# SnCl<sub>4</sub>-Induced Unsymmetrical Cleavage of Bis(*N,N*-diethylcarbamoyltelluro)arylmethanes: Generation of Tellurobenzaldehydes

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ABSTRACT: Tellurobenzaldehydes bearing an electron-withdrawing substituent were generated by way of SnCl<sub>4</sub>-induced unsymmetrical cleavage of bis(N,N-dialkylcarbamoyltelluro)arylmethanes, and were trapped using 2,3-dimethyl-1,3-butadiene. © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 24:482–489, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21115

# INTRODUCTION

Recently, a wide variety of studies on thio- and selenoaldehydes have been achieved in the light of their structural interests and the potentiality as new reactive intermediates for the organic reactions [1–4]. However, only limited research works on generation, trapping, or metal complexation of telluroaldehydes  $\mathbf{B}$  were reported [5–8]

due to the high instability of the target species toward air, light, and heating, as well as the lack of preparative methods of suitable and easily accessible precursors. In the course of our studies on the novel generation of higher-row chalcogenocarbonyl compounds, we previously reported a convenient preparation of stable ditelluroacetal derivatives **A** through the reaction of in situ generated tellurocarbamate ions with gemdihaloalkanes [9-11]. Actually, such ditelluroacetals A are recognized as potent precursors for telluroaldehydes **B** in the light of their symmetrical structures with an easily removable electronwithdrawing carbamoyl group on each tellurium atom, and compouds A are expected to undergo SnCl<sub>4</sub>-induced unsymmetrical C-Te bond cleavage to generate telluroaldehydes B through pushpull type removal of N,N-diethyltellurocarbamate in an analogous manner of our previous report on the generation of selenoaldehydes from bis(N,Ndimethylcarbamoylseleno)methanes [12, 13]. According to our expectation as mentioned above, we started our exploration on the reaction of **A** with SnCl<sub>4</sub> in the presence or absence of trapping agents. In this paper, we describe a new method for generation of tellurobenzaldehydes **B** from precursors **A** bearing an electron-withdrawing substituent on the aryl group.

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#### **RESULTS AND DISCUSSION**

Preparation of Bis(N,Ndialkylcarbamoyltelluro)arylmethanes (**1**, **4**, **5**,  $R^1 = CH_3$  or  $C_2H_5$ )

Bis(N,N-dimethylcarbamoyl) ditelluride (1) was at first prepared in moderate yield by treating N,N-dimethylformamide (DMF) with sodium and elemental tellurium under heating followed by aerobic oxidation of the reaction mixture [9–13]. Preparation of bis(N,N-diethylcarbamoyl) ditelluride (2,  $R^1 = C_2H_5$ ) was also carried out by treating N,Ndiethylformamide (DEF) with lithium metal and elemental tellurium through a similar procedure as shown in Scheme 1. However, ditelluride 2 was unstable on the contact with silica gel, and was only used for the further reactions without purification. Subsequently, when ditelluride 1 was subjected to sodium borohydride (NaBH<sub>4</sub>) reduction in ethanol followed by treatment with substituted benzal bromides (3), the corresponding ditelluroacetals 4 bearing a *N*,*N*-dimethylcarbamoyl group on each tellurium atom were obtained in moderate yields according to our previous reports [14-18]. In contrast, a similar treatment of crude ditelluride 2 with NaBH<sub>4</sub> and **3** only gave a complex mixture in which a trace amount of the corresponding ditelluroacetals **5** was contained.

In contrast, the yields of ditelluroacetals **4** and **5** were successfully improved by using a convenient one-pot procedure starting from DMF or DEF [(i) Na or Li metal; (ii) elemental tellurium,  $110^{\circ}$ C, 2 h; and (iii) substituted benzal halides **3** (i.e., benzal bromide (**3a**), *m*-chlorobenzal bromide (**3b**),

*p*-chlorobenzal bromide (**3c**), 2,4,6-trimethylbenzal chloride (**3d**), *p*-fluorobenzal chloride (**3e**), and *p*-trifluoromethylbenzal chloride (**3f**), respectively). All the results of the one-pot synthesis of **4** and **5** are shown in Table 1.

