

Stable germa- and stannaethenes

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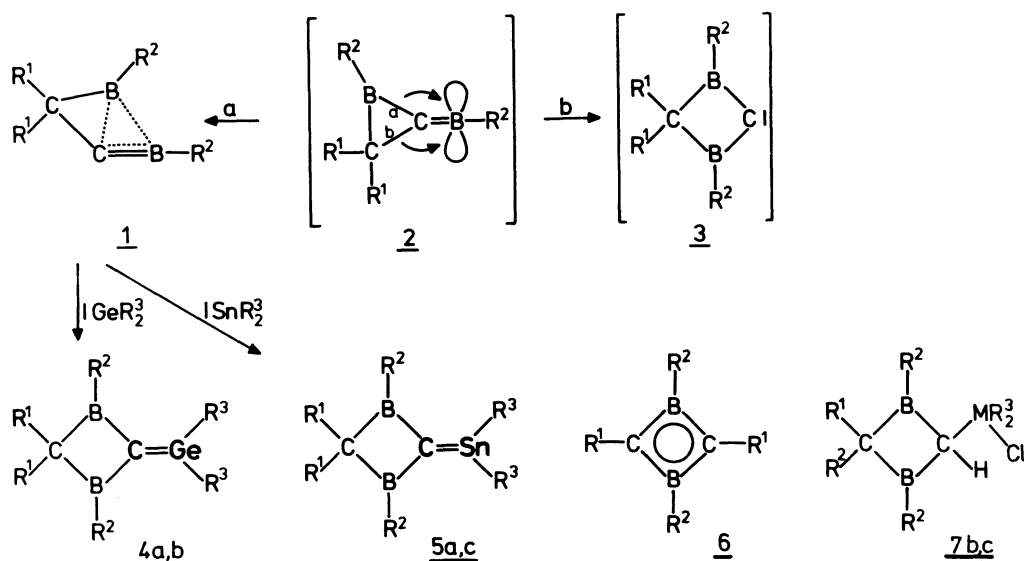
Abstract - Stable germa- and stannaethenes have been synthesized by addition of germylenes and stannylenes to a kryptodiborylcarbene. Extreme nmr-deshielding of tin is decisive proof for tricoordinated tin atoms in the stannaethenes. Considerable ylid character of germa- and stannaethenes is deduced from nmr-shielding of boron atoms adjacent to the tricoordinated carbon atom. X-ray analysis of a germa- and a stannaethene revealed strong distortion from planarity at the C=Ge and C=Sn bond: twisting of 36° and 61° and pyramidalization at carbon of 5° and 16° as measured by the fold angle. The distances from germanium and tin to the tricoordinated carbon (182.7(4) and 202.5(4) pm) are distinctly shorter (8.4 and 6.4%) than to tetracoordinated carbon atoms.

INTRODUCTION

In their introduction to a paper on the determination of heats of formation and π -bond energies of 1,1-dimethylmetallaethenes $(CH_3)_2M=CH_2$ (M = Si, Ge, Sn, Pb) Pietro and Hehre (ref. 1) stated in 1982, that stable, isolable compounds incorporating multiple bonds between carbon and germanium, tin or lead were nonexistent. In the meantime additional short-lived germaethenes (ref. 2) have been trapped, but the statement still holds. We now present synthesis, spectroscopic and X-ray characterization of stable germa- and stannaethenes.

