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## Introduction

Zero-valent, di-coordinated group-14-element compounds, the so-called ylidenes, have been extensively studied over the last decade, and C, Si, Ge, Sn, and Pb analogues have already been reported.<sup>1–10</sup> Ylidenes represent one of the isomers of the heavier analogues of allenes; however most ylidenes have been characterized as zero-valent compounds ( $E^0$ ) rather than allenes ( $E^{4+}$ ). The first 1-metallaallenes reported were the Si analogues (**A** in Fig. 1) synthesized by West *et al.* in 1993 and the Ge analogues (**B** and **C**) independently synthesized in 1998 by West as well as Tokitoh and Okazaki.<sup>11–13</sup> Subsequently, the synthesis, reactivity, and unique properties of their analogues were investigated.<sup>14–18</sup> Interestingly, an attempted synthesis of 1-stannapropadiene (**D**) along a similar synthetic route was reported by Escudié in 2004; however this led to an unprecedented stable distannirane (**E**) *via* a [2 + 1] cycloaddition between a transient stannylene and a 1-stannapropadiene (**D**).<sup>19</sup> This was the first tangible piece of evidence for the transient formation of a 1-stannapropadiene. In contrast, there is only one example each for the Si, Ge and Sn 2-metallaallene analogues (**F**, **G**, and **H**) using the same diphenylthiophosphinoyl groups ( $(Ph)_2(S)P-$ ) on the terminal carbon atoms of their allene moieties.<sup>20–22</sup> Importantly, the structural features of these compounds are not consistent with classical allene character due to the coordination of the sulfur atom in the substituents to the central metal atoms. Accordingly, tin analogues of allenes

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# A tin analogue of propadiene with cumulated C=Sn double bonds†

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The synthesis, structure, and properties of a stable, linear 2-stannapropadiene are reported. The identical C=Sn bonds in this 2-stannapropadiene are the shortest hitherto reported C–Sn bonds. This 2-stannapropadiene features a <sup>119</sup>Sn NMR signal at 507 ppm for the central tin atom, indicative of an unsaturated Sn<sup>4+</sup> oxidation state. Due to the inert-pair effect, the tin atom displays a pronounced preference for the +2 oxidation state over the +4 oxidation state. Nevertheless, by employing silyl substituents, it is possible to disrupt the inert-pair effect, leading to the formation of an isolable 2-stannapropadiene with a linear structure centered on a Sn<sup>4+</sup> atom. Treatment of this 2-stannapropadiene with SnBr<sub>2</sub>·dioxane resulted in the formation of a novel four-membered cyclic 1,1-dibromo-1,3-distannetane, which was subsequently reduced to afford the corresponding stable four-membered cyclic bis(stannylene).

with cumulative C=Sn  $\pi$ -bonds have remained elusive thus far. Earlier studies have reported on the isolation and characterization of a linear 2-germapropadiene (**1<sub>Ge</sub>**) by using bulky silyl substituents.<sup>23</sup> A single-crystal X-ray electron-density-distribution (EDD) analysis of **1<sub>Ge</sub>** allowed us to obtain the differential electron-density map of **1<sub>Ge</sub>**, which suggested two orthogonal  $\pi$ -bonds for the C=Ge=C moiety. Thus, **1<sub>Ge</sub>** represents the first example of a stable, structurally characterized germanium-centered heteroallene with a linear structure. Furthermore, the reactivity of **1<sub>Ge</sub>** is consistent with that of an allene rather than a tetrylene. To further investigate the properties of the corresponding 2-stannapropadiene, <sup>119</sup>Sn NMR

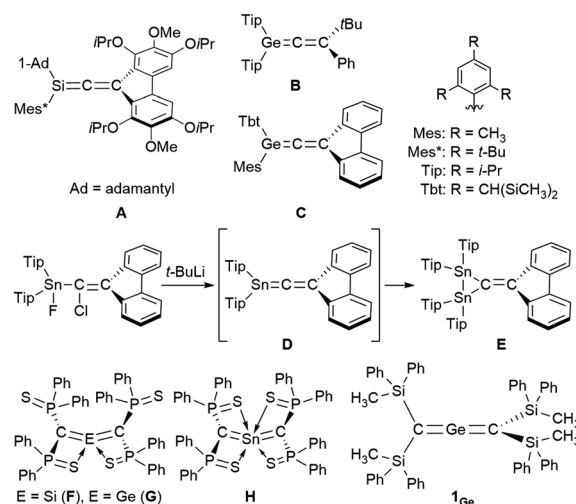


Fig. 1 Heteroallenes that contain heavier group-14 atoms and related compounds.

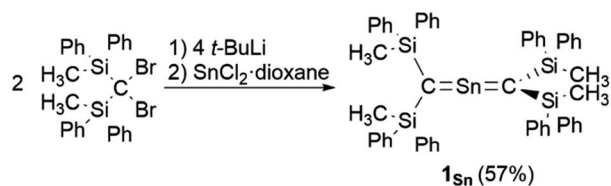


spectroscopy should offer a useful diagnostic tool for the determination of the electronic structure of the target compound. Herein, we report the synthesis and properties of a 2-stannapropadiene ( $\mathbf{1}_{\text{Sn}}$ ). The combined results of X-ray crystallographic and NMR spectroscopic analyses suggest that  $\mathbf{1}_{\text{Sn}}$  exists as an allene-type structure in the solid state and in solution. The linear structure of  $\mathbf{1}_{\text{Sn}}$  with cumulative C=Sn double bonds was confirmed by X-ray crystallography for the first time.

