Organotin Compounds

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Intramolecularly Coordinated Organotin Tellurides: Stable or Unstable?**

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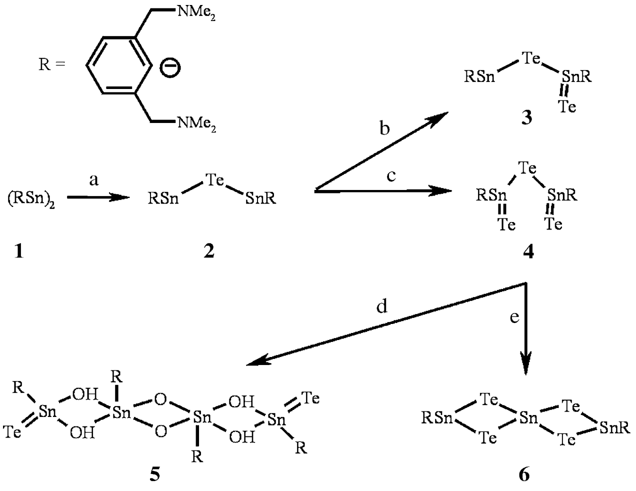
Increasing interest in the chemistry of organotin chalcogenides arises in part from their intriguing chemical and physical properties, providing possible technological applications such as semiconductivity, photoconductivity, or nonlinear optics.[1] Examples of tri- and diorganotin chalcogenides are known to form dimers or trimers with chalcogen atoms in the bridging positions. There are also rare examples of organotin chalcogenides containing terminal Sn=E (E = S, Se, Te) bonds.[2]

In recent years, monoorganotin chalcogenides have received increasing attention, and among these tin sesquichalcogenide cages of the general formula $[(RSn)_4E_6]$ containing both non-reactive organic groups R = alkyl, aryl, CF_3, C_6F_5 and functionalized organic substituents R = CH_2CH_2COOH, $CH(CH_2COOH)_2$ are the most popular.[3] These compounds usually have adamantane or double-decker structures (Supporting Information, Scheme S1). Dehnen and co-workers have shown that anionic tin chalcogenide polymers $[(RSn)_2E_3{}^{2-}]_\infty$ containing functionalized organic substituents may be prepared in this way as well.[4] Monomeric chalcogenides of Group 14 elements of the general formula $R_2M_2E_3$ (R = organic group, E = S, Se, Te) have a [1.1.1]propellane structure, as was either suggested theoretically[5] or shown experimentally (Supporting Information, Scheme S1).[6] Recently, compounds with the composition of $R_2Sn_2Te_5$ were isolated (R = bulky aryl substituent).[7] All of these structures, however, contain chalcogen atoms in the bridging positions with an M−E single bond, and most investigations are limited to sulfides or selenides (Supporting Information, Scheme S1). The corresponding tellurium compounds have not been investigated in detail, which is probably due to their thermal instability and sensitivity towards light.

Recently, we have reported the organotin(I) compound $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn]_2$ (**1**) and shown that the employment of intramolecularly coordinating pincer-type ligand is an alternative concept to the use of sterically demanding substituents for the stabilization of reactive distannyne derivatives.[8] The oxidation of compound **1** with elemental sulfur or selenium provided the unprecedented monoorganotin chalcogenides $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn]_2E$, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn(Se)]_2Se$, and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Sn_2(S)_7]$.[9]

In the course of systematic studies on the reactivity of distannyne **1**, we present here its reaction with elemental tellurium as a step-wise oxidation of the tin(I) atom (Scheme 1).

The addition of elemental tellurium to the dark red solution of compound **1** in *n*-hexane caused an immediate color change of the solution to pale yellow. From this solution, the bis(organotin(II)) telluride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn]_2Te$



Scheme 1. Synthesis of compounds **2**–**6**. a) Te, 4 h, hexane; b) Te, 24 h hexane; c) Te, 24 h, toluene; d) + moisture from toluene; e) *hν*, C_6D_6.

