

## Optimizing the Synthesis of Tetratellurafulvalene

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A systematic synthetic study of the  $\pi$ -donor tetratellurafulvalene (TTeF, **6**) has resulted in an optimized preparation producing repeatable yields of over 20%. The use of a "one-step" Li/Sn metal exchange/Te<sup>0</sup> insertion procedure and freshly prepared microcrystalline Te<sup>0</sup> serve to drive toward products, the equilibria converting (*Z*)-1,2-bis(trimethylstannyl)ethylene (**1**) to its corresponding metal-exchanged vinyl lithium species and subsequently to lithium ditellurolate **5**. Furthermore, the use of LiCl as an additive to enhance the reactivity of *n*-BuLi in these metal exchange reactions also increases yields and reproducibility. The slow addition of 1 equiv of tetrahaloethylene during the final cyclization step favors intramolecular reactions which produce TTeF vs intermolecular reactions that lead to oligomeric byproducts. The use of tetrabromoethylene in place of tetrachloroethylene in this step also reduces byproduct formation.

### Introduction

The synthetic study of tetrachalcogenafulvalene  $\pi$ -donors<sup>1</sup> and their various derived organic charge-transfer and radical cation salts has received much attention since the metallic properties of the charge-transfer complex formed between the  $\pi$ -donor tetrathiafulvalene (TTF) and the  $\pi$ -acceptor tetracyanoquinodimethane (TCNQ) were first elucidated in 1973.<sup>2</sup> Synthetic efforts have focused on ways to increase the bandwidths and dimensionality of materials derived from new donor and acceptor components.<sup>3</sup> In particular, incorporation of Se or Te in place of S in the heterofulvalene framework affects resulting materials in several important ways as exemplified by the physical parameters of the homologous TXF (X = S, Se, Te)–TCNQ series (Table 1).<sup>4</sup> As a result of the larger, more diffuse p and d atomic orbitals of Se and Te relative to those of S, *intrastack* orbital overlap is enhanced (the larger distance between adjacent molecules along the stacking axis, due to the increase in atomic dimensions upon progression from S to Se to Te, is more than offset by increased orbital size) leading to wider donor bandwidths ( $W_D$ ). The TCNQ acceptor bandwidth ( $W_A$ ) remains nearly constant throughout the series, thus the total bandwidth ( $W_T$ ) increase is approximated by the increase in  $W_D$ . In accordance with tight-binding band calculations, this increase in  $W_T$  is reflected in increased conductivity ( $\sigma$ ) as one moves from S to Se to Te.

Similarly, the theoretical prediction that conductivity will be roughly proportional to  $W_T^2$  is born out well in the TXF–TCNQ materials as demonstrated by the correlation between  $W_T^2$  and experimentally determined relative  $\sigma$ . The larger orbitals of Se and Te also allow for increased *interstack* overlap, which is reflected by increased complex dimensionality. This higher dimensionality leads to suppression, or entire elimination, of the inherent 1-D Peierls Distortion,<sup>5</sup> which frequently results in a metal to semiconductor phase transition at some temperature  $T_{\max}$ . The observed decrease in  $T_{\max}$  upon substitution of Se and Te for S is consistent with increased salt dimensionality. Suppression of these distortions allows for high conductivity to be observed to lower temperatures with the possibility of observing superconductivity. Superconductivity has, indeed, been observed in complexes containing the Se donor tetramethyltetraselenafulvalene (TMTSF) in combination with various inorganic counteranions<sup>6</sup> (e.g. TMTSF<sub>2</sub>X; X = PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>) and the S donor bis(ethylenedithio)tetrathiafulvalene (ET) in combination with numerous inorganic counteranions<sup>7</sup> (e.g. ET<sub>2</sub>X; X = I<sub>3</sub><sup>-</sup>, Cu(NCS)<sub>2</sub><sup>-</sup>, CuN(CN)<sub>2</sub>Y; Y = Cl<sup>-</sup>, Br<sup>-</sup>). Also, the greater polarizability of Se and Te relative to S allows for a reduction in the on-site Coulombic repulsion involved in the formation of doubly charged species. This reduction is observable in a decrease in the difference between the first and

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**Table 1. Physical Parameters for TXF–TCNQ**

