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Palladated Oligophenylene Thioethers: Synthesis and Reactivity toward Isocyanides, Carbon Monoxide, and Alkynes

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Supporting Information

ABSTRACT: Phenylene thioethers $XC_6H_4(SC_6H_4R\text{-}4)$-*a* (*a* = 2, 4; X = Br, I; R = H, OMe, NO_2) react with $Pd(dba)_2$ and 2 equiv of PPh_3 or 1 equiv of 2,2′-bipyridine (bpy) to afford *trans*-$[PdBr\{C_6H_4(SC_6H_4R\text{-}4)\text{-}a\}(PPh_3)_2]$ (for example, *a* = 2, R = H (**1**)) or *cis*-$[PdI\{C_6H_4(SC_6H_4R\text{-}4\}\text{-}a)(bpy)]$ (for example, *a* = 2, R = H (**5**)), respectively. Complex **1** (as well as some of its homologues) reacts (1) with 1 equiv of $[PdCl_2(NCPh)_2]$ to give a mixture of isomers of $[\{PdBr(PPh_3)\}_2(\mu\text{-}C,S\text{-}C_6H_4SPh\text{-}2)_2]$, (2) with 1 equiv of XyNC (Xy = $C_6H_3Me_2$-2,6) to render *SP-4-4*-$[PdBr\{C,S\text{-}C(=NXy)C_6H_4\text{-}2\text{-}SPh\}(PPh_3)]$, (3) with XyNC and TlTfO (TfO = O_3SCF_3; 1:2:1 molar ratios) to give *SP-4-3*-$[Pd\{C,S\text{-}C(=NXy)C_6H_4\text{-}2\text{-}SPh\}(CNXy)(PPh_3)]TfO$, (4) with 4 equiv of XyNC to give *SP-4-4*-$[Pd\{C,N\text{-}C(=NXy)C(=NXy)C(=NXy)C_6H_4(SPh)\text{-}2\}Br(CNXy)]$, or (5) with TlTfO (1:1 molar ratio) to afford a mixture of compounds from which a few single crystals of $(Ph_3PC_6H_4SPh\text{-}2)TfO$ could be obtained. Complexes with bpy ligands react with 2 equiv of PPh_3 to give *trans*-$[PdI\{C_6H_4(SC_6H_4R\text{-}4)\text{-}4\}(PPh_3)_2]$ or with 3 equiv of XyNC affording monoinserted complexes resulting from the replacement of the PdI(bpy) group by *trans*-$\{C(=NXy)\}Pd(CNXy)_2$. Dinuclear complexes are prepared by reacting diiodophenylene thioethers with $Pd(dba)_2$ and bpy. Complex **5** reacts with TlTfO and CO or various alkynes RC≡CR′ to afford, respectively, $[Pd\{C,S\text{-}C(O)C_6H_4SPh\text{-}2\}bpy]TfO$ or $[Pd\{C,S\text{-}C(R')=C(R)C_6H_4SPh\text{-}2\}bpy]$, the latter of which decompose thermally to give the benzothiophenes resulting from the C−S coupling. Crystal structures of some model complexes have been determined.

INTRODUCTION

We have recently reported the synthesis of a series of oligomeric phenylene thioethers $(X(C_6H_4S\text{-}a)_nC_6H_4R\text{-}4$, X = Br, I, *n* = 1−4, *a* = 2, 4, R = H, MeO, NO_2, NH_2, SMe, Br, I; 2-$XC_6H_4(SC_6H_4\text{-}4)_nSC_6H_4X\text{-}2$, *n* = 3, 5, X = Br; C_6HMe_3-2,4,6-$(SC_6H_4X\text{-}4)_2$-1,3 (X = Br, I)) using a new step-by-step method, each consisting first of a Pd-catalyzed reaction between ArI and HSAr′Br (Ar = aryl, Ar′ = arylene) to give ArXAr′Br, followed by a Cu-catalyzed replacement of Br by I to give ArXAr′I, which can in turn be reacted with HXAr′Br in the following step (Scheme 1).[1] We have also reported some of the corresponding sulfoxides. Polyarylene thioethers are produced commercially,[2] and some of their oligomeric analogues are used as ion-selective electrodes.[3]

In this paper we report the synthesis of mononuclear palladium(II) derivatives containing ortho- or para-bis(phenylene) monothioethers $[Pd]C_6H_4SC_6H_4R$ (*o*-*p*-**A** or *p*-*p*-**A**), tris(phenylene) dithioethers $[Pd]C_6H_4SC_6H_4SC_6H_4R$ (*p*-*p*-*p*-**B**), and dinuclear complexes containing mono(phenylene) monothioether $[Pd]_2(\mu\text{-}C,S\text{-}C_6H_4SPh)_2$ (*o*-**C**) or tris(phenylene) dithioethers $[Pd]C_6H_4S(C_6HR_3)SC_6H_4[Pd]$ (R = H (*p*-*p*-*p*-**C**), Me (*p*-*m*-*p*-**C**)), most of which are the only members of their families. Thus, only one metal complex of type *o*-*p*-**A** has been reported.[4]

Scheme 1

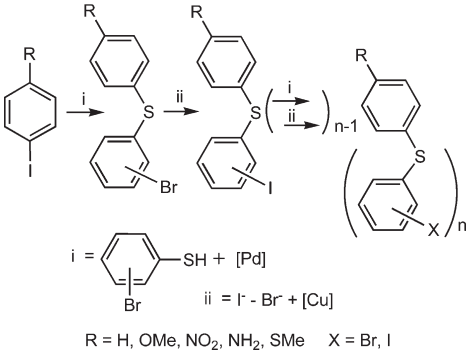

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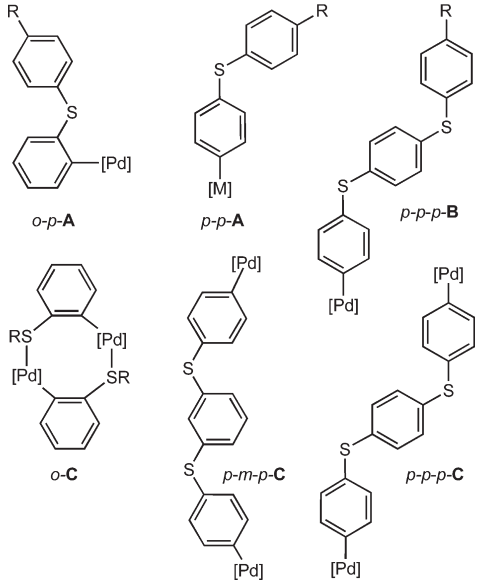
Chart 1

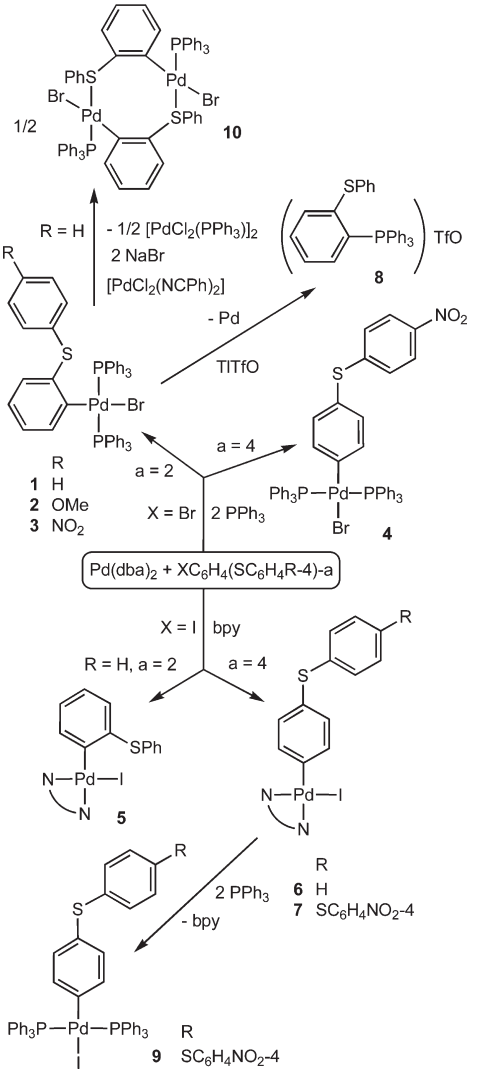


We report here the reactivity of some of our palladium complexes toward isocyanides, carbon monoxide, and alkynes. Although it is well known that these reagents insert into Pd—aryl bonds—including a few thioether-substituted derivatives[5−8]—we report here insertion reactions affording interesting new mono- and dinuclear complexes and also some 2,3-benzo[*b*]thiophenes.

RESULTS AND DISCUSSION

Synthesis of Mono- or Dinuclear Aryl Palladium Complexes Derived from Oligophenylene Thioethers. The reaction of a mixture of $Pd(dba)_2$ ($[Pd_2(dba)_3]\cdot$dba, dba = dibenzylideneacetone) and 2 equiv of PPh_3 with 1.2 equiv of the phenylene thioether $BrC_6H_4(SC_6H_4R\text{-}4)$-*n* (*n* = 2) in refluxing toluene afforded *trans*-$[PdBr\{C_6H_4S(C_6H_4R\text{-}4)\text{-}2\}(PPh_3)_2]$ (R = H (**1**), OMe (**2**), NO_2 (**3**); Scheme 2). Under the same reaction conditions, para-substituted phenylene thioethers (*n* = 4, R = H, MeO, NO_2) gave mixtures of compounds that could not be separated; however, using 1 equiv of the thioether and a shorter reaction time (10 min instead of 2−2.5 h) the expected complex *trans*-$[PdBr\{C_6H_4(SC_6H_4NO_2\text{-}4\}\text{-}4)(PPh_3)_2]$ (**4**) could be isolated. The other para-substituted phenylene thioethers (R = H, MeO) or the dithioethers $BrC_6H_4SC_6H_4$-4-SPh-4 or $BrC_6H_4SC_6H_4$-2-SPh-2 afforded complex mixtures even when $[Pd(PPh_3)_4]$ was used as the source of palladium. Under milder conditions the reactions did not take place. Probably, under the harsh reaction conditions used, the para-substituted aryl complexes decompose. It is well known that ortho-substituted aryl complexes are more stable (ortho effect) than para-substituted complexes[9,10] and that nitro groups confer a great stability to aryl complexes.[11] Our results suggest that a nitro group can influence the stability of an aryl palladium complex (**4**) even when the C—Pd and C—NO_2 bonds are separated by two para-phenylene groups and a S atom. The disappointing results from the ortho-substituted dithioether $BrC_6H_4SC_6H_4$-2-SPh-2 could be attributed to the overcrowded ortho position. We have reported the unexpected synthesis of *trans*-$[PdBr\{C_6H_4SPh\text{-}2\}(PPh_3)_2]$[12] by reacting the salt $PPh_4(SC_6H_4Br\text{-}2)$ with $Pd(dba)_2$ and PPh_3 (1:1:1).

Scheme 2



The oxidative addition reactions of *ortho*- or *para*-bromophenylene thioethers to $Pd(dba)_2$ in the presence of of 2,2′-bipyridine (bpy), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, or 4,4′-di-*tert*-butyl-2,2′-bipyridine led to palladium metal at temperatures < 90 °C. As iodoarenes are more reactive than bromoarenes in oxidative addition reactions, we reacted $Pd(dba)_2$ with IC_6H_4SPh-2, IC_6H_4SPh-4, or $I(C_6H_4S\text{-}4)_2C_6H_4NO_2$-4 at room temperature in the presence of bpy, affording *cis*-$[PdI\{C_6H_4(SC_6H_4R\text{-}4\}\text{-}n)(bpy)]$ (R = H, *n* = 2 (**5**), 4 (**6**), R = $SC_6H_4NO_2$-4, *n* = 4 (**7**)), respectively. Similarly, the dinuclear palladium complex $[\{PdI(bpy)\}_2\{\mu\text{-}(C_6H_4S\text{-}4)_2C_6H_4\text{-}4\}]$ (**11**; Scheme 3) or $[\{PdI(bpy)\}_2(\mu\text{-}C_6H_4\text{-}4\text{-}SC_6HMe_3\text{-}2,4,6\text{-}S\text{-}3\text{-}C_6H_4\text{-}4)]$ (**12**) was prepared by reacting diiodophenylene thioethers $I(C_6H_4S\text{-}4)_2C_6H_4I$-4 or C_6HMe_3-2,4,6-$(SC_6H_4I\text{-}4)_2$-1,3 with $Pd(dba)_2$ and bpy, respectively.

We have reported the synthesis of some triflato palladium complexes using different synthetic routes, e.g., by reacting acetylacetonato complexes with triflic acid[13] or halo complexes with TlTfO (TfO = O_3SCF_3).[14,15] These complexes, containing weakly bonding anionic ligands (also those with a perchlorato ligand), are useful as intermediates (not always isolated) in the synthesis of other complexes or as catalysts.[16] However, when such complexes contain a phosphine and an aryl ligand, they

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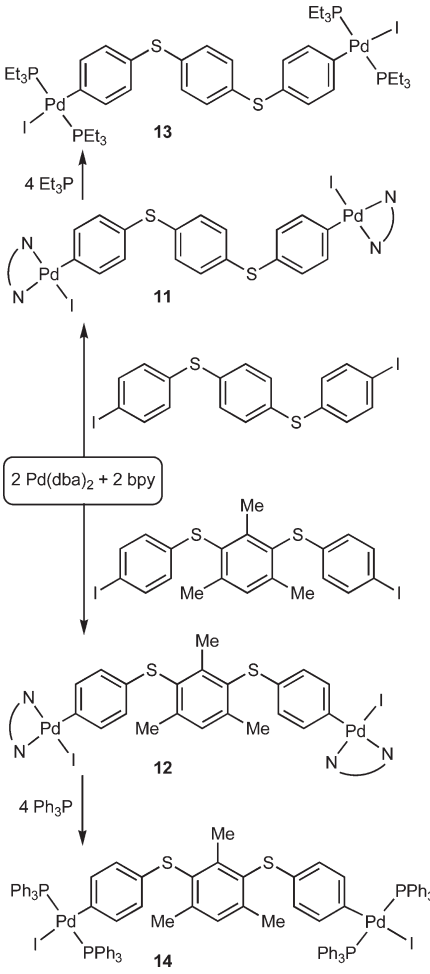
Scheme 3



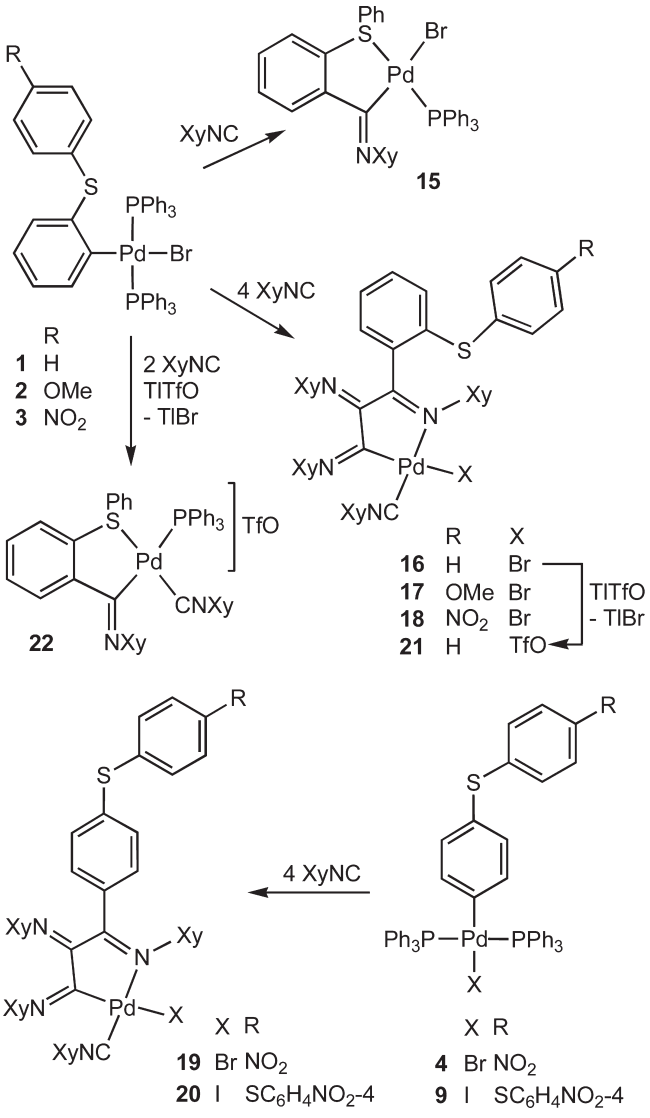
can decompose to give a phosphonium salt resulting from an aryl/PR_3 coupling.[17,18] Complex **1** reacted with TlTfO (1:1 molar ratio) to afford a mixture of compounds from which a few single crystals of $(Ph_3PC_6H_4SPh\text{-}2)TfO$ (**8**) (only permitting an X-ray diffraction study) could be obtained.

