

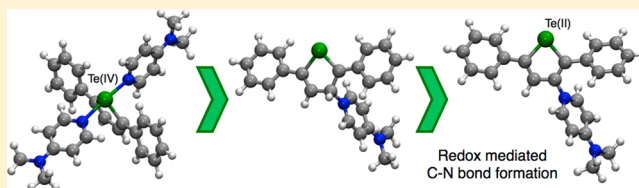
Te(II)/Te(IV) Mediated C–N Bond Formation on 2,5-Diphenyltellurophene and a Reassignment of the Product from the Reaction of $\text{PhI}(\text{OAc})_2$ with 2 TMS-OTf

Antonino Aprile, Kalon J. Iversen, David J. D. Wilson, and Jason L. Dutton*

Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Victoria, Australia, 3086

Supporting Information

ABSTRACT: We report a novel C–H to C–N bond metathesis at the 3-position of 1,2-diphenyltellurophene via oxidation of the Te(II) center to Te(IV) using the I(III) oxidant $[\text{PhI}(\text{4-DMAP})_2]^{2+}$. Spontaneous reduction of a transient Te(IV) coordination compound to Te(II) generates an electrophilic equivalent of 4-DMAP that substitutes at a C–H bond at the 3-position of the tellurophene. Theoretical and synthetic reaction pathway studies confirm that a Te(IV) coordination complex with 4-DMAP is an intermediate. In the course of these pathway studies, it was also found that the identity of the I(III) oxidant generated from $\text{PhI}(\text{OAc})_2$ and 2 TMS-OTf is $\text{PhI}(\text{OAc})(\text{OTf})$ and not $\text{PhI}(\text{OTf})_2$, as had been previously thought.



INTRODUCTION

The chemistry of tellurophenes, the Te analogues of thiophenes, has seen increasing interest in the past few years.¹ The interest has primarily been associated with luminescent properties of substituted tellurophenes (e.g., **1**)² and the electronic/optical properties of tellurophene containing polymers (e.g., **2**).^{3–9} In 2013, Seferos and co-workers reported that tellurophenes could be oxidized from Te(II) (**3**) to Te(IV) (**4**) using iodine based oxidants such as ICl or PhICl_2 (Scheme 1).¹⁰ Exposure of the oxidized compound to heat or green light resulted in reductive elimination of the dihalide from the Te center, which resulted in the regeneration of the Te(II) starting material. Extension to dibromo and difluoro Te(IV) derivatives of the simplified 2,5-diphenyltellurophene system followed.¹¹

Our group has been exploring the chemistry of the dicationic I(III) reagents $[\text{PhI}(\text{pyr})_2]^{2+}$ (**5R**; R = –H, –NMe₂, –CN) for simultaneously oxidizing transition metals and delivering pyridine ligands giving polycations, for example, generation of Au(III) trications **7R** from Au(I) starting material **6** (Scheme 2).^{12–14} This class of I(III) compounds was first reported in 1994 by Weiss and Seubert,¹⁵ later reinvestigated by Zhdankin et al.,^{16,17} and more recently used to oxidatively couple anilines.¹⁸ In transition metal chemistry, it has been demonstrated that the delivered pyridine ligands can be easily displaced by other two-electron donors, which was used to great effect in a high-profile report from Ritter on the generation of late-stage ¹⁸F labeling reagents for PET imaging.¹⁹ Pd(II) starting complex **8** was oxidized using SCH_3 to give **9**. Subsequent displacement of pyridine with ¹⁸F labeled KF gave **10**, which was later used to introduce electrophilic fluorine to organic reagents via reduction to Pd(II).

The tellurophene system (using 2,5-diphenyltellurophene **11** as a representative tellurophene) appeared an ideal choice to test the efficacy of compound **5** for the oxidation of main group centers and as a possible method for the straightforward generation of variously substituted Te(IV) derivatives of tellurophene, as well as potentially being a novel ligand stabilized Te polycation.²⁰ However, rather than simple oxidation of Te, an unusual C–H activation and C–N bond formation occurred at the 3-position of the tellurophene, mediated by the Te(II)/Te(IV) redox couple.

