ORGANOMETALLICS

Volume 16, Number 24, November 25, 1997

Communications

Synthesis and Structure of the First Alkylidenetelluragermirane

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Received September 15, 1997[⊗]

Summary: The first stable alkylidenetelluragermirane **4** *was synthesized by the reaction of an overcrowded diarylgermylene Tbt(Mes)Ge:* **2b** *(Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl) with 9-(dichloromethylene)fluorene,* **3**, *followed by addition of tributylphosphine telluride. X-ray crystallographic analysis of* **4** *shows that the geometry of its telluragermirane ring can be explained in terms of a π-complex binding model of a tellurium atom to a germanium–carbon double bond.*

In recent years, much attention has been paid to the synthesis, structure, and reactions of three-membered rings containing group 14 elements because of their unique structures and high strain energies. Until now, many of these types of compounds have been synthesized and their reactivities have been investigated.[1] Among them, ring compounds bearing an exocyclic double bond have been drawing special interest, since the introduction of an *exo*-methylene group to the three-membered ring is expected to increase the strain energy. In contrast to the extensive studies on alkylidenecyclopropanes and their heterocyclic analogues, e.g., allene oxides or allene episulfides,[2] the chemistry of germanium analogues has been less explored.[3]

Meanwhile, divalent germanium compounds (germylenes) are known to be highly reactive species and have been widely employed utilizing their insertion or cycloaddition reactions[1b,4] as useful building blocks for the synthesis of a variety of organogermanium compounds having new skeletons. We have reported some interesting reactions of extremely bulky germylenes, Tbt(R)Ge:, **2** (R = Tip, Mes, Dis), which were generated by (i) the sequential nucleophilic substitution reactions of germanium(II) iodide with TbtLi and RLi, (ii) the reductive dehalogenation of the corresponding dihalogermanes **1** with lithium naphthalenide in THF, or (iii) the thermal retrocycloaddition of the corresponding germirenes (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[5] R = Tip (2,4,6-triisopropylphenyl), Mes (mesityl), or Dis (bis(trimethylsilyl)methyl)).[6] For example,

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

[1] For recent reviews, see: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (c) Kabe, Y.; Ando, W. *Adv. Strain Org. Chem.* **1993**, *3*, 59. (d) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (e) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

[2] Ando, W.; Choi, N.; Tokitoh, N. in *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; p 173.

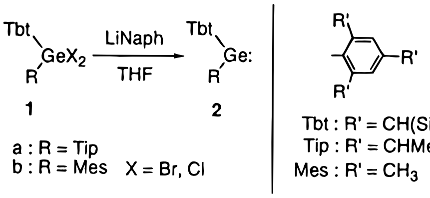
[3] Up to now, some examples of stable alkylidenegermiranes have been synthesized, see: (a) Ando, W.; Tsumuraya, T. *Organometallics* **1989**, *8*, 1467. (b) Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 659.

[4] For a review, see: (a) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. Recently, several stable alkyl- or aryl-substituted germylenes were isolated and their structures were determined by X-ray analysis. (b) Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 1647. (c) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H. G. *Organometallics* **1996**, *15*, 741. (d) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920. (e) Bender, J. E., IV; Holl, M. M. B.; Kampf, J. W. *Organometallics* **1997**, *16*, 2743 and references cited therein.

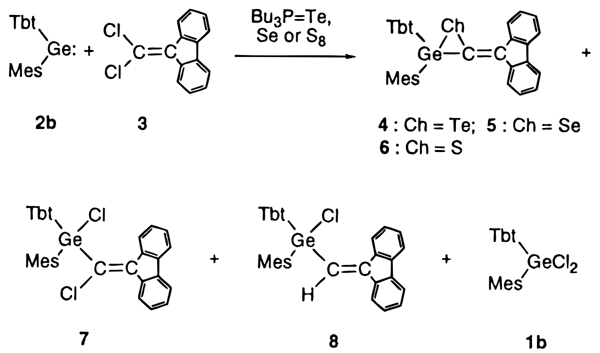
[5] We have recently succeeded in the synthesis of highly reactive species containing heavier main group elements by taking advantage of the effective protecting group, Tbt. For example, see: (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (b) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78. (c) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456 and references cited therein.

S0276-7333(97)00812-1 CCC: $14.00

Scheme 1



Scheme 2



we have succeeded in the synthesis of the first stable oxazagermete derivative by the reaction of **2a** (R = Tip) with 2,4,6-trimethybenzonitrile oxide, Scheme 1.[7] In this paper, we report the synthesis and structure of the first stable alkylidenetelluragermirane **4** derived from diarylgermylene **2b** (R = Mes).

