Catalytic and Stoichiometrically Directed Synthesis of Less Accessible Bromothiophenes and Bromobithiophenes. Trapping and Characterization of Catalytic Intermediates of *trans*-PdBr($C_4H_{4-n}Br_{n-1}S$-*C*)(PPh_3)$_2$ (n = 1−4), *trans*-PdBr($C_8H_4BrS_2$-*C*)(PPh_3)$_2$, and *trans,trans*-Pd_2Br_2(μ-$C_8H_{6-n}Br_{n-2}S_2$-*C,C′*)(PPh_3)$_4$ (n = 2, 4)

Yang Xie,[†] Bo-Mu Wu,[‡] Feng Xue,[‡] Siu-Choon Ng,*[,†] Thomas C. W. Mak,*[,‡] and T. S. Andy Hor*[,†]

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge, Singapore 119260, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received January 13, 1998

A facile one-pot procedure for synthesizing isomerically pure bromothiophenes and bromobithiophenes was achieved by palladium-catalyzed hydrodebromination. The compounds synthesized include 2,3,4-tribromothiophene (**2**), 3,4-dibromothiophene (**3**), 2,3-dibromothiophene (**7**), 3-bromothiophene (**4**), 3,3′,5-tribromo-2,2′-bithiophene (**10**), 3,3′-dibromo-2,2′-bithiophene (**11**), and 3-bromo-2,2′-bithiophene (**12**). The regioselectivity is catalytically dictated by the metalation site, whereas the extent of debromination is conveniently controlled by the stoichiometry and substrate quantity. Under favorable conditions, complete debromination takes place, giving rise to thiophene and bithiophene. The catalytic intermediates *trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (**16**), *trans,trans*-Pd_2Br_2(μ-$C_8H_2Br_2S_2$-*C,C′*)(PPh_3)$_4$ (**17**), *trans,trans*-Pd_2Br_2(μ-$C_8H_4S_2$-*C,C′*)(PPh_3)$_4$ (**18**), *trans*-PdBr($C_8H_4BrS_2$-*C*)(PPh_3)$_2$ (**19**), *trans*-PdBr(C_4H_3S-*C*)(PPh_3)$_2$ (**20**), and *trans*-PdBr(3,4,5-C_4Br_3S-*C*)(PPh_3)$_2$ (**21**) were isolated. Palladium insertion invariably occurs at the C(α)−Br bonds of the thiophene or bithiophene rings. Single-crystal X-ray crystallography analyses of **20**, **16**, and **21** gave three mononuclear square-planar Pd(II) thienyl structures with phosphines in *trans* orientations.

Introduction

Halothiophenes and halobithiophenes are widely used as substrates for a variety of C−C coupling reactions.[1] Especially common are the brominated derivatives, which serve as important intermediates in the syntheses of glassy materials,[2] conducting polymers,[3] and biologically active compounds.[4] These bromothiophenes and bromobithiophenes are usually prepared from direct bromination of thiophene or 2,2′-bithiophene with Br_2.[5] However, this usually gives a mixture of products, and the electronic factors favor the formation of 2-bromothiophene (**22**),[6] 2,5-dibromothiophene,[7] 2,3,5-tribromothiophene (**6**),[8] tetrabromothiophene (**1**),[9] 5-bromo-2,2′-bithiophene (**15**), 5,5′-dibromo-2,2′-bithiophene (**14**), or 3,3′,5,5′-tetrabromo-2,2′-bromothiophene (**9**).[10] For the syntheses of other isomers, alternative methods must be used. Common methodologies include the use of thienyllithium derivatives for the synthesis of 3-bromothiophene (**4**; from **6**), 2,3-dibromothiophene (**7**; from **6**),[11] 3,4-dibromothiophene (**3**; from **1**), and 2,3,4-tribro-

[†] National University of Singapore.
[‡] The Chinese University of Hong Kong.

(1) Dauria, M. *J. Photochem. Photobiol. A* **1995**, *91*, 187. Dagostini, A.; Dauria, M. *J. Chem. Soc., Perkin Trans.* **1994**, 1245. Zhang, Y. H.; Hornfeldt, A. B.; Gronowitz, S. *J. Heterocycl. Chem.* **1995**, *32*, 435.
(2) Whitaker, C. M.; McMahon, R. J. *J. Phys. Chem.* **1996**, *100*, 1081.
(3) Zhao, Z. S.; Pickup, P. G. *J. Electroanal. Chem.* **1996**, *404*, 55. Ng, S. C.; Chan, H. S. O.; Miao, P. *J. Mater. Sci. Lett.* **1997**, *16*, 1170. Chan, H. S. O.; Ng, S. C.; Seow, R. S. H.; Moderscheim, M. J. G. *J. Mater. Chem.* **1992**, *2*, 1135. Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476. Tanguy, J.; Pron, A.; Zargoska, M.; Kulszewics-Bajer, I. *Synth. Met.* **1991**, *45*, 81. Zargoska, M.; Kulszewics-Bajer, I.; Pron, A.; Firlej, I.; Bernier, P.; Galtier, M. *Synth. Met.* **1991**, *45*, 385. Roncali, J. *Chem. Rev.* **1992**, *92*, 711. Chan, H. S. O.; Ng, S. C. *Prog. Polym. Sci.*, in press. Chan, H. S. O.; Ng, S. C.; Huang, H. H.; *Prog. Pac. Polym. Sci., Proc. Pac. Polym. Conf.* **1994**, *3*, 237. Chan, H. S. O.; Ng, S. C.; Huang, H. H.; Seow, R. S. H. *J. Chem. Res., Synop.* **1996**, 232; *J. Chem. Res., Miniprint* **1996**, 1285.
(4) Kim, B. M.; Guare, J. P.; Vacca, J. P.; Michelson, S. R.; Darke, P. L.; Zugay, J. A.; Emini, E. A.; Schlief, W.; Lin, J. H.; Chen, I. W.; Vastag, K.; Anderson, P. S.; Huff, J. R. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 185. Gronowitz, S.; Zhang, Y.; Hornfeldt, A. *Acta Chem. Scand.* **1992**, *46*, 654. Prugh, J. D.; Hartman, G. D.; Mallorga, P. J.; McKeever, B. M.; Michelson, S. R.; Murcko, M. A.; Schwan, H.; Smith, R. L.; Sondey, J. M.; Springer, J. P.; Sugrue, M. F. *J. Med. Chem.* **1991**, *34*, 1805. D'Auria, M.; De Mico, A.; D'Onofrio, F.; Piancatelli, G. *J. Chem. Soc., Perkin Trans.* **1987**, *1*, 1777.
(5) Mozingo, R.; Harris, S. A.; Wolf, D. E.; Hoffhine, C. E.; Easton, N. R.; Folkers, K. *J. Am. Chem. Soc.* **1945**, *67*, 2092.
(6) Tamaru, Y.; Yamada, Y.; Yoshida, Z. *Tetrahedron* **1979**, *35*, 329.
(7) Markovitz, M. Dissertation, New York University, 1963; *Diss. Abstr.* **1964**, *24*, 3100.
(8) Gronowitz, S.; Raznikiewicz, T. *Org. Synth.* **1964**, *44*, 9. Gronowitz, S. *Acta Chem. Scand.* **1959**, *13*, 1045.
(9) Gronowitz, S.; Moses, P.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 267.
(10) Khor, E.; Ng, S. C.; Li, H. C.; Chai, S. *Heterocycles* **1991**, *32*, 1805.

