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Insertion of an Isolable Dialkylstannylene into C–Cl Bonds of Acyl Chlorides Giving Acyl(chloro)stannanes

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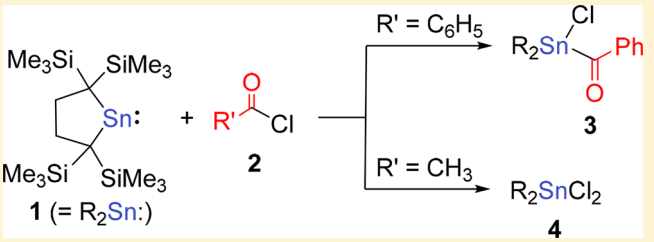
Supporting Information

ABSTRACT: The reactions of isolable dialkylstannylene **1** with 1-adamantanoyl, 2,2-dimethylpropanoyl, benzoyl, and substituted benzoyl chlorides afford the corresponding acyl(chloro)stannanes in good yields. Similar reactions with more reactive acetyl and propanoyl chlorides do not give the corresponding insertion products but the corresponding dichlorostannane by the overreaction. The benzoyl(chloro)stannane reacts with acetyl chloride to afford the corresponding 1,2-dione and the dichlorostannane quantitatively. Acyl(chloro)stannanes obtained were fully characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry, and by single-crystal X-ray diffraction studies.



INTRODUCTION

Acylsilanes and their heavier congeners, acylgermanes and acylstannanes, have been known as an electronically unique class of group-14 element compounds[1] with remarkably red-shifted n → π^* transition bands due to enhanced σ–n conjugation.[2] Since the first synthesis of a benzoylsilane by Brook,[3] a number of methods for the synthesis of various acylsilanes have been devised[4] and they have been applied for the organic synthesis[5,6] and for the synthesis of structurally interesting silicon compounds; acyltris(trimethylsilyl)silanes were utilized for the synthesis of the first stable silicon–carbon doubly bonded compounds (silenes).[7] More recently, an isolable silenyllithium was synthesized using an acyl(halo)silane.[8] On the contrary, less attention has been focused on the corresponding acylstannanes,[9] despite their great potential in synthetic organic chemistry. Acylstannanes have often been synthesized using the reactions of acyl chlorides (or carboxylic acid esters and thioesters) with stannyllithiums[9a,d] and those with hexamethyldistannane in the presence of palladium catalysts[9e] (eqs 1 and 2), and using some other specific reactions such as photolysis of stannylfuranes.[9f] A number of applications of the acylstannanes for the organic synthesis have been reported.[10]

$$Ph_3SnLi + RCOCl \longrightarrow Ph_3SnCOR + LiCl \quad (1)$$

$$Me_3SnSnMe_3 + RCOCl \longrightarrow Me_3SnCOR + Me_3SnCl \quad (2)$$

R = Ph, Me, ^{t}Bu, etc.

Insertion of isolable diamino- and dialkylstannylenes **A** and **B** (Chart 1) into acyl–Cl bonds of acyl chlorides, giving acyl(chloro)stannanes, has first reported by Lappert and coworkers in 1987.[11] Recently, a thermally less stable acyl(chloro)stannane was isolated through the reaction of a *C,N*-chelated stannylene (**C**) (Chart 1) with benzoyl chloride, and its molecular structure was determined by X-ray diffraction technique.[12]

We have recently reported a similar insertion of an isolable dialkylsilylene as a conventional synthetic method for the corresponding acyl(chloro)silanes **D** (Chart 1).[13] During the course of our studies of the reactions of isolable dialkylstannylene **1** (Chart 1) with various functional groups,[14] we have found that the stannylene inserts exclusively into the C–Cl bonds of acyl chlorides, providing a number of acyl(chloro)stannanes that are difficult to synthesize via conventional methods. They are expected to be more reactive than the corresponding acylsilanes and to serve as better synthetic reagents.

