ORGANOMETALLICS

Article

Cite This: Organometallics XXXX, XXX, XXX−XXX

pubs.acs.org/Organometallics

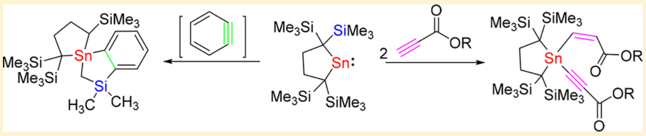
Reactions of an Isolable Dialkylstannylene with Propynoates and Benzyne

Jian Xu, Xu-Qiong Xiao, Chenting Yan, Zhifang Li,* Qiong Lu, Qian Yang, Guoqiao Lai,* and Mitsuo Kira*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, Zhejiang, People's Republic of China

Supporting Information

ABSTRACT: The reactions of stable monomeric dialkylstannylene **1** with methyl and ethyl propynoates give the corresponding 1:2 adducts, alkenyl(alkynyl)stannane **2** and **3** in high yields, while **1** does not react with parent acetylene or common mono- and disubstituted acetylenes such as phenylacetylene, trimethylsilylacetylene, diethyl 2-butynedioate, etc. Notably, **2** and **3** have the *Z*-configuration of the alkenyl moieties, in contrast to similar adducts obtained by the known reactions of silylenes with terminal acetylenes. It is suggested that the formation of a carbonyl oxygen-coordinate cyclic zwitterion as a key intermediate is essential for the reactions. Stannylene **1** adds to in situ generated benzyne, forming a 1:1 adduct having a unique 3-stanna-1-silaindane ring system.

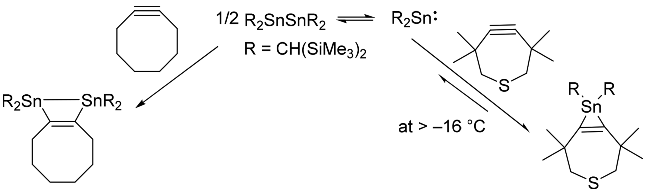


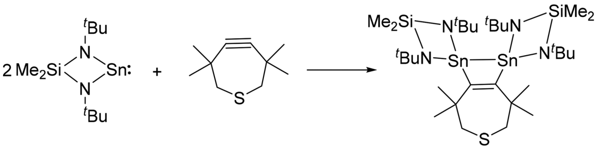
Much attention has been focused on the comparative chemistry of heavy congeners of carbenes, R_2E (E = Si, Ge, Sn, and Pb).[1] Knowledge and understanding of the chemistry of robust germylenes and stannylenes are however still limited in comparison to those of silylenes, while a number of isolable germylenes and stannylenes have been synthesized and their unique structures and reactions have been disclosed[1] since the pioneering works of Lappert et al.[2] One of the most intriguing difference in the reactivity between silylenes, germylenes, and stannylenes has been found in their reactivity toward alkenes and alkynes. While silylenes and germylenes are known to smoothly add to alkenes and alkynes giving the corresponding three-membered ring compounds, only a few addition reactions of stannylenes with alkenes and alkynes have been investigated.[1] The reactions of neither transient nor isolable stannylenes with simple alkenes and alkynes have been reported to date.[1e] Theoretical studies have shown that the addition reactions are almost thermo-neutral and an addition-dissociation equilibrium will be attained between the stannylene and the unsaturated C−C bonds.[3]

In 1988, Sita and his co-workers[4] have first reported that well-known Lappert's stannylene, $Sn[CH(SiMe_3)_2]_2$ equilibrated with the corresponding distannene,[2] reacts with a highly strained alkyne, 3,3,7,7-tetramethyl-6-thiacycloheptyne, giving a 1:1 adduct, the corresponding stannacyclopropene, at −16 °C as shown in Scheme 1. At elevated temperatures, it dissociates into the corresponding stannylene and the alkyne. A similar reaction of the stannylene with a strained, but less sterically hindered, cyclooctyne was found to give the corresponding 1,2-distannacyclobutene.[4b]

Similarly, Veith et al. have reported that an *N*-heterocyclic stannylene reacts with the strained alkyne, giving the corresponding 1,2-distannacyclobut-3-ene (eq 1).[5]

Scheme 1. Reactions of an Equilibrated Stannylene with Strained Alkynes





(1)

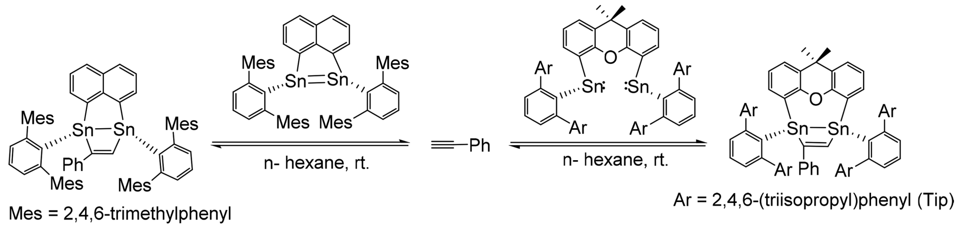
Though the 1,2-distannacyclobutenes would be formed by the consecutive addition of the stannylene molecules to the acetylene, direct [2 + 2] addition of the corresponding distannenes toward the strained alkynes is not ruled out; a number of stable heavy unsaturated tin−tin bonds have been found to react with various strained and less-strained alkynes, giving the corresponding 1,2-distannacyclobutenes.[6] Recently, Wesemann et al.[7] have also reported that both a nondissociative distannene and a nondimerizable bis(stannylene) afford the corresponding distannacyclobutenes during the reactions with alkynes (Scheme 2).

