

**Procedure for 2.** Phosphetane 1 (0.096 g, 0.465 mmol) and methylene chloride (1.5 mL, 13.3 mmol) were syringed into a Teflon-screw-top pressure NMR tube (Wilmad). The tube was heated in an oil bath at 90 °C for 68 h. The reaction is quantitative by  $^{31}\text{P}$  NMR spectroscopy. X-ray-quality crystals were obtained by reacting 0.960 g (4.65 mmol) of the phosphetane with 0.5 mL (4.44 mmol) of  $\text{CH}_2\text{Cl}_2$ . Crystals formed upon heating at 90 °C overnight. A partial X-ray structure was determined for 2. However, due to the presence of isomers of 1, there was disorder in the structural determination.  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  22.3 (s, *trans,trans*-2), 19.8 (AB quartet, *cis,trans*-2), 17.3 (s, *cis,cis*-2). The singlet peak assignments were made by assuming that the *cis* isomer remains upfield of the *trans* isomer.

**Procedure for 3.** To a solution of  $\text{Pt}(1,5\text{-COD})\text{Cl}_2$  (0.16 g, 0.45 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added the phosphetane 1 (0.17 mL, 0.86 mmol). The solution was stirred overnight, followed by removal of solvent under vacuum. The product was recrystallized by slow diffusion of ether into a  $\text{CH}_2\text{Cl}_2$  solution of 3.  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ ): isomer 3a,  $\delta$  3.44 (d,  $^1J(\text{Pt-P}) = 3453$  Hz,  $^2J(\text{P-P}) = 20.4$  Hz), 12.36 (d,  $^1J(\text{Pt-P}) = 3378$  Hz,  $^2J(\text{P-P}) = 20.0$  Hz); isomer 3b,  $\delta$  10.88 (s,  $^1J(\text{Pt-P}) = 3415$  Hz); isomer 3c,  $\delta$  5.56 (s,  $^1J(\text{Pt-P}) = 3418$  Hz).

**X-ray Structure Determination for 3.** X-ray-quality crystals of 3 were obtained by slow diffusion of ether into a  $\text{CH}_2\text{Cl}_2$  solution. The complex crystallized as 3-0.5 $\text{Et}_2\text{O}$  in the triclinic space group  $P\bar{1}$ , with  $a = 14.140$  (3) Å,  $b = 15.784$  (5) Å,  $c = 16.047$  (3)

Å,  $\alpha = 68.18$  (3)°,  $\beta = 83.47$  (2)°,  $\gamma = 69.94$  (2)°,  $V = 3122$  (1) Å<sup>3</sup>,  $Z = 4$ , and  $d_{\text{calcd}} = 1.522$  g/cm<sup>3</sup> for the formula  $\text{C}_{28}\text{H}_{43}\text{O}_{0.5}\text{P}_2\text{Cl}_2\text{Pt}$ . Crystal dimensions were  $0.63 \times 0.19 \times 0.10$  mm. A total of 8116 unique data were collected over the  $hkl$  limits  $-14$  to  $15$ ,  $-15$  to  $16$ ,  $0$ – $17$ . The structure was solved by MULTAN-least-squares-Fourier methods and was refined to  $R$  and  $R_w$  values of 0.033 and 0.040 for 289 variables and 6121 unique data with  $I > 3.0\sigma(I)$ . All programs were from the Enraf-Nonius SDP package. All calculations were performed on a micro-VAX computer.

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**Supplementary Material Available:** Tables of crystal data and data collection parameters, positional parameters, general temperature factor expressions, and bond distances and angles for 3 (22 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of Volatile Trifluoromethyl Alkyl Tellurides

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**Summary:** Ligand exchange reactions between bis(trifluoromethyl)tellurium and di-*tert*-butyl or dibenzyl telluride were used to prepare the odorless, unsymmetrical trifluoromethyl alkyl tellurides  $\text{CF}_3\text{TeC}(\text{CH}_3)_3$  and  $\text{CF}_3\text{TeC-H}_2\text{C}_6\text{H}_5$ , respectively. These new compounds, potentially useful as source reagents for chemical vapor deposition of tellurium alloys, are considerably more volatile than the corresponding  $\text{MeTeR}$  ( $R = \text{t-Bu, Bz}$ ) derivatives and decompose at comparable temperatures.