S0276-7333(98)00014-4 CCC: $15.00
Publication on Web 08/08/1998

Table 1. Catalytic Debromination of Bromothiophenes[a]

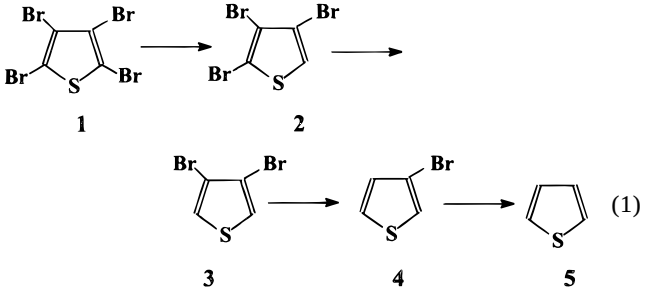
					product yield (%)						
entry no.	substrate	$NaBH_4$:substrate	time (h)	conversn (%)	**2**	**6**	**7**	**8**	**3**	**4**	**5**
1	**1**	2.5:1	6	100	93	0	0	0	7	0	0
2	**1**	5:1	8	100	0	0	0	0	95	4	trace
3[b]	**1**	2.5:1	6	91	72	0	0	0	10	8	trace
4[c]	**1**	2.5:1	6	85	70	0	0	0	8	6	trace
5	**2**	2:1	6	100			0	0	90	8	2
6	**6**	1.5:1	6	100			92	6	0	1	trace
7	**6**	3.3:1	7	100			2	trace	0	81	16
8	**7**	1.5:1	6	100						82	17
9	**8**	1.5:1	5	100						83	16
10	**3**	1.5:1	7	100						83	16
11	**1**	10:1	22	100							~100
12	**2**	7.8:1	18	100							~100
13	**3**	4.5:1	15	100							~100
14	**4**	2:1	8	100							~100
15	**6**	7:1	14	100							~100
16	**7**	4:1	10	100							~100
17	**8**	4.5:1	8	100							~100
18	**22**	1.5:1	3	100							~100

[a] Conditions: substrate, 1 mmol; catalyst, $Pd(PPh_3)_4$, 1 mol equiv of substrate; solvent, CH_3CN, 10 mL; 70 °C. The conversion and product distributions were analyzed by GC. [b] First recycle of catalyst used in entry 1. [c] Second recycle of catalyst used in entry 1.

mothiophene (**2**; from **1**),[12] Grignard reagents,[13,14] zinc reductive reactions[8] (for example, of **6**, **1**, and **9**, giving **4**, **3**, and **11**, respectively), and rearrangement of 2,5-dibromothiophene by $NaNHC_6H_5$ in liquid NH_3, giving **3**.[15] These approaches are generally handicapped by the required use of expensive and/or air-sensitive reagents and two-step or multistep synthetic routes. The synthetic utilities of these materials demand a simple preparative method which can give products in good yields and isomerically pure forms. In a recent communication, we reported a catalytic approach to the debromination of 2,3,5-tribromothiophene.[16] In this paper, we extended this strategy to other polybromothiophenes and polybromobithiophenes, whereby a facile one-pot synthesis for the less accessible brominated thiophene and bithiophene isomers is accomplished. The catalytic mechanism will also be discussed.

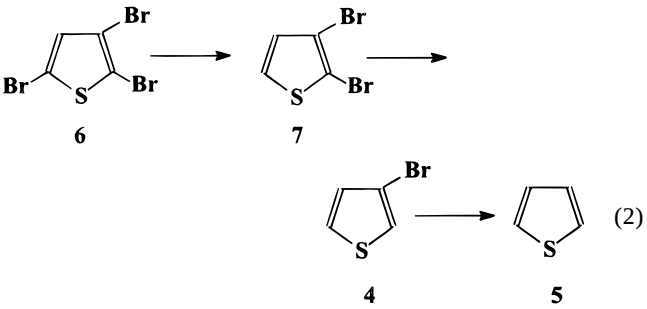
Results and Discussion

Our previous results established the efficiency of $Pd(PPh_3)_4$ as a catalyst when $NaBH_4$ is the reducing agent.[16] In this work, a series of bromothiophenes are examined for their debromination behaviors under catalytic conditions (Table 1). Debromination of tetrabromothiophene (**1**; eq 1) at a $NaBH_4$:substrate molar ratio of 2.5:1 in the presence of 1% of $Pd(PPh_3)_4$ catalyst at 70 °C results in a total (100%) conversion of the substrate, giving predominantly (93%) 2,3,4-tribromothiophene (**2**; Table 1, entry 1). Increasing the $NaBH_4$:substrate ratio to 5.0:1 remarkably gives almost exclusively (95%) 3,4-dibromothiophene (**3**; entry 2). When the catalyst (of entry 1) is recovered and recycled, it is still active, although the yields of **2** are generally



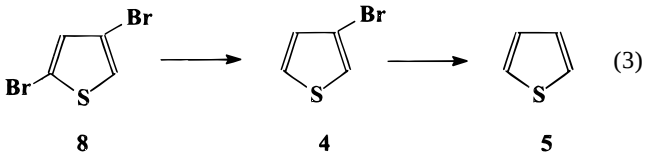
(1)

20−25% lower (entries 3 and 4). Similar work on **2** gives **3** (entry 5), which illustrates that **2** is a probable precursor to its lower brominated analogues. Similarly, 2,3,5-tribromothiophene (**6**) almost exclusively gives **7** (entry 6) or **4** (entry 7), depending on the $NaBH_4$ concentration (eq 2). The three dibromothiophene



(2)

isomers, *viz.* **3**, **7**, and **8**, inevitably give **4** as the isomerically pure monobromothiophene product (>80% yields) (entries 8−10) (eqs 1−3). Complete debromina-



(3)

tion of **3**, **6**, **7**, and **8** giving **4** and thiophene, **5**, as a side-product is also evident (entries 7−10) (eqs 1−3). In the presence of a 2−3-fold excess of $NaBH_4$, all bromothiophenes, **1**−**8**, regardless of the bromine con-

(11) Lawesson, S.-O. *Ark. Kemi* **1957**, *11*, 317, 325, 373.
(12) Decroix, B.; Morel, J.; Paulmier, C.; Paastour, P. *Bull. Soc. Chim. Fr.* **1972**, 1848.
(13) Troyanowsky, C. *Bull. Soc. Chim. Fr.* **1955**, 424. Gronowitz, S. *Ark. Kemi* **1954**, *7*, 267.
(14) Nemec, M.; Vopatrna, P.; Janda, M.; Srogl, J.; Stibor, I. *Synthesis* **1972**, 545.
(15) Reinecke, M. G.; Adickes, H. W.; Pyun, C. *J. Org. Chem.* **1971**, *36*, 2690.
(16) Xie, Y.; Ng, S. C.; Hor, T. S. A.; Chan, H. S. O. *J. Chem. Res., Synop.* **1996**, *3*, 150.

Table 2. Catalytic Debromination of Bromobithiophenes[a]

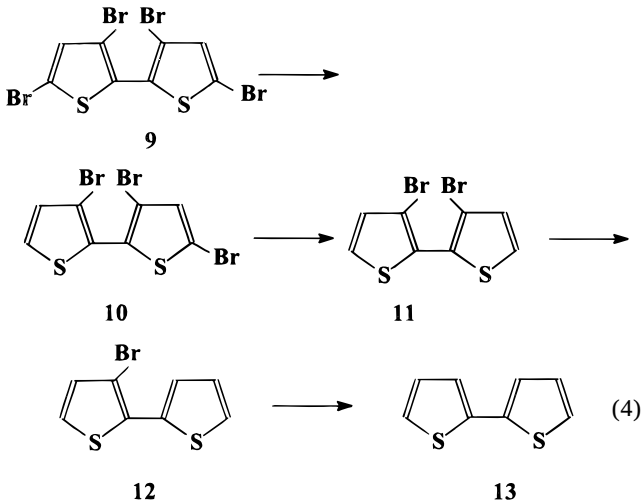
entry no.	sub-strate	$NaBH_4$: substrate	time (h)	conversn (%)	product yield (%)				
					10	**11**	**12**	**15**	**13**
1	**9**	1.5:1	4	100	80	20	trace	0	0
2	**9**	2.0:1	4	100	45	52	3	0	0
3	**9**	3.5:1	5	100	trace	88	12	0	0
4	**9**	5.0:1	6	100	0	14	80	0	6
5	**14**	1.5:1	3	100				81	19
6	**9**	8:1	12	100					~100
7	**14**	4:1	10	100					~100

[a] Conditions: substrate, 1 mmol; catalyst, $Pd(PPh_3)_4$, 1 mol equiv of substrate; solvent, CH_3CN, 10 mL; 70 °C. The conversion and product distributions were analyzed by GC using a HP5890 Series II Plus gas chromatograph with an HP-1 capillary column.

tent, undergo complete debromination to give near-quantitative yields of thiophene (**5**) after 24 h (entries 11−17). This demonstrates the high catalytic efficiency of the present system toward hydrodebromination.

