

# Reductive coupling of halogenothiophenes and halogenothiazoles catalysed by Pd<sup>II</sup> in a basic alcohol medium

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A catalytic reductive coupling method has been developed whereby 2- and 3-bromo- and 2-iodothiophenes, 2-bromothiazole and 2-bromofuran are converted into their corresponding bithiophene, bithiazole and bifuran derivatives. The use of a basic alcohol medium favours the reductive coupling pathway over the hydrodehalogenation pathway, which is generally more facile when other reducing agents are used. The catalytic mechanisms are discussed. The syntheses and characterization of the proposed intermediate complexes, *trans*-[PdBr(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] **1**, *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] **2** and *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3** support the proposed mechanism and the catalytic results. Single-crystal X-ray crystallographic structure determinations of **2** and **3** were carried out.

## Introduction

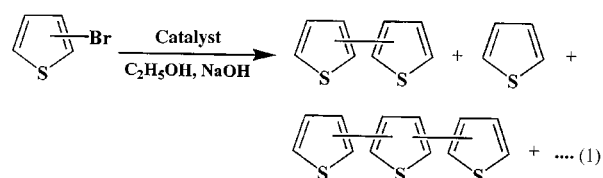
Bithiophenes and their derivatives are important synthetic precursors for conducting polymers<sup>1</sup> and biologically active materials.<sup>2</sup> Common synthetic methodologies for bithiophenes include Ullmann reaction,<sup>3</sup> Grignard coupling<sup>4</sup> and the use of Ni<sup>0</sup> as a coupling catalyst.<sup>5</sup> While each of these methods has its values, they also have their drawbacks. For example, the Ullmann method is non-selective, requires high temperatures and can produce erratic yields<sup>6</sup> whereas the other two methods, especially the use of nickel(0) catalysts, require careful preparation of the catalysts which are sensitive to air and heat. Recently, a more complex cross-coupling between stannyl and silyl bromothiophenes giving 3,4'-disubstituted-2,2'-bithiophene has also been reported.<sup>7</sup>

Recently we reported novel Pd-catalysed hydrodebromination reactions of polybrominated thiophenes which can be used to prepare a range of less accessible bromothiophene isomers.<sup>8</sup> A key intermediate in the proposed catalytic mechanism is a palladium–thienyl complex that undergoes rapid hydride transfer prior to elimination of the hydrodebrominated product.<sup>8</sup> In this paper we shall describe how we can suppress the hydrodebromination step and promote a bromo–thienyl ligand exchange in an alcohol medium. The success of the latter would pave a way for the facile synthesis of bithiophene through reductive coupling. The reaction conditions and the effects of the substrates used are described.

## Results and discussion

### Catalytic reaction

**Activity of different catalysts.** The palladium catalysts that are able to give a quantitative conversion of 2-bromothiophene under the specified conditions are given in the Experimental section (under **Catalytic reactions**). 2,2'-Bithiophene is invariably the main product and thiophene is the minor one. Trimer 2,2':5',2''-terthiophene, oligomers and small amounts of other products are also formed. The formation of these products suggests the occurrence of competing coupling, debromination and polymerization reactions [eqn. (1)]. The complex [PdCl<sub>2</sub>-



(dppf)] is the most efficient catalyst which gives the highest ratio (bithiophene : thiophene) of products in the shortest time. In spite of some success for nickel and copper complexes in related syntheses, the compounds [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub>, [Cu(BH<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>], [NiCl<sub>2</sub>(dppp)] [dppp = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>], [Ni{P(OEt)<sub>3</sub>}<sub>4</sub>] and [NiCl<sub>2</sub>(dppf)] exhibit no activity under the current conditions.

**Effects of different heterocyclic halide substrates and bases.** Different substrates *viz.* 2- and 3-bromothiophene, 2-iodothiophene,<sup>9</sup> 2-bromofuran<sup>10</sup> and 2-bromothiazole were studied with [PdCl<sub>2</sub>(dppf)], [Pd(PPh<sub>3</sub>)<sub>4</sub>] or Pd(OAc)<sub>2</sub> as catalysts (Table 1). Bromothiophenes, 2-iodothiophene and 2-bromofuran give quantitative conversions (entries 1–4 and 7, Table 1). 2-Iodothiophene undergoes dehalogenation more easily. The reactivity of 2-bromothiazole is lower (entries 5 and 6, Table 1).

Selectivity for coupling over hydrodehalogenation is best for bromothiophenes. In order to obtain quantitative conversion of 2-bromothiophene and maximum yield of bithiophene, at least one equivalent of NaOH is required per mole of 2-bromothiophene (Table 2). The effect of an additional quantity of a base on the yield is small, although the rate of reduction is accelerated. The effects of KOH, pyridine, aniline, DMF, NaOMe, NaOEt, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> were examined and compared with that of NaOH. Under similar conditions, the effects of NaOMe, NaOEt and KOH are similar to that of NaOH (entries 1–4, Table 2), whilst the conversion is significantly lower when the less basic Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> is used (entries 5 and 6, Table 2). There is no reaction with pyridine, aniline and DMF (entries 7–9, Table 2) or when a base is not added (entry 10, Table 2).

**Effects of alcohols.** An alcohol in this reaction serves both as a solvent and reducing agent. It solubilizes the substrates and

**Table 1** The [PdCl<sub>2</sub>(dppf)], [Pd(PPh<sub>3</sub>)<sub>4</sub>] or Pd(OAc)<sub>2</sub> catalysed coupling and debromination of different monohalogeno-substrates

Entry	Substrate	Conversion (%)	t/h	Product	Yield <sup>a</sup> (%)	Product	Yield (%)	b:t <sup>b</sup>
1	2-Bromothiophene	100	2.5	2,2'-Bithiophene	72	Thiophene	23	3.1
2	3-Bromothiophene	100	3.5	3,3'-Bithiophene	74	Thiophene	20	3.7
3	2-Iodothiophene	100	2	2,2'-Bithiophene	50	Thiophene	45	1.1
4 <sup>c</sup>	2-Iodothiophene	100	2.5	2,2'-Bithiophene	48	Thiophene	43	1.1
5 <sup>d</sup>	2-Bromothiazole	40	26	2,2'-Bithiazole	20	Thiazole	20	1.0
6 <sup>c</sup>	2-Bromothiazole	31	30	2,2'-Bithiazole	15	Thiazole	16	1.0
7	2-Bromofuran	100	5	2,2'-Bifuran	61	Furan	34	1.8

Conditions: EtOH, 10 cm<sup>3</sup>; substrate, 2.0 mmol; NaOH, 3.0 mmol; [PdCl<sub>2</sub>(dppf)], 1 mol%; 60 °C. <sup>a</sup> Obtained by GC analysis with anthracene as an internal standard. <sup>b</sup> The mole ratio of the coupling product to debromination product. <sup>c</sup> [Pd(PPh<sub>3</sub>)<sub>4</sub>] as catalyst. <sup>d</sup> Pd(OAc)<sub>2</sub> as catalyst.

