ORGANOMETALLICS

Volume 22, Number 2, January 20, 2003

Communications

Tetraarylstannagermene: A Molecule with a Ge═Sn Double Bond[1]

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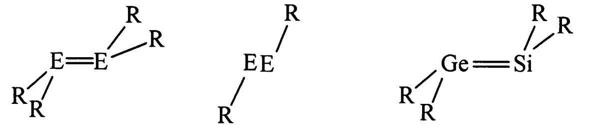
Received October 15, 2002

*Summary: The reaction of the Grignard compound RMgBr, R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, with GeCl$_2$·(dioxane) and SnCl$_2$ furnishes the stannagermene R$_2$Ge═SnR$_2$ (**4**) with a short Ge−Sn double bond length of 2.5065(5) Å. Treatment of **4** with dry oxygen at low temperature yields a 3,4-germastannadioxetane with a stretched O−O bond length.*

Since the isolation of the first distannene by Lappert et al. more than 25 years ago,[2] the synthesis and characterization of compounds with multiple bonds between the heavier elements of group 14 have been subjects of intensive research. Thus, not only have molecules of the type **1** (Chart 1) containing homonuclear double bonds between all elements of this group been prepared,[3] but also just recently the first examples of alkyne analogues **2** of germanium, tin, and lead were described. While the short bond lengths and the rather small trans-bent angles in the digermanium[4] and ditin[5] compounds support the existence of multiple bonds, the dilead compound must rather be considered as a diplumbylene with a Pb−Pb single bond on the basis of experimental findings and theoretical calculations.[6]

Chart 1



1 E = Si - Pb **2** E = Ge, Sn, Pb **3**

In contrast, stable molecules with heteronuclear multiple bonds between the heavier elements of group 14 were unknown until recently, due to their ready isomerization. For example, calculations on the parent compound of the germasilenes, H$_2$Si═GeH$_2$, revealed that the silylgermylene H$_3$Si(H)Ge: is appreciably more stable than the molecule with a heteronuclear double bond.[7] Even so, Sekiguchi et al. were recently able to isolate thermally stable germasilenes of the type **3**.[8] We now report on the formation and structural characterization of the first rather stable stannagermene **4**, which is formed surprisingly simply by the reaction of (2,4,6-

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[1] Compounds of Germanium, Tin, and Lead. 40. Part 39: Meiners, F.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.*, in press.

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[6] (a) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524. (b) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem.* **2001**, *113*, 2108; *Angew. Chem., Int. Ed.* **2001**, *40*, 2052.

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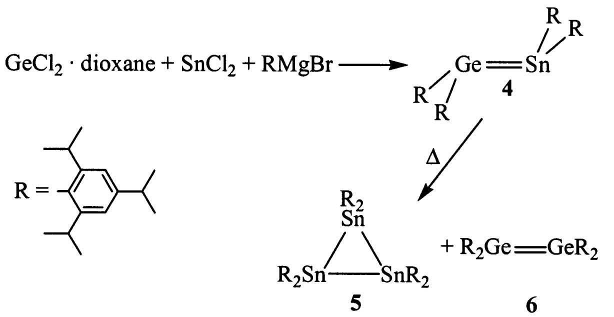
10.1021/om020855f CCC: $25.00 © 2003 American Chemical Society
Publication on Web 12/17/2002

Scheme 1



triisopropylphenyl)magnesium bromide with $GeCl_2$· (dioxane) and $SnCl_2$ at low temperature (Scheme 1).[9]

The ^{119}Sn−NMR spectrum, showing a typical signal for such compounds in the low-field region at 268 ppm, provided the first indication for the existence of a double bond. An X-ray crystallographic analysis[10] of the red crystals confirmed not only the structure of **4** but also revealed some interesting features (Figure 1). With a length of 2.5065 Å the Ge−Sn double bond is about 0.12 Å shorter than the average value for Ge−Sn single bonds[12] and, despite the bulky aryl groups, is even shorter than the value of 2.555 Å calculated for the parent compound $H_2Ge{=}SnH_2$.[13] As expected, the trans-bent angle between the R_2Sn plane and the Sn═Ge vector of 43.3° is larger than the corresponding angle of 30.2° at the germanium atom.