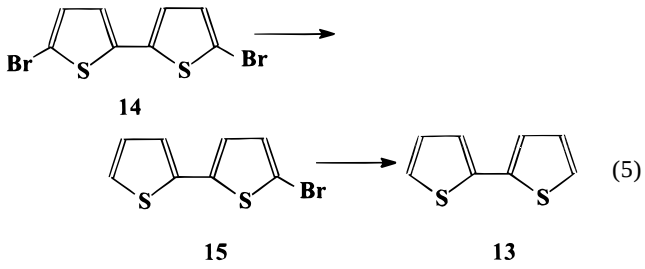
On the basis of these pilot results, large-scale preparations of 2,3,4-tribromothiophene (**2**), 2,3-dibromothiophene (**7**), 3,4-dibromothiophene (**3**), and 3-bromothiophene (**4**) have been achieved in yields of 82%, 83%, 86%, and 81% respectively. These catalytic yields are at least comparable with those literature yields of **2** (85%[11] or 70%,[12] both by *n*-C_4H_9Li from **1**), **3** (75%[14] by Mg, 68%[8] by Zn, or 75%[11] by *n*-C_4H_9Li on **1** or 80%[15] by $NaNHC_6H_4$ and NH_3 on 2,5-dibromothiophene), **7** (<12%[17] by C_2H_5MgBr on **6** or 97%[18] by Br_2 and CCl_4 on 3-bromothiophene (**4**)), and **4** (71%[8] by Zn or 84%[11] by *n*-C_4H_9Li on **6**). Our "one-pot" method avoids the use of expensive and/or air-sensitive reagents. It is notable that 2,3-dibromothiophene (**7**) can be obtained in good yield (92%, entry 6), whereas its preparation in a Grignard reaction is problematic and gives yields <12%.[17] Although **7** has been synthesized in good yield (97%) from the bromination of 3-bromothiophene (**4**), this method is not straightforward since **4** needs to be prepared carefully from another precursor **6**.[8,18]

This synthetic method can be extended to higher bromobithiophenes. For example, debromination of **9** giving **10** (eq 4) in 80% yield occurs at a $NaBH_4$: substrate molar ratio of 1.5:1 with **11** as a minor product (Table 2, entry 1). Increasing the molar ratio to 3.5:1



(4)

gives **11** as the dominant product (88%) and **12** as a byproduct (entry 3). Further increase to a 5:1 ratio gives chiefly **12** (80%) (entry 4). It is evident that this synthesis can be targeted at a specific product by controlling the extent of debromination through the measured use of the reductant. The same approach can be used to convert 5,5′-dibromo-2,2′-bithiophene (**14**) to 5-bromo-2,2′-bithiophene (**15**; 81%) (eq 5) (Table 2, entry



(5)

5). Complete debromination of **9** and **14**, giving bithiophene (**13**), is achieved when $NaBH_4$ is in excess (entries 6 and 7). These results prompted us to carry out preparative-scale synthesis of **10**−**12** (yields 75%, 85%, and 76%, respectively). The yields of **11** and **12** are comparable with those from other methods.[10] Compound **12** is a useful precursor for a series of 4-substituted 2,2′-bithiophenes.[19]

A distinct advantage of this catalytic approach is witnessed in the total conversion of the bromothiophenes or bromobithiophenes tested. The high regioselectivity of the products offers a synthetic advantage to this strategy. These results suggest that the conversion from higher to lower brominated thiophenes or bithiophenes is a sequential process driven by the catalyst and directed by the amount of the reductant used. Under catalytic influence, the α-position is most susceptible to substitution. The preferential formation of **7** (from **6**) over its isomers (**8** or **3**) has been described in our earlier communication.[16] Exclusive formation of **4** from both **6** and **7** without other monobromothiophene isomers is a manifestation of this α-directing effect. Degradation of **1**-**8** to thiophene (entries 11−17 in Table 1) and of **9** and **10** to 2,2′-bithiophene (entries 6 and 7 in Table 2) demonstrates a technological application of this system in the hydrodebromination of polybromothiophenes and polybromobithiophenes.

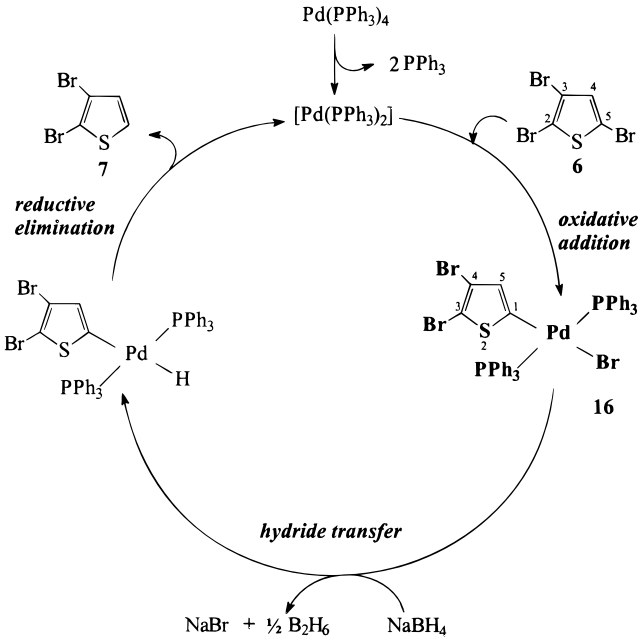
These catalytic reactions proceed through repetitive and sequential oxidative addition of the Pd(0) active catalyst with the C−Br bonds of the thiophene. The C−Br bond adjacent to the thiophenic sulfur is the most reactive and holds the key to the substitution at the α-position[20] (Scheme 1). This mechanism is supported by the trapping of the key intermediate *trans*-$PdBr(3,4\text{-}C_4HBr_2S\text{-}C)(PPh_3)_2$ (**16**), isolated from a stoichiometric reaction of **6** with $Pd(PPh_3)_4$. The single ^{31}P resonance (22.9 ppm) is consistent with a model containing *trans*-oriented phosphines. The high-field shift of the sole proton of **6** (i.e. the proton at the 4 (or *β*-)-position) (6.90 ppm) upon complex formation (5.56 ppm) is an indication of metalation at the adjacent carbon: *viz.*, at either the 3- or 5-position in **6** (numbering scheme illustrated

(17) Gronowitz, S. *Ark. Kemi* **1958**, *12*, 115.
(18) Gronowitz, S.; Dahlgren, K. *Ark. Kemi* **1963**, *21*, 201.
(19) Rasmussen, S. C.; Pichens, J. C.; Hutchison, J. E. *J. Heterocycl. Chem.* **1997**, *34*, 285.
(20) Xie, Y.; Ng, S. C.; Wu, B., Xue, F., Mak, T. C. W.; Hor, T. S. A. *J. Organomet. Chem.* **1997**, *531*, 175.