**Table 2** Effects of different bases on the debromination and coupling of 2-bromothiophene

Entry	Base	Reaction time/h	Conversion (%)	Yield <sup>a</sup> (%)		
				Thiophene (t)	Bithiophene (b)	b:t
1	NaOMe	2.5	100	30	70	2.3
2	NaOH	2.5	100	23	72	3.1
3	KOH	2.5	100	26	71	2.7
4	NaOEt	2.5	100	27	70	2.6
5	Na <sub>2</sub> CO <sub>3</sub>	2.5	40	10	30	3.0
6	NaHCO <sub>3</sub>	2.5	20	5	15	3.0
7	Pyridine	10	0	0	0	
8	Aniline	20	0	0	0	
9	DMF	30	0	0	0	
10	—	30	0	0	0	

Conditions: EtOH, 10 cm<sup>3</sup>; 2-bromothiophene, 2.0 mmol; base, 3.0 mmol; [PdCl<sub>2</sub>(dppf)], 1 mol%; 60 °C. <sup>a</sup> Obtained by GC analysis with anthracene as an internal standard.

**Table 3** Effects of alcohols on the coupling and debromination of 2-bromothiophene

Entry	Solvent	Reaction time/h	Conversion (%)	Yield <sup>a</sup> (%)		
				Thiophene (t)	bithiophene (b)	b:t
1	MeOH	2.5	100	43	57	1.3
2	EtOH	2.5	100	23	72	3.1
3	<i>n</i> -PrOH	2.5	64	16	48	3.0
4	<i>i</i> -PrOH	5.0	36	8	28	3.5
5	<i>n</i> -BuOH	5.0	41	8	33	4.1
6	<i>i</i> -BuOH	5.0	11	3	8	2.7
7	<i>t</i> -BuOH	24	0	0	0	
8	THF	24	0	0	0	

Conditions: alcohol, 10 cm<sup>3</sup>; 2-bromothiophene, 2.0 mmol; NaOH, 3.0 mmol; [PdCl<sub>2</sub>(dppf)], 1 mol%; 60 °C. <sup>a</sup> Obtained by GC analysis with anthracene as an internal standard.

the base. In MeOH and EtOH the reduction is completed after 2.5 h (entries 1 and 2, Table 3) whereas in PrOH and BuOH the conversion is significantly lower (entries 3–7, Table 3). The poorer solubility of bases in these solvents offers one of the explanations. The steric hindrance of the alcohol also plays a key role. For example, bulky alcohols tend to be less active than their lower homologues (*e.g.* comparing entries 3 and 4, and 5 and 6, Table 3). The ready availability of β-hydrogen in the alcohol also plays a key role. Thus *t*-BuOH without an active hydrogen or non-alcohol solvents like toluene, DMSO, 1,4-dioxane and THF show no reducing activity.

**Effects of temperature and duration.** As expected, the reaction rate increases as the temperature is raised from 20 to 78 °C (Fig. 1). The mole ratio of 2,2'-bithiophene to thiophene is however fairly constant over this temperature range but peaks at ≈60 °C. Refluxing conditions (78 °C) lead to more polymerization products and less bithiophene. There is an induction time of 5–10 min before any product is observed (Fig. 2). The light yellow or orange solution gradually turns to dark brown or black during the course of the reaction as the palladium catalyst gradually decomposes upon the consumption of 2-bromothiophene. The product yields peak at 2.5 h

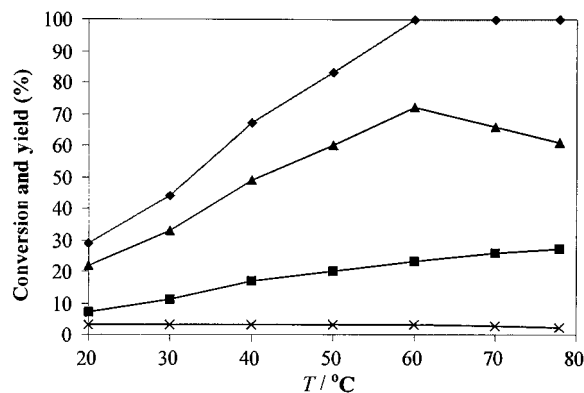
duration after which solid precipitates. It is significant that the relative proportion of 2,2'-bithiophene to thiophene remains essentially constant through the course of the reaction. This gives a clear indication that neither of these compounds is the precursor for the other in the reaction mechanism.

#### Preparative-scale syntheses of bithiophenes and bifuran

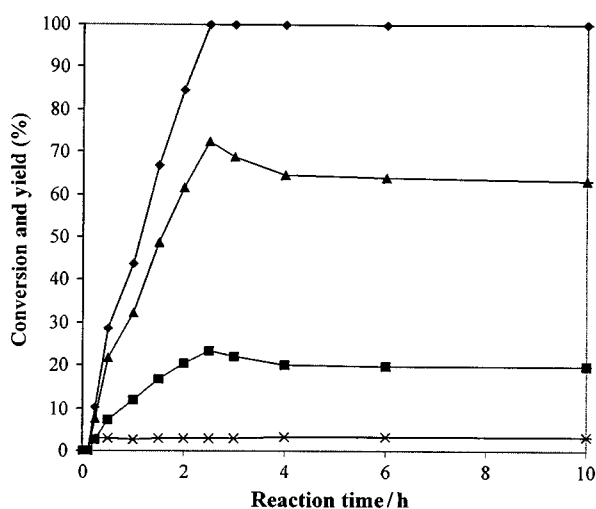
Based on the findings listed in Table 2, the coupling products 2,2'- and 3,3'-bithiophenes and 2,2'-bifuran have been synthesized on a preparative scale at 60 °C in the presence of 1 mol% [PdCl<sub>2</sub>(dppf)] and NaOH in EtOH. The products are isolated by standard methods, giving 2,2'- and 3,3'-bithiophenes and 2,2'-bifuran in 55, 65 and 50% yields respectively. The yields of bithiophenes are similar to those obtained from the Grignard coupling method,<sup>4,11</sup> but the present method offers a simpler procedure with the use of inexpensive reagents.

