APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 1041–1053
Published online 8 October 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1329

Synthesis and reactivity of thiophene palladium and thiophene dipalladium complexes with unsaturated molecules

Abdel-Sattar S. Hamad Elgazwy*

Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia 11566, Cairo, Egypt

Received 9 July 2007; Revised 16 August 2007; Accepted 16 August 2007

Reactions of 2,5-dibromothiophene, 1, with $[Pd_2(dba)_3]^{\bullet}$dba $[Pd(dba)_2$; dba = dibenzylideneacetone] in the presence of *N*-donor ligands such as 2,2′-bipyridine (bpy) and 4,4′-di-tert-butyl-2,2′-bipyridine (dtbbpy) give arylpalladium complexes of *cis*-[2-(5-BrC_4H_2S)$PdBrL_2$], 2a, b [L_2 = bpy (2a), L_2 = dtbbpy (2b)], and *cis*-*cis*-L_2PdBr[2,5-(C_4H_2S-)$PdBr(L_2)$], 3a, b [L_2 = bpy (3a), L_2 = dtbbpy (3b)]. Treatment of *cis* complexes 2a, b and 3a, b with CO causes the insertion of CO into the Pd–C bond to give the aroyl derivatives of palladium complexes of *cis*-[2-(5-BrC_4H_2S)$COPdBrL_2$], 4a, b [L_2 = bpy (4a), L_2 = dtbbpy (4b)], and *cis*-*cis*-[$(L_2)(CO)BrPdC_4H_2S$-$PdBr(CO)(L_2)$], 5a, b [L_2 = bpy (5a) and L_2 = dtbbpy (5b)], respectively. Treating complexes 2a, b with 1 mole equivalent of isocyanide XyNC (Xy = 2,6-dimethylphenyl) gave iminoacyl complexes *cis*-[2-(5-BrC_4H_2S)C=NXy$PdBrL_2$], 6a, b [L_2 = bpy (6a), L_2 = dtbbpy (6b)], and a 3-fold excess of isocyanide XyNC (Xy = 2,6-dimethylphenyl) gave triiminoacyl complexes [2-(5-BrC_4H_2S)$(C=NXy)_3$ PdBr], 7. Cyclization reactions of 6a, b with 3 mole equivalents of isocyanide XyNC (Xy = 2,6-dimethylphenyl) or cyclization reaction of 7 with 1 mole equivalent of isocyanide XyNC (Xy = 2,6-dimethylphenyl) both gave tetraiminoacyl complexes of [2-(5-BrC_4H_2S)$(C=NXy)_4PdBr$], 8, which was also obtained by the reaction of 1 or 2a, b with a 4-fold excess of isocyanide XyNC with or without add $Pd(dba)_2$. Similarly, complexes 3a and b were also reacted with 2 mole equivalents of isocyanide XyNC (Xy = 2,6-dimethylphenyl) to give iminoacyl complexes *cis*-*cis*-[$(L_2)(CNXy)BrPdC_4H_2S$-$PdBr(CNXy)(L_2)$], 10a, b [L_2 = bpy (10a), L_2 = dtbbpy (10b)] and an 8-fold excess of isocyanide XyNC (Xy = 2,6-dimethylphenyl) afforded tetraiminoacyl complexes of [2,5-$(C_4H_2S)(C=NXy)_8Pd_2Br_2$], 11. Complexes 2a, b and 3a, b reacted with TlOTf [(TfO = CF_3SO_3)] in CH_2Cl_2 to give 9a, b and 12a, b, respectively, in a moderate yield.

KEYWORDS: palladium; thiophene; dipalladium complex; carbon monoxide; isocyanide; bpy; dtbbpy

INTRODUCTION

The chemistry of aryl–palladium complexes is a topic of great interest because such compounds participate in many important palladium-catalyzed organic reactions.[1–3] In the last decade many carbon–carbon bond formation processes have been developed for which a fundamental step is the oxidative addition of an aryl halides to Pd(0) complexes. Among the best known are the palladium-catalyzed cross-coupling reactions of organic halides with organometallic nucleophiles, which are powerful tools in organic synthesis,[4–7] thus Pd(II) complexes play an important role in organic synthesis.[7] Insertion of unsaturated molecules into metal–carbon bonds constitutes a topic of current interest,[8] particularly those involving palladium species because of their important applications in many organic syntheses.[2,3] Thus, study of the insertion of CO and isocyanides into the palladium–carbon bond has attracted a great deal of interest, since it constitutes a key step in important processes such as the Heck reaction.[1,2–11] A few

*Correspondence to: Abdel-Sattar S. Hamad Elgazwy, Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia 11566, Cairo, Egypt.
E-mail: aelgazwy@egypt.com
Contract/grant sponsor: Higher Education Commission, Islamabad.

examples of insertion of CO into thiophene–palladium (II) complexes leading to acylpalladium (II) complexes have been reported.[12] In this paper, we wish to present the reactivity of novel thiophene–palladium complexes, in particular their reactions with different molarities of CO and isocyanides. Insertion reactions of isocyanides into the C–Pd bonds lead to isolation of the insertion species of iminoacyl complexes. The sequential insertion of two or more unsaturated species is of interest to us, because such processes constitute the first steps of important copolymerization reactions. Thus, copolymerization of CO and olefins using palladium catalysts takes place through alternating insertion of olefins and CO into the palladium carbon bond, and it constitutes a promising source of very interesting polymers.[13–16] Thus the insertion of CO into the Pd–C bond, resulting the formation of acylpalladium derivatives, constitutes a key step of the palladium-catalyzed carbonylation of organic substrates in laboratory synthesis and also in industrial processes. Insertion of isonitriles into Pd–C bonds also constitutes a subject of great interest, as it leads to new types of organopalladium complexes and because it is very important for organic synthesis. As we report here, mono-, di-, tri-, and tetrainsertion reactions of isocyanides produce thienylene palladium and thienylene-bridged dipalladium complexes. Although the monoinsertion reactions of isocyanides into the thiophene–platinum bond to give iminoacyl complexes are well known,[17] the sequential insertion reactions of isocyanides with thiophene palladium (II) complexes are rare.[18]

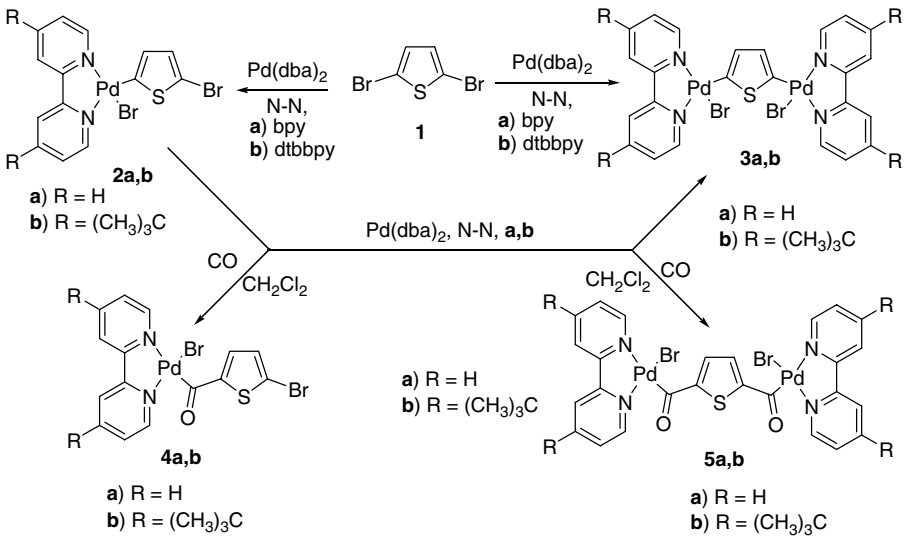
Thiophene-containing iminoacyl compounds are widely known as an important class of materials[19,20] which show intrinsic electronic properties such as luminescence,[21–23] redox activity,[24] nonlinear optical chromism[25] and electron transport.[26] While triarylamines generally carry a role of hole-transport for organic electroluminescent (EL) display devices,[27–33] thienylphenylene-containing triarylamines showed different properties.[19,20,25] Thus, insertion of XyNC into Pd–Me bonds followed by treatment with norbornadiene,[34,35] ethylene, propylene, allenes,[34] isocyanates or isothiocyanates[35,36] has been reported.

RESULTS AND DISCUSSION

Synthesis of thienylene palladium complexes of *cis*-[2-(5-BrC$_4$H$_2$S)BrPd(L$_2$)], 2a, b, and thienylene-bridged dipalladium complexes of *cis-cis*-[2,5-(C$_4$H$_2$S)Pd$_2$Br$_2$(L$_2$)$_2$], 3a, b [L$_2$ = 2, 2′-bipyridine (bpy) (a) and L$_2$ = 4, 4′-di-tert-butyl-2,2′-bipyridine (dtbbpy) (b)]

A method was used similar to the one described recently for the synthesis of *cis*-[Pd(C$_6$H$_4$OX-2)I(bpy)] (X = H, MeCO),[37] involving the reaction of 2-iodophenol with [Pd$_2$(dba)$_3$]·dba and bpy, or dtbbpy. Such a procedure has been shown to be useful for the synthesis of organopalladium complexes containing nitrogen[38,39] or phosphorus donor ligands,[40] and it was applied recently to the synthesis of palladated *o*-aniline derivatives.[41]

Similarly, we have synthesized a new derivative of *cis*-[2-(5-BrC$_4$H$_2$S)BrPd(L$_2$)] [L$_2$ = 2, 2′-bipyridine (bpy), (**2a**) and L$_2$ = 4, 4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy) (**2b**)] by oxidative addition reactions of the corresponding 2,5-dibromothiophene **1** to [Pd$_2$(dba)$_3$]·dba [Pd(dba)$_2$)] in the presence of a stoichiometric amount of nitrogen donor ligands such as bpy or dtbbpy with equimolar ratio in degassed acetone under nitrogen. The resulting mixture was stirred at 0 °C for 30 min and at room temperature for 3 h to give mononuclear σ-thienyl palladium (II) complexes **2a, b** in high yields, 98 and 91% respectively, as shown in Scheme 1. A similar reaction of 2,5-dibromothiophene **1** with



Scheme 1.

DOI: 10.1002/aoc

$Pd_2(dba)_3$·dba [$Pd(dba)_2$] in the presence of a stoichiometric amount of bpy or dtbbpy in a 1:2:2 molar ratio in degassed acetone under nitrogen led to oxidative addition of C–Br bonds to two Pd centers giving dinuclear palladium complexes with bridging thienylene ligand as *cis-cis*-L_2PdBr[μ–2, 5-(C_4H_2S-)$PdBr(L_2)$], **3a, b** [L_2 = bpy (**3a**), L_2 = dtbbpy (**3b**)] in high yields, 90 and 86% respectively, as outlined in Scheme 1.