### *Reaction of Bis(N,N-dialkylcarbamoyltelluro)arylmethanes* (**4**, **5**) *with* SnCl<sub>4</sub> *in the Presence of Dienes*

Treating a Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), a chloroform (CHCl<sub>3</sub>), or a benzene solution of bis(N,Ndimethylcartbamoyltellluro)phenylmethane (4a,  $R^2 = C_6H_5$  with SnCl<sub>4</sub> (2.0 mol) at room temperature (R.T.) under an Argon atmosphere in the presence of 2,3-dimethyl-1,3-butadiene, cyclopentadiene, or Danishefsky's diene only afforded a complex mixture along with extrusion of elemental tellurium in the reaction mixture and no products related to the corresponding [4+2] cycloadducts of tellurobenzaldehydes **B** were found at all in the crude mixture. Similar unsuccessful results were obtained through the reaction started from bis(N,Ndiethylcartbamoyltellluro)phenylmethane (5a.  $R^2 = C_6H_5$ ) bearing a bulky *N*,*N*-diethylcarbamoyl group on each tellurium atom or from bis(N,Ndiethylcarbamolytelluro)mesitylmethane (5d,  $R^2 =$ 2,4,6-trimethylphenyl (Mes)) bearing a bulky aryl group for the steric protection of telluroaldehydes.

In contrast, when substrate **5e** ( $R^2 = p$ -FC<sub>6</sub>H<sub>4</sub>) or **5f** ( $R^2 = p$ -CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) bearing an electronwithdrawing group on the aryl group was applied to the same reactions in a benzene solution at R.T.,



SCHEME 1 Preparation of (1) bis(*N*,*N*-dimethylcarbamoyl) ditelluride and (2) bis(*N*,*N*-diethylcarbamoyl) ditelluride.

	H		1) Na or Li (5 mol amt.) 2) Te (5 mol amt.), 100-110°C, Time 1 3) R <sup>2</sup> CHX <sub>2</sub> (3), R.T., Time 2			$\Rightarrow R_{2}^{1}N \xrightarrow{P} R_{2}^{1}N \xrightarrow{P} R_{2}^{1}N \xrightarrow{P} R_{2}^{1}N \xrightarrow{P} R_{2}^{1}$		
$\mathbb{R}^{1}$	Na or Li	Temp (° C)	Time 1 (h)	R <sup>2</sup> CHX <sub>2</sub> /	'3 X	Time 2 (h)	Product 4. 5	Yield (%)
$\begin{array}{c} \\ \hline \\ CH_3 \\ C_2H_5 \end{array}$	Na Li Li Li Li Li	100 110 110 110 110 110 110 110	1 2 2 2 2 2 2 2	$C_{6}H_{5}$ $C_{6}H_{5}$ <i>m</i> -CIC <sub>6</sub> H <sub>4</sub> H Mes <i>p</i> -FC <sub>6</sub> H <sub>4</sub> <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Br Br Br Cl Cl Cl	3 3 9 24 5 6 3	4a 5a 5b 5c 5d 5e 5f	Complex mixture 41 31 13 48 50 8

TABLE 1One-Pot Synthesis of Bis(N,N-dialkylcarbamoyltelluro)methanes (4, 5)

tellurapyranes **6e** and **6f** were obtained in 8% and 7% yields, respectively, in both cases as comparatively air-stable oily matters. All the physical and spectral data of **6e** and **6f**, involving MS, infrared (IR), <sup>1</sup>H nuclear magnetic resonance (NMR), and <sup>13</sup>C NMR spectra, as well as the elemental analysis data, were fully consistent with the structure of the [4+2] cycloadducts of the in situ generated tellurobenzaldehydes **B**. However, all attempts for the improvement of the yields of **6e** and **6f** by modifying the reaction procedure and conditions were not successful at all. All results on the attempts for generation and trapping of tellurobenzaldehydes **B** using 2,3-dimethyl-1,3-butadiene are shown in Table 2.

#### Reaction of Bis(N,N-dialkylcarbamoyltelluro)arylmethanes (**4**, **5**) with $SnCl_4$ in the Absence of Trapping Agents

We already reported that the reaction of bis(N,N-diethylcarbamoylseleno)methanes with SnCl<sub>4</sub> in the absence of trapping agents afforded  $\beta$ -1,3,5-triselenananes, the trimeric products of selenoaldehydes, in moderate-to-high yields [19, 20]. However, in spite of the exhaustive efforts, reaction of **5a–5d** with SnCl<sub>4</sub> only afforded a complex mixture containing the corresponding benzaldehydes and a trace amount of stilbene derivatives **7** along with the extrusion of elemental tellurium, and 1,3,5-tritelluranes were not obtained at all in contrast with the cases of

TABLE 2Generation and Trapping of Telluroaldehydes Bthrough the Reaction of Bis(N,N-diethylcarbamoyltelluro) methanes5 with  $SnCl_4$  in the Presence of 2,3-Dimethyl-1,3-butadiene