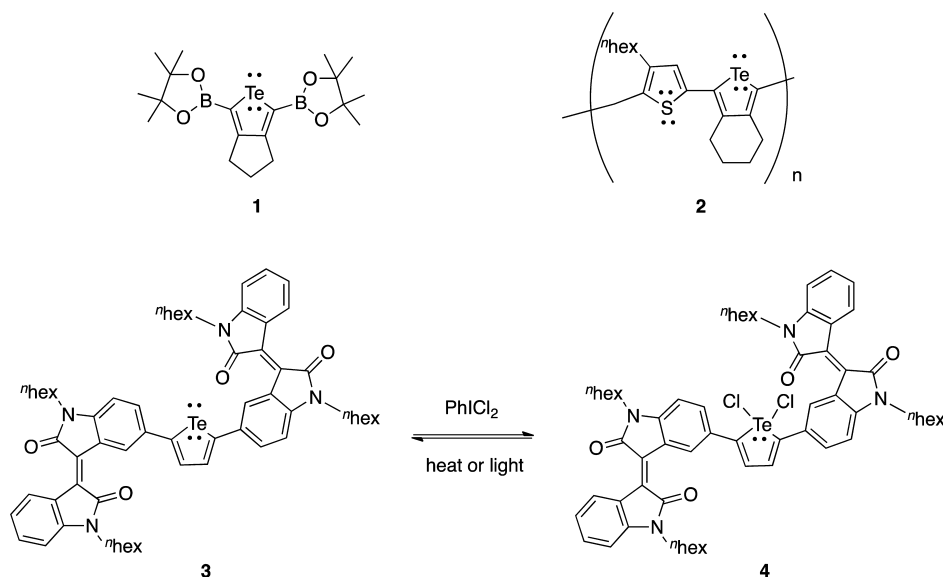
RESULTS AND DISCUSSION

The 1:1 stoichiometric reaction of 5NMe_2 with 2,5-diphenyltellurophene **11** in CDCl_3 resulted in the formation of an orange solution after stirring overnight. Proton NMR spectroscopy indicated the presence of two 4-DMAP containing compounds, one of which could be identified as likely protonated 4-DMAP based on a downfield proton resonance at ~12 ppm. One singlet at 8.29 ppm arising from the 3/4 tellurophene position protons indicated that one compound containing the tellurophene was present. Et_2O was added, resulting in precipitation of the protonated 4-DMAP. The remaining supernatant was placed in a –35 °C freezer in the glovebox, which resulted in the overnight growth of yellow colored single crystals. X-ray diffraction studies revealed the crystals to be cationic tellurophene **12**, with a 4-DMAP ligand having replaced a proton on the backbone at the 3-position of the ring (Figure 1). Based on the charge of the ring and the geometry about the Te, the oxidation state of tellurium in this

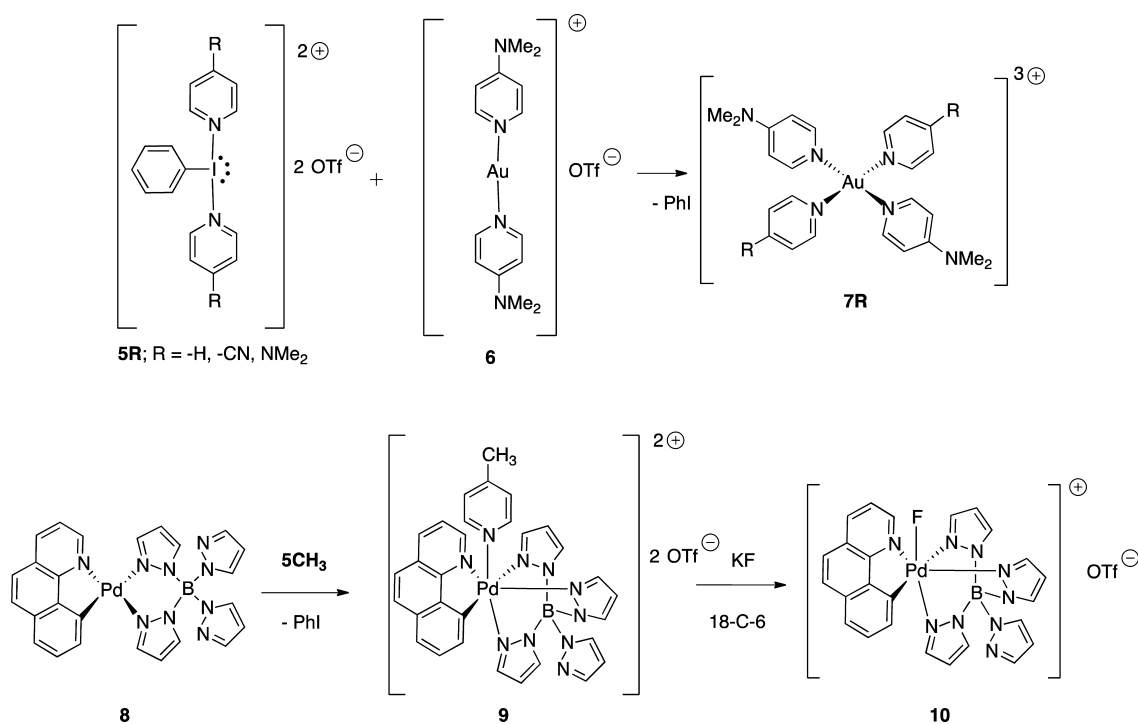
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Scheme 1. Tellurophenes Used As Building Blocks for Luminescent Compounds and Functionalized Polymers