In order to obtain insight into the pathway of the reaction, we examined the reaction of **2a, b** with Pd(0) complex [$Pd_2(dba)_3$]·dba [$Pd(dba)_2$)]. The reaction in degassed acetone in 1:1 molar ratio afforded a complex with the symmetrical structure of a thienylene-bridged dipalladium complex **3a, b** as a yellow solid in low yields as well as unidentified species as a minor product (Scheme 1), whereas the reaction in the presence of equimolar or excess of $Pd(dba)_2$ caused formation of **2a, b** or **3a, b** as sole product, and we did not observe unusual C–S bond cleavage of the thiophene ring. Complexes **3a** and **3b** were also obtained as byproducts in very low yields (8.6, 8%) during the reaction of 2,5-dibromothiophene **1** with equimolar bpy or dtbbpy and [$Pd_2(dba)_3$]·dba [$Pd(dba)_2$] at room temperature. This procedure has proved to be useful for the synthesis of similar organopalladium complexes.[42]

We observed that the yields are better if the molar ratios of 2,5-dibromothiophene **1** to Pd and L_2 to Pd are 1:1 or 1:2 or even greater. However, some decomposition to palladium metal always occurs. In this context, studies focused on the synthesis of novel thienylene palladium complexes *cis*-[2-(5-BrC4H2S)BrPd(L_2)] (**2a, b**) and thienylene-bridged dipalladium complexes of *cis-cis*-[Pd_2{C_4H_2S-(2, 4)}$Br_2(L_2)_2$] (**3a, b**) have shown that they undergo insertion of small molecules such as CO and isocyanide in different molarities.

Reaction of CO with thienylene palladium and bridging thienylene dipalladium complexes

The acylpalladium derivatives of 2-(5-BrC_4H_2S)$COPdBrL_2$, **4a, b** [L_2 = bpy (**4a**), L_2 = dtbbpy (**4b**)], and 2, 5-(C_4H_2S)$(CO)_2Pd_2Br_2(L_2)_2$, **5a, b** [L_2 = bpy (**5a**) and L_2 = dtbbpy (**5b**)], were obtained in moderate yields (70, 40 and 52, 36% respectively), when CO was bubbled through a CH_2Cl_2 solution of **2a, b** or **3a, b**. Treatment of **2a, b** with CO (1 atm) in CH_2Cl_2 at room temperature caused smooth CO insertion to give a complex with the unsymmetrical structure of the monoinserted species of monoacyl complexes *cis*-2-(5-BrC_4H_2S)$COPdBrL_2$], **4a, b** [L_2 = bpy (**4a**), L_2 = dtbbpy (**4b**)] in moderate yields (70 and 40% respectively). Similarly, complexes **3a, b** treated with CO gave a symmetrical structure of *cis-cis*-[(L_2)BrPd(CO)[-2,5-(C_4H_2S-)(CO)$PdBr(L_2)$] **5a, b** [L_2 = bpy (**5a**), L_2 = dtbbpy (**5b**)] in moderate yields (52 and 36%).

Complexes **4b** and **5b** have quite a similar solubility to the starting material and were not isolated by fractional crystallization; also, the lower yield of **4b, 5b** than **4a, 5a** may be due to the larger steric hindrance of 4,4′-di-tert-butyl-2,2′-bipyridine (dtbbpy) than 2,2′-bipyridine (bpy), for the CO insertion into a Pd–C bond in the thienylene briged complex. The reaction occurs selectively at one of the Pd–C bonds and shows no further CO insertion. Similar selective CO insertion into a Pd–C bond of arylene- or biarylene-bridged dinuclear Pd complexes was observed.[43] IR spectra for the crude product before purification show a strong νC═O absorption at 1598 cm^{-1} The ^{13}C NMR signals at δ221.6 support the single CO insertion into Pd–C bond of the thiophene palladium complexes.

Reaction of isocyanide with thienylene palladium and bridging thienylene dipalladium complexes

Monoinsertion of isonitrile (CNXy)

The reaction of complexes **2a, b** with 1 mole of isonitrile CNXy (1:1 molar ratio), Xy (Xy = 2, 6-$Me_2C_6H_3$) at room temperature gave a complex with the unsymmetrical structure of the monoinserted species of iminoacyl complexes *cis*-[2-(5-BrC_4H_2S)C═NRPdBrL_2], **6a, b** [L_2 = bpy (**6a**), L_2 = dtbbpy (**6b**), R = Xy] in excellent yield, 89 and 69%, as shown in Scheme 3. Similarly, insertion of isonitrile CNXy (Xy = 2, 6-$Me_2C_6H_3$) into complex **3a, b** gave a complex with the symmetrical structure of the iminoacyl complexes *cis-cis*-[(L_2)(CNXy)BrPdC_4H_2S-$PdBr$(CNXy)(L_2)], **10a, b** [L_2 = bpy (**10a**), L_2 = dtbbpy (**10b**)] in excellent yield (54.9 and 52% respectively; Scheme 3). The IR spectrum shows the ν(C═C) for the iminoacyl metal complex.[44–47] The crude product before purification shows an absorption band at 2160 cm^{-1} assigned to ν(C≡N) of the isonitrile coordinated to a Pd centre. These results suggest that the reaction gives not only **10a, b** but also cationic complexes such as [(L_2)(CN-R)Pd-C_4H_2S-Pd(CN-R)(L_2)]Br_2 or [(L_2)BrPd-C(═N-R)C_4H_2S-Pd(CN-R)(L_2)]Br [L_2 = bpy (**10a**), L_2 = dtbbpy (**10b**), R = Xy (Xy = 2, 6-$Me_2C_6H_3$)], which may be regarded as the intermediate for formation of **10a, b**. Thus the reactions with more bulky isocyanides such as CNXy (Xy = 2, 6-$Me_2C_6H_3$) with ligands such as L_2 = 2, 2′-bipyridine (bpy) (**10a**) and L_2 = 4, 4′-di-tert-butyl-2,2′-bipyridine (dtbbpy) (**10b**) gave the cationic adducts and the neutral complexes with the symmetrical structure *cis-cis*-[(L_2)BrPd-C(═N-R)C_4H_2S–C(═N-R)-$PdBr(L_2)$], **10a, b** [L_2 = bpy (**10a**), L_2 = dtbbpy (**10b**)]. Complexes **10a** and **b** were isolated by repeated recrystallization with yields of 49 and 60%, respectively. Sonogashira and co-workers[44] reported that insertion of aryl isocyanide into the Pt–C bonds of thienyl bridged diplatinum complexes occurred to give unsymmetric or symmetric iminodiplatinum complexes at much higher temperatures and their insertion was affected by the bulkiness of isocyanide and ligands on platinum. In our case, using bulky isocyanides such as CNXy (Xy = 2, 6-$Me_2C_6H_3$), iminoacyl palladium complexes with symmetrical structure were easily formed under mild conditions. These results indicate that isocyanide insertion into the Pd–C bonds of thienylene bridged dipalladium complexes occurs more easily than into the Pt–C bonds of thienylene bridged diplatinum complexes. Previous work by Mantovani

DOI: 10.1002/aoc

et al.[48] also showed that isocyanide insertion at room temperature occurs in the Pd–C bond of 2-thienylpalladium complex. Thus the reaction between isonitriles and Pd(0) complexes has been shown to give $Pd(CNXy)_2$ complex [equation (1) and as outlined in the following equations].[49]

$$Pd(dba)_2 + 2RXyNC \longrightarrow Pd(CNXy)_2 \quad (1)$$

$$Pd(CNXy)_2 + RX \longrightarrow [Pd(R)X(CNXy)_2] \quad (2)$$

$$[Pd(R)X(CNXy)_2] \longrightarrow 2/3\ [Pd\{C(=NXy)(R)\}X(CNXy)_2] + 1/3\ ''Pd(R)X \quad (3)$$

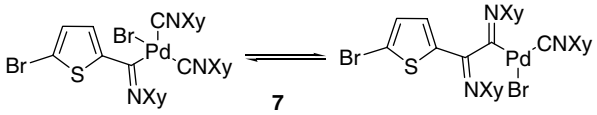
Reactions between acyl, aroyl and alkyl chlorides and $Pd(CN^tBu)_2$ give the complexes $[Pd(R)X(CN^tBu)_2]$ [equation (2); R = MeC(O), PhC(O), $(CH_2)_2CO_2Et$, $CH(Ph)CO_2Et$, CH_2CO_2Me, X = Cl], but not insertion products.[50] Otsuka showed that similar complexes with R = CH_2Ph, X = Br, I could be isolated by reacting $Pd(CN^tBu)_2$ with XR but with X = Cl the complex trans $[Pd\{C(=N^tBu)CH_2Ph\}Cl(CN^tBu)]_2$ was obtained.[51] Similarly, the reaction of $Pd(CN^tBu)_2$ with *trans* BrCH=$CHCO_2Me$ gave *trans* $[Pd\{C(=N^tBu)CH=CHCO_2Me\}Br(CN^tBu)]_2$.

Triinsertion of isonitrile (CNXy)

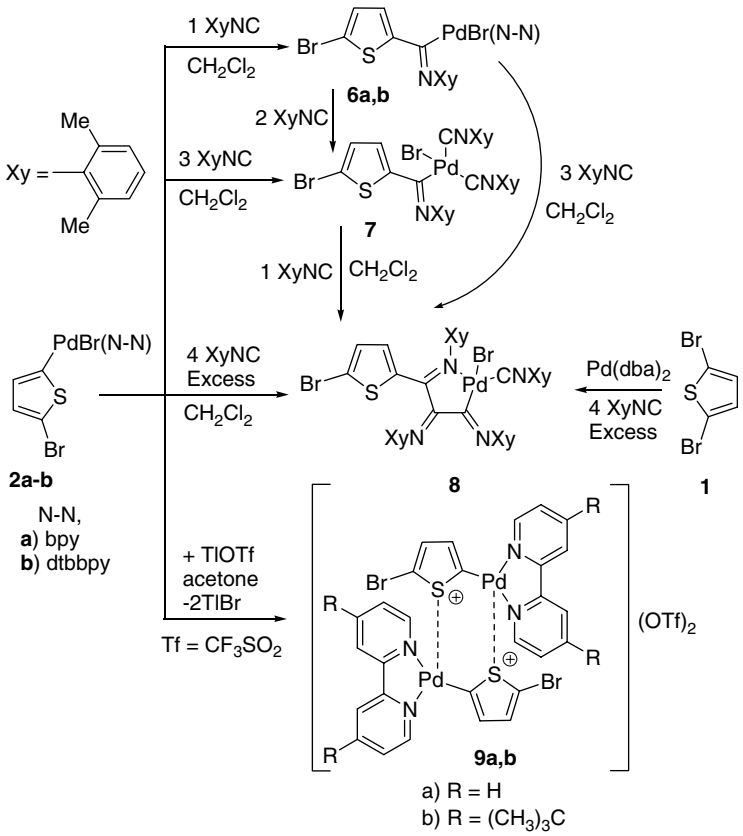
Complexes **2a, b** were treated with a 3-fold excess of isonitrile XyNC to give triiminoacyl complexes of [2-(5-BrC_4H_2S)(C=$NXy)_3$PdBr], **7**, in good yield (74%; Scheme 3), which was obtained also by cyclization reactions of complexes **6a, b** with 2 mole equivalent of isonitrile XyNC (Xy = 2,6-dimethylphenyl). The IR spectrum of complex **7** in the crude product shows two bands at 2180 and 2220 cm^{-1} assignable to the two ν(C≡N); two bands at 1603 and 1650 cm^{-1} may be due to the ν(C=N) group, and one of the remaining bands may be assignable to the ν(C=C) mode corresponding to the ν(thienyl) or to the ligands group coordinated to the palladium atom. This is attributed to the structure of the complex **7** and may be in two tautomeric forms as outlined in Scheme 2.

