

## Stannaacetylene (RSn≡CR') Showing Carbene-like Reaction Mode

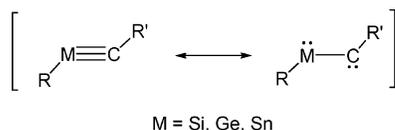
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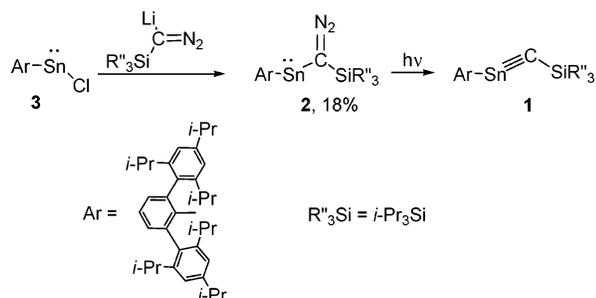
Many experimental and theoretical studies have been devoted to the chemistry of triple-bonded compounds of heavy group 14 elements.<sup>1</sup> Among them, silaisocyanide,<sup>2a</sup> silanitrile,<sup>2b</sup> silaacetylene,<sup>2c</sup> germaisocyanide,<sup>2d</sup> and disilaacetylene<sup>2e-g,3</sup> have been evidenced as short-lived species by various spectroscopic and trapping experiments. Only three acetylene analogues of heavy group 14 elements, [(2,6-Tip<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)Pb–Pb(C<sub>6</sub>H<sub>3</sub>-2,6-Tip<sub>2</sub>), (Tip = 2,4,6-*i*-Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>-)]<sup>4a</sup>, [(2,6-Dipp<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)Sn–Sn(C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>), (Dipp = 2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-)]<sup>4b</sup>, [(2,6-Dipp<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)Ge–Ge(C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>)]<sup>4c,d</sup> have been isolated as stable compounds recently by Power et al. Metallacetylenes (RM≡CR', M = Si, Ge, and Sn) are interesting because they are expected to have the carbene character perturbed electronically by a neighboring divalent heavy group 14 element through the resonance forms shown in Chart 1. Although a number of theoretical studies have been performed about metallacetylenes,<sup>5</sup> their carbene character has been discussed very rarely. Couret and co-workers have succeeded in the generation of a germaacetylene by the photolysis of a diazomethylgermylene.<sup>6</sup> The germaacetylene was trapped by alcohols, but no evidence was obtained for its carbene character.

### Chart 1



We report herein the first evidence for the successful generation of a stannaacetylene [**1**, Ar = 2,6-Tip<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, R' = *i*-Pr in Scheme 1] via the photolysis of the corresponding diazomethylstannylene **2**. Interestingly, stannaacetylene **1** thus generated showed a singlet carbene-like reaction mode.

### Scheme 1

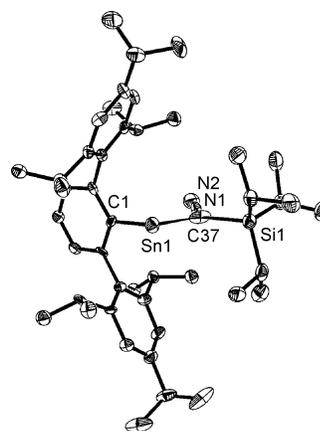


Diazomethylstannylene **2** was synthesized by the substitution of the corresponding arylchlorostannylene **3**<sup>7</sup> with silyldiazomethyl-

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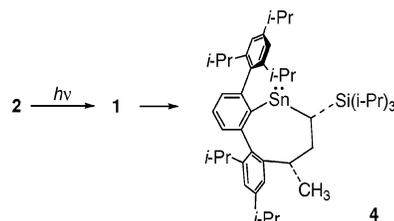


**Figure 1.** Molecular structure of aryldiazomethylstannylene **2** determined by X-ray crystallography (ORTEP, 30% thermal probability ellipsoid). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn1–C1 2.184(9); Sn1–C37 2.063(11); Si1–C37 1.858-(10); C37–N1 1.287(11); N1–N2 1.164(10); C1–Sn1–C37 99.2(3); C37–N1–N2 177.3(11); Sn1–C37–N1 119.8(7); Si1–C37–N1 115.5(8).