	(C <sub>2</sub> H <sub>5</sub> )	O R <sup>2</sup> O ₂N Te Te N(C₂I	$H_5)_2$ Lewis A	(10 mol amt.) Acid (2.0 mol amt.)		
		5		Ar, R.T.	6	
Substrate						Yield (%)
R	5	Lewis Acid (mol)	Solvent	Temp (° C)	Time (h)	6
$C_6H_5$ $C_6H_5$ $C_6H_5$ <i>m</i> -CIC <sub>6</sub> H <sub>4</sub> H Mes <i>p</i> -FC <sub>6</sub> H <sub>4</sub> <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	5a 5a 5b 5c 5d 5e 5f	BF <sub>3</sub> •OEt <sub>2</sub> (2.0) SnCl <sub>4</sub> (2.0)	CH <sub>2</sub> Cl <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub> Benzene Benzene Benzene Benzene Benzene Benzene	0 0 R.T. R.T. R.T. R.T. R.T. R.T.	1 1 3 2 1 4 2	Complex mixture Complex mixture Complex mixture Complex mixture Complex mixture <sup>a</sup> 8 7

<sup>a</sup>Uncharacterized oligomeric products containing Sn and Te atoms were mainly obtained.



SCHEME 2 Plausible pathway for the generation of tellurobenzaldehydes **B** through the reaction of bis(N,N-diethylcarbamoyltelluro)arylmethanes 5 with SnCl<sub>4</sub>.

the reaction starting from the selenium analogues. However, when **5a** ( $R^2 = C_6H_5$ ) was treated with SnCl<sub>4</sub> (1.5 mol) in CDCl<sub>3</sub> in an NMR tube and the reaction was monitored by using <sup>1</sup>H NMR at 298 K, a characteristic singlet signal at  $\delta = 5.23$ [19, 20], assignable to the methine proton of symmetrical  $\beta$ -1,3,5-tritellurane **8a**, was observed in the NMR spectrum of the reaction mixture. Furthermore, along with standing of the reaction mixture, a new singlet signal at  $\delta = 9.70$ , assigned to the formyl proton of benzaldehyde, was gradually increasing along with the extrusion of elemental tellurium. These results suggested the in situ formation of  $\beta$ -1,3,5-tritellurane **D** through trimerization of intermediary tellurobenzaldehude **B** as well as the subsequent oxidative decomposition of **D** to form aldehydes.

In addition, treatment of **5e** ( $R^2 = p$ -FC<sub>6</sub>H<sub>4</sub>) with SnCl<sub>4</sub> (1.5 mol) in benzene at R.T. afforded an unexpected triarylmethane **9e** ( $R^2 = p$ -FC<sub>6</sub>H<sub>4</sub>) [21–27] in 12% yield besides a complex mixture. Furthermore, the similar reaction of **5e** with SnCl<sub>4</sub> carried out in CH<sub>2</sub>Cl<sub>2</sub> in the presence of an excess amount of allyltrimethylsilane at –78°C afforded unstable *Te*allyl *N*,*N*-diethyltellurocarbamate (**10**) in 12% yield besides several uncharacterized products. The former results suggested the in situ generation of intermediary telluronium ions **E**, which would undergo Friedel–Crafts type reaction with benzene to form **9e** [28–35] via intermediary **F**. The formation of **10** was also explained by the nucleophilic attack of allyltrimethylsilane to the tellurium atom of substrates **5**. Therefore, a plausible formation mechanism of telluroaldehydes **B** involving an in situ generation of telluronium ions **E** through an SnCl<sub>4</sub>induced unsymmetrical cleavage of substrates **5**, as shown in Scheme 2, is proposed. However, all attempts for trapping of intermediates **E** were not successful.

#### CONCLUSION

In conclusion, we attempted the  $SnCl_4$ -induced unsymmetrical cleavage of bis(N,N-diethylcarbamoyltelluro)arylmethanes **5**, and trapping of tellurobenzaldehydes were only achieved in the case starting from **5** bearing an electron-withdrawing group on the aryl moiety. Further inspection for the reaction pathway to form telluroaldehydes **A**, as well as the further improvement of the reaction conditions, are under way in our laboratory.