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Supporting information for this article (Scheme S1 for different structural motives, Scheme S2 for exchange of the terminal tellurium atom of **3**, and Scheme S3 for decomposition process of **4**; Figure S1 for the transition state (**3 TS**) and Figure S2 for thermal decomposition of **4** and **6**; computational details of **2**–**6**; additional data on the NBO analysis and crystallographic details) is available on the WWW under http://dx.doi.org/10.1002/anie.201107666.

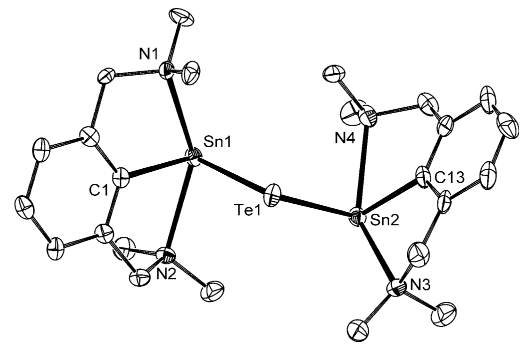

Figure 1. Molecular structure of **2**. Ellipsoids set at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–Te1 2.8218(7), Sn2–Te1 2.8334(8); Sn1-Te1-Sn2 95.32(2), Te1-Sn1-C1 95.1(2), Te1-Sn2-C13 95.0(2).

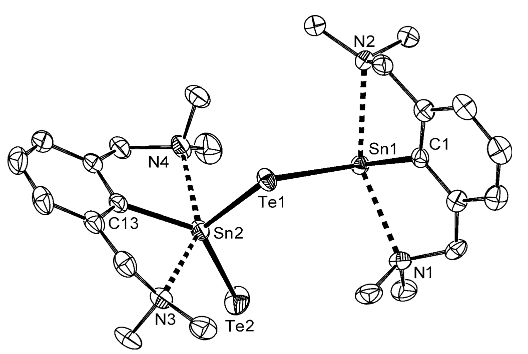

Figure 2. Molecular structure of **3**. Ellipsoids set at 50% probability, hydrogen atoms omitted for clarity. Selected bond distances [Å] and bond angles [°]: Sn1–Te1 2.8974(3), Sn2–Te2 2.6110(4), Sn2–Te1 2.7270(3); Sn1-Te1-Sn2 95.95(1), Te1-Sn1-C1 93.79(9), Te1-Sn2-C13 105.2(1).

(**2**) was obtained as yellow crystalline material in 78% yield. The molecular structure of **2** is shown in Figure 1.

Compound **2** is the first example of a structurally characterized telluride of low-valent Group 14 elements. The Sn1–Te1 (2.8218(7) Å) and Sn2–Te1 (2.8334(8) Å) bond lengths are similar and fall in the range expected for a Sn–Te single bond (sum of covalent radii $\Sigma_{\text{cov}}(\text{Sn,Te}) = 2.77$ Å).[10] The C1-Sn1-Te1 (95.1(2)°) and C13-Sn2-Te1 (95.0(2)°) angles are very similar to the C-Sn-E angles (range of 95.0(3)°) in the organotin(II) chalcogenides[9] and indicate that the s character of the lone pair is rather similar in these compounds.

The ^{119}Sn NMR spectrum of **2** in C_6D_6 revealed a resonance at $\delta = 67.8$ ppm and the ^{1}H NMR spectrum showed a singlet resonance at $\delta = 3.56$ ppm for the methylene groups CH_2N and a singlet resonance at $\delta = 2.42$ ppm for the methyl NCH_3 groups. Prolongation of the reaction time to 24 h gave a red solution from which the unprecedented compound [2,6-$(Me_2NCH_2)_2C_6H_3$(Te)Sn(μ-Te)Sn-2,6-$(Me_2NCH_2)_2C_6H_3$] (**3**) containing tin atoms in the oxidation states +II and +IV was isolated in 69% yield. The molecular structure of **3** is shown in Figure 2.

The Sn1–Te1 (2.8974(3) Å) and Sn2–Te1 (2.7270(3) Å) bond lengths are similar and fall in the range expected for a Sn–Te single bond ($\Sigma_{\text{cov}}(\text{Sn,Te}) = 2.77$ Å).[10] The Te2–Sn2 (2.6110(4) Å) bond distance is comparable to terminal Sn–Te bonds found in the diarylstannanetellurones (range of 2.5705(6)–2.618(1) Å).[11] The C1-Sn1-Te1 (93.79(9)°) angle resembles those found in **2**, and the C13-Sn2-Te1 (105.2(1)°) angle suggests the absence of the lone pair at the Sn2 atom.

