

σ -Thienyl complexes of palladium(II), *trans*-PdBr(C₄H_{4-n}Br_{n-1}S-C)(PPh₃)₂ (*n* = 1–4), from oxidative addition of bromothiophenes to Pd(PPh₃)₄. X-ray structural identification of key intermediates of catalytic debromination of 2-bromothiophene and tetrabromothiophene

Yang Xie ^a, S.C. Ng ^a, Bo-Mu Wu ^b, Feng Xue ^b, Thomas C.W. Mak ^b, T.S. Andy Hor ^{a,*}

^a Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 119260, Singapore

^b Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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Abstract

Oxidative addition reactions of Pd(PPh₃)₄ with bromothiophenes C₄H_{4-n}Br_nS (*n* = 1–4) occur readily at RT to give σ -thienyl complexes *trans*-PdBr(C₄H_{4-n}Br_{n-1}S-C)(PPh₃)₂ in yields $\geq$ 85%. The products are intermediates in the regioselective reduction of bromothiophenes catalyzed by Pd(0). Palladation invariably occurs at the carbon adjacent to the thienyl sulfur. Single crystal X-ray crystallographic determination was carried out on PdBr(2-thienyl)(PPh₃)₂, **1**, and PdBr(3,4,5-tribromo-2-thienyl)(PPh₃)₂, **6**. Crystal data for **1**: space group *Pbcn*, *a* = 19.354(1), *b* = 10.760(1), *c* = 16.451(1) Å, *Z* = 4, 3106 reflections, *R* = 0.0614; for **6**: space group *P2₁/n*, *a* = 11.361(2), *b* = 13.049(3), *c* = 26.670(5) Å, β = 102.00(3)°, *Z* = 4, 3577 reflections, *R* = 0.0375. Reduction of PdBr(3,4-dibromo-2-thienyl)(PPh₃)₂, **5**, by NaBH₄ gives 2,3-dibromothiophene.

Keywords: σ -Thienyl; Palladium; Oxidative addition; Bromothiophenes; Crystal structures; Catalysis; Reduction

1. Introduction

Bromothiophenes are important materials in drug [1] and polymer syntheses [2]. We have recently reported the synthesis of isomerically pure dibromothiophenes from tribromothiophenes catalyzed by palladium and nickel catalysts, and proposed that the high regioselectivity is accomplished by a selective oxidative addition process across the C(5)–Br bond as the energetically most favored pathway [3]. On the other hand, oxidative addition across the C(2)–Br and C(3)–Br bonds would selectively yield 2,4- and 2,5-dibromothiophenes respectively. Such manifestation of site reactivity through oxidative addition to a metal center is obviously a superior strategy compared to the classical organic reduction of 2,3,5-tribromothiophene. [Reduction of 2,3,5-tribromothiophenes using common commercially available reducing agents usually gives a mixture of di-

and monobromothiophenes and the parent thiophene. The poor selectivity is hardly surprising due to the interplay of contrasting steric and electronic effects.] Although a wealth of peripheral evidence is available regarding this oxidative addition step in Pd-catalyzed reduction, there are only a few cases in which the key oxidative addition products can be isolated and characterized crystallographically [4]. There is also no structural evidence that a similar pathway can occur in a thiophenyl substrate. An excellent review on thiophene chemistry was recently published by Rauchfuss [5]. The author also mentioned the poorly developed coordination chemistry of thienyl ligands C₄R₃S[−]. Chia and McWhinnie [6] described the oxidative addition of 2-bromothiophene to Pd(PPh₃)₄. In this paper, we report the isolation and spectroscopic characterization of the σ -thienyl intermediates arising from the regioselective reduction of a series of brominated thiophenes. Also included are the X-ray crystallographic analyses of two of these intermediates which provide firm evidence that

* Corresponding author.

oxidative addition represents a key step in the catalyst-directed reduction of halothiophenes.

