Synthesis and Stille Cross-Coupling Reactions of 2-(Tributylstannyl)- and 2,5-Bis(trimethylstannyl)tellurophene

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Abstract: Herein, we describe the synthesis and Stille cross-coupling reactions of 2-(tributylstannyl)- and 2,5-bis(trimethylstannyl)tellurophene. The reactions were most optimal when using aryl iodides as coupling partners, and a mixed catalyst system consisting of tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide, together with cesium fluoride as additive, in *N*,*N*-dimethylform-amide. This is the first reported synthesis and use of stannylated tellurophenes for cross-coupling reactions.

Key words: tellurophene, Stille reaction, cross-coupling, palladium, heterocyclic

Transition-metal catalyzed cross-coupling reactions are highly utilized in organic synthesis for the construction of carbon–carbon bonds.^{1,2} Of the various types of aryl–aryl cross-coupling reactions, the Stille reaction is one of the most used due to the stability and wide functional-group compatibility of arylstannanes.³ As a result, the synthesis of numerous aryl and heteroaryl stannanes and their subsequent use in cross-coupling reactions have now been described in the literature.^{1–3}

As part of an ongoing project involving the synthesis of di-cationic diarylchalcogenophenes,^{4,5} we were in recent need of an efficient synthesis of various 2,5-diaryltellurophenes. The most common route to such compounds, involving the cyclization of 1,4-diaryl-1,3-butadiynes to 2,5-diaryltellurophenes with sodium telluride (Na₂Te),⁶ was not sufficient in our hands. We thus considered the use of the Stille cross-coupling reactions of a distannylated tellurophene with an aryl halide. A literature review revealed that Stille reactions using stannylated tellurophenes have not been previously described, although reactions employing stannylated furans,⁷ thiophenes^{1b} and even selenophenes⁸ are known. Furthermore, although there have been recent examples of crosscoupling reactions involving halogenated tellurophenes as coupling partners,9 there have been no reports of crosscoupling reactions involving a metallated tellurophene as a coupling partner.¹⁰ We thus set out to develop this chemistry. As a result, we now describe the synthesis and crosscoupling reactions of 2-(tributylstannyl)tellurophene and 2,5-bis(trimethylstannyl)tellurophene for the convenient synthesis of 2-aryl- and 2,5-diaryltellurophenes.

Initially, we focused on the synthesis of 2-(tributylstannyl)tellurophene (1). Similar to furan and thiophene,⁸ standard monolithiation of tellurophene using butyllithium (1.1 equiv) in diethyl ether for 30 minutes at room temperature, followed by quenching with tributyltin chloride, gave the desired mono-tin tellurophene 1 in 57% yield as a pale-yellow liquid after vacuum distillation (Scheme 1). The use of N, N, N', N'-tetramethylethylenediamine (TMEDA) in the monolithiation did not improve the yield.

Next, we turned our attention to the synthesis of the di-tin tellurophene. In this case, we elected to prepare the bis(tri*methyl*stannyl) analogue (2), as this was expected to form a crystalline solid, considering the corresponding thiophene¹¹ and selenophene¹³ are solids. Our initial attempts at dilithiation using butyllithium (2.1 equiv) and TMEDA in diethyl ether at room temperature gave a poor yield of the di-stannyl tellurophene 2 (<20% yield), with a significant amount of the mono-stannyl product being isolated (27% yield) after quenching with trimeththyltin chloride. However, upon performing the dilithiation using sec-butyllithium and TMEDA¹¹ and heating in hexanes for 45 minutes before quenching, we were able to obtain a 42% yield of 2 as a colorless crystalline solid after recrystallization from methanol. Both the mono- and distannyl tellurophenes appear to be very stable compounds, with no visual evidence of decomposition upon prolonged storage at 0 °C. In contrast, tellurophene itself is prone to decomposition upon similar storage.