In contrast to the unsymmetrical structure of compound **3** found in the solid state, the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra at ambient temperature of **3** each showed one set of signals in C_6D_6. The ^{1}H NMR spectrum showed a singlet at $\delta = 3.14$ ppm for the methylene protons CH_2N and a singlet resonance at $\delta = 2.17$ ppm for methyl NCH_3 protons. The ^{119}Sn spectrum revealed a resonance at $\delta = -131.0$ ppm and the ^{125}Te NMR spectrum showed a single resonance at $\delta = -743.6$ ppm. This observation suggests the fast exchange of the terminal tellurium atom (Supporting Information, Scheme S2).

DFT calculations on compound **3** were performed and the geometry obtained reproduced the experimental values very well (see the Supporting Information). In accordance with the structure, the different charges were found on the Sn atoms (+1.102(Sn2)/+0.770 (Sn1)) as well as on the Te atoms (−0.640(Te2), −0.554 (Te1)). The Wiberg Sn2–Te2 bond index amounts to 1.345, which clarifies the donation of the terminal tellurium atom to the tin atom. Furthermore, there is a Te–Te interaction with a Wiberg bond index of 0.172, suggesting that the exchange of the tellurium atoms, as observed in solution, can be performed through the symmetrical transition state with a Sn_2Te_2 four-membered ring. DFT calculations gave a symmetrical transition state for **3TS** (Supporting Information, Figure S1).

The Sn–Te bond distances amount to 2.766 and 3.307 Å. The transition state is estimated to be 20 kcal mol^{-1} higher in energy than the minimum structure for **3**. This value can be regarded rather as the upper limit. The presence of the N donor atoms stabilizes compound **3** significantly: the donation to the formal tin(II) atom amounts to 23 kcal mol^{-1}, whereas the formal tin(IV) atom is stabilized by 28 kcal mol^{-1} per donor atom.

The complete oxidation of bis(organotin(II)) telluride **2** by Te to give the organotin(IV) telluride [2,6-$(Me_2NCH_2)_2C_6H_3$Sn(Te)]$_2$Te (**4**) in 71% yield was achieved after a reaction time of 24 h in toluene solution. The identity of **4** in solution was confirmed by ^{119}Sn and ^{125}Te NMR spectroscopy. The ^{119}Sn NMR spectrum of **4** in C_6D_6 revealed a resonance at $\delta = -84.6$ ppm flanked by $^1J(^{119}\text{Sn},^{125}\text{Te})$ satellites of 7418 Hz. This large coupling constant is consistent with the presence of a tellurium atom that is terminally bound to a tin atom.[11] The ^{125}Te NMR spectrum showed two signals at $\delta = -764.1$ ppm and $\delta = -1349.5$ ppm ($^1J(^{125}\text{Te},^{119}\text{Sn}) = 7418$ Hz). While the former signal corresponds to a bridging tellurium atom, the latter was assigned to the terminal atom.

DFT calculations on compound **4** were performed (see the Supporting Information). The charge on the Sn atoms is +1.106 and on the terminal Te atoms −0.632. Both terminal tellurium atoms donate additionally to the tin atom and strengthen the Sn–Te bonds to a bond order of 1.380/1.379. The stabilization provided by one N donor atom has been calculated to be approximately 26 kcal mol^{-1}. For a model compound that lacks the intramolecularly coordinating dimethylaminomethyl substituents, calculations reveal a decrease of the Sn–Te bond lengths (see the Supporting Information).