As mentioned above, para-substituted phenylene thioethers (R = H, MeO) or the dithioethers $BrC_6H_4SC_6H_4$-4-SPh-4 and $BrC_6H_4SC_6H_4$-2-SPh-2 afforded complex mixtures when reacted with $Pd(dba)_2$ and PPh_3 or when $[Pd(PPh_3)_4]$ was used as the source of palladium. The same occurred with $IC_6H_4SC_6H_4$-4-$S(C_6H_4NO_2$-4)-4. However, by reacting **7**, **11**, or **12** with 2 equiv of the corresponding phosphine, *trans*-$[PdI\{C_6H_4SC_6H_4$-4-S-$(C_6H_4NO_2$-4)-4$\}(PPh_3)_2]$ (**9**), $[\{trans\text{-}PdI(PEt_3)_2\}_2\{\mu\text{-}(C_6H_4S\text{-}4)_2\text{-}C_6H_4\text{-}4\}]$ (**13**), or $[\{trans\text{-}PdI(PPh_3)_2\}_2(\mu\text{-}C_6H_4$-4-$SC_6HMe_3$-2,4,6-S-3-$C_6H_4$-4)] (**14**), respectively, was prepared (Scheme 3).

In an attempt to prepare halide-bridged dinuclear complexes $[Pd(R)(PR_3)(\mu\text{-}X)]_2$, which are useful as starting materials,[10,19] we reacted **1** with 1 equiv of $[PdCl_2(NCPh)_2]$, affording instead $[\{PdBr(PPh_3)\}_2\{\mu\text{-}C,S\text{-}(C_6H_4SPh\text{-}2\}]$ (**10**), containing a bridging arylthioether ligand, which is the first member of this family. The reaction mixture contained two isomers in ratios depending on the temperature, one of which was characterized by an X-ray diffraction study (Scheme 1 and Figure 4). The same type of reaction was unsuccessful starting from complexes **2**−**4** because mixtures were obtained that we could not separate.

Reactivity toward Isocyanides and Carbon Monoxide. Complex **1** reacts with 1 equiv of XyNC (Xy = $C_6H_3Me_2$-2,6) to render a mixture of **1**, PPh_3, and *SP-4-4*-$[PdBr\{C,S\text{-}C(=NXy)C_6H_4$-2-SPh$\}(PPh_3)]$ (**15**, Scheme 4), which could be the result of the following three steps: the replacement of one of the phosphine ligands by XyNC, its insertion into the C−Pd bond, and coordination of the sulfur atom to give a C^S chelating ligand. The best yield of **15** (82%, isolated) was obtained by using 1.5 equiv of XyNC. When an XyNC:**1** molar ratio of 2 was used, a mixture of **15** and the palladacycle *SP-4-4*-$[PdBr\{C,N\text{-}C(=NXy)C(=NXy)C(=NXy)C_6H_4(SC_6H_4R$-4)-2$\}(CNXy)]$ (R = H (**16**), Scheme 4) was obtained. Complex **16** could be considered as being derived from **15** after an additional and fast double insertion of XyNC into the C−Pd bond and replacement of PPh_3 by XyNC. As a consequence of the increase of the ring size of the C^S palladacycle, from five to seven, a different five-membered C^N palladacycle is formed. Using the stoichiometric amount of XyNC (4 equiv) or excess (5 equiv) complex **16** was obtained in 90% yield. The analogous reaction with complex **2**, **3**, **4**, or **9** afforded **17**−**20** (Scheme 4), respectively, homologues of **16**. There are a few related complexes reported in the

Scheme 4



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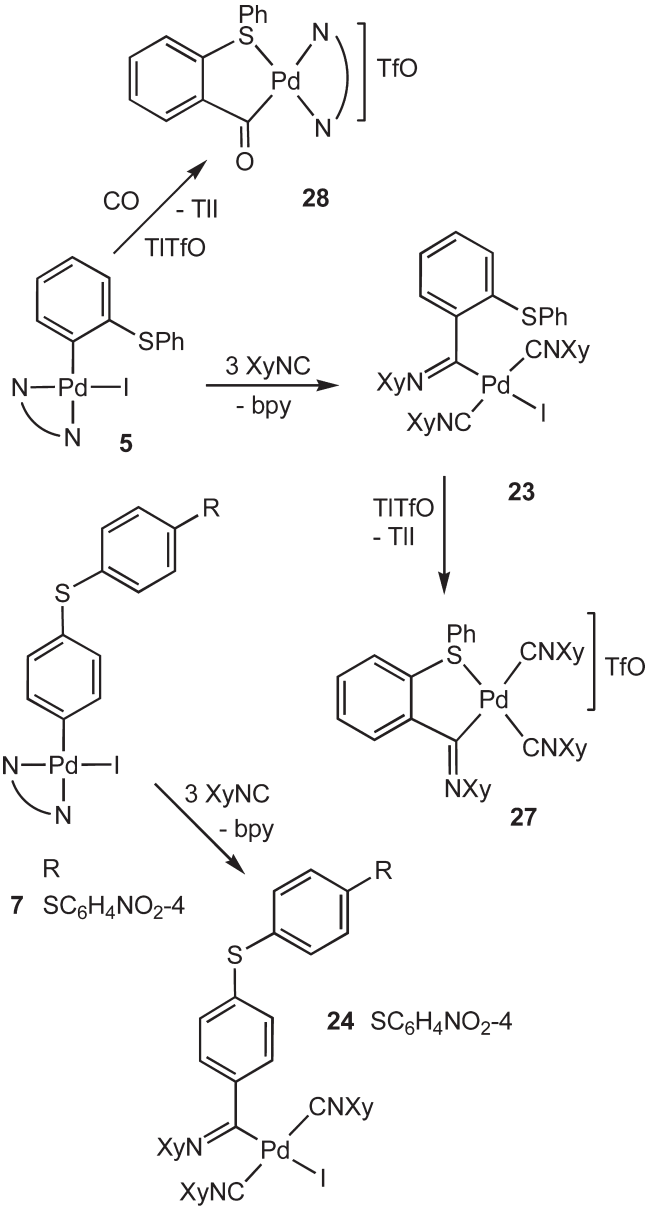
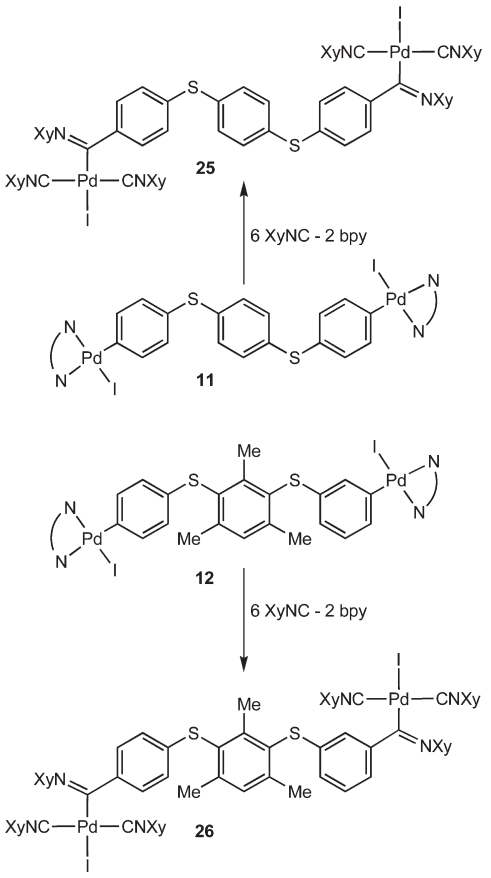
literature.[20,21] Complex **16** reacted with TlTfO to afford the triflato complex **21**, whereas the reaction of **1** with XyNC and TlTfO (1:2:1 molar ratio) afforded the complex *SP-4-3*-[Pd{*C,S*-C(=NXy)C_6H_4-2-SPh}(CNXy)(PPh_3)]TfO (**22**; Scheme 4). This product is the result of the replacement of Br, after its precipitation as TlBr by TlTfO, and one PPh_3 ligand by XyNC and the thioether sulfur atom and the insertion of one molecule of XyNC. The isomer obtained can be explained taking into account that C/C transphobia is greater than C/P transphobia.[15,18,21,22] When the same reaction was carried out using a XyNC:**1** molar ratio of 1 or 3, **16** was also obtained but with lower yield. Complex **2** or **3** reacted similarly, but the corresponding homologues of **16** could not be isolated in pure form.

A different behavior toward XyNC is observed in complexes with bpy ligands. Thus, mono- and dinuclear complexes **5**, **7** and **11**, **12** reacted with XyNC (1:3 or 1:6, respectively), affording complexes resulting from the replacement of the bpy ligand by two XyNC and the insertion of one isocyanide molecule into the C−Pd bond; that is, the PdI(bpy) group is transformed to *trans*-{C(=NXy)}Pd$(CNXy)_2$, giving **23**, **24** and **25**, **26** (Schemes 5 and 6), respectively, the former of which reacted with TlTfO to render the palladacycle [Pd{*C,S*-C(=NXy)C_6H_4SPh-2)}$(CNXy)_2$]-TfO (**27**; Scheme 5).

Scheme 5



Scheme 6

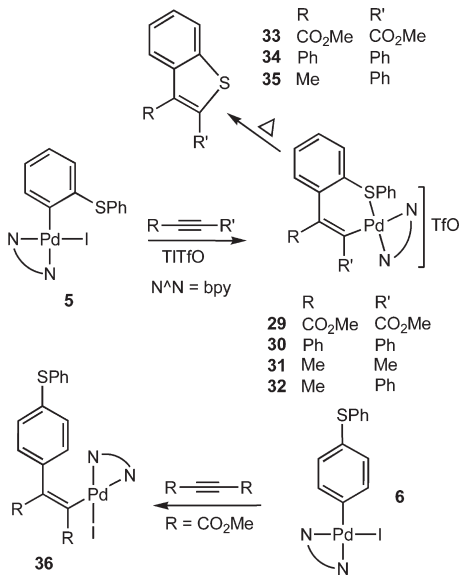


Reactivy toward Alkynes. Complexes **1**−**4** reacted with alkynes RC≡CR′ (R = R′ = CO_2Me, Ph, Me, R = Me, R′ = Ph) with or without TlTfO to give complex mixtures. However, complex **5** reacted with the same alkynes, in the presence of TlTfO at room temperature, to afford [Pd{*C,S*-C(R′)=C-(R)C_6H_4SPh-2}bpy] (R = R′ = CO_2Me (**29**), Ph (**30**), Me (**31**), R = Me, R′ = Ph (**32**); Scheme 7), resulting from the removal of the iodo ligand and the insertion of an alkyne molecule into the C−Pd bond, even if an excess of the alkyne was

Complexes **15**, **22**, and **27** are the only reported five-membered cyclopalladated iminoacyl thioether complexes. A few analogous six-membered ring complexes have been described.[7,8,23]

Complexes **1**−**4** and **7** do not react with CO, but **5** reacts with TlTfO and CO to give [Pd{*C,S*-C(O)C_6H_4SPh-2)}(bpy)]-TfO (**28**; ν(C=O): 1668 cm^{-1}), resulting from the removal of the bromo ligand, the insertion of CO into the aryl−Pd bond, and formation of a new S−Pd bond to give a C^S chelating ligand (Scheme 5). There is only one five-membered cyclopalladated iminoacyl thioether compound analogous to **28**, the neutral complex [Pd(*C,S*-C(O)C$(Me)_2CH_2$SMe], which, however, is not obtained by CO insertion but by oxidative addition of the corresponding acyl chloride to $Pd(dba)_2$.[24] A few analogous six-membered ring complexes have been reported, which in contrast to **28**, deinsert CO under very mild conditions.[8]

Scheme 7



used. In the case of **32**, only one of the two possible regioisomers was obtained, which we formulate in Scheme 7 as the isomer with the Ph group near the Pd atom because previous studies indicate such a preference when these insertions are regioselective.[25] A NOESY study on **35** (see below) proved this assignment. Complex **6** reacted with RC≡CR, in refluxing 1,2-dichloroethane, giving [Pd{C(R)═C(R)C_6H_4SPh-2}I(bpy)] (R = CO_2Me, **36**). The reaction in the presence of TlTfO gave complex mixtures and in acetone at room temperature (15 h) gave a mixture of **6** and **32**.

When a toluene solution of complex **29**, **30**, or **32** was refluxed, it decomposed to give the benzothiophene resulting from a C−S coupling and removal of the Ph group (Scheme 7, R = R′ = CO_2Me (**33**), Ph, (**34**), R = Me, R′ = Ph (**35**)). The syntheses of these benzothiophenes by cyclization reactions have been previously reported. Thus, **33** was prepared by the radical reaction of benzenethiol with dimethylacetylene dicarboxylate at 154 °C, which affords a mixture of the adduct MeO_2CC(SPh)═CHCO_2Me and **33**.[26] The best yield methods for the syntheses of compound **34** by cyclization involve (1) reaction of sulfenyl halogenides with silver trifluoromethanesulfonate and diphenylacetylene (94% yield),[27] (2) PhSC(Ph)═C(Ph)(OSO2Ar) catalyzed by boron trifluoride (>90% yield) or PhSCHPhC(O)Ph in polyphosphoric acid (85% yield),[28] and (3) Ph_2C═C(Ph)SH catalyzed by Cl_2Pd(COD) at 120 °C (85% yield).[29] The only cyclization reaction for the synthesis of compound **35**, involving (PhS)PhCHC(O)Me and Na_2CO_3, has been patented as an inhibitor of hepatitis C virus replication.[30] Alternatively, the thermolysis of 3-Me-1-phenylbenzo[*b*]thiophenium triflate has been reported to give **35** in 75% yield.[31] Related depalladation processes, affording a series of six- and seven-membered neutral and cationic sulfur-containing heterocycles, have been reported.[5,7]

Crystal Structures. The crystal structures of **2** (Figure 1), **3** (Figure 2), **8** (Figure 3), **10** (Figure 4), **14** (Figure 5), **16** (Figure 6), **17** (Figure 7), **21** (Figure 8), **22** (Figure 9), and **27** (Figure 10) have been determined. All compounds crystallize with no imposed symmetry and with one molecule in the asymmetric unit. The compounds will be grouped to discuss their common features. All palladium complexes show a slightly distorted square-planar geometry.

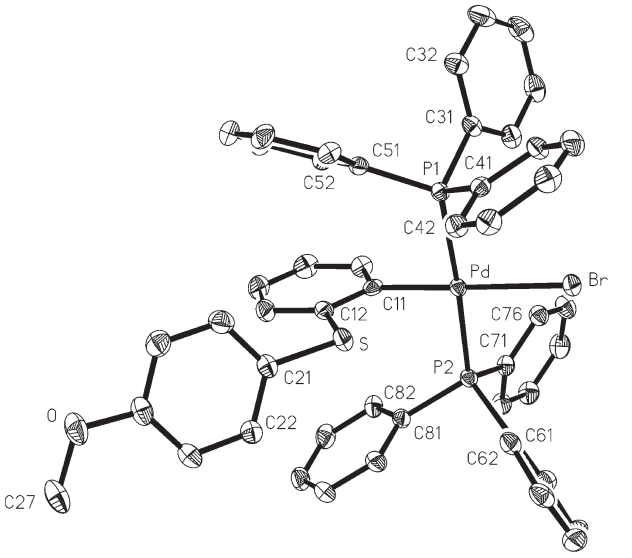


Figure 1. Thermal ellipsoid representation (50% probability) of complex **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(11) 2.011(2), Pd−P(2) 2.3198(6), Pd−P(1) 2.3411(6), Pd−Br 2.5205(3), C(11)−Pd−P(2) 86.15(6), C(11)−Pd−P(1) 90.65(6), P(2)−Pd−Br 92.938(16), P(1)−Pd−Br 90.337(16), C(21)−S−C(12) 103.75(10).