As a part of our recent studies on the reactivity of isolable dialkylstannylene **1**[8] that is monomeric and does not form the corresponding dimer in solution,[9,10] we have intended to shed

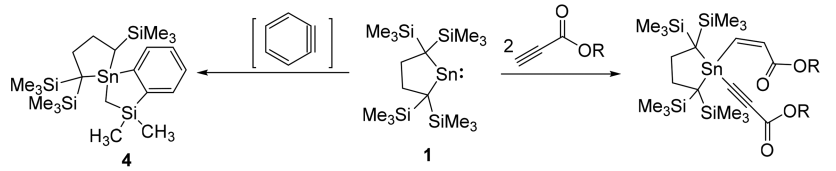
Received: April 4, 2018

DOI: 10.1021/acs.organomet.8b00197

Scheme 2. Reactions of Phenylacetylene with a Distannene and a Bis(stannylene)



Scheme 3. Reactions of Stannylene 1 with Propynoates and Benzyne



4

1

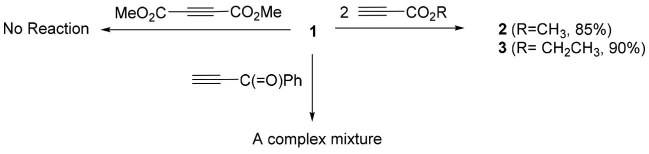
2, R = CH_3; **3**, R = CH_2CH_3

light on the generality of the reactivity of stannylenes toward alkynes. Unprecedentedly, stannylene **1** reacts with propynoate esters to afford the corresponding 1:2 adducts **2** and **3** (Scheme 3), while no reaction of **1** occurs with gaseous acetylene, phenylacetylene, trimethylsilylacetylene, 1,2-diphenylacetylene, or diethyl 2-butynedioate.[11] The reaction of **1** with in situ generated benzyne affords **4** with a unique 3-stanna-1-silaindane ring system, being accompanied by 1,4-silyl migration (Scheme 3).

■ RESULTS AND DISCUSSION

Reactions of Dialkylstannylene 1 with Methyl and Ethyl Propynoates. When **1** was treated with two molar amounts of methyl and ethyl propynoates in hexane at room temperature, the deep red color of **1** disappeared within 5 min, affording the corresponding 1:2 adducts, alkenyl(alkynyl)-stannanes **2** and **3**, in 85% and 90% isolated yields, respectively (Scheme 4).[12] In the similar conditions, **1** does not react with dimethyl 2-butynedioate even after a prolonged reaction time (5 h), probably owing to the severe steric hindrance during the reaction. Benzoylethyne reacts with **1** but gives a complex mixture.

Scheme 4. Reactions of Stannylenes 1 with Ethynylcarbonyl Compounds in Hexane at rt



The structures of **2** and **3** were fully characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopies, MALDI-TOF-MS, and finally X-ray crystallography. The ^{1}H NMR spectra of **2** and **3** show two doublet signals at 7.39 and 6.86 ppm and at 7.38 and 6.84 ppm, respectively, being assignable to their alkenyl protons with vicinal coupling constants ($^3J_{CH=CH}$) of 12 Hz. The *J* value is compatible with the *Z* configuration around the C═C double bond that is confirmed by the X-ray crystallography (*vide infra*). Their ^{13}C NMR spectra clearly show the presence of the C−C double and triple bonds. The alkenyl carbon resonances of **2** and **3** appear at δ 149.3 and 138.0 ppm, and at δ 152.9 and 134.4 ppm, respectively, and their alkynyl carbon signals are at 102.8 and 96.3 ppm and at 101.5 and 98.6 ppm. A ^{119}Sn NMR signal appears at −52.2 and −52.9 ppm for **2** and **3**, respectively.

The molecular structures of **2** and **3** determined by X-ray single-crystal analysis are consistent with the proposed. Yellow single crystals of **2** and **3** suitable for X-ray crystallography were obtained by slowly evaporating the solvent from their pentane solutions. The ORTEP drawings of the single crystals of **2** and **3**, which have the P_n and $C_{2/c}$ space groups, respectively, are depicted in Figures 1 and 2, together with pertinent structural parameters. Four independent molecules were found in an asymmetric unit of **2**; see the Supporting Information for the details. Because the molecular structures of

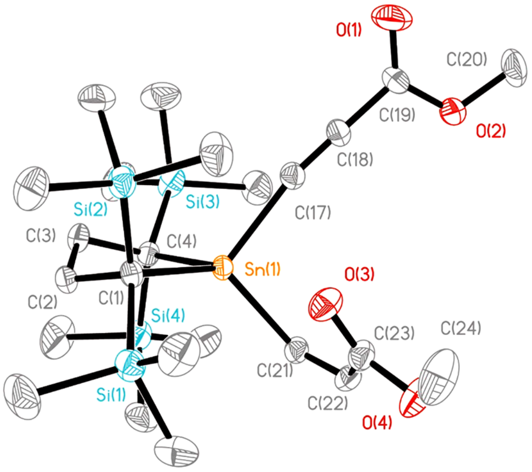


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−C(17) = 2.142(5), Sn(1)−C(21) = 2.151(5), Sn(1)−C(4) = 2.204(5), Sn(1)−C(1) = 2.196(5), Sn(1)−O(3) = 2.848(4), C(19)−O(1) = 1.167(7), C(23)−O(3) = 1.213(6), C(17)−C(18) = 1.180(7), C(21)−C(22) = 1.308(7), C(1)−Sn(1)−C(4) = 91.82(19), C(17)−Sn(1)−C(21) = 101.23(19), O(3)−Sn(1)−C(4) = 173.8(12), C(18)−C(17)−Sn(1) = 169.1(5), C(17)−C(18)−C(19) = 179.2(7), C(22)−C(21)−Sn(1) = 124.7(4), C(21)−C(22)−C(23) = 121.5(8). Dihedral angle (deg): Sn(1)−C(21)−C(22)−C(23) = 1.61(8), C(21)−C(22)−C(23)−O(3) = −4.42(9).