In solution, compound **4** is very sensitive and reacts with traces of moisture to give compound **5** as the partial hydrolysis product. The molecular structure of compound **5** is shown in Figure 3. The {Sn_4O_6} unit of compound **5** is composed of the chemically different entities [2,6-$(Me_2NCH_2)_2C_6H_3$]Sn(OH)O and [2,6-$(Me_2NCH_2)_2C_6H_3$]Sn(OH)Te that are linked by oxido/hydroxido bridges. While both molecules of stannonic acid [2,6-$(Me_2NCH_2)_2C_6H_3$]Sn(OH)O form the inner part of the {Sn_4O_6} moiety, the remaining two molecules of telluro(hydroxo)stannonic acid [2,6-$(Me_2NCH_2)_2C_6H_3$]Sn(OH)Te are located in the outer part.

The ^{119}Sn NMR spectrum of compound **5** in C_6D_6 revealed two resonances at $\delta = -424.0$ and -444.4 ppm. The ^{1}H NMR spectrum showed two AX spin systems for the methylene protons CH_2N at $\delta_A = 2.88$ ppm and $\delta_x = 5.55$ ppm, and at $\delta_A = 3.02$ ppm and $\delta_x = 4.17$ that are consistent with the molecular structure.

Further studies also showed that compound **4** is redox-unstable. When a sealed NMR tube containing the deep red solution of **4** in C_6D_6 was exposed to visible light for two weeks or heated at 40 °C for two days, the solution turned deep violet. From this solution, single crystals were obtained and identified as the unprecedented compound [2,6-$(Me_2NCH_2)_2C_6H_3Sn(\mu\text{-}Te)_2]_2Sn$ (**6**) containing both organotin and inorganic tin sites. The molecular structure of **6** is given in Figure 4 a.

The central Sn2 atom is coordinated by four tellurium atoms. Interestingly, the Sn2–Te1 (2.8979(5) Å) and Sn2–Te2 (3.2162(4) Å) bond lengths are rather different. While the Sn2–Te1 bonds fall in the range expected for a Sn–Te single bond, the Sn2–Te2 bond is substantially longer than the sum of the covalent radii of Sn (1.40 Å) and Te (1.37 Å) and can be interpreted in terms of the Te→Sn intramolecular interaction in **6**. The Sn1/Sn1a atoms coordinate to five atoms Te1,Te2/Te1a,Te2a, C1/C1a, N1,N2/N1a,N2a to give a distorted trigonal bipyramidal configuration. The nitrogen atoms occupy the axial and the carbon and tellurium atoms occupy the equatorial positions. The Sn1/Sn1a–Te (2.6926(5)/2.6633(5) Å) bond lengths are shorter than those of Sn2–Te and are comparable with terminal Sn–Te bonds.[11] The presence of different Sn–Te bonds in **6** is in direct contrast to structurally similar spiro[bis(ditelluradistannetane)], where all Sn–Te bond lengths are nearly equal (2.7445(13)–2.7661(13) Å) and define two Sn_2Te_2 four-membered rings with Sn–Te covalent bonds.[10f]

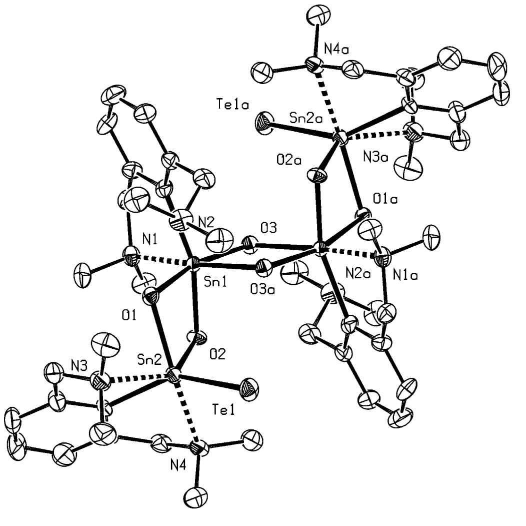

Figure 3. Molecular structure of **5**. Ellipsoids set at 50% probability, hydrogen atoms omitted for clarity.