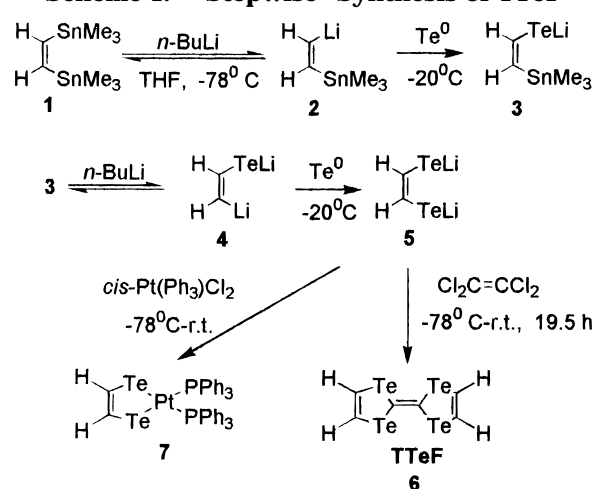
parameter	X = S	X = Se	X = Te
$\sigma_{300\text{ K}} (\Omega\text{ cm})^{-1}$	500	800	2200
relative $\sigma$	1	1.2–2.3	3.2–6.3
relative <sup>a</sup> $[W_T]^{1/2}$	1	1.5	3.1
$W_D$ (eV)	0.85	1.52	2.49
$W_A$ (eV)	1.37	1.31	1.36
$\sigma_{\text{max}}/\sigma_{300\text{ K}}$	≈14	≈12	≈9.5
$T_{\text{max}}$ (K)	59	40	<2 <sup>b</sup>
stacking axis (Å)	3.819	3.876	3.947
$\Delta E_{1/2}^c$ (V)	0.34	0.28	0.25

<sup>a</sup> Double- $\zeta$  Slater type orbitals. <sup>b</sup> No M–I transition observed to lowest temperature measured (2 K). <sup>c</sup> Volts vs SCE at Pt button electrode; 0.2 M TBA<sup>+</sup>BF<sub>4</sub><sup>–</sup> in CH<sub>2</sub>Cl<sub>2</sub>; 200 mV/s sweep rate.

second electrochemically determined donor oxidation potentials ( $\Delta E_{1/2}$ ). Unless the molecular component can transiently support a doubly charged species, only a correlated type of conduction can occur. This increase in polarizability also facilitates stacking of like-charged species in the segregated stacking motif typical of many of the fulvalene-containing materials.<sup>8</sup> With these concepts in mind, we have actively pursued the synthesis of unknown Se- and Te-containing fulvalenes<sup>9</sup> with the goal of incorporating such new donor components into novel organic metals and possibly superconductors.

Tetratellurafulvalene (TTeF, **6**), first synthesized by McCullough in our laboratories in 1987,<sup>10</sup> completed the homologous TXF (X = S, Se, Te) series and added to a relatively small, but growing, list of Te based donor components.<sup>11</sup> This initial synthesis of TTeF from (*Z*)-1,2-bis(trimethylstannyl)ethylene (**1**)<sup>12</sup> utilized a Li/Sn metal exchange reaction to form alkenyllithium **2**, followed by Te<sup>0</sup> insertion into the newly formed C–Li bond to produce lithium tellurolate **3**. This “stepwise” metal exchange, Te insertion procedure was repeated to yield sequentially organolithium species **4** and ditellurolate **5**. Cyclization using tetrachloroethylene (TCE) afforded TTeF (Scheme 1). Unfortunately, after the rigorous purification needed to obtain pure material necessary for high quality diffusion and electrochemical crystal growth (*at least* once chromatographed, usually twice, followed by recrystallization; see Experimental Section), yields were quite low and variable, typically on the order of only 1–5%.

Several features of this stepwise procedure have since been noted.<sup>13</sup> The three fundamental factors affecting the overall reaction process are the positions of the two Li/Sn metal exchange equilibria affording alkenyllithium species **2** and **4**, respectively, Te<sup>0</sup> uptake by alkenyllithium species **2** and **4**, and the success of the final cyclization of ditellurolate **5** with TCE. By trapping **5** with *cis*-Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> to yield platinum complex **7** in 28% purified yield, it was shown that the metal exchange/Te<sup>0</sup> insertion processes proceed at least to this extent. Thus,

**Scheme 1. “Stepwise” Synthesis of TTeF**

we focused our initial investigations on the final cyclization step. Important to this process was not only the absolute yield of the substitution process, but also the reduction of unwanted byproducts which complicated purification and, more importantly, increased the rate of TTeF decomposition. Whereas during initial chromatography of the crude reaction mixture significant loss of TTeF occurs, once the TTeF is purified it is moderately stable to chromatographic conditions (silica/CS<sub>2</sub>, see Experimental Section).

