Formation of a stannylstannylene *via* intramolecular carbene addition of a transient stannaacetylene (RSn≡CR′)†

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Photolysis of diazomethylstannylene [1, $Me_3SiC(=N_2)(Ar)Sn{:}$, Ar = C_6H_3-2,6-Tip_2, Tip = C_6H_2-2,4,6-(i-Pr)$_3$] afforded unusual stannylstannylene 3 *via* intramolecular carbene addition to an aromatic π bond of stannaacetylene 2; the structures of compounds 1 and 3 were fully characterized by X-ray crystallography.

In spite of a strong interest in acetylene analogs of heavy group 14 elements,[1] only a few studies describe thermally stable dimetallaacetylenes of silicon, germanium, tin and lead compounds.[2,3] The preparation and characterization of triply-bonded species of heavy group 14 elements still constitute a central research issue in the chemistry of main group elements. In a previous paper,[4] we have reported that the photolysis of triisopropylsilyl-substituted diazomethylstannylene **4** [(i-Pr)$_3$SiC(=N_2)(Ar)Sn:, Ar = 2,6-$Tip_2C_6H_3$, Tip = C_6H_2-2,4,6-(i-Pr)$_3$] generates efficiently the corresponding stannaacetylene **5** as shown in Scheme 1.[5] Stannaacetylene **5** gives cyclic alkylarylstannylene **6** *via* the facile intramolecular carbene insertion into a C–H bond of an isopropyl group of **5**, as expected by the contribution of a carbene-stannylene form in stannaacetylene (Chart 1).[4]

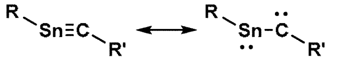

Chart 1

Herein, we report that a new stannaacetylene **2** formed by the photolysis of trimethylsilyl-substituted diazomethylstannylene **1** [$Me_3SiC(=N_2)(Ar)Sn{:}$] gives a quite unusual stannylstannylene **3** as the final product, indicating remarkable difference in the reaction modes between stannaacetylenes **2** and **5** due to the difference in the steric effects of the substituents.¶

Diazomethylstannylene **1** was synthesized by the reaction of the corresponding arylchlorostannylene **7** [Ar(Cl)Sn:] with (trimethylsilyl)diazomethyllithium[6] as thermally stable but air- and moisture-sensitive red crystals in 28% yield. The molecular structure of **1** is shown in Fig. 1.¶

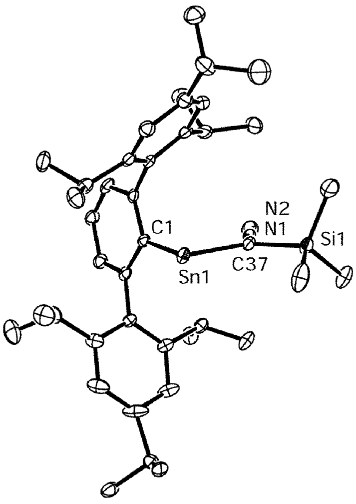

Fig. 1 Molecular structure of aryldiazomethylstannylene **1** determined by X-ray crystallography (ORTEP, 30% thermal probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1–C1 2.189(7), Sn1–C37 2.172(7), Si1–C37 1.866(8), C37–N1 1.303(11), N1–N2 1.137(10); C1–Sn1–C37 97.1(3), C37–N1–N2 179.6(9), Sn1–C37–N1 117.8(5), Si1–C37–N1 115.3(5).

Photolysis of a benzene solution of diazomethylstannylene **1** at ambient temperature in the absence of trapping reagents afforded unexpectedly red crystals of stannylstannylene **3** as a benzene trisolvate.[7] The molecular structure of **3** determined by X-ray crystallography is shown in Fig. 2.¶ The Sn2 atom in **3** is tetracoordinate with bonds to Sn1, C17, C41 and C77 atoms. On the other hand, the Sn1 atom is bonded to C1 and Sn2 atoms, and hence, is regarded as a divalent tin atom. The distance between Sn1 and C37 atoms is only 0.4 Å longer than that of the average of Sn–C covalent bonds in the molecule (Sn1–C1 Sn2–C41 Sn2–C77 and Sn2–C17) but significantly shorter than the sum of the van der Waals radii of Sn and C atoms (3.85 Å),[8] suggesting a significant interaction between the divalent Sn atom and cycloheptatrienyl π system. The structural characteristics are supported by a ^{119}Sn NMR