RESULTS AND DISCUSSION

When dialkylstannylene **1** was treated with an excess amount of benzoyl and 4-substituted benzoyl chlorides **2a**–**2c** in hexane at room temperature, the corresponding benzoyl(chloro)stannanes **3a**–**3c** were obtained in good yields, indicating that the C–Cl bond is much more reactive than the carbonyl group (eq 3). No significant difference was observed in the reactivity among benzoyl chlorides **2a**–**2c**. The results are summarized in Table 1.

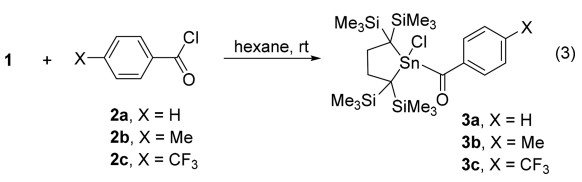


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Chart 1. Structural Formulae of Lappert's Stannylenes (A and B), Double *C,N*-Chelated Stannylene (C), Benzoyl(chloro)silanes (D), and 1

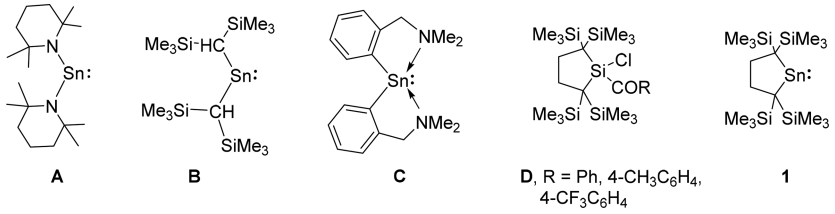

Table 1. Yields and Spectral Data of Acylstannanes

entry	compound	yield[a] (%)	δ (^{13}C)[b]	δ (^{119}Sn)[c]	ν (CO)[d] (cm^{-1})
1	**3a**	92	230.4	71.9	1639
2	**3b**	82	229.2	72.2	1628
3	**3c**	76	231.1	72.5	1634
4	**3d**	84	241.8	61.5	1652
5	**3e**	78	243.5	60.6	1655

[a]Isolated yields. [b]Spectra recorded in $CDCl_3$. Chemcial shifts (ppm) are based on external Me_4Si. [c]Based on external Me_4Sn. [d]Determined by ATR-FTIR.

Molecular structures of compounds **3a**–**3c** were determined by X-ray single-crystal diffraction analysis. Yellow single crystals of **3a**–**3c** suitable for X-ray crystallography were obtained by slowly evaporating the solvent from their hexane solutions. The ORTEP drawing of compound **3a** is depicted in Figure 1 together with pertinent structural parameters. Compound **3a** crystallizes in the $P2_1/c$ space group. The unit cell contains two independent molecules in an asymmetric unit with different torsion angles of C(1)Sn(1)C(17)O(1) and its equivalent, C(24)Sn(6)C(40)O(2), (130.8° and 134.8°, respectively). Because the other structural parameters of the two molecules are very similar, we will discuss the feature on the molecule with Sn(1). The sum of bond angles around C(17) is 360°, being in accord with the sp^2 character of the carbonyl carbon atom. The distance of the Sn(1)–Cl(1) (2.394(2) Å) bond is longer than that of chloro(triphenyl)tin (2.35 Å),[15] but shorter than those of trialkyl derivatives such as Cy_3SnCl (2.4558 Å, Cy = cyclohexyl)[16] and Me_3SnCl (2.43 Å).[17] The C(17)=O(1) bond distance of 1.192(7) Å is significantly shorter than those of the corresponding acyl(chloro)silanes (**D**, 1.217–1.223 Å).[13]

Similarly, compounds **3b** and **3c** were crystallized in space groups $P2_1/c$ and $P\bar{1}$, and their molecular structures are shown in Figures 2 and 3. In contrast to **3a** having two crystallographically independent molecules in an asymmetric unit, **3b** or **3c** has one molecule in a unit cell. Their structural parameters are similar to those of **3a**.