Tetrainsertion of isonitrile (CNXy)

Complex **8** was obtained in good yield (85%) either by direct oxidative addition reaction of 2,5-dibromothiophene **1** with a 4-fold isonitrile XyNC in the presence of $Pd(dba)_2$ or by indirect treatment of **2a, b** with 4-fold XyNC in CH_2Cl_2, as



Scheme 2.



Scheme 3.

DOI: 10.1002/aoc

shown in Scheme 3. Cyclization reactions of complexes **6a, b** in the presence of 3 mole equivalent of isonitrile XyNC (Xy = 2,6-dimethylphenyl) or by cyclization reaction of **7** in the presence of 1 mole equivalent of same isonitrile XyNC both gave an unsymmetrical structure of tetraiminoacyl complexes [2-(5-BrC_4H_2S)(C═NXy)$_4$PdBr], **8**, in same yield.

In a similar reaction, complex **3a, b** was reacted with a 8-fold or excess isocyanide XyNC (Xy = 2,6-dimethylphenyl) in CH_2Cl_2 to give symmetrical structure of tetraiminoacyl complexes of [2,5-(C_4H_2S)(C═NXy)$_8$$Pd_2Br_2$], **11**, in a moderate yield (49.8%).

These complexes, **8** and **11**, were confirmed by physical tools (IR, NMR, elemental analysis), which were consistent with the result described by Vicente *et al*.[52] for the tri- and tetra-insertion of an isocyanide XyNC (Xy = 2,6-dimethylphenyl) into the Pd–C bond of the *ortho*-substituted phenylpalladium complexes. There is no precedent for this type of ring structure, until confirmed by an X-ray structure analysis.[52]

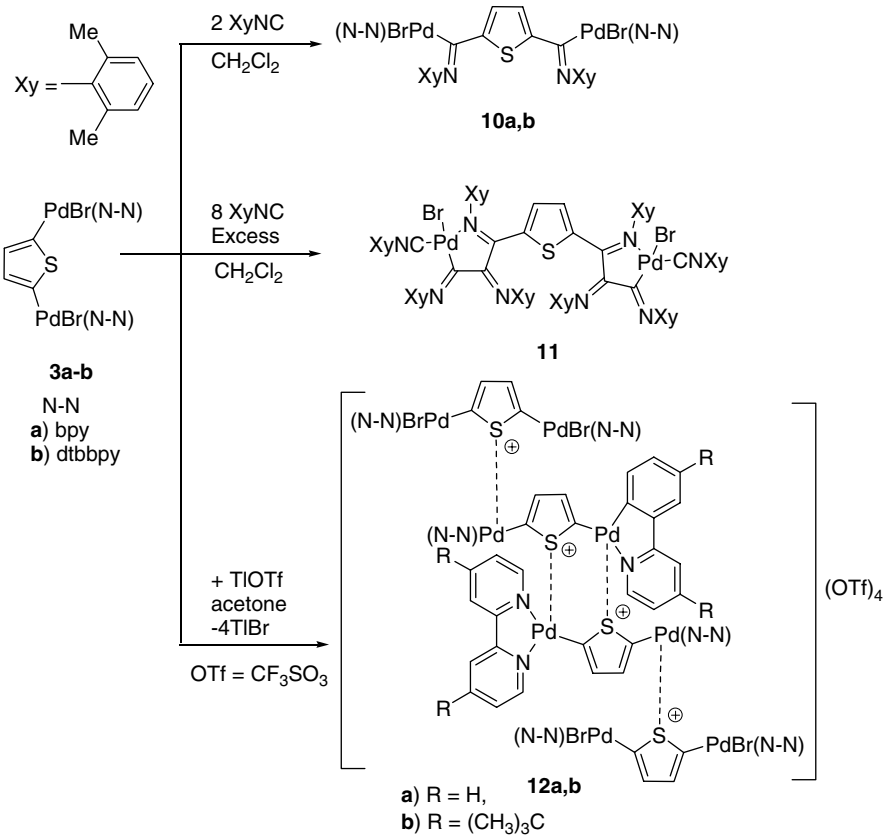
Reactions with TlOTf [(Tf = CF_3SO_2)]

Treatment of complexes **2a, b** with TlOTf [(Tf = CF_3SO_2)][7,37] in CH_2Cl_2 gave cyclopladate cation or palladocycle of **9a, b** in a moderate yield (43 and 25.5% respectively). According to the IR and ^{1}H NMR spectra, they seem to be dimers of the structure outlined in Scheme 3. The IR spectrum of the crude material shows one band assignable to ν(thienyl), two bands assignable to the ν(S═O), and one band assignable to the ν(C═N) mode corresponding to the ligands coordinated to the palladium atom.

Similarly, complexes **3a, b** were treated with TlOTf [(Tf = CF_3SO_2)][7,37] in CH_2Cl_2 to give cyclopalladated cation or palladacycle **12a, b** in moderate yield. According to the IR and ^{1}H NMR spectra, there seem to be four nuclear cations of palladacycle formed by coordination, although the sulfur atoms of the thiophene ring bond to the fragments that result from the loss of the Br bridges. The structure has a *trans* geometry of structure as outlined in Scheme 4. However, their elemental analyses, although close to the calculated values, are not correct and no suitable crystals for an X-ray diffraction study could be obtained, with the result that these compounds have not been characterized. However, coordination of the TfO anion cannot be discounted. To the best of our knowledge, few examples of insertion of an isocyanide into a Pd–C bond of the thienylene palladium complexes are known. Analytical and spectroscopic data are in agreement with the proposed formulation, as outlined in Scheme 4.

Spectroscopic properties

The bands assignable to ν(thienyl), ν(bpy) and ν(dtbbpy) in the IR spectra of the palladated thiophene complexes (those



Scheme 4.

DOI: 10.1002/aoc

containing the letter **a** and **b**) were observed within the range 1540–1731 cm^{-1}.

In the case of complex **2a**, two bands at 1602 and 1731 cm^{-1} were observed; this may be due to the existence of two different structural environments of the thienyl and bpy group in the solid state. Complexes having the bpy and dtbbpy showed the ν(C═N) and ν(C═C) bands in the region 1540–1731 cm^{-1}, while those having C═C groups showed one or two bands in the region 1614–1731 cm^{-1}. The IR spectrum of complex **2b** showed one band at 1544 cm^{-1} assignable to ν(thienyl) and two bands at 1715 and 1614 cm^{-1}; one of them may be due to the ν(C═N) group, and the other one of the remaining band may be assignable to the ν(C═C) mode corresponding to the dtbbpy ring coordinated to the palladium atom. The ^{1}H-NMR spectra of complexes **2a, b** show two doublet signals corresponding to the thienyl protons appearing in the different chemical shift region at δ6.64 and 6.99 ppm with the same coupling constant, $^3J_{HH} = 3.6$ Hz.

In the case of complex **3a**, two bands at 1542 and 1614 cm^{-1} were observed and are assignable to the ν(thienyl) and ν(C═N) groups of the ν(bpy). The IR spectrum of complex **3b** showed one band at 1540 cm^{-1} assignable to ν(thienyl) and one band at 1618 cm^{-1} assignable to the ν(C═N) group of the mode corresponding to the dtbbpy ring coordinated to the palladium atom. The ^{1}H-NMR spectra of complexes **3a, b** showed singlet signals corresponding to the theinyl protons appearing in the different chemical shift regions δ7.32, 7.42, 6.73, 7.16 ppm, showing that they slowly decompose in solution to the corresponding complexes (see the Experimental section).

The compounds **2a, b** and **3a, b** show fluxional behavior because the halves of dtbbpy and bpy, respectively, are equivalent at room temperature. However, at low temperature (−40 and −55 °C), the fluxional processes are slower than the ^{1}H-NMR time scale, showing the two different parts of those ligands. Such behavior has been observed previously, and it has been proposed that the rotation takes place through the dissociation of one Pd–N ligand, probably that *trans* to the carbon donor ligand, which exerts a greater *trans* influence, to give a Y-shaped intermediate.[53] The band assignable to ν(C═O) in the IR spectra of the acylpalladated complexes was observed within the range 1540–1598 cm^{-1}. In the case of **4a** and **4b**, one band at the same absorption, 1598 cm^{-1}, was observed; this may be due to the existence of two different structural environments of the ν(C═O) group in the solid state. In contrast, the analogous **5a** and **5b** showed only one band at 1601 and 1540 cm^{-1}, respectively, as expected. It was not possible to observe clearly the corresponding bands in complexes **6a** and**6b**, which showed bands assignable to ν(C═N) at different bands, 1645, 1584, 1506 cm^{-1} and 1644, 1585, 1502 cm^{-1}. In complex **7**, the IR spectrum showed one band at 2180 cm^{-1} assignable to ν(C≡N) and two bands at 1603 and 1650 cm^{-1}; one of them may be due to the ν(C═N) group, and the other remaining band may be assignable to the ν(C═C) mode corresponding to the ν(thienyl) or to the ligands group coordinated to the palladium atom. This proved that the complex was in two tautomeric forms. The ^{1}H-NMR spectra of complexes **7** showed two singlet signals at δ2.16 and 2.23 ppm, corresponding to those methyl groups of the Xy substitute, due probably to a restricted rotation around the C–N bond at room temperature.

In complex **8**, its IR spectrum showed one band at 2194 cm^{-1} assignable to ν(C≡N) and two bands at 1605 and 1642 cm^{-1}; one of them may be due to the ν(C═N), and one of the remaining bands may be assignable to the ν(C═C) mode corresponding to ν(thienyl) or to the ligands coordinated to the palladium atom. Something similar seemed to occur in complexes **8**, since they showed seven signals in the ^{1}H-NMR spectra at δ1.36, 2.14, 2.15, 2.25, 2.28, 2.29 and 2.63 ppm assignable to numbers of methyl groups, which implies that one of the Xy groups had a restricted rotation; we believe that it must also be the iminic Xy group. In the case of the complex **9a** and **b**, its IR spectrum showed bands at 1630 and 1544 cm^{-1} assignable to ν(thienyl) and two bands at 1715 and 1614 cm^{-1}; one of them may be due to the ν(C═C), and the other remaining band may be assignable to the ν(C═N) mode corresponding to the ligands coordinated to the palladium atom (Scheme 3).