## Results and discussion

As previously reported,  $\mathbf{1}_{\text{Ge}}$  can be obtained from the reaction between bis(silyl)carbenoid  $\text{R}^{\text{Si}}_2\text{CLiBr}$ , which is generated *in situ* from the reaction of  $\text{R}^{\text{Si}}_2\text{CBr}_2$  with *t*-BuLi (2 eq.) in THF at  $-95^\circ\text{C}$ , and  $\text{GeCl}_2\cdot\text{dioxane}$  (1.0 eq.) at  $-95^\circ\text{C}$ .<sup>24</sup> After removal of the generated LiBr and recrystallization from hexane and benzene,  $\mathbf{1}_{\text{Ge}}$  can be obtained as pale-yellow crystals in 50% yield. The tin analogue ( $\mathbf{1}_{\text{Sn}}$ ) was prepared in a similar manner, *i.e.*, the bis(silyl)carbenoid was generated using the previously outlined procedure, and  $\text{SnCl}_2\cdot\text{dioxane}$  (0.33 eq.) was added at low temperature (Scheme 1). After removal of all inorganic salts, recrystallization from hexane and benzene afforded 2-stannapropadiene ( $\mathbf{1}_{\text{Sn}}$ ) as yellow crystals in 57% yield. While  $\mathbf{1}_{\text{Ge}}$  forms the corresponding cyclic thermal isomer quantitatively in solution after 2 h at  $60^\circ\text{C}$  upon 1,3-migration of the phenyl group,  $\mathbf{1}_{\text{Sn}}$  does not undergo thermal decomposition, not even in solution after 12 h at  $100^\circ\text{C}$ .

The characterization of  $\mathbf{1}_{\text{Sn}}$  was accomplished using multinuclear NMR, ultraviolet-visible (UV-vis), and infrared (IR) spectroscopy as well as mass spectrometry and single-crystal X-ray diffraction analysis (Fig. 2). The solid-state structure of  $\mathbf{1}_{\text{Sn}}$  exhibits  $D_{2d}$  symmetry with a linear C–Sn–C moiety (C–Sn–C angle:  $178.06(6)^\circ$ ) and almost identical C–Sn bonds (C1–Sn1:  $1.9787(15)\text{ \AA}$ ; C2–Sn1:  $1.9827(16)\text{ \AA}$ ). These C–Sn bonds represent some of the shortest among the hitherto structurally characterized organotin species with C=Sn double bonds such as stannenes [ $2.003(5)$ – $2.073(10)\text{ \AA}$ ]<sup>25–29</sup> and are significantly shorter than those of a previously reported base-stabilized 2-stannapropadiene ( $2.063(2)\text{ \AA}$ ).<sup>20</sup> Furthermore, the allenic moiety of the base-stabilized 2-stannapropadiene is slightly bent ( $171.1(1)^\circ$ ) with pyramidal carbon atoms ( $\Sigma C_{\text{allene}}$ :  $354.6^\circ$ ). In contrast, the two terminal carbon atoms of  $\mathbf{1}_{\text{Sn}}$  are almost planar ( $\Sigma C1$ :  $359.6^\circ$ ;  $\Sigma C2$ :  $359.8^\circ$ ), indicating that the structural properties of  $\mathbf{1}_{\text{Sn}}$  are considerably different from those of the base-stabilized 2-stannapropadiene. The C1–Si1–Si2 and C2–Si3–Si4 planes slightly deviate from a perpendicular



Scheme 1 Synthesis of 2-stannapropadiene  $\mathbf{1}_{\text{Sn}}$ .