Scheme 2. Reactions of Au and Pd with Dicationic I(III) Oxidant 5R



product is +2, the same as in the starting material **11**. A re-examination of the proton NMR data from the reaction indicated that **12** and protonated 4-DMAP were the only products of the reaction (Scheme 3).

The isolation of **12** from the reaction poses several questions as to what is occurring in the reaction. To investigate whether an oxidative process was required, two equivalents of 4-DMAP were directly reacted with **11**, which resulted in no reaction and confirmed the requirement of an oxidizing agent. The next question was whether the C–H bond at the 3-position of the tellurophene was directly reacting with the iodine oxidant **5NMe₂**, or if the process was being mediated by oxidation of Te(II) to Te(IV). To investigate this issue, tellurophene **11** was reacted with the I(III) oxidant “PhI(OTf)₂” (generated from

PhI(OAc)₂ and two equivalents of TMS-OTf as per reported procedures)²¹ in CDCl₃, which immediately resulted in the generation of a bright orange solution (Scheme 4). Proton NMR spectroscopy indicated that this reaction generated a single, symmetric tellurophene containing product (with respect to the σ_v axis of the tellurophene bisecting the bond between carbons at positions 3 and 4), with the 3 and 4 position protons shifted to 7.74 ppm, slightly downfield from those in **11** (7.69 ppm). The ¹²⁵Te NMR chemical shift of the product was 900 ppm, substantially downfield from **11** at 412 ppm. The identity of the compound was tentatively assigned as a Te(IV) bistriflate complex **13OTf**, for which related complexes with dianionic chelating N-ligands are known to be stable.²² Two equivalents of 4-DMAP were added to the

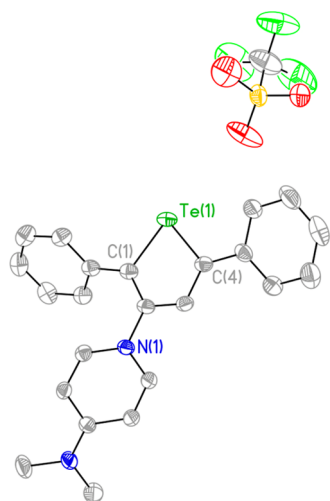


Figure 1. Solid-state structure of **12**. Et₂O solvate and hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 50% probability level.