In the case of the complex **10a** and **b**, its IR spectrum showed one band at 1603 and 1545 cm^{-1} assignable to ν(thienyl) and signal bands at 1732, 1717 and 1615 cm^{-1}; one of them may be due to ν(C═C), and one of the remaining bands may be assignable to the ν(C═N) mode corresponding to the ligands coordinated to the palladium atom (Scheme 4). It was not possible to observe clearly the corresponding bands in complex **10a** and**b**, which showed bands assignable to ν(C═N) at different bands, 1647, 1585, 1506 cm^{-1} and 1644, 1585, 1502 cm^{-1}. In the case of the complex **11**, its IR spectrum showed one band at 2197 cm^{-1} assignable to ν(C≡N) and two bands at 1605 and 1647 cm^{-1}; one of them may be due to the ν(C═N), and the other remaining band may be assignable to the ν(C═C) mode corresponding to the ν(thienyl) or to the ligands coordinated to the palladium atom (Scheme 4). The NMR spectra of complexes **11** showed seven singlet signal at δ1.36, 2.14, 2.15, 2.25, 2.28, 2.29 and 2.63 ppm, corresponding to the numbers of methyl groups of the Xy substituent, due probably to a restricted rotation around the C–N bond at room temperature. In the case of the complex **12a** and**b**, its IR spectrum showed bands at 1635 and 1555 cm^{-1} assignable to ν(thienyl) and two bands at 1716 and 1615 cm^{-1}; one of them may be due to the ν(C═C), and the other remaining band may be assignable to the ν(C═N) mode corresponding to the ligands coordinated to the palladium atom (Scheme 4).

CONCLUSIONS

We synthesized novel thienyl palladium and thienylene-bridged dipalladium complexes from the oxidative addition of 2,5-dibromothiophenes **1** with $Pd(dba)_2$ in the presence

DOI: 10.1002/aoc

of a stoichiometric amount of nitrogen donor ligands such as $L_2 = 2,2'$-bipyridine (bpy) (**1a**) and $L_2 = 4,4'$-di-tert-butyl-2,2′-bipyridine (dtbbpy) (**1b**), whereas the reaction in the presence of equimolar or excess $Pd(dba)_2$ caused the formation of **2a, b** or **3a, b** as the sole product. We did not observe unusual C–S bond cleavage of thiophene ring during the reaction process. These results do not provide any clue to elucidating the detailed mechanism of C–S bond cleavage of the thiophene ring. The thienyl palladium and thienylene-bridged dipalladium complexes underwent insertion of unsaturated molecules such as CO and isocyanide into their Pd–C bond at room temperature. Palladium complexes are an effective intermediate which were isolated smoothly and confirmed by IR, NMR and elemental analysis.

EXPERIMENTAL

Reactions were carried out without precautions to exclude atmospheric moisture, unless otherwise stated. The IR and C, H, N and S analyses and melting point determinations were carried out as described elsewhere.[54] NMR spectra were recorded on Varian Unity 300 and Bruker Unity 200 instruments. Chemical shifts were referred to TMS (^{1}H and ^{13}C{^{1}H}). ^{13}C NMR assignments were made with the help of DEPT techniques. Chromatographic separations were carried out by TLC on silica gel 60 ACC (70–230 mesh). Complex of Pd-$(dba)_2$ ($[Pd_2(dba)_3]dba$)[55,56] was prepared as previously reported.

Synthesis of *cis*-[2-(5-BrC_4H_2S)BrPd(bpy)] (2a)

Method A

2,5-Dibromothiophene, **1** (85 µl, 0.75 mmol), was added to a suspension of $Pd(dba)_2$ (432 mg, 0.75 mmol) and bpy (2,2 bipyridine; 120 mg, 0.75 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 3 h. The solvent was evaporated *in vacuo*, the residue extracted with CH_2Cl_2 (20 ml), and the resulting suspension filtered over anhydrous $MgSO_4$. The solvent was concentrated to dryness and the residue washed with diethyl ether (3 × 20 ml). The resulting solid was separated by filtration, washed with Et_2O (2 × 20 ml) and air-dried to give **2a** as a yellow solid. Yield: 375 mg, 98%. M.p.: 150–151 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 839 cm^{-1}; ν(thienyl) 1602.4 cm^{-1}; ν(bpy) 1731 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ6.64 (d, 1H, $J = 3.6$ Hz), 6.99 (d, 1H, $J = 3.6$ Hz), 7.26–7.46 (m, 1H), 7.54–7.59 (m, 1H), 8.01–8.08 (m, 4H), 8.13 (d, 1H, $J = 5.4$ Hz), 9.46 (d, 1H, $J = 5.6$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); d, 110.487 (s, thienyl of C–Br), 120.726 (s, C8 bpy), 121.262 (s, C8′ bpy), 125.650 (s, C10 and C10′ bpy), 128.884 (s, thienyl of C3), 129.238 (s, thienyl of C4), 137.946 (s, C9 or C9′ bpy), 138.150 (s, C9 or C9′ bpy), 149.800 (s, C11 or C11′ bpy), 150.181 (s, C11 or C11′ bpy), 151.180 (s, C7′ bpy), 152.655 (s, C7 bpy), 154.643 (s, C–Pd). Gc; $t_R = 14.738$ min; column; DB-5 6 m × 0.01 mm + 1 m guard column; temperature program: 50 °C/2 min/20 °C min^{-1}/250 °C/5 min; LRMS (EI); m/z 156 (M+, 100), 141 (<5), 132 (<5), 128 (35), 123 (<5), 102 (5), 78 (35), 74 (5), 63 (5), 51 (35). Anal. calcd for $C_{14}H_{10}N_2Br_2PdS$ (504.53): C, 33.33; H, 2.00; N, 5.55; S, 6.36. Found: C, 33.47; H, 1.98; N, 5.61; S, 5.96.

Synthesis of *cis*-[Pd_2{C_4H_2S-(2,4)}$Br_2(bpy)_2$] (3a)

Method A

2,5-Dibromothiophene, **1** (85 µl, 0.75 mmol), was added to a suspension of $Pd(dba)_2$ (864 mg, 1.5 mmol) and bpy (2,2 bipyridine; 240 mg, 1.5 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 24 h. The solvent was evaporated *in vacuo*, the residue washed with boiling *n*-hexane (4 × 10 ml), to eliminate dba, giving an orange solid. Since this solid contained some [$PdBr_2$(bpy)] [^{1}H-NMR, 9.83(d), 7.94(s), 7.51(dd)], it was re-dissolved in CH_2Cl_2 (2 ml), applied to a preparative TLC sheet, and eluted with CH_2Cl_2. The yellow band was extracted with acetone (25 ml). The resulting yellow solution was concentrated to dryness and the residue treated with CH_2Cl_2 (20 ml) and anhydrous $MgSO_4$ (1 h). The resulting suspension was filtered to give a solution, which was concentrated (2 ml). Addition of *n*-hexane (15 ml) caused the precipitation of a solid, which was separated by filtration, washed with *n*-hexane (2 × 5 ml) and air-dried to give **3a** as a yellow solid. Yield: 520 mg, 90%. M.p.: >300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 840 cm^{-1}; ν(thienyl) 1542 cm^{-1}; ν(bpy) 1614 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.32 (s, 2H), 7.42 (s, 2H), 7.49–7.51 (dd, 2H, $J = 2.1$ and 5.4 Hz), 7.72–7.78 (dd, 2H, $J = 4.8$ and 6.3 Hz), 7.81–7.86 (dd, 2H, $J = 3.6$ and 5.4 Hz), 8.05–8.10 (d, 2H, $J = 5.7$ Hz), 8.19 (m, 2H), 8.29–8.33 (d, 1H, $J = 7.2$ Hz), 8.54–8.57 (d, 1H, $J = 7.5$ Hz), 8.61–8.64 (d, 2H, $J = 7.2$ Hz), 8.88–8.90 (d, 2H, $J = 5.1$ Hz). Anal. calcd for $C_{24}H_{18}Br_2N_4Pd_2S$ (767.141): C, 37.58; H, 2.37; N, 7.30; S, 4.18. Found: C, 37.49; H, 2.28; N, 7.31; S, 4.01.

Synthesis of *cis*-[2-(5-BrC4H2S)BrPd(bpy)] (2a) and *cis*-[Pd_2{C_4H_2S-(2,4)}$Br_2(bpy)_2$] (3a)

Method B

2,5-Dibromothiophene, **1** (85 µl, 0.75 mmol), was added to a suspension of $Pd(dba)_2$ (432 mg, 0.75 mmol) and bpy (2,2 bipyridine; 120 mg, 0.75 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min and continue stirring at room temperature for 6 h. It was filtered to isolate the first portion of solid compound **3a** and the residue washed with boiling *n*-hexane (4 × 10 ml), to eliminate dba, giving an orange solid. Since this solid contained some [PdBr2(bpy)] [^{1}H-NMR, 9.83(d), 7.94(s), 7.51(dd)], it was re-dissolved in CH_2Cl_2 (2 ml), applied to a preparative TLC sheet, and eluted with CH_2Cl_2. The yellow band was extracted with acetone (25 ml). The resulting yellow solution was concentrated to dryness and the residue treated with CH_2–Cl_2 (20 ml) and anhydrous $MgSO_4$ (1 h). The resulting suspension was filtered to give a solution,

DOI: 10.1002/aoc

which was concentrated (2 ml). Addition of *n*-hexane (15 ml) caused the precipitation of a solid, which was separated by filtration, washed with *n*-hexane (2 × 5 ml), and air-dried to give **3a** as a yellow solid. Yield: 50 mg, 8.6%. M.p.: >300 °C dec. The filtrate (mother liquor) was evaporated *in vacuo*, the residue extracted with CH_2Cl_2 (20 ml), and the resulting suspension filtered over anhydrous $MgSO_4$. The solvent was concentrated to dryness and the residue washed with diethyl ether (3 × 20 ml) to eliminate dba. The resulting solid was separated by filtration, washed with Et_2O (2 × 20 ml) and air-dried to give **2a** as a yellow solid. Yield: 325 mg, 85%. M.p.: 150–152 °C dec.

Synthesis of *cis*-[2-(5-BrC4H2S)BrPd(dtbbpy)] (2b)

Method A

2,5-Dibromothiophene (85 µl, 0.75 mmol) was added to a suspension of $Pd(dba)_2$ (432 mg, 0.75 mmol) and dtbpy(4,4-di-tert-butyl-2,2 bipyridine; 210 mg, 0.75 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 3 h. The solvent was evaporated *in vacuo*, the residue extracted with CH_2Cl_2 (20 ml), and the resulting suspension filtered over anhydrous $MgSO_4$. The solvent was concentrated to dryness and the residue was heed with diethyl ether (3 × 20 ml). The resulting solid was separated by filtration, washed with Et_2O (2 × 20 ml) and air-dried to give **2b** as a yellow solid, in a yield of 420 mg, 91%. M.p.:160–162 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 852 cm^{-1}; ν(thienyl) 1544 cm^{-1}; ν(dtbbpy) 1715 and 1614 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.41 (s, 9H), 1.43 (s, 9H), 6.64 (d, 1H, $J = 3.46$ Hz), 6.98 (d, 1H, $J = 3.46$ Hz), 7.38–7.42 (dd, 1H, $J = 1.75$ and 4.06 Hz), 7.51–7.55 (dd, 1H, $J = 1.73$ and 5.77 Hz), 7.95–8.00 (m, 3H), 9.33 (d, 1H, $J = 5.79$ Hz). Anal. calcd for $C_{22}H_{26}N_2Br_2SPd\text{-}Et_2O$: C, 45.21; H, 5.21; N, 4.05; S, 4.63. Found: C, 45.19; H, 4.41; N, 4.13; S, 4.61 [1 mole of diethyl ether incorporating in the complex **2b**].