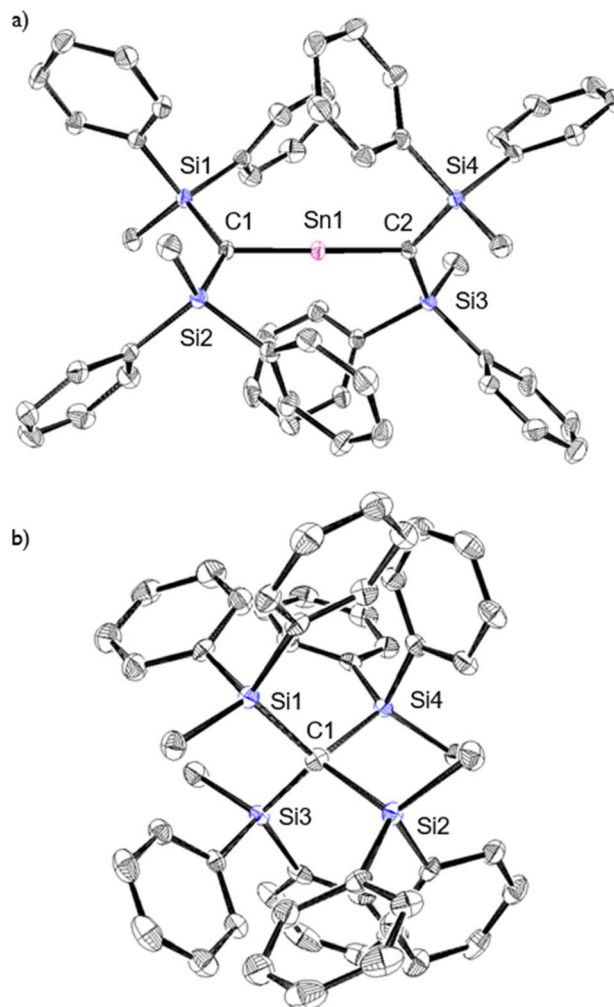


Fig. 2 (a) Top and (b) side views of the molecular structure of  $\mathbf{1}_{\text{Sn}}$  in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\mathbf{1}_{\text{Sn}}$ : C1–Sn1:  $1.9787(15)$ , C2–Sn1:  $1.9827(16)$ , C1–Si1:  $1.8410(16)$ , C1–Si2:  $1.8336(16)$ , C2–Si3:  $1.8423(16)$ , C2–Si4:  $1.8428(16)$ , C1–Sn–C2:  $178.06(6)$ , Si1–C1–Si2:  $130.90(9)$ , Si1–C1–Sn1:  $114.62(8)$ , Si2–C1–Sn1:  $114.07(8)$ , Si3–C2–Si4:  $133.33(9)$ , Si3–C2–Sn1:  $112.17(8)$ , and Si4–C2–Sn1:  $114.29(8)$ .

arrangement relative to each other ( $79.9^\circ$ ), probably due to the steric repulsion among the silyl groups.

The molecular structure of  $\mathbf{1}_{\text{Sn}}$  was further examined using theoretical calculations. The structural characteristics of  $\mathbf{1}_{\text{Sn}}$ , which were optimized at the B3PW91-D3(bj)/Def2TZVP level for Sn and the 6-311G(2d,p) level for the rest of the atoms, are in good agreement with those obtained experimentally (Fig. S45<sup>†</sup>), *i.e.*, the linear geometry of the C=Sn=C moiety (C–Sn–C =  $180.0^\circ$ ) and the two C–Sn bond lengths ( $1.959\text{ \AA}$ ) are close to the values obtained from the XRD analysis (C1–Sn1:  $1.9787(15)\text{ \AA}$ ; C2–Sn1:  $1.9827(16)\text{ \AA}$ ). The introduction of  $\text{H}_3\text{Si}$  substituents on the 2-stannapropadiene ( $\mathbf{1}_{\text{Sn}}^{\text{H}_3\text{Si}}$ ) resulted in an optimized linear structure, whereas the  $\text{H}$ -,  $\text{H}_3\text{C}$ -, and  $\text{H}_2\text{N}$ -substituted 2-stannapropadienes  $\mathbf{1}_{\text{Sn}}^{\text{H}}$ ,  $\mathbf{1}_{\text{Sn}}^{\text{H}_3\text{C}}$ , and  $\mathbf{1}_{\text{Sn}}^{\text{H}_2\text{N}}$  exhibit bent structures, suggesting that the presence of silyl substituents on the terminal carbon affect the linear C=Sn=C structure of  $\mathbf{1}_{\text{Sn}}$ .



That is, the  $\pi$ -electron accepting ability of the silyl groups on the terminal carbons would be crucial for the formation of the linear structure of 2-stannapropadiene. Apeloig and co-workers have reported the synthesis of a tetrasilyl-substituted distannene with a non-twisted structure that exhibits an almost perfect planar geometry due to the suitable steric effect and the silyl substituent effect.<sup>30</sup> The frontier Kohn–Sham orbitals of  $\mathbf{1}_{\text{Sn}}$  provided further information on the nature of the cumulated C=Sn bonds. The HOMO ( $\pi$ ), HOMO-1 ( $\pi$ ), LUMO+1 ( $\pi^*$ ), and LUMO+2 ( $\pi^*$ ) of  $\mathbf{1}_{\text{Sn}}$  reveal features typical of compounds with a linear allene-type structure (Fig. 3b). A natural bond orbital (NBO) analysis of the optimized structure of  $\mathbf{1}_{\text{Sn}}$  showed two C–Sn  $\pi$ -bonds that consist of almost pure 5p orbitals of the tin atom and 2p orbitals of the carbon atoms on the allene moiety.<sup>31</sup> The calculated natural-population-analysis (NPA) charges on the tin atom (+2.06) and on each of the terminal carbon atoms (−1.95) indicate a stronger polarization in the allene moiety of  $\mathbf{1}_{\text{Sn}}$  compared to that of the germanium derivative  $\mathbf{1}_{\text{Ge}}$  (Ge: +1.76; C: −1.86).<sup>23</sup>

To investigate the multiple-bond character of  $\mathbf{1}_{\text{Sn}}$  by vibrational spectroscopy, we recorded the IR spectrum (KBr, pellet) of  $\mathbf{1}_{\text{Sn}}$  in the solid state (Fig. S53†). The C=Sn=C asymmetric stretching