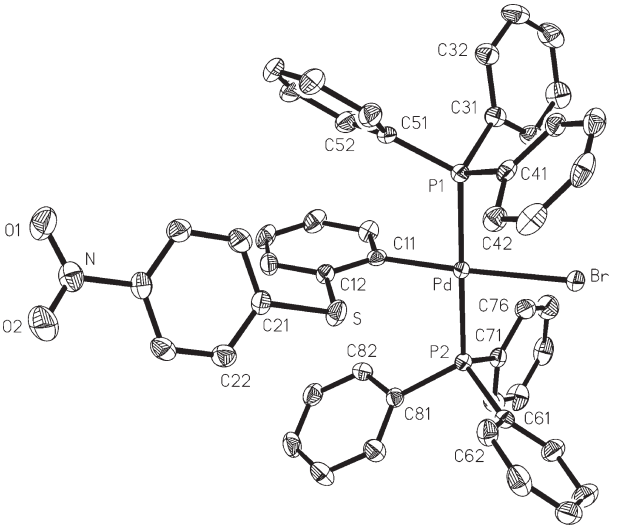


Figure 2. Thermal ellipsoid representation (50% probability) of complex **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(11) 2.014(2), Pd−P(2) 2.3206(6), Pd−P(1) 2.3297(6), Pd−Br 2.5353(3), N−O(2) 1.212(3), N−O(1) 1.235(3), N−C(24) 1.474(3), C(11)−Pd−P(2) 90.89(6), C(11)−Pd−P(1) 89.80(6), P(2)−Pd−Br 88.808(18), P(1)−Pd−Br 90.572(18), C(12)−S−C(21) 103.18(11), O(2)−N−O(1) 124.4(2), O(2)−N−C(24) 118.5(2), O(1)−N−C(24) 117.0(2).

1. *Complexes trans-[Pd{C_6H_4(SAryl)-4}X{(PPh_3)$_2$}] (X = Br, Aryl = C_6H_4OMe-4 (**2**), $C_6H_4NO_2$-4 (**3**)) and trans-[{PdI(PPh_3)$_2$}$_2${μ-C_6H_4(SC_6HMe_3-2,4,6-S-3)C_6H_4-4}-4] (**14**).* The Pd−P bond distances are similar to each other (2.3198(6)−2.3411(6) Å) and to those in *trans*-[Pd{C_6H_4(SPh)-4}Br{(PPh_3)$_2$}]

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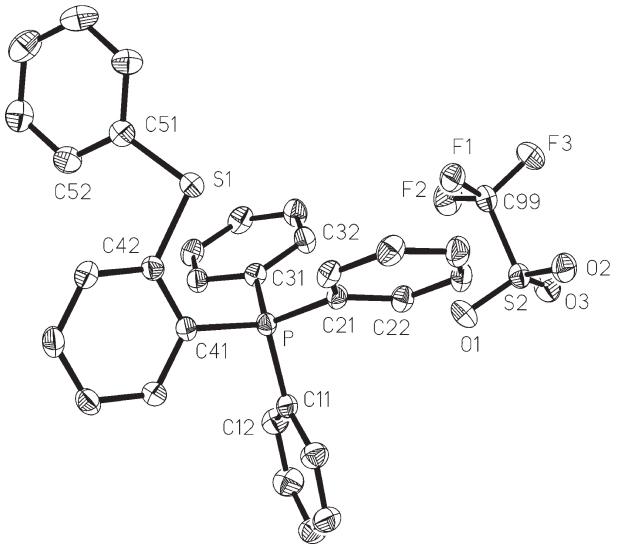


Figure 3. Thermal ellipsoid representation (50% probability) of complex **8**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P−C(31) 1.7944(16), P−C(21) 1.7957(16), P−C(41) 1.8026(16), P−C(11) 1.8026(17), S(1)−C(42) 1.7672(17), S(1)−C(51) 1.7815(18), C(31)−P−C(21) 113.87(8), C(31)−P−C(41) 109.61(7), C(21)−P−C(41) 111.35(7), C(31)−P−C(11) 106.74(8), C(21)−P−C(11) 106.40(8), C(41)−P−C(11) 108.59(8).

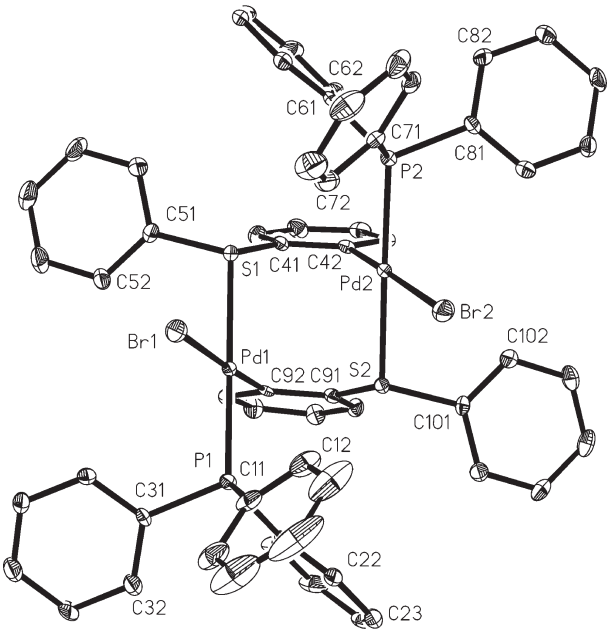


Figure 4. Thermal ellipsoid representation (30% probability) of complex **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(92) 2.005(6), Pd(1)−P(1) 2.2725(16), Pd(1)−S(1) 2.3774(15), Pd(1)−Br(1) 2.5115(11), Pd(2)−C(42) 2.013(6), Pd(2)−P(2) 2.2652(16), Pd(2)−S(2) 2.3711(15), Pd(2)−Br(2) 2.5187(9), S(1)−C(51) 1.783(6), S(1)−C(41) 1.790(6), S(2)−C(91) 1.773(6), S(2)−C(101) 1.782(5), C(92)−Pd(1)−P(1) 88.98(14), C(92)−Pd(1)−S(1) 91.25(14), P(1)−Pd(1)−Br(1) 94.45(4), S(1)−Pd(1)−Br(1) 85.32(4), C(42)−Pd(2)−P(2) 89.66(15), C(42)−Pd(2)−S(2) 91.73(15), P(2)−Pd(2)−Br(2) 94.02(4), S(2)−Pd(2)−Br(2) 84.57(4), C(51)−S(1)−C(41) 103.6(3), C(51)−S(1)−Pd(1) 107.71(19), C(41)−S(1)−Pd(1) 109.58(18), C(91)−S(2)−C(101) 104.7(3), C(91)−S(2)−Pd(2) 110.65(18), C(101)−S(2)−Pd(2) 106.76(18).

(2.3337(7)−2.3366(7) Å).[12] The Pd−Br bond lengths increase slightly as the para-substituent of the aryl group becomes more electron-withdrawing (NO_2 (2.5353(3) Å) > H (2.5296(3) Å)[12] > OMe (2.5205(3) Å)), which should increase the Br to Pd π-back-bonding.

*2. [PPh_3(C_6H_4SPh-4)]TfO (**8**).* This phosphonium salt shows the expected distorted tetrahedral geometry around the P atom (C−P−C range 113.87(8)−106.40(8)°). The C−P bond distances lie in the narrow range 1.7944(16)−1.8026(16) Å.

*3. Complex [{PdBr(PPh_3)}$_2$(μ-C,S-C_6H_4SPh-2)$_2$] (**10**).* As mentioned above, complex **10** is the first reported complex containing a bridging arylthioether. The molecule displays approximate 2-fold symmetry (root-mean-square deviation 0.15 Å). Some bond distances in this complex are different from those in the above group 1 complexes. Thus, the Pd−P bond distances are shorter in **10** (2.2725(16) and 2.2652(16) Å vs 2.3198(6)−2.3411(6) Å), which indicates that the trans influence of the thioether ligand is weaker than that of PPh_3. The Pd−Br bond lengths in **10** (2.5115(11), 2.5187(9) Å) are similar to that in **2** (2.5205(3) Å), which has the shorter Pd−Br bond distance in the group 1 complexes. The Pd−S bond lengths (2.3774(15), 2.3711(15) Å) are longer than those present in the only palladium complex characterized by X-ray diffraction containing mutually trans thioether and P-donor ligands (2.358(2), 2.342(2) Å), although the latter is an aminobis(phosphonite) ligand instead of PPh_3.[32]

*4. Complexes SP-4-4-[Pd{C,N-C(=NXy)C(=NXy)C(=NXy)C_6H_4-(SC_6H_4R-4)-2}X(CNXy)] (X = Br, R = H (**16**), OMe (**17**), X = TfO, R = H (**21**)).* The C−N−C−Pd group of atoms of the coordinated XyNC ligand is almost linear (angle range 171.4(2)−176.25(15)°). In **16**, the Xy ring of the N(5)Xy group is adjacent to the isocyanide ligand at N(6) rather than to N(4)Xy. Interplanar angles and intercentroid distances for the relevant rings are 16.4° and 4.83 Å. Similarly, the N(4)Xy ring is close to the N(5)Xy group rather than to the XyC(10) ring. The same is observed in complex **17**. The ranges of bonding distances of PdC≡NXy (1.153(3)−1.148(3) Å), Pd−CNXy (1.9703(18)−1.945(3) Å), PdC=N(Xy) (1.260(3)−1.261(2) Å), and XyN−Pd (2.0903(19)−2.075(2) Å) include the corresponding average values in similar complexes (1.153, 1.941, 1.278, 2,102 Å, respectively).[21,33] The Pd−C(=NXy) bond distance depends on the nature of the trans ligand, being 1.996(3) or 2.002(2) Å for Br (**16**, **17**, respectively; in analogous complexes 1.9936(15), 2.0037(18) Å)[21] and 1.9748(16) Å for TfO (**21**; 1.9772(19), 1.9681(18) Å in similar complexes),[21] which means that the trans influence of Br is slightly greater than that of TfO. The Pd−Br bond distance (**16**: 2.5173(5), **17**: 2.5295(4) Å) is similar to those in analogous complexes (2.5390(2), 2.5282(3) Å).[21]

*5). Complexes SP-4-3-[Pd{C,S-C(=NXy)C_6H_4-2-SPh}(CNXy)-(PPh_3)]TfO (**22**) and [Pd{C,S-C(=NXy)C_6H_4SPh-2)}(CNXy)$_2$]TfO (**27**).* As mentioned above, there are no precedents for these types of Pd complexes. The bonding distances PdC≡NXy (1.149(3)−1.144(3) Å) and PdC=N(Xy) (1.258(3), 1.266(2) Å) are similar to the corresponding values in the above group of complexes (1.153(3)−1.148(3) and 1.260(3)−1.261(2) Å, respectively). The Pd−CNXy bond lengths depend on the trans ligand. Thus, the Pd−CNXy bond distance trans to S (**22**: 1.974(2), **27**: 1.986(2) Å) is shorter that that trans to C in **27** (2.0636(19) Å) because of the greater trans influence of the

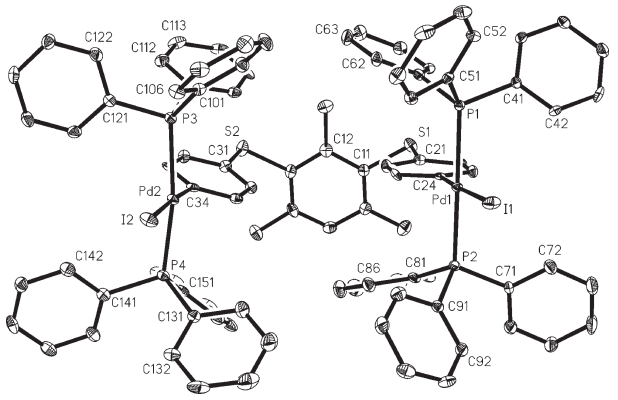


Figure 5. Thermal ellipsoid representation (30% probability) of complex **14**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(24) 2.007(5), Pd(1)−P(2) 2.3313(15), Pd(1)−P(1) 2.3364(15), Pd(1)−I(1) 2.6820(7), Pd(2)−C(34) 2.029(6), Pd(2)−P(4) 2.3210(16), Pd(2)−P(3) 2.3665(16), Pd(2)−I(2) 2.6917(7), S(1)−C(21) 1.785(6), S(1)−C(11) 1.790(6), S(2)−C(13) 1.783(6), S(2)−C(31) 1.789(6), C(24)−Pd(1)−P(2) 86.38(15), C(24)−Pd(1)−P(1) 85.60(15), P(2)−Pd(1)−I(1) 93.74(4), P(1)−Pd(1)−I(1) 94.10(4), C(34)−Pd(2)−P(4) 89.28(16), C(34)−Pd(2)−P(3) 89.63(16), P(4)−Pd(2)−I(2) 89.56(4), P(3)−Pd(2)−I(2) 92.07(4), C(21)−S(1)−C(11) 102.0(3), C(13)−S(2)−C(31) 102.6(3).

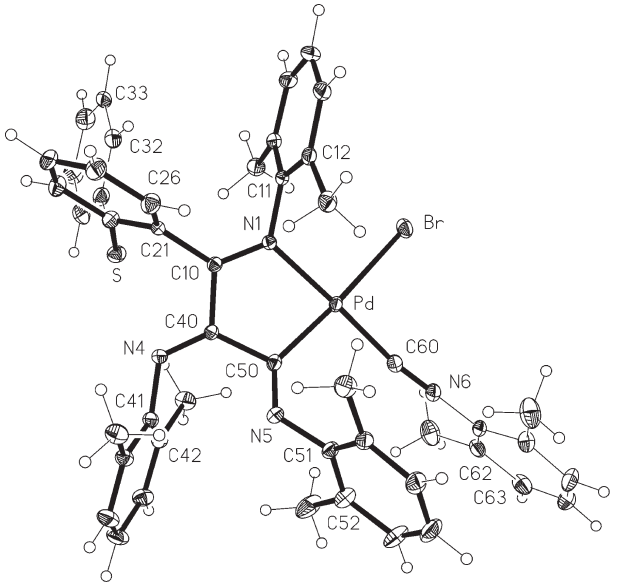


Figure 6. Thermal ellipsoid representation (30% probability) of complex **16**. Selected bond lengths (Å) and angles (deg): Pd−C(60) 1.945(3), Pd−C(50) 1.996(3), Pd−N(1) 2.075(2), Pd−Br 2.5173(5), S−C(22) 1.777(3), S−C(31) 1.777(3), N(1)−C(10) 1.292(3), N(1)−C(11) 1.445(3), N(4)−C(40) 1.270(3), N(4)−C(41) 1.428(3), N(5)−C(50) 1.260(3), N(5)−C(51) 1.418(3), N(6)−C(60) 1.148(3), N(6)−C(61) 1.394(3), C(60)−Pd−C(50) 96.57(11), C(50)−Pd−N(1) 80.66(9), C(60)−Pd−Br 87.00(8), N(1)−Pd−Br 95.81(6), C(22)−S−C(31) 103.17(13), C(10)−N(1)−C(11) 121.9(2), C(10)−N(1)−Pd 115.93(16), C(11)−N(1)−Pd 122.12(15), C(40)−N(4)−C(41) 124.3(2), C(50)−N(5)−C(51) 125.4(2), C(60)−N(6)−C(61) 176.4(3).

latter. The Pd−C(=NXy) bond distance trans to PPh_3 (2.077(2) Å) is longer than that trans to XyNC (2.0373(18) Å), which must be caused by the greater trans influence of PPh_3.

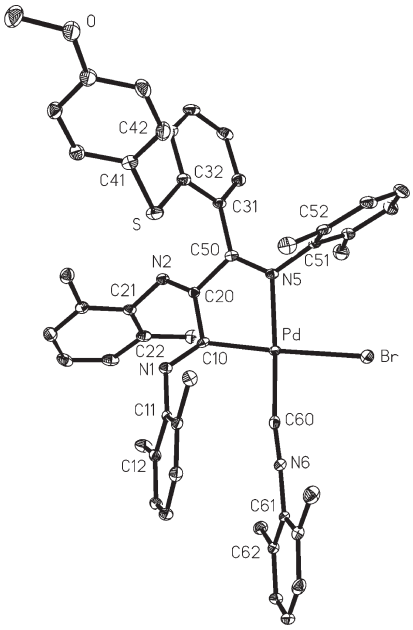


Figure 7. Thermal ellipsoid representation (30% probability) of complex **17**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(60) 1.951(3), Pd−C(10) 2.002(2), Pd−N(5) 2.0903(19), Pd−Br 2.5295(4), S−C(41) 1.775(3), S−C(32) 1.782(3), N(1)−C(10) 1.260(3), N(1)−C(11) 1.422(3), N(2)−C(20) 1.270(3), N(2)−C(21) 1.423(3), N(5)−C(50) 1.277(3), N(5)−C(51) 1.457(3), N(6)−C(60) 1.153(3), N(6)−C(61) 1.406(3), C(60)−Pd−C(10) 96.47(10), C(60)−Pd−N(5) 177.19(10), C(10)−Pd−N(5) 81.08(9), C(60)−Pd−Br 86.17(7), C(10)−Pd−Br 175.77(7), N(5)−Pd−Br 96.20(6), C(41)−S−C(32) 102.53(13), C(10)−N(1)−C(11) 123.6(2), C(20)−N(2)−C(21) 123.8(2), C(50)−N(5)−C(51) 122.6(2), C(50)−N(5)−Pd 116.50(16), C(51)−N(5)−Pd 120.88(15), C(60)−N(6)−C(61) 172.2(3).