Synthesis of *cis*-[Pd_2{C_4H_2S-(2,4)}Br_2(dtbbpy)$_2$] (3b)

Method A

2,5-Dibromothiophene(85 µl, 0.75 mmol) was added to a suspension of $Pd(dba)_2$ (864 mg, 1.5 mmol) and dtbpy (4,4-di-tert-butyl-2,2 bipyridine; 420 mg, 1.5 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 1 h and then stirred at room temperature for 24 h. The solvent was evaporated *in vacuo*, then the residue washed with boiling *n*-hexane (4 × 10 ml), to eliminate dba, giving an orange solid. Since this solid contained some [$PdBr_2$(dtbbpy)] [^{1}H-NMR, 9.83 (d), 7.95 (s), 7.52 (dd), 1.45 (s)], it was re-dissolved in CH_2Cl_2 (2 ml), applied to a preparative TLC sheet, and eluted with CH_2Cl_2. The yellow band was extracted with acetone (25 ml). The resulting yellow solution was concentrated to dryness and the residue treated with CH_2Cl_2 (20 ml) and anhydrous $MgSO_4$ (1 h). The resulting suspension was filtered to give a solution, which was concentrated (2 ml). Addition of Et_2O (25 ml) caused the precipitation of a solid, which was separated by filtration, washed with Et_2O (2 × 5 ml), and air-dried to give **3b** as a yellow solid. Yield: 640 mg, 86%. M.p.: >300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 855.5 cm^{-1}; ν(thienyl) 1540 cm^{-1}; ν(dtbbpy) 1618 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ1.44 (s, 18H), 1.56 (s, 18H), 6.73 (s, 2H), 7.16 (s, 2H), 7.38 (bs, 2H), 7.51–7.53 (m, 4H), 7.89 (d, 1H, $J = 6.35$ Hz), 8.00 (bs, 1H), 9.56 (d, 2H, $J = 6.09$ Hz). Anal. calcd for $C_{40}H_{50}Br_2N_4Pd_2S$ (991.566): C, 48.45; H, 5.08; N, 5.65; S, 3.23. Found: C, 44.93; H, 4.74; N, 5.62; S, 3.61.

Synthesis of *cis*-[2-(5-BrC4H2S)BrPd(dtbbpy)] (2b) and *cis*-[Pd_2{C_4H_2S-(2,4)}Br_2(dtbbpy)$_2$] (3b)

Method B

2,5-Dibromothiophene (85 µl, 0.75 mmol) was added to a suspension of $Pd(dba)_2$ (432 mg, 0.75 mmol) and dtbpy(4,4-di-tert-butyl-2,2 bipyridine; 210 mg, 0.75 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min, then stirred at room temperature for 6 h. It was filtered to isolate the first portion of solid compound **3b**, then the residue washed with boiling *n*-hexane (4 × 10 ml) to eliminate dba, giving an orange solid. Since this solid contained some [$PdBr_2$(dtbbpy)] [^{1}H-NMR, 9.83 (d), 7.95 (s), 7.52 (dd), 1.45 (s)], it was re-dissolved in CH_2Cl_2 (2 ml), applied to a preparative TLC sheet, and eluted with CH_2Cl_2. The yellow band was extracted with acetone (25 ml). The resulting yellow solution was concentrated to dryness and the residue treated with CH_2Cl_2 (20 ml) and anhydrous $MgSO_4$ (1 h). The resulting suspension was filtered to give a solution, which was concentrated (2 ml). Addition of Et_2O (25 ml) caused the precipitation of a solid, which was separated by filtration, washed with Et_2O (2 × 5 ml), and air-dried to give **3b** as a yellow solid. Yield: 60 mg, 8%. M.p.: >300 °C dec.

The filtrate (mother liquor) was evaporated *in vacuo*, the residue extracted with CH_2Cl_2 (20 ml), and the resulting suspension filtered over anhydrous $MgSO_4$. The solvent was concentrated to dryness and the residue washed with Et_2O (3 × 20 ml) to eliminate dba. The resulting solid was separated by filtration, washed with Et_2O (2 × 20 ml) and air-dried to give **2b** as a yellow solid.

Yield: 300 mg, 65%. M.p.: 160–162 °C dec.

Reactions of complexes 2a, b and 3a, b with carbon monoxide

General procedure

Complexes **2a, b, 3a, b** (0.23 mmol) was dissolved in CH_2Cl_2 (2 ml) at room temperature (r.t.) after evacuation of the system. CO (1 atm) was introduced and the initial pale yellow solution immediately turned orange-yellow. After the solution was stirred for 4 h at r.t., the solvent was evaporated under a reduced pressure to give a yellow residue, which was recrystallized from THF–hexane to give a yellow solid of **4a, b** and **5a, b,** as described below.

Reaction of CO with **2a** (104 mg, 0.23 mmol) was carried out analogously to give *cis*-[2-(5-BrC_4H_2S)COPdBr(bpy)] (**4a**)

DOI: 10.1002/aoc

in a yield of 70 mg, 70%. M.p.: >300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 839 cm^{-1}; νC=O, 1598 cm^{-1}, ν(thienyl) 1602.4 cm^{-1}; ν(bpy) 1731 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ6.65 (d, 1H, $J = 3.6$ Hz), 6.98 (d, 1H, $J = 3.6$ Hz), 7.25–7.48 (m, 1H), 7.55–7.60 (m, 1H), 8.01–8.10 (m, 4H), 8.14 (d, 1H, $J = 5.4$ Hz), 9.45 (d, 1H, $J = 5.6$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ110.487 (s, thienyl of C*ipso*-Br), 120.726 (s, CH bpy), 121.262 (s, CH bpy), 125.650 (s, 2CH bpy), 128.884 (s, thienyl of HC-3), 129.238 (s, thienyl of HC-4), 137.946 (s, CH bpy), 138.150 (s, CH bpy), 149.800 (s, CH bpy), 150.181 (s, CH bpy), 151.180 (s, C*ipso* bpy), 152.655 (s, C*ipso* bpy), 154.643 (s, thienyl C*ipso*-Pd), 221.6 (s, C=O). Anal. calcd for $C_{15}H_{10}N_2Br_2OPdS$ (432.62); C, 33.83; H, 1.89; N, 5.26; S, 6.02. Found: C, 33.75; H, 1.85; N, 5.25; S, 6.01.

Reaction of CO with **2b** (104 mg, 0.23 mmol) was carried out analogously to give *cis*-[2-(5-BrC_4H_2S)COPdBr(dtbbpy)] (**4b**), a yellow solid, in a yield of 60 mg, 40%. M.p.: >300 °C dec. air-dried. IR (Nujol): ν(CH δ oop, thienyl) 852 cm^{-1}; ν(thienyl) 1544 cm^{-1}; νC=O, 1598 cm^{-1}, ν(dtbbpy) 1715 and 1614 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.42 (s, 9H), 1.44 (s, 9H), 6.65 (d, 1H, $J = 3.46$ Hz), 6.98 (d, 1H, J = 3.46 Hz), 7.38–7.43 (dd, 1H, $J = 1.75$ and 4.06 Hz), 7.51–7.55 (dd, 1H, $J = 1.73$ and 5.77 Hz), 7.95–8.09 (m, 3H), 9.35 (d, 1H, $J = 5.79$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ57.5 (CMe_3), 58.0 (CMe_3), 109.8 (s, thienyl of C*ipso*-Br), 122.7 (s, CH bpy), 121.26 (s, CH bpy), 125.65 (s, 2CH bpy), 129.1 (s, thienyl of HC-3), 130.2 (s, thienyl of HC-4), 138.1 (s, C*ipso* bpy), 138.3 (s, C*ipso* bpy), 149.8 (s, CH bpy), 151.4 (s, CH bpy), 151.2 (s, C*ipso* bpy), 152.6 (s, C*ipso* bpy), 155.7 (s, thienyl C*ipso*-Pd), 223.1 (s, C=O). Anal. calcd for $C_{23}H_{26}N_2Br_2SOPd$ (644.74): C, 42.85; H, 4.06; N, 4.34; S, 4.97. Found: C, 42.19; H, 4.41; N, 4.30; S, 4.94.

Reaction of CO with **3a** (208 mg, 0.46 mmol) was carried out analogously to give *cis-cis*-[2,5-$(C_4H_2S)(CO)_2Pd_2Br_2(bpy)_2$] (**5a);** Yield: 100 mg, 52%. M.p.: >300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 840 cm^{-1}; ν(thienyl) 1542 cm^{-1}; νC=O, 1601 cm^{-1}; ν(bpy) 1614 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.32 (s, 2H, thienylene), 7.42 (s, 2H), 7.49–7.51 (dd, 2H, $J = 2.1$ and 5.4 Hz), 7.72–7.78 (dd, 2H, $J = 4.8$ and 6.3 Hz), 7.81–7.86 (dd, 2H, $J = 3.6$ and 5.4 Hz), 8.05–8.10 (d, 2H, $J = 5.7$ Hz), 8.19 (m, 2H), 8.29–8.33 (d, 1H, $J = 7.2$ Hz), 8.54–8.57 (d, 1H, $J = 7.5$ Hz), 8.61–8.64 (d, 2H, $J = 7.2$ Hz), 8.88–8.90 (d, 2H, $J = 5.1$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ122.7 (s, CH bpy), 123.5 (s, CH bpy), 126.65 (s, 2CH bpy), 126.8 (s, thienyl of C*ipso*), 132.3 (s, thienyl of CH), 138.1 (s, CH bpy), 138.2 (s, CH bpy), 150.1 (s, CH bpy), 150.5 (s, CH bpy), 151.2 (s, C*ipso* bpy), 152.66 (s, C*ipso* bpy), 219.9 (s, C=O). Anal. calcd for $C_{26}H_{18}Br_2N_4O_2Pd_2S$ (823.12): C, 37.94; H, 2.20; N, 6.81; S, 3.89. Found: C, 37.89; H, 2.28; N, 6.61; S, 3.91.

Reaction of CO with **3b** (208 mg, 0.46 mmol) was carried out analogously to give *cis-cis*-[2,5-$(C_4H_2S)(CO)_2Pd_2Br_2$ (dtbbpy)$_2$] (**5b**); as a yellow solid. Yield: 87 mg, 36%. M.p.:>300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 855.5 cm^{-1}; ν(thienyl) 1540 cm^{-1}; νC=O, 1615 cm^{-1}; ν(dtbbpy) 1618 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ1.44 (s, 18H), 1.56 (s, 18H), 6.73 (s, 2H), 7.16 (s, 2H), 7.38 (bs, 2H), 7.51–7.53 (m, 4H), 7.89 (d, 1H, $J = 6.35$ Hz), 8.00 (bs, 1H), 9.56 (d, 2H, $J = 6.09$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ58.9 (CMe_3), 58.4 (CMe_3), 122.72 (s, CH bpy), 121.26 (s, CH bpy), 125.65 (s, 2CH bpy), 126.8 (s, thienyl of C*ipso*), 132.3 (s, thienyl of CH), 138.1 (s, C*ipso* bpy), 138.3 (s, C*ipso* bpy), 149.8 (s, CH bpy), 151.4 (s, CH bpy), 151.2 (s, C*ipso* bpy), 152.6 (s, C*ipso* bpy), 222.21 (s, C=O). Anal. calcd for $C_{42}H_{50}N_4Br_2SO_2Pd_2$: (1047.55)C, 48.16; H, 4.81; N, 5.35; S, 3.06. Found: C, 48.13; H, 4.74; N, 5.52; S, 3.01.