ADDITION OF GERMYLENES AND STANNYLENES TO A KRYPTODIBORYLCARBENE

Our starting material for the synthesis of stable germa- and stannaethenes is the nonclassical (ref. 3, 4) boranediylborirane **1**. Structure and reactivity of **1** are best understood on the basis of the classical boranediylborirane **2** (ref. 5). Interaction of the empty p-orbital at the dicoordinated boron with the adjacent B-C- σ -bond (a) of the 3-membered ring yields **1**. Stronger interaction with the C-C- σ -bond (b) can lead to carbene **3**, which has recently been calculated to be only 42 kJ/mol higher in energy than **1** for model compounds with R(1) = SiH₃ and R(2) = CH₃ (ref. 3). Experimentally we had shown (ref. 6) that **1** behaves as if it were the electrophilic carbene **3** in reactions with bis(trimethylsilyl)ethine, triphenylphosphine and triphenylarsine. We now reacted **1** with germylenes (ref. 7, 8) and stannylenes (ref. 9,10) in pentane at room temperature and obtained crystalline germaethenes **4a** and **4b** (ref. 11) and stannaethenes **5a** and **5c** (ref. 12). While **4a**, **4b** and **5c** were formed as the sole products, **5a** had to be separated from a reaction mixture by crystallization. The nature of the additional product is still unknown. The colour of the metallaethenes varies from pale yellow (**4a**) to lemon yellow (**4b**) to orange (**5a**) to indian red (**5c**). **4a** and **4b** melt without, **5c** with partial decomposition into the corresponding stannylene and the 1,3-dihydro-1,3-diborete **6**. Crystals of **4b** and **5c** decolorize only slowly (**4b**: within 3 days, **5c**: within 2 hours) when brought into normal atmosphere. **4b** and **5c** add hydrogen chloride to give the corresponding 1,3-diboretanes **7b,c** with the proton attached to the diboretane and the chlorine to the metal.

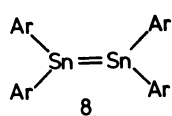


SPECTROSCOPIC AND X-RAY RESULTS

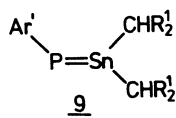
Decisive spectroscopic proof for tricoordinated tin atoms in 5a and 5c are their extreme low field nmr-chemical shifts $\delta\text{Sn}(119) = 647$ and 835 ppm. For the tricoordinated tin atoms of 8 and 9 $\text{Sn}(119)$ -chemical shifts of 427 (ref. 13) and 658 ppm (ref. 14) have been observed. The tetracoordinated tin atom in 7c shows $\delta\text{Sn}(119) = 75$ ppm. Chemical shifts of the tricoordinated carbon atoms of 4 and 5 are at the lower limit (see table 1) of the range to be expected.

TABLE 1. Chemical shifts of the tricoordinated carbon and of boron atoms of 4, 5 and 7 (in ppm)

	<u>4a</u>	<u>4b</u>	<u>5a</u>	<u>5c</u>	<u>7a,b</u>
$\delta^{13}\text{C}$	93	115	91	142	-
$\delta^{11}\text{B}$	65	66	50	64	82,83

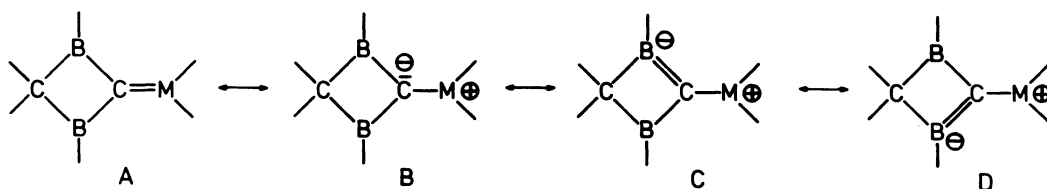


Ar = 2,4,6-triisopropylphenyl



Ar' = 2,4,6-tri-tert-butylphenyl

The shielding of the boron atoms of 4a-5c (50-66 ppm) as compared to 82-83 ppm for 7a,b indicates negative π -charge at the boron atoms, which in turn points to considerable contribution of ylid resonance structures B-D.



The results of the X-ray structure analysis of 4b and 5c are shown in Fig. 1.