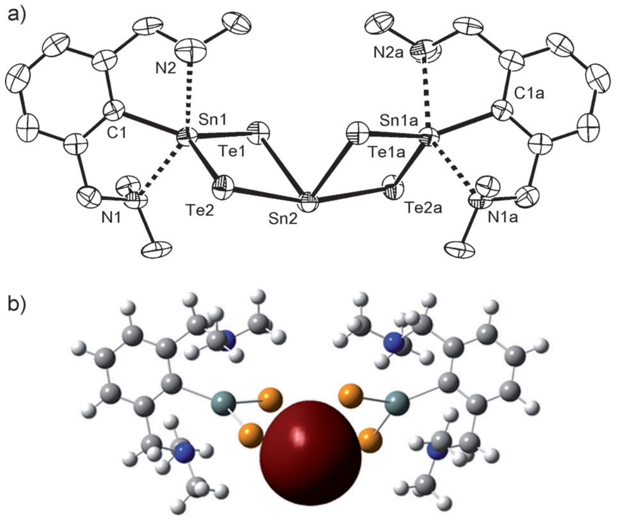

Figure 4. a) Molecular structure of **6**. Selected bond distances [Å] and bond angles [°]: Sn1–Te1 2.6926(5), Sn2–Te1 2.8979(5), Sn2–Te2 3.2162(4), Sn1–Te2 2.6633(5); Te1-Sn1-Te2 107.23(2), Sn1-Te2-Sn2 78.39(2). Ellipsoids set at 50% probability, hydrogen atoms omitted for clarity. b) The electron lone pair of the central Sn^{II} atom (red).

The identity of compound **6** was confirmed by NMR spectroscopy. The ^{119}Sn NMR spectrum in C_6D_6 revealed equally intense resonances at $\delta = -294.4$ ppm and $\delta = -295.0$ ppm that were assigned to terminal Sn atoms Sn1/Sn1a and at $\delta = -379.3$ ppm assigned to the Sn2 atom that suggests a distortion of the molecular structure of **6** in solution, which is most probably due to the weakening of the Te→Sn intramolecular interaction in C_6D_6 solution. As result, all the Te atoms are equivalent in solution, as shown by the ^{125}Te NMR spectrum: one signal at $\delta = -394.9$ ppm with $^1J(^{125}Te,^{119}Sn) = 4142$ Hz was observed. This dynamic behavior of **6** is in contrast to spiro[bis(ditelluradistannetane)], where the structural rigidity resulted in the presence of three signals in the ^{119}Sn NMR spectrum at $\delta = -149$, -384, and -387 ppm, together with four signals in the ^{125}Te NMR spectrum at $\delta = 762.9$, 765.0, 766.0, and 771.3 ppm.[10f]

The overall composition of **6** may be best described as an insertion product of in situ generated tin(II) telluride, SnTe, into one of the two Sn–Te bonds of [2,6-$(Me_2NCH_2)_2C_6H_3Sn(Te)]_2Te$ (**4**). The tin(II) telluride originates from reduction of a part of **4**, and consequently there must also be an oxidation product. To identify the oxidation product, the crude reaction mixture was monitored by ^{125}Te NMR spectroscopy. The spectrum revealed two signals at $\delta = 300$ ppm and $\delta = 350$ ppm that fall in the range that is typical for intramolecularly coordinated organotellurium(II) compounds.[12] The signals were tentatively assigned to [2,6-

$(Me_2NCH_2)_2C_6H_3]_2Te$ and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Te_2$, respectively. These observations show that compound **4** is indeed redox-unstable and decomposes to organotellurium(II) and organotellurium(I) compounds and SnTe, which in turn interacts with **4** to produce complex **6** (Supporting Information, Scheme S3). Interestingly, an alternative synthesis of compound **4** by reaction of the monoorganotin(IV) compound $2,6\text{-}(Me_2NCH_2)_2C_6H_3SnClI_2$ with Li_2Te produced a mixture of similar composition. The heating of **4** at 350 °C for 2 h under vacuum resulted in the complete decomposition providing SnTe and Te as the final products (for powder X-ray diffraction, see the Supporting Information, Figure S2).

