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The First Synthesis of Bisgermylene and Bisstannylene with Acyclic Structure

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A bisgermylene and a bisstannylene with acyclic structure were synthesized for the first time by one-pot, two-step ligand substitution reactions from the corresponding germanium and tin dichlorides. The products were easily isolated by crystallization from diethyl ether and are stable at ambient temperatures under argon. Oxidative addition of the bisgermylene or bisstannylene to organic halides was examined.

The heavier analogues of carbenes, germylenes and stannylenes, are very important chemical species in organometallic chemistry and have been extensively studied in recent years.[1] These species are normally highly reactive yet unstable. Therefore, they are to be stabilized by using a bulky ligand such as -N(SiMe3)2 for the isolation.[2] So far, there has been no report on the synthesis of such compounds with two divalent germanium or tin moieties having an acyclic structure.

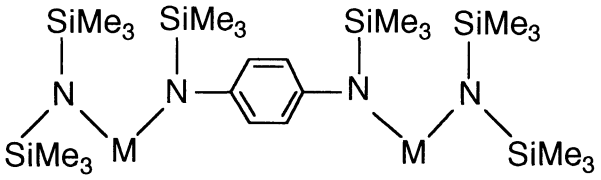
In our investigations on the polymer synthesis using divalent compounds of the group 14 elements as monomer, we have found new copolymerizations involving an oxidation-reduction process[3-5] and a ligand substitution polymerization.[6] In order to extend our research scope, new germylene or stannylene species have been desired. This leads us to explore the first and convenient synthesis of a "bisgermylene" and a "bisstannylene" with an acyclic structure. In relevant to the present study, a cyclic germetane [Ge{μ-N(2,4,6-*t*-Bu3C6H2)}]2[7] and a cyclic germanazene [GeN(2,6-*i*-Pr2C6H3)]3[8] were recently reported.

The synthesis of bisgermylene **5a** or bisstannylene **5b** was carried out in THF at 0 °C under argon by one-pot, two-step ligand substitutions from the 1,4-dioxane complex of germanium dichloride(**1a**) or tin dichloride(**1b**). The lithium amide compounds **2** and **4** were prepared from the corresponding amines, 1,1,1,3,3,3-hexamethyldisilazane and *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine, respectively, in THF at -78 °C, and directly used in situ. The latter diamine was prepared from *p*-phenylenediamine and trimethylsilyl chloride using triethylamine as a base under refluxing in toluene and purified by recrystallization from diethyl ether.[9] Here, the half-substituted compound **3** (M=Ge or Sn) was prepared in the first step and directly used for the substitution reaction without isolation in the second step.

For the synthesis of bisgermylene **5a**, 3.50 g (15.1 mmol) of **1a**[10] was dissolved in 30 mL of THF and cooled to 0 °C. To this solution, 30 mL of THF solution containing 15.1 mmol of lithium amide **2** was added. The reaction mixture was stirred at 0 °C for 1 h, and then another 30 mL of THF solution containing 7.55 mmol of compound **4** was added. After further stirring for 3 h at 0 °C, the reaction solvent THF was removed under reduced pressure and the residue was extracted by using 50 mL of toluene. Lithium chloride

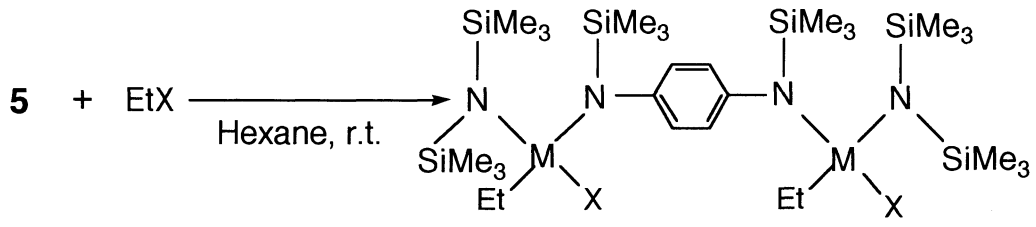
was removed by filtrating the toluene solution. Toluene was further removed under reduced pressure and the crude product was then dissolved into 20 mL of diethyl ether. Crystallization from diethyl ether solution at -20 °C gave 2.63 g (48.6% yield) of pale yellow product after drying. Both ^{1}H and ^{13}C NMR spectra supported the structure of **5a**(Fig.1).[11] Bisstannylene **5b**,[12] a pale orange crystal, was prepared in a similar manner in 45.8% isolated yield. Compound **5a** showed a melting point of 80.5 °C under argon. Compound **5b** showed no clear melting point and started to decompose at around 160 °C.