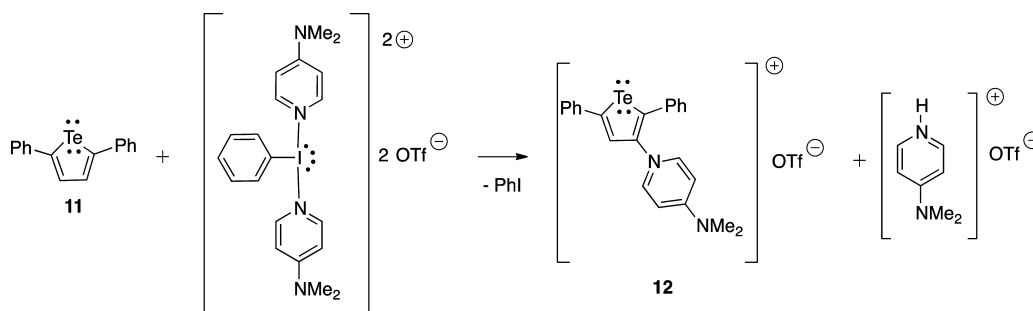
reaction mixture, which resulted in the immediate production of **12** as ascertained from ¹H NMR spectroscopy, via a presumed Te(IV)-bis-4-DMAP adduct (**14**) resulting from the displacement of triflates. The adduct **14** would be the same product arising from direct oxidation of **11** with 5NMe₂. We propose that the transformation of the intermediate adduct **14** to **12** occurs as outlined in Scheme 4, with the overall effect of the reaction being an electrophilic aromatic substitution on the 3-position of tellurophene with the Te(IV) intermediate generating an electrophilic equivalent of 4-DMAP via reduction to Te(II). To confirm that formation of an adduct with 4-DMAP at the Te(IV) center was required, tellurophene **11** was reacted with PhI(OAc)₂, which resulted in the straightforward isolation of **13OAc**. The identity of **13OAc** was confirmed by X-ray crystallography (Figure 2). Acetate is a much poorer leaving group than triflate, and the addition of two equivalents of 4-DMAP to **13OAc** resulted in no reaction, confirming that interaction of the 4-DMAP with the Te(IV) center is required for the activation of the 3-position C–H to proceed. Computational studies lend support to the proposed mechanism, with a calculated ΔG of –114 kJ/mol in the oxidation step to generate **14**. Intermediate **15** is calculated to be higher in energy by 58 kJ/mol compared to **14**, but elimination of protonated 4-DMAP to form **12** is favorable by 219 kJ/mol, giving an overall ΔG from **11** to **12** of –275 kJ/mol. Intermediate **15** is calculated to be in equilibrium with **15'**, the corresponding 4-DMAP adduct with **15'** lower in energy by

26 kJ/mol, allowing sufficient **15** to be present to act as the base driving the reaction forward. Reduction to Te(II) in **15** is supported by an examination of the molecular orbitals, where the HOMO–3 is clearly a p-based orbital centered on the Te atom (Figure 3), consistent with Te(II). There is some amount of π-backbonding from Te to the formally cationic α-carbon in **15** (Te–C 1.99 Å), which is somewhat more pronounced in the adduct **15'** (Te–C 1.96 Å).

Compound **13OTf** was found to be an extremely air/moisture sensitive material, as is typical of Te-OTf bound compounds.^{22,23} Attempts to isolate a bulk solid of **13OTf** from the reaction mixture also resulted in decomposition. The ¹²⁵Te NMR chemical shift of 900 ppm measured for **13OTf** is indicative, but not absolutely confirming of the assignment of a +4 oxidation state for the Te atom.²⁴ For verification, single bright orange crystals were grown from a solution of what was presumed to be **13OTf** at –35 °C. The crystals were highly moisture sensitive, decomposing rapidly even in Na dried paratone-n oil; however we were able to successfully mount a sample on the X-ray diffractometer. Solution and refinement of the data unexpectedly gave compound **16**, a mixed triflate/acetate ligated Te(IV) species rather than the expected bis-triflate species (Figure 4). Proton NMR of single crystals picked in the glovebox showed an identical spectrum to that obtained from a freshly prepared solution of PhI(OAc)₂, 2 TMS-OTf, and tellurophene **11**. While **13OAc** was inert with respect to the addition of 4-DMAP, we propose that the addition of 4-DMAP to **16** displaces the triflate group, which in turn weakens the Te–O bond to the acetate owing to the much stronger *trans* influence of 4-DMAP over triflate. This allows for the second equivalent of 4-DMAP to displace the acetate group generating intermediate **14**, allowing the substitution reaction to proceed.