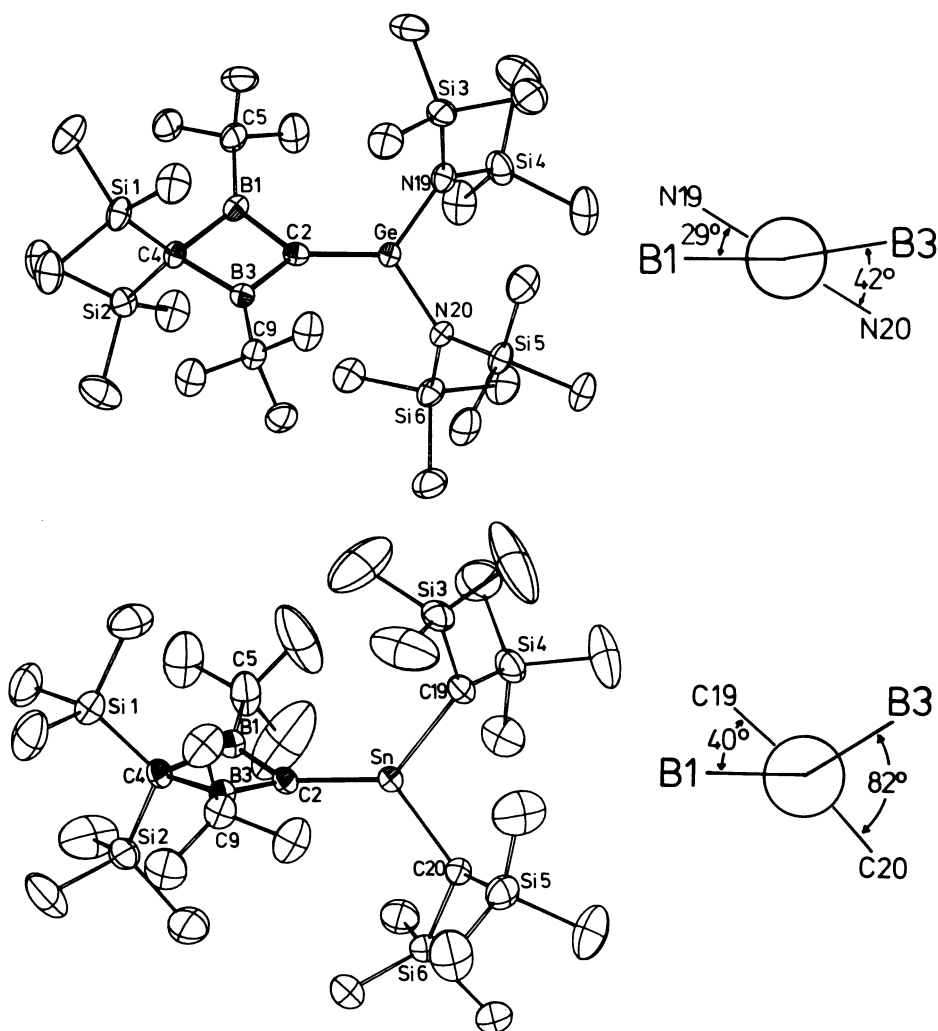
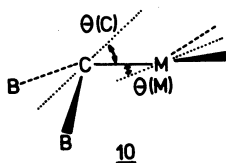


Fig. 1. ORTEP plots of the crystal structures of germaethene **4b** (above) and stannaethene **5c** (below) and stereographic projections along the C2-Ge and C2-Sn bond, respectively. Reproduced from (ref.11,12) with permission of VCH Verlagsgesellschaft, Weinheim.

Short distances between the tricoordinated carbon atom C2 and the adjacent boron atoms B1 and B3 (149.4(7) to 153.4(7) pm) confirm the importance of the ylid resonance forms C and D for **4b** and **5c**. The geometry around the C=Ge and C=Sn bond is strongly distorted from planarity. From the torsion angles B1-C2-Ge-N19 (29°), B3-C2-Ge-N20 (42°), B1-C2-Sn-C19 (40°) and B3-C2-Sn-C20 (82°) mean twist angles of 36° and 61° are calculated. Pyramidalization as measured by the fold angles $\theta(M)$ and $\theta(C)$ - see **10** - between the C=Ge or C=Sn bond and planes Ge,N19,N20, Sn,C19,C20 and C2,B1,B3 is negligible at germanium (2°), tin (5°) and C2 of the germaethene **4b** (5°) but considerable at C2 of the stannaethene **5c** (16°).



germanium and tin and the tricoordinated carbon C2 (182.7(4) and (202.5(4) pm) are distinctly (8.4 and 6.4%) shorter than those between germanium or tin and tetracoordinated carbon atoms: Ge-C 198 pm in $\text{Ge}(\text{CH}_3)_4$ (ref. 17), Sn-C 214 pm in $\text{Sn}(\text{CH}_3)_4$ (ref. 18), Sn-C19 215.2(5) and Sn^2C_{20} 217.2(4) pm in 5c. They are only slightly longer than those calculated for $\text{H}_2\text{C}=\text{GeH}_2$ (177.3 pm) and $\text{H}_2\text{C}=\text{SnH}_2$ (198.2 pm) (ref. 19).

Preliminary results on a plumbaethene (ref. 20) suggest that the high yield character of 4 and 5 is to a considerable part due to the sterically induced twisting of the carbon-metal bond.

Acknowledgement

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