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From Chelate *C,N*-Cyclopalladated Oximes to *C,N,N′*-, *C,N,S*-, or *C,N,C′*-Pincer Palladium(II) Complexes by Formation of Oxime Ether Ligands

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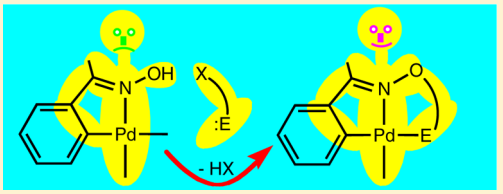
Supporting Information

ABSTRACT: Pincer complexes of the types [Pd{*C,N,N′*-Ar{C(Me)=NOCH$_2$py-2}-2}X] or [Pd{*C,N,S*-C$_6$H$_4$}{C(Me)=NOCH$_2$SMe}-2}Cl] (Ar = C$_6$H$_4$, C$_6$H(OMe)$_3$-4,5,6; py-2 = 2-pyridyl; X = Cl, Br) have been prepared by reacting cyclopalladated oxime complexes [Pd{*C,N*-Ar{C(Me)=NOH}-2}(μ-Cl)]$_2$ with XCH$_2$py-2 or ClCH$_2$SMe, respectively, in the presence of K^{t}BuO. Various neutral and cationic derivatives have been synthesized as well as iminobenzoyl complexes resulting from the insertion of isocyanide into their Pd−C$_{aryl}$ bond. The cycloaddition of MeO$_2$CC≡CCO$_2$Me to the oximato complex [Pd{*C,N*-C$_6$H$_4$}{C(Me)=NO}-2}(^{t}Bubpy)] (^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in the presence of various neutral L ligands produces pincer complexes [Pd{*C,N,C′*-C$_6$H$_4$}{C(Me)=NOC(CO$_2$Me)=C(CO$_2$Me)}-2}L]. Complexes of each one of the new types have been characterized by X-ray diffraction methods.



INTRODUCTION

Ortho-functionalized aryl palladium complexes are of interest because of their remarkable reactivity.[1,2] In particular, we have focused our ongoing research on such complexes[3−7] in the study of their reactions with unsaturated species. The modified reactivity imposed by the metal on both the pre-existing ortho group and that resulting from the insertion process allowed us to prepare interesting organic compounds resulting from depalladation processes,[4,5,8−12] as well as various types of chelate[13,14] and pincer[12,15−17] complexes, including the first family of stable Pd(IV) pincer complexes prepared by oxidizing the corresponding Pd(II) derivatives[18,19] and the first *C,N,C*-imidocarbene[14] and *C,N,O*-acyl[14,15] complexes of any metal.

The continuous growth in the development of pincer complexes[15−17,20] can be attributed to their applications in organic synthesis, as catalysts[12,18,21] or in stoichiometric reactions,[19,22] or as materials.[23] Although the most common complexes involve symmetrical pincer ligands, the presence of different donor groups provides unsymmetrical pincer complexes with unique properties and reactivity.[24]

A few examples have been reported of chelate organometal complexes converting into pincer derivatives. However, in all cases, this transformation occurs as a consequence of the chelating ligand bearing a pendant aryl group that metalates.[25,26] In a few other reports, preexisting pendant groups different from aryl in the chelating ligand have been suggested to participate in chelate-to-pincer complex conversion processes.[18,26,27] However, the generation of a coordinating side arm on a chelate complex giving rise to a pincer complex is unprecedented. We report here the first results obtained applying this strategy, namely, the nucleophilic attack of oximato chelate complexes to XCH$_2$py-2 (X = Cl, Br; py-2 = 2-pyridyl) or ClCH$_2$SMe to give *C,N,N′*- or *C,N,S*-pincer derivatives, respectively. We have reported a different, but related, approach when reacting a 2-formylaryl palladium complex with ortho-phenylenediamine.[28] The same type of condensation reaction has been used to prepare chelate[29] or pincer palladium complexes from monocoordinated formylaryl complexes and primary amines.[30] Very recently,[31] the formation of the pincer complexes [MCl{*P,C,P*-C(PPh$_2$CH$_2$PPh$_2$)$_2$}] (M = Ni, Pd, Pt) from MCl$_2$, CS$_2$, and dppm has been suggested to occur by attack of dppm to chelate complexes of the type [M]{*P,C*-C(S)PPh$_2$CH$_2$PPh$_2$)$_2$} with abstraction of dppmS.