#### EXPERIMENTAL

#### Instruments

The melting points were determined with a Büchi 535 micromelting-point apparatus. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-400P (400 MHz) spectrometer (Bruker Biospin, Karlsruhe, Germany), and the chemical shifts of the <sup>1</sup>H NMR spectra are given in  $\delta$  relative to internal tetramethylsilane. <sup>13</sup>C NMR spectra were recorded on a Bruker AC-400P (101 MHz; Bruker Biospin). Mass spectra were recorded on a Hitachi M-2000 mass spectrometer (Hitachi High-Technologies, Tokyo, Japan) with electron-impact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer (JASCO, Tokyo, Japan). Elemental analyses were performed using a Yanagimoto CHN corder MT-5 (Yanaco, Kyoto, Japan).

### Materials

Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385, Merck, Darmstadt, Germany) without a pretreatment. CH<sub>2</sub>Cl<sub>2</sub> (Kanto Chemical, Tokyo, Japan) and CHCl<sub>3</sub> (Kanto Chemical) were dried over P<sub>4</sub>O<sub>10</sub> (Kanto Chemical), and were freshly distilled before use. Hexane (Kanto Chemical), benzene (Kanto Chemical), DMF (Kanto Chemical), and DEF (Tokyo Chemical Industry, Tokyo, Japan) were dried over calcium hydride (CaH<sub>2</sub>, Kanto Chemical) and freshly distilled before use. Ethanol (Wako Pure Chemical Industries, Tokyo, Japan) was dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>, Kanto Chemical), and were freshly distilled before use. All of the substrates and reagents, including elemental tellurium (Wako Pure Chemical Industries), benzal bromide, (Wako Pure Chemical Industries), m-chlorobenzal bromide (Wako Pure Chemical Industries), pfluorobenzal chloride (Wako Pure Chemical Industries), p-trifluoromethylbenzal chloride (Wako Pure Chemical Industries), dibromomethane (Wako Pure Chemical Industries), 2,4,6-trimethylbenzaldehyde (Wako Pure Chemical Industries), 2,3-dimethyl-1,3butadiene (Wako Pure Chemical Industries), allyltrimethylsilane (Wako Pure Chemical Industries), boron trifluoride diethyl ether complex (BF<sub>3</sub>·OEt<sub>2</sub>, Wako Pure Chemical Industries), stannic chloride (SnCl<sub>4</sub>, Wako Pure Chemical Industries), lithium metal (Wako Pure Chemical Industries), sodium metal (Wako Pure Chemical Industries), sodium borohydride (NaBH<sub>4</sub>, Wako Pure Chemical Industries), anhydrous sodium sulfate powder (Na<sub>2</sub>SO<sub>4</sub>, Kanto Chemical), and molecular sieves 4A (MS-4A,

Nacalai Tesque, Kyoto, Japan) were commercially available reagent grade, and were used without any pretreatment.

## Preparation of Bis(N,N-dialkylcarbamoyl) Ditellurides (1, 2)

Bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**1**) was prepared according to our previous report [8]. DEF (20 mL) was treated with lithium (347 mg, 50.0 mmol) and elemental tellurium (1.29 g, 10.1 mmol) at 110°C for 20 h, and then oxygen gas was bubbled into the reaction mixture at 0°C for 1.5 h. The reaction was quenched with a small amount of water. The reaction mixture was extracted with chloroform, and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> powder. After removal of the solvent in vacuo, crude bis(*N*,*N*-diethylcarbamoyl) ditelluride (**2**, 610 mg, 27% yield) was obtained as a black oil. However, chromatographic purification of **2** was unsuccessful due to the facile decomposion through the contact with silica gel.

**1** (R<sup>1</sup> = CH<sub>3</sub>) [8]: Yellow needles, melting point (mp) 121.0–122.0°C; MS (*m*/*z*) 404 (M<sup>+</sup>; 0.4%, <sup>130</sup>Te); IR (KBr) 2908, 1657, 1399, 1350, 1248, 1074, 870 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 3.08 (6H, s), 3.11 (6H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 36.2 (q), 40.7 (q), 145.6 (s). Calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: C, 18.04; H, 3.03; N, 7.01. Found: C, 18.06; H, 2.95; N, 7.03.

**2** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>): Black oil; MS (*m*/*z*) 456 (M<sup>+</sup>; 0.3%, <sup>130</sup>Te), 100 (Et<sub>2</sub>NCO; bp); IR (neat) 2987, 1693, 1471, 1301, 1205, 1067, 828 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 1.11$ –1.32 (12H, m), 3.42–3.51 (8H, m).