DFT calculation of compound **6** was performed to give insight into the bonding situation. Starting from the crystal structure, the geometry of **6** was fully optimized and it reproduced the experimental values very well. Natural bond orbital analysis reveals a lone pair on the central Sn atom with 95 % s character (Figure 4 b). Wiberg Te–Sn1/Sn1a bond orders are in the range 1.000–1.1552, which exceeds the normal single-bond character and hints that the tin atoms Sn1/Sn1a strongly bind to tellurium atoms. In contrast, Wiberg Te1/Te1a–Sn2 bond orders amount to 0.715, which agrees with a single bond. Finally, the Wiberg Te2/Te2a–Sn2 bond orders amount to 0.387 only, which proves the absence of a single bond and supports that the bond can be interpreted as a Te→Sn donor–acceptor interaction. As in compound **4**, the N-donor stabilization in **6** is again 26 $kcal\,mol^{-1}$ per donor atom.

In conclusion, we have shown a stepwise oxidation of distannyne **1** by tellurium, which easily inserts into the Sn–Sn bond to give the bis(organotin(II))telluride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn]_2Te$ (**2**). The further oxidation process is slow and can be tuned easily. Slow oxidation of compound **2** produced the unprecedented compound $[2,6\text{-}(Me_2NCH_2)_2C_6H_3(Te)Sn(\mu\text{-}Te)Sn\text{-}2,6\text{-}(Me_2NCH_2)_2C_6H_3]$ (**3**), containing tin atoms in the oxidation states +II and +IV, and led to the final oxidation product $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sn(Te)]_2Te$ (**4**). Compound **4** is the first example of an intramolecularly coordinated tritellurostannonic acid anhydride with two terminal Sn–Te bonds. In solution, compound **4** is thermodynamically unstable and decomposes to give compound **6**, which can formally be regarded as a complex of **4** with tin(II) telluride, SnTe. DFT calculations of compounds **3**, **4**, and **6** revealed highly positive charges at the Sn atoms and negative charges at the terminal Te atoms. Consequently, the terminal Sn–Te bond can be interpreted as a formal "single" bond, where the bond order is increased owing to the strong electrostatic interaction between Sn^+ and Te^-. The presence of the N,C,N-chelating ligand $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$ is thus crucial for the stabilization of the positive charge at the tin atom by strong N→Sn donation.

Experimental Section

Unless otherwise stated, all manipulations were carried out under anaerobic and anhydrous conditions. The ^1H, ^{13}C, ^{119}Sn, and ^{125}Te NMR spectra were recorded on a Bruker Avance 500 spectrometer and referenced to known standards ($SiMe_4$, $SnMe_4$, $TeMe_2$). Compound **1**[8a] and $2,6\text{-}(Me_2NCH_2)_2C_6H_3SnClI_2$[13] were prepared according to the literature procedures.

2: Te powder (0.20 g, 1.6 mmol) was added at room temperature with stirring to a solution of **1** (0.20 g, 0.3 mmol) in hexane (20 mL). The reaction mixture was stirred for an additional 4 h and the color changed from deep red to colorless. The solution was filtered and the filtrate was concentrated to a volume of approximately 5 mL. Storage overnight at 5 °C gave yellow crystals of **2** (0.188 g, 78 % yield). M.p. 146–148 °C. ^1H NMR (500.18 MHz, [D$_6$]benzene, 25 °C): $\delta = 2.42$ (br s, 12 H, NCH_3), 3.56 (s, 4 H, CH_2), 7.05 (d, 2 H, ArH), 7.17 ppm (t, 1 H, ArH). ^{13}C NMR (125.77 MHz, [D$_6$]benzene, 25 °C): $\delta = 46.9$ (NCH_3), 67.1 (CH_2N), 124.7 (C3,5), 127.4, (C4), 146.4 (C2,6), 168.7 ppm (C1). ^{119}Sn NMR (186.49 MHz, [D$_6$]benzene, 25 °C): $\delta = 67.8$ ppm. ^{125}Te NMR (157.84 MHz, [D$_6$]benzene) not found.