Volatile organotellurium compounds are commonly used as source reagents for metal organic chemical vapor deposition (MOCVD) of mercury cadmium telluride (MCT). Fabrication of devices based on MCT requires the ability to grow abrupt junctions over large areas at low temperatures (<300 °C). High growth temperatures coupled with low growth rates result in diffusion of mercury across the heterojunction, thus destroying its integrity and usefulness.<sup>1</sup> In this note we report the synthesis of two novel highly volatile trifluoromethyl alkyl tellurides potentially suitable as tellurium source reagents for growth of mercury cadmium telluride.

MOCVD of mercury cadmium telluride is presently limited by the availability of appropriate tellurium source reagents. Volatility of the tellurium source reagent and efficient, low-temperature decomposition of the source reagent to elemental tellurium, without incorporation of

Table I. Trends in Volatility and Decomposition Temperatures of Organotellurium Compounds

compd	vapor pressure, mmHg (temp, °C)	growth temp, °C
dimethyl telluride	760 (82)	>450
diisopropyl telluride	5.6 (30)	390
di- <i>tert</i> -butyl telluride	4 (40)	320
diallyl telluride	3.5 (45)	280
methyl allyl telluride	8 (30)	290

\*Growth temperatures are from literature data and are the temperatures at which the growth rate becomes temperature-independent.<sup>4,17</sup>

Table II. Boiling Points of Selected Organometallic Compounds at 1 atm

compd	bp, °C	perfluoro compd	bp, °C
$(\text{CH}_3)_2\text{S}$	37.3	$(\text{CF}_3)_2\text{S}$	-22
$(\text{CH}_3)_2\text{Se}$	54.5	$(\text{CF}_3)_2\text{Se}$	
$(\text{CH}_3)_2\text{Te}$	82	$(\text{CF}_3)_2\text{Te}$	23

impurities into the product film, are among the most important criteria for effective tellurium source reagents. Competing trends in volatility and decomposition temperature currently require a compromise between growth rate and temperature (Table I).<sup>2</sup>

The absence of intermolecular forces in perfluoroalkyl compounds often leads to increased volatility as compared to the hydrocarbon analogues (Table II).<sup>3</sup> We sought to

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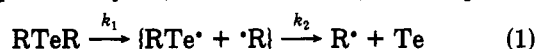
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take advantage of this increased volatility in the design of novel tellurium precursors, while maintaining the required low decomposition temperature. The temperature dependence of film growth for the compounds in Table I was consistent with a stepwise homolysis decomposition pathway.<sup>4</sup> In this mechanism, the energy required to break the first tellurium-carbon bond was rate-limiting and was proportional to the stability of the carbon-centered radical formed upon homolysis (reaction 1). Thus, it was expected



that the bond energy of a Te-CF<sub>3</sub> bond would lie somewhere between those of Te-CH<sub>3</sub> and vinyl-Te bonds on the basis of the relative stability of the corresponding radicals. If the ease of formation of the carbon-centered radical were the most crucial factor in the decomposition of organotellurides, then unsymmetrical tellurium derivatives of formula CF<sub>3</sub>TeR (where R = CH<sub>3</sub>, <sup>t</sup>Bu, Bz) would be predicted to be more volatile than the corresponding MeTeR compounds without significant changes in the decomposition temperature.

### Experimental Section

Compound manipulations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques, vacuum lines, and a Vacuum Atmospheres drybox. Bis(trifluoromethyl)mercury,<sup>5</sup> diallyl telluride,<sup>6</sup> dibenzyl telluride,<sup>6</sup> di-*tert*-butyl telluride,<sup>7</sup> and bis(trifluoromethyl) ditelluride<sup>8</sup> were prepared using literature methods. Bis(trifluoromethyl)tellurium was prepared from bis(trifluoromethyl)mercury and tellurium(IV) chloride by the method of Ganja, Ontiveros, and Morrison.<sup>9</sup> Tellurium(IV) chloride was purchased from Aldrich and used as received.