A Typical Procedure for the One-Pot Synthesis of Bis(N,N-dialkylcarbamoyltelluro)arylmethanes (4, 5) from DMF and DEF. A 50 mL DEF was treated with lithium metal (1.402 g, 202 mmol) and elemental tellurium (5.117 g, 40.1 mmol) under 110°C for 2 h under an Argon atmosphere. After cooling the reaction mixture to 0°C, the reaction mixture was treated with a substituted benzal halide 3 (33.0 mmol) under R.T. for 3 h. The reaction was guenched by the addition of water, and the reaction mixture was extracted with hexane-dichloromethane (3:1), and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvents in vacuo, the residual crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding bis(*N*,*N*-diethylcarbamoyltelluro)arylmethanes (5) as a yellow-to-brown powder or oil.

**5a** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>): Pale yellow powder, mp 93.5–95.0°C (decomposion); MS (FAB<sup>+</sup>, m/z) 547 (M<sup>+</sup>+1; 0.3%, <sup>128</sup>Te); 544 (M<sup>+</sup>; 0.3%, <sup>128</sup>Te, <sup>126</sup>Te), 448 (M<sup>+</sup>-CONEt<sub>2</sub>; 2%, <sup>130</sup>Te, <sup>128</sup>Te), 100 (CONEt<sub>2</sub>; bp); IR (KBr) 2973, 1636, 1452, 1399, 1297, 1244, 1209, 1105, 1071, 832, 646 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 1.17$  (6H, t, J = 7.1 Hz), 1.18 (6H, t, J = 7.1 Hz), 3.08 (2H, q, J = 7.1 Hz), 3.09 (2H, q, J = 7.1 Hz), 3.49 (2H, dq, J = 13.9, 7.1 Hz), 3.53 (2H, dq, J = 13.9, 7.1 Hz), 5.93 (1H, s), 7.02–7.49 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = -4.4$  (d), 13.4 (q), 14.5 (q), 41.4 (t), 44.4 (t), 126.3 (d), 127.9 (d), 128.0 (d), 149.8 (s), 159.0 (s). Calcd for C<sub>17</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: C, 37.42; H, 4.80; N, 5.13. Found: C, 37.19; H, 4.66; N, 5.05.

**5b** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = *m*-ClC<sub>6</sub>H<sub>4</sub>): Black oil; MS (FAB<sup>+</sup>, *m/z*) 583 (M<sup>+</sup>+1; 22%, <sup>130</sup>Te, <sup>128</sup>Te), 581 (M<sup>+</sup>; 22%, <sup>128</sup>Te), 100 (CONEt<sub>2</sub>; bp); IR (neat) 2978, 1662, 1466, 1396, 1300, 1246, 1208, 1111, 834, 784, 694, 648 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.18 (6H, t, *J* = 7.1 Hz), 1.19 (6H, t, *J* = 7.1 Hz), 3.07 (2H, q, *J* = 7.1 Hz), 3.08 (2H, q, *J* = 7.1 Hz), 3.48 (2H, dq, *J* = 13.8, 7.1 Hz), 3.54 (2H, dq, *J* = 13.8, 7.1 Hz), 5.85 (1H, s), 7.01–7.48 (4H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = -6.2 (d), 13.2 (q), 14.3 (q), 41.3 (t), 44.1 (t), 125.9 (d), 126.1 (d), 127.8 (d), 128.8 (d), 132.9 (s), 151.7 (s), 158.3 (s). HRMS (FAB<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>26</sub>ClN<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: *m/z* 582.9780. Found: *m/z* 582.9778.

**5c** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = H): Yellow oil; MS (EI<sup>+</sup>, *m*/*z*) 470 (M<sup>+</sup>; 21%, <sup>128</sup>Te), 468 (M<sup>+</sup>; 13%, <sup>128</sup>Te, <sup>126</sup>Te), 330 (M<sup>+</sup>-2NEt<sub>2</sub>; 29%, <sup>130</sup>Te), 328 (M<sup>+</sup>-2NEt<sub>2</sub>; 29%, <sup>130</sup>Te, <sup>128</sup>Te), 100 (CONEt<sub>2</sub>; bp), 72 (Et<sub>2</sub>N; 25%); IR (neat) 2974, 1644, 1399, 1244, 1097, 836 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.18 (6H, t, *J* = 7.1 Hz), 1.23 (6H, t, *J* = 7.1 Hz), 3.12 (4H, q, *J* = 7.1 Hz), 3.51 (4H, q, *J* = 7.1 Hz), 3.91 (2H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = -31.0 (t), 13.3 (q), 14.4 (q), 41.3 (t), 44.3 (t), 157.1 (s). Calcd for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: C, 28.14; H, 4.72; N, 5.97. Found: C, 27.69; H, 4.50; N, 5.89.