Compound **4** is relatively stable in the solid state. It decomposes slowly in solution with formation of the cyclotristannane **5**[14] and the digermene **6**,[15] as detected by their ^{1}H NMR spectra and, in the case of **5**, ^{119}Sn NMR spectrum. Even after 4 weeks in toluene solution **4** can still be detected together with **5** and **6**. Thus, **4** behaves differently from the stannagermene, in which merely the triisopropylphenyl groups at germanium have been replaced by mesityl groups. Although the latter compound can be characterized by trapping reactions and its ^{119}Sn NMR signal at 360 ppm, it has not yet been isolated.[16]

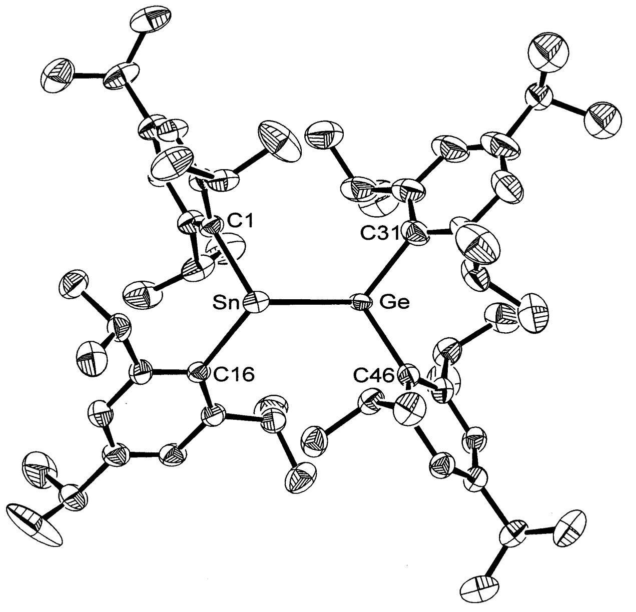


Figure 1. Molecule of **4** in the crystal state (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge−Sn = 2.5065(5), Ge−C(31) = 2.056(4), Ge−C(46) = 2.051(4), Sn−C(1) = 2.150(4), Sn−C(16) = 2.158(4); C(1)−Sn−C(16) = 104.92(14), C(31)−Ge−C(46) = 108.13(17), C(1)−Sn−Ge = 111.50(11), C(16)−Sn−Ge = 120.90(11), C(31)−Ge−Sn = 123.49(12), C(46)−Ge−Sn = 117.45(10).

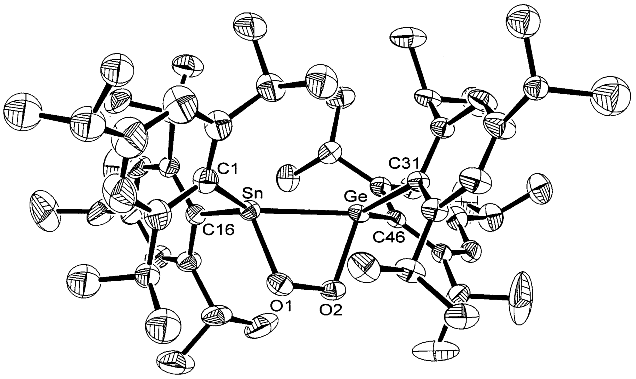


Figure 2. Molecule of **7** in the crystal state (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Ge−Sn = 2.6347(7), O(1)−O(2) = 1.521(3).