Table 3. Crystallographic Data and Structure Refinement Details for *trans*-PdBr(C_4H_3S-*C*)(PPh_3)$_2$ (20), *trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (16), and *trans*-PdBr(3,4,5-C_4Br_3S-*C*)(PPh_3)$_2$ (21)

	20	16	21
formula	$C_{40}H_{33}BrP_2PdS$	$C_{40}H_{31}Br_3P_2PdS$	$C_{40}H_{30}Br_4P_2PdS$
mol wt	794.0	951.7	1030.7
color and habit	yellow prism	yellow prism	yellow prism
cryst size (mm^3)	0.30 × 0.30 × 0.40	0.30 × 0.24 × 0.18	0.20 × 0.20 × 0.30
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbcn* (No. 60)	*C*2/*c* (No. 15)	$P2_1/n$
T, K	294	294	294
a, Å	19.354(1)	25.681(1)	11.361(2)
b, Å	10.760(2)	13.546(1)	13.049(3)
c, Å	16.451(1)	11.619(1)	26.670(5)
β, deg	90	113.87(1)	102.00(3)
F(000)	1600	1872	2008
V, $Å^3$	3426(2)	3696(2)	3867(2)
Z	4	4	4
abs coeff, mm^{-1}	1.891	3.939	4.777
ρ_{calcd}, g cm^{-3}	1.539	1.710	1.770
index ranges	$-24 \le h \le 24$, $-13 \le k \le 13$, $0 \le l \le 20$	$0 \le h \le 32$, $-17 \le k \le 17$, $-14 \le l \le 13$	$0 \le h \le 13$, $0 \le k \le 15$, $-31 \le l \le 30$
no. of rflns collected	11 410	6356	7181
no. of indep rflns	3606 (R_{int} = 2.36%)	3696 (R_{int} = 6.77%)	6815 (R_{int} = 2.69%)
final *R* Indices (obsd data)	R = 6.14%, wR = 5.93%	R = 5.29%, wR = 13.45%	R = 3.75%, wR = 4.00%
goodness of fit	1.49	1.12	1.12
largest diff peak and hole (e $Å^{-3}$)	0.75 and −0.87	0.69 and −0.88	0.42 and −0.52

Scheme 1. Proposed Catalytic Mechanism for the Debromination of 2,3,5-Tribromothiophene



in Scheme 1). The metalated carbon is deshielded (148.1 ppm) compared to other carbon resonances (110.6−132.2 ppm), although the exact position of palladation in the thienyl moiety cannot be unambiguously assigned on the basis of these spectra.

A single-crystal X-ray analysis was carried out to confirm the solid-state structure of **16** (Figure 1, Table 3). It reveals a *trans* Pd(II) square-planar thienyl complex arising from oxidative addition of **6** to Pd(0). This structure provides unequivocal evidence that metalation occurs preferentially at the carbon between the sulfur atom and the 4 (or β-)-carbon. Subsequent hydrodebromination of **16** followed by proton transfer would account for the formation of **7** (Scheme 1). Reaction of **16** with $NaBH_4$ in CD_3CN in an NMR tube at 60 °C gives a weak and short-lived singlet at −11.06 ppm attributed to the fragile Pd−H moiety. In $CDCl_3$,

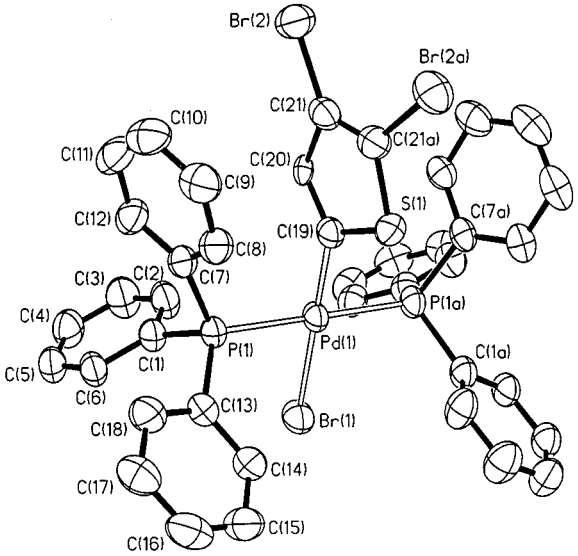


Figure 1. ORTEP plot of the molecular structure of *trans*-PdBr-σ-3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (**16**) (30% probability ellipsoids).

the ^1H spectrum shows two species (δ −9.73 ppm, dd, $^2J_{PH}$ = 82.5 Hz, $^2J_{PH}$ = 3.3 Hz; δ −11.86 ppm, t, $^2J_{PH}$ = 8.7 Hz) attributable to the *cis* and *trans* hydrido thienyl complexes. Similar palladium hydrido complexes have been reported.[21] The hydrido resonances are not sustainable. GC/MS assay of the resultant mixture confirms **7** as the predominant product.

The substrate **6** is an ideal model for crystallographic analysis because it contains the maximum regioselectivity information. Although α-substitution (i.e. at the 2- and 5-positions) is expected, the β-position cannot be ignored, as it also offers some steric and electronic (activation from neighboring bromine) advantages. Be-

(21) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554. Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *Inorg. Chem.* **1991**, *30*, 2005. Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803. Saito, T.; Munakata, H.; Imoto, H. *Inorg. Synth.* **1977**, *17*, 83. Green, M. L. H.; Munakata, H. *J. Chem. Soc., Dalton Trans.* **1974**, 269.

tween the two α-bromine atoms, the one at the 2-position is electronically favored because of possible activation from both neighboring atoms, *viz*. Br and S; the 5-bromine has an advantage from a steric viewpoint. These differences are subtle, but they decide the metalation site and hence determine the regioselectivity of the reaction.

Despite the presence of sterically demanding ligands, **16** maintains a near-ideal square-planar geometry with virtually linear disposition of the *trans* ligands (∠P(1)−Pd(1)−P(1a) = 179.5(1)° and ∠Br(1)−Pd(1)−C(19) = 180.0°) (Figure 1, Table 4). To minimize repulsion between the thienyl and phenyl planes so as to support a strong Pd−thienyl interaction (Pd(1)−C(19) = 1.998(3) Å), the thienyl plane is tilted at a dihedral angle of 109.6° to the Pd(II) coordination plane. There is no indication of η^1(S) coordination or any η^2− or η^4−metal interaction using the π-bonds on the thienyl ring, even though such coordination modes are commonly found in other metals.[22] The strong *trans* influence of the thienyl group gives a significantly long Pd−Br bond (2.5089(8) Å) compared to many other Pd^{II}−Br bonds, e.g. in *trans*-[$PdBr_2(PPh_3)_2$] (2.425(1) Å)[23] and *trans*-$PdBr_2$[2-(2′-thienyl)pyridine)]$_2$ (2.431(1) Å).[24] The weakness of this Pd−Br bond also supports the ready hydroreduction of **16**, which is a crucial step governing the efficiency of the catalyst. To confirm that the regioselective attack is independent of the degree of bromination of the thiophene ring, we have also determined the X-ray crystallographic structures of *trans*-PdBr(C_4H_3S-*C*)(PPh_3)$_2$ (**20**) (Figure 2) and *trans*-PdBr(3,4,5-C_4Br_3S-*C*)(PPh_3)$_2$ (**21**) (Figure 3), which are obtained similarly from **22** and **1**, respectively. Both reveal similar σ-thienyl structures with metalation at the C atom next to the thiophene sulfur and two *trans*-directing phosphines. The slight and progressive weakening of the Pd−C bonds from **20** (1.993(4) Å) to **16** (1.998(3) Å) and to **21** (2.004(8) Å) is consistent with the weaker donicity of the thienyl ligand as its size or bromo content increases. The corresponding strengthening of the Pd−P bonds also emphasizes the importance of electronic over steric effects. Very notably, the weaker σ-effect of the (higher) bromothienyl derivative weakens its *trans* influence. This is translated to a progressive strengthening of the Pd−Br bonds from **20** (2.526(1) Å) to **16** (2.5089(8) Å) and to **21** (2.483(1) Å). The weakness of the Pd−Br bonds (in **20** and **16**) is consistent with the ease of debromination of **22** and **6**, respectively. It takes a shorter time and/or less $NaBH_4$ to complete the degradation of **22** and **6** compared to that of **1** (Table 1, entries 1, 6, and 18).