**5d** ( $R^1 = C_2H_5$ ,  $R^2 = Mes$ ): Pale brown solid, mp 105.0–106.0°C (decomposition); MS (FAB<sup>+</sup>, m/z) 589 (M<sup>+</sup>+1; 2%, <sup>128</sup>Te), 587 (M<sup>+</sup>; 2%, <sup>128</sup>Te, <sup>126</sup>Te), 488 (M<sup>+</sup>-CONEt<sub>2</sub>; 6%, <sup>128</sup>Te), 486 (M<sup>+</sup>-CONEt<sub>2</sub>; 6%, <sup>128</sup>Te, <sup>126</sup>Te), 362 (M<sup>+</sup>-TeCONEt<sub>2</sub>; 42%, <sup>128</sup>Te), 360 (M<sup>+</sup>-TeCONEt<sub>2</sub>; 40%, <sup>128</sup>Te, <sup>126</sup>Te), 261 (MesCHTe+1; 10%, <sup>128</sup>Te), 259 (MesCHTe+1; 10% <sup>126</sup>Te), 100 (CONEt<sub>2</sub>; bp), 72 (Et<sub>2</sub>N; 38%); IR (KBr) 2975, 1653, 1467, 1380, 1243, 1107, 835 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 1.12 - 1.19$  (12H, m), 2.24 (3H, s), 2.48 (3H, s), 2.66 (3H, s), 3.05 (4H, q, J = 6.9 Hz), 3.48-3.50 (4H, m), 6.57 (1H, s), 6.77 (1H, s), 6.81 (1H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = -6.4$  (d), 13.4 (q), 14.5 (q), 20.7 (q), 21.0 (q), 23.2 (q), 41.3 (t), 43.8 (t), 128.7 (d), 129.6 (d), 133.9 (s), 135.7 (s), 136.7 (s), 140.4 (s), 157.2 (s). Calcd for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: C, 40.87; H, 5.49; N, 4.77. Found: C, 40.48; H, 5.32; N, 4.71.

**5e** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = *p*-FC<sub>6</sub>H<sub>4</sub>): Pale yellow powder, mp 61.0–63.2°C (decomposition); MS (EI<sup>+</sup>, *m*/*z*) 564 (M<sup>+</sup>, 0.04%, <sup>128</sup>Te), 562 (M<sup>+</sup>; 0.03%, <sup>128</sup>Te, <sup>126</sup>Te), 236 (FC<sub>6</sub>H<sub>4</sub>CHTe; 17%, <sup>128</sup>Te), 234 (FC<sub>6</sub>H<sub>4</sub>CHTe; 10%, <sup>126</sup>Te), 100 (Et<sub>2</sub>NCO; bp), 72 (Et<sub>2</sub>N; 8%); IR (KBr) 2976, 2933, 1666, 1603, 1503, 1460, 1399, 1301, 1214, 1102, 837, 757, 649 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.17 (6H, t, *J* = 7.1 Hz), 1.18 (6H, t, *J* = 7.1 Hz), 3.077 (2H, q, *J* = 7.1 Hz), 3.078 (2H, q, *J* = 7.1 Hz), 3.44–3.58 (4H, m), 5.90 (1H, s), 6.84 (2H, t, *J* = 8.7 Hz), 7.46 (2H, dd, *J* = 8.7, 5.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = -6.2 (d), 13.4 (q), 14.5 (q), 41.4 (t), 44.3 (t), 114.5 (dd, *J*<sub>C-F</sub> = 21.8 Hz), 129.4 (dd, *J*<sub>C-F</sub> = 8.6 Hz), 145.8 (d, *J*<sub>C-F</sub> = 2.9 Hz), 158.8 (s), 161.1 (d, *J*<sub>C-F</sub> = 245.4 Hz). HRMS (EI<sup>+</sup>, *m*/*z*): Calcd for C<sub>17</sub>H<sub>25</sub>FN<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: 565.0062. Found: 565.0060.