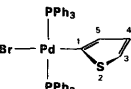
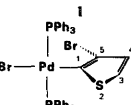
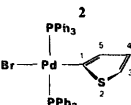
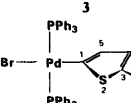
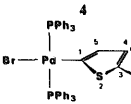
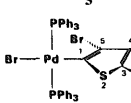
2. Results and discussion

$\text{Pd}(\text{PPh}_3)_4$ reacts readily with 2-bromothiophene in benzene or toluene at RT to give $\text{PdBr}(2\text{-thienyl})(\text{PPh}_3)_3$, **1**, in near-quantitative yield. Similar reactions with 2,3-dibromothiophene, 2,4-dibromothiophene, 2,5-dibromothiophene, 2,3,5-tri-

bromothiophene and tetrabromothiophene give $\text{PdBr}(5\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **2**, $\text{PdBr}(4\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **3**, $\text{PdBr}(3\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **4**, $\text{PdBr}(3,4\text{-dibromo-2-thienyl})(\text{PPh}_3)_3$, **5** and $\text{PdBr}(3,4,5\text{-tribromo-2-thienyl})(\text{PPh}_3)_3$, **6** respectively (Scheme 1). All the reactions readily proceed to completion at RT. The ^1H , ^{13}C and ^{31}P NMR spectral data are summarized in Table 1. The ^{31}P shifts (22.6–23.7 ppm) fall into a narrow band which is consistent with those observed in the *trans*-oriented phosphines found in *trans*- $\text{PdXPh}(\text{PPh}_3)_2$ [7]. Palladation invari-

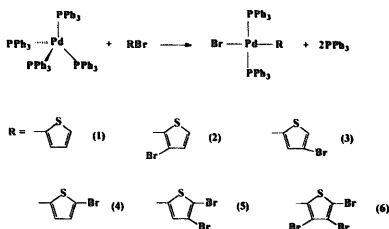
Table 1

NMR data of $\text{PdBr}(2\text{-thienyl})(\text{PPh}_3)_3$, **1**, $\text{PdBr}(5\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **2**, $\text{PdBr}(4\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **3**, $\text{PdBr}(3\text{-bromo-2-thienyl})(\text{PPh}_3)_3$, **4**, $\text{PdBr}(3,4\text{-dibromo-2-thienyl})(\text{PPh}_3)_3$, **5** and $\text{PdBr}(3,4,5\text{-tribromo-2-thienyl})(\text{PPh}_3)_3$, **6**

Spectroscopic assignments	^1H NMR δ (ppm)					^{13}C NMR δ (ppm)					^{31}P NMR δ (ppm)
Complexes ^a	PPh_3	H^1	H^2	H^3	J (Hz)	PPh_3	C^1	C^2	C^3	C^4	PPh_3
	7.52 (m, 12H) 7.30 (t, 18H)	6.84 (d, 1H)	6.34 (dd, 1H)	5.93 (d, 1H)	$(\text{H}^1\text{--H}^2)$ 4.88 $(\text{H}^2\text{--H}^3)$ 3.00	134.6 143.3 127.1 128.5 127.8					23.0
	7.56 (m, 12H) 7.32 (t, 18H)	6.67 (d, 1H)	6.18 (d, 1H)		$(\text{H}^1\text{--H}^2)$ 4.89	134.8 148.2 127.0 129.7 113.3 128.0					23.7
	7.50 (m, 12H) 7.34 (t, 18H)	6.63 (d, 1H)		5.70 (d, 1H)	$(\text{H}^1\text{--H}^2)$ 0.99	134.6 148.3 125.9 109.9 131.9 128.0					23.2
	7.58 (m, 12H) 7.36 (t, 18H)		6.19 (d, 1H)	5.64 (d, 1H)	$(\text{H}^1\text{--H}^2)$ 3.69	134.7 145.6 112.0 130.6 132.1 128.0					22.6
	7.59 (m, 12H) 7.36 (t, 18H)			5.56 (s, 1H)		134.6 148.1 110.6 114.0 132.2 128.0					22.9
	7.59 (m, 12H) 7.35 (t, 18H)					134.7 146.8 110.5 114.7 115.8 127.9					23.2

6

^a The metalated carbon of the thienyl ring is assigned at 1-position. In free thiophenes, this carbon atom is at 2- or 5-position depending on the positioning of the bromine atom(s). Sulfur is at 1-position in free thiophenes.