Spectroscopic Properties of Complexes. The NMR spectra of all prepared complexes were consistent with the proposed structures. The low solubility of complexes **1** and **2** prevented the recording of their ^{13}C NMR spectra.

^{1}H, ^{31}P, and ^{13}C NMR spectra of the mixture obtained by reacting **1** with $[PdCl_2(NCPh)_2]$ (Scheme 2) showed the presence of two isomers in approximately 3:2 molar ratio at room temperature. The most abundant could be isolated and characterized by X-ray diffraction (complex **10**; $\delta(^{31}P)$, 31.08 (br s) ppm, at room temperature), but the other, **10′**, which is fluxional ($\delta(^{31}P)$, 30.88 (br s) ppm, at room temperature), could not be separated from the mixture. Both products are in equilibrium in $CDCl_3$ or toluene-d_6 (^{1}H and ^{31}P NMR). Thus, at −30 °C only traces of **10′** could be detected, while at 55 °C the **10**:**10′** molar ratio decreased to 1:3; only traces of **10** could be detected at 65 °C. Probably, this equilibrium is established between the dimer **10** and a monomer (**10′**, Scheme 8), which agrees with the temperature dependence of the equilibrium. The fluxionality of **10′**, which probably involves an equilibrium with its isomer **10″**, could not be studied because the signals are broad in the range of its existence in solution ($T > -35$ °C), which suggests a fast **10′** ⇆ **10″** equilibrium. The small difference between the $\delta(^{31}P)$ in **10** and that of the **10′** + **10″** mixture suggests that the **10′** ⇆ **10″** equilibrium is considerably displaced to the left, because in **10** and **10′** P is trans to S and the $\delta(^{31}P)$ in **10″** is expected to be quite different from that in **10′** given the very different trans

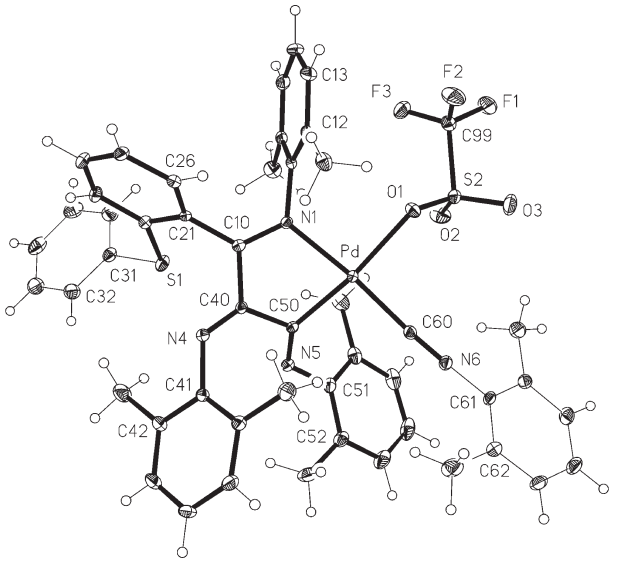


Figure 8. Thermal ellipsoid representation (30% probability) of complex **21**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(60) 1.9703(18), Pd−C(50) 1.9748(16), Pd−N(1) 2.0781(13), Pd−O(1) 2.1975(12), S(1)−C(31) 1.7731(18), S(1)−C(22) 1.7758(17), N(1)−C(10) 1.295(2), N(1)−C(11) 1.450(2), N(4)−C(40) 1.273(2), N(4)−C(41) 1.428(2), N-(5)−C(50) 1.261(2), N(5)−C(51) 1.419(2), N(6)−C(60) 1.149(2), N(6)−C(61) 1.409(2), C(60)−Pd−C(50) 94.45(7), C(50)−Pd−N(1) 80.82(6), C(60)−Pd−O(1) 92.70(6), N(1)−Pd−O(1) 92.06(5), C(31)−S(1)−C(22) 103.74(8), C(10)−N(1)−C(11) 120.29(14), C-(10)−N(1)−Pd 115.19(10), C(11)−N(1)−Pd 124.46(11), C(40)−N(4)−C(41) 124.95(15), C(50)−N(5)−C(51) 124.36(15), C(60)−N(6)−C(61) 175.62(17).

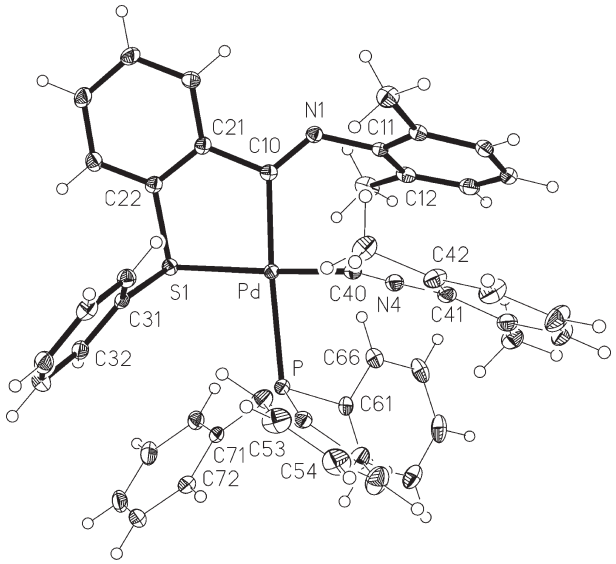


Figure 9. Thermal ellipsoid representation (50% probability) of complex **22**. Selected bond lengths (Å) and angles (deg): Pd−C(40) 1.974(2), Pd−C(10) 2.077(2), Pd−S(1) 2.3220(5), Pd−P 2.4215(6), S(1)−C(22) 1.787(2), S(1)−C(31) 1.792(2), N(1)−C(10) 1.258(3), N(1)−C(11) 1.415(3), N(4)−C(40) 1.149(3), N(4)−C(41) 1.404(3), C(40)−Pd−C(10) 93.03(8), C(10)−Pd−S(1) 84.91(6), C(40)−Pd−P 85.67(6), S(1)−Pd−P 97.36(2), C(22)−S(1)−C(31) 100.51(10), C(22)−S(1)−Pd 99.63(7), C(31)−S(1)−Pd 100.89(7), C(10)−N(1)−C(11) 126.68(18), C(40)−N(4)−C(41) 177.3(2).

influence of an aryl with respect to a thioether ligand. In addition, the stronger C/P transphobia[34] than that of C/Br or S/P suggests that **10″** should be an unstable complex.

In complexes **16**−**26** (Schemes 4−6) both Me groups of the coordinated XyNC are equivalent, as are those in the iminoacyl groups of complexes resulting from the monoinsertion of XyNC (**22**−**26**), which indicates free rotation around the Xy−N bond. However, in **15** (Scheme 4) such rotation is slow because the Me singlet is broad at room temperature and at −50 °C two resonances are observed, probably because of the appreciable steric requirements of PPh_3; in fact, its related complex **22** (Scheme 4) shows only one iminoacyl Me singlet because its cis ligand (XyCN) is smaller than PPh_3. The restricted rotation of the Xy group around the C−N bond also indicates that, at low temperatures, the S atom is a chiral center because of the slowing of inversion at this atom. In complex **27** (Scheme 5), ^{1}H and ^{13}C NMR spectra show two Me resonances at room temperature, one corresponding to four and the other to two Me groups (at 2.14, 2.19 ppm in ^{1}H NMR, respectively). When the temperature is lowered (to −50 °C), the first resonance is split into three 1:1:2 singlets. Our interpretation is that the inserted XyNC and its cis-coordinated XyNC interchange at room temperature and, when the temperature is lowered, the process is slowed to make both XyNC inequivalent on the NMR time scale; the 1:1 singlets are assigned to the two methyls of the iminoacyl Xy group made inequivalent at low temperature.

In some complexes derived from the triinsertion of XyNC (**16**−**18**, **21**) the rotation of the Xy iminoacyl groups and that around the C−$C_6H_4SC_6H_4R$ bond are prevented or very slow at room temperature, causing the observation of three pairs of inequivalent Me groups of the inserted isocyanides. In the case of complex **19** or **20** the free rotation around the C_6H_4−SC_6H_4R bond provides it with a symmetry plane, thus making equivalent the pair of Me of each Xy iminoacyl group.

EXPERIMENTAL SECTION

$Pd(dba)_2$,[35] $[PdCl_2(PhCN)_2]$,[36] and thioethers[1] were prepared as reported in the literature. Unless otherwise stated, the reactions were carried out and NMR spectra recorded at room temperature. Xy(i) and Xy(c) refer to Xy groups of inserted and coordinated XyNC, respectively.

Synthesis of *trans*-[PdBr{C_6H_4(SC_6H_4R-4)-*a*}(PPh_3)$_2$] (*a* = 2, R = H (1), OMe (2), NO_2 (3); *a* = 4, R = NO_2 (4)). A mixture of $[Pd(dba)_2]$ (100−200 mg), PPh_3, and the corresponding thioether (1:2:*x* molar ratio; *x* = 1.2 (**1**), 1.1 (**2**), 1.3 (**3**), 1 (**4**)) in toluene (50 mL) under N_2 was refluxed for 2 h (10 min for **4**). The solvent of the resulting mixture was evaporated, the residue extracted with CH_2Cl_2 (4 × 5 mL), and the suspension filtered through Celite. The red filtrate was concentrated to dryness, and the residue washed with Et_2O (20 mL) and filtered to afford yellow (**1**, **3**, **4**) or orange (**2**) solids.

1: 76%. Mp: 178 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (m, 12 H, *ortho*-PPh_3), 7.35−7.18 (several m, 21 H), 6.96 (m, 1 H), 6.70 (dd, 2 H, Ph, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.7 Hz), 6.31 (m, 2 H), 5.58 (m, 1 H, C_6H_4). ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 152.40 (t, CPd, C_6H_4, $^3J_{PC}$ = 3.62 Hz), 144.99 (t, CS, $^2J_{PC}$ = 3.77 Hz), 135.00 ("t", *ortho*-PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 12.6 Hz), 134.86 (CH, Ph), 133.17 (t, CS, Ph, $^5J_{PC}$ = 1.1 Hz), 131.45 ("t", *ipso*-PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 45.7 Hz), 129.75 (*para*-PPh_3), 128.86 (CH), 128.06 (CH), 127.72 ("t", *meta*-PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10.2 Hz), 124.77 (CH, C_6H_4), 123.48 (CH), 123.19 (CH). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.58 (s, PPh_3). Anal. Calcd for $C_{48}H_{39}BrP_2SPd$: C, 64.33; H, 4.39; S, 3.58. Found: C, 63.98; H, 4.53; S, 3.41. Single crystals were obtained by slow diffusion of Et_2O into a solution of **1** in CH_2Cl_2.

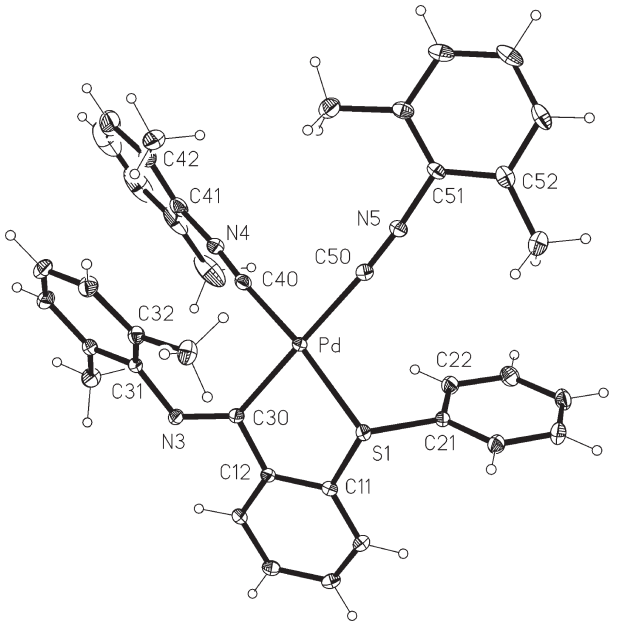
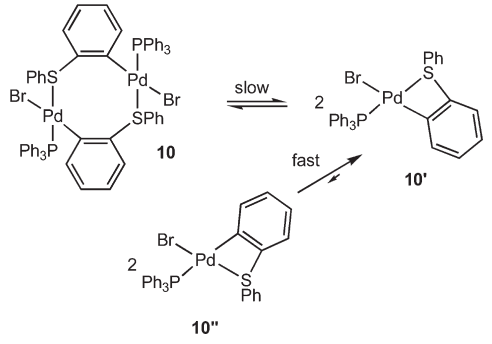


Figure 10. Thermal ellipsoid representation (30% probability) of complex **27**. Selected bond lengths (Å) and angles (deg): Pd−C(40) 1.986(2), Pd−C(30) 2.0373(18), Pd−C(50) 2.0636(19), Pd−S(1) 2.3358(5), S(1)−C(11) 1.7833(19), S(1)−C(21) 1.7864(19), N-(3)−C(30) 1.266(2), N(3)−C(31) 1.415(2), N(4)−C(40) 1.144(3), N(4)−C(41) 1.411(3), N(5)−C(50) 1.146(2), N(5)−C(51) 1.408(2), C(40)−Pd−C(30) 90.40(7), C(40)−Pd−C(50) 91.85(8), C(30)−Pd−C(50) 176.01(8), C(40)−Pd−S(1) 169.97(5), C(30)−Pd−S(1) 81.90(5), C(50)−Pd−S(1) 96.22(6), C(11)−S(1)−C(21) 103.52(9), C(11)−S(1)−Pd 97.04(6), C(21)−S(1)−Pd 107.59(6), C(30)−N(3)−C(31) 126.21(16), C(40)−N(4)−C(41) 175.3(2), C(50)−N(5)−C(51) 174.3(2).

Scheme 8



2: 77%. Mp: 185 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 12 H, *ortho*-PPh_3), 7.31 (m, 6 H, *para*-PPh_3), 7.25 (m, 12 H, *meta*-PPh_3), 6.94 (d, 1 H, H3 or H6, C_6H_4Pd, $^3J_{HH}$ = 6 Hz), 6.70 (d, 2 H, C_6H_4OMe, $^3J_{HH}$ = 9 Hz), 6.62 (d, 2 H, C_6H_4OMe, $^3J_{HH}$ = 9 Hz), 6.31 (m, 2 H, H4 + H5, C_6H_4Pd), 5.44 (d, 1 H, H3 or H6, C_6H_4Pd, $^3J_{HH}$ = 6 Hz), 3.77 (s, 3 H, OMe). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 159.72 (COMe), 151.41 (t, CPd, J_{PC} = 3.67 Hz), 145.94 (t, CS, C_6H_4Pd, J_{PC} = 3.67 Hz), 136.85 (CH, C2, C_6H_4OMe), 134.90 (t, *ortho*-PPh_3, $[^2J_{PC} + {}^4J_{PC}]$ = 12.8 Hz), 131.28 (t, *ipso*-PPh_3, $[^1J_{PC} + {}^3J_{PC}]$ = 45.3 Hz), 129.61 (*para*-PPh_3), 127.59 (t, *meta*-PPh_3, $[^3J_{PC} + {}^5J_{PC}]$ = 10.4 Hz), 124.20 (CH, C_6H_4Pd), 123.51 (C), 123.50 (CH, C_6H_4Pd), 122.74 (CH, C_6H_4Pd), 114.31 (CH, C3, C_6H_4OMe), 55.19 (OMe). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.16 (s, 2 PPh_3). Anal. Calcd for $C_{49}H_{41}BrOPdP_2S$: C, 63.54; H, 4.46; S, 3.46. Found: C, 63.37; H, 4.43; S, 3.05. Single crystals were obtained by slow diffusion of Et_2O into a solution of **2** in CH_2Cl_2.