**5f** (R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>): Yellow oil; MS (*m*/*z*) 618 (M<sup>+</sup>; 1%, <sup>130</sup>Te), 616 (M<sup>+</sup>; 4%, <sup>130</sup>Te, <sup>128</sup>Te), 614 (M<sup>+</sup>; 3%, <sup>128</sup>Te), 460 (M<sup>+</sup>-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCO; 3%, <sup>130</sup>Te), 458 (M<sup>+</sup>-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCO; 6%, <sup>130</sup>Te, <sup>128</sup>Te), 456 (M<sup>+</sup>-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCO; 4%, <sup>128</sup>Te), 330 (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHTe; bp, <sup>130</sup>Te), 328 (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHTe; 99%, <sup>128</sup>Te); IR (neat) 2973, 2855, 1634, 1611, 1400, 1323, 1244, 1212, 1163, 1108, 1066, 835 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 1.15$ -1.22 (12H, m), 3.09 (4H, br.q, *J* = 7.0 Hz), 3.40–3.60 (4H, m), 5.85 (1H, s), 7.41 (2H, br.d, *J* = 8.0 Hz), 7.60 (2H, br.d, *J* = 8.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = -6.0$  (d), 13.3 (q), 14.5 (q), 41.5 (t), 44.4 (t), 124.0 (q, *J*<sub>C-F</sub> = 240.0 Hz), 124.8 (br.d), 128.2 (d), 154.1 (s), 158.6 (s). HRMS (EI<sup>+</sup>, *m*/*z*): Calcd for C<sub>18</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Te<sub>2</sub>: 617.9993. Found: 617.9995.

A Typical Procedure for the Treatment of *Bis*(*N*,*N*-*dialkylcarbamoyltelluro*)*arylmethanes* (4. **5**) with  $SnCl_4$  in the Presence of 2,3-Dimethyl-1,3-Butadiene. A 10 mL benzene solution of bis(N,Ndiethylcarbamoyltelluro)-4-fluorophenylmethane (5e, 564 mg, 1.00 mmol) was treated with  $SnCl_4$ (1M benzene solution, 2.00 mL, 2.00 mmol, 2.00 mol) in the presence of an excess amount of 2,3dimethyl-1,3-butadiene (821 mg, 10.0 mol) under R.T. for 4 h, and the reaction mixture was quenched by the addition of saturated NaHCO<sub>3</sub> solution. The reaction mixture was extracted with chloroform, and the organic layer was dried over anhydrous  $Na_2SO_4$ . After removing the solvent in vacuo, the residual crude mixture was subjected to column chromatographic separation on silica gel to afford the [4+2] cycloadduct 6e (25 mg, 8% yield) as vellow oil.

**6e** ( $\mathbb{R}^2 = p$ -FC<sub>6</sub>H<sub>4</sub>): Yellow oil; MS (m/z) 320 (M<sup>+</sup>: 19%, <sup>130</sup>Te), 318 (M<sup>+</sup>; 10%, <sup>128</sup>Te), 238 (p-FC<sub>6</sub>H<sub>4</sub>CHTe; 18%, <sup>130</sup>Te), 236 (p-FC<sub>6</sub>H<sub>4</sub>CHTe; 20%, <sup>128</sup>Te), 189 (bp); IR (neat) 2856, 2345, 1601, 1507, 1447, 1375, 1227, 1155, 832, 732 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.84 (3H, s), 1.87 (3H, s), 2.46 (1H, dd, J = 13.8, 3.6 Hz), 2.96 (1H, dd, J = 13.8, 11.6 Hz), 3.16 (1H, d, J = 11.9 Hz), 3.81 (1H, br.d, J = 11.9 Hz), 4.86 (1H, dd, J = 11.6, 3.6 Hz), 6.94 (2H, br.t, J = 8.8 Hz), 7.35 (2H, br.dd, J = 8.8, 5.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 4.4$  (dd), 18.2 (q), 20.4 (q), 33.7 (br.s), 43.0 (dd), 115.2 (dd,  $J_{C-F} = 21.8$  Hz), 129.2 (dd,  $J_{C-F} = 7.2$  Hz), 129.8 (s), 132.2 (s), 141.3 (d,  $J_{C-F} = 4.6$  Hz), 161.2 (d,  $J_{C-F} = 243.6$  Hz). HRMS (EI<sup>+</sup>; m/z) Calcd for C<sub>13</sub>H<sub>15</sub>FTe: 318.0203. Found: 328.0208.