To a THF solution of germylene **2b**, prepared from Tbt(Mes)$GeCl_2$, **1b** (1.23 g, 1.51 mmol), and 2 equiv of LiNaph (0.60 M, 5 mL), was added at room temperature 1.1 equiv of 9-(dichloromethylene)fluorene, **3**[8] (418 mg, 1.69 mmol), and then tributylphosphine telluride (303 mg, 0.92 mmol).[9] After removal of the solvent, purification of the residue afforded dichlorogermane, **1b** (24%), (1-chlorovinyl)germane, **7** (5%), vinylgermane, **8** (12%), and alkylidenetelluragermirane, **4** (10%, orange crystals).[10] The use of elemental tellurium instead of tributylphosphine telluride as a tellurium source gave almost similar reaction products, but compound **4** was not obtained, probably due to the low solubility of elemental tellurium. On the other hand, the alkylidenechalcogenagermiranes **5** and **6**, the selenium and sulfur analogues of **4**, were readily obtained together with **1b**, **7**, and **8** by the reactions of germylene **2b** with 9-(dichloromethylene)fluorene, **3**, followed by the addition of elemental sulfur and selenium, respectively, Scheme 2. The structures of chalcogenagermiranes **4**−**6** obtained here were determined by ^1H NMR, ^{13}C NMR, and FAB-MS spectroscopy and elemental analysis. Chalcogenagermiranes **4**−**6** are presumably formed by the initial insertion of germylene **2** into the C−Cl bond of **3** followed by dechlorination with **2** leading to 1-germaallene and subsequent chalcogenation.

Chalcogenagermiranes **4** and **5** represent the first examples of three-membered ring systems of this kind, although Ando et al. reported the synthesis of a 3-alkylidene-1,2-thiagermirane via cycloaddition of a germylene with a thioketene.[3a] All of the compounds **4**−**6** are stable at room temperature, even upon exposure to atmospheric oxygen, light, and moisture. Selena- and thiagermiranes **5** and **6** were found to be thermally very stable up to 200 °C, as in the case of the Ando's alkylidenethiagermirane which does not decompose at its melting point (120−121 °C).[3a] In contrast to these compounds, telluragermirane **4** gradually decomposed in solution at 120 °C.

The molecular structure of **4** was determined by X-ray crystallographic analysis.[11] The ORTEP drawing is shown in Figure 1 along with selected bond lengths and angles.

The length of the Ge(1)−Te(1) bond (2.591(3) Å) in **4** is similar to that of the Ge−Te bond reported for a

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(6) (a) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167. (b) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1425. (c) Tokitoh, N.; Kishikawa, K.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 827. (d) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 1087. (e) Tokitoh, N.; Kishikawa, K.; Manmaru, K.; Okazaki, R. *Heterocycles* **1997**, *44*, 149. (f) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337.

(7) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Chem. Commun.* **1997**, 1553.

(8) Combret, J. C.; Villiéras, J.; Lavielle, G. *Tetrahedron Lett.* **1971**, *12*, 1035.

(9) Quite recently, a similar type of reactions (reaction of a germylene with vinyl chloride) was reported, see: Ohgaki, H.; Ando, W. *J. Orgamomet. Chem.* **1996**, *521*, 387.