When tetrabromoethylene (TBE) was substituted for TCE in Scheme 1 and low temperatures were maintained *throughout* the Te<sup>0</sup> insertions, purified yields of TTeF of up to 12% were obtained (entry 2 in Table 2). Byproduct formation was reduced to the point where reasonably pure material was obtained after only one chromatographic sequence, and product suitable for crystal growth was accessible after a subsequent recrystallization from degassed CS<sub>2</sub>/hexane. Although average yields were significantly increased, this stepwise process was still plagued by frequent inconsistencies and a more reliable procedure was desirable for repeated preparations.

We therefore undertook a systematic study of several factors deemed critical to the consistent conversion of distannane **1** to TTeF: (1) the use of *freshly prepared* microcrystalline Te<sup>0</sup> for the chalcogen insertion reactions, (2) optimization of the position of the two Li/Sn metal exchange equilibria through the use of alternate metal exchange/Te<sup>0</sup> insertion conditions, (3) the use of various additives to enhance the reactivity of *n*-BuLi in the metal exchange processes, and (4) utilization of a slow TXE (X = Cl, Br) addition rate and the optimal number of equivalents of tetrahaloethylene cyclizing reagent.

## Results and Discussion

**Use of Microcrystalline Tellurium at Low Temperature.** As noted, it is generally desirable to maintain low temperatures during chalcogen insertion reactions in order to avoid competing side reactions of both the initial alkenyllithium **2** and the subsequently generated lithium tellurolate **3** (Scheme 2).

Most published procedures for accomplishing Te<sup>0</sup> insertion into a C–Li bond, and indeed our own initial synthesis of TTeF, call for warming of the alkenyllithium solution to various temperatures up to 25 °C in order to facilitate Te<sup>0</sup> uptake. In the case of the reactions depicted in Scheme 1, the addition of Te<sup>0</sup> in the conversion of **2** to

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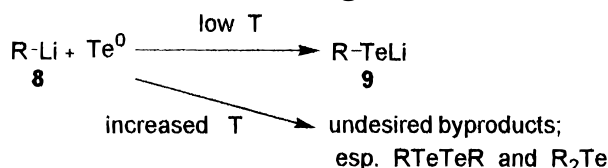
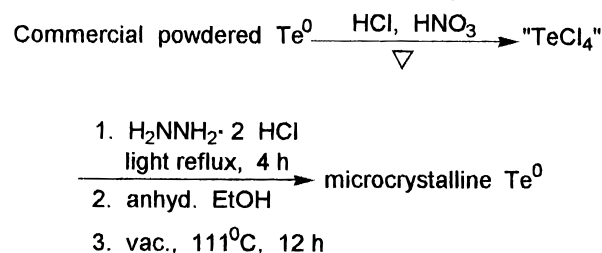
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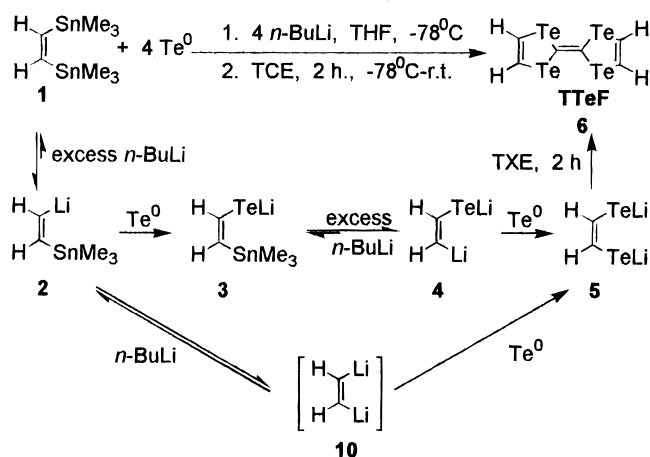
**Scheme 2. Chalcogen Insertion****Scheme 3. Preparation of Microcrystalline  $\text{Te}^0$** 

**3** and **4** to **5** was accompanied by a warming of the reaction mixture from its initial temperature of  $-78^\circ\text{C}$  to a final temperature of  $-20^\circ\text{C}$ . The suspension was stirred until all gray  $\text{Te}^0$  was consumed, at which point the solution was recooled to  $-78^\circ\text{C}$ . This warming technique used to facilitate  $\text{Te}^0$  uptake undoubtedly increased the rate of formation of byproducts such as di-*n*-butylmono- and ditelluride and alkyltelluride oligomers ( $\text{R}_2\text{Te}_n$ ), which complicate the isolation and purification of TTeF.