frequency of  $\mathbf{1}_{\text{Sn}}$  is observed at 930  $\text{cm}^{-1}$  and the assignment of this IR shift was supported by DFT calculations (925  $\text{cm}^{-1}$ ). This frequency is slightly lower than the C=Ge=C asymmetric stretching frequency of  $\mathbf{1}_{\text{Ge}}$  (973  $\text{cm}^{-1}$ ) and significantly lower than the C=C=C asymmetric stretching frequency of 1,1,3,3-tetrakis(trimethylsilyl)allene (1870  $\text{cm}^{-1}$ ).<sup>32,33</sup> It can thus be concluded that the frequency of the stretching vibration reflects the bond strength of the allene moieties. In the  $^1\text{H}$  NMR spectrum of  $\mathbf{1}_{\text{Sn}}$  in  $\text{C}_6\text{D}_6$ , the signal for the protons of the methyl groups was observed as a sharp singlet at 0.39 ppm, indicating a highly symmetric structure for  $\mathbf{1}_{\text{Sn}}$  in solution. The resonance for the carbon nuclei of the terminal carbons in the allene moiety was observed at 107 ppm, *i.e.*, shifted slightly down-field relative to those of previously reported 2-germapropadiene  $\mathbf{1}_{\text{Ge}}$  (86 ppm) and tetrakis(trimethylsilyl)allene (64 ppm).<sup>32,33</sup> Moreover, the  $^{119}\text{Sn}$  NMR signal for the tin atom was observed at 507 ppm in  $\text{C}_6\text{D}_6$ , indicating unsaturated  $\text{Sn}^{4+}$  character, similar to those of the stable stannenes (270–835 ppm) and stannaaromatic compounds (264–491 ppm) shown in Fig. 4.<sup>34–37</sup> However, this value is significantly lower than those of previously reported stannylenes ((−1147)–64 ppm), which are zero-valent tin species, and higher than those of kinetically stabilized stannylenes (2235–2323 ppm), which are  $\text{Sn}^{2+}$  species.<sup>38,39</sup> The central tin atom of a tristannaallene has been observed at 2233 ppm due to the considerable unsaturated character that is similar to that in stannylenes, and a stereochemically active lone pair of electrons.<sup>40</sup> In contrast to the resonance of the  $^{119}\text{Sn}$  nucleus in the base-stabilized 2-stannapropadiene (−401 ppm), the resonance of  $\mathbf{1}_{\text{Sn}}$  is characteristic for an unsaturated tin compound.<sup>21</sup> Moreover, the  $^{119}\text{Sn}$  NMR signal of  $\mathbf{1}_{\text{Sn}}$  in THF at 20 °C was observed as a broadened peak at 497 ppm. With decreasing temperature, this signal gradually shifts to a higher field (Fig. S38†), suggesting a dynamic process. At −50 °C, the signals were observed at 475 ppm and 362 ppm. Gauge-independent atomic orbital (GIAO)  $^{119}\text{Sn}$  NMR calculations for the optimized structure of  $\mathbf{1}_{\text{Sn}}$  afforded a value of 849 ppm. When the solvent effect for THF was considered using the SCRf method, no significant shift in the signal was observed (847 ppm). However, for  $\mathbf{1}_{\text{Sn}}\cdot\text{THF}$ , wherein one molecule of THF is coordinated to the central tin atom, a significant signal shift to 539 ppm was observed. The optimized structure of  $\mathbf{1}_{\text{Sn}}\cdot\text{THF}$

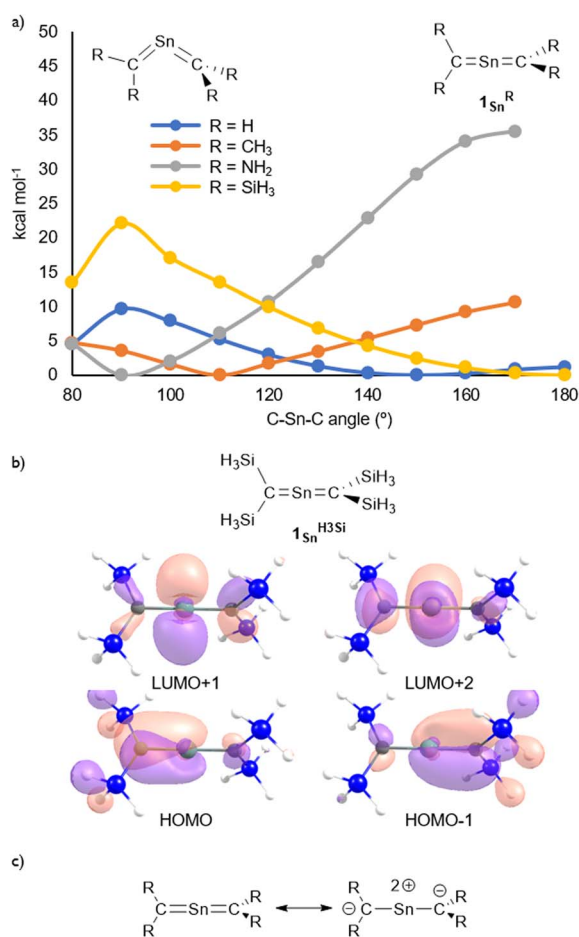


Fig. 3 (a) Optimized structures of 2-stannapropadienes calculated at the B3PW91-D3(bj)/Def2TZVP level for Sn and the 6-311G(2d,p) level for the remaining atoms. (b) Kohn–Sham orbitals of  $\mathbf{1}_{\text{Sn}}^{\text{H}_3\text{Si}}$ . (c) Canonical resonance structures of linear 2-stannapropadienes.



Fig. 4  $^{119}\text{Sn}$  NMR chemical shifts of  $\mathbf{1}_{\text{Sn}}$  and related compounds.



revealed a bent C–Sn–C moiety (Fig. S46<sup>†</sup>), and this distortion in the molecular geometry around the tin atom would feasibly account for the observed changes of the chemical shifts. To investigate the dynamics of **1**<sub>Sn</sub> in THF, variable-temperature (VT) <sup>1</sup>H NMR experiments were carried out. As shown in Fig. S37,<sup>†</sup> the methyl protons of **1**<sub>Sn</sub> were observed as a broadened peak (0.20 ppm) at room temperature. At –50 °C, these protons were observed as two independent sharp singlet signals (0.31/0.16) with a 1:3 ratio. However, at 40 °C, all methyl protons appeared as a sharp singlet, suggesting rapid dissociation of the coordinated THF molecule from the central tin atom of **1**<sub>Sn</sub>.