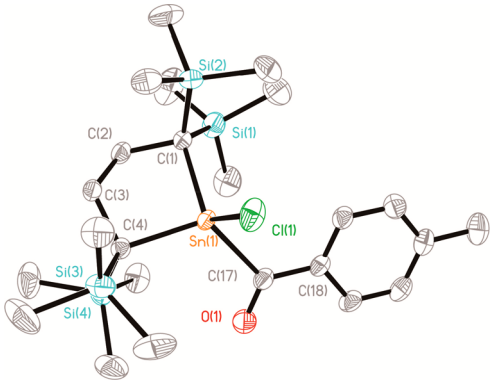

Figure 2. ORTEP drawing of compound **3b**. (Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.) Selected bond lengths (Å) and angles (deg): Sn(1)–C(4) 2.174(3), Sn(1)–C(1) 2.186(3), Sn(1)–C(17) 2.235(3), Sn(1)–Cl(1) 2.3841(8), C(18)–C(17) 1.485(4), O(1)–C(17) 1.203(4), C(4)–Sn(1)–C(1) 93.37(10), C(4)–Sn(1)–C(17) 115.78(11), C(1)–Sn(1)–C(17) 129.95(11), C(4)–Sn(1)–Cl(1) 110.05(8), C(1)–Sn(1)–Cl(1) 110.95(8), C(17)–Sn(1)–Cl(1) 96.67(8), O(1)–C(17)–C(18) 122.8(3), O(1)–C(17)–Sn(1) 115.2(2), C(18)–C(17)–Sn(1) 122.0(2).

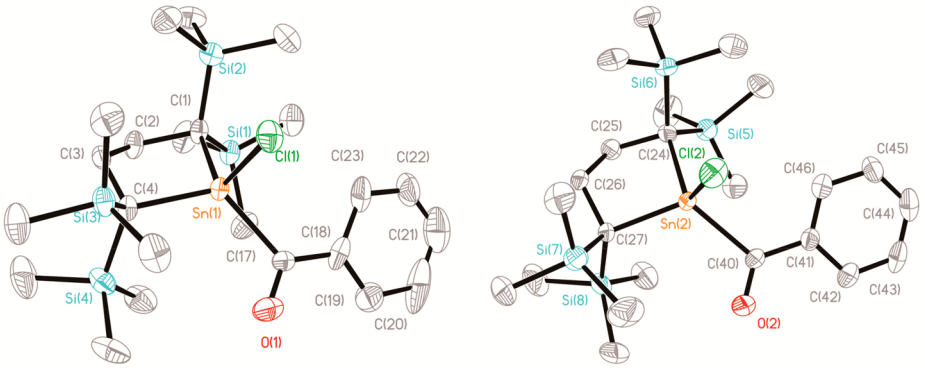

Figure 1. ORTEP drawing of compound **3a**. (Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.) Selected bond lengths (Å) and angles (deg): Sn(1)–C(4) 2.165(5), Sn(1)–C(1) 2.183(6), Sn(1)–C(17) 2.219(6), Sn(1)–Cl(1) 2.394(2), O(1)–C(17) 1.192(7), C(17)–C(18) 1.457(9), C(4)–Sn(1)–C(1) 94.4(2), C(4)–Sn(1)–C(17) 119.5(2), C(1)–Sn(1)–C(17) 126.5(2), C(4)–Sn(1)–Cl(1) 110.94(16), C(1)–Sn(1)–Cl(1) 111.10(17), C(17)–Sn(1)–Cl(1) 94.83(18), O(1)–C(17)–C(18) 120.3(6), O(1)–C(17)–Sn(1) 116.7(5), C(18)–C(17)–Sn(1) 123.0(5), C(19)–C(18)–C(17) 122.7(8).