It was known that microcrystalline  $\text{Te}^0$ , formed *via* the reduction of  $\text{TeCl}_4$  with hydrazine<sup>14</sup> (Scheme 3; see Experimental Section), exhibited significantly higher reactivity toward the chalcogen insertion process relative to commercially available material. Although in previous syntheses microcrystalline  $\text{Te}^0$  had been employed, we verified that when *freshly prepared* metal was used the conversion of **2** to **3** and **4** to **5** could be consistently accomplished without warming of the reaction solution, thereby reducing byproduct formation. The use of fresh microcrystalline  $\text{Te}^0$  thus facilitates the reliable overall conversion of distannane **1** to ditellurolate **5** without increasing reaction temperature above  $-78^\circ\text{C}$ .

The significantly enhanced reactivity of microcrystalline  $\text{Te}^0$  is ascribed to its finely divided, oxide-free character in the same vein as the much greater reactivity of Reike Mg relative to commercial metal.<sup>15</sup> Occasionally, despite the fact that the microcrystalline material was stored in the dark in an inert atmosphere glove box, decreases in reactivity were observed. It is therefore advisable to prepare a fresh batch of  $\text{Te}^0$  at least every month. The reason for this loss of reactivity is currently unknown, but it is likely responsible for a portion of the varying yields often observed in the course of repeated TTeF syntheses. Similar decreases in reactivity during the use of Reike Mg have been attributed to atomic aggregation or to changes in crystal structure. Microcrystalline  $\text{Te}^0$  was used for *all* experiments included in Table 1.

**Optimization of the Li/Sn Metal Exchange Reactions.** The Li/Sn metal exchange reaction is an equilibrium process, the position of which is obviously critical to synthetic utility.<sup>16</sup> General factors which influence the position of this equilibrium are stannane structure,

**Scheme 4. Basic "One-step" Metal Exchange/ $\text{Te}^0$  Insertion TTeF Synthesis**

alkyllithium reactivity and structure, and reaction temperature.<sup>16b,17</sup> In the synthesis of TTeF, stannane configuration and low reaction temperatures are essentially fixed. Thus, we investigated the role of the alkyllithium reagent in the metal exchange process. As previously noted, the sequential Li/Sn exchange processes used to convert distannane **1** to vinylolithium species **2** and alkenylstannane **3** to alkenyllithium species **4** (Scheme 1) proceed in at least 28% yield as demonstrated through the trapping of ditellurolate **5** to form Pt complex **7**. We reasoned that higher yields from these exchange processes could be obtained if optimal conditions in relation to factors involving the alkyllithium reagent could be determined.

It is well known that the use of excess alkyllithium reagent often exerts the expected effect of shifting the Li/Sn exchange equilibrium toward metal-exchanged organolithium products. This effect, in combination with the observation by Reich that the reaction of MeLi with vinylstannanes at  $-78^\circ\text{C}$  is fast relative to its reaction with  $\text{Se}^0$  also present in the reaction mixture<sup>18</sup> prompted us to examine how the use of excess *n*-BuLi in the presence of  $\text{Te}^0$  affected the yield of TTeF obtained from distannane **1**. A twofold excess (4 equiv relative to **1**) of both alkyllithium and  $\text{Te}^0$  were utilized in a "one-step" metal exchange/ $\text{Te}^0$  insertion TTeF synthesis, the  $\text{Te}^0$  being combined with ditin **1** *prior* to addition of *n*-BuLi (Scheme 4).

Use of a "one-step" procedure was envisioned to affect the synthesis in several ways relative to the "stepwise" procedures previously utilized. First, the use of excess *n*-BuLi in both Li/Sn metal exchange processes should shift the equilibria toward alkenyllithium products **2** or **4**. Second, we hoped that the presence of  $\text{Te}^0$  in the reaction mixture from the very start of the addition of *n*-BuLi might serve to effectively remove the alkenyllithium species **2** and **4** from the metal exchange equilibrium as they are formed to produce tellurolates **3** and **5**, respectively. This removal would again serve to shift the Li/Sn exchange equilibrium toward products. Third,

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Table 2. Purified Yields of TTeF (6) Using Various Synthetic Procedures

expt no.	metal exchange/ insertion procedure	<i>cis</i> -distannane <b>1</b> (equiv)	total Te <sup>0</sup> (equiv)	total <i>n</i> -BuLi (equiv)	TCE/TBE (equiv)	additive (equiv)	yield purified TTeF ( <b>6</b> )
1	stepwise <sup>a</sup>	1	1.86	2.2	0.5 TCE	—	5
2	stepwise	1	1.86	2.2	0.5 TBE	—	12
3	one-step <sup>b</sup>	1	4	4	1 TCE	—	6
4	one-step	1	4	4	1 TBE	—	13
5	one-step	1	4	4	1 TCE	2 LiCl	23
6	one-step	1	4	4	1 TBE	2 LiCl	26
7	one-step	1	4	4	1 TCE	2 TMEDA <sup>c</sup>	16
8	one-step	1	4	4	1 TCE	12 HMPA <sup>d</sup>	<1
9	one-step	1	4	4	0.5 TCE	2 LiCl	<1
10	one-step	1	4	4	4 TCE	—	5