**6f** (R<sup>2</sup> = *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>): Yellow oil; MS (*m/z*) 370 (M<sup>+</sup>; 8%, <sup>130</sup>Te), 368 (M<sup>+</sup>; 12%, <sup>128</sup>Te), 288 (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHTe; 16%, <sup>130</sup>Te), 286 (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHTe; 14%, <sup>128</sup>Te), 239 (bp); IR (neat) 3010, 2860, 1324, 1165, 1127, 1068 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.84 (3H, br.s), 1.89 (3H, br.s), 2.50 (1H, dd, *J* = 13.5, 3.5 Hz), 2.95–3.05 (1H, dd, *J* = 13.5, 10.5 Hz), 3.19 (1H, br.d, *J* = 12.0 Hz), 3.87 (1H, br.d, *J* = 12.0 Hz), 4.91 (1H, d, *J* = 10.5, 3.5 Hz), 7.47 (2H, br.d, *J* = 8.7 Hz), 7.50 (2H, br.d, *J* = 8.7 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 4.7 (d), 18.3 (q), 20.4 (q), 33.8 (t), 42.2 (dd), 124.5 (q, *J*<sub>C-F</sub> = 210.6 Hz), 126.3 (br.d), 128.0 (d), 130.0 (s), 132.1 (s), 149.9 (s). HRMS (EI<sup>+</sup>; *m/z*) Calcd for C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>Te: 370.0188. Found: 370.0192.

Treatment of Bis(N,N-dialkylcarbamoyltelluro)arylmethane **5e** with  $SnCl_4$  in the Absence of Trapping Agents. A 10 mL benzene solution of bis(N,Ndiethylcarbamovltelluro)-p-fluorophenylmethane (5e, 2.64 g, 4.68 mmol) was treated with  $SnCl_4$ (1M benzene solution 18.7 mL, 18.7 mmol, 4.00 mol) under R.T. for 3 h, and the reaction mixture was quenched by the addition of saturated NaHCO<sub>3</sub> solution. The reaction mixture was extracted with chloroform, and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent in vacuo, the residual crude complex mixture was subjected to column chromatographic separation on silica gel to afford 1,1-diphenyl-1*p*-fluorophenylmethane **9e** (98 mg, 8% yield) as colorless needles.

**9e** ( $\mathbb{R}^2 = p$ -FC<sub>6</sub>H<sub>4</sub>) [21]: Colorless needles, mp 58.7–59.5°C (lit. 62.0–63.0°C); MS (*m/z*) 262 (M<sup>+</sup>; bp), 185 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>; 71%), 165 (M<sup>+</sup>-ArH; 48%); IR (KBr) 3024, 1598, 1501, 1445, 1227, 1156, 1086, 1024, 806, 742 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 5.52 (1H, s), 6.96–7.30 (14H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 56.0 (d), 115.1 (dd,  $J_{C-F}$  = 21.8 Hz), 126.4 (d), 128.4 (d), 129.3 (d), 130.8 (dd,  $J_{C-F}$  = 8.7 Hz), 139.6 (s), 143.7 (s), 161.4 (d,  $J_{C-F}$  = 243.6 Hz).

Treatment of Bis(N,N-diethylcarbamoyltelluro)arylmethane **5e** with  $SnCl_4$  in the Presence of Allyltrimethylsilane. A 10 mL CH<sub>2</sub>Cl<sub>2</sub> solution of bis(N,N-diethylcarbamoyltelluro)-pfluorophenylmethane (**5e**, 564 mg, 1.00 mmol) was treated with SnCl<sub>4</sub> (1M CH<sub>2</sub>Cl<sub>2</sub> solution, 4.0 ml, 4.00 mmol, 4.00 mol) in the presence of allyltrimethylsilane (571 mg, 5.00 mmol, 5.00 mol) under  $-78^{\circ}$ C for 4 h, and the reaction mixture was quenched by the addition of saturated NaHCO<sub>3</sub> solution. The reaction mixture was extracted with chloroform, and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent in vacuo, the residual crude mixture was subjected to column chromatographic separation on silica gel to afford *Te*-allyl *N*,*N*-diethyltellurocarbamate **10e** (33 mg, 12% yield) as unstable yellow oil. The structure of compound **10e** was confirmed by independent synthesis through the reaction of in situ generated *N*,*N*-diethyltellurocarbamate ion with ally bromide through a similar method shown above.

**10** ( $\mathbb{R}^1 = \mathbb{C}_2\mathbb{H}_5$ ): Yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta =$ 1.15 (3H, t, J = 7.1 Hz), 1.22 (3H, t, J = 7.1 Hz), 3.15 (2H, q, J = 7.1 Hz), 3.48 (2H, q, J = 7.1 Hz), 3.68 (2H, d, J = 8.0 Hz), 4.84 (1H, br.d, J = 9.8 Hz), 5.09 (1H, br.d, J = 17.0 Hz), 6.09 (1H, ddt, J = 17.0, 9.8, 8.0 Hz).

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