#### The reaction mechanism

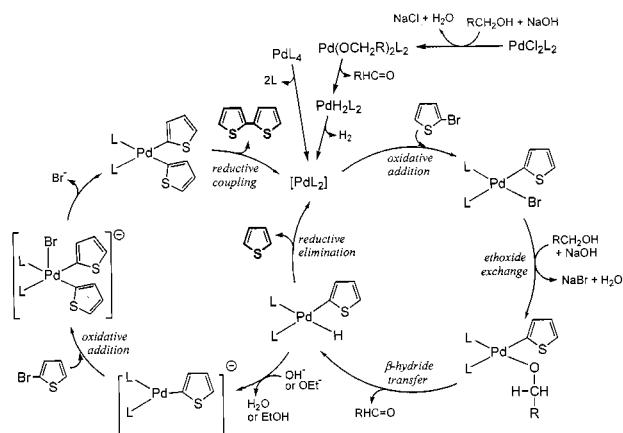
The above results allow us to propose two competing mechanisms for reductive coupling and hydrodebromination (Scheme 1). In either mechanism the use of a palladium(0) precursor would enter directly as a palladium(0) catalyst whilst



**Fig. 1** Effects of temperature on the coupling and hydrodebromination of 2-bromothiophene. Conditions: EtOH, 10 cm<sup>3</sup>; 2-bromothiophene, 2.0 mmol; NaOH, 3.0 mmol; [PdCl<sub>2</sub>(dppf)], 1 mol%. The yield was obtained by GC analysis with anthracene as an internal standard. ◆, Conversion; ■, yield of thiophene (t); ▲, yield of bithiophene (b); ×, b : t.

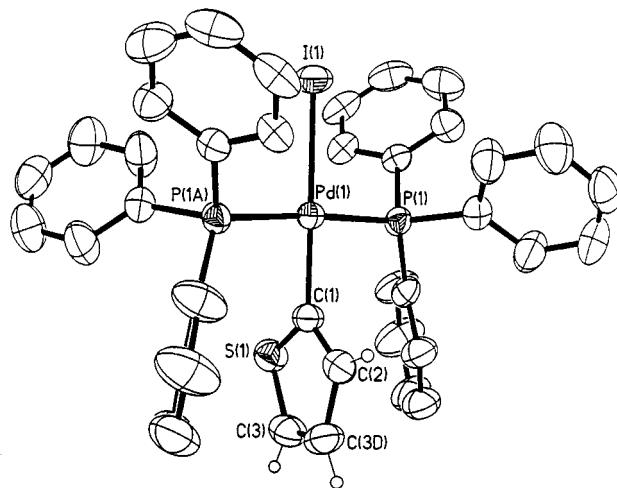


**Fig. 2** Effects of reaction time on the coupling and hydrodebromination of 2-bromothiophene at 60 °C. Other conditions and symbols as in Fig. 1.



**Scheme 1** Proposed catalytic coupling and hydrodebromination mechanisms of 2-bromothiophene.

a palladium(II) pre-catalyst can be reduced easily in the presence of NaOH (or other strong base) and alcohol. Both go through an oxidative addition process to give a bromothiophenyl palladium(II) complex, followed by base-assisted alkoxylation to give an alkoxy thiophenyl complex. This key intermediate either undergoes a β-H elimination to give a hydride complex,



**Fig. 3** An ORTEP<sup>17</sup> plot of the molecular structure of *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] 2 (50% probability ellipsoids).

which leads to thiophene through reductive elimination, or bithiophene through deprotonation, oxidative addition and finally reductive elimination. The latter type of mechanism, especially the involvement of a five-co-ordinated palladate,<sup>12</sup> has been discussed.<sup>13</sup>

The observed lower efficiency of the bulkier and less acidic alcohols and those that do not have active β-H is consistent with this mechanism. The higher yield of thiophene in MeOH compared to EtOH (Table 3) is consistent with the higher acidity and the larger number of β-hydrogens of the former. The ease of β-H elimination,<sup>14</sup> ligand exchange<sup>15</sup> and reductive elimination<sup>16</sup> on Pd<sup>II</sup> has been well established.

We have also substantiated this mechanism by using CD<sub>3</sub>OD and C<sub>2</sub>D<sub>5</sub>OD in the reduction of 2-bromothiophene to 2,2'-bithiophene or thiophene; GC-MS analysis showed that all the thiophene is deuterated.

#### Isolation and characterization of the intermediates

In order to have a better understanding of the catalytic mechanism we have isolated the proposed key catalytic intermediates *trans*-[PdBr(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] 1,<sup>8</sup> *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] 2 and *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2,N</sup>)(PPh<sub>3</sub>)<sub>2</sub>]·½CHCl<sub>3</sub> 3 from the stoichiometric reactions between [Pd(PPh<sub>3</sub>)<sub>4</sub>] and 2-bromothiophene, 2-iodothiophene and 2-bromothiazole respectively. These compounds were characterized by NMR and X-ray single-crystal crystallography. Complex 1 has recently been reported.<sup>8</sup> Complexes 1, 2 and 3 were treated with bromothiophene or bromothiazole and NaOH in EtOH at 60 °C respectively. The GC and GC-MS assays confirmed the generation of bithiophene and thiophene from 1 or 2, and bithiazole and thiazole from 3.† This suggests that these complexes are possible intermediates of the reduction of the respective heterocyclic halides.