<sup>1</sup>H and <sup>125</sup>Te NMR spectra were recorded at room temperature in benzene-*d*<sub>6</sub> on a WP 200SY NMR spectrometer equipped with a VSP200 broad-band probe. <sup>125</sup>Te spectra were referenced to external neat Me<sub>2</sub>Te at 0 ppm, and <sup>1</sup>H spectra were referenced to C<sub>6</sub>D<sub>5</sub>H (7.15 ppm). Mass spectra were obtained on a Hewlett-Packard HP5890A/HP5970 gas chromatograph/mass spectrometer equipped with a 60-m poly((methylphenyl)silicone) column. Molecular weights for ions containing tellurium are reported for <sup>130</sup>Te. GC analyses were performed using a Perkin-Elmer Sigma 2000 gas chromatograph on a 30-m poly((methylphenyl)silicone) column equipped with a LCI-100 integrator.

Vapor pressure measurements were carried out using an apparatus constructed at ATM with an MKS Baratron differential pressure sensor (Model 315BH) and a Leybold-Heraeus D2A vacuum pump with an ultimate vacuum of 0.01 Torr.

A Lindberg decomposition furnace in conjunction with a Perkin-Elmer Sigma 2000 gas chromatograph was used to study the thermal decomposition of the tellurium compounds. With this system, compounds were delivered into a decomposition furnace using a specified carrier gas. Typical conditions consisted of a flow of 30 sccm (sccm = standard cubic centimeters per minute) through the reagent bubbler into a pyrolysis tube with a volume of 35 mL, giving a residence time of 1.17 min. Reaction products from the decomposition were then carried to the gas chromatograph and injected onto the column. Identification of the volatile components of the decomposition was accomplished by comparing their retention times with those of authentic samples. Confirmation was achieved by withdrawing samples for GC-MS. Additional decomposition experiments were done using the injection port of a Hewlett-Packard HP5890A gas chromatograph as the pyrolysis chamber. The volatile products passed immediately into the gas chromatograph and were separated on

a 60-m poly((methylphenyl)silicone) column. The products were identified using a Hewlett-Packard HP5970 mass spectrometer.

**Synthesis of (Trifluoromethyl)benzyltellurium.** Dibenzyltellurium (2.44 g, 0.00788 mol) was placed in a 50-mL flask equipped with a vacuum stopcock and magnetic stirrer. Bis(trifluoromethyl)tellurium (1.93 g, 0.00727 mol) was condensed into the flask, and the mixture was stirred at room temperature, exposed to artificial room light, for 65 h. The flask was fitted with a short-path distillation head, and (trifluoromethyl)benzyltellurium (3.0 g, 72% yield) was distilled from the reaction mixture under vacuum (bp 80–82 °C/4 Torr). NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H, δ 6.95 (m, 5 H), 3.94 (s, 2 H); <sup>13</sup>C, δ 12 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>TeCF<sub>3</sub>, J<sub>C-H</sub> = 146 Hz), 102 (q, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>TeCF<sub>3</sub>, J<sub>C-F</sub> = 351 Hz), 126–138 (m, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>TeCF<sub>3</sub>); <sup>125</sup>Te, δ 980 (q of t, J<sub>Te-F</sub> = 91 Hz, J<sub>Te-H</sub> = 23 Hz); <sup>19</sup>F, δ 24.0 ppm. MS: *m/z* 290 (M<sup>+</sup>), 199 (CF<sub>3</sub>Te<sup>+</sup>), 130 (Te<sup>+</sup>), 91 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup>). Exact mass: calculated for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>Te (<sup>130</sup>Te) 289.9567, found 289.9592.

**Synthesis of (Trifluoromethyl)-*tert*-butyltellurium.** Using the method described for (trifluoromethyl)benzyltellurium, <sup>t</sup>Bu<sub>2</sub>Te (18.9 g, 0.0778 mol) was reacted with (CF<sub>3</sub>)<sub>2</sub>Te (14.8 g, 0.055 mol) for 6 days at room temperature and exposed to light. Vacuum distillation gave (trifluoromethyl)-*tert*-butyltellurium, bp 60–61 °C/114 mm (22.9 g, 82% yield). NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H, δ 1.48 (s, 9 H); <sup>13</sup>C, δ 36 (q, CF<sub>3</sub>TeC(CH<sub>3</sub>)<sub>3</sub>, J<sub>C-H</sub> = 127 Hz), 103 (q, CF<sub>3</sub>TeC(CH<sub>3</sub>)<sub>3</sub>, J<sub>C-F</sub> = 351 Hz); <sup>125</sup>Te, δ 1162 (m); <sup>19</sup>F, δ 21.6. MS: *m/z* 256 (M<sup>+</sup>), 199 (CF<sub>3</sub>Te<sup>+</sup>), 130 (Te<sup>+</sup>), 69 (CF<sub>3</sub><sup>+</sup>), 57 (C<sub>4</sub>H<sub>9</sub><sup>+</sup>). Exact mass: calculated for C<sub>5</sub>H<sub>9</sub>F<sub>3</sub>Te (<sup>126</sup>Te) 251.9688, found 251.9713.