We are studying the reactivity of ortho-substituted aryl palladium complexes with alkynes. These reactions generally give organic compounds[4,5,7,8,11,32−34] or products resulting from the insertion of the alkyne into the Pd−C bond[3,8,11,12,32−36] or its attack on the aryl ligand.[4,8,17,32,37] The latter are most probably obtained through the intermediacy of insertion products, with only one exception, in which the alkyne attacks to an aryl substituent.[17] In this work, we report the unprecedented reaction of an aryl complex with MeO$_2$CC≡CCO$_2$Me (DMAD). When reacted with this alkyne, aryl palladium complexes typically give the product of insertion into the Pd−C bond.[2,9,11,12,34,36,38] However, the reaction with some of our oximato complexes afforded the

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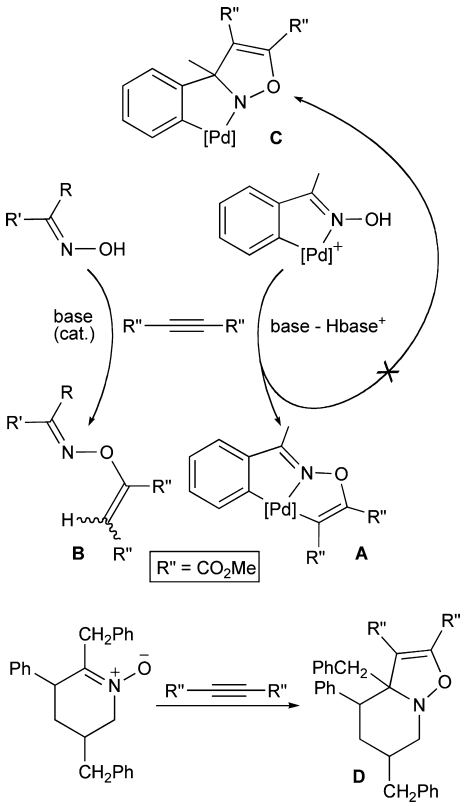
products of a cycloaddition (**A**, Scheme 1). This behavior differs also from the typical behavior of ketoximes

Scheme 1



RR′C═NOH when reacted with DMAD in the presence of catalytic amounts of base. The products are the result of a hydro-oximation reaction, (*E*+*Z*)-$MeO_2CCH{=}C(ON{=}CRR')CO_2Me$ (**B**, Scheme 1), that convert upon heating into pyrroles.[39] When designing this reaction, we also considered the possibility that a different cycloaddition occurred to give **C** (Scheme 1), taking into account the formation of **D** in the reaction of DMAD with 1,2-dihydroquinazoline 3-oxide.[40]

RESULTS AND DISCUSSION

Synthesis. We have previously reported the synthesis of cyclopalladated aryloxime complexes **1** (Scheme 2) and their reactions with base to give oximato derivatives, for instance **2**.[13] We decided to study the potential reactivity of these oximato complexes toward XCH_2py-2 (X = Cl, Br) or $ClCH_2SMe$ in the hope that an oxime ether would form, giving a *C,N,N′*- or *C,N,S*-pincer complex after coordination of the N or S atom. The results were as expected, and complex **3aBr** was obtained when $BrCH_2$py-2 (prepared *in situ* from the commercially available ($BrCH_2$pyH-2)Br and K^{t}BuO) was reacted with **2a** (Scheme 2). However, a more straightforward method for obtaining good yields of pincer complexes was the reaction of the oxime complexes **1** with 1 equiv of base and an appropriate alkyl halide, such as XCH_2py-2 or $ClCH_2SMe$, which afforded complexes **3** or **4**, respectively.[41]

Replacement of the chloro ligand in complex **3aCl** or **4aCl** by monodentate neutral ligands was achieved by reacting them with equimolar amounts of $MClO_4$ (M = Ag, Na (for **5a3**)) and the appropriate ligand to give cationic complexes **5a1**−**5a4** or **6a1**−**6a4**, respectively. The reactions were carried out in acetone or CH_2Cl_2 (**5a4**) and, when using silver salts, protected from light.