3: Yield: 81%. Mp: 183 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.91 (d, 2 H, H3, $C_6H_4NO_2$, $^3J_{HH}$ = 10 Hz), 7.55−7.21 (several m, 30 H, PPh_3), 6.99 (d, 1 H, H3 or H6, C_6H_4Pd, $^3J_{HH}$ = 6 Hz), 6.68 (d, 2 H, H2, $C_6H_4NO_2$, $^3J_{HH}$ = 10 Hz), 6.46 (m, 2 H, H4 + H5, C_6H_4Pd), 6.09 (d, 1 H, H3 or H6, C_6H_4Pd, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} APT NMR (75.48 MHz, $CDCl_3$): δ 156.97 (t, CS or CPd, C_6H_4Pd, $^2J_{PC}$ = 3.67 Hz or $^3J_{PC}$ = 3.67 Hz), 145.87 (C), 145.20 (C), 139.73 (t, CS or CPd, C_6H_4 Pd, $^2J_{PC}$ = 3.67 Hz or $^3J_{PC}$ = 3.67 Hz), 137.30 (t, C6, C_6H_4Pd, $^3J_{PC}$ = 3.67 Hz), 134.90 ("t", *ortho*-PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 15 Hz), 131.26 ("t", *ipso*-PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 45.3 Hz), 130.50 (CH, $C_6H_4NO_2$), 129.91 (*para*-PPh_3), 128.2 (CH, C_6H_4Pd), 127.91 ("t", *meta*-PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10.4 Hz), 125.46 (CH, C_6H_4Pd), 123.89 (CH, C_6H_4Pd), 123.72 (CH, $C_6H_4NO_2$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.13 (s, 2 PPh_3). Anal. Calcd for $C_{48}H_{38}BrNO_2PdP_2S$: C, 61.26; H, 4.07; N, 1.49; S, 3.41. Found: C, 61.05; H, 4.21; N, 1.56; S, 3.04. Single crystals were obtained by slow diffusion of Et_2O into a solution of **3** in CH_2Cl_2.

4: Yield: 95 mg, 64%. Mp: 164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, 2 H, H3, $C_6H_4NO_2$, $^3J_{HH}$ = 9 Hz), 7.59 (m, 12 H, *ortho*-PPh_3), 7.43 (m, 18 H, *meta*- + *para*-PPh_3), 6.94 (m, 4 H, H2, C_6H_4Pd + H2, $C_6H_4NO_2$), 6.44 (d, 2 H, H3, C_6H_4Pd, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 161.5 (t, CPd, $^2J_{PC}$ = 5 Hz), 149.9 (CS, $C_6H_4NO_2$), 144.8 (CS, C_6H_4Pd), 137.8 (t, CH, C2, C_6H_4Pd, $^3J_{PC}$ = 5 Hz), 134.9 ("t", *ortho*-PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 10 Hz), 133.5 (CH, C3, C_6H_4Pd), 131.21 ("t", *ipso*-PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 50 Hz), 130.0 (*para*-PPh_3), 128.1 ("t", *meta*-PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10 Hz), 125.6 (CH, C2, $C_6H_4NO_2$), 123.7 (CH, C3, $C_6H_4NO_2$), 121.9 (CNO_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.00 (s, PPh_3). Anal. Calcd for $C_{48}H_{38}BrNO_2PdP_2S$: C, 61.26; H, 4.07; N, 1.49; S, 3.41. Found: C, 60.93; H, 4.38; N, 1.76; S, 3.57

Synthesis of *cis*-[PdI{$C_6H_4(SC_6H_4R$-4)-*a*}(bpy)] (R = H, *a* = 2 (5), 4 (6), R = $SC_6H_4NO_2$-4, *a* = 4 (7)), [{PdI(bpy)}$_2$-μ-{C_6H_4-(SC_6H_4-4)$_2$-4}] (11), and [{PdI(bpy)}$_2$-μ-{$C_6H(SC_6H_4$-4)$_2$-1,3-Me_3-2,4,6}] (12). A mixture of [Pd(dba)$_2$] (40−65 mg), bpy, and the corresponding thioether (1:2:*y* molar ratio; *y* =2.2 (**5**), 2.3 (**6**), 2 (7), 1 (**11**, **12**)) in toluene under N_2 was stirred for 18 h. The solvent of the resulting mixture was evaporated, the residue extracted with CH_2Cl_2 (3 × 5 mL), and the suspension filtered through Celite. The filtrate was concentrated to dryness, and the residue washed with Et_2O (5 mL) and filtered to afford yellow (**5**−7, **12**) or orange (**11**) solids.

5: Yield: 96%. Mp: 196 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.65 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 8.11−7.97 (m, 4H, H3 + H3′ + H4 + H4′, bpy), 7.70 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 7.54 (td, 1 H, H5 or H5′, bpy, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.45−7.35 (m, 2 H, C_6H_4 + 1H, H5 or H5′, bpy), 7.27 (m, 4 H, Ph), 7.17 (m, 2 H, C_6H_4 + 1 H, Ph). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 156.1 (C2, bpy), 154.0 (C2′, bpy), 153.4 (CH, C6 or C6′, bpy), 150.5 (CH, C6 or C6′, bpy), 147.6 (C), 139.2 (CH, C4 or C4′, bpy), 139.1 (CH, C4 or C4′, bpy), 138.5 (C), 137.9 (CH, C_6H_4), 132.1 (CH, C_6H_4), 129.3 (CH, Ph), 129.3 (CH, Ph), 128.3 (C), 127.2 (CH, C5 or C5′, bpy), 126.9 (CH, C5 or C5′, bpy), 126.3 (CH, C4, Ph), 122.5 (CH, C3 or C3′, bpy), 122.1 (CH, C3 or C3′, bpy). Anal. Calcd for $C_{22}H_{17}IN_2PdS$: C, 45.97; H, 2.98; S, 5.58; N, 4.87. Found: C, 45.64; H, 2.86; S, 5.40; N, 4.88.

6: Yield: 87%. Mp: 196 °C (dec). ^{1}H NMR (300 MHz, acetone-d_6): δ 9.57 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 6 Hz), 8.52 (d, 1 H, H3 or H3′, bpy, $^3J_{HH}$ = 4 Hz), 8.50 (d, 1 H, H3 or H3′, bpy, $^3J_{HH}$ = 4 Hz), 8.24 (m, 2 H, H4 + H4′, bpy), 7.77 (td, 1 H, H5 or H5′, bpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.60 (m, 1 H, H5 or H5′ + 1 H, H6 or H6′, bpy), 7.38 (m, 1 H, C_6H_4 or Ph), 7.34 (d, 2 H, Ph), 7.21−7.12 (several m, 2 H, Ph + 1 H, C_6H_4 or Ph), 6.89 (m, 3 H, C_6H_4 or Ph). ^{13}C{^{1}H} APT NMR (50.32 MHz, acetone-d_6): δ 156.8 (C), 155.1 (C), 153.2 (CH, C6 or C6′, bpy), 150.2 (CH, C6 or C6′, bpy), 149.0 (C), 143.5 (C), 140.4 (CH, C4 or

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C4′, bpy), 140.4 (CH, C4 or C4′, bpy), 139.2 (CH), 138.1 (C), 132.3 (CH, Ph), 130.5 (CH), 129.7 (CH, Ph), 127.9 (CH, C5 or C5′, bpy), 127.7 (CH, C5 or C5′, bpy), 127.3 (CH), 125.5 (CH), 124.8 (CH), 123.9 (CH, C3 or C3′, bpy), 123.6 (CH, C3 or C3′, bpy). Anal. Calcd for $C_{22}H_{17}IN_2PdS$: C, 45.97; H, 2.98; S, 5.58; N, 4.87. Found: C, 46.15; H, 2.99; S, 5.52; N, 5.08.

7: Yield: 69%. Mp: 207 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.66 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 8.08−8.00 (m, 4 H, H3 + H3′ + H4 + H4′, bpy +2 H, C_6H_4), 7.69 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 7.54 (m, 1 H, H5 or H5′, bpy +2 H, C_6H_4), 7.39 (m, 1 H, H5 or H5′, bpy +2 H, C_6H_4), 7.24 (d, 4 H, C_6H_4), 7.16 (d, 2 H, C_6H_4). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 155.9 (C), 153.7 (C), 153.2 (CH, C, 6 or C, 6′, bpy), 150.1 (CH, C6 or C6′, bpy), 149.5 (C), 149.0 (C), 145.3 (C), 142.6 (C), 138.9 (CH, C4 or C4′, bpy), 138.8 (CH, C4 or C4′, bpy), 138.1 (CH C_6H_4), 135.3 (CH C_6H_4), 133.1 (CH C_6H_4), 128.4 (CH C_6H_4), 127.0 (CH, C5 or C5′, bpy), 126.6 (CH, C5 or C5′, bpy), 126.4 (CH C_6H_4), 125.9 (C), 125.3 (C), 124.1 (CH C_6H_4), 122.2 (CH, C3 or C3′, bpy), 121.7 (CH, C3 or C3′, bpy). Anal. Calcd for $C_{28}H_{20}I\,N_3O_2PdS_2$: C, 46.19; H, 2.75; S, 8.80; N, 5.77. Found: C, 46.53; H, 2.85; S, 8.70; N, 5.65.

11: Yield: 54%. Mp: 190 °C (dec). ^{1}H NMR (200 MHz, dmso-d_6): δ 9.37 (m, 2 H, H6 or H6′, bpy), 8.63 (d, 4 H, H3 + H3′, bpy, $^3J_{HH}$ = 8 Hz), 8.27 (t, 4 H, H4 + H4′, bpy, $^3J_{HH}$ = 8 Hz), 7.76 (m, 2 H, bpy), 7.68 (m, 2 H, bpy), 7.48 (m, 2 H, bpy), 7.34 (d, 4 H, H2 or H3, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 7.23 (s, 4 H, C_6H_4), 7.08 (d, 4 H, H2 or H3, C_6H_4Pd, $^3J_{HH}$ = 8 Hz). **11** is not sufficiently soluble in organic solvents to allow the recording of its ^{13}C NMR. Anal. Calcd for $C_{38}H_{28}I_2N_4PdS_2$: C, 42.60; H, 2.63; S, 5.99; N, 5.23. Found: C, 42.32; H, 2.64; S, 5.80; N, 4.84.

12: Yield: 252 mg, 68%. Mp: 198 °C (dec). ^{1}H NMR (400 MHz, d_6-dmso): δ 9.32 (s, 2 H, H6 or H6′, bpy), 8.58 (d, 4 H, H13 + H13′, bpy, $^3J_{HH}$ = 8 Hz), 8.23 (t, 4 H, H14 + H14′, bpy, $^3J_{HH}$ = 8 Hz), 7.77 (s, 2 H, bpy), 7.59 (s, 2 H, bpy), 7.45 (s, 2 H, bpy), 7.32 (s, 1 H, C$_6$H), 7.14 (d, 4 H, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 6.66 (d, 4 H, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 2.68 (s, Me), 2.42 (s, 2 Me). **12** is not sufficiently soluble in organic solvents to allow the recording of its ^{13}C NMR. Anal. Calcd for $C_{41}H_{34}I_2N_4Pd_2S_2$: C, 44.22; H, 3.08; S, 5.76; N, 5.03. Found: C, 44.40; H, 2.83; S, 5.51; N, 4.68.

Synthesis of [Pd{$C_6H_4SC_6H_4$-4-S($C_6H_4NO_2$-4)-4}I(PPh_3)$_2$] (9), [{*trans*-PdI(PEt_3)$_2$}$_2$-μ-{C_6H_4(SC_6H_4-4)$_2$-4}] (13), and [{*trans*-PdI(PPh_3)$_2$}$_2$-μ-{C_6H(SC_6H_4-4)$_2$-1,3-Me_3-2,4,6}] (14). To a suspension of the homologous bpy complex in CH_2Cl_2 (10 mL) was added the corresponding phosphine (1:*x* molar ratio; *x* = 2 (**9**), 4 (**13**), 3.8 (**14**)), and the resulting solution was stirred for 10 min. The solvent was evaporated and the residue washed with *n*-pentane (5 mL) to afford the complex as a yellow solid.

9: Yield: 67%. Mp: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, 2 H, H3, $C_6H_4NO_2$, $^3J_{HH}$ = 9 Hz), 7.56 (m, 12 H, PPh_3), 7.36 (m, 6 H, PPh_3 + 2 H, C_6H_4), 7.28 (d, 12 H, PPh_3, $^3J_{HH}$ = 8 Hz), 7.13 (d, 2 H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.03 (d, 2 H, C_6H_4, $^3J_{HH}$ = 9 Hz), 6.78 (d, 2 H, C_6H_4, $^3J_{HH}$ = 7 Hz), 6.43 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 162.6 (t, CPd, $^2J_{PC}$ = 3.5 Hz), 148.9 (C, C_6H_4), 145.5 (C, C_6H_4), 142.4 (C, C_6H_4), 137.3 (t, C2, C_6H_4Pd, $^3J_{CP}$ = 10 Hz), 135.1 ("t", *ortho*-PPh_3, $|^2J_{CP} + {}^4J_{CP}|$ = 15 Hz), 133.3 (CH, C_6H_4), 132.2 ("t", *ipso*-PPh_3, $|^1J_{CP} + {}^3J_{CP}|$ = 45.3 Hz), 130.1 (*para*-PPh_3), 128.5 (CH, C_6H_4), 128.0 ("t", *meta*-PPh_3, $|^3J_{CP} + {}^5J_{CP}|$ = 10 Hz), 126.4 (CH, C_6H_4), 126.2 (C, C_6H_4), 124.2 (CH, C_6H_4), 124.0 (C, C_6H_4). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.03 (s, PPh_3). Anal. Calcd for $C_{54}H_{42}INO_2PdP_2S_2$: C, 59.16; H, 3.83; S, 5.84; N, 1.28. Found: C, 59.01; H, 3.85; S, 5.86; N, 1.36.

13: Yield: 56%. Mp: 178 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.23 (d, 4 H, H2, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 7.11 (d, 4 H, H3, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 7.02 (s, 4 H, C_6H_4), 1.68 (m, 24 H, CH_2, Et_3P), 1.06 (t, 36 H, Me, Et_3P, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 159.3 (t, CPd, $^2J_{CP}$ = 5.0 Hz), 137.6 (t, CH, C2, C_6H_4Pd, $^3J_{CP}$ = 5.0 Hz), 136.2 (C), 132.8 (CH, C3, C_6H_4Pd), 128.8 (CH, C_6H_4), 126.7 (C), 16.2 ("t", CH_2, PEt_3, $|^1J_{CP} + {}^3J_{CP}|$ = 13.6 Hz), 8.31 (s, CH_3, PEt_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 11.14 (s, PEt_3). Anal. Calcd for $C_{42}H_{72}I_2Pd_2P_4S_2$: C, 40.96; H, 5.89; S, 5.21. Found: C, 40.73; H, 5.90; S, 5.09.

14: Yield: 95%. Mp: 148 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69 (m, 24 H, *ortho*-PPh_3), 7.19 (m, 36 H, *meta*- + *para*-PPh_3), 7.05 (s, 1 H, C_6H), 6.44 (d, 4 H, H2, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 5.89 (d, 4 H, H3, C_6H_4Pd, $^3J_{HH}$ = 8 Hz), 2.57 (s, 3 H, Me), 2.34 (s, 6 H, 2 Me). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 154.0 (t, CPd, $^2J_{CP}$ = 5.0 Hz), 149.2 (CS), 144.9 (2 *C*Me), 136.2 (t, C2, C_6H_4Pd, $^3J_{CP}$ = 5.0 Hz), 134.9 ("t", *ortho*-PPh_3, $|^2J_{CP} + {}^4J_{CP}|$ = 15 Hz), 132.2 ("t", *ipso*-PPh_3, $|^1J_{CP} + {}^3J_{CP}|$ = 50.3 Hz), 129.9 (s, *para*-PPh_3), 127.9 ("t", *meta*-PPh_3, $|^3J_{CP} + {}^5J_{CP}|$ = 10 Hz), 125.8 (CH, C3, C_6H_4Pd), 22.5 (2 Me), 21.4 (Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.41 (s, PPh_3). Anal. Calcd for $C_{93}H_{78}I_2Pd_2P_4S_2$: C, 60.37; H, 4.25; S, 3.47. Found: C, 60.09; H, 4.20; S, 3.20. Single crystals were obtained by slow diffusion of *n*-hexane into a solution **14** in CH_2Cl_2.

($Ph_3PC_6H_4SPh$-2)TfO (8). A mixture of **1** (90 mg, 0.1 mmol) and TlTfO (40 mg, 0.1 mmol) in CH_2Cl_2 was refluxed for 2 h and filtered. The filtrate was concentrated to dryness and the residue washed five times with Et_2O. The resulting brown solid was a mixture that could not be separated. The main ^{31}P NMR resonance appears at 22.03 ppm. Slow diffusion of Et_2O into a CH_2Cl_2 solution of this mixture afforded a few single crystals of **8**.