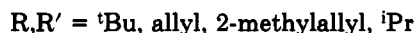
**Reaction of Diallyltellurium with Bis(trifluoromethyl)tellurium.** Equimolar amounts of diallyltellurium and bis(trifluoromethyl)tellurium were combined under vacuum in a flame-sealed NMR tube. After the mixture was kept 14 days at room temperature, exposed to light, a new resonance in the <sup>125</sup>Te NMR spectrum was seen at 893 ppm (q of t, J<sub>Te-F</sub> = 92 Hz, J<sub>Te-H</sub> = 30 Hz). GC/MS of the mixture confirmed the presence of (trifluoromethyl)allyltellurium: *m/z* 240 (M<sup>+</sup>), 199 (CF<sub>3</sub>Te<sup>+</sup>), 171 (C<sub>3</sub>H<sub>5</sub>Te<sup>+</sup>), 130 (Te<sup>+</sup>), 69 (CF<sub>3</sub><sup>+</sup>), 41 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>).

### Results and Discussion

Mixed trifluoromethyl alkyl tellurides have been previously prepared by photolysis of dimethyl telluride in the presence of perfluoroalkyl iodides<sup>10</sup> and addition of bis(trifluoromethyl)tellurium to cyclohexene.<sup>11</sup> The former method produced an inseparable mixture of compounds, while the latter was clearly unsuitable for the compounds desired in this study.

Unsymmetrical tellurides have also been prepared by reaction of dimethylmercury with dialkyl ditellurides.<sup>12</sup> However, the reaction of (CF<sub>3</sub>)<sub>2</sub>Hg with ditellurides R'TeTeR' (R' = Me, <sup>t</sup>Bu) in benzene failed to yield the unsymmetrical trifluoromethyl alkyl telluride derivatives even at 80 °C.

In a previous study we observed that a number of alkyl tellurides underwent facile ligand exchange reactions at low temperatures. In all cases equilibrium favored the unsymmetrical telluride, with Δ*G* values for reaction 2 ranging from -0.89 to -2.1 kcal/mol.<sup>13,14</sup> Bis(trifluoro-



methyl)tellurium was readily prepared by published procedures from bis(trifluoromethyl)mercury and tellurium tetrachloride.<sup>15</sup> The novel unsymmetrical tellurium com-

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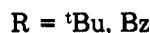
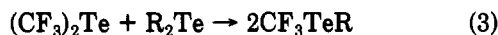
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Table III. Vapor Pressures of Selected *tert*-Butyl Tellurides<sup>18</sup>

compd	vapor pressure, mmHg (temp, °C)
CF <sub>3</sub> Te <sup>t</sup> Bu	13 (17)
CH <sub>3</sub> Te <sup>t</sup> Bu	0.8 (17)
<sup>t</sup> BuTe <sup>t</sup> Bu	4 (40)

pounds CF<sub>3</sub>Te(<sup>t</sup>Bu) and CF<sub>3</sub>TeBz were then successfully synthesized by ligand exchange reactions between (CF<sub>3</sub>)<sub>2</sub>Te and R<sub>2</sub>Te (reaction 3). Curiously, the CF<sub>3</sub>TeR compounds do not possess the distinctive foul odor associated with volatile, low-molecular-weight alkyl tellurides.