Scheme 1. Oxidative additions of bromothiophenes to $\text{Pd(PPh}_3)_4$.

ably 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 3- (or β -) position adjacent to the metalated site are inevitably shielded with respect to the parent thiophenes. For example, the β -protons of 2-bromothiophene, 2,4-dibromothiophene, 2,5-dibromothiophene and 2,3,5-tribromothiophene at 7.04, 6.98, 6.83 and 6.90 ppm are high-field shifted to 5.93, 5.70, 5.64 and 5.56 ppm in **1**, **3**, **4** and **5** respectively. Support of this comes from the β -proton resonance of **2** (6.18 ppm) which is only slightly shifted compared to that in 2,3-dibromothiophene (6.91 ppm) in the absence of any neighboring metalation effect. The metalation effect is also exemplified in the ^{13}C NMR data. The metalated carbon is characterized by a low-field shift to 143.3–148.3 ppm for **1–6**. The non-metalated α -carbons resonate at 109.5–132.3 ppm.

Complex **1** is a stable and rare unsubstituted σ -thienyl complex. Complex **6** derived from a completely substituted thiophene is an ideal structural model for examination of the preferential site for oxidative palladation. Chia and McWhinnie [6] reported the reaction between 2-bromothiophene and $\text{Pd(PPh}_3)_4$ to give a *trans* product, but similar reaction with 2-bromo-3-methylthiophene gives a mixture of *cis* and *trans* isomers. Similar trichlorothiényl complexes have also been obtained from metal–halogen exchange between 2- $\text{LiC}_4\text{Cl}_3\text{S}$ and metal halides [8]. There is however no crystallographic report on these species. To confirm the metalation site and geometry of the oxidative addition product including the *trans*-disposition of the phosphine groups, single crystal X-ray structure analysis was carried out on both complexes. They represent the first crystallographically characterized thienyl complexes of palladium. Many thienyl complexes are formed from lithiated thienyls or thienylic Grignard reagents, both of which are unstable for isolation. Although palladium complexes are documented catalysts for the syntheses of many functional thiophenes [9], there appears to be no report on the isolation and structural characterization of the intermediates involved.

Complex **1** shows a Pd(II) σ -thienyl complex with near-ideal square-planar geometry with two phosphines ($\angle\text{P(1)}-\text{Pd}-\text{P(1a)}$ 177.5(1) $^\circ$) and thienyl and bromide ($\angle\text{Br}-\text{Pd}-\text{C(19)}$ 180.0(1) $^\circ$) *trans* to each other (Fig. 1, Tables 2 and 3). To achieve a strong Pd –thienyl interaction ($\text{Pd}-\text{C(19)}$ 1.993(4) Å), the thienyl plane makes a dihedral angle of 96.1 $^\circ$ with the Pd(II) coordination plane to avoid steric interactions with the phenyl groups.

Table 2
Crystal data and details of the data collection and refinement for **1** and **6**

	$\text{C}_{40}\text{H}_{13}\text{BrP}_2\text{PdS}$	$\text{C}_{40}\text{H}_{30}\text{Br}_2\text{P}_2\text{PdS}$
Molecular formula	794.0	1030.7
Molecular weight	yellow prism	yellow prism
Color and habit	0.30 × 0.30 × 0.40	0.20 × 0.20 × 0.30
Crystal size (mm ³)	orthorhombic	monoclinic
Crystal system	<i>Pbcn</i> (No. 60)	<i>P2</i> ₁ / <i>n</i>
Space group	294	294
Temperature (K)		
Unit cell parameters	<i>a</i> (Å) 19.354(1)	11.361(2)
	<i>b</i> (Å) 10.760(2)	13.049(3)
	<i>c</i> (Å) 16.451(1)	26.670(5)
	β ($^\circ$)	102.00(3)
<i>F</i> (000)	1600	2008
<i>V</i> (Å ³)	3426(2)	3867(2)
<i>Z</i>	4	4
Absorption coefficient (mm ^{−1})	1.891	4.777
Density (calc.) (g cm ^{−3})	1.539	1.770
Index ranges	−24 ≤ <i>h</i> ≤ 24, −13 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 15, −31 ≤ <i>l</i> ≤ 30
Reflections collected	11410	7181
Independent reflections	3606 (<i>R</i> _{int} = 2.36%)	6815 (<i>R</i> _{int} = 2.69%)
Final <i>R</i> indices (obs. data)	<i>R</i> = 6.14%, <i>wR</i> = 5.93%	<i>R</i> = 3.75%, <i>wR</i> = 4.00%
Goodness-of-fit	1.49	1.12
Largest difference peak and hole (e Å ^{−3})	0.75 and −0.78	0.42 and −0.52