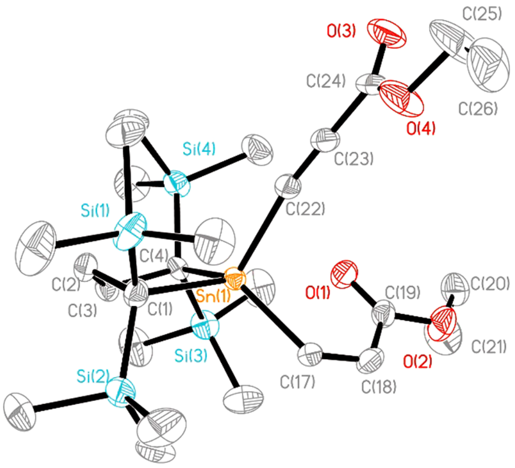


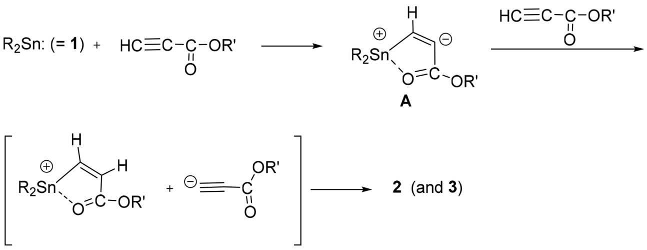
Figure 2. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−C(17) = 2.119(6), Sn(1)−C(22) = 2.123(7), Sn(1)−C(4) = 2.170(5), Sn(1)−C(1) = 2.197(6), Sn(1)···O(1) = 2.767(5), C(19)−O(1) = 1.197(8), C(19)−O(2) = 1.314(7), C(24)−O(3) = 1.174(9), C(24)−O(4) = 1.298(9), C(17)−C(18) = 1.322(9), C(22)−C(23) = 1.191(9), C(1)−Sn(1)−C(4) = 91.5(2), C(17)−Sn(1)−C(22) = 99.4(2), O(1)−Sn(1)−C(1) = 173.7 (2), C(18)−C(17)−Sn(1) = 124.4(5), C(17)−C(18)−C(19) = 119.7(6), C(23)−C(22)−Sn(1) = 168.7(6), C(22)−C(23)−C(24) = 179.1(8). Dihedral angle Sn(1)−C(17)−C(18)−C(19) = −2.75(9), C(17)−C(18)−C(19)−O(1) = −3.33(10).

2 and **3** are very similar to each other, we discuss herein only the structural characteristics of **2**. The *Z* configuration around the C═C double bond and the *s*-cis enone conformation are shown by the small dihedral angles Sn(1)−C(21)−C(22)−C(23) [1.61(8)°] and C(21)−C(22)−C(23)−O(3) [−4.42(9)°]. Though the *s*-cis conformation, the Sn···O distance of 2.848(4) Å, which is significantly smaller than the sum of van der Waals radii of Sn (2.25 Å) and O atoms (1.55 Å),[13] and the O(3)−Sn(1)−C(4) angle of 173.8(2)° are suggestive of a trigonal bipyramidal pentacoordinate tin structure of **2**. A theoretical study suggests however that the stabilization by the coordination may be unimportant (vide infra). The stannacyclopentane ring of **2** adopts an envelope conformation with one of the ring CH$_2$ groups out of a plane formed by the other four ring atoms. The C21−C22 and C17−C18 bond lengths, 1.308(7) and 1.180(7) Å, indicate the existence of one C═C double bond and one C≡C triple bond.

The reactions of stannylenes with terminal acetylenes giving the corresponding 1:2 adducts have never been known up to date, while similar 1:2 addition reactions of base-stabilized silylenes with phenylacetylene have recently been reported.[14] Interestingly, the geometry around the double bonds of **2** and **3** adopts *Z*-configuration, though in the above silylene reactions,[14] the corresponding (*E*)-phenylethenylsilanes are produced. To figure out reasonable pathways for rather unexpected formation of **2** (and **3**), optimized structures and free energies of possible products and intermediates for the model reaction of stannylene **1′** with methyl propynoate were determined using the dispersion-corrected DFT calculations (B3PW91-GD3) in heptane and THF; all the trimethylsilyl groups of **1** were replaced to trihydrosilyl groups in **1′**.[15] As shown in Scheme 5, while the optimized structures of (*Z*)-**2′**(*s*-cis) with the Sn···O(C═O) distance of 2.62 Å in heptane (2.63 Å in THF) are similar to that of **2** observed in the crystal (Figure 1), the isomer is 3−6 kcal/mol less stable than the other three isomers; no large difference is observed in the relative free energies among the other three structures. It is suggested that the extra-coordination of carbonyl oxygen toward tin does not contribute to stabilizing the system. The reaction of **1′** + 2(methyl propynoate) giving **2′** is highly exergonic with the ΔG larger than −28 kcal/mol in the two solvents.