3: Te powder (0.20 g, 1.6 mmol) was added at room temperature with stirring to a solution of **1** (0.20 g, 0.3 mmol) in *n*-hexane (20 mL). The reaction mixture was stirred for an additional 24 h and the color changed from deep red to orange. The solution was filtered and the filtrate was concentrated to a volume of approximately 8 mL. Storage overnight at 5 °C gave orange crystals of **3** (0.195 g, 69 % yield). M.p. 160 °C decomp. ^1H NMR (500.18 MHz, [D$_8$]toluene, 25 °C): $\delta = 2.17$ (s, 12 H, NCH_3), 3.14 (s, 4 H, CH_2), 6.61 (d, 2 H, ArH), 6.82 (t, 1 H, ArH) ppm. ^{13}C NMR (125.77 MHz, [D$_8$]toluene, 25 °C): $\delta = 46.6$ (NCH_3), 65.5 (CH_2N), 124.8 (C3,5), 127.9, (C4), 137.4 (C2,6), 145.1 ppm (C1). ^{119}Sn NMR (186.49 MHz, [D$_8$]toluene, 25 °C): $\delta = -131$ ppm. ^{125}Te NMR (157.84 MHz, [D$_8$]toluene, 25 °C) $\delta = -743.6$ ppm.

4: Te powder (0.25 g, 1.9 mmol) was added at room temperature with stirring to a solution of **1** (0.25 g, 0.4 mmol) in toluene (3 × freeze–pump–thaw, 20 mL). The reaction mixture was stirred for 24 h. The resulting suspension was filtered and the dark red filtrate was concentrated to approximately 5 mL. Storage overnight at −20 °C gave dark red crystals of **4** (0.29 g, 71 % yield). M.p. 205 °C decomp. ^1H NMR (500.18 MHz, [D$_6$]benzene, 25 °C): $\delta = 2.45$ (s, 12 H, NCH_3), 3.38 (s, 4 H, CH_2), 6.95 (d, 2 H, ArH), 7.33 ppm (t, 1 H, ArH). ^{13}C NMR (125.77 MHz, [D$_6$]benzene, 25 °C): $\delta = 46.4$ (NCH_3), 64.4 (CH_2N), 124.7 (C3,5), 128.2 (C4), 138.9 (C1), 144.3 ppm (C2,6). ^{119}Sn NMR (186.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -84.6$ ppm ($^1J(^{119}Sn,^{125}Te) = 7418$ Hz). ^{125}Te NMR (157.84 MHz, [D$_6$]benzene, 25 °C): $\delta = -764.1$ and -1349.5 ppm ($^1J(^{125}Te,^{119}Sn) = 7418$ Hz).

5: Compound **4** (0.1 g, 0.11 mmol) was dissolved in 5 mL of wet toluene. After the filtration of black precipitate, the resulting orange solution was stored three days at room temperature to give colorless crystals of **5** (10.5 mg, 12 % yield). M.p. 75 °C decomp. ^1H NMR (500.18 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.15$ (6 H, d, NCH_3), 2.22 (6 H, s, NCH_3), 2.38 (6 H, s, NCH_3), 2.63 (6 H, s, NCH_3), 2.88 (2 H, AX system, CH_2N), 5.55 (2 H, AX system, CH_2N), 3.02 (2 H, AX system, CH_2N), 4.17 (2 H, AX system, CH_2N), 6.78–7.26 (6 H, m, ArH), 11.82 (2 H, s, SnOH), 11.84 ppm (2 H, s, SnOH). ^{119}Sn NMR (186.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -424$, -444 ppm. ^{125}Te NMR (C_6D_6, 157.84 MHz) not found.

6: A Young valve NMR tube containing the C_6D_6 solution of **4** (50 mg, 0.05 mmol) was exposed to visible light for two weeks. During this period the solution became dark violet and the crystals suitable for X-ray diffraction analysis were grown. This material was identified as compound **6**. Alternatively, compound **6** was prepared by following procedure. $2,6\text{-}(Me_2NCH_2)_2C_6H_3SnClI_2$ (0.34 g, 0.57 mmol) was added with stirring at room temperature to a solution of Li_2Te (0.11 g Te, 0.93 mmol, 1.73 mL 1 M lithium triethylborohydride) in THF (3 × freeze–pump–thaw, 20 mL) at room temperature. The reaction mixture was stirred for 24 h. The resulting suspension was filtered and the dark violet filtrate was concentrated to approximately 5 mL. Storage overnight at −20 °C gave dark violet crystals of **6** (0.15 g, 43 % yield). M.p. 223.3–226.0 °C. ^1H NMR (500.18 MHz, [D$_8$]THF, 25 °C): $\delta = 2.48$ (s, 12 H, NCH_3), 4.38 (bs, 4 H, CH_2), 6.96 (d, 2 H, ArH), 7.09 ppm (t, 1 H, ArH). ^{13}C NMR (125.77 MHz, [D$_8$]THF, 25 °C): $\delta = 45.8$ (NCH_3), 62.4 (CH_2N), 124.8 (C3,5), 127.4 (C4), 143.1 ppm (C2,6); signal for C1 not found; ^{119}Sn NMR (186.49 MHz, [D$_8$]THF, 25 °C): $\delta = -294.4$, -295.0, and -379.3 ppm. ^{125}Te NMR (157.84 MHz, [D$_8$]THF, 25 °C): $\delta = -394.9$ ppm ($^1J(^{125}\text{Te},^{119}\text{Sn})$: 4142 Hz).