Reactivity of complex 2a, b toward isocyanide (XyNC): monoinsertion

General procedure

Isonitrile XyNC (Xy = 2, 6-$Me_2C_6H_3$) (52 mg, 0.39 mmol) was added to a suspension of *cis* complexes of **2a, b** (0.20 mmol) in CH_2Cl_2 (20 ml). The suspension was stirred for 16 h at room temperature. The color changed from pale yellow into pale red and then dark red during monitoring of the reaction mixture. After this time the workup was carried out in air. The solvents was filtered over anhydrous $MgSO_4$/Silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, giving a red complex.

*Synthesis of cis-[2-(5-BrC_4H_2S)C=NXyPdBr(bpy)]**6a***

Reaction of isonitrile XyNC (Xy = 2, 6-$Me_2C_6H_3$) (52 mg, 0.39 mmol) with **2a** (116 mg, 0.23 mmol) was carried out analogously to give **6a** as a red solid, in a yield of 130 mg, 89%. M.p.: >300 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 840 cm^{-1}; ν(thienyl) 1603 cm^{-1}; ν(bpy) 1732, cm^{-1}, $\surd$(C=N) 1645, 1584, 1506. ^{1}H NMR (300 MHz, $CDCl_3$): δ2.08 (s, 6H, 2Me), 6.64 (d, 1H, $J = 3.6$ Hz, thieny-H), 6.95 (d, 2H, $^3J_{HH} = 7.5$ Hz, Ar-H_m), 6.99 (d, 1H, $J = 3.6$ Hz, thieny-H), 7.17–7.11 (t, 1H, $^3J_{HH} = 7.5$ Hz, Ar-H_P), 7.28–7.46 (m, 1H), 7.55–7.60 (m, 1H), 8.01–8.10 (m, 4H), 8.15 (d, 1H, $J = 5.4$ Hz), 9.48 (d, 1H, $J = 5.6$ Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ18.5 (Me), 18.6 (Me), 111.2 (s, thienyl of C*ipso*-Br), 121.7 (s, CH bpy), 122.3 (s, CH bpy), 126.50 (s, 2CH bpy), 127.9 (s, CHmeta), 128.3 (s, CH*para*)129.4 (s, thienyl of HC3), 130.28 (s, thienyl of HC4), 138.46 (s, CH bpy), 138.5 (s, C*ipso-ortho* C–Me),138.6 (s, CH bpy), 148.6 (s, C*ipso*C–N=C), 150.80 (s, CH bpy), 152.18 (s, CH bpy), 153.38 (s, C*ipso* bpy), 153.8 (s, C*ipso* bpy), 156.63 (s, thienyl C*ipso*)175.9 (s, C=N). Anal. calcd for $C_{23}H_{19}N_3Br_2PdS$ (635.711): C, 43.45; H, 3.01; N, 6.61; S, 5.04. Found: C, 43.47; H, 2.98; N, 6.76; S, 5.06.

*Synthesis of cis-[2-(5-BrC_4H_2S)C=NXyPdBr(dtbbpy)]**6b***

Reaction of isonitrile XyNC (Xy = 2, 6-$Me_2C_6H_3$) (52 mg, 0.39 mmol) with **2b** (141 mg, 0.23 mmol) was carried out analogously to give **6b** as a red solid, in a yield of 120 mg, 69%. M.p.: >300 °C dec. IR (Nujol): ν(CH δ oop, thienyl) 852 cm^{-1}; ν(thienyl) 1545 cm^{-1}; ν(dtbbpy) 1717 and 1615 cm^{-1}, $\surd$(C=N) 1644, 1585, 1502. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.41 (s, 9H), 1.43 (s, 9H), 2.08 (s, 6H, 2Me), 6.64 (d, 1H, $J = 3.46$ Hz,

DOI: 10.1002/aoc

thieny-H), 6.95 (d, 2H, $^3J_{HH} = 7.5$ Hz, Ar-H_m), 6.98 (d, 1H, J = 3.46 Hz, thieny-H), 7.17–7.11 (t, 1H, $^3J_{HH} = 7.5$ Hz, Ar-H_P), 7.38–7.42 (dd, 1H, $J = 1.75$ and 4.06 Hz), 7.51–7.55 (dd, 1H, $J = 1.73$ and 5.77 Hz), 7.95–8.00 (m, 3H), 9.33 (d, 1H, $J = 5.79$ Hz). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$); δ18.4 (Me), 18.5 (Me), 57.6 (CMe_3), 58.2 (CMe_3), δ110.9 (s, thienyl of C*ipso*-Br), 121.8 (s, CH bpy), 122.42 (s, CH bpy), 126.9 (s, 2CH bpy), 127.3 (s, CHmeta), 128.6 (s, CH*para*), 129.5 (s, thienyl of HC3), 130.4 (s, thienyl of HC4), 138.45 (s, CH bpy), 138.76 (s, C*ipso-ortho* C–Me),138.33 (s, CH bpy), 148.72 (s, C*ipso*C–N=C), 151.20 (s, CH bpy), 152.23 (s, CH bpy), 153.41 (s, C*ipso* bpy), 153.48 (s, C*ipso* bpy), 156.89 (s, thienyl C*ipso*), 176.9 (s, C=N). Anal. calcd for $C_{31}H_{35}Br_2N_3PdS$ (747.92); C, 49.78; H, 4.72; N, 5.62; S, 4.29. Found: C, 49.59; H, 4.42; N, 5.43; S, 4.11.

Reactions with isocyanide (XyNC): triinsertion

*Synthesis of [2-(5-BrC_4H_2S)(C=NXy)$_3$PdBr] **7**: general procedure*

Isonitrile XyNC (156 mg, 1.17 mmol) was added to a suspension of *cis* complexes of **2a** or **2b** (0.20 mmol) in CH_2Cl_2 (20 ml) at 0 °C, and the resulting suspension was warmed slowly to room temperature and stirred overnight. The solvent was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, to give red complex **7** in a yield of 150 mg, 74%. M.p.: >300 °C dec. IR (Nujol, cm^{-1}): ν(CH δ oop, thienyl) 840 cm^{-1}; ν(thienyl) 1603 cm^{-1}; √(C=N) 1650, √(C≡N). 2180; ^1H NMR (300 MHz, $CDCl_3$): δ2.16 (s, 6H, 2 Me), 2.23 (s, 12H, 4 Me), 6.64 (d, 1H, $^3J_{HH} = 3.6$ Hz, thieny-H), 6.85 (d, 2H, $^3J_{HH} = 8.0$ Hz, Ar-H_m), 6.99 (d, 1H, $^3J_{HH} = 3.6$ Hz, thieny-H), 7.17 (t, 1H, $^3J_{HH} = 8.0$ Hz, Ar-H_P), 7.30–7.46 (m, 6H, XyNC). Anal. calcd for $C_{31}H_{29}N_3Br_2PdS$ (741.876): C, 50.19; H, 3.94; N, 5.66; S, 4.32. Found: C, 50.34; H, 3.98; N, 5.76; S, 4.16.

*From complex cis-[2-(5-BrC_4H_2S)C=NXyPdBrL_2]**6a, b***

Isonitrile XyNC (Xy = 2, 6-$Me_2C_6H_3$) (104 mg, 0.78 mmol) was added to a suspension of complexes of **6** (0.23 mmol) in CH_2Cl_2 (20 ml). The suspension was stirred for 16 h at room temperature. The color was changed from red–yellow into pale red and then dark red during monitor the reaction mixture. After this time the workup was carried out in air. The solvent was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3) and air-dried, giving red complex **7**, in a yield of 150 mg, 74%.

Synthesis of ***cis*-[2-(5-BrC_4H_2S)(C=NXy)$_4$PdBr]8: tetrainsertion**

General procedure; method A

Isonitrile XyNC (208 mg, 1.56 mmol) was added to a suspension of *cis* complexes of **2a** and/or **2b** (0.20 mmol) in CH_2Cl_2 (20 ml) at 0 °C, and the resulting suspension was warmed slowly to room temperature and stirred overnight. The solvent was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3) and air-dried, to give red complex **8** in a yield of: 150 mg, 85%. M.p.: >300 °C dec. IR (Nujol): ν (CH δoop, thienyl) 840 cm^{-1}; ν(thienyl) 1605 cm^{-1}, √(C=N) 1642, √(C≡N) 2194; ^1H NMR (300 MHz, $CDCl_3$): δ1.36 (s, 3H, Me), 2.14 (s, 3H, Me), 2.15 [s, 6H, 2Me(Xy)], 2.25 (s, 3H, Me), 2.28 (s, 3H, Me), 2.29 (s, 3H, Me), 2.63 (s, 3H, Me), 6.33 (t, 1H, $^3J_{HH} = 7.5$ Hz, Ar-H_P), 6.41–6.43 (m, 1H), 6.64 (d, 1H, $^3J_{HH} = 3.6$ Hz, thieny-H), 6.79 (d, 1H, $J = 3.6$ Hz, thieny-H), 6.88–7.22 (m, 10H); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$); δ176.3 (C=N), 172.3 (C=N), 169.2 (C=N), 149.7 (quaternary C*ipso*–N=C), 149.5 (quaternary C*ipso*–N=C),148.5 (quaternary C*ipso*–N=C), 138.5 (quaternary C*ipso*–Me), 135.9 (quaternary C*ipso*–Me), 135.8 (quaternary C*ipso*–Me), 135.7 (quaternary C*ipso*–Me), 129.1 (XyCH*o,p*), 128.9 (XyCH*o,p*), 128.2 (XyCH*o,p*), 127.6 (XyCH*o,p*), 127.4 (XyCH*o,p*), 127.3 (quaternary XyC*ipso*–NC–Pd), 127.1 (XyCH*o,p*), 126.7 (XyCH*o,p*), 126.6. (XyCH*o,p*), 108.4 (thienyl of C*ipso*–Br), 130.4 (thienyl of HC-3), 126.5 (thienyl of C-4), 131.3 (thienyl-C*ipso*), 20.5 (Me, Xy), 19.9 (Me, Xy), 18.6 (Me, Xy), 18.4 (Me, Xy). Anal. calcd for $C_{40}H_{38}N_4Br_2PdS$ (873.05): C, 55.03; H, 4.39; N, 6.42; S, 3.67. Found: C, 55.07; H, 4.45; N, 6.36; S, 3.56.