<sup>a</sup> See Scheme 1. <sup>b</sup> See Scheme 4. <sup>c</sup> *N,N,N',N'*-Tetramethylethylenediamine. <sup>d</sup> Hexamethylphosphoramide.

it is possible that direct formation of dilithio species **10** could occur in the presence of two or more equivalents of *n*-BuLi, followed by two Te<sup>0</sup> insertion reactions to afford ditelluroolate **5**. Although we feel the *in situ* stepwise repeated metal exchange/insertion process is more likely, the formation of dianions similar in structure to **10** is not unprecedented and cannot be ruled out in the present case.<sup>18,19</sup> Use of this basic “one-step” procedure (entry 3 of Table 2) enhanced net yields slightly relative to the analogous “stepwise” procedure (entry 1 of Table 2), other conditions held constant. More importantly, the “one-step” synthesis proved to be a more reliable preparation, i.e. yields varied less from run to run. Separation of TTeF from the byproducts inevitably produced by the use of excess reagents in the “one-step” procedure proved no more difficult than when an analogous “stepwise” process was used.

The increased reliability of the “one-step” procedure allowed us to systematically examine the effects of various additives on the involved Li/Sn exchange equilibria. The use of additives to increase alkylolithium reactivity is a common synthetic technique. Increases in reactivity are frequently ascribed to a decrease in aggregation state of the alkylolithium reagent similar to that observed as one moves from a noncoordinating to coordinating solvent,<sup>20</sup> or to the formation of Li halide/alkylolithium mixed aggregates.<sup>21</sup> In situations involving the formation of “ate” complexes, such as pentacoordinate stannates in the case of Li/Sn metal exchange, the increase in complex formation and, subsequently, metal-exchanged product has also been ascribed to increased solvation of the “ate” complex in the presence of coordinating additives.<sup>17,22</sup> In examining the effect of such additives on the TTeF synthesis, we utilized exclusively the more reliable “one-step” procedure.

Surprisingly, the use of 12 equiv of HMPA (relative to distannane **1**), in accordance with conditions shown to be favorable for pentacoordinate stannate complex formation in exchange reactions involving tetramethyltin and MeLi,<sup>17</sup> resulted in essentially no yield of TTeF (entry 8 of Table 2). Conversely, the use of LiCl or TMEDA significantly enhanced reaction yields and produced a pronounced increase in reproducibility. The use of 2 equiv of TMEDA produced TTeF in 16% purified yield

(entry 7 of Table 2). Even more encouraging were yields of up to 23% when LiCl was utilized as the additive and TCE was used in the cyclization step (entry 5 of Table 2). More than 2 equiv of LiCl or TMEDA seemed to have little effect on reaction yields. Because of its greater ease of purification and handling, LiCl was chosen over TMEDA for subsequent investigations. Routine yields using procedure 5 (i.e. the procedure used to obtain entry 5) of Table 2 were slightly lower than the best yield obtained, typically ranging from 15–17% after rigorous purification.

Numerous additional experiments, not reflected in the entries of Table 2, were performed investigating the use of MeLi in place of *n*-BuLi to affect Li/Sn exchange. MeLi is frequently utilized in Li/Sn metal exchange, and its lower steric requirements relative to *n*-BuLi during pentacoordinate stannate complex formation warranted its investigation. Somewhat surprisingly, very little TTeF was obtained by use of either the “stepwise” or “one-step” syntheses or any variations thereof. Experimental results conclusively demonstrating the failure of MeLi to participate readily in these metal exchange processes indicate that the relative basicity of the alkylolithium reagent, and thus the difference in energy between the reactant alkylolithium and product alkenylolithium, may be the dominant factor affecting these particular exchange equilibria. A hexane solution of *n*-BuLi was thus selected as the reagent of choice for all metal exchange reactions included in Table 1.