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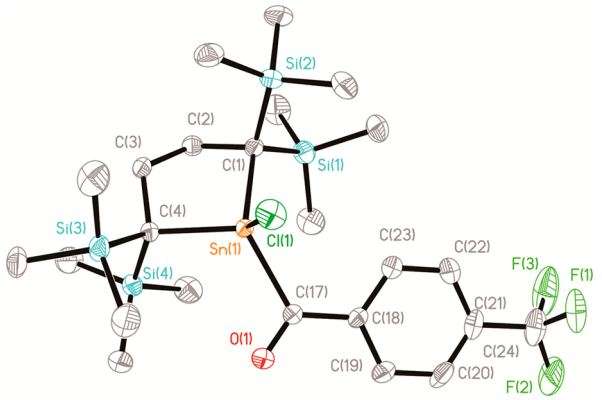
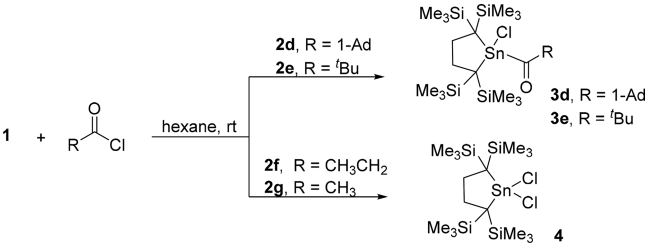


Figure 3. ORTEP drawing of compound **3c**. (Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.) Selected bond lengths (Å) and angles (deg): Sn(1)−C(4) 2.168(3), Sn(1)−C(1) 2.184(3), Sn(1)−C(17) 2.226(3), Sn(1)−Cl(1) 2.3891(9), C(17)−O(1) 1.195(4), C(17)−C(18) 1.497(4), C(4)−Sn(1)−C(1) 93.49(10), C(4)−Sn(1)−C(17) 116.22(10), C(1)−Sn(1)−C(17) 132.25(11), C(4)−Sn(1)−Cl(1) 111.88(8), C(1)−Sn(1)−Cl(1) 111.30(8), C(17)−Sn(1)−Cl(1) 92.12(9), O(1)−C(17)−C(18) 121.6(3), O(1)−C(17)−Sn(1) 115.3(2), C(18)−C(17)−Sn(1) 123.0(2), C(23)−C(18)−C(17) 121.2(3), C(19)−C(18)−C(17) 119.5(3).

The NMR spectra of **3a**−**3c** in $CDCl_3$ are consistent with their structures in the solid states. Typically, the ^{1}H NMR spectrum reveals two singlet signals for the four trimethylsilyl groups in the region of 0.1−0.3 ppm [0.16, 0.28 (**3a**); 0.17, 0.28 (**3b**); 0.17, 0.29 (**3c**)], indicating that there are two types of trimethylsilyl groups because of their *Cs* symmetry of **3**. In accord with the observation, two singlet ^{13}C and ^{29}Si NMR signals were observed for the trimethylsilyl groups in **3a**−**3c**, at 3.1.and 3.6 ppm in the ^{13}C NMR, and at ca. 5.7 and 3.2 ppm in the ^{29}Si NMR. The signals at 230.4 (**3a**), 229.2 (**3b**), and 231.1 (**3c**) ppm in ^{13}C NMR spectra are ascribed to the carbonyl carbon signals, which are at higher field than those of the typical acylstannanes (δ ca. 240 ppm)[9d] but at lower field than those of the corresponding acyl(chloro)silanes (δ 224.5−225.3 ppm).[13] The ^{119}Sn NMR resonances due to the ring tin atom of **3a**−**3c** appear at the similar chemical shifts of 72 ppm. In the IR spectra of **3**, a strong absorption was observed at around 1630 or 1650 cm^{-1}, which can be attributed to the C═O stretching mode. The frequencies are lower than those for usual ketones such as PhCO^{t}Bu (ν (CO) = 1675 cm^{-1})[18a] but a little higher than those for related acylmetals like $PhCOSiMe_3$ (ν (CO) = 1618 cm^{-1}),[18b] $PhCOGeEt_3$ (ν (CO) = 1629 cm^{-1}),[4a] and $PhCOSnMe_3$ (ν (CO) = 1620 cm^{-1}).[9d]