Synthesis of [PdBr(μ-C_6H_4SPh-2)(PPh_3)]$_2$ (10). To a solution of **1** (80 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was added solid [$PdCl_2$(PhCN)$_2$] (17 mg, 0.04 mmol). The resulting suspension was stirred for 30 min, and then 3 equiv of NaBr was added and the mixture stirred for 10 min. The suspension was filtered through Celite, and the solid washed with CH_2Cl_2 (3 × 5 mL); the resulting solution was concentrated to dryness, and Et_2O (15 mL) added to give a yellow solid containing a mixture of isomers **10** + **10′** (Scheme 8). Yield: 38 mg, 67%. Mp: 145 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): **10**, δ 7.70 (m, 12 H, *ortho*-PPh_3), 7.40−7.17 (several m, 30 H, *meta*- + *para*-PPh_3 + 10 H, Ph + 2 H, H3 or H6, C_6H_4), 6.41 (t, 2 H, H4 or H5, C_6H_4, $^3J_{HH}$ = 8 Hz), 6.17 (t, 2 H, H4 or H5, C_6H_4, $^3J_{HH}$ = 8 Hz), 5.35 (d, 2 H, H3 or H6, C_6H_4, $^3J_{HH}$ = 8 Hz); **10′**, δ 7.56 (m, 12 H, *ortho*-PPh_3), 7.40−7.17 (several m, 26 H, H_m + *para*-PPh_3 + 8 H, Ph), 6.98 (m, 4 H, C_6H_4), 6.56 (m, 4 H, C_6H_4), 6.25 (m, 2 H, Ph). ^{13}C{^{1}H} APT NMR (300 MHz, $CDCl_3$): **10**, δ 158.7 (C), 140.1 ("t", C−Pd, $|^2J_{CP} + {}^4J_{CP}|$ = 7 Hz), 135.4 (d, *ortho*-PPh_3, $^2J_{CP}$ = 15 Hz), 131.0 (d, *ipso*-PPh_3, $^1J_{CP}$ = 53 Hz), 130.3 (d, *para*-PPh_3, $^4J_{CP}$ = 7 Hz), 129.0 (CH, Ph), 128.2 (d, *meta*-PPh_3, $^3J_{CP}$ = 14 Hz), 127.1 (CH, C3 or C6, C_6H_4), 124.8 (CH, C4 or C5, C_6H_4), 123.9 (CH, C4 or C5, C_6H_4); **10′**, δ 149.7 (C), 135.0 (d, *ortho*-PPh_3, $^2J_{CP}$ = 15 Hz), 133.1 (CH), 130.3 (s, *para*-PPh_3), 128.0 (d, *meta*-PPh_3, $^3J_{CP}$ = 14 Hz), 127.0 (CH), 124.1 (CH, C_6H_4). ^{31}P NMR (121 MHz, $CDCl_3$): **10**: δ 31.08 (s, PPh_3). **10′**: δ 30.88 (br s, PPh_3). Anal. Calcd for ($C_{30}H_{24}BrPPdS$)$_2$: C, 56.84; H, 3.82; S, 5.06. Found: C, 56.60; H, 3.90; S, 4.96. Single crystals of **10** were obtained by slow diffusion of Et_2O into a solution of the **10** + **10′** mixture in CH_2Cl_2.

Synthesis of *SP-4-4*-[Pd{κ^2-*C,S*-C(=NXy)C_6H_4SPh-2}Br(PPh_3)] (15), *SP-4-4*-[Pd{*C,N*-C(=NXy)C(=NXy)C(=NXy)C_6H_4-(SC_6H_4R-4)-*n*}X(CNXy)] (X = Br, *n* = 2, R = H (16), OMe (17), NO_2 (18); X = Br, *n* = 4, R = NO_2 (19); X = I, *n* = 4, R = $SC_6H_4NO_2$-4 (20)). A mixture of the corresponding *trans*-[Pd(arylthioether)X(PPh_3)$_2$] (**1**−**4**; 22−150 mg) and XyNC (1:*x* molar ratio; *x* = 1.4 (**15**), 4 (**16**−**20**)) in CH_2Cl_2 (15 mL) was stirred (24 h (**15**), 5 h (**16**), 12 h (**17**, **18**), 4 h (**19**), 1.5 h (**20**)). The solution was concentrated (1 mL), Et_2O (15 mL; **15**) or *n*-pentane (15 mL; **16**−**19**) was added, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL; **15**) or *n*-pentane (3 × 15 mL; **16**) to give a yellow (**15**), reddish purple (**16**), purple (**17**, **20**), or red (**18**, **19**) solid.

15: Yield: 82%. Mp: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 2 H, C_6H_4), 7.55 (m, 2 H, C_6H_4), 7.29 (several m, 20 H, PPh_3 + Ph),

6.91 (t, 1 H, *para*-Xy, $^3J_{HH}$ = 7 Hz), 6.83 (d, 2 H, *meta*-Xy, $^3J_{HH}$ = 7 Hz), 1.60 (s, 6 H, 2 Me). $^{13}C\{^1H\}$ APT NMR (100.64 MHz, $CDCl_3$): δ 180.77 (C═N), 155.94 (C), 145.58 (C), 145.52 (C), 134.42 (C, *ortho*-Xy), 134.25 (d, CH, *ortho*-PPh_3, $^2J_{PC}$ = 12.4 Hz), 132.64 (CH, C_6H_4), 132.12 (d, C, *ipso*-PPh_3, $^1J_{PC}$ = 45.4 Hz), 131.44 (CH, C_6H_4), 130.81 (CH, C_6H_4), 130.25 (CH, Ph), 130.22 (CH, Ph), 129.52 (CH, *para*-PPh_3), 128.20 (d, CH, *meta*-PPh_3, $^3J_{PC}$ = 10.8 Hz), 128.13 (CH, *meta*-Xy), 127.36 (CH, Ph), 127.01 (CH, C_6H_4), 124.25 (CH, *para*-Xy), 18.85 (bs, 2 Me, XyNC). ^{31}P NMR (121 MHz, $CDCl_3$): δ 28.74 (s, PPh_3). Anal. Calcd for $C_{39}H_{33}BrNPdPS$: C, 61.23; H, 4.35; N, 1.83; S, 4.19. Found: C, 60.85; H, 4.50; N, 1.86; S, 3.86.

16: Yield: 90%. Mp: 230 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (s, 4 H), 7.23−6.81 (several m, 15 H), 6.34 (m, 2 H), 2.62 (s, 3 H, Me), 2.42 (s, 3 H, Me), 2.30 (s, 6 H, 2 Me), 2.19 (s, 3 H, Me), 2.13 (s, 6 H, 2 Me), 1.13 (s, 3 H, Me). ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 174.28 (C═N), 172.87 (C═N), 168.79 (C═N), 150.83 (C), 147.83 (C), 143.58 (C), 135.12 (C), 134.62 (C), 133.89 (C), 132.16 (C), 130.99 (CH), 130.86 (CH), 130.65 (C), 129.45 (CH), 129.10 (CH), 128.87 (C), 128.65 (CH), 128.07 (CH), 127.95 (CH), 127.85 (CH), 127.71 (CH), 127.51 (CH), 127.41 (CH), 127.11 (C), 127.00 (CH), 126.80 (CH), 126.34 (CH), 125.38 (C), 123.76 (CH), 123.73 (CH), 121.86 (C), 20.22 (Me, XyNC), 19.94 (Me, XyNC), 19.26 (Me, XyNC), 19.03 (Me, XyNC), 18.90 (Me, XyNC), 18.52 (2 Me, XyNC), 17.41 (Me, XyNC). Anal. Calcd for $C_{48}H_{45}BrN_4PdS$: C, 64.32; H, 5.06; N, 6.25; S, 3.58. Found: C, 64.02; H, 4.96; N, 5.75; S, 3.29. Single crystals were obtained by slow diffusion of *n*-pentane into a solution of **16** in $ClCH_2CH_2Cl$.

17: Yield: 80%. Mp: 213 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.37 (d, 2 H, C_6H_4OMe, $^3J_{HH}$ = 8 Hz), 7.09−6.83 (several m, 16 H, C_6H_4, C_6H_4OMe + XyNC), 6.36 (m, 2 H, C_6H_4 and/or XyNC), 3.83 (s, 3 H, OMe), 2.63 (s, 3 H, Me), 2.47 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.33 (s, 3 H, Me), 2.28 (s, 3 H, Me), 2.13 (s, 6 H, 2 Me), 1.11 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 174.33 (C═N), 172.8 (C═N), 168.6 (C═N), 160.3 (COMe), 150.8 (C), 147.8 (C), 143.5 (C), 138.0 (C), 135.2 (CH, C_6H_4OMe), 134.6 (C), 130.8 (C), 130.8 (CH), 129.9 (C), 129.0 (CH), 128.8 (C), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (C), 127.5 (CH), 127.4 (CH), 127.1 (C), 126.9 (CH), 126.7 (CH), 125.4 (C), 125.1 (CH), 123.7 (CH), 122.3 (C), 121.8 (C), 115.2 (CH, C_6H_4OMe), 55.4 (OMe), 20.18 (Me, XyNC), 20.05 (Me, XyNC), 19.37 (Me, XyNC), 19.07 (Me, XyNC), 18.88 (Me, XyNC), 18.49 (2 Me, XyNC), 17.32 (Me, XyNC). Anal. Calcd for $C_{49}H_{47}BrN_4OPdS$: C, 63.53; H, 5.11; N, 6.05; S, 3.46. Found: C, 63.19; H, 5.26; N, 5.97; S, 3.17. Single crystals were obtained by slow diffusion of *n*-pentane into a solution of **17** in CH_2Cl_2.

18: Yield: 76%. Mp: 222 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, 2 H, $C_6H_4NO_2$, $^3J_{HH}$ = 8 Hz), 7.49−7.34 (several m, 4 H, C_6H_4 and XyNC), 7.02 (d, 2 H, $C_6H_4NO_2$, $^3J_{HH}$ = 8 Hz), 7.08−6.79 (several m, 10 H, C_6H_4 and XyNC), 6.37 (m, 2 H, C_6H_4 or XyNC), 2.59 (s, 3 H, Me), 2.21 (s, 3 H, Me), 2.19 (s, 3 H, Me), 2.16 (s, 3 H, Me), 2.12 (s, 6 H, 2 Me), 2.04 (s, 3 H, Me), 1.30 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 174.5 (C═N), 173.7 (C═N), 168.3 (C═N), 152.3 (C), 147.7 (C), 146.1 (C), 145.9 (C), 143.8 (C), 135.6 (C), 134.9 (CH), 134.6 (C), 131.5 (CH), 130.2 (C), 129.9 (C), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.7 (C), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.7 (C), 125.8 (C), 125.3 (C), 124.1 (CH), 123.9 (CH), 123.8 (CH), 122.2 (C), 20.17 (Me, XyNC), 19.44 (Me, XyNC), 19.04 (Me, XyNC), 18.89 (Me, XyNC), 18.71 (Me, XyNC), 18.47 (2 Me, XyNC), 17.71 (Me, XyNC). Anal. Calcd for $C_{48}H_{44}BrN_5O_2PdS$: C, 61.25; H, 4.71; N, 7.44; S, 3.41. Found: C, 61.61; H, 4.87; N, 7.16; S, 3.10.

19: Yield: 87%. Mp: 213 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 8.10 (d, 2 H, H3, $C_6H_4NO_2$, $^3J_{HH}$ = 8 Hz), 7.48 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.33 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.29 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.10−6.92 (several m, 9 H, XyNC), 6.62 (d, 2 H, XyNC, $^3J_{HH}$ = 8 Hz), 6.43 (t, 1 H, XyNC, $^3J_{HH}$ = 8 Hz), 2.36 (s, 6 H, 2 Me), 2.22 (s, 6 H, 2 Me), 2.14 (s, 6 H, 2 Me), 1.76 (s, 6 H, 2 Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 174.8 (C═N), 171.8 (C═N), 167.6 (C═N), 150.7 (C), 148.0 (C), 146.5 (C), 144.7 (C), 144.0 (C), 137.2 (C), 134.7 (C), 131.1 (CH, C_6H_4), 130.8 (C), 130.4 (CH, C_6H_4), 129.6 (CH, C_6H_4), 129.3 (CH, *para*-Xy), 129.2 (C), 128.2 (CH, *meta*-Xy), 127.9 (CH), 127.8 (CH, *meta*-Xy), 127.5 (2 CH, *meta*-Xy), 126.1 (C), 124.4 (CH, C3, $C_6H_4NO_2$), 124.0 (CH, *para*-Xy), 123.9 (C), 123.8 (CH, *para*-Xy), 19.4 (2 Me, XyNC), 18.8 (2 Me, XyNC), 18.7 (2 Me, XyNC), 18.6 (2 Me, XyNC). Anal. Calcd for $C_{48}H_{44}BrN_5O_2PdS$: C, 61.25; H, 4.71; N, 7.44; S, 3.41. Found: C, 60.91; H, 4.66; N, 7.22; S, 3.34.

20: Yield: 77%. Mp: 139 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, 2 H, H3, $C_6H_4NO_2$, $^3J_{HH}$ = 8 Hz), 7.45 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.39 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.37 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.26 (d, 2 H, $^3J_{HH}$ = 8 Hz), 7.18 (d, 2 H, $^3J_{HH}$ = 8 Hz), 7.06 (m, 4 H), 6.99 (d, 2 H, $^3J_{HH}$ = 8 Hz), 6.94 (d, 2 H, $^3J_{HH}$ = 8 Hz), 6.89 (t, 1 H, XyNC, $^3J_{HH}$ = 8 Hz), 6.59 (d, 2 H, XyNC, $^3J_{HH}$ = 8 Hz), 6.40 (t, 1 H, XyNC, $^3J_{HH}$ = 8 Hz), 2.31 (s, 6 H, 2 Me), 2.21 (s, 6 H, 2 Me), 2.13 (s, 6 H, 2 Me), 1.73 (s, 6 H, 2 Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 176.2 (C═N), 171.5 (C═N), 167.6 (C═N), 150.3 (C), 148.0 (C), 147.0 (C), 146.1 (C), 145.9 (C), 140.9 (C), 135.1 (C), 135.0 (CH, C_6H_4), 134.9 (C), 133.5 (CH, C_6H_4), 131.6 (C), 130.3 (CH, C_6H_4), 129.2 (C), 129.0 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.3 (C), 124.3 (CH, C3, $C_6H_4NO_2$), 124.1 (C), 124.0 (CH), 123.9 (CH), 19.7 (2 Me), 18.8 (2 Me), 18.7 (2 Me), 18.6 (2 Me). Anal. Calcd for $C_{54}H_{48}IN_5O_2PdS_2$: C, 59.15; H, 4.41; N, 5.85; S, 6.39. Found: C, 59.46; H, 4.49; N, 5.67; S, 6.12.

Synthesis of [Pd{κ²-C(═NXy)C(═NXy)C[C_6H_4SPh-2](═NXy)}(TfO)(CNXy)] (21). To a solution of **16** (80 mg, 0.08 mmol) in CH_2Cl_2 (15 mL) was added TlTfO (30 mg, 0.08 mmol), and the mixture was stirred for 5 h. The suspension was filtered through Celite and the filtrate concentrated (1 mL). Addition of pentane (15 mL) gave a suspension that was filtered; the solid was washed with *n*-pentane (3 × 5 mL) to give **21** as an orange-red solid. Yield: 62 mg, 72%. Mp: 131 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.33 (s, 5 H), 7.21−6.90 (several m, 14 H), 6.51 (m, 1 H), 6.24 (m, 1 H), 2.61 (s, 3 H, Me), 2.49 (s, 3 H, Me), 2.34 (s, 3 H, Me), 2.28 (s, 3 H, Me), 2.18 (s, 3 H, Me), 2.14 (s, 6 H, 2 Me), 1.06 (s, 3 H, Me). ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 174.43 (C═N), 166.66 (C═N), 162.76 (C═N), 149.10 (C), 147.66 (C), 141.07 (C), 135.66 (C), 135.56 (C), 133.36 (C), 131.50 (CH), 131.35 (CH), 131.10 (C), 130.78 (CH), 130.35 (C), 129.80 (CH), 129.66 (CH), 128.88 (C), 128.72 (CH), 128.63 (CH), 128.40 (CH), 128.25 (CH), 128.10 (CH), 127.92 (CH), 127.72 (CH), 127.67 (CH), 127.48 (CH), 127.34 (C), 127.05 (CH), 126.51 (CH), 125.21 (C), 124.44 (CH), 124.30 (CH), 121.65 (C), 20.07 (Me, XyNC), 19.37 (Me, XyNC), 19.31 (Me, XyNC), 19.08 (Me, XyNC), 18.56 (Me, XyNC), 18.40 (2 Me, XyNC), 17.31 (Me, XyNC). Anal. Calcd for $C_{49}H_{45}F_3N_4O_3PdS_2$: C, 60.96; H, 4.70; N, 5.80; S, 6.64. Found: C, 60.82; H, 4.93; N, 5.81; S, 6.31. Single crystals were obtained by slow diffusion of *n*-pentane into a solution of **21** in CH_2Cl_2.