The ultraviolet-visible (UV-vis) spectrum of **1**<sub>Sn</sub> in benzene exhibits an absorption maximum at  $\lambda_{\text{max}} = 328 \text{ nm}$  ( $\epsilon$  8000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), indicating the presence of  $\pi$ -bonding without conjugation between the two C=Sn double bonds (Fig. 5). This value differs significantly from those of our previously reported  $\text{R}^{\text{Si}}_2\text{C}=\text{C}=\text{CR}^{\text{Si}}_2$  compounds (Ch = S: 449 nm, Se: 523 nm, and Te: 610 nm) with bent structures, suggesting strong interactions between each of the C–Ch multiple bonds due to their bent structures.<sup>41–43</sup> And, the  $\lambda_{\text{max}}$  value of **1**<sub>Sn</sub> is red-shifted relative to those of **1**<sub>Ge</sub> [265 nm ( $\epsilon$  11 000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 272 nm ( $\epsilon$  12 000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), and 283 nm ( $\epsilon$  11 000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )] and tetrakis(trimethylsilyl)allene<sup>32,33</sup> (273 nm,  $\epsilon$  36 000  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), indicating a narrowing of the HOMO–LUMO gap of **1**<sub>Sn</sub> relative to that of the germanium analogue **1**<sub>Ge</sub> due to the insufficient orbital overlap of  $5p\pi$ – $2p\pi$  in **1**<sub>Sn</sub> relative to that of  $4p\pi$ – $2p\pi$  in **1**<sub>Ge</sub> (Fig. S51<sup>†</sup>). Furthermore, the absorption maxima at 265–283 nm in 2-germapropadiene are expected to overlap with the  $\pi$ – $\pi^*$  transitions of phenyl groups. In contrast, the absorption peak of 2-stannapropadiene appears at 328 nm, which does not overlap with the  $\pi$ – $\pi^*$  transitions of phenyl

groups. Therefore, the epsilon value of 2-stannapropadiene is smaller than that of the germanium analogue. The UV-vis spectrum of **1**<sub>Sn</sub> in THF at room temperature exhibited a pronounced shoulder peak at 430 nm, which can be attributed to the coordination of a THF molecule to the central tin atom of **1**<sub>Sn</sub> (Fig. S56<sup>†</sup>). However, at 50 °C, the shoulder peak at 430 nm disappeared due to the dissociation of the coordinated THF molecule. Similarly, when donor molecules such as pyridine and 4-dimethylaminopyridine (DMAP) were added to a benzene solution of **1**<sub>Sn</sub>, similar shoulder peaks were observed in the respective spectra (Fig. S55<sup>†</sup>). Time-dependent density functional theory (TD-DFT) calculations were performed for compounds **1**<sub>Sn</sub> and **1**<sub>Sn</sub>·donor at the B3PW91/Def2tzvp level for Sn and the 6–311++G(2d,p) level for all other atoms. The results indicate a mixture of two  $\pi$ – $\pi^*$  transitions, *i.e.*, one at 333 nm ( $f = 0.0178$ ) and another at 306 nm ( $f = 0.1589$ ), which is in good agreement with the observed  $\lambda_{\text{max}}$  value for **1**<sub>Sn</sub>. For **1**<sub>Sn</sub>·THF, the calculations suggested a mixture of two  $\pi$ – $\pi^*$  transitions associated with the bent allene moiety, whereby one occurs at 443 nm ( $f = 0.0067$ ), consistent with the experimentally observed  $\lambda_{\text{max}}$  value. According to the theoretical calculations, the coordination of the donor molecule to **1**<sub>Sn</sub> to form **1**<sub>Sn</sub>·donor (donor: THF, pyridine, or DMAP) is expected to be exothermic for all cases except for THF (for details, see Table S52<sup>†</sup>). While the coordination of the donor molecule THF to the central tin atom of **1**<sub>Sn</sub> is endothermic, it is still likely that THF coordinates to the central tin atom in solution. The coordinated molecules of THF readily dissociate upon solvent distillation to regenerate **1**<sub>Sn</sub>. Recrystallization in the presence of THF or DMAP leads to the formation of **1**<sub>Sn</sub>, indicating that the coordination of these donors to **1**<sub>Sn</sub> in the crystalline solid state is not favorable. The higher positive charge on the central tin atom in **1**<sub>Sn</sub>, coupled with its lower steric demand compared to that of germanium derivative **1**<sub>Ge</sub>, suggests a preference for the coordination of donor molecules to the central tin atoms.

The reaction of **1**<sub>Sn</sub> with H<sub>2</sub>O immediately produces stannanediol **2** (Scheme 2). Subsequently, the reaction of **1**<sub>Sn</sub> with 2 eq. of MeLi followed by H<sub>2</sub>O affords the corresponding dimethylated compound **3**. As expected, **1**<sub>Sn</sub> readily reacts with hydrogen chloride under mild conditions to quantitatively form the corresponding dichlorostannane (**4Cl**). These reactivity patterns are similar to those of 2-germapropadiene (**1**<sub>Ge</sub>), indicating that the central tin atom can be expected to be the most electrophilic atom in the C=Sn=C allene moiety. In order to further explore the reactivity of **1**<sub>Sn</sub>, we undertook an investigation involving the reaction between **1**<sub>Sn</sub> and the SnX<sub>2</sub>·dioxane complex. This reaction was motivated by our previous syntheses of four-membered cyclic compounds derived from bis(methylene)- $\lambda^4$ -chalcogenanes using GeX<sub>2</sub>·dioxane (X = Cl, Br).<sup>43</sup> The reaction of **1**<sub>Sn</sub> with SnX<sub>2</sub>·dioxane proceeded smoothly even at room temperature to afford the corresponding four-membered stannylenes (**5X**) as light brown solids, which are thermally stable but sensitive to H<sub>2</sub>O, which selectively affords decomposed **4X**.