It was hypothesized that OTf/OAc exchange at Te(IV) from the target bistriflate complex **13OTf** and TMS-OAc could result in the observed product **16**. Thermodynamic calculations on the equilibrium between **13OTf** and **16** indeed indicated that the potential equilibrium would lie on the product side by 46 kJ/mol (Scheme 5). We then performed the same calculation on the analogous I(III) equilibrium, which also indicated that the equilibrium for I(III) was also on the product side (ΔG –14 kJ/mol; K = 284 at 298 K). Therefore, the predicted dominant I(III) compound in the reaction between PhI(OAc)₂ and 2 TMS-OTf is the mixed species PhI(OTf)(OAc) reported some years ago by Zhdankin.²⁵ Recently, Wirth and Farid described a low-temperature ¹H NMR study on the formation of PhI(OTf)₂ by reaction of PhI(OAc)₂ with a variety of stoichiometric equivalents of TMS-OTf.²¹ We repeated their experiments at room temperature, matching

Scheme 3. Reaction of Tellurophene **11** with 5NMe₂ Giving **12**



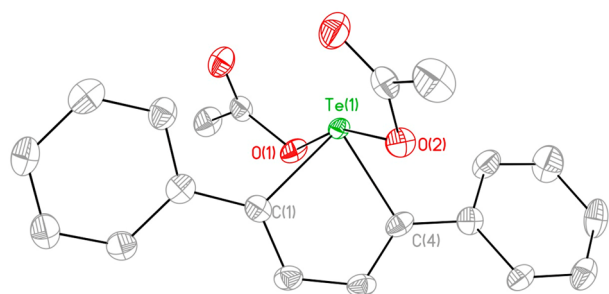
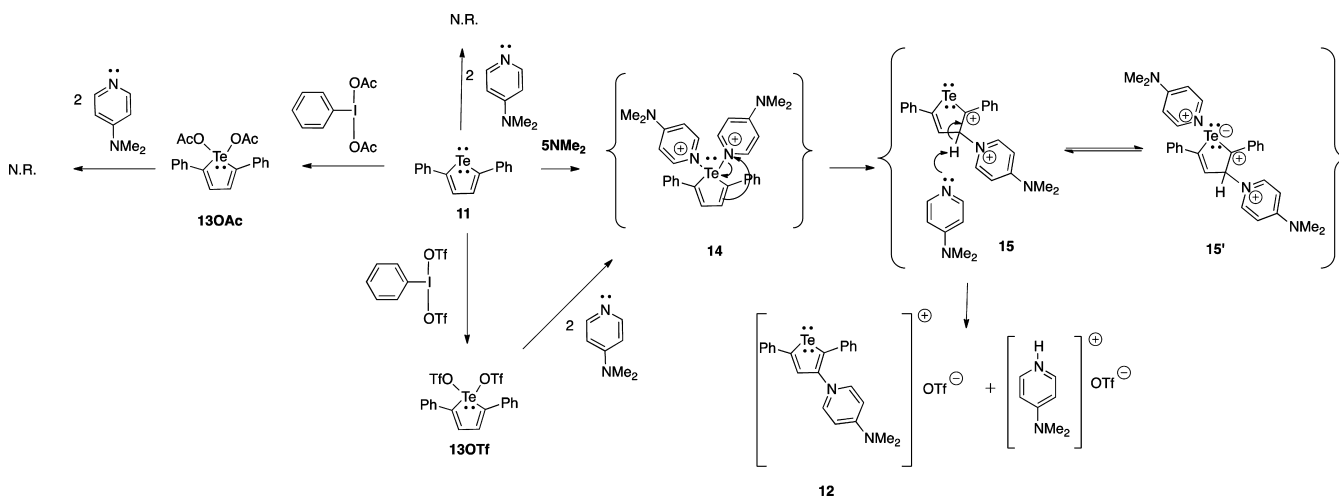
Scheme 4. Reaction Pathway Studies on the Reactions of **11** with I(III) Oxidants and Subsequent Reactions with 4-DMAP

Figure 2. Solid-state structure of **13OAc**. Hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å): Te(1)–O(1) 2.145(5); Te(1)–O(2) 2.152(5).