From the reaction of 2,5-dibromothiophene 1 with isocyanide (XyNC); method B

2,5-Dibromothiophene **1** (85 µl, 0.75 mmol) was added to a suspension of $Pd(dba)_2$ (432 mg, 0.75 mmol) and XyNC (Xy = 2,6-$Me_2C_6H_3$) (393 mg, 3.00 mmol) in degassed acetone (25 ml) under nitrogen, and the resulting mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 3 h. The solvent was evaporated *in vacuo*, the residue extracted with CH_2Cl_2 (20 ml), and the resulting suspension filtered over anhydrous $MgSO_4$. The solvent was concentrated to dryness and the residue washed with diethyl ether (3 × 20 ml). The resulting solid was separated by filtration, washed with Et_2O (2 × 20 ml) and air-dried to give **8** as a red solid in a yield of 150 mg, 85%.

*From reaction of complex **6a, b** with isocyanide (XyNC)*

Isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$) (156 mg, 1.17 mmol) was added to a suspension of complexes of **6a, b** (0.20 mmol) in CH_2Cl_2 (20 ml). The suspension was stirred for 16 h at room temperature. The color changed from red–yellow to pale red and then dark red during monitor the reaction mixture. After this time the workup was carried out in air. The solvents was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, giving red complex **8**, in the same yield: 144 mg, 82%.

DOI: 10.1002/aoc

From reaction of complex **7** *with isocyanide; method C*

Isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$) (52 mg, 0.39 mmol) was added to a suspension of complexes of **7** (148 mg, 0.20 mmol) in CH_2Cl_2 (20 ml). The suspension was stirred for 16 h at room temperature. The color changed from red–yellow into pale red and then dark red during monitoring of the reaction mixture. After this time the workup was carried out in air. The solvents was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, giving red complex **8**, in a yield of 144 mg, 82%.

Reactivity of complex 2a, b toward Tl(OTf) [(Tf = CF_3SO_2)]

Reaction of complex ***2a*** *with Tl(OTf)*

A mixture of **2a** (51 mg, 0.001 mmol) and TlOTf (35 mg, 0.0002 mmol) in acetone (3 ml) was allowed to react at room temperature with stirring for 3 h, then filtered through the celiet and the solvent evaporated to isolate the air-dried, semi-solid product, to give yellow complex porphyrine **9a** in a yield of 50 mg, 43%. M.p.: >300 °C dec. IR (Nujol, cm^{-1}): ν (CH δ oop, thienyl) 840 cm^{-1}; ν (thienyl) 1630 cm^{-1}; $\surd$(S═O) 1039, 1277; ^{1}H NMR (200 MHz, $CDCl_3$): δ6.92 (d, 1H, J = 3.5 Hz, thienyl), 6.99 (d, 1H, J = 3.8 Hz, thienyl), 7.02 (d, 1H, J = 3.5 Hz, thienyl), 7.07 (d, 1H, J = 3.8 Hz, thienyl), 7.16 (s, 1H), 7.36 (s, 1H), 7.58 (bs, 3H), 7.78 (s, 1H), 8.11–8.17 (m, 6H), 8.82 (s, 1H), 9.40 (bs, 2H), 9.64 (s, 1H). Anal. calcd for {$C_{30}H_{20}Br_2F_6N_4O_6Pd_2S_4$}: C, 31.40; H, 1.76; N, 4.88; S, 11.18. Found: C, 31.57; H, 1.84; N, 5.25; S, 11.42.

Reaction of complex ***2b*** *with Tl(OTf)*

A mixture of **2b** (51 mg, 0.001 mmol) and TlOTf (35 mg, 0.0002 mmol) in acetone (3 ml) was allowed to react at room temperature with stirring for 3 h, then filtered through the celiet and the solvent evaporated to isolate the air-dried, semi-solid product, to give yellow complex porphyrine **9b** in a yield of 35 mg, 25.5%. M.p.: >300 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 852 cm^{-1}; ν (thienyl) 1544 cm^{-1}; ν (dtbbpy) 1715 and 1614 cm^{-1}, $\surd$(S═O) 1039, 1277 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ1.41 (s, 9H), 1.42 (s, 9H), 1.43 (s, 9H), 1.44 (s, 9H), 6.92 (d, 1H, J = 3.7 Hz, thienyl), 6.99 (d, 1H, J = 3.9 Hz, thienyl), 7.02 (d, 1H, J = 3.7 Hz, thienyl), 7.07 (d, 1H, J = 3.9 Hz, thienyl), 7.16 (s, 1H), 7.36 (s, 1H), 7.38–7.42 (dd, 1H, J = 1.75 and 4.06 Hz), 7.51–7.55 (dd, 1H, J = 1.73 and 5.77 Hz), 7.58 (bs, 3H), 7.78 (s, 1H), 8.11–8.17 (m, 2H), 9.40 (bs, 1H), 9.64 (d, 1H, J = 5.79 Hz). Anal. calcd for {$C_{46}H_{52}$ $Br_2F_6N_4O_6Pd_2S_4$} (1371.83): C, 40.27; H, 3.82; N, 4.08; S, 9.35. Found: C, 40.13; H, 3.86; N, 4.25; S, 9.37.

Synthesis of
cis-[2,5-(C_4H_2S)(C═NXy)$_2$$Pd_2Br$(bpy)] ***10a***

Reaction of isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$) (102 mg, 0.78 mmol) with **3a** (176 mg, 0.23 mmol) was carried out analogously to give **10a** as a red solid, in a yield of 130 mg, 54.9%. M.p.: >300 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 840 cm^{-1}; ν (thienyl) 1603 cm^{-1}; ν (bpy) 1732, cm^{-1}, $\surd$(C═N) 1647, 1585, 1506. ^{1}H NMR (300 MHz, $CDCl_3$): δ2.08 (s, 12H, 4Me), 6.64 (d, 1H, J = 3.7 Hz, thieny-H), 6.95 (d, 4H, $^3J_{HH}$ = 7.5 Hz, Ar-H_m), 6.99 (d, 1H, J = 3.7 Hz, thieny-H), 7.17–7.11 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar-H_P), 7.28–7.46 (m, 2H), 7.55–7.60 (m, 2H), 8.01–8.10 (m, 8H), 8.15 (d, 2H, J = 5.4 Hz), 9.48 (d, 2H, J = 5.6 Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ18.3 (Me), 18.4 (Me), 122.5 (s, CH bpy), 123.4 (s, CH bpy), 126.65 (s, 2CH bpy), 126.82 (s, thienyl of C*ipso*),127.9 (s, XyCHmeta), 128.3 (s, XyCH*para*), 132.3 (s, thienyl of HC-4), 138.16 (s, CH bpy), 138.5 (s, XyC*ipso-ortho*-Me),138.6 (s, CH bpy), 149.91 (s, XyC*ipso*–N═C), 150.80 (s, CH bpy), 151.22 (s, CH bpy), 153.66 (s, C*ipso* bpy), 153.68 (s, C*ipso* bpy), 176.9 (s, C═N). Anal. calcd for $C_{42}H_{36}N_6Br_2Pd_2S$ (1029.49): C, 49.00; H, 3.52; N, 8.16; S, 3.11. Found: C, 49.47; H, 3.98; N, 8.36; S, 3.06.

Synthesis of
cis-[2,5-(C_4H_2S)(C═NXy)$_2$$Pd_2Br$(dtbbpy)] ***10b***

Reaction of isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$) (102 mg, 0.78 mmol) with **3b** (228 mg, 0.23 mmol) was carried out analogously to give **10b** as a red solid, in a yield of 150 mg, 52%. M.p.: >300 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 852 cm^{-1}; ν (thienyl) 1545 cm^{-1}; ν (dtbbpy) 1717 and 1615 cm^{-1}, $\surd$(C═N) 1644, 1585, 1502. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.41 (s, 18H), 1.43 (s, 18H), 2.08 (s, 12H, 4Me), 6.64 (d, 1H, J = 3.5 Hz, thieny-H), 6.95 (d, 4H, $^3J_{HH}$ = 7.5 Hz, Ar-H_m), 6.98 (d, 1H, J = 3.5 Hz, thieny-H), 7.17–7.11 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar-H_P), 7.38–7.42 (dd, 2H, J = 1.75 and 4.06 Hz), 7.51–7.55 (dd, 2H, J = 1.73 and 5.77 Hz), 7.95–8.00 (m, 6H), 9.33 (d, 2H, J = 5.79 Hz). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ18.5 (Me), 18.6 (Me), 58.81 (CMe_3), 58.52 (CMe_3), 121.28 (s, CH bpy), 122.81 (s, CH bpy), 126.4 (s, thienyl of C*ipso*), 126.15 (s, 2CH bpy), 127.9 (s, XyCHmeta), 128.3 (s, XyCH*para*), 132.32 (s, thienyl of HC-4), 138.1 (s, C*ipso* bpy), 138.15 (s, XyC*ipso-ortho*–Me), 138.63 (s, C*ipso* bpy), 148.6 (s, CH bpy), 149.6 (s, XyC*ipso*–N═C), 151.40 (s, CH bpy), 151.45 (s, C*ipso* bpy), 153.58 (s, C*ipso* bpy), 176.6 (s, C═N). Anal. calcd for $C_{58}H_{68}Br_2N_6Pd_2S$ (1253.915); C, 55.56; H, 5.47; N, 6.70; S, 2.56. Found: C, 55.59; H, 5.42; N, 6.43; S, 2.31.

Reactions of complexes 3a, b with isocyanide (XyNC): tetrainsertion

Synthesis of cis-{*2,5-(C_4H_2S)(C═NXy)$_4$$PdBr_2$*}, ***11:*** *general procedure*

Isonitrile XyNC (205 mg, 1.56 mmol) was added to a suspension of *cis* complexes of **3a** and/or **3b** (0.20 mmol) in CH_2Cl_2 (20 ml) at 0 °C, and the resulting suspension was warmed slowly to room temperature and stirred overnight. The solvents was filtered over anhydrous $MgSO_4$:silica gel (1 : 3). The resulting red solution was evaporated and the residue was triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, to give red complex **11** in a yield of 130 mg, 49.8%. M.p.: 215–217 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 840 cm^{-1}; ν (thienyl) 1605 cm^{-1}, $\surd$(C═N) 1647, $\surd$(C≡N) 2197; ^{1}H NMR (300 MHz, $CDCl_3$): δ1.36 (s, 6H, 2Me), 2.14 (s, 6H,

DOI: 10.1002/aoc

2Me), 2.15 [s, 12H, (2MeXy)2], 2.25 (s, 6H, 2Me), 2.28 (s, 6H, 2Me), 2.29 (s, 6H, 2Me), 2.63 (s, 6H, 2Me), 6.33 (t, 2H, $^3J_{HH} = 7.5$ Hz, Ar-H$_P$), 6.41–6.43 (m, 4H), 6.64 (d, 1H, $^3J_{HH} = 3.6$ Hz, thieny-H), 6.79 (d, 1H, $J = 3.6$ Hz, thieny-H), 6.88–7.79 (m, 18H). ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$); δ178.0 (C═N), 173.1 (C═N), 172.3 (C═N), 149.7 (quaternary Xy*Cipso*–N═C), 149.5 (quaternary *Cipso*–N═C),148.5 (quaternary *Cipso*–N═C), 138.5 (quaternary *Cipso*–Me), 135.9 (quaternary *Cipso*–Me), 135.8 (quaternary *Cipso*–Me), 135.7 (quaternary *Cipso*–Me), 129.1 (XyCH*o,p*), 128.9 (XyCH*o,p*), 128.2 (XyCH*o,p*), 127.6 (XyCH*o,p*), 127.4 (XyCH*o,p*), 127.3 (quaternary Xy*Cipso*–N–Pd), 127.1 (XyCH*o,p*), 126.7 (XyCH*o,p*), 126.6. (XyCH*o,p*), 125.4 (thienyl of HC-3), 131.3 (thienyl-C*ipso*), 20.4 (Me, Xy), 19.8 (Me, Xy), 18.8 (Me, Xy), 18.6 (Me, Xy). Anal. calcd for $C_{76}H_{74}N_8Br_2Pd_2S$ (1504.169): C, 60.69; H, 4.96; N, 7.45; S, 2.13. Found: C, 60.27; H, 4.55; N, 7.36; S, 2.16.