One of the most interesting reactions of compounds of type **1** is their oxidation in air, which, in the case of digermenes, leads to stable 3,4-digermadioxetanes.[17] We thus addressed the question of whether compound **4** would react analogously, despite the greater Ge═Sn bond length, or whether other reaction pathways would dominate. Passage of dry air through a solution of **4** in *n*-hexane at 0 °C gave the compound **7** in quantitative yield (Scheme 2). This product was characterized by its ^{119}Sn NMR spectrum (δ 128 ppm) and an X-ray crystallographic analysis (Figure 2).[18]

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(9) To a suspension of $GeCl_2$·(dioxane) (0.55 g, 2.37 mmol) and $SnCl_2$ (0.45 g, 2.37 mmol) in THF (35 mL) and dioxane (5 mL) was added at −78 °C dropwise a solution of the Grignard compound, prepared from 1-bromo-2,4,6-triisopropylbenzene (3.0 g, 10.6 mmol) and magnesium turnings in THF (30 mL). The mixture was allowed to come to −10 °C. At −40 °C the color changed from light yellow to red. After the mixture was stirred for 30 min at −10 °C, the solvents were distilled off, the residue was redissolved in cooled *n*-pentane (80 mL), and the precipitated salts were filtered off. Concentration of the solution to a minimum amount at −20 °C afforded 0.90 g (37% yield) of red crystals of **4**. Because of the low stability of **4** no reliable spectral and analytical data could be obtained.

(10) Crystal data for **4**: $(C_{60}H_{92}GeSn)_2$, fw = 2009.23, monoclinic, space group $P2_1/n$, $a = 14.4059(6)$ Å, $b = 37.5545(14)$ Å, $c = 21.6693(11)$ Å, $\beta = 95.804(6)°$, $Z = 4$, $V = 11663.1(9)$ Å^3, $D_{calcd} = 1.144$ g cm^{-3}, $\mu = 0.977$ mm^{-1}, $T = 193(2)$ K, crystal size 0.80 × 0.38 × 0.27 mm^3, Stoe-IPDS area detector, structure solution by direct methods, refinement on F^2 ($2\theta_{max} = 52°$), 22 569 unique reflections, R1 = 0.0500, wR2 (all data) = 0.1502, GOF (F^2) = 1.031.[11]

(11) The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-192 690 (**4**) and CCDC-192 691 (**7**).

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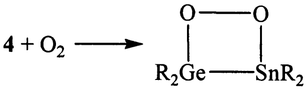
Scheme 2



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While the Ge−Sn bond length of 2.6347(7) Å is in the same range as other single bonds of this type,[12] the O−O bond length of 1.521(3) Å is markedly stretched. In addition, the four-membered heterocyclic ring is appreciably folded, as can be seen from the torsion angle Ge−O−O−Sn of 31.4°. Similar to compound **4**, product **7** is relatively stable in the solid state, whereas in solution at room temperature the formation of subsequent products occurs. According to the ^{119}Sn NMR signals at −92.4, −102.5, −111.7, and −122.1 ppm these products are in the typical region of oligostannoxanes[14] and probably -germoxanes, which cannot be characterized by NMR data.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Lists of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Crystal data for **7**: $C_{60}H_{92}GeO_2Sn$, fw = 1036.62, monoclinic, space group $P2_1/n$, $a = 12.465(3)$ Å, $b = 28.216(7)$ Å, $c = 17.473(3)$ Å, $\beta = 104.43(2)°$, $Z = 4$, $V = 5951(2)$ Å^3, $D_{calcd} = 1.157$ g cm^{-3}, $T = 193(2)$ K, crystal size 0.55 × 0.26 × 0.16 mm^3, Stoe-IPDS area detector, structure solution by direct methods, refinement on F^2 ($2\theta_{max} = 52°$), 10 904 unique reflections, R1 = 0.0350, wR2 = 0.0912 (all data), GOF (F^2) = 1.018. The Ge and Sn atoms are disordered and were refined on two positions with an occupancy factor of 0.5 each.[11]