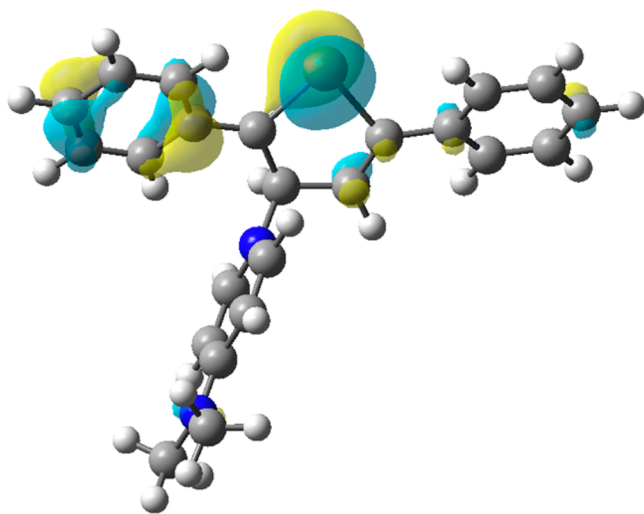


Figure 3. Calculated HOMO–3 of intermediate **15**.

their results. Critically, at the 1:2 stoichiometry prescribed in the literature for synthesis of $\text{PhI}(\text{OTf})_2$, there are two separate resonances for the $-\text{CH}_3$ arising from acetate and two resonances for the $-\text{SiMe}_3$ groups of trimethylsilyl substituents (see Supporting Information). If the reaction proceeded to give $\text{PhI}(\text{OTf})_2$ and 2 TMS-OAc as reported, there should be only one acetate $-\text{CH}_3$ resonance, arising from TMS-OAc. One acetate group in the mixture of $\text{PhI}(\text{OAc})_2 + 2 \text{TMS-OTf}$ can be assigned to TMS-acetate (as can one $-\text{SiMe}_3$ group) by

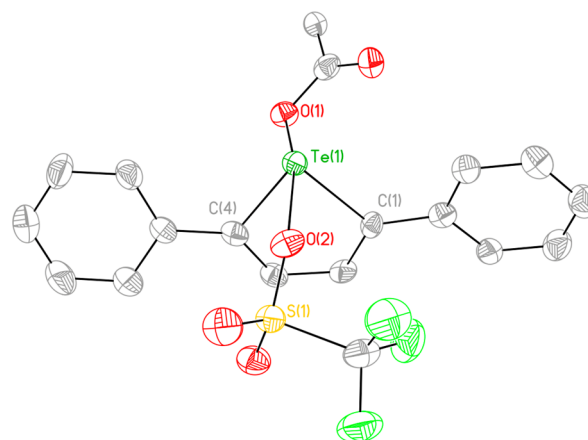


Figure 4. Solid-state structure of **16**. Chloroform solvate and hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å): Te(1)–O(1) 2.013(3); Te(1)–O(2) 2.453(3).

examination of a reported spectra.²⁶ The other TMS resonance was assigned to TMS-OTf by comparison with a genuine sample. It is likely that in most cases the mixture of $\text{PhI}(\text{OTf})(\text{OAc}) + \text{TMS-OTf}$ will act as an equivalent of $\text{PhI}(\text{OTf})_2$, but based on our observations the actual I(III) species present is clearly $\text{PhI}(\text{OTf})(\text{OAc})$, which in our case did give a different outcome in the chemistry.

CONCLUSIONS

In summary we have described a new type of reaction—a C–H to C–N bond metathesis reaction mediated by reduction of a Te(IV) coordination complex generating an electrophilic equivalent of 4-dimethylaminopyridine. Spontaneous reduction of higher oxidation state chalcogen compounds induced by ligands is well-known, but in all other cases this involves S, Se, and Te tetrahalides (e.g., SeCl_4 , TeI_4), typically with unproductive and deleterious elimination of X_2 ($\text{X} = \text{Cl}$, I).^{27–31} As discussed in the Introduction, current interest around tellurophenes is based on their electronic properties. While our work is clearly at the model stage, the functionalization of 2,5-diphenyltellurophene into cationic C–N functionalized **12** results in a narrowing of the calculated HOMO–LUMO gap from 3.97 to 3.46 eV (M06-2X/def2-