Scheme 1 Synthesis of mono- and di-stannyltellurophenes

With the mono- and di-stannyl tellurophenes in hand, we turned to the Stille cross-coupling reactions. Our first coupling involved the reaction of mono-tin tellurophene **1** with 4-bromobenzonitrile (1 equiv) in the presence of tet-

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rakis(triphenylphosphine)palladium(0) (2-3 mol%) in toluene, which are typical conditions³ for a Stille coupling (Scheme 2). This reaction proved sluggish, and after heating for two days at near reflux, the yield of 2-(4-cyanophenyl)tellurophene (**3a**) was only 36% following purification. In our previous work, these standard conditions gave much higher yields when the analogous monostannyl furan,⁷ thiophene¹² and even selenophene⁴ were coupled with 4-bromobenzonitrile, with no noticeable differences in reactivity observed within the series. On the other hand, Tierney and co-workers¹³ have recently observed a lower reactivity of a stannylated selenophene compared to the analogous thiophene. In the end, our results here suggest a relatively low reactivity for stannylated tellurophene **1** in Stille couplings.



Scheme 2 Stille coupling of mono-stannyl tellurophene 1 with 4-bromo- or 4-iodobenzonitrile

In an attempt to improve the yield of the coupling reaction, we explored the use of an aryl iodide as coupling partner, instead of the aryl bromide. We also included copper(I) iodide as co-catalyst and cesium fluoride as additive, and changed the solvent to *N*,*N*-dimethylformamide, conditions which have been shown to improve certain Stille couplings.¹⁴ Under these conditions (Scheme 2), the reaction was complete after heating over-

 Table 2
 Yields for Various 2,5-Diaryltellurophenes Prepared by Stille Coupling

Me ₃ Sn Te SnMe ₃ 2	R (2 equiv) Pd(PPh ₃) ₄ , Cul, CsF DMF, 60 °C, ~16 h		R	
Entry	Compd	R	Yield (%)	Mp (°C)
1	4 a	CN	88	231–232
2	4b	Н	42	224–225
3	4c	Me	47	239–240
4	4d	NO ₂	67	271–272
5	4e	OMe	42	278

night (16 h) at just 60 °C, with a 64% yield of coupling product **3a** being obtained after purification. Satisfied with this result, we explored the use of other aryl iodides in this reaction. Table 1 shows the results obtained from the synthesis of a number of 2-aryltellurophenes that were prepared in this manner, with purified yields ranging from 61-88%.



Te Sr	n(<i>n</i> -Bu) ₃ -	Pd(PPh ₃) ₄ , Cul, Cs DMF, 60 °C, ~16 h	→ F 3a-e	R R
Entry	Compd	R	Yield (%)	Mp (°C)
1	3a	CN	64	65–66
2	3b	Н	61	45–46
3	3c	Me	62	47–48
4	3d	NO_2	88	102
5	3e	OMe	63	106–107

The mixed catalyst conditions were next applied to crosscoupling reactions with of di-stannyl tellurophene 2. Here again, aryl iodides were used as coupling partners. As shown in Table 2, the yields obtained for the symmetrical 2,5-diaryltellurophenes ranged from moderate to excellent (42-88%), with yields being highest for those products containing an electron-withdrawing group (entries 1 and 4). The lower yields for the other products may partly be a consequence of our purification method (recrystallization), although the electronic nature of the substituents could have affected the coupling reaction. Ultimately, this Stille approach has allowed us to prepare these 2,5-diaryltellurophenes in a very convenient manner, where the traditional tellurophene ring-forming approach had generally failed in our hands.

In summary, novel mono- and di-stannyl tellurophenes have been prepared and used for the convenient preparation of 2-aryl- and 2,5-diaryltellurophenes by Stille coupling with aryl iodides. The mixed copper-palladium catalyst system, with cesium fluoride as additive, was found to give moderate to excellent yields of the coupling products and appears to perform better than the standard Stille conditions that employ a palladium catalyst alone. This chemistry, which is the first example of the use of stannylated tellurophenes for coupling reactions, has allowed the preparation of arylated derivatives that were not readily available by other methods.