Synthesis of [Pd{κ²-*C*,*S*-C(═NXy)C_6H_4SPh-2}(PPh_3)(CNXy)]TfO (22). A mixture of **1** (80 mg, 0.09 mmol), XyNC (23 mg, 0.18 mmol), and TlTfO (31 mg, 0.09 mmol) in acetone (15 mL) was stirred for 1 h. The suspension was filtered through Celite, and the filtrate was concentrated to dryness. The residue was washed with Et_2O (3 × 5 mL) to give **22** as a yellow solid. Yield: 56 mg, 60%. Mp: 155 °C. Λ_M (acetone, 4.84 × 10^{-4} mol L^{-1}): 136 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 1 H, H3 or H6, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.56−7.50 (m, 3 H, C_6H_4 and/or Ph), 7.45 (m, 4 H, C_6H_4 and/or Ph and/or XyNC), 7.32 (td, 6 H, *meta*-PPh_3, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 3 Hz), 7.26 (m, 3 H, *para*-PPh_3), 7.18 (m, 6 H, *ortho*-PPh_3), 6.90 (m, 2 H, Ph + 2 H, *meta*-Xy(i) + 2 H, *meta*-Xy(c)), 6.79 (m, 1 H, *para*-Xy(i)), 2.19 (s, 6 H, 2 Me), 1.68 (s, 6 H, 2 Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 152.2 (C), 151.2 (C), 150.8 (C), 134.2 (C), 133.5 (d, CH, *ortho*-PPh_3, $^2J_{PC}$ = 12.4 Hz), 133.5 (CH, C_6H_4 or Ph), 131.8 (CH),

Table 1. Crystal Data and Structure Refinement of Complexes 2, 3, 8, and 10

	2	3	8	10·CH_2Cl_2.C_6H_{14}
formula	$C_{49}H_{41}BrOP_2PdS$	$C_{48}H_{38}BrNO_2P_2PdS$	$C_{31}H_{24}F_3O_3PS_2$	$C_{67}H_{64}Br_2Cl_2P_2Pd_2S_2$
fw	926.13	941.10	596.59	1438.76
temperature (K)	133	133	133	133
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (Å)	12.8982(12)	12.9620(14)	10.8871(12)	18.203(3)
b (Å)	14.8492(14)	14.5561(14)	17.038(2)	15.410(3)
c (Å)	21.869(2)	21.838(2)	14.922(2)	22.325(3)
α (deg)	90	90	90	90
β (deg)	90	90	97.992(4)	105.56(3)
γ (deg)	90	90	90	90
volume (Å^3)	4188.5	4120.3	2741.1	6032.6
Z	4	4	4	4
ρ_{calcd} (Mg m^{-3})	1.469	1.517	1.446	1.584
μ (mm^{-1})	1.6	1.6	0.31	2.2
$F(000)$	1880	1904	1232	2896
cryst size (mm)	0.33 × 0.25 × 0.20	0.21 × 0.10 × 0.06	0.24 × 0.15 × 0.13	0.14 × 0.08 × 0.07
θ range (deg)	1.7 to 30	1.7 to 30	1.8 to 28.3	1.2 to 26.4
no. of rflns coll	81 991	65 727	27 635	62 445
no. of indep rflns/R_{int}	12 254/0.050	12 043/0.059	6780/0.041	12 344/0.0920
transmissn	0.86−0.73	0.90−0.78		0.86−0.69
restraints/params	0/497	0/505	0/361	197/653
goodness-of-fit on F^2	1.02	0.93	1.05	0.98
R_1 ($I > 2\sigma(I)$)	0.025	0.028	0.037	0.049
wR_2 (all reflns)	0.060	0.048	0.103	0.139
largest diff. peak/hole (e Å^{-3})	1.2/−0.60	0.76/−0.53	0.42/−0.41	1.8/−1.5

131.8 (CH), 131.7 (CH), 131.6 (CH), 131.5 (CH, C_6H_4 or Ph), 131.0 (CH, C_6H_4 or Ph), 130.4 (CH, *para*-PPh_3), 129.4 (d, CH, *meta*-PPh_3, $^3J_{PC}$ = 10.4 Hz), 128.7 (C, *ipso*-PPh_3, $^1J_{PC}$ = 35 Hz), 128.6 (CH, C3 or C6, C_6H_4), 128.1 (CH, *meta*-Xy), 128.0 (CH, *meta*-Xy), 127.1 (C), 124.9 (CH, *para*-Xy(i)), 19.6 (2 Me, XyNC), 18.3 (2 Me, XyNC) ^{31}P NMR (121 MHz, $CDCl_3$): δ 13.9 (s, PPh_3). Anal. Calcd for $C_{49}H_{42}F_3N_2O_3PdS_2$: C, 60.96; H, 4.39; N, 2.90; S, 6.64. Found: C, 60.66; H, 4.33; N, 3.02; S, 6.29. Single crystals were obtained by slow diffusion of Et_2O into a solution of **22** in CH_2Cl_2.

Synthesis of *trans*-[Pd{C(═NXy)C_6H_4SPh-2}$(CNXy)_2$I] (23), *trans*-[Pd{C(═NXy)(C_6H_4S-4)$_2C_6H_4NO_2$-4}$(CNXy)_2$I] (24), [{*trans*-Pd[C(═NXy)$(CNXy)_2$I]}$_2$-μ-{$C_6H_4(SC_6H_4$-4)$_2$-4}] (25), and [{*trans*-Pd[C(═NXy)$(CNXy)_2$I]}$_2$-μ-{$C_6H_4(SC_6H_4$-4)$_2$-4}] (26). A mixture of the corresponding *cis*-[PdI(arylthioether)(bpy)] (**5**−**7**; 25−50 mg) and XyNC (1:*x* molar ratio; *x* = 3 (**23**, **24**), 6 (**25**, **26**)) in CH_2Cl_2 (15 mL) was stirred for 1 h (**23**−**25**) or 0.5 h (**26**). The solution was concentrated (1 mL), and Et_2O (10 mL, **23**, **25**) or *n*-pentane (10 mL, **24**, **26**) added. The suspension was filtered, and the solid washed with Et_2O (3 × 5 mL, **23**, **25**) or *n*-pentane (3 × 5 mL, **24**, **26**) to give a yellow solid.

23: Yield: 79%. Mp: 152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 1 H, C_6H_4 or Ph), 7.45 (m, 2 H, C_6H_4 and/or Ph), 7.29 (m, 6 H, C_6H_4 and Ph), 7.18 (t, 2 H, *para*-Xy(c), $^3J_{HH}$ = 7 Hz), 7.03 (d, 4 H, *meta*-Xy(c), $^3J_{HH}$ = 7 Hz), 6.83 (d, 2 H, *meta*-Xy(i), $^3J_{HH}$ = 7 Hz), 6.68 (t, 1 H, *para*-Xy(i), $^3J_{HH}$ = 7 Hz), 2.23 (s, 12 H, 4 Me), 2.19 (s, 6 H, 2 Me). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 176.9 (C═N), 150.9 (C), 148.0 (C), 135.5 (C, *ortho*-Xy), 134.8 (C), 132.1 (CH), 130.9 (CH), 130.1 (CH), 129.7 (CH, Ph), 129.5 (CH, *para*-Xy(c)), 128.9 (CH), 128.2 (CH), 128.0 (CH, *meta*-Xy(i)), 127.9 (CH, *meta*-Xy(c)), 127.6 (CH), 127.2 (C, *ipso*-Xy(c)), 123.7 (CH, *para*-Xy(i)), 19.28 (2 Me, XyNC), 18.88 (4 Me, 2 XyNC). Anal. Calcd for $C_{39}H_{36}IN_3PdS$: C, 57.68; H, 4.47; N, 5.17; S, 3.95. Found: C, 57.29; H, 4.49; N, 5.10; S, 3.75.

24: Yield: 76%. Mp: 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 8.10 (d, 2 H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.48 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.40 (m, 4 H, C_6H_4), 7.22 (m, 2 H, C_6H_4 + 2 H, *para*-Xy(c)), 7.06 (d, 4 H, *meta*-Xy(c), $^3J_{HH}$ = 8 Hz), 6.93 (m, 1 H, *para*-Xy(i) + 2 H, *meta*-Xy(i)), 2.23 (s, 12 H, 4 Me), 2.12 (s, 6 H, 2 Me). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 176.4 (C═N), 149.7 (C), 147.7 (C), 145.6 (C), 144.4 (C), 138.3 (C), 136.3 (C), 135.9 (C, *ortho*-Xy(c)), 135.0 (CH, C_6H_4), 131.4 (CH, C_6H_4), 131.2 (CH, C_6H_4), 130.6 (CH, C_6H_4), 130.2 (CH, C_6H_4), 129.4 (C), 128.1 (CH, 4 CH, *meta*-Xy(c) + 2 CH, *meta*-Xy(i)), 127.2 (CH, *para*-Xy(c)), 126.5 (C, *ipso*-Xy(c)), 124.2 (CH, C_6H_4), 123.5 (CH, *para*-Xy(i)), 18.86 (2 Me, XyNC), 18.79 (4 Me, 2 XyNC). Anal. Calcd for $C_{45}H_{39}IN_4O_2PdS_2$: C, 55.99; H, 4.07; N, 6.64; S, 5.80. Found: C, 55.70; H, 3.92; N, 6.43; S, 5.77.

25: Yield: 20 mg, 56%. Mp: 187 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.24 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.41 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.33 (s, 4 H, C_6H_4), 7.19 (t, 4 H, *para*-Xy(c)), $^3J_{HH}$ = 8 Hz), 7.03 (d, 8 H, *meta*-Xy(c), $^3J_{HH}$ = 8 Hz), 6.92 (m, 6 H, 2 H, *para*-Xy(i) + 4 H, *meta*-Xy(i)), 2.21 (s, 24 H, 8 Me), 2.11 (s, 12 H, 4 Me). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 176.0 (C═N), 149.7 (C), 143.9 (C), 137.9 (C), 136.0 (C, 6 C, *ortho*-Xy), 134.5 (C), 132.2 (CH, C_6H_4), 130.5 (CH, C_6H_4), 130.2 (CH, *para*-Xy(c)), 130.1 (CH, C_6H_4), 128.2 (CH, *meta*-Xy(c+i)), 126.6 (C, *ipso*-Xy(c)), 123.5 (CH, *para*-Xy(i)), 18.91 (4 Me, 2 XyNC), 18.82 (8 Me, 4 XyNC). Anal. Calcd for $C_{72}H_{66}I_2N_6Pd_2S_2$: C, 55.93; H, 4.30; N, 4.15; S, 5.44. Found: C, 55.65; H, 4.26; N, 4.00; S, 5.36.

26: Yield: 20 mg, 56%. Mp: 165 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.28 (s, 1 H, C_6H), 7.20 (t, 4 H, *para*-Xy(c), $^3J_{HH}$ = 8 Hz), 7.06 (d, 8 H, *meta*-Xy(c), $^3J_{HH}$ = 8 Hz),

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Table 2. Crystal Data and Structure Refinement of Complexes 14, 16, and 17

	14·3/2CH_2Cl_2	16	17
formula	$C_{94.5}H_{81}Cl_3I_2P_4Pd_2S_2$	$C_{48}H_{45}BrN_4PdS$	$C_{49}H_{47}BrN_4OPdS$
fw	1977.54	896.25	926.28
temperature (K)	133	133	133
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	14.505(2)	12.8797(15)	13.2572(14)
b (Å)	17.404(3)	15.2802(15)	14.1029(14)
c (Å)	18.296(3)	21.356(3)	14.1107(14)
α (deg)	69.526(5)	90	112.513(4)
β (deg)	88.976(5)	95.79(2)	115.224(4)
γ (deg)	82.322(5)	90	91.839(4)
volume (Å^3)	4286.2	4181.6	2143.7
Z	2	4	2
ρ_{calcd} (Mg m^{-3})	1.532	1.424	1.435
μ (mm^{-1})	1.4	1.5	1.5
F(000)	1978	1832	948
cryst size (mm)	0.18 × 0.11 × 0.08	0.28 × 0.25 × 0.05	0.19 × 0.11 × 0.03
θ range (deg)	1.2 to 28.3	1.6 to 30	1.6 to 28.3
no. of rflns coll	78 661	64 427	23 477
no. of indep rflns/R_{int}	21 156/0.080	12 230/0.048	10 560/0.038
transmissn	0.90−0.74	0.93−0.78	0.89−0.74
restraints/params	365/997	0/504	0/523
goodness-of-fit on F^2	1.07	1.04	0.90
R_1 ($I > 2\sigma(I)$)	0.064	0.037	0.034
wR_2 (all reflns)	0.150	0.104	0.069
largest diff peak/hole (e Å^{-3})	1.8/−1.5	1.65/−0.90	0.73/−0.75

6.99 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 6.91 (m, 2 H, *para*-Xy(i) + 4 H, *meta*-Xy(i)), 2.68 (s, 3 H, Me), 2.47 (s, 6 H, 2 Me), 2.20 (s, 24 H, 8 Me, XyNC), 2.08 (s, 12 H, 4 Me, XyNC). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 176.0 (C═N), 171.6 (C), 149.7 (C), 149.6 (C), 145.9 (C), 141.9 (C), 140.5 (C), 135.9 (C, *ortho*-Xy), 131.2 (CH, C_6H), 130.5 (CH, C_6H_4), 130.1 (CH, *para*-Xy(c)), 128.9 (C), 128.1 (CH, *meta*-Xy-(c+i)), 126.7 (C, *ipso*-Xy(c)), 124.8 (CH, C_6H_4), 123.4 (CH, *para*-Xy(i)), 22.3 (2 Me, C_6H_1), 20.8 (Me, C_6H), 18.9 (4 Me, 2 XyNC), 18.8 (8 Me, 4 XyNC). Anal. Calcd for $C_{75}H_{72}I_2N_6Pd_2S_2$: C, 56.72; H, 4.57; N, 4.04; S, 5.29. Found: C, 57.07; H, 4.38; N, 4.28; S, 5.09.

Synthesis of [Pd{κ^2-*C*,*S*-C(═NXy)C_6H_4SPh-2}(CNXy)$_2$]TfO (27). To a solution of **23** (70 mg, 0.09 mmol) in acetone (15 mL) was added TlTfO (31 mg, 0.09 mmol), and the mixture was stirred for 1 h. The resulting suspension was filtered through Celite, and the filtrate concentrated (1 mL). Addition of Et_2O (5 mL) gave a suspension, which was filtered, and the solid was washed with Et_2O (3 × 5 mL) to give **27** as a yellow solid. Yield: 62 mg, 83%. Mp: 127 °C. Λ_M (acetone, 3.84 × 10^{-4} mol L^{-1}): 147 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (m, 1 H), 7.68 (m, 2 H), 7.54 (m, 6 H), 7.25 (t, 2 H, *para*-Xy(c), $^3J_{HH}$ = 8 Hz), 7.07 (d, 4 H, *meta*-Xy(c), $^3J_{HH}$ = 8 Hz), 6.84 (d, 2 H, *meta*-Xy(i), $^3J_{HH}$ = 8 Hz), 6.62 (t, 1 H, *para*-Xy(i), $^3J_{HH}$ = 8 Hz), 2.19 (s, 6 H, 2 Me), 2.14 (s, 12 H, 4 Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 151.8 (C), 150.5 (C), 133.4 (CH), 132.4 (C), 131.4 (CH), 130.9 (CH), 128.7 (CH, C_6H_4), 128.4 (CH, *para*-Xy(c)), 128.1 (CH, *meta*-Xy(i+c)), 127.1 (C), 125.2 (CH, *para*-Xy(i)), 123.0 (C), 118.8 (C), 19.4 (2 Me, XyNC), 18.4 (4 Me, 2 XyNC). Anal. Calcd for $C_{40}H_{36}F_3N_3O_3PdS_2$: C, 57.59; H, 4.35; N, 5.69; S, 5.04. Found: C, 57.27; H, 4.38; N, 7.48; S, 5.09. Single crystals were obtained by slow diffusion of Et_2O into a solution of **27** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*,*S*-C(O)C_6H_4SPh-2}(bpy)]TfO (28). CO was bubbled for a few seconds through a solution of **5** (30 mg, 0.05 mmol) in acetone (15 mL); TlTfO (20 mg, 0.06 mmol) was added, and the CO bubbling was continued for up to 30 min. Then the suspension was stirred for up to 1 h and filtered through Celite, and the filtrate concentrated (1 mL). Et_2O (5 mL) was added, the suspension filtered, and the solid washed with Et_2O (3 × 5 mL), giving **28** as a yellow solid. Yield: 20 mg, 64%. Mp: 205 °C (dec). Λ_M (acetone, 4.7 × 10^{-4} molL^{-1}): 137 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (400 MHz, d_6-dmso): δ 8.97 (s, 2 H, H6 + H6′, bpy), 8.61 (d, 2 H, H13 + H13′, bpy, $^3J_{HH}$ = 8 Hz), 8.32 (t, 2 H, H14 + H14′, bpy, $^3J_{HH}$ = 8 Hz), 8.04 (d, 2 H, Ph, $^3J_{HH}$ = 7 Hz), 7.98 (d, 1 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.85 (m, 2 H, H15 + H15′, bpy), 7.76 (m, 2 H, C_6H_4 and/or Ph), 7.59 (t, 1 H, C_6H_4 and/or Ph, $^3J_{HH}$ = 8 Hz), 7.50 (m, 3 H, C_6H_4 and/or Ph). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, d_6-dmso): δ 207.0 (CO), 154.1 (C), 149.6 (CH, C6 + C6′, bpy), 148.3 (C), 141.7 (CH, C4 + C4′, bpy), 136.6 (C), 136.3 (CH, C_6H_4 or Ph), 133.0 (CH, Ph), 131.8 (CH, C_6H_4 and/or Ph), 131.3 (C), 130.6 (CH, Ph), 130.3 (CH, C_6H_4), 127.5 (CH, C5 + C5′, bpy), 125.8 (CH, C_6H_4 or Ph), 123.9 (CH, C3 + C3′, bpy). Anal. Calcd for $C_{24}H_{17}F_3N_2O_4PdS_2$: C, 46.13; H, 2.74; N, 4.48; S, 10.26. Found: C, 45.81; H, 2.82; N, 4.51; S, 10.09.