The mononuclear acetato complex **7a** (Scheme 2) was prepared from equimolar amounts of **3aCl** and AgAcO, while the dinuclear bridging acetato complex **8a** was isolated from the reaction of **3aCl** with AgTfO and AgAcO in 2:1:1 molar ratio. The latter is the first complex in which two palladium atoms are connected only by a bridging acetato ligand.

The reaction of complex **3aCl** with excess isocyanide RNC caused its insertion in the Pd−C_{aryl} bond to give the iminobenzoyl pincer complex **9a1** (R = Xy; Scheme 3) or **9a2** (R = ^{t}Bu). A similar reaction starting from the cationic complex **5a1** or **5a2** produced the cationic iminoacyl-(isocyanide) complex **10a1** (R = Xy) or **10a2** (R = ^{t}Bu), respectively. Complex **11a1**, the analogue of **10a1** containing the *C,N,S*-pincer ligand, was prepared in high yield from the acetonitrile complex **6a4** and XyNC. However, this procedure did not allow us to isolate pure its ^{t}BuNC homologue **11a2**. This complex deinserts ^{t}BuNC in solution at room temperature, giving a mixture of **6a2** and **11a2**. However, pure **11a2** was obtained by reacting the isocyanide complex **6a2** with ^{t}BuNC. Excess isocyanide over the required amount was used in all these insertion reactions (see Experimental Section), but a larger excess was necessary to complete the reaction (1) when ^{t}BuNC was used instead of XyNC and (2) when the insertion occurred in a neutral complex (for example, **3aCl** to give **9**) than in a cationic derivative (for example, **5** or **6** to give complex **10** or **11**, respectively). This confirms that the insertion process is facilitated by the presence of an electron-withdrawing substituent in the isocyanide and of a higher positive charge at the metal, both favoring the nucleophilic attack of the aryl carbon on the isocyanide one.

The reaction of complex **2a** with DMAD was carried out in the hope that, apart from the common insertion of the alkyne in the Pd−C_{aryl} bond, two alternative processes, namely, a hydro-oximation or a cycloaddition, could occur. The former would be analogous to that observed in the reaction of ketoximes RR′C═NOH with DMAD in the presence of catalytic amounts of base to give compounds (*E*+*Z*)-$MeO_2CCH{=}C(ON{=}CRR')CO_2Me$ (**B**, Scheme 1), which, under heating, transform into pyrroles,[39] while the latter could afford **C** in a similar way to that observed in the attack of DMAD to 1,2-dihydroquinazoline 3-oxide (**D**, Scheme 1).[40] However, the reaction of **2a** with an equimolar amount of DMAD produced a mixture from which complex **12** was the only product that we could isolate pure, in 52% yield (Scheme 4). Although the NMR spectra and elemental analyses of **12** showed that it was an adduct, they did not allow us to fully determine its structure. With the purpose of knowing if the oximato function had participated in the process, we reacted **12** with $ClCH_2$py-2. The reaction produced complex **13**, resulting from replacement of ^{t}Bubpy by $ClCH_2$py-2, which we could isolate in good yield and fully characterize including its crystal structure. Therefore, formation of **12** can be explained by the nucleophilic attack of the oximate oxygen on one alkyne carbon of DMAD followed by the attack of the resulting carbanion on the Pd atom, which must be more electrophilic than the C═N carbon atom. Complex **12** can be a tetra- (as represented in Scheme 4) or pentacoordinated complex depending on the role of the ligand ^{t}Bubpy in the complex. Complex **12** reacted also with isocyanides RNC (R = Xy, ^{t}Bu; 1:1 molar ratio), at room temperature, to give complexes **14** and **15**, respectively, which were isolated in moderate yield. In the case of **15**, the yield