While the unsubstituted thienyl ring (in **20**) and the bromide thienyl rings (in **16**) are essentially planar (mean deviation 0.008 and 0.031 Å, respectively), the tribromothienyl ring (in **21**) forces a slight but noticeable distortion on the metal coordination plane (mean deviation 0.069 Å, with the P atoms on one side and the Br(1) and C(19) atoms on the other), as well as some angular distortions from linearity in ∠P(1)−Pd(1)−P(2) (174.6(1)°) and ∠C(1)−Pd(1)−Br(1) (176.7(2)°). The metalation imparts little effect on the strength of the thienyl C−Br bonds (e.g. mean C−Br = 1.854(5) Å in **16**, and mean C−Br = 1.868 Å in **21**, compared to C−Br = 1.865 Å in 2-bromothiophene[25]). This is consistent with the proposal that activation of the C−Br bond takes place via complex formation.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *trans*-PdBr(C_4H_3S-*C*)(PPh_3)$_2$ (20), *trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (16), and *trans*-PdBr(3,4,5-C_4Br_3S-*C*)(PPh_3)$_2$ (21)

(a) *trans*-PdBr(C_4H_3S-*C*)(PPh_3)$_2$ (**20**)

Bond Lengths

Pd(1)−C(19)	1.993(4)	Pd(1)−Br(1)	2.526(1)
Pd(1)−P(1)	2.351(1)	C(21)−C(21a)	1.361(1)
S(1)−C(19)	1.710(3)	S(1)−C(21a)	1.709(3)
C(19)−C(20)	1.363(5)	C(20)−C(21)	1.430(4)
P(1)−C(6)	1.826(4)	P(1)−C(18)	1.838(5)
P(1)−C(12)	1.826(4)		

Bond Angles

C(19)−Pd(1)−P(1)	88.8(1)	P(1)−Pd(1)−P(1a)	177.5(1)
S(1)−C(19)−Pd(1)	120.7(1)	C(20)−C(19)−Pd(1)	136.2(2)
C(19)−S(1)−C(21a)	93.2(2)	S(1)−C(19)−C(20)	103.1(3)
C(19)−C(20)−C(21)	125.5(5)	C(20)−C(21)−C(21a)	100.6(3)
S(1)−C(21a)−C(21)	117.5(1)	C(6)−P(1)−Pd(1)	113.3(2)
C(12)−P(1)−Pd(1)	110.7(1)	C(18)−P(1)−Pd(1)	120.5(1)

(b) *trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (**16**)

Bond Lengths

Pd(1)−C(19)	1.998(3)	Pd(1)−Br(1)	2.5089(8)
Pd(1)−P(1)	2.340(1)	S(1)−C(19)	1.710(5)
S(1)−C(21a)	1.710(5)	C(21)−Br(2)	1.854(5)
C(21)−C(21a)	1.362(6)	P(1)−C(1)	1.825(5)
P(1)−C(7)	1.828(5)	P(1)−C(13)	1.830(5)

Bond Angles

C(19)−Pd(1)−P(1)	89.8(1)	P(1)−Pd(1)−P(1a)	179.5(1)
S(1)−C(19)−C(20)	107.6(3)	C(20)−C(19)−Pd(1)	133.4(2)
S(1)−C(19)−Pd(1)	119.0(1)	C(19)−S(1)−C(21a)	90.5(2)
C(19)−C(20)−C(21)	120.9(3)	C(20)−C(21)−C(21a)	102.5(1)
S(1)−C(21a)−C(21)	118.4(3)	Br(2)−C(21)−C(21a)	125.5(5)
S(1)−C(21a)−Br(2a)	116.0(3)	C(1)−P(1)−Pd(1)	109.4(4)
C(7)−P(1)−Pd(1)	116.3(1)	C(13)−P(1)−Pd(1)	116.1(1)

(c) *trans*-PdBr(3,4,5-C_4Br_3S-*C*)(PPh_3)$_2$ (**21**)

Bond Lengths

Pd(1)−C(1)	2.004(8)	Pd(1)−Br(1)	2.483(1)
Pd(1)−P(1)	2.329(2)	Pd(1)−P(2)	2.339(2)
C(1)−C(2)	1.357(10)	S(1)−C(1)	1.730(7)
S(1)−C(4)	1.719(9)	C(2)−C(3)	1.425(11)
C(3)−C(4)	1.360(10)	C(2)−Br(2)	1.871(7)
C(3)−Br(3)	1.865(7)	C(4)−Br(4)	1.868(8)
P(1)−C(5)	1.833(8)	P(1)−C(11)	1.804(7)
P(1)−C(17)	1.812(7)	P(2)−C(23)	1.813(7)
P(2)−C(29)	1.822(8)	P(2)−C(35)	1.816(9)

Bond Angles

C(1)−Pd(1)−P(1)	90.1(2)	C(1)−Pd(1)−P(2)	91.7(2)
Br(1)−Pd(1)−P(1)	89.0(1)	Br(1)−Pd(1)−P(2)	89.5(1)
Br(1)−Pd(1)−C(1)	176.7(2)	P(1)−Pd(1)−P(2)	174.6(1)
S(1)−C(1)−Pd(1)	121.3(4)	C(2)−C(1)−Pd(1)	129.3(5)
C(1)−S(1)−C(4)	92.7(4)	S(1)−C(1)−C(2)	109.3(6)
C(1)−C(2)−C(3)	115.0(6)	C(2)−C(3)−C(4)	111.5(7)
S(1)−C(4)−C(3)	111.5(6)	C(1)−C(2)−Br(2)	122.4(6)
C(3)−C(2)−Br(2)	122.6(5)	C(2)−C(3)−Br(3)	123.9(5)
C(4)−C(3)−Br(3)	124.5(6)	S(1)−C(4)−Br(4)	121.0(4)
C(3)−C(4)−Br(4)	127.5(6)	C(5)−P(1)−Pd(1)	120.0(3)
C(11)−P(1)−Pd(1)	105.4(2)	C(17)−P(1)−Pd(1)	116.7(2)
C(23)−P(2)−Pd(1)	115.0(3)	C(29)−P(2)−Pd(1)	111.8(3)
C(35)−P(2)−Pd(1)	115.7(3)		

(22) A typical example of η^1(S) coordination is found in $ReCp^*(CO)_2$-(C_4H_4S), which reacts with $Fe_2(CO)_9$ to give a η^1:η^4-bridging complex. See: (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753. η^2 complexes are also known. See: (b) Cordone, R.; Harman, W. B.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. (c) Deeming, A. J.; Arse, A. J.; de Sanctis, Y.; Day, M. W.; Hardcastle, K. I. *Organometallics* **1989**, *8*, 1408. (d) Arse, A. J.; Deeming, A. J.; de Sanctis, Y.; Machada, R.; Rivas, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1568.

(23) Xie, Y.; Ng, S.-C.; Mak, T. C. W.; Hor, T. S. A. Unpublished results.

(24) Giordano, T. J.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1978**, *17*, 1917.