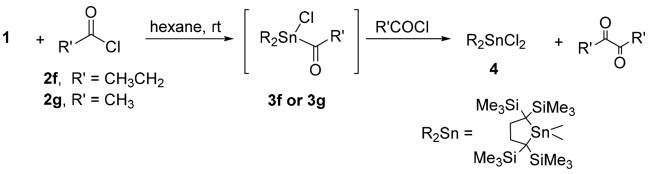
Similarly to aroyl chlorides, 1-adamantanoyl **2d** and 2,2-dimethylpropanoyl chlorides **2e** also readily furnished the corresponding 1:1 adducts **3d** and **3e** in good yields (Scheme 1). Products **3d** and **3e** were fully characterized by NMR, DODI-TOF, IR, and EA. In contrast to **2a**−**2e**, propanoyl chloride **2f** and acetyl chloride **2g** reacted with **1** under similar reaction conditions but did not give the corresponding acylstannanes. Thus, the reactions of **1** with 2 mol of **2f** and **2g** afforded the corresponding dichlorostannane **4** in 78% and 76% yields, respectively. The formation of the corresponding 1,2-diones, hexane-3,4-dione, and butane-1,2-dione, in 30% and 40%, was shown by GC−MS analysis of the reaction mixture. In the reactions of **1** with more reactive acyl chlorides, **2f** and **2g**, **3f** and **3g** once formed would be decomposed by another acyl chloride molecule to give **4** (Scheme 2), indicating

Scheme 1. Reactions of Alkanoyl Chlorides 2d−2g with Dialkylstannane 1

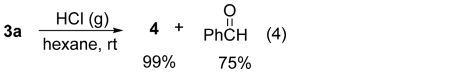


umpolung of a nucleophilic acyl chloride into an electrophilic acylstannane.[8]

Scheme 2. Pathway of the Formation of 4

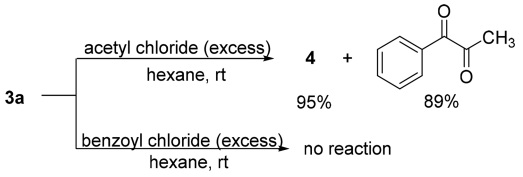


Due to the umpolung, an acyl(chloro)stannane may react with HCl and another acyl chloride to give the corresponding aldehyde and 1,2-dione, respectively. Actually, benzoyl(chloro)-stannane **3a** reacts with HCl in hexane at room temperature to afford benzaldehyde together with **4** in good yields (eq 4).



The reaction of **3a** with acetyl chloride gave 1-phenyl-propane-1,2-dione in a high yield, while **3a** did not react with less reactive benzoyl chloride in the similar conditions (Scheme 3). The reactions of acylstannanes with acyl chlorides have

Scheme 3. Reaction of 3a with Acetyl Chloride or Benzoyl Chloride



been reported to occur in the presence of palladium catalysts, giving the corresponding 1,2-diones.[10a] The reaction would occur concertedly through the nucleophilic attack of the anionic chlorine atom of acetyl chloride to the tin atom of **3a** leaving benzoyl group, which would be captured simultaneously by the cationic acetyl carbon to form the 1,2-dione; it is interesting to note that the benzoyl group may be regarded as an equivalent to a chlorine atom similarly to ethoxyethyl group.[19]

In conclusion, the reactions of isolable dialkylstannylene **1** with acyl chlorides (aroyl, 1-adamantanoyl, and 2,2-dimethyl-propanoyl chlorides) afforded acylstannanes **3a**−**3e** exclusively. Propanoyl and acetyl chlorides react with **1** to give the corresponding dichlorostannane **4** by overreaction. Aroyl-(chloro)stannane **3a** further reacted with acetyl chloride to be transformed into the corresponding 1,2-dione and **4** quantitatively.