The experimental molecular structure and theoretical calculations suggest that **5Cl** contains a Sn<sup>2+</sup> and a Sn<sup>4+</sup> atom (Fig. 6). The shortest distance between divalent tin atoms in **5Cl** is 7.20 Å, which indicates that **5Cl** is monomeric in the solid

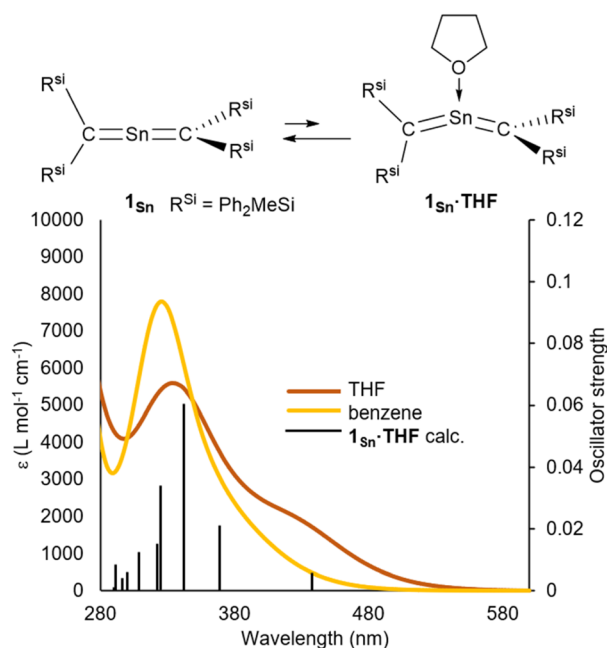
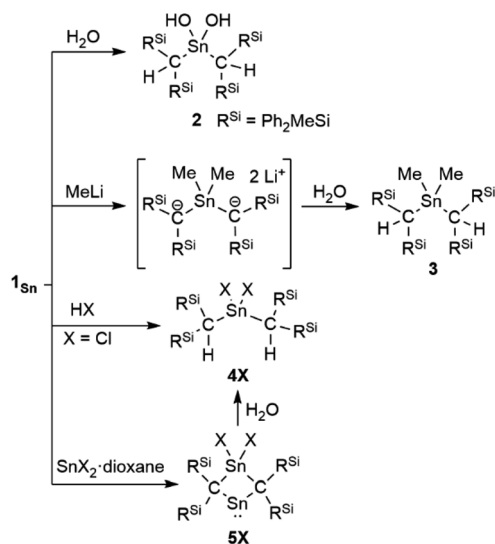


Fig. 5 (a) UV-vis spectra of **1**<sub>Sn</sub> in benzene and THF at room temperature, and simulated UV-vis absorption spectrum of **1**<sub>Sn</sub>·THF obtained from TD-DFT calculations, together with theoretical oscillator-strength values (black vertical lines).





Scheme 2 Reactivity patterns of  $1_{\text{Sn}}$ .

state. In contrast, there is a weak intermolecular interaction between  $\text{Sn1}\cdots\text{Sn2}$  in  $5\text{Cl}$  ( $3.1022(5)$  Å), which is shorter than the sum of the van der Waals radii ( $4.34$  Å).<sup>44</sup> The Sn1 center adopts a typical di-coordinated  $\text{Sn}^{2+}$  geometry, and the Sn2 center shows a typical tetra-coordinated  $\text{Sn}^{4+}$  geometry. The C1–Sn1–C2 bond angle of  $5\text{Cl}$  ( $87.93(5)^\circ$ ) is similar to that of a previously reported five-membered dialkylstannylene ( $86.7(2)^\circ$ ).<sup>38</sup> The Sn1–C bonds in  $5\text{Cl}$  ( $2.313(2)$  Å and  $2.300(2)$  Å) are significantly longer than those of a hitherto reported dialkylstannylene ( $2.218(7)$  Å and  $2.223(7)$  Å), indicating small amounts of strain due to the four-membered ring in  $5\text{Cl}$ . The bond length of Sn2–C ( $2.163(2)$  Å and  $2.173(2)$  Å) is identical to that of typical Sn–C bonds ( $2.16$  Å), indicating an increased p-character of the central  $\text{Sn}^{2+}$  atom in the Sn1–C single bonds

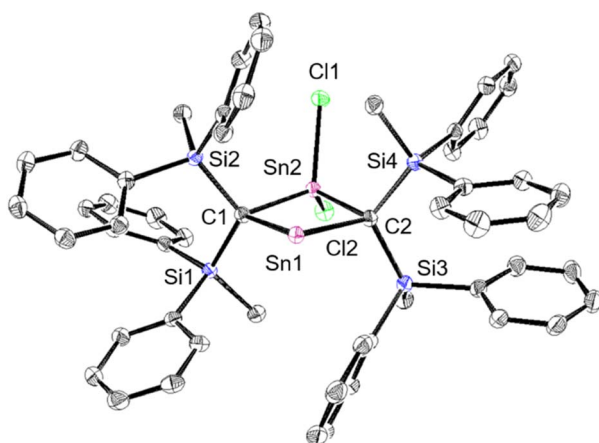
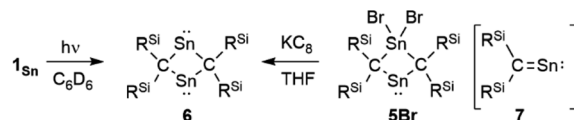