**Structure of *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] 2.** Complex 2, similar to 1,<sup>8</sup> is a palladium(II) σ-thienyl complex with a near-ideal square-planar geometry with two phosphines [P(1)–Pd–P(1A) 176.09(7)°] as well as thiophenyl and iodide [I–Pd–C(1) 180.0°] *trans* to each other (Fig. 3, Table 4). The neutral molecule possesses crystallographically imposed 2-fold rotational

† No vigorous effort was spent to determine the product ratio of hydrodebromination and coupling products. These ratios would not necessarily be the same as those obtained from the catalytic reactions because the reaction conditions are different. For example, in a catalytic reaction, there is a higher chance for the hydride, *e.g.* [PdH(C<sub>4</sub>H<sub>3</sub>S)L<sub>2</sub>], to undergo proton abstraction (which leads to bithiophene) than for it to undergo intramolecular elimination of thiophene.

**Table 4** Selected bond lengths (Å) and angles (°) for *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] **2** and *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3**

(a) *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] **2**

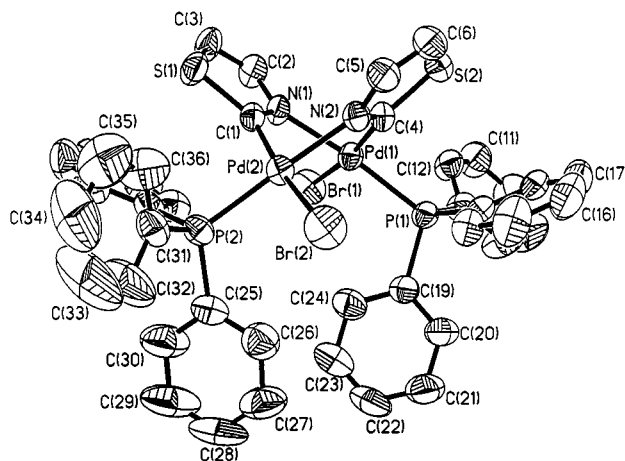
Pd(1)–C(1)	2.019(7)	Pd(1)–I(1)	2.6953(7)
Pd(1)–P(1)	2.3618(12)	C(3)–C(3D)	1.364(12)
S(1)–C(1)	1.696(6)	S(1)–C(3)	1.645(8)
C(1)–C(2)	1.414(7)	C(2)–C(3D)	1.510(3)
P(1)–C(1A)	1.831(5)	P(1)–C(1B)	1.848(5)
P(1)–C(1C)	1.832(5)		

C(1)–Pd(1)–P(1)	88.05(3)	P(1)–Pd(1)–P(1A)	176.09(7)
I(1)–Pd(1)–P(1)	91.95(3)	I(1)–Pd(1)–C(1)	180.0
S(1)–C(1)–Pd(1)	120.6(2)	C(2)–C(1)–Pd(1)	127.9(3)
C(1)–S(1)–C(3)	92.4(4)	S(1)–C(1)–C(2)	104.3(6)
C(1)–C(2)–C(3D)	111.1(6)	C(2)–C(3D)–C(3)	106.7(4)
S(1)–C(3)–C(3D)	118.2(3)	C(1A)–P(1)–Pd(1)	113.6(2)
C(1B)–P(1)–Pd(1)	119.6(2)	C(1C)–P(1)–Pd(1)	111.2(2)

(b) *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3**

A		B	
Pd(1)–Br(1)	2.4897(8)	Pd(1A)–Br(1A)	2.4779(8)
Pd(2)–Br(2)	2.4725(8)	Pd(2A)–Br(2A)	2.4901(8)
Pd(1)–N(1)	2.081(4)	Pd(1A)–N(1A)	2.078(5)
Pd(2)–N(2)	2.071(5)	Pd(2A)–N(2A)	2.082(5)
Pd(1)–C(4)	1.981(6)	Pd(1A)–C(4A)	1.987(6)
Pd(2)–C(1)	1.978(6)	Pd(2A)–C(1A)	1.978(6)
Pd(1)–P(1)	2.274(2)	Pd(1A)–P(1A)	2.269(2)
Pd(2)–P(2)	2.266(2)	Pd(2A)–P(2A)	2.270(2)
N(1)–C(2)	1.377(7)	N(1A)–C(2A)	1.393(8)
N(1)–C(1)	1.328(7)	N(1A)–C(1A)	1.320(7)
S(1)–C(1)	1.718(6)	S(1A)–C(1A)	1.721(6)
S(1)–C(3)	1.696(7)	S(1A)–C(3A)	1.701(8)
C(2)–C(3)	1.330(8)	C(2A)–C(3A)	1.344(9)
N(2)–C(4)	1.315(7)	N(2A)–C(4A)	1.330(7)
N(2)–C(5)	1.379(7)	N(2A)–C(5A)	1.380(7)
S(2)–C(4)	1.715(6)	S(2A)–C(4A)	1.719(6)
S(2)–C(6)	1.707(7)	S(2A)–C(6A)	1.710(6)
C(5)–C(6)	1.329(9)	C(5A)–C(6A)	1.333(9)
C(4)–Pd(1)–N(1)	84.2(2)	C(4A)–Pd(1A)–N(1A)	84.9(2)
C(4)–Pd(1)–P(1)	92.1(2)	C(4A)–Pd(1A)–P(1A)	92.4(2)
N(1)–Pd(1)–P(1)	170.45(1)	N(1A)–Pd(1A)–P(1A)	174.47(14)
C(4)–Pd(1)–Br(1)	170.6(2)	C(4A)–Pd(1A)–Br(1A)	170.8(2)
N(1)–Pd(1)–Br(1)	88.92(13)	N(1A)–Pd(1A)–Br(1A)	90.21(13)
P(1)–Pd(1)–Br(1)	95.51(5)	P(1A)–Pd(1A)–Br(1A)	91.16(5)
C(1)–Pd(2)–P(2)	93.7(2)	C(1A)–Pd(2A)–P(2A)	93.4(2)
C(1)–Pd(2)–N(2)	83.4(2)	C(1A)–Pd(2A)–N(2A)	84.2(2)
N(2)–Pd(2)–P(2)	175.21(14)	N(2A)–Pd(2A)–P(2A)	170.77(14)
C(1)–Pd(2)–Br(2)	171.1(2)	C(1A)–Pd(2A)–Br(2A)	172.3(2)
P(2)–Pd(2)–Br(2)	93.09(5)	P(2A)–Pd(2A)–Br(2A)	91.56(5)
N(2)–Pd(2)–Br(2)	90.17(13)	N(2A)–Pd(2A)–Br(2A)	91.79(14)
C(1)–N(1)–Pd(1)	117.2(4)	N(1A)–N(1A)–Pd(1A)	119.1(4)
N(1)–C(1)–Pd(2)	124.5(4)	N(1A)–C(1A)–Pd(2A)	124.5(4)
C(2)–N(1)–Pd(1)	129.9(4)	C(2A)–N(1A)–Pd(1A)	128.0(4)
C(4)–N(2)–Pd(2)	118.0(4)	C(4A)–N(2A)–Pd(2A)	118.1(4)
C(5)–N(2)–Pd(2)	128.1(4)	C(5A)–N(2A)–Pd(2A)	129.5(4)
S(1)–C(1)–Pd(2)	124.6(3)	S(1A)–C(1A)–Pd(2A)	124.0(3)
N(2)–C(4)–Pd(1)	124.1(4)	N(2A)–C(4A)–Pd(1A)	124.9(4)
S(2)–C(4)–Pd(1)	124.5(3)	S(2A)–C(4A)–Pd(1A)	123.7(3)