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EXPERIMENTAL SECTION

Manipulation of air-sensitive compounds was performed under a controlled dry argon atmosphere using standard Schlenk techniques. Hexane was distilled from sodium−benzophenone. All the other reagents were obtained from commercial suppliers and used without further purification. Dialkylstannylene **1** was prepared according to literature procedures.[14a] Stannlylene **1** and other air-sensitive materials were handled in an MBraun glovebox. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{29}Si (79 MHz), and ^{119}Sn (187 MHz) NMR spectra were recorded on a BRUKER AV-400 MHz instrument using Me_4Si (^{1}H, ^{13}C, and ^{29}Si) and Me_4Sn (^{119}Sn) as external standards. Mass spectra were measured with a Bruker Daltonics Autoflex IITMMALDI-TOF spectrometer. IR spectra were recorded by attenuated total reflection with a diamond single reflection plate using a Bruker Vertex 70 instrument. Elemental analyses were performed on a VARIO EL-III instrument.

The full ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra of all new compounds (**3a**−**3e**) are provided in the Supporting Information (SI).

Synthesis of 3a−3e. A hexane solution of acyl chloride (0.96 mmol) was added to a hexane solution of dialkylstannylene **1** (0.3 g, 0.64 mmol) at room temperature. The color of the solution changed from red to yellow quickly. The reaction mixture was allowed to stir for 2−3 h, and then the solvent was removed under vacuum. The resulting residue was purified by a preparative silica-gel column to give **3** as a yellow solid.

3a, Yield: (0.36g, 92%); mp: 99.0−99.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−8.00 (m, 2H,), 7.56−7.63 (m, 3H), 2.35−2.16 (m, 4H), 0.28 (s, 18H), 0.16 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 230.3, 138.5, 134.3, 130.3, 129.0, 33.8, 21.5, 3.6, 3.1; ^{29}Si NMR (79 MHz) δ 5.71, 3.37; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ 71.9; MALDI-TOF-MS m/z Calcd for $C_{23}H_{45}ClOSi_4Sn$: 604; Found: 604; Anal. Calcd for $C_{23}H_{45}ClOSi_4Sn$: C, 45.73; H, 7.51; O, 2.65. Found: C, 45.69; H, 7.53; O, 2.62.

3b, Yield: (0.33g, 82.5%); mp: 142.8−143.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.89 (d, J = 8 Hz, 2H), 7.36−7.38 (d, J = 8 Hz, 2H), 2.45 (s, 3H), 2.15−2.32 (m, 4H), 0.28 (s, 18H), 0.17 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 229.2, 145.5, 136.1, 130.5, 129.8, 33.8, 21.8, 21.3, 3.6, 3.1; ^{29}Si NMR (79 MHz) δ 5.68, 3.35; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ 72.2; MALDI-TOF-MS m/z Calcd for $C_{24}H_{47}ClOSi_4Sn$: 618; Found:618; Anal. Calcd for $C_{24}H_{47}ClOSi_4Sn$: C, 46.63; H, 7.66; O, 2.59. Found: C, 46.57; H, 7.58; O, 2.66.

3c, Yield: (0.11 g, 76%); mp: 126.2−126.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.13 (d, J = 8 Hz, 2H), 7.84−7.86 (d, J = 8 Hz, 2H), 2.17−2.36 (m, 4H), 0.29 (s, 18H), 0.17 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 231.0, 140.7, 135.0, 130.1, 126.1, 124.7, 33.7, 22.0, 3.6, 3.1; ^{29}Si NMR (79 MHz) δ 5.82, 3.46; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ 72.5; MALDI-TOF-MS m/z Calcd for $C_{24}H_{44}ClF_3OSi_4Sn$: 672; Found:672; Anal. Calcd for $C_{24}H_{44}ClF_3OSi_4Sn$: C, 42.89; H, 6.60; O, 2.38. Found: C, 42.97; H, 6.58; O, 2.33.