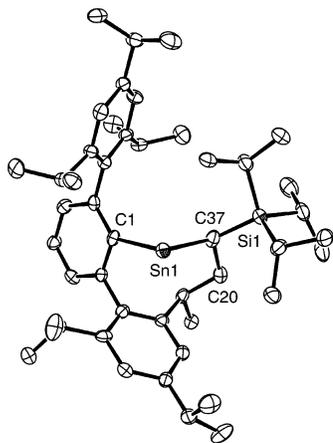
lithium<sup>8</sup> as thermally stable but air- and moisture-sensitive red crystals in 18% yield (Scheme 1).<sup>9,10</sup> The molecular structure of **2** in the solid state is shown in Figure 1. Notably, the much shorter Sn–C(=N<sub>2</sub>) bond length (2.063(11) Å) than the Sn–C<sub>ar</sub> bond length (2.184(9) Å) as well as the rather high <sup>119</sup>Sn NMR resonance (1323 ppm) is suggestive of the significant electron-donating effects of the diazomethyl substituent.

The photolysis of a benzene solution of **2** without any trapping reagent using a 500-W high-pressure mercury arc lamp at room temperature gave red crystals of cyclic stannylene **4** in 70% yield (Scheme 2).<sup>11,12</sup> The <sup>119</sup>Sn resonance appearing at δ 1426 is a little

### Scheme 2



higher field than that of a known alkyl(aryl)stannylene [(C<sub>6</sub>H<sub>3</sub>-2,6-Tip<sub>2</sub>)(*t*-Bu)Sn: δ 1904],<sup>13,14</sup> probably due to the π coordination of a benzene ring to the divalent tin atom in **4**. The molecular structure of **4** with a twist-crown stannacyclooctadiene ring is shown in Figure 2. The photoreaction is highly stereoselective to give only cyclic stannylene **4** with *cis* arrangement between methyl and triisopropylsilyl substituents on the stannacyclooctadiene ring; no *trans* isomer was detected in the reaction mixture.



**Figure 2.** Molecular structure of **4** in the unit cell (ORTEP, 30% thermal probability ellipsoid). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn1–C1 2.201(7); Sn1–C37 2.231(8); C20–C37 1.557(11); C1–Sn1–C37 94.4(3); Sn1–C37–Si1 111.2(4); Sn1–C37–C20 115.0(6).

The formation of **4** by the photolysis of **2** is explained straightforwardly by the intermediacy of stannaacetylene **1** followed by the intramolecular insertion of the carbene moiety of **1** to a proximate methyl C–H bond in an isopropyl group as shown in Scheme 2. The stereoselective formation of **4** is consistent with the severe steric repulsion between the triisopropylsilyl group and a triisopropylphenyl ring caused during the formation of the *trans* isomer. The present results afford the evidence not only for the generation of **1** but also for its high carbene-like reactivity.

The photolysis ( $\lambda > 330$  nm) of **2** in a 3-methylpentane glass matrix at 77 K showed new absorption maxima at 350 nm (strong) and 453 nm (weak) assignable to **1**.<sup>15</sup> In accord with the result, a similar transient absorption maximum was observed at 355 nm with the lifetime of 50 ms during the laser flash photolysis (XeCl, 190 mJ, 308 nm) of **2** in benzene at room temperature.<sup>16</sup> No triplet ESR spectrum was observed during the photolysis of **2** in a low-temperature glass matrix. In accord with the experimental results, our preliminary calculations at the QCISD/3-21G\* level have shown that the singlet of HSnCH is 4.9 kcal mol<sup>-1</sup> more stable than the triplet and characterized as an Sn≡C triple-bonded compound with a significant stannylene–carbene character.<sup>17</sup>