Crystallography: Analysis of a yellow crystal of **2**·(0.56×0.21×0.18 mm^3), an orange crystal of **3**·(0.30×0.14×0.13 mm^3), a colorless crystal of **5** (0.14×0.10×0.10 mm^3), and a red crystal of **6** (0.22×0.16×0.08 mm^3) was performed on a Nonius KappaCCD diffractometer at 150(1) K. Crystal data for **2**: $C_{24}H_{38}N_4TeSn_2$, $M = 747.56\ \text{g mol}^{-1}$, monoclinic, space group $P2_1/c$, $a = 6.7710(5)$, $b = 45.553(3)$, $c = 9.5530(5)$ Å; $\beta = 108.255(5)°$; $V = 2798.2(3)$ Å^3, $Z = 4$, $\mu = 2.824\ \text{mm}^{-1}$, 23782 independent reflections ($\theta_{\min} = 2.14$, $\theta_{\max} = 27.50$), 5846 with $I \geq 2\sigma(I)$, $R_1 = 0.042$, $wR2$ (all data) $= 0.0692$. Crystal data for **3**: $C_{24}H_{38}N_4Te_2Sn_2 \cdot 0.13\,C_4H_8O$, $M = 884.18\ \text{g mol}^{-1}$, orthorombic, space group $Pbca$, $a = 12.1250(8)$, $b = 18.2339(15)$, $c = 27.8581(15)$ Å; $V = 6159.0(7)$ Å^3, $Z = 8$, $\mu = 3.498\ \text{mm}^{-1}$, 67649 independent reflections ($\theta_{\min} = 1.75$, $\theta_{\max} = 27.49$), 7042 with $I \geq 2\sigma(I)$, $R_I = 0.0394$, $wR2$ (all data) $= 0.0551$. Crystal data for **5**: $C_{48}H_{80}N_8O_6Te_2Sn_4 \cdot 2\,C_7H_8$, $M = 1779.43\ \text{g mol}^{-1}$, monoclinic, space group $P2_1/c$, $a = 14.6871(12)$, $b = 13.3910(12)$, $c = 21.0689(14)$ Å; $\beta = 120.95(3)$; $V = 3554.1(9)$ Å^3, $Z = 2$, $\mu = 2.245\ \text{mm}^{-1}$, 34982 independent reflections ($\theta_{\min} = 2.14$, $\theta_{\max} = 27.50$), 8097 with $I \geq 2\sigma(I)$, $R_1 = 0.0408$, $wR2$ (all data) $= 0.0785$. Crystal data for **6**: $C_{24}H_{38}N_4Te_4Sn_3$, $M = 1249.05\ \text{g mol}^{-1}$, monoclinic, space group $P2/c$, $a = 24.8331(6)$, $b = 9.2740(2)$, $c = 14.9088(12)$ Å; $\beta = 93.093(7)$; $V = 3428.5(3)$ Å^3, $Z = 4$, $\mu = 5.524\ \text{mm}^{-1}$, 14391 independent reflections ($\theta_{\min} = 2.14$, $\theta_{\max} = 27.50$), 3922 with $I \geq 2\sigma(I)$, $R_1 = 0.0330$, $wR2$ (all data) $= 0.0785$. CCDC 847113 (**6**), 847114 (**2**), 847115 (**3**), and 847116 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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