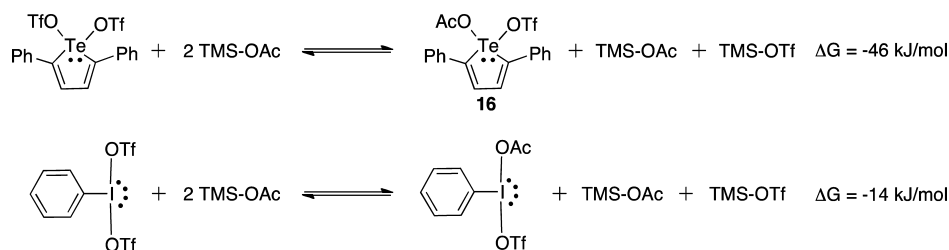
Scheme 5. Calculated ΔG of Reaction for the Mixtures of 13OTf and 2 TMS-OAc and PhI(OTf)₂ and 2 TMS-OAc

Table 1. Refinement Details for X-ray Structural Determinations

compound	12·Et ₂ O	13OAc	16·CHCl ₃
empirical formula	C ₂₆ H ₂₆ N ₂ F ₃ O _{3.5} S ₁ Te ₁	C ₂₀ H ₁₈ O ₄ Te ₁	C ₂₀ H ₁₆ Cl ₃ F ₃ O ₅ S ₁ Te ₁
FW (g/mol)	639.15	449.94	659.34
crystal system	monoclinic	triclinic	triclinic
space group	<i>I</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.3566(7)	8.526(2)	10.840(2)
<i>b</i> (Å)	10.5736(6)	10.197(2)	11.056(2)
<i>c</i> (Å)	35.407(2)	10.315(3)	12.188(2)
α (deg)	90	91.18(3)	71.11(3)
β (deg)	92.060(4)	99.60(3)	75.36(3)
γ (deg)	90	94.89(3)	62.77(3)
<i>V</i> (Å ³)	5371.4(5)	880.4(3)	1219.3(4)
<i>Z</i>	8	2	2
<i>R</i> 1[<i>I</i> > 2 σ <i>I</i>]	0.0338	0.0628	0.0449
<i>wR</i> 2(<i>F</i> ²)	0.0924	0.1733	0.1067
GOF (<i>S</i>)	1.046	1.075	1.095

TZVP), indicating the potential to use this method to modulate the properties of tellurophene containing compounds. In the course of our work it was also determined that the product of the reaction between PhI(OAc)₂ and 2 TMS-OTf is PhI(OTf)(OAc) and not PhI(OTf)₂, which has the potential to effect the chemistry within this system, as shown in the generation of 16.

EXPERIMENTAL DETAILS

Chloroform and acetonitrile were obtained from Caledon Laboratories and dried using an Innovative Technologies Solvent Purification System with dual columns packed with solvent appropriate drying agents. The dried solvents were stored under an N₂ atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy (CDCl₃, CD₃CN) were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH₂, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. Reagents were purchased from Alfa Aesar or Sigma-Aldrich and used as received. Tellurophene 11 and [PhI(DMAP)₂][OTf]₂ were synthesized via literature procedures.^{11,15}

Synthesis and Isolation of 12 [PhTe(DMAP)]₂[OTf]. Tellurophene 11 (50 mg, 1.5 mmol) was dissolved in CH₂Cl₂ (1 mL) and added to a suspension of [PhI(DMAP)₂][OTf]₂ (112 mg, 1.5 mmol) in CH₂Cl₂ (1 mL). The mixture was stirred overnight, resulting in an orange colored solution. Et₂O was added to the solution resulting in a precipitation of a solid which was confirmed by ¹H NMR to be protonated 4-DMAP. The yellow supernatant was placed in the -35 °C freezer, resulting in precipitation of 12 as pale yellow crystals. The supernatant was decanted and the crystals dried *in vacuo* (70 mg, 77% yield). M.P.: 92–96 °C. ¹H NMR (400 MHz, CD₃CN): δ 8.29 (s, 1H), 7.96 (d, 2H, *J* = 8 Hz), 7.58 (d, 2H, *J* = 8 Hz), 7.44–7.42 (m, 3H), 7.34 (d, 3H, *J* = 8 Hz), 7.18 (d, 2H, *J* = 8 Hz), 6.82 (d, 2H, *J* = 8 Hz), 3.19 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 156.5, 149.8, 141.8, 141.2, 140.8, 137.8, 134.6, 129.7, 129.4, 129.3, 129.2, 128.9, 128.4, 128.6, 108.3, 40.7. ¹⁹F NMR (376 MHz, CDCl₃): -78.2. ¹²⁵Te NMR

(126 MHz, CDCl₃): δ 540. ESI-MS [*M*]⁺: *m/z* 455.0 [PhTe(DMAP)]⁺.