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† Electronic supplementary information (ESI) available: 1: An NMR study of photoreaction of diazomethylstannylene (**1**). 2: Preliminary theoretical calculations of relative energies of intermediates. 3: Laser flash photolysis experiment for diazomethylstannylene. CCDC 697285 and 697286. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814801e

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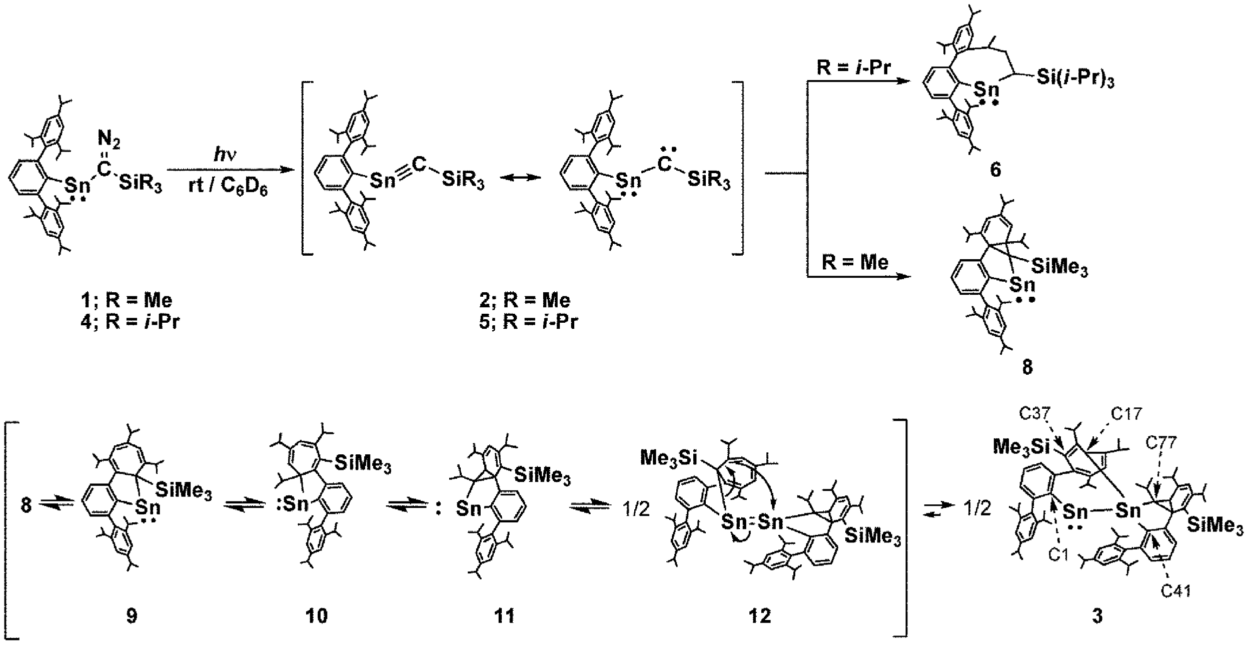

Scheme 1

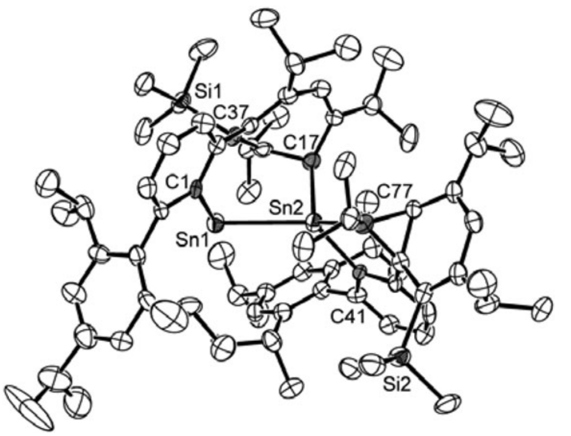

Fig. 2 Molecular structure of stannylstannylene **3** determined by X-ray crystallography (ORTEP, 30% thermal probability ellipsoids). Hydrogen atoms and solvated benzenes are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1–Sn2 2.9034(13), Sn1–C1 2.201(12), Sn2–C41 2.197(12), Sn2–C77 2.171(11), Sn2–C17 2.270(11); C1–Sn1–Sn2 94.9(3), C41–Sn2–C77 83.8(5), C77–Sn2–C17 119.1(5), C41–Sn2–C17 107.9(5), C77–Sn2–Sn1 137.9(3), C41–Sn2–Sn1 124.2(3), C17–Sn2–Sn1 84.4(3); Sn1···C37 distance (Å) 2.594(13).