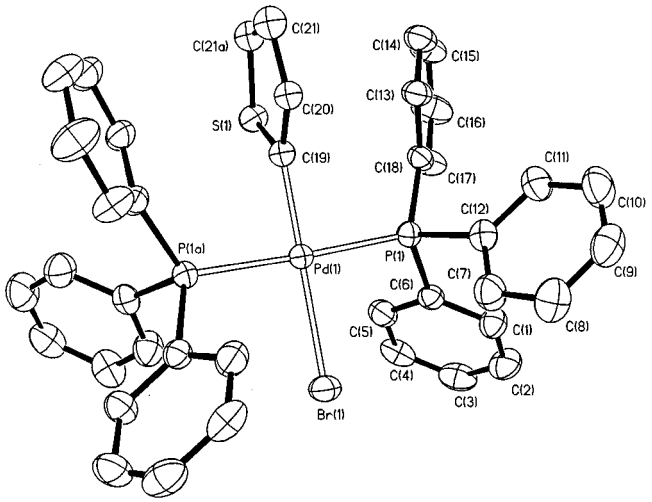


Figure 2. ORTEP plot of the molecular structure of *trans*-$PdBr(C_4H_3S\text{-}C)(PPh_3)_2$ (**20**) (30% probability ellipsoids).

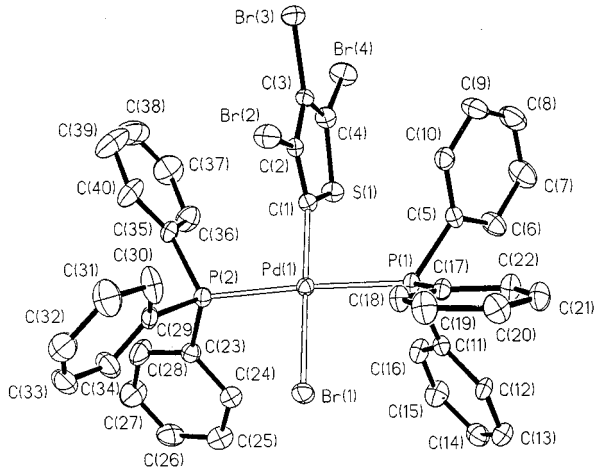
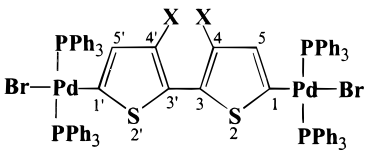
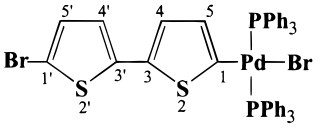


Figure 3. ORTEP plot of the molecular structure of *trans*-$PdBr(3,4,5\text{-}C_4Br_3S\text{-}C)(PPh_3)_2$ (**21**) (30% probability ellipsoids).

To verify that the synthesis and mechanism can be extended to the bithiophene systems, we have trapped the debromination intermediates *trans*,*trans*-$Pd_2Br_2(\mu\text{-}4,4'\text{-}C_8H_2Br_2S_2\text{-}C,C')(PPh_3)_4$ (**17**) from the stoichiometric reaction of **9** with $Pd(PPh_3)_4$ and, similarly, *trans*,*trans*-$Pd_2Br_2(\mu\text{-}C_8H_4S_2\text{-}C,C')(PPh_3)_4$ (**18**) and *trans*-$PdBr(C_8H_4BrS_2\text{-}C)(PPh_3)_2$ (**19**) from **14** and $Pd(PPh_3)_4$. Complex



17: X = Br
18: X = H



19

19 is an intermediate of **18**. Isolation of these complexes shows clearly the sequential proceedings of the oxidative addition and hydrodebromination steps. The ^{31}P shifts (22.5−22.8 ppm) fall into a narrow band, which is consistent with what is observed for the *trans*-oriented phosphines found in *trans*,*trans*-$Pd_2X_2(\mu\text{-}4,4'\text{-biphenyl})(PPh_3)_4$.[26] Palladation invariably occurs at the carbon at the 2 (or α-)-position, i.e. adjacent to the sulfur. This regioselectivity is indicated in the ^1H NMR spectra, in which the resonances of the protons at the 5 (or *β*-)-position adjacent to the metalated site are inevitably shielded with respect to those of the parent bithiophenes. Similarly, the metalated carbon is characterized by a low-field shift to 142.3−148.0 ppm for **17**−**19**, whereas the nonmetalated α-carbons resonate at 111.4−132.1 ppm. Formation of **11** and **13** can similarly be explained by a selective insertion of the $[Pd(PPh_3)_2]$ moieties into the C−Br bonds at the α-position of the bithiophene sulfur in **9** and **14**. Formation of **19** over **18** can be controlled stoichiometrically. Reaction of **9** with $Pd(PPh_3)_4$ takes place rapidly, giving only **17** as the isolated product.

The present results suggest that isomerically pure bromothiophenes and bromobithiophenes can be synthesized by a Pd-catalyzed reduction method, whereby the degree of hydrodebromination can be controlled conveniently by a measured use of the reductant. The easy trapping of some reaction intermediates would pave a way for us to introduce other functionalities to the thienyl complexes. Such work could lead to a significant methodology, on the basis of which nucleophilic substitutions of thiophenes and bithiophenes and the designed synthesis of thiophene-containing oligomers and polymers can be carried out. Current work in our laboratory is directed at these initiatives.

Experimental Section

2-Bromothiophene, 2,4-dibromothiophene, 2,3,5-tribromothiophene, tetrabromothiophene, and $NaBH_4$ were commercial products and were used without further purification. $Pd(PPh_3)_4$ was prepared according to published procedures.[27] 5,5′-Dibromo-2,2′-bithiophene and 3,3′,5,5′-tetrabromo-2,2′-bithiophene were synthesized by direct bromination of 2,2′-bithiophene with 2 and 4 molar equiv of bromine, respectively, in a chloroform−acetic acid mixture.[10] Reagent-grade acetonitrile was distilled from CaH_2 under argon. Toluene, benzene, and diethyl ether were distilled from Na/benzophenone under argon. NMR spectra were acquired on a Bruker ACF300 spectrometer. ^1H NMR spectra had $SiMe_4$ as the internal reference with $CDCl_3$ as solvent. ^{13}C NMR spectra were referenced to the same solvent. ^{31}P NMR spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software with the standard 85% H_3PO_4−D_2O.

General Procedure for the Catalytic Debromination of Bromothiophenes and Bromobithiophenes. An oxygen-free mixture of bromothiophenes or bromobithiophene (1 mmol) and $Pd(PPh_3)_4$ (0.011 g, 0.01 mmol) in CH_3CN (10 mL) was stirred for about 5 min, after which $NaBH_4$ was added. (Tables 1 and 2). The mixture was stirred at 70 °C under argon for a specified period of time. At the conclusion of the reaction, an internal standard, anthracene, was added to the mixture, and the conversion and yield of products were

(25) Harshbarger, W. B.; Bauer, S. H. *Acta Crystallogr.* **1970**, *B26*, 1010. Derissen, J. L.; Kocken, J. W. M.; Weelden, R. H. *Acta Crystallogr.* **1971**, *B27*, 1692. Karl, R. R.; Bauer, S. H. *Acta Crystallogr.* **1972**, *B28*, 2619.
(26) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J. *Organometallics* **1997**, *16*, 1897.
(27) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

determined by capillary GC (Hewlett-Packard 5890 Series II Plus, 25 m × 0.32 mm HP-1 column, 80−300 °C).

Recycle Use of the Catalyst. At the end of the catalytic reaction, the mixture was filtered under argon and the residual solid was washed with CH_3CN (2 mL × 2). This solid was used as the catalyst in a recycled debromination reaction.

General Procedure for the Preparative Synthesis of Bromothiophenes and Bithiophenes. An oxygen-free mixture of bromothiophenes or bromobithiophenes and $Pd(PPh_3)_4$ (0.231 g, 0.2 mmol) in CH_3CN was stirred at 70 °C under nitrogen for about 10 min. A specified quantity of $NaBH_4$ was added in small portions over a period of time (*t*). The mixture was continuously stirred at 70 °C for that period of time. Upon completion of reaction (monitored by TLC), the solvent was removed and the crude compound distilled *in vacuo* (for the liquid product). Solid products were washed with water, dried, and recrystallized from hexane.