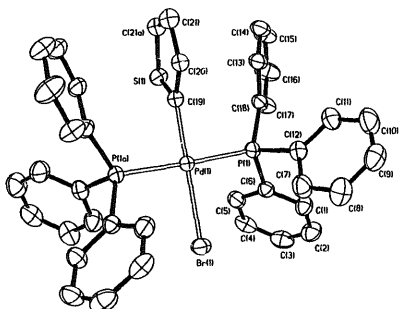


Fig. 1. ORTEP plot (30% thermal ellipsoids) of the molecular structure of $\text{PdBr}(\text{2-thienyl})(\text{PPh}_3)_2$, **1**. A crystallographic C_2 axis passes through $\text{Br}(1)$, $\text{Pd}(1)$, $\text{C}(19)$ and the mid-point of the $\text{C}(21)$ – $\text{C}(21a)$ bond, and only one orientation of the disordered 2-thienyl group is shown for the sake of clarity.

There is no indication of $\eta^1\text{-S}$ 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. [A typical example of $\eta^1\text{-S}$ coordination is found in $\text{ReCp}^+(\text{CO})_3(\text{C}_4\text{H}_4\text{S})$ which reacts with $\text{Fe}_2(\text{CO})_9$ to give an η^1, η^4 -bridging complex, see Ref. [10]; η^2 -complexes are also known, see Ref. [11].] In spite of the metalation at one of the two carbon atoms neighboring the sulfur, the two C–S bonds are identical ($\text{C}(19)$ – $\text{S}(1)$ 1.710(3) and $\text{C}(21a)$ – $\text{S}(1)$ 1.709(3) Å). The thienyl ring is essentially planar (mean deviation 0.008 Å) with the inner C–C bond ($\text{C}(20)$ – $\text{C}(21)$ 1.430(4) Å) significantly longer than the outer ones (mean $\text{C}(19)$ – $\text{C}(20)$ and $\text{C}(21)$ – $\text{C}(21a)$ 1.362(3) Å). The strong *trans* influence of the thienyl group gives a significantly long Pd–Br bond (2.526(1) Å

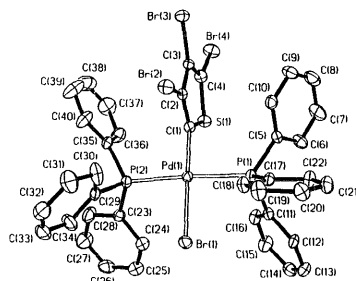


Fig. 2. ORTEP plot (30% thermal ellipsoids) of the molecular structure of $\text{PdBr}(3,4,5\text{-tribromo-2-thienyl})(\text{PPh}_3)_2$, **6**.

compared to many other $\text{Pd}(\text{II})$ –Br bonds, e.g. in $[\text{PdBr}_2(\text{CO})]^-$ (2.413(4)–2.432(4) Å) [12] and *trans*- $\text{PdBr}_2[2\text{-}(2'\text{-thienyl})\text{pyridine}]_2$ (2.431(1) Å) [13]. The weakness of this Pd–Br bond also supports the ready reduction (or H-exchange) of **1** with subsequent elimination to give thiophene.

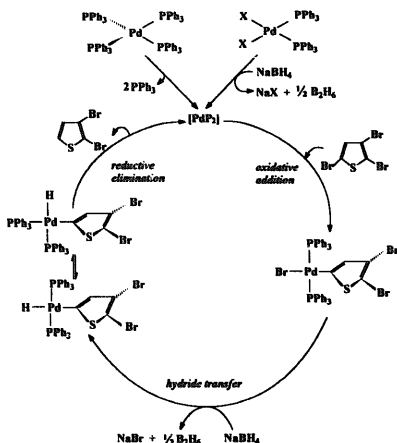
The X-ray structure of **6** proves unequivocally that C–Br insertion occurs preferentially at the 2- (or α -) position (Fig. 2, Tables 2 and 4). Interestingly, similar C–H insertion on an Rh(I) complex under photolytic conditions can occur at both 2- and 3- (or β -) positions [14]. Among all the thiophenes examined, we have no evidence that the 3-positions are susceptible to such attack. Complex **6** has all the essential features found in **1**. Notable differences are found in the significantly stronger Pd–Br bond (2.483(1) Å). The weaker *trans* influence of a weaker σ -donor due to the electron-withdrawing effect of bromide is probably responsible.