Synthesis of [Pd{κ^2-*C*,*S*-C(R′)═C(R)C_6H_4SPh-2}(bpy)]TfO (R = R′ = CO_2Me (29), Ph (30), Me (31), R = Me, R′ = Ph (32)). To a mixture of **5** (0.08 mmol) and the alkyne (0.32 mmol) in acetone (15 mL) was added TlTfO (27 mg, 0.08 mmol), and the mixture was stirred for 1 h. The suspension was filtered, and the filtrate concentrated (1 mL). Et_2O (5 mL) was added, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) to give a yellow solid.

29: Yield: 40 mg, 67%. Mp: 259 °C (dec). Λ_M (acetone, 4.33 × 10^{-4} mol L^{-1}): 129 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, acetone): δ 9.21 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 4 Hz), 8.73 (d, 2 H, H3 + H3′, bpy, $^3J_{HH}$ = 8 Hz), 8.61 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 4 Hz), 8.44 (m, 2 H,

Table 3. Crystal Data and Structure Refinement of Complexes 21, 22, and 27

	21	22	27·C_3H_6O
formula	$C_{49}H_{45}F_3N_4O_3PdS_2$	$C_{49}H_{42}F_3N_2O_3PPdS_2$	$C_{43}H_{42}F_3N_3O_4PdS_2$
fw	965.41	965.34	892.32
temperature (K)	133	133	133
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	11.7151(6)	14.6913(11)	10.0675(6)
b (Å)	12.2861(8)	10.4189(8)	10.6815(6)
c (Å)	16.9683(11)	29.827(2)	19.9274(12)
α (deg)	104.251(4)	90	99.712(4)
β (deg)	91.167(4)	103.535(4)	92.707(4)
γ (deg)	108.462(4)	90	105.616(4)
volume (Å^3)	2232.4	4438.7	2024.5
Z	2	4	2
ρ_{calcd} (Mg m^{-3})	1.436	1.445	1.464
μ (mm^{-1})	0.57	0.61	0.62
$F(000)$	992	1976	916
cryst size (mm)	0.27 × 0.11 × 0.08	0.40 × 0.11 × 0.05	0.25 × 0.10 × 0.10
θ range (deg)	1.3 to 30	1.4 to 28.3	2.0 to 30.5
no. of rflns coll	43547	61154	44545
no. of indep rflns/R_{int}	13 029/0.037	11 007/0.049	12 299/0.041
transmissn	0.93−0.82	0.96−0.82	0.94−0.86
restraints/params	0/567	161/554	103/552
goodness-of-fit on F^2	0.97	0.96	1.03
R_1 ($I > 2\sigma(I)$)	0.031	0.031	0.036
wR_2 (all reflns)	0.070	0.077	0.084
largest diff peak/hole (e Å^{-3})	0.52/−0.43	1.2/−0.5	0.55/−0.51

H14 + H14′, bpy), 8.19 (dd, 1 H, H3 or H6, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.97 (m, 1 H, H5 or H5′, bpy), 7.90 (m, 2 H, H5 or H5′, bpy + H3 or H6, C_6H_4), 7.76 (td, 1 H, H4 or H5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.65 (td, 1 H, H4 or H5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.58 (m, 2 H, Ph), 7.43 (m, 3 H, Ph), 3.66 (s, 3 H, OMe), 3.51 (s, 3 H, OMe). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, $CDCl_3$): δ 169.6 (CO), 166.3 (CO), 157.2 (C), 155.7 (C), 152.3 (CH, C6 or C6′, bpy), 151.0 (CH, C6 or C6′, bpy), 149.0 (C), 144.3 (C), 143.0 (CH, C4 or C4′, bpy), 142.7 (CH, C4 or C4′, bpy), 138.4 (C), 134.3 (CH, C3 or C6, C_6H_4), 133.8 (CH, C4 or C5, C_6H_4), 132.3 (CH, C3 or C6, C_6H_4), 131.2 (CH, C4 or C5, C_6H_4), 130.7 (CH, C4, Ph), 130.5 (CH, C2 or C3, Ph), 130.0 (CH, C2 or C3, Ph), 129.0 (CH, C5 or C5′, bpy), 128.7 (CH, C5 or C5′, bpy), 125.1 (CH, C3 or C3′, bpy), 125.0 (CH, C3 or C3′, bpy), 124.1 (C), 52.9 (OMe), 52.5 (OMe). Anal. Calcd for $C_{29}H_{23}F_3N_2O_7PdS_2$: C, 47.13; H, 3.14; N, 3.79; S, 8.68. Found: C, 47.22; H, 3.10; N, 3.81; S, 8.31.

30: Yield: 60 mg, 97%. Mp: 136 °C. Λ_M (acetone, 4.64 × 10^{-4} mol L^{-1}): 121 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1 H, H6 or H6′, bpy), 8.61 (d, 2 H, H3 + H3′, bpy, $^3J_{HH}$ = 8 Hz), 8.25 (m, 2 H, H4 + H4′, bpy), 7.83 (m, 1 H), 7.75 (m, 1 H), 7.65 (m, 1 H), 7.49−7.18 (several m, 12 H, C_6H_4 and Ph), 6.94 (d, 3 H, $^3J_{HH}$ = 8 Hz), 6.79 (t, 4 H, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ APT NMR (75.48 MHz, $CDCl_3$): δ 156.8 (C), 155.5 (C), 153.8 (C), 150.3 (CH, C6 or C6′, bpy), 149.9 (C), 149.2 (CH, C6 or C6′, bpy), 141.77 (CH, C4 or C4′, bpy), 141.3 (CH, C4 or C4′, bpy), 140.7 (C), 140.6 (C), 137.7 (C), 132.9 (CH, C_6H_4 or Ph), 131.8 (CH, C_6H_4 or Ph), 130.5 (CH, Ph), 130.4 (CH, Ph), 129.9 (CH, Ph), 129.4 (CH, C_6H_4 or Ph), 128.4 (CH, Ph), 128.3 (CH, C_6H_4 or Ph), 127.7 (CH, Ph), 127.2 (CH, C_6H_4 or Ph), 127.1 (CH, C_6H_4 or Ph), 124.6 (CH, C3 or C3′, bpy), 124.3 (CH, C3 or C3′, bpy), 123.1 (C), 118.9 (C). Anal. Calcd for $C_{37}H_{27}F_3N_2O_3Pd\,S_2$: C, 57.33; H, 3.51; N, 3.62; S, 8.27. Found: C, 57.32; H, 3.37; N, 3.56; S, 7.87.

31: Yield: 50 mg, 96%. Mp: 174 °C (dec). Λ_M (acetone, 5.5 × 10^{-4} mol L^{-1}): 115 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.11 (m, 1 H, H6 or H6′, bpy), 8.66 (m, 3 H, H6 or H6′ + H3 + H3′, bpy), 8.36 (t, 2 H, H4 + H4′, $^3J_{HH}$ = 8 Hz), 8.04−7.83 (several m, 3 H, H5 + H5′, bpy +1 H, C_6H_4 and/or Ph), 7.71 (t, 2 H, Ph, $^3J_{HH}$ = 8 Hz), 7.44 (s, 6 H, C_6H_4 and Ph), 2.05 (s, 3 H, Me), 2.01 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (50.32 MHz, acetone-d_6): δ 156.4 (C), 154.8 (C), 152.7(C), 152.1 (CH, C6 or C6′, bpy), 150.7 (CH, C6 or C6′, bpy), 142.3 (CH, C4 or C4′, bpy), 141.9 (CH, C4 or C4′, bpy), 133.3 (CH, C_6H_4 and/or Ph), 133.2 (CH, C_6H_4 and/or Ph), 130.4 (CH, Ph), 129.8 (CH, C_6H_4 and/or Ph), 128.7 (CH, C5 or C5′, bpy), 128.5 (CH), 128.4 (CH, C5 or C5′, bpy), 127.9 (CH, Ph), 124.6 (CH, C3 or C3′, bpy), 124.3 (CH, C3 or C3′, bpy), 23.0 (Me), 18.2 (Me). Anal. Calcd for $C_{27}H_{23}F_3N_2O_3Pd\,S_2$: C, 49.81; H, 3.56; N, 4.30; S, 9.85. Found: C, 49.86; H, 3.45; N, 4.24; S, 9.77.

32: Yield: 45 mg, 90%. Mp: 133 °C. Λ_M (acetone, 4.5 × 10^{-4} mol L^{-1}): 125 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (m, 1 H, H3 or H3′, bpy), 8.46 (m, 1 H, H3 or H3′, bpy), 8.32 (m, 1 H, H6 or H6′, bpy), 8.22 (m, 1 H, H4 or H4′, bpy), 8.06 (m, 1 H, H4 or H4′, bpy), 7.74 (m, 2 H), 7.61 (m, 1 H), 7.50−7.27 (several m, 11 H), 7.09 (m, 3 H), 2.25 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100.64 MHz, $CDCl_3$): δ 155.8 (C), 155.1 (C), 150.5 (CH, C6 or C6′, bpy), 149.7 (CH, C6 or C6′, bpy), 142.1 (C), 141.4 (CH, C4 + C4′, bpy), 130.1 (CH), 128.1 (CH), 128.35 (CH, Ph and/or C_6H_4), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.8 (CH), 126.2 (C), 124.3 (CH, C3 or C3′, bpy), 124.1 (CH, C3 or C3′, bpy), 123.6 (C), 120.0 (C), 20.8 (Me). Anal. Calcd for $C_{32}H_{25}F_3N_2O_3Pd\,S_2$: C, 53.90; H, 3.51; N, 3.93; S, 8.98. Found: C, 53.93; H, 3.75; N, 4.15; S, 8.76.

Synthesis of 2-R′-3-R-benzo[*b*]thiophene (R = R′ = CO_2Me (33), Ph (34); R = Me, R′ = Ph (35)). A suspension of **29** (50 mg,

0.07 mmol), **30** (80 mg, 0.10 mmol), or **32** (80 mg, 0.11 mmol) in toluene was stirred at 130 °C for 16 h. The solvent was evaporated, and the residue was washed with CH_2Cl_2 (3 × 5 mL) and filtered through Celite. The filtrate was concentrated (2 mL) and subjected to preparative TLC on silica gel (70−200 mesh) with 5% fluorescent GF_{254} and as eluent a 2:1 (**33**), 1:1 (**34**), or 1:2 (**35**) v/v mixture of CH_2Cl_2−hexane. The appropriate band (R_f = 0.35 (**33**), 0.66 (**34**), 0.70 (**35**)) was extracted with acetone, the solution was stirred with $MgSO_4$ and filtered, and the filtrate was concentrated to dryness to give the thiophene as a colorless solid.

33: Yield: 12 mg, 71%. The NMR data coincide with those reported in the literature.[26]

34: Yield: 25 mg, 87%. The NMR data coincide with those reported in the literature.[31,37]

35: Yield: 19 mg, 76%. The NMR data coincide with those reported in the literature.[37]

Synthesis of [PdI(bpy){C(CO$_2$Me)=C(CO$_2$Me)C$_6$H$_4$SPh-4}] (36). A mixture of **6** (40 mg, 0.07 mmol) and dimethylacetylenedicarboxylate (14 μL, 0.14 mmol) in 1,2-dichloroethane (20 mL) was refluxed for 16 h, and the mixture was filtered through Celite (1 mL). The filtrate was concentrated (1 mL), and Et_2O (5 mL) added. The suspension was filtered, and the solid washed with Et_2O (3 × 5 mL) to give **36** as a yellow solid. Yield: 30 mg, 60%. Mp: 239 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 8.92 (d, 1 H, H6 or H6′, bpy, $^3J_{HH}$ = 5 Hz), 7.96 (m, 4 H, H3 + H3′ + H14 + H14′, bpy), 7.65 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.54 (t, 1 H, H5 or H5′, bpy, $^3J_{HH}$ = 5 Hz), 7.43 (t, 1 H, H5 or H5′, bpy, $^3J_{HH}$ = 5 Hz), 7.18 (m, 5 H, Ph), 7.12 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 3.84 (s, 3 H, OMe), 3.72 (s, 3 H, OMe). ^{13}C{^{1}H} APT NMR (50.32 MHz, $CDCl_3$): δ 173.5 (C), 164.1 (C), 160.0 (C), 155.7 (C), 154.2 (C), 154.0 (CH, C6 or C6′, bpy), 151.6 (CH, C6 or C6′, bpy), 139.3 (CH, C4 and C4′, bpy), 139.0 (C), 135.6 (C), 134.1 (C), 131.2 (CH, Ph), 130.0 (CH, C_6H_4), 129.2 (CH, C_6H_4), 127.2 (CH, C5 or C5′, bpy and Ph), 126.9 (CH, C5 or C5′, bpy), 122.2 (CH, C3 or C3′, bpy), 122.1 (CH, C3 or C3′, bpy), 117.8 (C), 52.29 (Me), 52.08 (Me). Anal. Calcd for $C_{28}H_{23}IN_2O_4PdS$: C, 46.91; H, 3.23; N, 3.91; S, 4.47. Found: C, 46.89; H, 3.12; N, 3.89; S, 4.12.

X-ray Structure Determinations. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of a Bruker SMART 1000 CCD diffractometer. Data were recorded at low temperature using monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected for absorption using the multiscan method. Structures were refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122). Hydrogen atoms were included using rigid methyl groups or a riding model. Numerical data are summarized in Tables 1 and 2. *Special features and exceptions*: For the isotypic compounds **2** and **3**, which are achiral but crystallize by chance in the Sohncke space group $P2_12_12_1$, the Flack parameter refined to −0.001(4) and 0.025(4), respectively. For **3**, the absorption correction was based on indexed faces. For **8**, no absorption correction was made. For **10**, the solvent molecules (dichloromethane and two half hexanes) display some high U values; a system of restraints was used to improve the stability of refinement. Hexane hydrogens were not included in the refinement. For **14**, one dichloromethane is disordered over an inversion center and its dimensions are unsatisfactory. For **27**, the acetone is disordered over two positions.

CONCLUSION

We report the synthesis of the first family of palladated oligophenylene thioethers, which includes mono- and dinuclear, neutral, and cationic complexes. Those containing *trans*-PdX(PPh$_3$)$_2$ or *cis*-PdX(bpy) moieties show different behavior toward XyNC: the first afford products resulting from the tri-insertion of XyNC, whereas those of the second group give monoinserted products. Symmetrical and unsymmetrical alkynes lead to monoinsertion products, some of which decompose thermally to give benzothiophenes. Some new types of bridging thioaryl and chelating iminoacyl palladium have been prepared and fully characterized.

ASSOCIATED CONTENT

Supporting Information. Cif files of the reported X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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