**Optimizing the Cyclization of Ditelluroolate 5 with TXE (X = Cl, Br).** The “one-step” TTeF synthesis shown in Scheme 4 utilizes a slow addition of TXE over the course of 1 h relative to “stepwise” procedures in which the tetrahaloethylene is added in one portion (see Experimental Section). Such slow addition under relatively dilute conditions were utilized to facilitate intramolecular cyclization of lithium telluroolate **11** to yield ring closed product **12** as opposed to intermolecular reaction to produce oligomeric byproducts such as **13** (Scheme 5). In order to maximize formation of ring closed product **12** and subsequently TTeF, during “one-step” preparations the reaction was held at –78 °C for an additional 2 h after the TXE addition was complete. Thin layer chromatography (SiO<sub>2</sub>/CS<sub>2</sub>) of the reaction mixture at low temperatures revealed the presence of TTeF soon after the addition of TXE, indicating cyclization is a kinetically competitive process as might be expected.

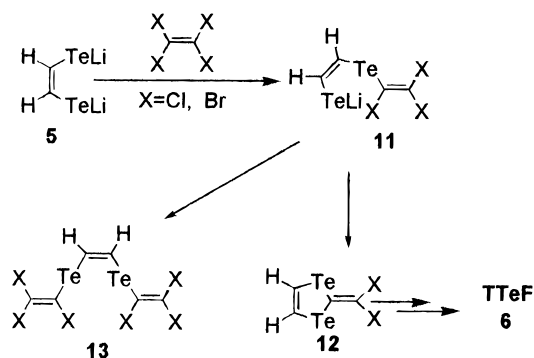
The use of TBE in place of TCE enhanced the yield of TTeF obtained *via* the “one-step” procedure as we had previously demonstrated for the “stepwise” procedure.<sup>13</sup> Using the “one-step” synthesis *without additives* the purified yield of TTeF increased from 6% with TCE to

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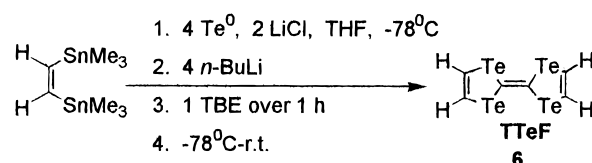
**Scheme 5. Ditelluroate Cyclization with TXE (X = Cl, Br)**

13% with TBE (entries 3 and 4, respectively, in Table 2). When LiCl was added prior to *n*-BuLi addition, yields increased modestly from 23% to 26% (entries 5 and 6 in Table 2). As previously noted, yields obtained using TCE were typically slightly lower than 23% (ca. 15–17%), thus the difference noted upon utilization of TBE in place of TCE is often accordingly more pronounced. Undesired byproduct formation is significantly reduced when TBE is used as the cyclizing reagent. It is clear that at least a portion of TBE's greater efficiency as a cyclizing reagent is attributable to this reduction in side reactions, as in many cases highly pure TTeF was obtained after only one chromatographic sequence. This, obviously, minimizes losses due to decomposition during purification procedures. Interestingly, yields of less than 1% are obtained using tetraiodoethylene in the cyclization step, indicating higher yields are not simply a consequence of the enhanced leaving group ability of Br relative to Cl, and that radical mechanisms and/or side reactions may be involved. Wudl has noted that the reaction of telluroates with TCE is most likely not a straightforward addition–elimination, but a more complicated process.<sup>23</sup>

Various equivalents of TXE cyclizing reagent were also investigated for yield optimization in the “one-step” cyclization sequence. The best yields were obtained when 1 equiv of tetrahaloethylene was used per 1 equiv of distannane. Although stoichiometrically only 0.5 equiv of TXE are required, yields were significantly reduced when less than 1 equiv was used (entry 9 vs entry 5 in Table 2). This outcome is an indication that, even at low temperatures, undesired anionic species present in solution (e.g. *n*-BuTe<sup>-</sup>, *n*-BuTeTe<sup>-</sup>, *n*-Bu<sup>-</sup>) are in kinetic competition with the desired ditelluroate **5** for reaction with TXE. The use of greater than 1 equiv of TXE has a much less pronounced negative effect on reaction yield (entry 10 vs entry 3 of Table 2).

### Conclusions

A systematic study of the synthesis of the  $\pi$ -donor TTeF (**6**) has improved the yield of purified fulvalene product from values (at best) around 12% to quite repeatable values as high as 26% if TBE is used in the final cyclization step. If the more readily available TCE is used for cyclization, yields have been improved from 1–5% to 15–17% or better. The observed improvements in yield and reproducibility are a result of (1) the use of freshly prepared microcrystalline Te<sup>0</sup>, which allows low temperature (–78 °C) to be maintained throughout the

**Scheme 6. Optimal Conditions for the Synthesis of TTeF**

entire metal exchange/insertion processes, thus suppressing byproduct formation, (2) the use of a twofold excess of *n*-BuLi to shift the Li/Sn metal exchange equilibria toward alkenyllithium products **2** and **4**, (3) the combination of Te<sup>0</sup> and distannane **1** prior to addition of *n*-BuLi in a “one-step” procedure, which allows for effective removal of alkenyllithium intermediates **2** and **4** from the metal exchange equilibria to form telluroates, and (6) the use of TBE in place of TCE to reduce byproduct formation and TTeF decomposition during purification.