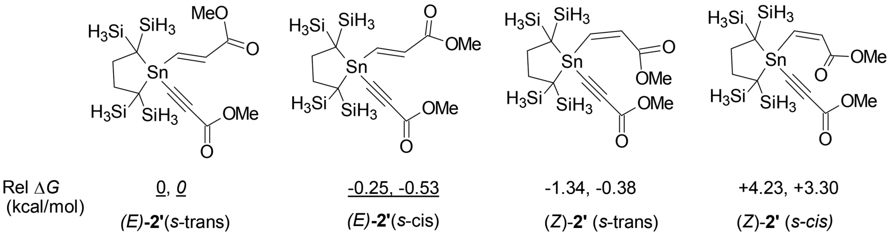
The mechanism for the formation of **2** (and **3**) would be similar to that for the reactions of the NHC-stabilized silylenes with phenylacetylene.[14] Thus, the 1:2 adduct **2** (and **3**) may be formed via the initial nucleophilic attack of **1** on a propynoate ester, giving an alkenyl anion-tin cation zwitterionic intermediate (**A**), which abstracts an acidic proton of the second propynoate ester, followed by combining the resulting alkynyl anion and the cationic tin atom (Scheme 6). The formation of the cyclic zwitterion **A** is indispensable for producing the Z-isomer of **2** and **3**.

Scheme 6. A Plausible Mechanism for the Formation of 2 (and 3) by the Reactions of 1 with Propynoate Esters

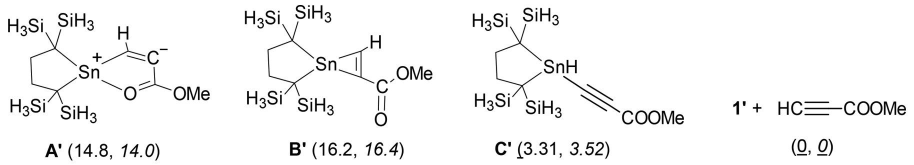


Relative stabilities of possible model 1:1 adducts of **1′** to methyl propynoate, **A′**, **B′**, and **C′** are calculated in heptane and THF as shown in Scheme 7.[15] In accord with the experimental results, the cyclic zwitterionic intermediate **A′** with the Sn···O distance of 2.23 Å in heptane (2.20 Å in THF)

Scheme 5. Relative Free Energies (kcal/mol) of the Isomers of a Model Stannylene-Methyl Propynoate 1:2 Adduct in Heptane and THF (*Italics*)



Scheme 7. Relative Stabilities of A′−C′ in Reference to 1′ + Methyl Propynoate[a]

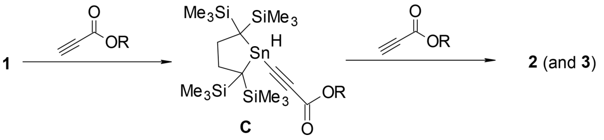


[a]Relative free energies (ΔG in kcal/mol) in heptane and THF (*italics*) are shown in parentheses.

is located as a minimum. Intermediate **A′** is 1.4 and 2.4 kcal/mol more stable than stannacyclopropene **B′** in heptane and THF, respectively. Compounds **A′** and **B′** are more than 10 kcal/mol less stable than CH insertion product **C′** in the two solvents. The formation of **A** as the key intermediate would be essential for the reactions of **1** with propynoates, and it may explain why only the (*Z*)-isomers of the products **2** and **3** are formed and why phenyl- and other common terminal acetylenes do not react with **1**.

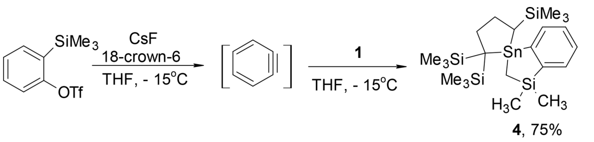
The theoretical calculations show that the reactions of **1′** + methyl propynoate giving **A′** and **B′** are both highly endergonic at 298.15 K (Scheme 7), suggesting that, without the subsequent addition of the secondary propynoate to the intermediates, the reactions may not proceed.

Another pathway in which the reaction occurs via the initial insertion of **1** into the C−H bond of the propynoate, followed by the hydrostannation of the resulting hydrostannane **C** with the second propynoate (eq 2), is improbable because neither the CH-insertion nor the hydrostannation without catalysts or activators has been known. Actually, our studies showed that neither the insertion of **1** into the acetylenic CH bond of phenylaceylene nor the hydrostannation of diphenyldihydrostannane to methyl propynoate was observed.



(2)

Reaction of Dialkylstannylene 1 with Benzyne. When **1** was treated with benzyne generated by the reaction of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate with cesium fluoride at −15 °C,[16] the reaction took place smoothly, and the color of the mixture changed from deep green to colorless within 10 min and yielded **4** in 75% isolated yield (eq 3).



(3)

The product was fully characterized by multinuclear NMR spectroscopy, elemental analysis, and finally confirmed by single crystal X-ray diffraction studies. The molecular structure of **4** determined by X-ray single-crystal analysis is shown in Figure 3 together with pertinent structural parameters.