Fig. 6 Molecular structure of  $5\text{Cl}$  in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [ $^\circ$ ] for  $5\text{Cl}$ :  $\text{Sn1}\cdots\text{Sn2}$ :  $3.1022(5)$ , C1–Sn1:  $2.313(2)$ , C2–Sn1:  $2.301(2)$ , C1–Sn2:  $2.163(2)$ , C2–Sn2:  $2.173(2)$ , C1–Si1:  $1.905(2)$ , C1–Si2:  $1.888(2)$ , C2–Si3:  $1.902(2)$ , C2–Si4:  $1.909(2)$ , C1–Sn1–C2:  $87.93(8)$ , C1–Sn2–C2:  $95.22(8)$ , Sn1–C1–Sn2:  $87.67(8)$ , and Sn1–C2–Sn2:  $78.76(8)$ .

in  $5\text{Cl}$  relative to that in  $1_{\text{Sn}}$ . The four-membered ring of  $5$  deviates slightly from planarity (sum of the interior angles:  $358.58^\circ$ ). The molecular structure of  $5\text{Br}$  is isostructural to that of  $5\text{Cl}$  (Fig. S43<sup>†</sup>). In the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra of  $5\text{X}$  in  $\text{C}_6\text{D}_6$  at room temperature, a signal for only one set of silyl groups was observed, suggesting a flipping of the four-membered ring of  $5\text{X}$ . The  $^{119}\text{Sn}$  NMR spectrum of  $5\text{Cl}$  in  $\text{C}_6\text{D}_6$  exhibits signals at 1355 ppm for the  $\text{Sn}^{2+}$  nucleus and at 61 ppm for the  $\text{Sn}^{4+}$  nucleus. The signal for the  $\text{Sn}^{2+}$  nucleus of  $5\text{Cl}$  is shifted upfield relative to those of the kinetically stabilized stannylenes (**I**: 2323 ppm; **J**: 2299 ppm; Fig. 4),<sup>38,39</sup> indicating some kind of interaction with the  $\text{Sn}^{2+}$  nucleus. Unfortunately, the  $^{119}\text{Sn}$  NMR spectrum of  $5\text{Br}$  could not be recorded due to prohibitively low solubility. To investigate the interactions with  $\text{Sn}^{2+}$ , NBO calculations were conducted at the B3PW91-D3(bj)/Def2tzvp level for Sn and the 6-311+G(2d,p) level for all other atoms. The vacant p orbital of  $\text{Sn}^{2+}$  in  $5\text{X}$  receives electron donation not only from the C–Si  $\sigma$ -bonds but also from the C– $\text{Sn}^{4+}$  bonds, X– $\text{Sn}^{4+}$  bonds, and  $\pi$  orbitals of the phenyl groups. This would increase the electron density on  $\text{Sn}^{2+}$ , resulting in a significant upfield shift of the  $^{119}\text{Sn}$  signal of  $5\text{Cl}$ . In Fig. S28,<sup>†</sup> the UV-vis spectra of  $5\text{X}$  in benzene show absorption maxima at  $\lambda_{\text{max}} = 466$  nm for  $5\text{Cl}$  ( $\epsilon$   $1300$   $\text{dm}^3$   $\text{mol}^{-1}$   $\text{cm}^{-1}$ ) and  $\lambda_{\text{max}} = 472$  nm for  $5\text{Br}$  ( $\epsilon$   $1300$   $\text{dm}^3$   $\text{mol}^{-1}$   $\text{cm}^{-1}$ ), which are slightly blue-shifted compared to that of the five-membered cyclic stannylene **I** ( $484$  nm;  $\epsilon$   $400$   $\text{dm}^3$   $\text{mol}^{-1}$   $\text{cm}^{-1}$ ) in Fig. 4. Moreover, the absorption coefficients of  $5\text{X}$  are significantly higher than that of **I**, suggesting an expansion between the phenyl moieties and the vacant p orbital of  $\text{Sn}^{2+}$  obtained from the DFT calculations on  $5\text{X}$ .

To investigate the photostability of  $1_{\text{Sn}}$ , we carried out photoreactions in  $\text{C}_6\text{D}_6$  under irradiation from a 100 W high-pressure mercury lamp (Fig. S36<sup>†</sup>). After 3 days, one of the products obtained in the photochemical reaction was the four-membered cyclic bis(stannylene) (**6**). The formation of **6** implies the generation of a stannavinylidene (**7**) via cleavage of the C=Sn bond in  $1_{\text{Sn}}$  under irradiation. The reduction of  $5\text{Br}$  with  $\text{KC}_8$  also afforded bis(stannylene) **6** as a purple solid in 26% yield (Scheme 3). The shortest intermolecular distance between the tin atoms in **6** ( $7.1223(4)$  Å) indicates that **6** is monomeric in the solid state (Fig. 7). The intramolecular Sn1 $\cdots$ Sn1' distance ( $3.311(1)$  Å) is similar to those of related four-membered cyclic tin analogues ( $3.132(2)$ – $3.4413(2)$  Å) as shown in Fig. 8.<sup>45–54</sup> The Sn1–C bonds in **6** ( $2.281(2)$  Å/ $2.301(1)$  Å) are similar to those of  $5\text{Br}$  ( $2.289(5)$  Å/ $2.310(5)$  Å). The four-membered ring of **6** exhibits perfect planar geometry (sum of the interior angles:  $360^\circ$ ). The NMR spectra of **6** suggested that **6** adopts a highly symmetric structure in a solution: the  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  exhibits one set of signals due to four equivalent  $\text{Ph}_2\text{MeSi}$

Scheme 3 Photolysis of  $1_{\text{Sn}}$  and reduction of  $5\text{Br}$ .