Scheme 6 summarizes the conditions we have found to produce optimal yields and reproducibility in the TTeF synthesis. The ability to reliably prepare useful quantities of TTeF should facilitate both the study of its derived charge-transfer salts and cation radical complexes and the investigation of its potential utility as a building block for functionalized tellurafulvalene electron donors.

### Experimental Section

**General Methods.** All reactions were performed under a positive pressure of prepurified grade Ar (>99.998%) in oven-dried glassware either assembled in a high purity He (>99.997%) atmosphere glovebox or under a strong flow of Ar while hot. Flasks were stoppered with Suba-Seal brand rubber septa unless otherwise indicated. Reagents were of the highest grade available from Aldrich and used without further purification unless otherwise noted. Tetrabromoethylene (Alfbro Chemicals, 97%) was recrystallized three times from anhyd ethanol. Tetrachloroethylene was distilled from crushed 4 Å molecular sieves prior to each use and stored in the dark. Lithium chloride was dried in an Abderhalden drying apparatus at 110 °C for 14 h. *n*-BuLi was titrated with 2,5-dimethoxybenzyl alcohol according to a literature procedure.<sup>24</sup> TMEDA and HMPA were vacuum distilled from calcium hydride. THF was freshly distilled from sodium benzophenone ketyl. CS<sub>2</sub> (EM Science Omni-Solv) for extractions and chromatography was degassed with Ar for 30 min prior to use. Recrystallizations were performed with similarly degassed CS<sub>2</sub> (Aldrich HPLC Grade) and HPLC Grade hexane (Fisher Scientific). Column chromatography was performed with VWR EM 60 (70–230 Mesh ASTM) silica gel. <sup>1</sup>H NMR spectra were obtained at either 300 MHz or 400 MHz, and <sup>13</sup>C were spectra were acquired at 75.5 MHz. EI mass spectra were obtained at 70 eV at The Johns Hopkins University or at The Washington University Resource for Biomedical and Bio-organic Mass Spectrometry, St. Louis, MO. Elemental analyses were performed by Gailbraith Laboratories, Inc. Experimental procedures are for representative “stepwise” and “one-step” preparations; modifications involving equivalents of reagents and/or additives follow in a straightforward way from these procedures.

**Microcrystalline Te.**<sup>14</sup> To powdered Te<sup>0</sup> (13.02 g, 102 mmol) in a 500 mL beaker was cautiously added 12 M HCl

(23) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*(4), 1154–1156.

(24) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87–88.

(153 mL) and 16 M HNO<sub>3</sub> (13.4 mL) with vigorous stirring. The mixture was heated to distill off volatiles until ca. 100 mL of bright yellow TeCl<sub>4</sub> solution remained. This solution was poured into 4 M HCl (225 mL concd HCl in 450 mL degassed H<sub>2</sub>O) under Ar. To this solution was added H<sub>2</sub>NNH<sub>2</sub>·HCl (8.36 g, 122 mmol) cautiously with vigorous stirring. The resulting suspension was brought to mild reflux for ca. 4 h, or until the liquid portion is essentially clear. This suspension was filtered through a coarse glass fritted filter funnel under Ar, and the gray Te<sup>0</sup> filtrant was washed with degassed anhyd EtOH (7 × 100 mL). The Te<sup>0</sup> so obtained was dried overnight in an Abderhalden drying apparatus at 110 °C and stored in an inert atmosphere glove-box in the dark. Recovery was nearly quantitative.