symmetry. To achieve a strong Pd–thienyl interaction [Pd–C(1) 2.019(7) Å], the thienyl plane makes a dihedral angle of 95.0° with the palladium(II) co-ordination plane to avoid steric interactions with the phenyl groups. There is no indication of η<sup>1</sup>-S co-ordination or any η<sup>2</sup> or η<sup>4</sup> metal interaction using the π bonds on the thienyl ring. Metallation at one of the two carbon atoms neighbouring the sulfur gives rise to two C–S bonds of slightly different lengths [C(1)–S(1) 1.696(6) and C(3)–S(1) 1.645(8) Å]. The strong *trans* influence of the thienyl group gives an unusually long Pd–I bond [2.6953(7) Å compared to many other Pd<sup>II</sup>–I bonds, e.g. in the red isomer of [PdI<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>] [2.638(3) and 2.619(3) Å],<sup>18</sup> yellow isomer of [PdI<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>] [2.59(3) Å],<sup>18</sup> *trans*-[PdI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [2.587(1) Å]<sup>19</sup> and [Pd<sub>2</sub>(μ-dppm)<sub>2</sub>(μ-I)(CH<sub>3</sub>)I]<sup>+</sup> [2.577(6) Å].<sup>20</sup> The weakness of this Pd–I bond also supports the ready reduction (or



**Fig. 4** An ORTEP plot of the molecular structure of one of the two independent molecules (A) in the asymmetric unit of *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3** (50% probability ellipsoids).

hydrogen exchange) of **2** with subsequent elimination to give thiophene.

**Structure of *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3**.** Elemental analysis suggests that complex **3** contains only one phosphine group per metal atom which is different from that in either **1** or **2**. The <sup>1</sup>H and <sup>13</sup>C NMR data suggest that palladation occurs at the thiazole rings. The single <sup>31</sup>P NMR resonance indicates a mononuclear structure or a dinuclear structure with two symmetric PPh<sub>3</sub> groups. An array of structures are possible depending on the nuclearity and the relative disposition of the four different donor atoms on the Pd *viz.* Br, C, N and P. In order to obtain a definitive assignment, an X-ray single-crystal diffraction study was carried out on **3**. There are two crystallographically independent molecules A (Fig. 4) and B in the unit cell, but they are similar. They contain a dinuclear structure with two metal atoms bridged by two thiazole groups co-ordinated through C and N. Each Pd<sup>II</sup> is essentially planar with one PPh<sub>3</sub> and Br completing the square plane. This structure can also be viewed as a modified “face-to-face A-frame” structure. It clearly indicates that the thiazole N is preferentially bonded instead of S and that the phosphine ligand prefers to be *trans* to the N donor, which has a lower *trans* influence.

To our knowledge, **3** is the first palladium complex of thiazole to be characterized by NMR and single crystal X-ray crystallography. Among the few complexes of thiazole or its derivatives,<sup>21</sup> **3** is one of two with a dinuclear bridged structure. The other was prepared by electrophilic attack on a thiazole ring with methyl lithium.<sup>22</sup>

An alternative view of the Pd<sub>2</sub> structure is a six-membered metal–thiazole ring folded along the Pd···Pd hinge at an angle of 88.5(2) (A) or 82.6(2)° (B). The two co-ordination planes around the metal atoms are significantly skewed from coplanarity to a dihedral angle 87.3(2) (A) or 90.1(2)° (B). With two phosphines opting to bind selectively *trans* to the N-donor, it gives a molecular C<sub>2</sub> symmetry and the P(2)–Pd(2)···Pd(1)–P(1) dihedral angle of 99.3(2) (A) or 96.6(2)° (B). No direct Pd–Pd bond is envisaged which is consistent with the observed distance of 3.407 (A) or 3.459 Å (B). The average Pd–C (1.981), Pd–N (2.078) and Pd–Br (2.4825 Å) lengths are in agreement with reported values.<sup>23</sup> The Pd–Br lengths are intermediate between those in e.g. *trans*-[PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [2.425(1) Å]<sup>24</sup> and *trans*-dibromobis[2-(2-thienyl)pyridine]palladium [2.431(1) Å]<sup>25</sup> and in e.g. *trans*-[Pd(Et)(Br)(PMe<sub>3</sub>)<sub>2</sub>] [2.554(1) Å]<sup>26</sup> and [PdBr(C<sub>5</sub>H<sub>4</sub>N-C<sup>2</sup>, -C<sup>3</sup> or C<sup>4</sup>)(PEt<sub>3</sub>)<sub>2</sub>] [2.522(1)–2.563(3) Å].<sup>27</sup> This suggests that the *trans* influence of thiazole is stronger than bromide but weaker than ethyl or pyridyl. The Pd–P lengths (average 2.270 Å) on the contrary are slightly shorter

than those found elsewhere (2.306–2.350 Å).<sup>23</sup> Palladation imparts a very slight structural or geometric effect on the thiazolyl group when compared with free thiazole.<sup>28</sup>

The isolation of complex **3** suggests that a dinuclear structure could also exist in equilibrium with mononuclear intermediates in the catalytic cycles for reductive dehalogenation or coupling of difunctional heterocycles. The higher stability of dinuclear complexes could explain the lower reactivity of bromothiazole compared to halogenothiophenes. Current research in our laboratory is directed at the isolation of the reaction intermediates of other multifunctional heterocycles and the study of their synthetic utilities.