2,3,4-Tribromothiophene (2): CH_3CN (100 mL), tetrabromothiophene (**1**; 8.0 g, 20 mmol), $NaBH_4$ (1.9 g, 50 mmol). *t*: 2 h. Yield: 5.3 g (82%). Bp: 131−132 °C /10 mmHg (lit.[11] 132−134 °C/10 mmHg). ^{1}H NMR: δ 7.36 (s, 1H). MS: *m*/*z* 318/320/322/324 (M^+: 60/100/100/60). Purity: in excess of 95% (determined by GC).

2,3-Dibromothiophene (7): 2,3,5-tribromothiophene (**6**; 6.42 g, 20 mmol), $NaBH_4$ (1.2 g, 30 mmol), CH_3CN (100 mL). *t*: 1.5 h. Yield: 4.0 g (83%). Bp: 92−94 °C/10 mmHg (lit.[11] 88−90 °C/9 mmHg). ^{1}H NMR: δ 7.25 (d, 1H, J = 5.6 Hz), 6.91 (d, 1H, J = 5.6 Hz). MS: *m*/*z* 240/242/244 (M^+: 50/100/50). Purity: in excess of 95%.

3,4-Dibromothiophene (3): tetrabromothiophene (**1**; 8.0 g, 20 mmol), $NaBH_4$ (3.8 g, 100 mmol), CH_3CN (100 mL). Adding time: 3 h. Yield: 4.2 g (86%). Bp: 92−93 °C/10 mmHg (lit.[11] 93−93 °C/10 mmHg). ^{1}H NMR: δ 7.30 (s, 2H). MS: *m*/*z* 240/242/244 (M^+: 60/100/60). Purity: in excess of 96%.

3-Bromothiophene (4): 2,3,5-tribromothiophene (**6**; 6.42 g, 20 mmol), $NaBH_4$ (2.5 g, 6.6 mmol), CH_3CN (100 mL). *t*: 3 h. Yield: 2.64 g (81%). Bp: 50−52 °C/20 mmHg (lit.[11] 44−46 °C/11 mmHg). ^{1}H NMR: δ 7.27 (d, 1H, J = 5.0 Hz), 7.21 (d, 1H, J = 1.3 Hz), 6.98 (d, 1H, J = 3.1 Hz). MS: *m*/*z* 162/164 (M^+: 100/100). Purity: in excess of 95%.

3,3′-Dibromo-2,2′-bithiophene (11): 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**9**; 9.64 g, 20 mmol), $NaBH_4$ (2.7 g, 70 mmol), CH_3CN (120 mL). *t*: 2.5 h. Yield: 5.51 g (85%). Mp: 96−97 °C (lit.[10] mp 95−97 °C). ^{1}H NMR: δ 7.41 (d, 2H, J = 5.4 Hz), 7.09 (d, 2H, J = 5.4 Hz). MS: *m*/*z* 322/324/326 (M^+: 80/100/80).

3-Bromo-2,2′-bithiophene (12): 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**9**; 9.64 g, 20 mmol), $NaBH_4$ (3.8 g, 100 mmol), CH_3CN (120 mL). *t*: 4 h. Yield: 3.72 g (76%). Bp: 123−125 °C/0.05 mmHg. ^{1}H NMR: $\delta_{H3'}$ 7.42 (dd, 1H, J = 1.1, 3.7 Hz), $\delta_{H5'}$ 7.35 (dd, 1H, J = 1.1, 5.1 Hz), δ_{H5} 7.19 (d, 1H, J = 5.4 Hz), $\delta_{H4'}$ 7.09 (dd, 1H, J = 3.7, 5.1 Hz), δ_{H4} 7.02 (d, 1H, J = 5.4 Hz). MS: *m*/*z* 244/246 (M^+: 100/100).

3,3′,5-Tribromo-2,2′-bithiophene (10): 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**9**; 9.64 g, 20 mmol), $NaBH_4$ (1.2 g, 30 mmol), CH_3CN (100 mL). *t*: 2 h. Yield: 6.07 g (75%). Mp: 85−87 °C. ^{1}H NMR: $\delta_{H5'}$ 7.41 (d, 1H, J = 5.3 Hz), $\delta_{H4'}$ 7.07 (d, 1H, J = 5.3 Hz), δ_{H4} 7.06 (s, 1H). MS: *m*/*z* 400/402/404/406 (M^+: 70/100/100/70).

General Procedure for the Synthesis of 16−19. A mixture of $Pd(PPh_3)_4$ and bromothiophene or bromobithiophenes in benzene or toluene was deoxygenated and stirred overnight in a Schlenk flask under argon at room temperature. The resultant yellow solution or suspension was evaporated to dryness *in vacuo*. The solid residue was triturated with Et_2O and the ether solution discarded. The washing was repeated twice and the residual product purified further by recrystallization from $CHCl_3$−hexane.

***trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (16).** $Pd(PPh_3)_4$ (1.156 g, 1.0 mmol), 2,3,5-tribromothiophene (**6**; 0.390 g, 1.2 mmol), benzene (20 mL). Yield: 0.85 g (90%). Mp: ∼235 °C dec. ^{1}H NMR: δ 7.59 (m, 12H, PPh_3), 7.36 (t, 18H, PPh_3), 5.56 (s, 1H, H_5−Pd). ^{31}P NMR: δ 22.9. ^{13}C{^{1}H} NMR: δ 134.6 (t, $^3J_{CP}$ = 6.3 Hz, C_o-P), 130.5 (s, C_p−P), 130.3 (t, $^2J_{CP}$ = 24.3 Hz, C_i−P), 128.0 (t, $^4J_{CP}$ = 5.3 Hz, C_m−P); 148.1 (t, $^2J_{CP}$ = 8.3 Hz, C_1−Pd), 110.6 (s, C_3−Pd), 114.0 (s, C_4−Pd), 132.2 (s, C_5−Pd). Anal. Calcd for $C_{40}H_{31}Br_3P_2PdS$: C, 50.48; H, 3.28; Br, 25.18; P, 6.51; Pd, 11.18; S, 3.37. Found: C, 50.72; H, 3.32; Br, 24.70; P, 6.13; Pd, 10.84; S, 3.22.

***trans,trans*-Pd_2Br_2(μ-4,4′-$C_8H_2Br_2S_2$-*C*,*C*′)(PPh_3)$_4$ (17):** $Pd(PPh_3)_4$ (1.156 g, 1.0 mmol), 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**9**; 0.484 g, 1.0 mmol), toluene (30 mL). Yield: 0.80 g (92%). Mp: ∼220 °C dec. ^{1}H NMR: δ 7.57 (m, 24H, PPh_3), 7.29 (t, 36H, PPh_3), 5.42 (s, 2H, C_5−Pd). ^{31}P NMR: δ 22.6. ^{13}C NMR: δ 134.6 (t, $^3J_{CP}$ = 6.1 Hz, C_o−P), 130.8 (s, C_p−P), 130.3 (t, $^2J_{CP}$ = 24.8 Hz, C_i−P), 128 (t, $^4J_{CP}$ = 5.2 Hz, C_m−P); 148.0 (t, $^2J_{CP}$ = 8.0 Hz, C_1−Pd), 111.4 (s, C_3−Pd), 128.6 (s, C_4−Pd), 133.0 (s, C_5−Pd). Anal. Calcd for $C_{80}H_{62}Br_4P_4Pd_2S_2$: C, 55.10; H, 3.58; Br, 18.33; P, 7.10; Pd, 12.21; S, 3.68. Found: C, 55.28; H, 3.71; Br, 18.01; P, 6.87; Pd, 11.21; S, 3.20.