Table 3
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
$\text{Pd}(1)$ – $\text{C}(19)$	1.993(4)	$\text{Pd}(1)$ – $\text{Br}(1)$	2.526(1)
$\text{Pd}(1)$ – $\text{P}(1)$	2.351(1)	$\text{Pd}(1)$ – $\text{P}(1a)$	2.351(1)
$\text{C}(19)$ – $\text{C}(20)$	1.363(5)	$\text{S}(1)$ – $\text{C}(19)$	1.710(3)
$\text{S}(1)$ – $\text{C}(21a)$	1.709(3)	$\text{C}(20)$ – $\text{C}(21)$	1.430(4)
$\text{C}(21)$ – $\text{C}(21a)$	1.361(1)	$\text{P}(1)$ – $\text{C}(6)$	1.826(4)
$\text{P}(1)$ – $\text{C}(12)$	1.826(4)	$\text{P}(1)$ – $\text{C}(18)$	1.838(5)
Bond angles			
$\text{C}(19)$ – $\text{Pd}(1)$ – $\text{P}(1)$	88.8(1)	$\text{C}(19)$ – $\text{Pd}(1)$ – $\text{P}(1a)$	88.8(1)
$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{P}(1)$	91.2(1)	$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{P}(1a)$	91.2(1)
$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{C}(19)$	180.0(1)	$\text{P}(1)$ – $\text{Pd}(1)$ – $\text{P}(1a)$	177.5(1)
$\text{S}(1)$ – $\text{C}(19)$ – $\text{Pd}(1)$	120.7(1)	$\text{C}(20)$ – $\text{C}(19)$ – $\text{Pd}(1)$	136.2(2)
$\text{C}(19)$ – $\text{S}(1)$ – $\text{C}(21a)$	93.2(2)	$\text{S}(1)$ – $\text{C}(19)$ – $\text{C}(20)$	103.1(3)
$\text{C}(19)$ – $\text{C}(20)$ – $\text{C}(21)$	125.5(5)	$\text{C}(20)$ – $\text{C}(21)$ – $\text{C}(21a)$	100.6(3)
$\text{S}(1)$ – $\text{C}(21a)$ – $\text{C}(21)$	117.5(1)	$\text{C}(6)$ – $\text{P}(1)$ – $\text{Pd}(1)$	113.3(2)
$\text{C}(12)$ – $\text{P}(1)$ – $\text{Pd}(1)$	110.7(1)	$\text{C}(18)$ – $\text{P}(1)$ – $\text{Pd}(1)$	120.5(1)