Tellurophene was prepared according to our published procedure.¹⁵ Et₂O was distilled from a sodium/benzophenone still prior to use. Hexanes was dried over CaH₂ and distilled prior to use. Anhydrous DMF was purchased and used as received. ¹H NMR spectra were recorded on a Bruker Avance spectrometer at 300 MHz using the residual solvent peak as an internal standard (δ = 7.26 ppm for CDCl₃, 2.49 ppm for DMSO-*d*₆). ¹³C NMR spectra were recorded at 75 MHz using the residual solvent peak as an internal standard (δ = 77.5 ppm for CDCl₃; 39.5 ppm for DMSO-*d*₆). Melting points were obtained using a Mel-Temp 1201D apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc. High resolution mass spectra were provided by the Mass Spectrometry Laboratory at the University of Alabama. IR was performed with a Perkin–Elmer Spectrum 100 FT-IR spectrometer using ATR.

2-(Tributylstannyl)tellurophene (1)

To a three-neck, round-bottom flask (100 mL) was added tellurophene (3.58 g, 20 mmol) and anhyd Et_2O (50 mL). An addition funnel loaded with (*n*-Bu)₃SnCl (7.16 g, 22 mmol) was placed on the flask. At r.t. and under nitrogen, BuLi (13.75 mL, 1.6 M in hexanes, 22 mmol) was added slowly by syringe to the tellurophene solution, and the resulting tan-colored mixture was stirred at r.t. for 45 min. The mixture was then chilled in a salt-water–ice bath, and the (*n*-Bu)₃SnCl was slowly added. After stirring overnight (~18 h), a small amount of EtOH was added and the mixture was washed with H₂O (3 × 50 mL). The dark-red organic layer was dried over Na₂SO₄ and concentrated by rotary evaporation to give a thin oil. Vacuum distillation (8 cm vigreux fractionating column at ~1 Torr) gave the product **1**, which was pure by GC/MS.

Yield: 5.3 g (57%); pale-yellow liquid; bp 160 °C.

¹H NMR (300 MHz, CDCl₃): δ = 9.28 (d, *J* = 6.4 Hz, 1 H), 8.15 (d, *J* = 3.6 Hz, 1 H), 8.02 (d, *J* = 6.4 Hz, 1 H), 1.60–1.40 (m, 6 H), 1.38–1.33 (m, 6 H), 1.14–1.08 (m, 6 H), 0.95–0.90 (m, 9 H).

¹³C NMR (75 MHz, CDCl₃): δ = 146.0, 140.4, 140.2, 130.5, 29.5, 27.8, 14.2, 12.1.

HRMS (EI): m/z [M⁺] calcd for C₁₆H₃₀¹¹⁸Sn¹³⁰Te: 470.0275; found: 470.0289.

2,5-Bis(trimethylstannyl)tellurophene (2)

To a three-neck, round-bottom flask (500 mL) was added tellurophene (6.1 g, 34 mmol), TMEDA (8.33 g, 71.6 mmol) and hexanes (100 mL). Under nitrogen, the mixture was chilled in an icewater bath and *s*-BuLi (51.1 mL, 1.4 M in cyclohexane) was added dropwise by addition funnel. The resulting light colored suspension was then heated to near reflux for 45 min. The dark-brown mixture was then chilled in an ice-bath again and Me₃SnCl (71.6 mL, 1.0 M in hexanes) was slowly added by addition funnel. After stirring overnight at r.t., sat. aq NH₄Cl (80 mL) was added to the reaction. The layers were separated and the organic layer was washed with aq CuSO₄ until no more precipitate appeared. The extract was filtered over Celite, washed with H_2O (2 × 50 mL), dried over Na_2SO_4 and concentrated to approximately 50 mL on a rotary evaporator. After chilling on ice, crystals (6.8 g) were collected by suction. Concentration of the filtrate and trituration with MeOH gave a second crop of crystals (1.2 g). Both sets of crystals were combined and recrystallized from MeOH.