spectrum of **3** (Fig. 3), in which two resonances appeared at 71.4 and 788.7 ppm are assignable to tetracoordinate Sn2 and base-coordinate divalent Sn1 nuclei, respectively. In accord with the assignment, the signal at 71.4 ppm split into a doublet due to the coupling with a proton at C17 in a non-decoupled ^{119}Sn NMR ($^{2}J_{\mathrm{Sn-H}}$ = 80.8 Hz). The signal at 788.7 ppm with the ^{119}Sn–^{119}Sn coupling ($^{1}J_{\mathrm{Sn-Sn}}$) of 6240 Hz would be reasonable as that due to divalent Sn2 coordinated by a cycloheptatriene π base; a typical base-coordinate stannylstannylene [:Sn{2-(Me$_3$Si)$_2$C–C$_5$H$_4$N}{Sn(SiMe$_3$)$_3$}] has been reported to show the divalent ^{119}Sn nucleus at 897 Hz with a $^{1}J_{\mathrm{Sn-Sn}}$ value of 6746 Hz.[7a,b]

A speculative mechanism for the formation of **3** is shown in Scheme 1. Photolysis of **1** generates the highly reactive stannaacetylene **2**, which undergoes intramolecular carbene addition to a π bond of a triisopropylphenyl group affording norcaradiene **8** followed by the ring expansion into stannylene **9**, instead of the C–H insertion of stannaacetylene **5** generated by the photolysis of **4**.[5,9] Stannylene **9** isomerizes into stannylenes **10** and **11** *via* 1,3-tin migration[10] and a norcaradiene–cycloheptatriene rearrangement.[11] Recombination between stannylenes **8** (or **9**) and **11** will give distannene **12**, which rearranges into stannylstannylene **3**. In accord with this mechanism, when the photoreaction of stannylene **1** was monitored by ^{119}Sn NMR spectroscopy, the initial ^{119}Sn signal at δ 1286 due to **1** disappeared gradually with appearance and increase of a new broad signal at δ 2113 that is assignable to the intermediary stannylenes.[10]

In a previous paper, we have reported that a transient absorption maximum assignable to a π(SnC)–π*(SnC) transition of stannaacetylene **5** is observed at 355 nm with the lifetime of 50 ms during the laser flash photolysis (LFP) of **4** using an XeCl laser (190 mJ, 308 nm) in benzene at room temperature.[5] LFP experiments of a benzene solution of **1**

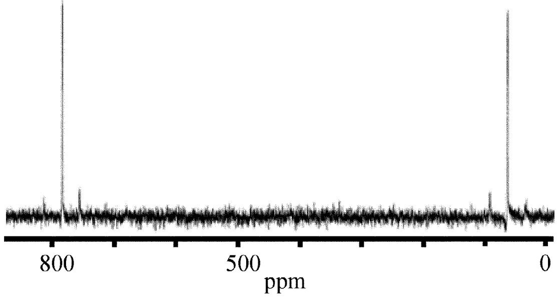

Fig. 3 ^{119}Sn{^{1}H} NMR spectrum of stannylstannylene **3** in benzene-d_6.

(5.0×10^{-4} M) under similar conditions showed a transient band at 355 nm assignable to a π(SnC)–π^*(SnC) transition of **2** but with very short lifetime (3.7 μs). The 10^{-4} times shorter lifetime of **2** than that of **5** indicates that the lifetime or the kinetic stability of stannaacetylene is very sensitive to the steric bulk of the trialkylsilyl substituent. Carbene **2** with a less bulky silyl substituent adds preferably to an aromatic π bond, while a similar addition of carbene **5** is sterically prohibited.

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Notes and references

¶ **1**: A solution of trimethylsilyldiazomethyllithium (1.0 mmol) in tetrahydrofuran (10 mL) was added to a solution of arylchlorostannylene ((2,6-$Tip_2C_6H_3$)SnCl) (640 mg, 1.0 mmol) in tetrahydrofuran (10 mL) at −78 °C. After stirring for 20 h, the volatile materials were removed under reduced pressure and the residual solid was extracted with hexane, filtered, and concentrated. The residue was allowed to stand at ambient temperature to afford **1** as red crystals (200 mg, 0.28 mmol, 28% yield): mp 158–160 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.00 (s, 9 H), 1.16 (d, J = 6.9 Hz, 24 H), 1.46 (d, J = 6.9 Hz, 12 H), 2.73 (septet, J = 6.9 Hz, 2 H), 3.39 (septet, J = 6.9 Hz, 4 H), 7.16 (s, 4 H), 7.2–7.4 (m, 3 H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 0.7 (Si*Me*), 22.9 (*p*-CHMe_2), 24.2 (*o*-CHMe_2), 26.9 (*C*N_2), 31.0 (*p*-*C*HMe$_2$), 34.7 (*o*-*C*HMe$_2$), 121.4 (*m*-H(Tip)), 128, 130.3, 135.3, 145.8, 149.2, 176.7; ^{29}Si NMR (59 MHz, C_6D_6, 298 K) δ 0.4; ^{119}Sn NMR (112 MHz, C_6D_6, 298 K) δ 1286; MS (EI, 70 eV): m/z 714 (M^+, 10), 686 ($M^+ - N_2$, 0.5), 601 ($ArSn^+$, 100), 481 (Ar^+, 50), 73 ($SiMe_3{}^+$, 25).