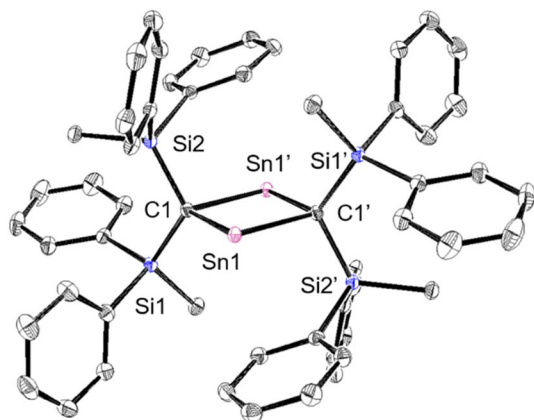


Fig. 7 Molecular structure of **6** in the crystalline state with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **6**: Sn1...Sn1': 3.311(1), C1–Sn1: 2.2812(13), C–Sn1': 2.3015(14), C1–Si1: 1.8620(13), C1–Si2: 1.8707(13), C1–Sn1–C1': 87.47(5), Sn1–C1–Sn1': 92.53(5), and Si1–C1–Si2: 117.60(7).

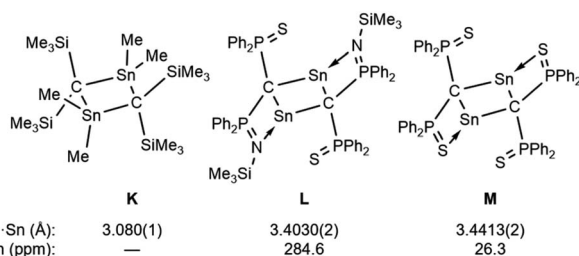


Fig. 8 Four-membered cyclic compound **K** and base-stabilized bis(stannylenes) **L** and **M**.

groups, while the <sup>119</sup>Sn NMR spectrum of **6** shows only one signal at 2003 ppm. The chemical shift of the divalent tin nuclei in **6** is slightly upfield shifted compared to those of cyclic alkyl stannylenes **I** (2323 ppm)<sup>38</sup> and **J** (2299 ppm)<sup>39</sup> in Fig. 4, but significantly downfield shifted compared to that of precursor **5Cl** (1355 ppm) and those of base-stabilized bis(stannylene)s (284.6–(–11) ppm).<sup>45–54</sup>

The frontier Kohn–Sham orbitals of **6** provide further information on the nature of the divalent tin moieties (Fig. 9). The HOMO represents lone pairs on two tin atoms, while the LUMO

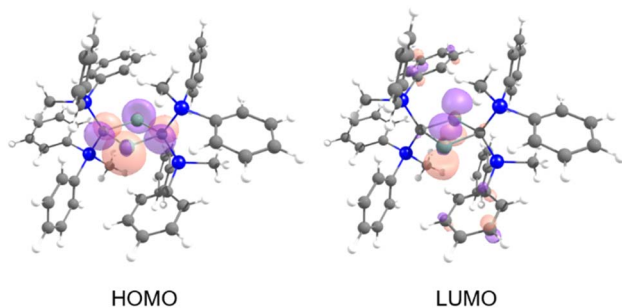


Fig. 9 Kohn–Sham orbitals of **6**.

consists of the vacant p orbitals on the tin atoms, indicating the typical molecular orbitals of a stannylene. The UV-vis spectrum of **6** in benzene exhibits an absorption maximum at  $\lambda_{\text{max}} = 558 \text{ nm}$  ( $\epsilon 700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). Further studies on the reactivity patterns of **6** are currently in progress.

## Conclusions

We have reported the successful synthesis of the first stable 2-stannapropadiene (**1<sub>sn</sub>**) with a linear allene-type structure. The bulky silyl groups dominate the structural features and govern the stability of the 2-stannapropadiene due to the high steric demand and negative hyperconjugation by the silyl groups. A multinuclear NMR analysis of the linear heteroallene confirmed the unsaturated Sn<sup>4+</sup> oxidation state of the central Sn atom. The reaction of **1<sub>sn</sub>** with SnX<sub>2</sub>·dioxane afforded a four-membered cyclic stannylene (**5X**), indicating a unique reactivity that stands in contrast to that of a previously reported 2-germapropadiene. The photolysis of **1<sub>sn</sub>** afforded bis(stannylene) **6**, which is most likely obtained from the dimerization of stannavinylidene **7**. Further investigations into the reactivity of **1<sub>sn</sub>** and bis(stannylene) **6** are currently in progress in our laboratories.

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

## Author contributions

The project was designed by K. S. The synthesis and characterization are conducted by T. A. All authors contributed to the writing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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