Yield: 7.1 g (42%); colorless crystals; mp 120 °C (MeOH).

¹H NMR (300 MHz, CDCl₃): δ = 8.31 (s, 2 H), 0.26 (s, 18 H).

¹³C NMR (75 MHz, CDCl₃): δ = 147.3, 146.0, -7.3.

Anal. Calcd for $C_{10}H_{20}Sn_2Te: C, 23.77; H, 3.99$. Found: C, 23.86; H, 4.01.

Synthesis of 2-Aryltellurophenes by Stille Coupling; Typical Procedure

2-(4-Cyanophenyl)tellurophene (3a)

To a 25 mL round-bottom flask was added 4-iodobenzonitrile (0.192 g, 0.84 mmol), Pd(PPh_3)₄ (0.048 g, 42 μ mol), CsF (0.255 g, 1.68 mmol), CuI (0.016 g, 84 μ mol), and then DMF (2 mL). After purging with nitrogen, tellurophene **1** (0.436 g, 0.93 mmol) was added and the mixture was heated at 50–60 °C overnight. After this time, TLC (hexanes–EtOAc, 3:1) showed the disappearance of 4-iodobenzonitrile. The reaction was then extracted with CH₂Cl₂ and washed with H₂O (3 × 10 mL). The extract was dried over Na₂SO₄ and concentrated on a rotary evaporator. The yellow solid was then recrystallized from hexanes (30 mL) to give the product **3a**.

Yield: 0.15 g (64%); fine yellow solid; mp 63 °C.

IR: 3093, 3027, 2919, 2847, 2226, 1598, 1439, 1255, 825, 676 cm⁻¹.

¹H NMR (300 MHz, DMSO-*d*₆): δ = 9.01 (dd, *J* = 1.0, 6.7 Hz, 1 H), 8.20 (dd, *J* = 1.0, 4.1 Hz, 1 H), 7.88 (dd, *J* = 4.1, 6.7 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 8.5 Hz, 2 H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ = 147.3, 144.3, 138.6, 136.2, 133.0, 131.7, 172.2, 119.0, 109.3.

Anal. Calcd for C₇H₁₁NTe: C, 47.05; H, 2.51; N, 4.99. Found: C, 46.82; H, 2.45; N, 4.90.

2-Phenyltellurophene (3b)

Yield: 0.130 g (61%); golden sheets; mp 45–46 °C (MeOH–H₂O). IR: 3071, 3045, 3009, 1592, 1483, 1444, 1256, 1209, 1071, 1033, 843, 752, 679 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.81 (dd, *J* = 3.7, 4.4 Hz, 1 H), 7.82 (d, *J* = 4.2 Hz, 1 H), 7.51–7.48 (m, 1 H), 7.35–7.26 (m, 5 H). ¹³C NMR (75 MHz, CDCl₃): δ = 150.2, 140.6, 139.2, 133.8, 129.4, 128.0, 127.6, 126.0.

HRMS (EI): m/z calcd for C₁₀H₈Te: 253.9659 (¹²⁶Te), 255.9671 (¹²⁸Te), 257.9688 (¹³⁰Te). Found: 253.9655 (¹²⁶Te), 255.9677 (¹²⁸Te), 257.9685 (¹³⁰Te).

2-(4-Methylphenyl)tellurophene (3c)

Yield: 0.115 g (62%); yellow solid; mp 47–48 °C (MeOH–H₂O). IR: 3081, 3056, 3017, 2917, 2860, 1725, 1603, 1535, 1504, 1445, 1256, 1120, 807, 746, 706, 688 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.76 (dd, *J* = 1.5, 6.6 Hz, 1 H), 7.78 (m, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.14 (m, 2 H), 2.36 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 150.3, 139.1, 138.1, 136.8, 133.2, 130.1, 127.4, 125.2, 21.6.

