Cl (**8**), a model structure $L^2Ge^+\cdots Cl^-$ corresponding to a divalent germanium species weakly coordinated with the Cl atom was proposed. However,



8

the interatomic Ge−N and Ge−Cl distances measured for this chloride (Table 1) both lie between the donor−acceptor and covalent bond lengths. Therefore the choice between the two structures in this case seems somewhat arbitrary. The same could be said about the structure of the complex [(i-Pr)$_2$ATI]Ge^{II}Cl [16] (ATI = aminotroponiminate), which exhibited similar Ge−N and Ge−Cl bond lengths. Perusal of Ge−N and Ge−Cl bond distances in the complexes of the type L^2GeX suggests that the nature of these bonds strongly depends on the ligand type and the substituents. The shorter (more covalent) the Ge−N bond, the longer (more coordinate) the Ge−X bond. In the case of diimino complex **7**, we encounter a coordinate Ge−N and a covalent Ge−Cl bond, the latter being elongated due to interionic coordination with a Ge atom of a neighboring anion.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM050860U

---

(15) Probst, T.; Steigelmann, O.; Riede, J.; Schmidbaur H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1397.

(16) (a) Saur, I.; Miqueu, K.; Rima, G.; Barrau, J.; Lemierre, V.; Chrostowska, A.; Sotiropoulos, J.-M.; Pfister-Guillouzo, G. *Organometallics* **2003**, *22*, 3143. (b) Chrostowska, A.; Lemierre, V.; Pigot, T., Pfister-Guillouzo, G.; Saur, I.; Miqueu, K.; Rima, G.; Barrau, J. *Main Group Met. Chem.* **2002**, *25*, 469.

(17) For a review on N-heterocyclic germylenes and their complexes, see: Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411.

(18) (a) Ayers, A. E.; Klapötke, T. M.; Dias, R. H. V. *Inorg. Chem.* **2001**, *40*, 1000. (b) Dias, R. H. V.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67.