Table 4
Selected bond lengths (Å) and angles (°) for **6**

$\text{Pd}(1)$ – $\text{C}(1)$	2.004(8)	$\text{Pd}(1)$ – $\text{Br}(1)$	2.483(1)
$\text{Pd}(1)$ – $\text{P}(1)$	2.329(2)	$\text{Pd}(1)$ – $\text{P}(2)$	2.339(2)
$\text{C}(1)$ – $\text{C}(2)$	1.357(10)	$\text{S}(1)$ – $\text{C}(1)$	1.730(7)
$\text{S}(1)$ – $\text{C}(4)$	1.719(9)	$\text{C}(2)$ – $\text{C}(3)$	1.425(11)
$\text{C}(3)$ – $\text{C}(4)$	1.360(10)	$\text{C}(2)$ – $\text{Br}(2)$	1.871(7)
$\text{C}(3)$ – $\text{Br}(3)$	1.865(7)	$\text{C}(4)$ – $\text{Br}(4)$	1.868(8)
$\text{P}(1)$ – $\text{C}(5)$	1.833(8)	$\text{P}(1)$ – $\text{C}(11)$	1.804(7)
$\text{P}(1)$ – $\text{C}(17)$	1.812(7)	$\text{P}(2)$ – $\text{C}(23)$	1.813(7)
$\text{P}(2)$ – $\text{C}(29)$	1.822(8)	$\text{P}(2)$ – $\text{C}(35)$	1.816(9)
$\text{C}(1)$ – $\text{Pd}(1)$ – $\text{P}(1)$	90.1(2)	$\text{C}(1)$ – $\text{Pd}(1)$ – $\text{P}(2)$	91.7(2)
$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{P}(1)$	89.0(1)	$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{P}(2)$	89.5(1)
$\text{Br}(1)$ – $\text{Pd}(1)$ – $\text{C}(1)$	176.7(2)	$\text{P}(1)$ – $\text{Pd}(1)$ – $\text{P}(2)$	174.6(1)
$\text{S}(1)$ – $\text{C}(1)$ – $\text{Pd}(1)$	121.3(4)	$\text{C}(2)$ – $\text{C}(1)$ – $\text{Pd}(1)$	129.3(5)
$\text{C}(1)$ – $\text{S}(1)$ – $\text{C}(4)$	92.7(4)	$\text{S}(1)$ – $\text{C}(1)$ – $\text{C}(2)$	109.3(6)
$\text{C}(1)$ – $\text{C}(2)$ – $\text{C}(3)$	115.0(6)	$\text{C}(2)$ – $\text{C}(3)$ – $\text{C}(4)$	111.5(7)
$\text{S}(1)$ – $\text{C}(4)$ – $\text{C}(3)$	111.5(6)	$\text{C}(5)$ – $\text{P}(1)$ – $\text{Pd}(1)$	120.0(3)
$\text{C}(11)$ – $\text{P}(1)$ – $\text{Pd}(1)$	105.4(2)	$\text{C}(17)$ – $\text{P}(1)$ – $\text{Pd}(1)$	116.7(2)
$\text{C}(23)$ – $\text{P}(2)$ – $\text{Pd}(1)$	115.0(3)	$\text{C}(29)$ – $\text{P}(2)$ – $\text{Pd}(1)$	111.8(3)
$\text{C}(35)$ – $\text{P}(2)$ – $\text{Pd}(1)$	115.7(3)		



Scheme 2. Proposed catalytic mechanism of regioselective debromination of 2,3,5-tribromothiophene to 2,3-dibromothiophene via an intermediate $\text{PdBr}(\text{3,4-dibromo-2-thienyl})(\text{PPh}_3)_2$, **5**.

Despite the presence of three bromides on a highly substituted thieryl ring, there appears no bond weakening effect on either the Pd–thienyl ($\text{Pd}–\text{C}(1)$ 2.004(8) Å) or Pd–phosphine (mean $\text{Pd}–\text{P}$ 2.334(2) Å) interactions. This is facilitated by an essentially orthogonal relationship between the thienyl ring and the Pd coordination plane (dihedral angle 96.4°). The bromothieryl ring however forces a slight but noticeable (mean deviation 0.069 Å, with the P atoms on one side and the Br(1) and C(19) atoms on the other) distortion of metal–ligand bonds, as well as minor angular distortion of $\angle \text{P}(1)–\text{Pd}–\text{P}(2)$ (174.6(1)°) and $\angle \text{C}(1)–\text{Pd}–\text{Br}(1)$ (176.7(2)°) from linearity.

The exclusive insertion of $[\text{Pd}(\text{PPh}_3)_2]$ into the C–Br bond at the 2-position determines the regioselectivity of the debromination reaction (Scheme 2). For example, reduction of 2,3,5-tribromothiophene gives good yields of 2,3-dibromothiophene when catalyzed by $\text{Pd}(0)$. To show that the oxidation addition products **1–6** are intermediates in the debromination reactions, complex **5** was treated with an equimolar amount of NaBH_4 in CD_3CN at RT. ^{31}P NMR and GC/MS assay confirmed the generation of 2,3-dibromothiophene as the predominant thiophene product. In the presence of two-fold excess of PPh_3 and under similar conditions, the same product is formed.

The delocalization effect imparted by bromide is expected to stabilize the bromothieryl complexes with respect to the unsubstituted thienyl complex **1**. This electronic effect appears to offset the steric problems

associated with the highly substituted thienyl complex. The X-ray structure of **1** also points to a polarization and weakening of the Pd–Br bond. The reactions of the thiophenes with $\text{Pd}(\text{PPh}_3)_4$ were followed by ^{31}P and ^1H NMR; the reactivity order descends from highly substituted thiophenes to unsubstituted thiophene. Conversely, the stability of the isolated complexes decreases as follows: $6 > 5 > 4 \approx 3 \approx 2 > 1$. Among the dibromothiophenes, the 2,5-isomer is the most reactive whereas the 2,3-derivative is the least; the steric effects appear to be a governing factor.