HRMS (EI): m/z calcd for $C_{11}H_{10}$ Te: 267.9816 (¹³⁰Te), 269.9827 (¹²⁸Te), 271.9845 (¹²⁶Te). Found: 267.9816 (¹³⁰Te), 269.9828 (¹²⁸Te), 271.9848 (¹²⁶Te).

2-(4-Nitrophenyl)tellurophene (3d)

Yield: 0.220 g (88%); yellow-orange crystals; mp 102 $^{\circ}\mathrm{C}$ (hexanes).

IR: 3097, 3071, 1584, 1522, 1500, 1430, 1370, 1317, 1260, 1207, 1184, 1113, 850, 828, 749, 686, 679 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 9.02 (dd, *J* = 1.2, 6.8 Hz, 1 H), 8.20 (d, *J* = 8.8 Hz, 2 H), 7.98 (dd, *J* = 1.2, 4.1 Hz, 1 H), 7.88 (dd, *J* = 4.0, 6.5 Hz, 1 H), 7.60 (d, *J* = 8.8 Hz, 2 H).

¹³C NMR (75 MHz, CDCl₃): δ = 147.2, 146.9, 139.5, 136.6, 132.1, 130.0, 127.8, 124.9.

Anal. Calcd for $C_{10}H_7NO_2Te$: C, 39.93; H, 2.35; N, 4.66. Found: C, 40.00; H, 2.24; N, 4.61.

2-(4-Methoxyphenyl)tellurophene (3e)

Yield: 0.150 g (63%); golden sheets; mp 106–107 °C (hexanes) (Lit. 16 111–112 °C).

IR: 3083, 3019, 2968, 2936, 2913, 2840, 1600, 1571, 1554, 1533, 1501, 1442, 1415, 1307, 1283, 1257, 1241, 1178, 1022, 824, 812, 793, 686 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.72 (dd, *J* = 6.8, 1.2 Hz, 1 H), 7.77 (dd, *J* = 6.8, 4.0 Hz, 1 H), 7.68 (d, *J* = 1.2, 4.0 Hz, 1 H), 7.42 (dd, *J* = 6.7, 2.2 Hz, 2 H), 6.87 (dd, *J* = 6.7, 2.2 Hz, 2 H), 3.83 (s, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 159.8, 149.9, 139.1, 133.5, 132.7, 128.6, 124.7, 114.8, 55.9.

Anal. Calcd for $C_{11}H_{10}$ OTe: C, 46.23; H, 3.53. Found: C, 46.17; H, 3.49.

2,5-Diaryltellurophenes by Stille Coupling; Typical Procedure 2,5-Bis(4-cyanophenyl)tellurophene (4a)

To a 25 mL round-bottom flask was added 4-iodobenzonitrile (0.498 g, 2 mmol), Pd(PPh₃)₄ (0.107 g, 93 µmol), CsF (0.565 g, 3.72 mmol), CuI (0.035 g, 186 µmol) and then DMF (4 mL). After purging with nitrogen, 2,5-bis(trimethylstannyl)tellurophene (**2**; 0.467 g, 0.93 mmol) was added and the mixture was heated at 50–60 °C overnight (~16 h). The reaction was then diluted with MeOH and the resulting precipitate was collected by suction. This precipitate was dissolved in CH₂Cl₂ and gravity filtered to remove Pd catalyst. The filtrate was then partially concentrated on a rotary evaporator (to about half volume) and diluted with hexanes (about equal volume). The solution was then further concentrated until nearly all the CH₂Cl₂ had evaporated. The resulting solid (0.302 g, 88%) was collected by suction and recrystallized from MeOH (~130 mL) to give the product **4a**.

Yield: 0.302 g (88%); fibrous golden-red crystals; mp 231-232 °C.