**Supporting Information Available:** X-ray structural information on **2** and **4** (CIF) and experimental details of the photolysis of **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) **2**: mp 169–172 °C dec. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  0.87 (d, *J* = 7.2 Hz, 18 H), 1.03 (septet, *J* = 7.2 Hz, 3 H), 1.23 (d, *J* = 6.9 Hz, 12 H), 1.47–1.50 (m, 12 H), 2.79 (septet, *J* = 6.9 Hz, 2 H), 3.3–3.5 (m, 4 H), 7.18 (s, 4 H), 7.2–7.4 (m, 3 H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  12.4 [Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>], 18.8 [Si(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>], 23.1 [*p*-CH(CH<sub>3</sub>)<sub>2</sub>], 24.2 [*o*-CH(CH<sub>3</sub>)<sub>2</sub>], 27.3 (CN<sub>2</sub>), 31.0 [*p*-CH(CH<sub>3</sub>)<sub>2</sub>], 34.7 [*o*-CH(CH<sub>3</sub>)<sub>2</sub>], 121.6 (*m*-CH), 128, 130.4, 135.2, 146.0, 149.1, 176.9; <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  5.4; <sup>119</sup>Sn NMR (112 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1323; MS (EI, 70 eV) *m/z* 798 (M<sup>+</sup>, 20), 601 (100), 481 (10). See the Supporting Information for the details of the synthesis of **2**.
- (10) X-ray crystallographic analysis of **2**: Diffraction data were collected from single crystals of dimensions (0.2 mm × 0.2 mm × 0.1 mm) in sealed glass capillaries on a Bruker SMART 1000 CCD system using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Crystal data (120 K): C<sub>46</sub>H<sub>70</sub>N<sub>2</sub>SiSn, FW = 797.82, monoclinic, space group P2<sub>1</sub>/c, *a* = 12.384(5) Å, *b* = 21.871(9) Å, *c* = 16.751(7) Å,  $\beta = 104.875(9)^\circ$ , *V* = 4385(3) Å<sup>3</sup>, density (calcd) 1.209 Mg/m<sup>3</sup>, *Z* = 4. Final *R* indices R1 = 0.0601 for 2547 reflections with *I* > 2 $\sigma$ (*I*), wR2 = 0.1288 for all data, 4712 unique reflections.
- (11) <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  0.96 (d, *J* = 6.9 Hz, 18 H), 1.0–1.4 (m, 37 H), 2.68–2.85 (m, 3 H), 3.28 (septet, *J* = 6.9 Hz, 2 H), 3.52–3.66 (m, 2 H), 3.84–3.92 (m, 1 H), 7.1–7.4 (m, 7 H); <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  5.6; <sup>119</sup>Sn NMR (112 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1426; MS (EI, 70 eV) *m/z* 770 (M<sup>+</sup>, 100). See the Supporting Information for the <sup>1</sup>H and <sup>13</sup>C NMR data obtained by a 600 MHz NMR spectrometer.
- (12) Diffraction data were collected from a single crystal of dimensions 0.4 mm × 0.3 mm × 0.2 mm. Crystal data for **4** (120 K): C<sub>46</sub>H<sub>70</sub>SiSn, FW = 769.80, monoclinic, space group P2<sub>1</sub>/n, *a* = 16.407(4) Å, *b* = 21.904(5) Å, *c* = 24.092(5) Å,  $\beta = 106.357(4)^\circ$ , *V* = 8308(3) Å<sup>3</sup>, density (calcd) 1.231 Mg/m<sup>3</sup>, *Z* = 8. Final *R* indices (all data) R1 = 0.0972, wR2 = 0.1676 for 9535 unique reflections.
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- (17) In the optimized structure of HSnCH, the four atoms are coplanar with *trans*-bent arrangement. Therefore, the stannylene–carbene structure in the resonance scheme (Chart 1) should be taken as (ground state)–stannylene–(doubly excited)carbene instead of (ground state)stannylene–(ground state)carbene structure. See the Supporting Information for the details of the theoretical calculations.

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