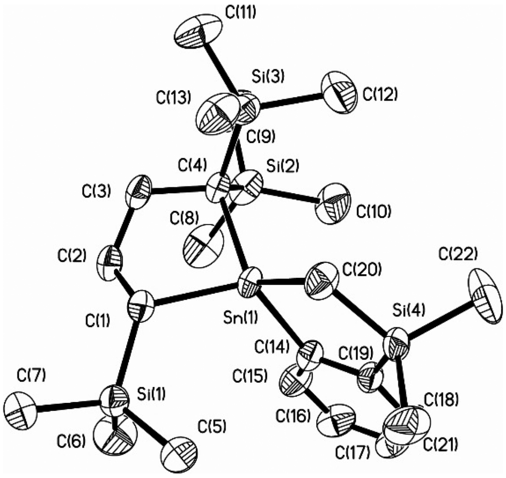
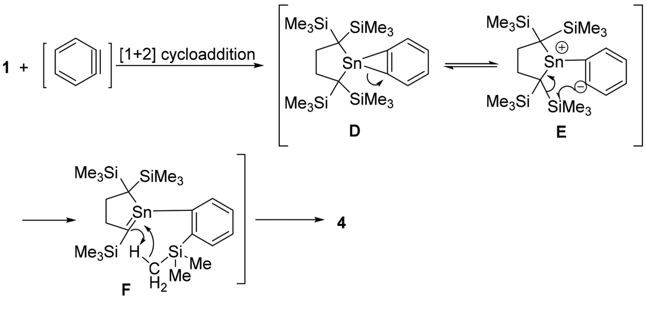


Figure 3. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) = 2.162(3), Sn(1)−C(4) = 2.203(3), Sn(1)−C(14) = 2.173(3), Sn(1)−C(20) = 2.150(3), C(19)−Si(4) = 1.887(4), C(20)−Si(4) = 1.853(4), C(14)−C(19) = 1.409(4), C(14)−C(15) = 1.386(5), C(20)−Sn(1)−C(14) = 93.74(13), C(1)−Sn(1)−C(4) = 88.56(11), C(15)−C(14)−Sn(1) = 128.10(2), C(19)−C(14)−Sn(1) = 112.7(2), Si(4)−C(20)−Sn(1) = 107.33(2), C(14)−C(19)−Si(4) = 120.5(2), C(20)−Si(4)−C(19) = 105.669(14).

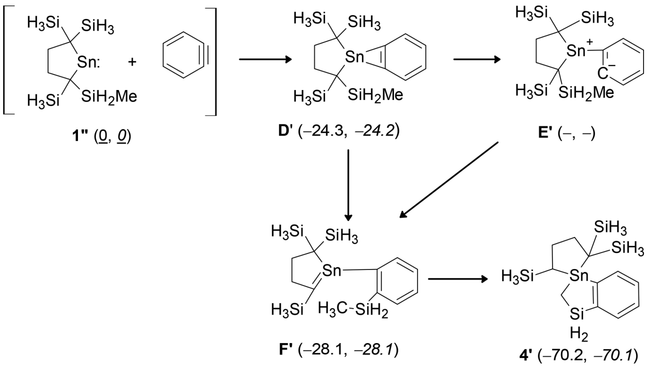
Scheme 8. Pathway Proposed for the Reaction of Stannylene 1 with Benzyne



The reaction pathway is not fully understood, but a plausible mechanism is proposed as follows (Scheme 8): Stannacyclopropene **D** would initially form through the reaction of **1** with benzyne having a strained and hence highly reactive triple bond. Intermediate **D** may then form the ring-opened 1,3-zwitterionic intermediate **E**, in which stannylene tin and phenyl *ortho*-carbon are positively and negatively charged. 1,4-Trimethylsilyl migration to the anionic carbon gives stannene **F**. Final product **4** would be formed via the insertion of the C═Sn bond of **F** into a C−H bond of a trimethylsilyl group.[17]

Optimized structures of **D′**, **F′**, and **4′**, as models of **D**, **F**, and **4** in Scheme 8 were determined using the B3PW91-GD3 calculations in heptane and THF. Relative free energies of these compounds are compared with those of the starting **1″** + benzyne in Scheme 9; in stannylene **1″**, one silyl group of **1′** was replaced to a methylsilyl group. Expectedly, all the reactions giving **D′**, **F′**, and **4′** from **1″** + benzyne are found to be highly exergonic. Several attempts to locate **E′** as a minimum failed and were terminated by the formation of **D′**. Compound **E′** may be in a shallow minimum between **D′** and **F′** or may not be formed as an intermediate. Further works are

Scheme 9. A Pathway for the Reaction of Stannylene 1′′ with Benzyne Giving 4′[a]



[a]Relative free energies (ΔG in kcal/mol) of the intermediates **D′**, **F′**, and product **4′** in heptane and in THF are given in parentheses (heptane, THF in *italics*). **E′** is not located as an energy minimum.

required for obtaining the reasonable profile for the whole reaction.

In conclusion, not only strained C−C triple bonds like benzyne but also polar mono-alkoxycarbonyl-substituted acetylenes have been found to react with isolable dialkylstannylene **1**. In the latter reactions giving the corresponding 1:2 adducts, a neighboring alkoxycarbonyl substituent is essential to facilitate the initial nucleophilic attack of **1**, forming the key zwitterionic intermediate due to the intramolecular coordination of the carbonyl oxygen to the tin center.

■ EXPERIMENTAL SECTION

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{29}Si (79 MHz), and ^{119}Sn (187 MHz) NMR were recorded using tetramethylsilane (^{1}H, ^{13}C, and ^{29}Si) and tetramethyltin (^{119}Sn) as external standards on a BRUKER AV-400 MHz instrument. GC−MS spectra were measured with an Agilent 7890a gas chromatography instrument coupled to an Agilent 5975c mass spectrometer. Mass spectra were measured with a Bruker Daltonics Autoflex II TM MALDI-TOF spectrometer. Elemental analyses were performed on a VARIO EL-III instrument. Stannylene **1** was prepared according to the literature procedures.[8] Stannylene **1** and other air-sensitive materials were handled in an MBraun glovebox.

The full ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra of all new compounds (**2**−**4**) are provided in the Supporting Information (SI).