Most of the reported α -thienyl complexes are synthesized from electrophilic attack on the thiophene ring [15] or metal exchange with lithiated thienyls [16]. It is surprising that nucleophilic attack on halo-substituted thiophenes has rarely been exploited as an alternative synthetic path. The present study illustrates this idea and charts our future work on a variety of low-valent unsaturated complexes.

3. Experimental details

3.1. General

All reactions were performed using standard Schlenk techniques. 2-Bromothiophene, 2,3-, 2,4- and 2,5-dibromothiophenes, 2,3,5-tribromothiophene and tetrabromothiophene were commercial products and used without further purification. $\text{Pd}(\text{PPh}_3)_4$ was prepared according to published procedures [17]. Reagent-grade benzene and diethyl ether were distilled from Na/benzophenone under argon.

3.2. Analytical methods

NMR spectra were acquired on a Bruker ACF300 spectrometer. ^1H NMR spectra were referenced to the internal reference SiMe_4 with CDCl_3 as solvent. ^{13}C NMR spectra were referenced to the 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% $\text{H}_3\text{PO}_4–\text{D}_2\text{O}$.

Gas chromatographic data were obtained on a Hewlett–Packard 5890 Series II Plus Gas Chromatograph (GC) with a HP-1 capillary column (25 m $\times$ 0.32 mm ID, 0.25 μm phase thickness, 25 m length). A split/splitless injector was used in the splitless mode. Nitrogen was used as the carrier gas and the flow rate was 1.28 ml min^{-1} . The temperatures for injector and detector were 280 and 300 °C respectively. The temperature program for the analysis of the reaction mixture of complex **5** with NaBH_4 was as follows: initial oven temperature held at 60 °C for 5 min, increased to 300 °C at a rate of 10 °C min^{-1} , with final temperature held for 2 min. For mass spectrometric analysis of the reaction mixture, a Hewlett–Packard 5890 Series I Gas Chro-

matograph was equipped with a Hewlett–Packard 5988A Mass Spectrometer (MS) installed with a Continuous Dynode Electron Multiplier (CDEM). The GC–MS was operated with a Hewlett–Packard 59970 MS ChemStation system and an NBS library database (version 3.1). The column used was a 25 m × 0.32 mm ID (0.25 μm phase thickness, 25 m length) HP-5 capillary column (Hewlett–Packard). Helium was the carrier gas and the flow rate was 1.29 ml min⁻¹. The temperatures for injector, transfer line and ion source were 280, 280 and 200°C respectively. The mass spectrometer was tuned to perfluorotributylamine (PFTBA). The following temperature program was used: 50°C held for 5 min, followed by a linear increase to a final temperature of 280°C with a rate of 10°C min⁻¹ and held there for another 10 min.

Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department at the National University of Singapore.

3.3. Synthesis of PdBr(2-thienyl)(PPh₃)₂, 1

A mixture of Pd(PPh₃)₄ (1.156 g, 1.0 mmol) and 2-bromothiophene (0.198 g, 1.2 mmol) in benzene (10 ml) was deoxygenated and stirred overnight in a 50 ml Schlenk flask under argon at RT. The resultant yellow solution was evaporated to dryness in vacuo. The solid residue was triturated with Et₂O and the ether solution discarded. The washing was repeated twice and the residual product purified further by recrystallization from chloroform–hexane.

3.4. Syntheses of PdBr(5-bromo-2-thienyl)(PPh₃)₂, 2, PdBr(4-bromo-2-thienyl)(PPh₃)₂, 3, PdBr(3-bromo-2-thienyl)(PPh₃)₂, 4, PdBr(3,4-dibromo-2-thienyl)(PPh₃)₂, 5, PdBr(3,4,5-tribromo-2-thienyl)(PPh₃)₂, 6

These complexes were prepared by a method similar to that described for 1. Their yields, physical properties and elemental analytical data are listed in Table 5.