(10) All of the new organogermanium compounds obtained here showed satisfactory spectral and analytical data, which are described in the Supporting Information together with the experimental details for their preparation. In the following, the preparation of diarylgermylene **2b** and its reaction with 9-(dichloromethylene)fluorene, **3**, followed by addition of tributylphosphine telluride are described as representative examples. To a solution of Tbt(Mes)Ge:, **2b**, prepared from Tbt(Mes)$GeCl_2$, **1b** (1.23 g, 1.51 mmol), and LiNaph (0.60 M, 3 mmol) at −78 °C in THF (50 mL), was added a THF solution (20 mL) of 9-(dichloromethylene)fluorene, **3** (418 mg, 1.69 mmol), at room temperature. The solution was stirred for 5 min. To the solution was added tributylphosphine telluride (303 mg, 0.92 mmol), and the reaction mixture was stirred overnight. The solution was purified roughly by short column chromatography (SiO_2 with $CHCl_3$). After removal of the solvent, the reaction residue was subjected to gel permeation liquid chromatography (GPLC) to remove naphthalene and tributylphosphine telluride. The orange yellow solid thus obtained was chromatographed by flash column chromatography (FCC) (SiO_2 with hexane-10/1 hexane/$CHCl_3$) to afford dichlorogermane, **1b** (293 mg, 0.36 mmol), and telluragermirane, **4** (153 mg, 0.15 mmol). Other fractions were further purified by preparative thin-layer chromatography (PTLC) (SiO_2 with hexane) to afford (1-chlorovinyl)germane, **7** (75 mg, 0.076 mmol), and vinylgermane, **8** (174 mg, 0.18 mmol). **4**: orange crystals, mp 209.0−217.0 °C (dec); ^1H NMR (500 MHz, $CDCl_3$, 300K) δ −0.17 (s, 9H), −0.13 (s, 9H), −0.08 (s, 9H), −0.04 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 1.33 (s, 1H, *p*-CH), 2.22 (s, 3H, *p*-Me), 2.49 (s, 1H, *o*-CH), 2.64 (br s, 3H, *o*-Me), 2.73 (br s, 3H, *o*-Me), 2.74 (s, 1H, *o*-CH), 6.33 (s, 1H, arom H Tbt), 6.42 (s, 1H, arom H Tbt), 6.82 (s, 2H, arom H Mes), 7.09 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 8.36 (d, J = 7.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ 0.76 (q), 0.88 (q), 1.25 (q), 1.41 (q), 1.62 (q), 1.77 (q), 20.90 (q), 27.84 (d), 28.01 (q × 2), 28.64 (d), 30.73 (d), 119.23 (d), 119.46 (d), 121.90 (s), 122.35 (d), 122.73 (s), 122.83 (d), 123.59 (d), 126.03 (d), 126.75 (d), 127.23 (d), 127.73 (d), 128.46 (d), 129.37 (d × 2), 136.50 (s), 137.53 (s), 138.32 (s), 139.59 (s), 140.64 (s), 140.68 (s), 141.58 (s), 142.39 (s), 143.74 (s), 145.64 (s), 152.87 (s), 153.04 (s); ^{125}Te NMR (158 MHz, $CDCl_3$, Me_2Te) δ 13.77. Anal. Calcd for $C_{50}H_{78}GeSi_6Te$: C, 57.31; H, 7.50. Found: C, 57.23; H, 7.41. **1b**: white crystals, mp 216.0−218.0 °C. **5**: pale orange crystals, mp 263.0−269.0 °C (dec); ^{77}Se NMR (95 MHz, $CDCl_3$, Me_2Se) δ 127.56. **6**: yellow crystals, mp 274.0−276.0 °C (dec). **7**: yellow crystals, mp >300 °C. **8**: pale yellow crystals, mp 286−299 °C (dec).

(11) Crystallographic data for **4**: $C_{50}H_{78}GeSi_6Te$, fw = 1047.87, monoclinic, space group $P2_1/n$ (No. 14), a = 12.863(4) Å, b = 11.012(10) Å, c = 39.56(3) Å, β = 92.57(5)°, V = 5598(5) Å^3, Z = 4, D_c = 1.243 g cm^{-3}, μ(Mo Kα) = 12.16 cm^{-1}, R (R_w) = 0.085 (0.057). An orange prismatic crystal of **4** having approximate dimensions of 0.20 × 0.10 × 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 296 K and a rotating anode generator. The structure was solved by direct methods with SHELXS-86.[12] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated position but not refined. The final cycle of full-matrix least-squares refinement was based on 2326 observed reflections ($I > 2.00\sigma(I)$) and 523 variable parameters.