3: A benzene-d_6 (0.4 mL) solution of **1** (30 mg, 0.04 mmol) was sealed in a Pyrex NMR tube and then irradiated ($\lambda > 360$ nm) using a high-pressure mercury lamp (500 W) equipped with a Pyrex cut filter. The reaction was monitored by ^{1}H NMR spectroscopy. Upon completion of the reaction, the solvent was partially removed under reduced pressure. The residue was allowed to stand at ambient temperature to afford red crystals of **3** as a benzene trisolvate (*ca.* 20 mg, 0.03 mmol, *ca.* 70% yield). Unfortunately, because of monomer-dimer equilibrium, the ^{1}H NMR and ^{13}C NMR data were very complicated. ^{119}Sn NMR (112 MHz, C_6D_6, 298 K): δ 71.4 ($^2J_{Sn-H}$ = 80.8 Hz, $^1J_{Sn-Sn}$ = 6240 Hz), 788.7 ($^1J_{Sn-Sn}$ = 6240 Hz).

X-Ray structural data: Diffraction data were collected from a single crystal in a sealed grass capillary on a Bruker SMART 1000 CCD system using graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å). The structures were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97.

Crystal data for **1** (120 K): $C_{40}H_{58}N_2SiSn$, M = 1605.62, triclinic, space group $P\bar{1}$, 0.4 × 0.3 × 0.3 mm, a = 10.155(3), b = 10.299(3), c = 21.771(6) Å, α = 83.444(5), β = 82.344(6), γ = 62.356(5)°, V = 1995.5(10) Å^3, D_c = 1.188 Mg m^{-3}, Z = 2. Final R indices $R1$ = 0.0766 for 5479 reflections with $I > 2\sigma(I)$, $wR2$ = 0.2056 for all data, 6943 unique reflections.

Crystal data for **3** (220 K): $C_{80}H_{116}Si_2Sn_2 \cdot 3C_6H_6$, M = 1605.61, monoclinic, space group $P2_1/c$, 0.4 × 0.3 × 0.2 mm, a = 12.628(2), b = 41.255(7), c = 17.126(3), β = 95.001(4)°, V = 8888(3) Å^3, D_c = 1.200 Mg m^{-3}, Z = 4. Final R indices $R1$ = 0.1150 for 6792 reflections with $I > 2\sigma(I)$, $wR2$ = 0.2678 for all data, 15 721 unique reflections. The C22–C24 distance has been restrained by means of DFIX, because of unresolved disordered position.

1 For recent reviews of stable triply bonded species of heavy main group elements, see: A. Sekiguchi, *Pure Appl. Chem.*, 2008, **80**, 447; P. P. Power, *ACS Symp. Ser.*, 2006, **917**, 179; P. P. Power, *Chem. Commun.*, 2003, 2091; M. Weidenbruch, *Angew. Chem., Int. Ed.*, 2003, **115**, 2222; M. Weidenbruch, *J. Organomet. Chem.*, 2002, **646**, 39; R. West, *Polyhedron*, 2002, **21**, 467; P. Jutzi, *Angew. Chem., Int. Ed.*, 2000, **39**, 3797; P. P. Power, *Chem. Rev.*, 1999, **99**, 3463; G. H. Robinson, *Acc. Chem. Res.*, 1999, **32**, 773.

2 Isolable dimetallaacetylenes: L. Pu, B. Twamley and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 3524; A. D. Philips, R. J. Wright, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2002, **124**, 5930; M. Stender, A. D. Phillips, R. J. Wright and P. P. Power, *Angew. Chem., Int. Ed.*, 2002, **41**, 1785; L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 11626; A. Sekiguchi, R. Kinjo and M. Ichinohe, *Science*, 2004, **305**, 1755; N. Wiberg, S. K. Vasisht, G. Fischer and P. Mayer, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1823; Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase and N. Tokitoh, *J. Am. Chem. Soc.*, 2006, **128**, 1023.