1a: $GeCl_2 C_4H_8O_2$
b: $SnCl_2$



5a: M=Ge
b: M=Sn

It has been known that a germylene or a stannylene can be easily inserted into a carbon-halogen σ-bond.[13,14] In order to further characterize the bisgermylene **5a** and the bisstannylene **5b**, the oxidative addition of organic halides was examined. Both of **5a** and **5b** easily reacted with ethyl iodide or ethyl bromide in hexane at room temperature under argon to give the oxidative addition products, **6a** and **6b**, respectively. **6a** and **6b** were isolated by crystallization from the hexane solution. The isolated yields of **6a** (X=I) and **6b** (X=I) were 42.3 and 34.3%, respectively, and those of **6a** (X=Br) and **6b** (X=Br) were 31.5



6a: M=Ge (X=I,Br)
b: M=Sn (X=I,Br)

and 42.3%, respectively. The compound **6a** (X=I)[15] was white crystals with no clear melting point and decomposed at 168 °C, while the compound **6b** (X=I)[16] was pale brown crystals with a melting point of 149.4 °C. The compound **6a** (X=Br)[17] was white crystals melting at 142.6 °C, while the compound **6b** (X=Br)[18] was brown crystals (mp, 139.8 °C). Oxidative additions of *n*-propyl chloride to **5a** and **5b** did not take place under similar reaction conditions.