## Experimental

### General

All reactions were performed using standard Schlenk techniques. All solvents were degassed before use. Reagent-grade toluene and diethyl ether were distilled from sodium-benzophenone under nitrogen. The compound Pd(OAc)<sub>2</sub>, 2- and 3-bromothiophene and 2-bromothiazole were commercial products used without further purification. 2-Iodothiophene,<sup>9</sup> 2-bromofuran,<sup>10</sup> [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>],<sup>29</sup> [PdCl<sub>2</sub>(dppf)],<sup>30</sup> [Pd(PPh<sub>3</sub>)<sub>4</sub>],<sup>31</sup> [PdCl<sub>2</sub>(dppr)],<sup>‡</sup><sup>32</sup> [Pd(dba)<sub>2</sub>],<sup>‡</sup><sup>33</sup> [PdCl<sub>2</sub>(MeCN)<sub>2</sub>],<sup>34</sup> [NiCl<sub>2</sub>(dppp)],<sup>35</sup> [NiCl<sub>2</sub>(dppf)],<sup>36</sup> [Ni{P(OEt)<sub>3</sub>}<sub>4</sub>],<sup>37</sup> [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub><sup>38</sup> and [Cu(BH<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>39</sup> were prepared according to published procedures.

### GC and GC-MS

Gas chromatographic analyses were carried out on a Hewlett-Packard (HP) 5890 Series II Plus gas chromatograph with an HP-1 capillary column (25 m × 0.32 mm, id, 0.25 μm phase thickness) with a flame ionization detection system. A split/splitless injector was used in the splitless mode. Nitrogen was used as the carrier gas and the flow rate was 1.28 cm<sup>3</sup> min<sup>-1</sup>. The temperatures for injector and detector were 280 and 300 °C respectively. The temperature programme for the analysis of the catalytic reaction mixture was as follows: initial oven temperature held at 50 °C for 5 min, increased to 300 °C at a rate of 10 °C min<sup>-1</sup>, final temperature held for 2 min.

For mass spectrometric analysis of the reaction mixture a Hewlett-Packard 5890 Series I gas chromatograph equipped with an HP 5988A mass spectrometer installed with a Continuous Dynode Electron Multiplier (CDEM) was used. The ionization mode was EI. The system was operated with an HP 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) HP-5 capillary column. Helium was the carrier gas and the flow rate was 1.29 cm<sup>3</sup> min<sup>-1</sup>. The temperatures for the injector, transfer line, and ion source were 280, 280 and 200 °C respectively. The mass spectrometer was tuned to perfluorotributylamine (PFTBA). The following temperature programme was used: 50 °C held for 5 min, followed by a linear increase (10 °C min<sup>-1</sup>) to a final temperature of 280 °C, held for another 10 min.

### NMR analysis

The NMR spectra were acquired on a Bruker ACF 300 spectrometer, <sup>1</sup>H spectra being referenced to the internal reference SiMe<sub>4</sub> with CDCl<sub>3</sub> as solvent, <sup>13</sup>C to the same solvent and <sup>31</sup>P internally relative to the deuterium lock signal using the SR Command of Standard Bruker Software with the standard 85% H<sub>3</sub>PO<sub>4</sub>-D<sub>2</sub>O. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department at National University of Singapore.

‡ dppr = 1,1'-Bis(diphenylphosphino)ruthenocene; dba = dibenzylideneacetone.

### Catalytic reactions

The catalytic reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Magnetic stirring was used for all reactions. A typical procedure was as follows: 10 cm<sup>3</sup> of degassed alcohol, 20 mmol of substrate and 30 mmol of NaOH were added to a Schlenk flask which was connected to the nitrogen gas supply and a reflux condenser. The flask was then flushed with nitrogen gas and the rate of gas flow monitored by means of a bubbler fitted at the neck of the reflux condenser. The solution was stirred for ≈5 min before a 1 mol% amount of the catalyst was added. The flask was immersed in an oil-bath maintained at 60 °C for a designated duration with stirring. The reaction mixtures were analysed by GC with anthracene as an internal standard. The products were assayed by gas chromatography, identified by GC-MS analysis and confirmed by comparisons with authentic samples.

Debromination of 2-bromothiophene was tested by ten palladium {viz. Pd(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub> + L (L = PPh<sub>3</sub> or dppe), [Pd(dba)<sub>2</sub>], [Pd(dba)<sub>2</sub>] + dppe, [PdCl<sub>2</sub>L] (L = 2PPh<sub>3</sub>, 2MeCN, dppf or dppr), [Pd(PPh<sub>3</sub>)<sub>4</sub>]} and other copper and nickel catalytic systems. Only the palladium systems showed any measurable activities. The complex [PdCl<sub>2</sub>(dppf)] was the best performer in terms of the time taken for completion (2½ h) and the yields of 2,2'-bithiophene (b) (72%) with respect to thiophene (t) (23%), which gives a b:t ratio of 3.1; [PdCl<sub>2</sub>(PPh<sub>3</sub>)], [PdCl<sub>2</sub>(dppf)] and [Pd(PPh<sub>3</sub>)<sub>4</sub>] also showed a reasonable b:t ratio of 2.7–2.8:1 taking 3 h for completion. Other palladium systems were less satisfactory (b:t 2.2–2.4:1; 3–6 h).