3.5. Reaction of PdBr(3,4-dibromo-2-thienyl)(PPh₃)₂, 5 with NaBH₄

To a CD₃CN solution (5 ml) of 5 (0.0192 g, 0.02 mmol) in a 40 ml Schlenk flask was added an equimolar quantity of NaBH₄ (0.0008 g, 0.02 mmol) and the mixture was stirred for 4 h under argon at RT. The resultant dark-colored mixture was filtered and analyzed by NMR and GC/MS. The ³¹P NMR spectrum of the filtrate showed that 5 was consumed and PPh₃ (δ = -5 ppm) was formed. GC and GC/MS analysis with the help of standard samples showed that 2,3-dibromothiophene, PPh₃ and OPPh₃ were formed as the main products.

The above experiment was repeated in the presence of two-fold excess of PPh₃. The resultant mixture, which is almost colorless, was analyzed. Similarly, 2,3-dibromothiophene, PPh₃ and OPPh₃ were detected. The solution is not stable, changing gradually to dark-red and finally liberating Pd metal. Attempts to isolate any palladium complexes from this mixture were unsuccessful.

3.6. X-ray crystallography

Single crystals of PdBr(2-thienyl)(PPh₃)₂, 1, and PdBr(3,4,5-tribromo-2-thienyl)(PPh₃)₂, 6, were grown respectively from CH₃CN–C₆H₅CH₃–CHCl₃ and C₆H₅CH₃–CHCl₃ mixtures. Crystals suitable for X-ray diffraction were mounted on thin-walled glass capillaries under an atmosphere of nitrogen. Intensity data were measured on a Rigaku RAXIS IIC imaging plate and a Rigaku AFC7 diffractometer respectively, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For complex 1, 31 oscillation frames were used with φ = 0–180°, Δφ = 6.0° and a scan rate of 8 min per frame. For complex 2, the variable ω-scan technique was used with a scan rate of 2.00 to 32.00° min⁻¹. Empirical absorption corrections were applied to the raw intensities. The structures were solved

Table 5
Physical properties and elemental analytical data for 1–6

Complexes (formula)	Color	M.p. (°C)	Yield (%)	Analysis (%)						
				C	H	Br	P	Pd	S	
1 (C ₄₀ H ₃₃ BrP ₂ PdS)	yellow	~ 185 (dec.)	85	Found	60.72	4.34	9.55	7.60	13.44	4.44
				Calc.	60.51	4.19	10.06	7.80	13.40	4.04
2 (C ₄₀ H ₃₂ Br ₂ P ₂ PdS)	light yellow	~ 200 (dec.)	88	Found	55.17	3.59	18.52	7.25	12.10	3.58
				Calc.	55.04	3.70	18.31	7.10	12.19	3.67
3 (C ₄₀ H ₃₂ Br ₂ P ₂ PdS)	light yellow	~ 205 (dec.)	91	Found	55.28	4.09	17.93	7.01	11.98	3.92
				Calc.	55.04	3.70	18.31	7.10	12.19	3.67
4 (C ₄₀ H ₃₂ Br ₂ P ₂ PdS)	light yellow	~ 200 (dec.)	93	Found	55.13	3.69	18.11	6.95	11.76	3.28
				Calc.	55.04	3.70	18.31	7.10	12.19	3.67
5 (C ₄₀ H ₃₁ Br ₃ P ₂ PdS)	light yellow	~ 235 (dec.)	90	Found	50.72	3.32	24.70	6.13	10.84	3.22
				Calc.	50.48	3.28	25.18	6.51	11.18	3.37
6 (C ₄₀ H ₃₀ Br ₄ P ₂ PdS)	light yellow	~ 260 (dec.)	95	Found	46.40	2.99	30.50	5.68	9.77	3.40
				Calc.	46.61	2.93	31.01	6.01	10.32	3.11

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. Molecule 1 has a crystallographic two-fold axis passing through Br(1), Pd(1), C(19) and the mid-point of the C(21)–C(21a) bond; the X-ray scattering power of the disordered thienyl group is thus represented by C(19) and C(21) at full site occupancy together with S(1) and C(20) at half site occupancy. All calculations were performed on a PC 486 with the SHELXTL-PC program package [18]. Crystal data, data collection parameters and results of the analyses are listed in Table 2. Selective bond lengths and bond angles for 1 and 6 are listed in Tables 3 and 4 respectively.

4. Supplementary material available

Lists of thermal parameters and structure factors for complexes 1 and 6 are available from the authors.

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