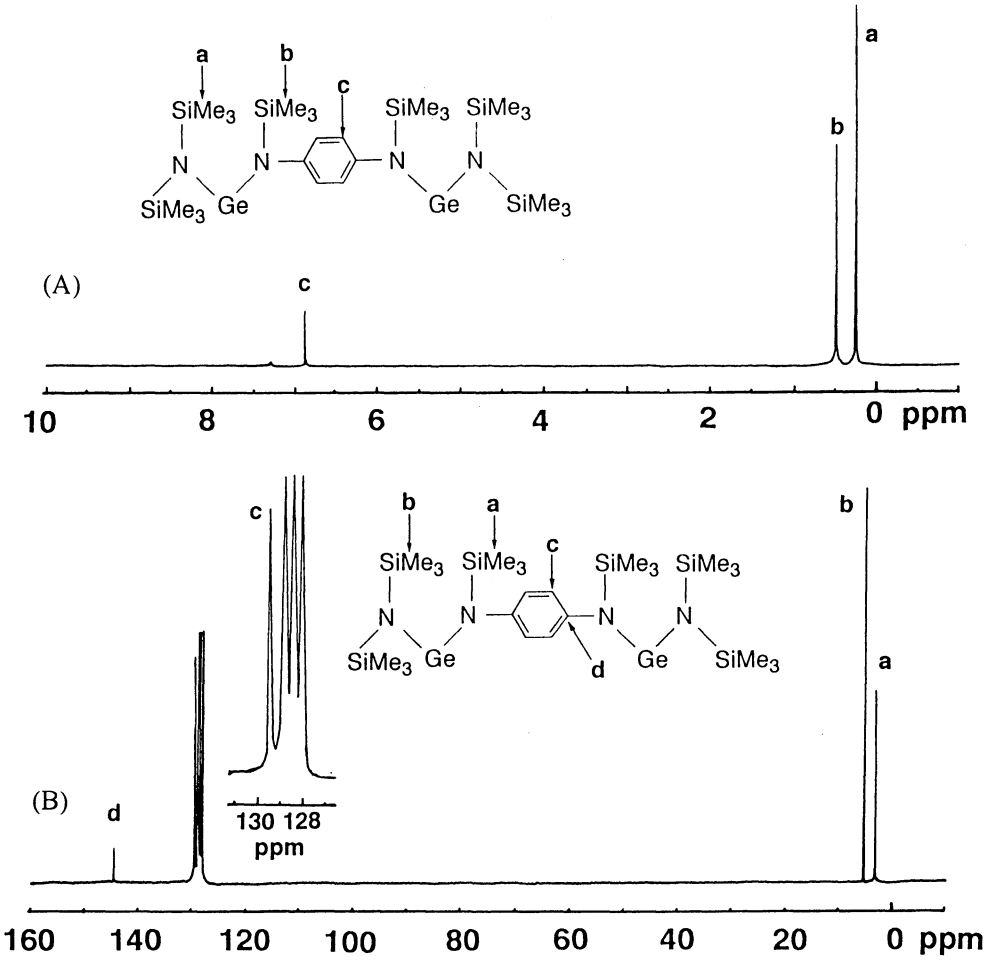


Fig.1. ^{1}H (A) and ^{13}C (B) NMR spectra of the bisgermylene **5a** (both in C_6D_6).

Further investigations of the polymer synthesis and other organometallic reactions of bisgermylene **5a** and bisstannylene **5b** are now in progress.

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11) ^{1}H NMR(C_6D_6, δ in ppm): 0.23(36H, -N[Si*Me*3]2, s); 0.47(18H, Ar-N-Si*Me*3, s); 6.87(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 2.89(Ar-N-Si*Me*3); 4.98(-N[Si*Me*3]2); 129.43(Ar*C*H); 144.27(Ar*C*).

12) ^{1}H NMR(C_6D_6, δ in ppm): 0.23(36H, -N[Si*Me*3]2, s); 0.45(18H, Ar-N-Si*Me*3, s); 6.84(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 3.47(Ar-N-Si*Me*3); 5.40(-N[Si*Me*3]2); 129.24(Ar*C*H); 145.62(Ar*C*).

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15) ^{1}H NMR(C_6D_6, δ in ppm): 0.38(18H, Ar-N-Si*Me*3, s); 0.47(36H, -N[Si*Me*3]2, s); 1.17(6H, -CH_2 CH_3, t); 1.61(4H, -CH_2CH_3,q); 7.35(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 2.47(Ar-N-Si*Me*3); 6.84(-N[Si*Me*3]2); 9.81(-CH_2CH_3); 26.04(-CH_2CH_3); 130.75(Ar*C*H); 143.90(Ar*C*). Anal. Found: C, 32.25; H, 6.64; N, 5.04%. Calcd for $C_{28}H_{68}N_4Si_6Ge_2I_2$: C, 32.70; H, 6.66; N, 5.45%.

16) ^{1}H NMR(C_6D_6, δ in ppm): 0.39(18H, Ar-N-Si*Me*3, s); 0.43(36H, -N[Si*Me*3]2, s); 1.24(6H, -CH_2 CH_3,t); 1.52(4H, -CH_2CH_3,q); 7.22(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 2.52(Ar-N-Si*Me*3); 6.40(-N[Si*Me*3]2); 11.19(-CH_2CH_3); 23.43(-CH_2CH_3); 130.39(Ar*C*H); 145.03(Ar*C*). Anal. Found: C, 28.57; H, 6.10; N, 4.99%. Calcd for $C_{28}H_{68}N_4Si_6Sn_2I_2$: C, 30.01; H, 6.12; N, 5.00%.

17) ^{1}H NMR(C_6D_6, δ in ppm): 0.35(18H, Ar-N-Si*Me*3, s); 0.47(36H, -N[Si*Me*3]2, s); 1.20(6H, -CH_2 CH_3, t); 1.46(4H, -CH_2CH_3, m); 7.27(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 2.50(Ar-N-Si*Me*3); 6.46(-N[Si*Me*3]2); 9.19(-CH_2CH_3); 23.30(-CH_2CH_3); 131.11(Ar*C*H); 143.72(Ar*C*).

18) ^{1}H NMR(C_6D_6, δ in ppm): 0.38(18H, Ar-N-Si*Me*3, s); 0.41(36H, -N[Si*Me*3]2, s); 1.28(6H, -CH_2 CH_3, t); 1.48(4H, -CH_2CH_3,q); 7.18(4H, C_6H_4, s). ^{13}C NMR(C_6D_6, δ in ppm): 2.42(Ar-N-Si*Me*3); 6.05(-N[Si*Me*3]2); 10.48(-CH_2CH_3); 22.10(-CH_2CH_3); 130.58(Ar*C*H); 144.77(Ar*C*).

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