Synthesis and Isolation of 13OAc. Tellurophene 11 (100 mg, 3.0 mmol) was dissolved in CH₃CN (5 mL) and added to a solution of PhI(OAc)₂ (104 mg, 3.0 mmol) in CH₃CN (5 mL). The mixture was stirred overnight, resulting in a bright yellow solid. The mixture was placed in a -35 °C freezer to complete precipitation. The solid was filtered and dried *in vacuo* to yield 13OAc (49 mg, 79% yield). Yellow crystals of 13OAc were grown from a saturated CH₃CN solution stored at -35 °C overnight. ¹H NMR (400 MHz, CD₃CN): δ 7.71–7.68 (m), overlapping with singlet at 7.69, 7.48–7.41 (m, 6H), 1.78 (s, 6H). ¹³C NMR (100 MHz, CD₃CN): δ 178.5, 158.9, 140.4, 134.9, 130.4, 129.8, 128.5, 21.3. ¹²⁵Te NMR (126 MHz, CD₃CN): δ 683.

Synthesis of 16. To a solution of PhI(OAc)₂ (104 mg, 3.0 mmol) in CDCl₃ (2 mL) was added TMS-OTf (108 μ L, 6 mmol) and left to stir for 30 min. This solution was then added to a suspension of tellurophene 11 (100 mg, 3.0 mmol) in CDCl₃ (2 mL), resulting in the immediate formation of a dark red solution. The mixture was examined by ¹H NMR, ¹⁹F NMR, and ¹²⁵Te NMR spectroscopy. The solution was stored at -35 °C overnight, resulting in square red crystals of 16. ¹H NMR (400 MHz, CDCl₃): δ 7.74 (s, 2H), 7.62 (m, 4H), 7.46–7.44 (m, 6H) 2.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 176.8, 155.9, 141.5, 137.5, 136.3, 134.1, 132.6, 131.9, 130.7, 130.3, 129.6, 127.7, 127.5, 19.5. ¹⁹F NMR (376 MHz, CDCl₃): δ -77.3. ¹²⁵Te NMR (126 MHz, CDCl₃): δ 900.

X-ray Crystallography Details. Single crystals were selected under *n*-paratone oil, mounted on nylon loops, and placed into a cold stream (172 K) of N₂ on an Oxford CCD diffractometer using Mo *K* α radiation. Structure solution and refinement were performed using the SHELXTL suite of software. Structure and refinement information is found in Table 1.

COMPUTATIONAL DETAILS

Theoretical calculations were performed within the Gaussian 09 program.³² All of the compounds were optimized using the M06-2X density functional³³ employing the def2-TZVP basis set.³⁴ Analysis

using other density functionals (B3LYP,^{35,36} wB97XD³⁷) and basis sets (def2-SVP)³⁸ produced analogous geometries and energetic trends, so they are not reported. Frequency calculations indicate that all compounds were at a minimum with zero imaginary frequencies. All reported calculations include solvent effect correction using the integral equation formulation of the polarizable continuum model (IEFPCM)^{39–41} with acetonitrile solvent parameters. Single-point calculations (including MP2, SOS-MP2,⁴² and SCS-MP2⁴³ energies) were performed using the M06-2X/def2-TZVP optimized geometries. ΔG values reported in the manuscript are the SCS-MP2 electronic energies including solvent effects incorporating the M06-2X/def2-TZVP gas-phase thermochemical corrections (standard $T = 298.15$ K and $p = 1$ atm).

■ ASSOCIATED CONTENT

● Supporting Information

Cartesian coordinates and energies for optimized geometries. Proton, ¹³C, and ¹²⁵Te NMR spectra of synthesized compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.dutton@latrobe.edu.au.

Notes

The authors declare no competing financial interest.

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