Reaction of 1 with Methyl and Ethyl Propynoates. When methyl propynoate (75.6 mg, 0.9 mmol) or ethyl propynoate (88.2 mg, 0.9 mmol) was added dropwise into a hexane (5 mL) solution of stannylene **1** (200 mg, 0.432 mmol) at room temperature, the color of the reaction mixture turned quickly from red to green, and 1 h later, to yellow. Removal of the solvent under vacuum and then preparative silica column chromatography gave pure **2** or **3** in the yield of 85% and 90%, respectively.

2: white solid (232 mg); mp:104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 12 Hz, 1H), 6.86 (d, J = 12 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.17−2.04 (m, 4H), 0.26 (s, 18H), 0.10 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 152.9, 149.3, 138.0, 102.8, 96.3, 52.6, 51.9, 34.7, 17.4, 3.7, 3.4; ^{29}Si NMR (79 MHz, $CDCl_3$) δ 4.91, 3.74; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ −52.2; MALDI-TOF-MS m/z Calcd for $C_{24}H_{48}O_4Si_4Sn$: 632; Found:632; Anal. Calcd for $C_{24}H_{48}O_4Si_4Sn$: C, 45.63; H, 7.66; O, 10.13. Found: C, 45.58; H, 7.57; O, 10.08.

3: white solid (257 mg); mp:107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 12 Hz, 1H), 7.84 (d, J = 12 Hz, 1H), 4.34 (q, J = 8 Hz, 2H), 4.15 (q, J = 8 Hz, 2H), 2.16−2.04 (m, 4H), 1.36 (t, J = 8 Hz, 3H), 1.26 (t, J = 8 Hz, 3H), 0.25 (s, 18H), 0.10 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 157.2, 152.9, 134.4, 101.5, 98.6, 61.9, 61.3, 34.2, 14.2, 14.0, 13.8, 3.5, 3.0; ^{29}Si NMR (79 MHz, $CDCl_3$) δ 4.86, 3.70; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ −52.9; MALDI-TOF-MS m/z Calcd for $C_{26}H_{52}O_4Si_4Sn$: 660; Found:660; Anal. Calcd for $C_{26}H_{52}O_4Si_4Sn$: C, 47.33; H, 7.94; O, 9.70. Found: C, 47.26; H, 7.89; O, 9.72.

Reaction of Stannylene 1 with Benzyne. Cesium fluoride (0.164 g, 1.08 mmol) was charged into a Schlenk tube and dried with a heat gun under reduced pressure. The tube was cooled to room temperature under an argon atmosphere. To the tube were added 18-crown-6 ether (0.57 g, 2.15 mmol) and dry THF (6 mL). The resulting solution was stirred at −15 °C for 10 min. To the solution was quickly added a solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.161 g, 0.540 mmol) in dry THF (1 mL), and the mixture was stirred for 20 min at −15 °C. Then stannylene **1** (0.1 g, 0.216 mmol) in THF (1 mL) was added to the mixture. After the reaction mixture was stirred for half an hour at −15 °C, the solvent was removed under vacuum. The residue was purified by preparative silica column chromatography, giving 3-stanna-1-silaindane **4** in the yield of 75%.

White solid (83.4 mg); mp: 205.3−206.5 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.86 (d, J = 8 Hz, 1H), 7.46 (d, J = 8 Hz, 1H), 7.20−7.24 (m, 2H), 2.34−2.38 (m, 2H), 1.55−1.67(m, 2H), 0.36 (s, 3H), 0.31 (s, 3H), 0.29 (t, J = 6 Hz, 1H), 0.20 (s, 9H), 0.10 (s, 9H), 0.02−0.06 (m, 2H), −0.02 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 152.3, 151.5, 137.2, 133.5, 128.7, 128.4, 34.7, 32.8, 17.2, 16.0, 2.7, 2.0, 1.4, 1.1, 0.0, −6.8; ^{119}Sn NMR (187 MHz, C_6D_6) δ 148.1; MALDI-TOF-MS m/z Calcd for $C_{22}H_{44}Si_4Sn$: 540; Found:540; Anal. Calcd for $C_{22}H_{44}Si_4Sn$: C, 48.97; H, 8.22. Found: C, 48.89; H, 8.15.

DFT Calculations. All calculations were performed using the Gaussian 09 package. Geometry optimizations and vibrational frequency calculations of all stationary points were performed using a dispersion-corrected DFT method, B3PW91-GD3 using the basis sets of 6-31+G(d,p) for C, H, O, and Si atoms + SDD for Sn. To evaluate the effects of a polar solvent in the reactions investigated, all the calculations were performed in heptane and THF as well as in gas phase using the polarizable continuum model (PCM).[18] See the Supporting Information for the calculation details and full reference of Gaussian 09.

X-ray Structure Determination. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo−Kα radiation (λ = 0.71073 Å) using the ω-2θ scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-2000.[19] The crystal and refinement data are described in the SI. The supplementary crystallographic data for **2**, **3**, and **4** are deposited with the CCDC; the nos. are 1817474, 1817475, and 1817473, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00197.

^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra of **2**−**4** and X-ray crystallography of compounds **2**−**4** and details of the theoretical calculations (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1817473−1817475 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhifanglee@hznu.edu.cn (Z.L.).
*E-mail: gqlai@hznu.edu.cn (G.L.).
*E-mail: mitsuo.kira.e2@tohoku.ac.jp (M.K.).

ORCID

Zhifang Li: 0000-0002-9548-2158

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21472032, 21771048) and the Natural Science Foundation of Zhejiang Province (Grant No. LY17B010002). We are grateful to Prof. Takeaki Iwamoto, Department of Chemistry, Tohoku University, for helping us perform theoretical calculations at the B3PW91-GD3 level.