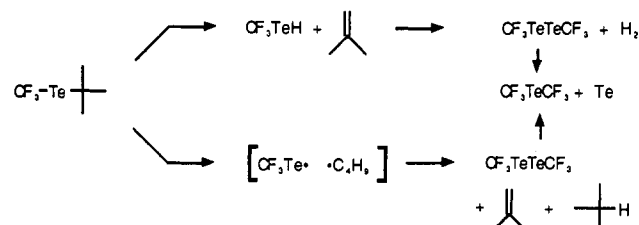


Similar experiments with (CF<sub>3</sub>)<sub>2</sub>Te and diallyl telluride led to spectroscopic identification of up to 30% CF<sub>3</sub>Te(allyl) after 10 days at 70 °C. Considerable decomposition to tellurium metal and 1,5-hexadiene was also observed. Although the desired compound was readily identified in these mixtures by gas chromatography/mass spectrometry (GC/MS) and <sup>128</sup>Te NMR spectroscopy, this compound could not be isolated in a pure form. The problem with this synthesis may be kinetic, i.e. decomposition of the starting material or product to 1,5-hexadiene occurs at a rate comparable to or faster than the desired rearrangement, or it may be that the equilibrium in this instance favors the symmetrical tellurides. The preparation of CF<sub>3</sub>Te(allyl) from reactions of (CF<sub>3</sub>)<sub>2</sub>Hg with diallylmethyltellurium bromide or triallyltellurium iodide were also unsuccessful.

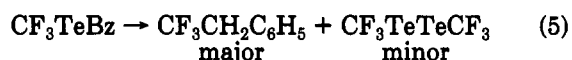
As expected, the trifluoromethyl alkyl tellurides showed significant increases in volatility as compared to the alkyl tellurides (Table III). Decomposition of CF<sub>3</sub>Te(<sup>t</sup>Bu) both in a flow-tube system and in a GC/MS injection port yielded isobutane, isobutene, and bis(trifluoromethyl)tellurium (reaction 4).<sup>16</sup> In the GC/MS experiments

$$CF_3Te{}^t\text{Bu} \rightarrow C_4H_{10} + C_4H_8 + (CF_3)_2Te + CF_3TeTeCF_3 \quad (4)$$

bis(trifluoromethyl) ditelluride was also observed. The ditelluride was presumably present in both systems but due to the longer residence time underwent further decomposition in the flow tube to (CF<sub>3</sub>)<sub>2</sub>Te. The decomposition of CF<sub>3</sub>TeTeCF<sub>3</sub> to CF<sub>3</sub>TeCF<sub>3</sub> was confirmed using

Figure 1. Possible pathways for decomposition of CF<sub>3</sub>Te<sup>t</sup>Bu.

a small sample of the ditelluride prepared via photolysis of CF<sub>3</sub>TeCF<sub>3</sub>.<sup>8</sup> Extrusion of tellurium and formation of dimethyl telluride have been proposed for the decomposition of dimethyl ditelluride.<sup>17</sup> The decomposition of CF<sub>3</sub>TeTeCF<sub>3</sub> in the GC/MS instrument occurred at slightly lower temperatures than were required to decompose CF<sub>3</sub>Te<sup>t</sup>Bu. These results were consistent with those observed for both MeTe<sup>t</sup>Bu and <sup>t</sup>Bu<sub>2</sub>Te, where competing bond homolysis and β-hydrogen elimination pathways were present (Figure 1).<sup>13</sup> Decomposition of (trifluoromethyl)benzyltellurium yielded 2,2,2-trifluoroethylbenzene as the primary product and bis(trifluoromethyl) ditelluride as the minor product (reaction 5). Smaller amounts of



toluene and bis(trifluoromethyl)tellurium were also seen, as well as trace amounts of benzene and (trifluoromethyl)benzene. These products were consistent with the bond homolysis mechanism followed by radical recombination or abstraction. Interestingly, CF<sub>3</sub>Te(<sup>t</sup>Bu) was *less* stable than CF<sub>3</sub>TeBz, the former being completely decomposed in the flow tube at an oven temperature of 335 °C whereas the latter required 450 °C for complete decomposition. The absence of a β-hydrogen-elimination pathway may be responsible for the greater stability of the benzyl derivative. Chemical vapor deposition experiments and further investigation of the thermal decomposition pathways of these new compounds are in progress.

**Acknowledgment.** The financial support of the National Science Foundation is gratefully acknowledged. We also thank Dan Pentek of Yale University for carrying out the exact-mass measurements.

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