Reactivity of complexes 3a, b toward Tl(OTf) [Tf = CF_3SO_2]

Reaction of complex 3a with Tl(OTf)

A mixture of **3a** (76 mg, 0.001 mmol) and TlOTf (70 mg, 0.0004 mmol) in acetone (3 ml) was allowed to react at room temperature with stirring for 3 h, then filtered through the celiet and the solvent evaporated to isolate the air-dried, semi-solid product, to give 30 mg of yellow complex porphyrine **12a**. M.p.: >300 °C dec. IR (Nujol, cm^{-1}): ν (CH δ oop, thienyl) 841 cm^{-1}; ν (thienyl) 1635 cm^{-1}; $\surd$(S═O) 1040, 1280; ^{1}H NMR (200 MHz, $CDCl_3$): δ6.90 (d, 2H, $J = 3.5$ Hz, thienyl), 6.97 (d, 2H, $J = 3.8$ Hz, thienyl), 7.05 (d, 2H, $J = 3.5$ Hz, thienyl), 7.09 (d, 2H, $J = 3.8$ Hz, thienyl), 7.17 (bs, 4H), 7.35 (bs, 4H), 7.59 (m, 12H), 7.78 (bs, 4H), 8.05–8.17 (m, 24H), 8.82 (bs, 4H), 9.41 (m, 8H), 9.65 (bs, 4H).

Reaction of complex 3b with Tl(OTf)

A mixture of **3b** (100 mg, 0.001 mmol) and TlOTf (70 mg, 0.0004 mmol) in acetone (3 ml) was allowed to react at room temperature with stirring for 3 h, then filtered through the celiet and the solvent evaporated to isolate the air-dried, semi-solid product, to give 30 mg of yellow complex **12b**. M.p.: >300 °C dec. IR (Nujol): ν (CH δ oop, thienyl) 853 cm^{-1}; ν (thienyl) 1555 cm^{-1}; ν (dtbbpy) 1716 and 1615 cm^{-1}, $\surd$(S═O) 1039, 1278 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ1.40 (bs, 36H), 1.42 (bs, 36H), 1.44 (bs, 36H), 1.45 (bs, 36H), 6.92 (d, 2H, $J = 3.7$ Hz, thienyl), 6.99 (d, 2H, $J = 3.9$ Hz, thienyl), 7.02 (d, 2H, $J = 3.7$ Hz, thienyl), 7.07 (d, 2H, $J = 3.9$ Hz, thienyl), 7.16 (s, 4H), 7.36 (s, 4H), 7.38–7.42 (dd, 4H, $J = 1.75$ and 4.06 Hz), 7.51–7.55 (dd, 4H, $J = 1.73$ and 5.77 Hz), 7.58 (bs, 12H), 7.78 (s, 4H), 8.11–8.17 (m, 8H), 9.40 (bs, 4H), 9.64 (d, 4H, $J = 5.79$ Hz).

Acknowledgements

We are grateful to the Higher Education Commission, Islamabad, Pakistan for financial support during the author's stay as visiting Professor at the University of Balochistan, Quetta, Pakistan.

REFERENCES

1. Heck RF. *Palladium Reagents in Organic Synthesis.* Academic Press: New York, 1985.
2. Hartwig JF. *Angew. Chem., Int. Edn* 1998; **37**: 2047.
3. Tsuji J. *Palladium Reagents and Catalysis.* Wiley: Chichester, 1995.
4. Elgazwy A-SSH. *Phosphorus, Sulfur Silicon* 2000; **164**: 131.
5. Elgazwy A-SSH. *J. Sulf. Chem.* 2004; **25**: 257.
6. Elgazwy A-SSH. *J. Heterocyc. Chem.* 2004; **41**: 755.
7. Vicente J, Arcas A, Fernández-Hernández JM, Bautista D, Jones PG. *Organometallics* 2004; **24**(10): 2516.
8. Ryabov AD. *Synthesis* 1985; 233.
9. Whitcombe NJ, Hii KK, Gibson SE. *Tetrahedron* 2001; **57**: 449.
10. Crisp GT. *Chem. Soc. Rev.* 1998; **27**: 427.
11. Beletskaya IP, Cheprakov AV. *Chem. Rev.* 2000; **100**: 3009.
12. Kim Y-J, Lee S-C, Cho MH, Lee S-W. *J. Organomet. Chem.* 1999; **588**: 268.
13. Abu-Surrah A, Rieger B. *Angew. Chem., Int. Edn Engl.* 1996; **35**: 2475.
14. Mecking S, Johnson LK, Wang L, Brookhart M. *J. Am. Chem. Soc.* 1998; **120**: 888.
15. Vicente J, Abad JA, Fortsch W, Lopez-Saez MJ, Jones PG. *Organometallics* 2004; **23**: 4414.
16. Markies BA, Kruis D, Rietveld MHP, Verkerk KAN, Boersma J, Kooijman H, Lakin MT, Spek AL, van Koten G. *J. Am. Chem. Soc.* 1995; **117**: 5263.
17. Onitsuka K, Murakami K, Matsukawa K, Sonogashira K, Adachi T, Yoshida T. *J. Organomet. Chem.* 1995; **490**: 117.
18. Xie Y, Wu BM, Xue F, Ng SC, Mak TCW, Hor TSA. *Organometallics* 1998; **17**: 3988.
19. Elgazwy A-SSH. *Tetrahedron* 2003; **59**: 7445.
20. Elgazwy A-SSH. *Tetrahedron Report* 650.
21. Noda T, Ogawa H, Noma N, Shirota Y. *Appl. Phys. Lett.* 1997; **70**: 699.
22. Noda T, Imae I, Noma N, Shirota Y. *Adv. Mater.* 1997; **9**: 239.
23. Constable EC, Housecroft CE, Schofield ER, Encinas S, Armaroli N, Barigelletti F, Flamigni L, Figgemeier E, Vos JG. *Chem. Commun.* 1999; 869.
24. Kurata H, Inase M, Oda M. *Chem. Lett.* 1999; 519.
25. Thayumanavan S, Mendez J, Marder SR. *J. Org. Chem.* 1999; **64**: 4289.
26. Cui Y, Zhang X, Jenekhe SA. *Macromolecules* 1999; **32**: 3824.
27. Tang CW, VanSlyke SA. *Appl. Phys. Lett.* 1987; **51**: 913.
28. Tang CW, VanSlyke SA, Chen CH. *J. Appl. Phys.* 1989; **65**: 3610.
29. VanSlyke SA, Chen CH, Tang CW. *Appl. Phys. Lett.* 1996; **69**: 2160.
30. Shirota Y, Kuwabara Y, Inada H, Wakimoto T, Nakada H, Yonemoto Y, Kawami S, Imai K. *Appl. Phys. Lett.* 1994; **65**: 807.
31. Kuwabara Y, Ogawa H, Inada H, Noma N, Shirota Y. *Adv. Mater.* 1994; **6**: 677.
32. Tokito S, Tanaka H, Okada A, Taga Y. *Appl. Phys. Lett.* 1996; **69**: 878.
33. Inada H, Yonemoto Y, Wakimoto T, Imai K, Shirota Y. *Mol. Cryst. Liq. Cryst.* 1996; **280**: 331.
34. Delis JGP, Aubel PG, Vrieze K, van Leeuwen P, Veldman N, Spek AL. *Organometallics* 1997; **16**: 4150.
35. Owen GR, Vilar R, White AJP, Williams DJ. *Organometallics* 2002; **21**: 4799.
36. Owen GR, Vilar R, White AJP, Williams DJ. *Organometallics* 2003; **22**: 4511.
37. Vicente J, Abad JA, Förtsch W, Jones PG, Fischer AK. *Organometallics* 2001; **20**: 2704.
38. Van Asselt R, Vrieze K, Elsevier CJ. *J. Organomet. Chem.* 1994; **480**: 27.
39. Markies BA, Canty AJ, Degraaf W, Boersma J, Janssen MD, Hogerheide MP, Smeets WJJ, Spek AL, van Koten G. *J. Organomet. Chem.* 1994; **482**: 191.

DOI: 10.1002/aoc

40. Wallow TI, Goodson FE, Novak BM. *Organometallics* 1996; **15**: 3708.
41. Vicente J, Abad JA, Frankland AD, Ramírez de Arellano MC. *Chem. Commun.* 1997; 959.
42. Vicente J, Abad JA, Martínez-Viviente E, Ramírez de Arellano MC. *Organometallics* 2000; **19**: 752.
43. Kim Y-J, Song S-W, Lee S-W, Lee S-W, Osakada K, Yamamoto T. *J. Chem. Soc. Dalton Trans* 1998; 1775.
44. Onitsuka K, Murakami K, Matsukawa K, Sonogashira K, Adachi T, Yoshida T. *J. Organomet. Chem.* 1995; **490**: 117.
45. Treichel PM. *Adv. Organomet. Chem.* 1973; **11**: 21.
46. Yamamoto Y, Yamazaki H. *Coord. Chem. Rev.* 1980; **32**: 193.
47. Singlton E, Oosthnzen EH. *Adv. Organomet. Chem.* 1983; **22**: 209.
48. Mantovani A, Calligato L, Pasquetto A. *Inorg. Chim. Acta* 1983; **76**: L145.
49. Otsuka S, Nakamura A, Tatsuno Y. *J. Am. Chem. Soc.* 1969; **91**: 6994.
50. Otsuka S, Nakamura A, Yoshida T, Naruto M, Ataka K. *J. Am. Chem. Soc.* 1973; **95**: 3180.
51. Otsuka S, Ataka K. *J. Chem. Soc. Dalton Trans.* 1976; 327.
52. Vicente J, Abad JA, Viviente EM J, Jones PG. *Organometallics* 2002; **21**: 4454.
53. Delis JGP, Aubel PG, Vrieze K, van Leeuwen P, Veldman N, Spek AL, van Neer FJR. *Organometallics* 1997; **16**: 2948.
54. Vicente J, Abad JA, Gil-Rubio J, Jones PG. *Organometallics* 1995; **14**: 2677.
55. Heck RF. *Palladium Reagents in Organic Synthesis*. Academic Press: New York, 1985.
56. Yatsimirsky AK, Kazankov GM, Ryabov AD. *J. Chem. Soc., Perkin Trans. 2* 1992; 1295.

DOI: 10.1002/aoc