REFERENCES

(1) For recent reviews of heavy carbenes, see: (a) Lee, V. Ya.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds*; John Wiley & Sons: Chichester, U.K., 2010. (b) Asay, M.; Jones, C.; Driess, M. *N*-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligand. *Chem. Rev.* **2011**, *111*, 354−396. (c) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Stable Heavier Carbene Analogues. *Chem. Rev.* **2009**, *109*, 3479−3511. (d) Barrau, J.; Rima, G. Stable Germanium Analogs of Carbenes, Imines, Ketones, Thiones, Selones and Tellones. *Coord. Chem. Rev.* **1998**, *178−180*, 593−622. (e) Lappert, M. F. Recent Advances in the Chemistry of Bivalent Organic Compounds of Germanium, Tin and Lead. *Main Group Met. Chem.* **1994**, *17*, 183−208. (f) Neumann, W. P. Germylenes and Stannylenes. *Chem. Rev.* **1991**, *91*, 311−344.

(2) (a) Harris, D. H.; Lappert, M. F. Monomeric, Volatile Bivalent Amides of Group IV$_B$ Elements, M(NR$^1{}_2$)$_2$ and M(NR^{1}R^2)$_2$(M=Ge, Sn, or Pb; R^1=Me$_3$Si, R^2=Me$_3$C. *J. Chem. Soc., Chem. Commun.* **1974**, 895−896. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. Subvalent Group 4B Metal Alkyls and Amides. Part I. The Synthesis and Physical Properties of Kinetically Stable Bis[bis(trimethysilyl)-methyl]-Germanium(II), -Tin(II), and -Lead(II). *J. Chem. Soc., Dalton Trans.* **1976**, 2268−2274. (c) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. Subvalent Group 4B Metal Alkyls and Amides. Part II. The Chemistry and Properties of Bis[bis(trimethylsilyl)methyl]tin(II) and Its Lead Analogue. *J. Chem. Soc., Dalton Trans.* **1976**, 2275−2286.

(3) Boatz, J. A.; Gordon, M. S.; Sita, L. R. Theoretical Studies of the Metallacyclopropenes c-[MX$_2$C$_2$H$_2$] (M = C, Si, Ge, Sn; X = H, F). *J. Phys. Chem.* **1990**, *94*, 5488−5493.

(4) (a) Sita, R. L.; Bickerstaff, R. D. Synthesis and Crystal Structure of the First Stannacyclopropene Derivative. *J. Am. Chem. Soc.* **1988**, *110*, 5208−5209. (b) Sita, L. R.; Bickerstaff, R. D. Investigation of the Factors Influencing the Structure and Stability of Stannacyclopropenes: The Synthesis and Molecular Structure of Two Derivatives. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 31−36. (c) Sita, R. L.; Kinoshita, I.; Lee, P. S. Reactions of Stannylenes with Alkynes: Synthesis and Chemical Reactivity of a Stable 1,2-Distannacyclobut-3-ene Derivative. *Organometallics* **1990**, *9*, 1644−1650.

(5) Krebs, A.; Jacobsen-Bauer, A.; Haupt, E.; Veith, M.; Huch, V. Synthesis and Structure of Digerma- and Distannacyclobutenes. *Angew. Chem.* **1989**, *101*, 640−642.

(6) (a) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. Compounds of Germanium and Tin. 10. Thermolysis of a Cyclotristannane: Stannylene Versus Distannene Reactions. *Chem. Ber.* **1992**, *125*, 563−566. (b) Lee, V. Y.; Fukawa, T.; Nakamoto, M.; Sekiguchi, A.; Tumanskii, B. L.; Karni, M.; Apeloig, Y. (*t*Bu$_2$MeSi)$_2$Sn:Sn(SiMetBu$_2$)$_2$: A Distannene with a >Sn:Sn< Double Bond That Is Stable Both in the Solid State and in Solution. *J. Am. Chem. Soc.* **2006**, *128*, 11643−11651. (c) Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. Reversible Reactions of Ethylene with Distannynes Under Ambient Conditions. *Science* **2009**, *325*, 1668−1670. (d) Hardwick, J. A.; Baines, K. M. The Addition of Nitriles to a Molecular Digermene: Reversible Addition and Comparison to Surface Reactivity. *Angew. Chem., Int. Ed.* **2015**, *54*, 6600−6603.

(7) Schneider, J.; Henning, J.; Edrich, J.; Schubert, H.; Wesemann, L. Reversibility in Reactions of Linker-Bridged Distannenes with Terminal Alkynes at Ambient Temperature. *Inorg. Chem.* **2015**, *54*, 6020−6027.

(8) (a) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. Synthesis and X-ray Structure of the First Dicoordinate Dialkylstannylene That Is Monomeric in The Solid State. *J. Am. Chem. Soc.* **1991**, *113*, 7785−7787. (b) Kira, M.; Ishida, S.; Iwamoto, T.; Yauchibara, R.; Sakurai, H. New Synthesis of a Stable Dialkylstannylene and Its Reversible Complexation with Tetrahydrofuran. *J. Organomet. Chem.* **2001**, *636*, 144−147. (c) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. Addition of Stable Nitroxide Radical to Stable Divalent Compounds of Heavier Group 14 Elements. *J. Am. Chem. Soc.* **2003**, *125*, 9300−9301. (d) Kira, M.; Ishida, S.; Iwamoto, T. Comparative Chemistry of Isolable Divalent Compounds of Silicon, Germanium, and Tin. *Chem. Rec.* **2004**, *4*, 243−253.