3d, Yield: (0.24g, 84%); mp: 104.2−105.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28−2.18 (m, 3H), 2.13 (s, 4H), 2.05 (s, 6H), 1.76 (s, 6H), 0.22 (s, 18H), 0.18 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 242.1, 54.9, 37.8, 36.5, 33.7, 28.2, 22.8, 3.8, 3.4; ^{29}Si NMR (79 MHz) δ 5.69, 3.11; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ 61.5; MALDI-TOF-MS m/z Calcd for $C_{27}H_{55}ClOSi_4Sn$: 662; Found: 662; Anal. Calcd for $C_{27}H_{55}ClOSi_4Sn$: C, 48.97; H, 8.37; O, 2.42. Found: C, 48.89; H, 8.45; O, 2.35.

3e, Yield: (0.22g, 78%); mp: 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29−2.13(m, 4H), 1.34 (s, 9H), 0.22 (s, 18H), 0.18 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 243.5, 52.5, 33.7, 25.9, 22.6, 3.7, 3.3; ^{29}Si NMR (79 MHz) δ 5.70, 3.18; ^{119}Sn NMR (187 MHz, $CDCl_3$) δ 60.6; Anal. Calcd for $C_{21}H_{49}ClOSi_4Sn$: C, 43.18; H, 8.46. Found: C, 43.09; H, 8.55.

Reaction of Dialkylstannylene 1 with Acetyl Chloride or Propanoyl Chloride. A hexane solution of HCl-free acetyl chloride (39.3 mg, 0.5 mmol) or propanoyl chloride (46.25 mg, 0.5 mmol) was added to a solution of dialkylstannylene **1** (0.1 g, 0.2 mmol) in hexane at room temperature. The color of the solution changed from red to colorless quickly. The reaction mixture was allowed to stir for 2 h. Then, the reaction mixtures were checked by GC−MS directly, and found the formation of biacetyl (30%) or hexane-3,4-dione (40%) in addition to dichlorostannane **4**, which was obtained by recrystallization from a 1:1 mixture of hexane and EtOH as a colorless solid in 78% or 76%. **4**: mp: 190 °C (lit.[14b]187−188 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 4H), 0.25 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.5, 24.9, 3.3; ^{29}Si NMR (79 MHz) δ 4.81; ^{119}Sn NMR (187 MHzCDCl$_3$) δ 182.6.

Reaction of 3a with Acetyl Chloride. A hexane solution of acetyl chloride (78.5 mg, 1 mmol) was added dropwise into **3a** (121 mg, 0.2 mmol) in hexane (210 mL) in a Schlenk tube at room temperature, and then the reaction mixture was stirred for 12 h. The solvent was removed under vacuum, and the products were isolated as pure substances from the resulting residue by flash chromatography. Dichlorostannane **4** and phenylpropane-1,2-dione were isolated in 95% and 89%, respectively. 1-Phenylpropane-1,2-dione: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.95 (d, J = 8.0 Hz, 2H), 7.42−7.57 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 191.3, 134.4, 131,8, 130.2, 128.7, 26.2.

Reaction of 3a with HCl. In a Schlenk tube (25 mL) was placed **3a** (121 mg, 0.2 mmol) and hexane (10 mL), and then HCl gas was bubbled into the tube for 30 min. The mixture was stirred at room temperature for an additional 2 h. After separation using column chromatography, compound **4** and benzaldehyde were obtained in 99% and 75%, respectively; the latter yield was determined by GC−MS.

X-ray Structure Determination. Single crystals of **3a**, **3b**, and **3c** suitable for X-ray analysis were obtained by the recrystallization from hexane. 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.[20] Crystal and refinement data for **3a**−**3c** are described in the SI. The supplementary crystallographic data for **3a**, **3b**, and **3c** are deposited with the CCDC; the Nos. are 1534786, 1534785, and 1534784, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00549.

^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra of **3a**−**3e** and **4** and X-ray crystallography of compounds **3a**, **3b**, and **3c** (PDF)

Accession Codes

CCDC 1534784−1534786 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.

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The authors declare no competing financial interest.

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