### Preparative-scale syntheses

**2,2'-Bithiophene.** An oxygen-free mixture of 2-bromothiophene (8.1 g, 50 mmol) and NaOH (3.0 g, 75 mmol) in EtOH (100 cm<sup>3</sup>) was stirred at 60 °C under nitrogen for about 10 min to allow NaOH to dissolve. The complex [PdCl<sub>2</sub>(dppf)] (0.36 g, 0.5 mmol) was then added and the mixture stirred continuously at 60 °C for 2.5 h. Upon completion of reaction (monitored by TLC) the mixture was evaporated to about 20 cm<sup>3</sup> and the solid was separated by filtration. Ice-water was then added to the filtrate to precipitate 2,2'-bithiophene, which was collected by filtration to give a yield of 50%, mp 31–33 °C. Owing to the low melting point of 2,2'-bithiophene, which made filtration difficult, the filtrate can be treated alternatively by removing the solvent and distilling the crude compound *in vacuo*. The main fraction which distilled at bp 87–88 °C (1.5 mmHg) (lit.,<sup>4</sup> bp 144 °C, 25 mmHg) was collected, giving pure 2,2'-bithiophene (4.5 g, 55%). δ<sub>H</sub>(CDCl<sub>3</sub>) 7.20 (dd, 2 H, J = 5.1, 1.2), 7.17 (dd, 2 H, J = 3.6, 1.2) and 7.01 (dd, 2 H, J = 5.1, 3.6 Hz). *m/z* 166 (M<sup>+</sup>, 100%).

**3,3'-Bithiophene.** An oxygen-free mixture of 3-bromothiophene (8.1 g, 50 mmol) and NaOH (3.0 g, 75 mmol) in EtOH (100 cm<sup>3</sup>) was stirred at 60 °C under nitrogen for about 10 min to allow NaOH to dissolve. The complex [PdCl<sub>2</sub>(dppf)] (0.36 g, 0.5 mmol) was then added. The mixture was stirred continuously at 60 °C for 2.5 h. Upon completion of reaction (monitored by TLC) the mixture was evaporated to about 20 cm<sup>3</sup> and the solid separated by filtration. Ice-water was then added to the filtrate to precipitate 3,3'-bithiophene which was collected on a filter in 65% yield (5.3 g), mp 131–133 °C.<sup>40</sup> δ<sub>H</sub>(CDCl<sub>3</sub>) 7.38 (m, 2 H) and 7.35 (m, 4 H). *m/z* 166 (M<sup>+</sup>, 100%).

**2,2'-Bifuran.** An oxygen-free mixture of 2-bromofuran (2.9 g, 20 mmol) and NaOH (1.4 g, 35 mmol) in EtOH (50 cm<sup>3</sup>) was stirred at 60 °C under nitrogen for about 10 min to allow NaOH to dissolve. The complex [PdCl<sub>2</sub>(dppf)] (0.144 g, 0.2 mmol) was then added. The mixture was stirred continuously at 60 °C for

**Table 5** Crystallographic data and refinement details for *trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] **2** and *trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> **3**

	<b>2</b>	<b>3</b>
Molecular formula	C <sub>40</sub> H <sub>33</sub> IP <sub>2</sub> PdS	C <sub>42</sub> H <sub>34</sub> Br <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> S <sub>2</sub> ·½CHCl <sub>3</sub>
<i>M</i>	840.96	1125.58
Colour and habit	Yellow prism	Colourless block
Crystal size/mm	0.25 × 0.23 × 0.13	0.25 × 0.10 × 0.08
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$
<i>T</i> /K	293(2)	293(2)
<i>a</i> /Å	19.4193(4)	13.2315(2)
<i>b</i> /Å	10.9234(3)	16.6131(4)
<i>c</i> /Å	16.4094(3)	20.0065(4)
<i>a</i> <sup>o</sup>		88.055(1)
<i>β</i> <sup>o</sup>		83.110(1)
<i>γ</i> <sup>o</sup>		86.919(1)
<i>F</i> (000)	1672	2214
<i>V</i> /Å <sup>3</sup>	3480.84(14)	4358.0(2)
<i>Z</i>	4	4
<i>μ</i> /mm <sup>-1</sup>	1.600	2.953
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.605	1.716
Reflections collected	20238	25796
Independent reflections	4377 ( <i>R</i> <sub>int</sub> = 0.0227)	19089 ( <i>R</i> <sub>int</sub> = 0.0231)
Final <i>R</i> , <i>R</i> ' indices (observed data)	0.0541, 0.1050	0.0567, 0.0983
Goodness of fit	1.252	1.064
Largest difference peak and hole/e Å <sup>-3</sup>	0.674 and -0.926	0.976 and -0.770

2.5 h. Upon completion of reaction (monitored by TLC) the mixture was evaporated to about 10 cm<sup>3</sup> and the solid separated by filtration. The solvent was removed from the filtrate and the crude product distilled *in vacuo*. The main fraction which distilled at bp 65–67 °C (11 mmHg) (lit.,<sup>41</sup> bp 63–64 °C, 11 mmHg) was collected, giving pure 2,2'-bifuran (1.34 g, 50%). δ<sub>H</sub>(CDCl<sub>3</sub>) 6.10 (dd, 2H), 7.01 (d, 2 H, *J* = 1.1) and 7.23 (d, 2 H, *J* = 3.3 Hz). *m/z* 134 (M<sup>+</sup>, 100%).