**Tetratellurafulvalene (6). "Stepwise" Procedure (entry 1 of Table 2).** A THF (90 mL) solution of freshly distilled (*Z*)-1,2-bis(trimethylstannyl)ethylene (**1**)<sup>12</sup> (2.65 g, 7.50 mmol) in a 250 mL three-necked flask equipped with two solid addition flasks, each containing microcrystalline Te<sup>0</sup> (0.89 g, 6.97 mmol), was cooled to -78 °C with stirring. To this solution was added dropwise a 2.48 M hexane solution of *n*-BuLi (3.33 mL, 8.25 mmol) *via* gastight syringe and syringe pump over the course of 15 min. The resulting pale yellow solution was stirred at -78 °C for 1.5 h. The contents of one of the solid addition flasks was then added in one portion to the reaction solution with vigorous stirring. The resulting gray slurry was stirred at -78 °C for ca. 1.5 h until no solid Te<sup>0</sup> was observable in the reaction solution. A second portion of *n*-BuLi was added as described above, and the solution was stirred at -78 °C for an additional 0.5 h after the addition was complete. The contents of the second solid addition flask was then added to the solution, followed by stirring at -78 °C for 2.5 h. A solution of TCE (0.63 g, 3.80 mmol) in THF (5 mL) was added to the reaction in one portion *via* gastight syringe at -78 °C, and the solution was stirred for 15 h while its internal temperature was allowed to slowly rise to 25 °C. The reaction slurry was then transferred under Ar *via* cannula onto degassed MeOH (500 mL) with stirring. The MeOH suspension was filtered through a glass-fritted funnel under Ar pressure. The resulting solids were washed with degassed hexanes (2 × 50 mL) and the remaining solids extracted with degassed CS<sub>2</sub> (3 × 100 mL) under Ar. CS<sub>2</sub> was removed *in vacuo* to afford a red-brown solid (950 mg, 43%). This crude product was chromatographed under Ar (SiO<sub>2</sub>/degassed CS<sub>2</sub>) to produce a yellow-green band (*R<sub>f</sub>* = 0.80) which was collected to yield crude TTeF (**6**) (221 mg, 10%). A second chromato-

graphic sequence provided a brilliant green CS<sub>2</sub> solution of spectroscopically pure product (110 mg, 5%). Further purification can be effected by recrystallization from degassed CS<sub>2</sub>/hexane under Ar: <sup>1</sup>H NMR (1:1; CDCl<sub>3</sub>/CS<sub>2</sub>) δ 8.85 (s). IR (KBr) 2960, 2900, 1633, 1503, 1398, 1265, 1100, 810, 647, 602, 596. UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> = 332 nm. MS *m/z* (rel intensity) 588 (M<sup>+</sup>; 60), 562 (30), 306 (50), 282 (100), 256 (60), 130 (40). High res MS: calcd for C<sub>6</sub>H<sub>4</sub><sup>130</sup>Te<sub>4</sub>: 595.6562; found: 595.6554; calcd for C<sub>4</sub>H<sub>2</sub><sup>128</sup>Te<sup>130</sup>Te<sub>3</sub>: 593.6445; found: 563.6539. Anal. Calcd for C<sub>6</sub>H<sub>4</sub>Te<sub>4</sub>: C, 12.29; H, 0.69; Te, 87.03. Found: C, 12.27; H, 0.71; Te, 87.41.

**Tetratellurafulvalene (6). "One-Step" Procedure (entry 6 of Table 2).** Distannane **1** (1.00 g, 2.83 mmol), Te<sup>0</sup> (1.44 g, 11.00 mmol), and LiCl (0.24 g, 5.66 mmol) were combined in a 100 mL three-necked flask and slurried in THF (40 mL) under Ar. The suspension was cooled to -78 °C, and a 2.48 M hexane solution of *n*-BuLi (4.44 mL, 11.00 mmol) was added dropwise *via* gastight syringe over 30 min with a syringe pump. The solution was stirred for an additional 45 min. Unreacted Te<sup>0</sup> was frequently still present in the reaction suspension. To this slurry was added TBE (0.97 g, 2.83 mmol) in THF (7 mL) *via* gastight syringe and syringe pump over 1 h, followed by stirring at -78 °C for 2 h. The reaction was quickly warmed to 25 °C by removal of the low temperature bath and replacement with a room temperature bath 15 min after removal. The resulting suspension was transferred under Ar *via* cannula onto stirred, degassed anhyd MeOH (300 mL). The MeOH slurry was filtered under Ar pressure through a glass-fritted filter funnel, and the filtrant was washed with degassed hexanes (2 × 100 mL). The remaining solids were extracted with degassed CS<sub>2</sub> (5 × 100 mL) under Ar. Solvent was removed *in vacuo* to leave a red-brown solid (230 mg, 28%). This crude product was chromatographed under Ar (SiO<sub>2</sub>/degassed CS<sub>2</sub>) to yield TTeF (**6**) spectroscopically identical to that obtained using the "stepwise" procedure (214 mg, 26%). If TCE is used in the cyclization step, a second chromatographic sequence is frequently required to obtain highly pure tellurafulvalene.

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