(12) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

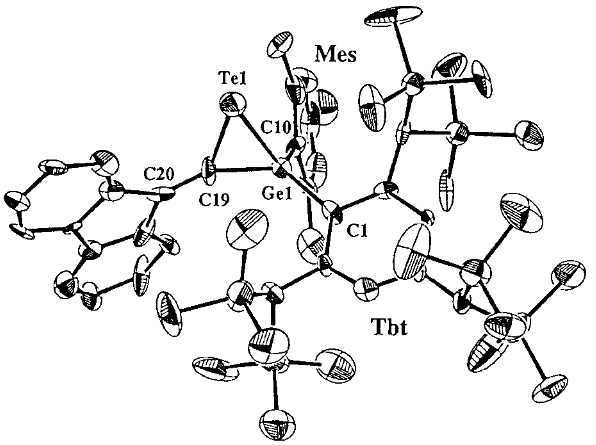

Figure 1. The ORTEP drawing of alkylidenetelluragermirane **4** with thermal ellipsoid plots (30% probability). Selected bond lengths (Å) and angles (deg): Ge(1)—C(19) 1.88(2), Ge(1)—Te(1) 2.591(3), C(19)—Te(1) 2.11(2), C(19)—Ge(1)—Te(1) 53.5(7), Ge(1)—Te(1)—C(19) 45.8(5), Ge(1)—C(19)—Te(1) 80.6(7), Ge(1)—C(19)—C(20) 149(1), Te(1)—C(19)—C(20) 129(1), C(1)—Ge(1)—C(10) 119.7(7), C(1)—Ge(1)—C(19) 119.5(7), C(10)—Ge(1)—C(19) 115.2(8), Te(1)—Ge(1)—C(19)—C(20) 179(3).

telluradigermirane (2.597(2) Å).[13] The C(19)—Te(1) bond length (2.11(2) Å) is in the range of Te—C single bond lengths for two-coordinate tellurium compounds previously reported (2.025—2.298 Å;[14b] an average of 2.158 Å).[15] However, its length is shorter than that in $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ (2.21(2) Å)[14b] and longer than that in a tellurocarbonyl η^1-tungsten complex (1.987(5) Å).[16] The Ge(1)—C(19) bond length (1.88(2) Å) is slightly shorter than the reported Ge—C single bond length (1.92—2.07 Å) of germirane derivatives[3b] or that of the calculated value for $H_3GeCH{=}CH_2$ (1.943 Å).[17] The interior bond angles at Ge(1), Te(1), and C(19) are 53.5(7)°, 45.8(5)°, and 80.6(7)°, respectively, and the bond angle of Ge(1)—C(19)—C(20) is 149(1)°. The dihedral angles between the telluragermirane ring plane and the aromatic planes of Tbt and Mes groups are 71.1° and 74.5°, respectively. In addition, the two benzene rings of the Tbt and Mes groups are almost perpendicular to each other. A dihedral angle between the three-membered ring and the fluorenyl group is 17.4°. The sum of the bond angles around the Ge atom (C(1)—Ge(1)—C(10), C(1)—Ge(1)—C(19), and C(10)—Ge(1)—C(19)) is 354.4°, suggesting considerable sp^2 character of the germanium center of **4**.

In connection with the molecular structure of **4**, it should be pointed out that many examples of digermirane derivatives $\overline{\mathrm{Ge{-}Ge{-}X}}$ (X = S,[18] C,[19] N,[19] and Te[13]), show remarkable shortening in their Ge—Ge bonds compared with a typical Ge—Ge single bond as well as planarity around the germanium atoms. This characteristic geometry for digermirane derivatives is most likely interpreted in terms of a π-complex binding model of the corresponding digermenes with the chalcogen atom, carbene, and nitrene.[20] We think that the shortening of the Ge(1)—C(19) bond and the notable planarity around the Ge(1) atom in telluragermirane **4** can be explained similarly using the π-complex binding model of a tellurium atom with a germanium—carbon double bond of a germaallene. In other words, the Ge(1)—C(19) bond in **4** might have a partial π-bond character.

The chalcogenagermiranes obtained here are potentially useful precursors for the synthesis of a germaallene, a novel class of a germanium—carbon double bond compound. Investigations on the reactivities of the newly obtained chalcogenagermiranes **4**—**6** are currently in progress.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research (Grant Nos. 05236102 and 07454193) from the Ministry of Education, Science, Sports, and Culture of Japan. K.K. thanks Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We are also grateful to Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gift of the chlorosilanes and alkyllithiums, respectively.

Supporting Information Available: Text giving detailed experimental and spectral data for all new compounds, tables of complete bond lengths and angles, atomic coordinates, and positional and thermal parameters, and an ORTEP diagram for **4** (41 pages). Ordering information is given on any current masthead page.

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(14) Tellurocarbonyl η^2-metal complexes have been reported. See, for example: (a) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Orgamomet. Chem.* **1988**, *340*, 161. (b) Shin, J. H.; Parkin, G. *Organometallics* **1994**, *13*, 2147.

(15) Allen, F.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(16) Minoura, M.; Kawashima, T.; Tokitoh, N.; Okazaki, R. *Chem. Commun.* **1996**, 123.

(17) Basch, H.; Hoz, T. in *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1995; p 1.

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(19) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1990**, *9*, 2061.

(20) Interestingly, the telluradigermirane ring system shows almost no bond shortening for the Ge—Ge bond as compared with a typical Ge—Ge single bond but a remarkable planarity at the Ge atoms. See, ref 13.