***trans*-[PdI(C<sub>4</sub>H<sub>3</sub>S-C)(PPh<sub>3</sub>)<sub>2</sub>] 2.** A mixture of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (1.156 g, 1.0 mmol) and 2-iodothiophene (0.252 g, 1.2 mmol) in toluene (20 cm<sup>3</sup>) was deoxygenated and stirred overnight in a 50 cm<sup>3</sup> Schlenk flask under argon at room temperature (r.t.). The resultant yellow solution was evaporated to dryness *in vacuo*. The solid residue was triturated with Et<sub>2</sub>O and the ether solution discarded. The washing was repeated twice to remove PPh<sub>3</sub> and the residual product purified further by recrystallization from chloroform–hexane. Complex **2** was obtained as yellow crystals (0.71 g, 86%), mp ≈180 °C (decomp.) (Found: C, 57.1; H, 3.7; I, 15.0; P, 7.0; Pd, 12.2; S, 3.5. C<sub>40</sub>H<sub>33</sub>IP<sub>2</sub>PdS requires C, 57.1; H, 3.9; I, 15.1; P, 7.4; Pd, 12.7; S, 3.8%); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.53 (m, 12 H), 7.28 (t, 18 H, PPh<sub>3</sub>), 6.82 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 4.82, H<sup>3</sup>-Pd), 6.33 (dd, 1 H, H<sup>4</sup>-Pd) and 5.89 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 3.25 Hz, H<sup>5</sup>-Pd); δ<sub>p</sub>(CDCl<sub>3</sub>) 21.9; δ<sub>c</sub>(CDCl<sub>3</sub>) 134.7 (t, <sup>3</sup>*J*<sub>CP</sub> = 6.3, C<sub>o</sub>-P), 130.4 (s, C<sub>p</sub>-P), 130.0 (t, <sup>2</sup>*J*<sub>CP</sub> = 24.3, C<sub>i</sub>-P), 127.7 (t, <sup>4</sup>*J*<sub>CP</sub> = 5.3, C<sub>m</sub>-P), 146.1 (t, <sup>2</sup>*J*<sub>CP</sub> = 8.3 Hz, C<sup>1</sup>-Pd), 126.9 (s, C<sup>3</sup>-Pd), 128.3 (s, C<sup>4</sup>-Pd) and 132.0 (s, C<sup>5</sup>-Pd).

***trans*-(*N,P*)-[PdBr(μ-C<sub>3</sub>H<sub>2</sub>NS-C<sup>2</sup>,*N*)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·½CHCl<sub>3</sub> 3.** A mixture of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.58 g, 0.5 mmol) and 2-bromothiazole (0.41 g, 2.5 mmol) in toluene (30 cm<sup>3</sup>) was deoxygenated and stirred overnight in a 50 cm<sup>3</sup> Schlenk flask under argon at r.t. The resultant yellow suspension was evaporated to about 5 cm<sup>3</sup> *in vacuo*. The pale solid residue was filtered off and washed with ethanol (2 × 5 cm<sup>3</sup>) and then Et<sub>2</sub>O (2 × 5 cm<sup>3</sup>). The solid was recrystallized from a CHCl<sub>3</sub>–EtOH mixture. Complex **3** was obtained as colourless crystals (0.46 g, 82%), mp ≈265 °C (decomp.) (Found: C, 45.2; H, 3.4; Br, 14.0; Cl, 4.5; N, 2.6; P, 5.8; Pd, 17.9; S, 5.3. C<sub>42</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>2</sub>·½CHCl<sub>3</sub> requires C, 45.4; H, 3.1; Br, 14.2; Cl, 4.7; N, 2.5; P, 5.5; Pd, 18.9; S, 5.7%); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.80 (m, H<sub>p</sub>-P, 12 H), 7.34 (m, H<sub>m</sub>-P, H<sub>p</sub>-P, 18 H), 6.87 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 3.54, H<sup>4,4'</sup>-Pd) and 7.88 (d, 2 H, <sup>3</sup>*J*<sub>HH</sub> = 3.54 Hz, H<sup>5,5'</sup>-Pd); δ<sub>p</sub>(CDCl<sub>3</sub>) 30.2 (s, PPh<sub>3</sub>); δ<sub>c</sub>(CDCl<sub>3</sub>) 134.8 (d, <sup>3</sup>*J*<sub>CP</sub> = 11.4, C<sub>o</sub>-P), 130.8 (d, <sup>2</sup>*J*<sub>CP</sub> = 44.6, C<sub>i</sub>-P), 130.7 (s, C<sub>p</sub>-P),

128.5 (t, <sup>4</sup>*J*<sub>CP</sub> = 11.2, C<sub>m</sub>-P), 183.8 (d, <sup>2</sup>*J*<sub>CP</sub> = 2.7, C<sup>2,2'</sup>-Pd), 142.5 (s, C<sup>5,5'</sup>-Pd) and 120.0 (d, <sup>2</sup>*J*<sub>CP</sub> = 5.4 Hz, C<sup>4,4'</sup>-Pd).

#### X-Ray crystallography

Single crystals of complex **2** were grown by the diffusion method with hexane layered onto the sample solution in CHCl<sub>3</sub>, while those of **3** were grown by slow evaporation of a MeOH–CHCl<sub>3</sub> mixture at r.t. The data crystals were mounted at the end of glass fibres. The diffraction experiments were carried out on a Siemens SMART CCD diffractometer with a Mo-Kα sealed tube at 23 °C. Preliminary cell constants were obtained from 45 frames (width of 0.3° in ω) of data. Final cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The software SMART<sup>42</sup> was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT<sup>42</sup> for integration of intensity of reflections and scaling, SADABS<sup>43</sup> for absorption correction and SHELXTL<sup>44</sup> for space group and structure determination, refinements, graphics and structure reporting. For **2**, the space group *Pbcn* was determined unambiguously from the systematic absences. For *Z* = 4, there is a crystallographically imposed 2-fold symmetry present in the neutral molecule and the 2-fold rotation axis runs through Pd(1), I(1) and C(1) of thiophene. As a consequence, the thiophene ligand is disordered which has been modelled successfully. All the non-hydrogen atoms were assigned anisotropic thermal parameters and refined in the least-squares cycles. Riding models were used to place the hydrogen atoms. For **3** the space group is *P* $\bar{1}$ . For *Z* = 4 there are two independent molecules present in the asymmetric unit. In the Fourier-difference routine a chloroform molecule was located and the chlorine atoms were found to be disordered along the C<sub>3</sub> axis. Two disordered structures were resolved (occupancies 0.55/0.45) and included in the refinement cycles. The occupancy factors were obtained from the ratios of the electron densities of Cl atoms in the Fourier-difference map and not refined. Common isotropic thermal parameters were refined for each group and an isotropic thermal parameter was refined for the carbon atom of the solvate. Anisotropic thermal parameters were refined for all the non-hydrogen atoms in the neutral molecule. Riding models were used to place the hydrogen atoms in the neutral molecule. Differences in the orientations of the phenyl rings were found when the two independent molecules

were superimposed onto each other. The program MISSYM<sup>45</sup> did not find any additional symmetry in the crystal lattice. The crystallographic data and refinement details are shown in Table 5.

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