***trans,trans*-Pd_2Br_2(μ-$C_8H_4S_2$-*C*,*C*′)(PPh_3)$_4$ (18):** Pd(PPh_3)$_4$ (1.156 g, 1.0 mmol), 5,5′-dibromo-2,2′-bithiophene (**14**; 0.162 g, 0.5 mmol), toluene (30 mL). Yield: 0.67 g (85%). Mp: ∼195 °C dec. ^{1}H NMR: δ 7.52 (m, 24H, PPh_3), 7.23 (t, 36H, PPh_3), 5.84 (d, 2H, $^3J_{HH}$ = 3.4 Hz, H_4−Pd), 5.58 (d, 2H, $^3J_{HH}$ = 3.4 Hz, H_5−Pd); ^{31}P NMR: δ 22.5. ^{13}C NMR: δ 134.6 (t, $^3J_{CP}$ = 6.1 Hz, C_o−P), 131.1 (s, C_p−P), 129.8 (t, $^2J_{CP}$ = 24.8 Hz, C_i−P), 127.7 (t, $^4J_{CP}$ = 5.2 Hz, C_m−P); 142.3 (t, $^2J_{CP}$ = 8.0 Hz, C_1−Pd), 132.1 (s, C_3−Pd), 124.5 (s, C_4−Pd), 131.3 (s, C_5−Pd). Anal. Calcd for $C_{80}H_{64}Br_2P_4Pd_2S_2$: C, 60.58; H, 4.07; Br, 10.07; P, 7.81; Pd, 13.42; S, 4.04. Found: C, 61.10; H, 4.24; Br, 9.93; P, 7.52; Pd, 12.98; S, 4.00.

***trans*-PdBr($C_8H_4BrS_2$-*C*)(PPh_3)$_2$ (19):** Pd(PPh_3)$_4$ (1.156 g, 1.0 mmol), 5,5′-dibromo-2,2′-bithiophene (**14**: 0.324 g, 1.0 mmol), toluene (30 mL). Reaction time: 2 h. Yield: 0.79 g (83%). Mp: ∼180 °C dec. ^{1}H NMR: δ 7.56 (m, 12H, PPh_3), 7.27 (t, 18H, PPh_3), 6.32 (d, 1H, $^3J_{HH}$ = 5.3 Hz, H_4−Pd), 5.82 (d, 1H, $^3J_{HH}$ = 5.3 Hz, H_5−Pd), 6.28 (d, 1H, $^3J_{HH}$ = 3.8 Hz, $H_{4'}$−Pd), 6.78 (d, 1H, $^3J_{HH}$ = 3.8 Hz, $H_{5'}$-Pd). ^{31}P NMR: δ 22.8. ^{13}C NMR: δ 134.7 (t, $^3J_{CP}$ = 6.1 Hz, C_o−P), 130.9 (s, C_p−P), 130.1 (t, $^2J_{CP}$ = 24.8 Hz, C_i−P), 127.9 (t, $^4J_{CP}$ = 5.2 Hz, C_m−P); 146.8 (t, $^2J_{CP}$ = 8.0 Hz, C_1−Pd), 132.1 (s, C_3−Pd), 128.5 (s, C_4−Pd), 132.1 (s, C_5−Pd), 108.4 (s, $C_{1'}$−Pd), 131.3 (s, $C_{3'}$−Pd), 125.4 (s, $C_{4'}$−Pd),130.4 (s, $C_{5'}$−Pd). Anal. Calcd for $C_{44}H_{34}Br_2P_2PdS_2$: C, 55.34; H, 3.59; Br, 16.73; P, 6.49; Pd, 11.14; S, 6.71. Found: C, 56.01; H, 3.91; Br, 16.11; P, 6.95; Pd, 11.76; S, 5.91.

Reaction of *trans*-PdBr(3,4-C_4HBr_2S-*C*)(PPh_3)$_2$ (16) with $NaBH_4$. Complex **16** (6 mg, 0.006 mmol) and $NaBH_4$ (4 mg, 0.01 mmol) were added to CD_3CN (0.6 mL) in an NMR tube under an argon atmosphere. The tube was warmed to 60 °C for 1 h with shaking. ^{1}H NMR data were then obtained at ambient temperature: δ −11.06 ppm (s, Pd−H). Under otherwise identical conditions in $CDCl_3$, both the *trans* and *cis* structures were detected. ^{1}H NMR (ppm): *cis* δ −9.73 (dd, $^2J_{PH}$ = 82.5 Hz, $^2J_{PH}$ = 3.3 Hz, H−Pd); *trans* δ −11.86 (t, $^2J_{PH}$ = 8.7 Hz, H−Pd) (∼ 1:3 ratio). The reaction of **16** with $NaBH_4$ was also performed in CH_3CN for 5 h at 60 °C, and the resultant dark mixture was filtered. GC/MS analysis with the help of standard samples revealed that 2,3-dibromothiophene, PPh_3, and $OPPh_3$ were formed as the main products.

X-ray Crystallography. Single crystals of **16** were grown by a diffusion method with hexane layered on a sample solution in $CHCl_3$ at room temperature and those of **20** and **21** were grown similarly from $CH_3CN/C_6H_5CH_3/CHCl_3$ and $C_6H_5CH_3/CHCl_3$ mixtures, respectively. Crystals suitable for X-ray diffraction were mounted on thin-walled Lindemann glass capillaries under a nitrogen atmosphere. Intensity data were measured on a Rigaku RAXIS IIC imaging plate for **16** and **20** and on a Rigaku AFC7 diffractometer for complex **21**, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73

Å). For complex **16**, 36 oscillation frames were used with $\phi = 0-180°$, $\Delta\phi = 5.0°$, and scan rate 8 min per frame; for complex **20**, 31 oscillation frames were used with $\phi = 0-180°$, $\Delta\phi = 6.0°$, and scan rate 8 min per frame; for complex **21**, the variable ω-scan technique was used with a scan rate of 2.00−32.00°/min. Empirical absorption corrections were applied to the raw intensities. The structures were solved by direct methods and refined by full-matrix least squares. The anisotropic thermal parameters of all non-hydrogen atoms were varied, and hydrogen atoms were introduced in their idealized positions with assigned isotropic temperature factors. In **16**, a crystallographic C_2 axis passes through the Pd(1) and Br(1) atoms, so that the 3,4-dibromo-2-thienyl group is subjected to 2-fold disorder. In the model chosen for refinement, the C_2 axis is taken to pass through the C(19) atom and the midpoint of the C(21)−C(21a) bond, and the X-ray scattering power of the disordered thienyl group is accordingly represented by C(19) and C(21) at full site occupancy together with S(1) and C(20) at half site occupancy. In view of the close overlap between the S(1) and *ipso* C(20a) atoms of the two possible orientations of the thienyl ring, bond length restraints of 1.712(1), 1.424(2), and 1.362(1) Å, respectively, were imposed on the carbon−sulfur and formal single and double carbon−carbon bonds. Likewise, complex **20** has a crystallographic 2-fold axis passing through Br(1), Pd(1), C(19), and the midpoint of the C(21)−C(21a) bond, and refinement was handled in the same manner. The atoms in complex **21** were all well-behaved. All calculations were performed on a PC 486 with the SHELXTL-PC program package[28] for **20** and **21** and SHELXL-93 for **16**.[29] Crystal data, data collection parameters, and results of the analyses are listed in Table 3. Selected bond lengths and bond angles are listed in Table 4.

Acknowledgment. We thank the National University of Singapore (Grant Nos. RP950695 and RP960613) and The Chinese University of Hong Kong (Hong Kong Research Grants Council Ref. CUHK 311/94P) for financial support and the technical staff in the Department of Chemistry of NUS for general help. Stenographic assistance from Y. P. Leong and valuable discussions with S. Li and P. M. N. Low are appreciated. Y.X. thanks NUS for a scholarship award.

Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, bond distances and angles, and thermal parameters for **16**, **20**, and **21** (18 pages). Ordering information is given on any current masthead page.

OM9800142

(28) Sheldrick, G. M. In *Computational Crystallography*; Sayre, D., Ed.; Oxford University Press: New York, 1982; pp 506−514.

(29) Sheldrick, G. M. SHELX-93: A Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993.