3 Reactivity and properties of isolable dimetallacetylenes: M. Stender, A. D. Phillips and P. P. Power, *Chem. Commun.*, 2002, 1312; C. Cui, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2004, **126**, 5062; C. Cui, M. Brynda, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2004, **126**, 6510; C. Cui, M. M. Olmstead, J. C. Fettinger, G. H. Spikes and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 17530; G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232; G. H. Spikes, Y. Peng, J. C. Fettinger, J. Steiner and P. P. Power, *Chem. Commun.*, 2005, 6041; A. Sekiguchi, M. Ichinohe and R. Kinjo, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 825; V. Kravchenko, R. Kinjo, A. Sekiguchi, M. Ichinohe, R. West, Y. S. Balazs, A. Schmidt, M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 2006, **128**, 14472; R. Kinjo, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2007, **129**, 26; G. H. Spikes and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 85; R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto and S. Nagase, *J. Am. Chem. Soc.*, 2007, **129**, 7766.

4 (*a*) Couret and co-workers have reported on the preparation of base-stabilized germaacetylene *via* photolysis of diazomethylgermylene: C. Bibal, S. Mazières, H. Gornizka and C. Couret, *Angew. Chem., Int. Ed.*, 2001, **40**, 952; (*b*) intramolecular insertion of a transient carbene stabilized by neighboring P and N atoms intoa C–H bond has been reported: F. E. Hahn, D. L. Van, M. C. Moyes, T. v. Fehren, R. Fröhlich and E. U. Würthwein, *Angew. Chem., Int. Ed.*, 2001, **40**, 3144.

5 W. Setaka, K. Hirai, H. Tomioka, K. Sakamoto and M. Kira, *J. Am. Chem. Soc.*, 2004, **126**, 2696.

6 (*a*) G. Bertrand, in *Organosilicon Chemistry III: From Molecules to Materials*, eds. N. Auner and J. Weis, Wiley-VCH, Weinheim, 1998, p. 223; (*b*) T. Aoyama, S. Inoue and T. Shioiri, *Tetrahedron Lett.*, 1984, **25**, 433; (*c*) D. Seyferth and T. C. Flood, *J. Organomet. Chem.*, 1971, **29**, C25.

7 A few base-free and base-coordinated stannylstannylenes have been reported: (*a*) C. J. Cardin, D. J. Cardin, S. P. Constantine, A. K. Todd, S. J. Teat and S. Coles, *Organometallics*, 1998, **17**, 2144; (*b*) S. Benet, C. J. Cardin, D. J. Cardin, S. P. Constantine, P. Heath, H. Rashid, S. Teixeira, J. H. Thorpe and A. K. Todd, *Organometallics*, 1999, **18**, 389; (*c*) B. E. Eichler and P. P. Power, *Inorg. Chem.*, 2000, **39**, 5444; (*d*) B. E. Eichler, B. L. Phillips, P. P. Power and M. P. Augustine, *Inorg. Chem.*, 2000, **39**, 5450; (*e*) See also: W. Setaka, K. Sakamoto, M. Kira and P. P. Power, *Organometallics*, 2001, **20**, 4460.

8 E. John, *The Elements*, Oxford University Press, NY, 3rd edn, 1998.

9 For trimethylsilylcarbene addition to a π bond of a benzene ring, see: A. J. Ashe, III, *J. Org. Chem.*, 1972, **37**, 2053.

10 The 1,3-tin migration may occur as a photochemical or a thermal process. For the thermal suprafacial 1,3-silyl migration, see: L. C. Zhang, C. Kabuto and M. Kira, *J. Am. Chem. Soc.*, 1999, **121**, 2925 and references cited in. Because preliminary calculations at the RHF/3-21G* level suggest that **8** and **11** are more stable than other isomers, the NMR signal at δ 2113 may be assigned to **8** and/or **11** (see ESI†). Thermal 1,5-tin migration would be eliminated on the basis of the theoretical calculations. The theoretical calculations were performed using Gaussian 03 program: M. J. Frisch, *et al.*, *GAUSSIAN 03 (Revision D.01)*.

11 R. B. Larrabee, *J. Am. Chem. Soc.*, 1971, **93**, 1510; H. D. Gridnev, O. L. Tok, N. A. Gridneva, Y. N. Bubnov and P. R. Schreiner, *J. Am. Chem. Soc.*, 1998, **120**, 1034, and references cited therein.