(9) (a) Yan, C.; Xu, Z.; Xiao, X.-Q.; Li, Z.; Lu, Q.; Lai, G.; Kira, M. Reactions of an Isolable Dialkylstannylene with Carbon Disulfide and Related Heterocumulenes. *Organometallics* **2016**, *35*, 1323−1328. (b) Yan, C.; Li, Z.; Xiao, X.-Q.; Wei, N.; Lu, Q.; Kira, M. Reversible Stannylenoid Formation from the Corresponding Stannylene and Cesium Fluoride. *Angew. Chem., Int. Ed.* **2016**, *55*, 14784−14787. (c) Lu, Q.; Yan, C.; Xiao, X.-Q.; Li, Z.; Wei, N.; Lai, G.; Kira, M. Insertion of an Isolable Dialkylstannylene Into C-Cl Bonds of Acyl Chlorides Giving Acyl(chloro)stannanes. *Organometallics* **2017**, *36*, 3633−3637. For some other interesting reactions of **1**, see ref 10.

(10) (a) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak-Holl, M. M. A Stannylene/Aryl Iodide Reagent for Allylic C-H Activation and Double Bond Addition Chemistry. *Organometallics* **2008**, *27*, 1041−1043. (b) Kavara, A.; Kampf, J. W.; Banaszak-Holl, M. M. Direct Formation of Propargyltin Compounds via C-H Activation. *Organometallics* **2008**, *27*, 2896−2897. (c) Kavara, A.; Boron, T. T., III; Ahsan, Z. S.; Banaszak-Holl, M. M. C-H Activation of Alkanes, Alkenes, Alkynes, Arenes, and Ethers Using a Stannylene/Aryl Halide Mixture. *Organometallics* **2010**, *29*, 5033−5039. (d) Kavara, A.; Kheir, M. M.; Kampf, J. W.; Banaszak-Holl, M. M. Aryl Halide Radical Clocks as Probes of Stannylene/Aryl Halide C-H Activation Rates. *J. Inorg. Organomet. Polym. Mater.* **2014**, *24*, 250−257. (e) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. Persistent Dialkyl(silyl)stannylium Ions. *J. Am. Chem. Soc.* **2011**, *133*, 14562−14565.

(11) As suggested by a referee, the reaction of stannylene **1** with the substituted acetylenes may form the corresponding stannacyclopropenes that equilibrate with the starting compounds, and hence, the cyclic adduct may exist at low temeratures. However, the initial red color of **1** in a 0.01 M solution of **1** with an excess of phenylacetylene in hexane does not fade even at −78 °C, indicating no appreciable amount of the stannacyclopropene forms in the solution.

(12) The reaction of **1** with 1 equiv of methyl propynoate in C$_6$D$_6$ in similar conditons gave a mixture of **1**, **3**, and several unidentified products, as monitored by ^{1}H NMR (Figure S13). No evidence for the existence of intermediary 1:1 adduct was obtained, suggesting that the formation of the 1:2 adduct **3** from the 1:1 adduct may be faster than the formation of the initial 1:1 adduct. At the low concentration of methyl propynoate, the 1:1 adduct may decompose to the unidentified products..

(13) Batsanov, S. S. Van der Waals Radii of Elements. *Inorg. Mater.* **2001**, *37*, 871−885.

(14) (a) Gao, Y.; Zhang, J.; Hu, H. D.; Cui, C. M. Base-Stabilized 1-Silacyclopenta-2,4-dienylidenes. *Organometallics* **2010**, *29*, 3063−3065. (b) Ahmad, S. U.; Szilvási, T.; Inoue, S. A Facile Access to a

Novel NHC-Stabilized Silyliumylidene Ion and C-H Activation of Phenylacetylene. *Chem. Commun.* **2014**, *50*, 12619−12622. (c) Eisenhut, C.; Szilvási, T.; Breit, N. C.; Inoue, S. Reaction of an *N*-Heterocyclic Carbene-Stabilized Silicon(II) Monohydride with Alkynes: [2+2+1] Cycloaddition versus Hydrogen Abstraction. *Chem. - Eur. J.* **2015**, *21*, 1949−1954. (d) Walewska, M.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T. Alkyne Addition and Insertion Reactions of $[(Me_3Si)_3Si]_2Ge\cdot PMe_3$0020. *Chem. - Eur. J.* **2016**, *22*, 18512−18521.

(15) See the Experimental Section and the Supporting Information for the details of the theoretical calculations. We thank a referee for recommending the use of a dispersion-corrected DFT method and inclusion of solvation effects for the present theoretical caculations. Typically, the relative free energies of the four 1:2 adducts are meaningfully modified from those of the B3LYP/6-31+G(d, p) without dispersion using the basis sets of 6-31+G(d, p) for C, H, O, and Si atoms + LanL2DZ for Sn.

(16) Dockendorff, C.; Sahli, S.; Olsen, M.; Milhau, L.; Lautens, M. Synthesis of Dihydronaphthalenes via Aryne Diels-Alder Reactions: Scope and Diastereoselectivity. *J. Am. Chem. Soc.* **2005**, *127*, 15028−15029.

(17) No analogous reaction to the formation of **4** from intermediate **F** is known until now. A polar or radical nature of the C═Sn bond may allow the abstraction of the proton or hydrogen of a proximate methyl group.

(18) Tomasi, J.; Persico, M. Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent. *Chem. Rev.* **1994**, *94*, 2027−2094.

(19) (a) Picou, C. L.; Stevens, E. D.; Shah, M.; Boyer, J. H. Structure of 4,4-Difluoro-1,3,5,7,8-pentamethyl-3a,4a-diaza-4-bora-s-indacene. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 1148−1150. (b) *SMART, SAINT, SADABS and SHELXTL*; Bruker AXS Inc.: Madison, WI, 2000.