IR: 3025, 2220, 1920, 1680, 1595, 1547, 1537, 1491, 1456, 1408, 1201, 1174, 898, 837, 797 $\rm cm^{-1}.$

¹H NMR (300 MHz, DMSO- d_6): δ = 8.30 (s, 2 H), 7.89 (d, J = 8.0 Hz, 4 H), 7.75 (d, J = 8.0 Hz, 4 H).

¹³C NMR (75 MHz, CDCl₃): δ = 148.3, 143.4, 137.3, 133.0, 127.3, 118.9, 109.9.

Anal. Calcd for $C_{18}H_{10}N_2$ Te: C, 56.61; H, 2.64; N, 7.34. Found: C, 56.74; H, 2.64; N, 7.36.

2,5-Diphenyltellurophene (4b)

Yield: 0.130 g (42%); light-yellow sheets; mp 224–225 °C (CHCl₃– MeOH) (Lit. 17 220–224 °C).

IR: 3052, 3008, 1592, 1481, 1461, 1439, 887, 809, 743, 683 cm⁻¹.

¹H NMR (300 MHz, DMSO- d_6): δ = 8.02 (s, 2 H), 7.57–7.54 (m, 4 H), 7.39–7.29 (m, 6 H).

¹³C NMR (75 MHz, DMSO- d_6): $\delta = 148.1$, 139.7, 134.9, 129.6, 128.3, 126.9.

2,5-Bis(4-methylphenyl)tellurophene (4c)

Yield: 0.158 g (47%); grey sheets; mp 239–240 °C (CH₂Cl₂–hexanes).

IR: 3014, 2911, 2855, 2722, 1893, 1545, 1497, 1462, 1287, 1122, 893, 796 $\rm cm^{-1}.$

¹H NMR (300 MHz, DMSO-*d*₆): δ = 7.92 (s, 2 H), 7.42 (d, J = 7.8 Hz, 4 H), 7.16 (d, J = 7.8 Hz, 4 H), 2.29 (s, 6 H).

¹³C NMR (75 MHz, DMSO- d_6): $\delta = 147.8$, 138.1, 137.4, 134.6, 130.5, 127.1, 21.6.

Anal. Calcd for $C_{18}H_{16}$ Te: C, 60.07; H, 4.48. Found: C, 59.79; H, 4.51.

2,5-Bis(4-nitrophenyl)tellurophene (4d)

Yield: 0.261 g (67%); dark-red solid; mp 271–272 °C (CH₂Cl₂– hexanes).

IR: 3109, 3063, 2911, 1581, 1539, 1495, 1446, 1322, 1294, 1276, 1109, 841, 796, 725, 683 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.24 (d, *J* = 9.4 Hz, 4 H), 8.05 (s, 2 H), 7.61 (d, *J* = 9.4 Hz, 4 H).

¹³C NMR (75 MHz, CDCl₃): δ = 148.9, 147.5, 146.0, 137.2, 127.6, 125.0.

Anal. Calcd for $C_{16}H_{10}N_2O_4\text{Te:}$ C, 45.55; H, 2.39; N, 6.64. Found: C, 45.43; H, 2.38; N, 6.65.

2,5-Bis(4-methoxyphenyl)tellurophene (4e)

Yield: 0.154 g (42%); golden sheets; mp 278 °C (acetone).

IR: 3016, 2949, 2836, 1600, 1567, 1544, 1498, 1466, 1439, 1411, 1273, 1240, 1178, 1113, 1028, 1006, 831, 822, 799, 790 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.66 (s, 2 H), 7.40 (d, *J* = 6.7 Hz, 4 H), 6.87 (d, *J* = 6.7 Hz, 4 H), 3.83 (s, 6 H).

¹³C NMR (75 MHz, CDCl₃): δ = 159.3, 146.7, 133.0, 132.8, 127.8, 114.3, 55.4.

Anal. Calcd for $C_{18}H_{16}O_2Te: C, 55.16; H, 4.11$. Found: C, 55.09; H, 4.16.

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