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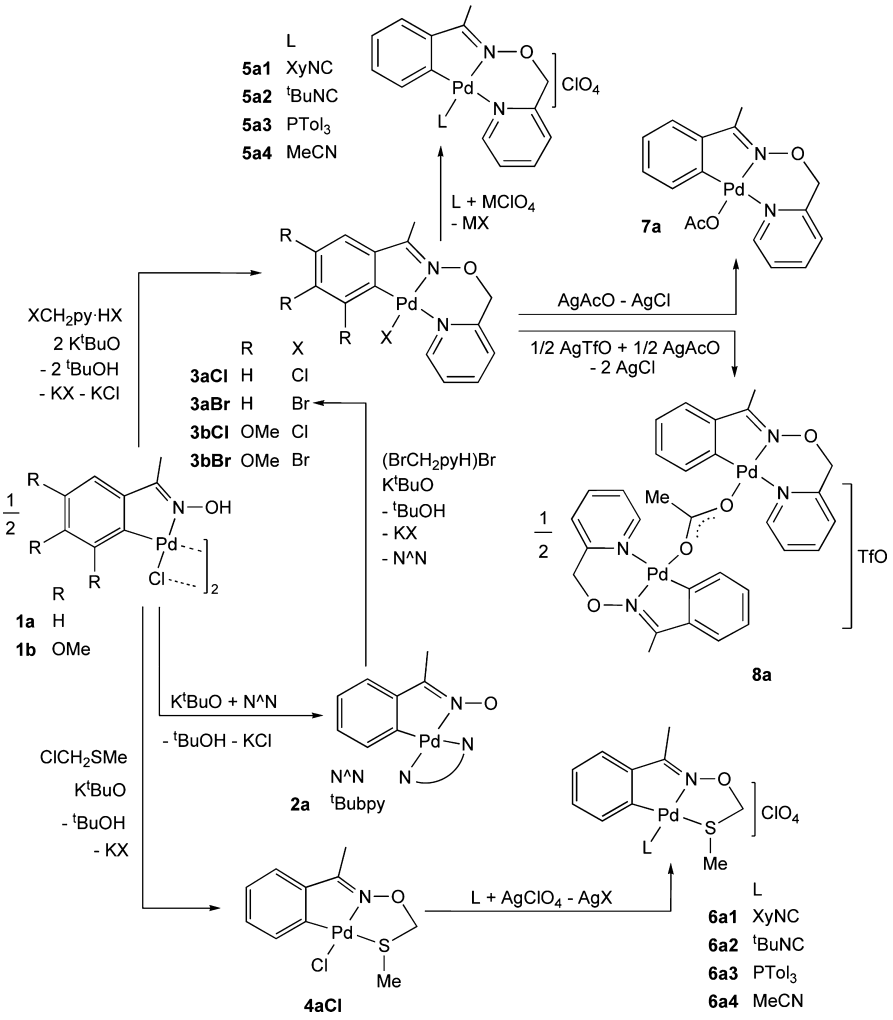
Scheme 2



improves when using excess isocyanide. Not even traces of iminobenzoyl derivatives were obtained when **14** or **15** was treated with excess isocyanide. In fact, **14** did not react with ^{t}BuNC under any reaction conditions, and this was also the case for **15** and XyNC below 60 °C, while, upon heating at 80 °C, an intractable mixture formed along with elemental palladium.

Complexes **4a**, **5a3**, **6a3**, **7a**, **9a1**, and **10a1** crystallized with various amounts of water in spite of being heated in a vacuum oven. The water content deduced from their elemental analyses was confirmed in all cases by their ^{1}H NMR spectra.

The reaction of **3bCl** with CO, aimed to produce the corresponding acyl complex, did not occur at room temperature in toluene, and when the reaction mixture was heated at 80 °C for 3 h, decomposition was observed. After removing the colloidal palladium by filtration through a short pad of anhydrous $MgSO_4$, a solution was obtained containing the previously unreported ligand $C_6H_2\{C(Me)=NOCH_2py\text{-}2\}(OMe)_3$-3,4,5 (**L**) along with very small amounts of unknown impurities. **L** was identified by its exact mass and ^{1}H and ^{13}C NMR spectra.[42] An attempt to prepare **L** by alkylation of the oxime $C_6H_2\{C(Me)=NOH\}(OMe)_3$-3,4,5 with ($ClCH_2$pyH-2)Cl and K^{t}BuO (1:1:2), carried out under the same reaction conditions used for the synthesis of **3bCl**, produced a mixture containing only a small amount of **L** (<20%), along with unreacted oxime, $ClCH_2$py-2, and other unidentified products.

X-ray Crystal Structures. The crystal structures of complexes **3aBr** (Figure 1), **3bCl** (Figure 2), **5a3** (Figure 3), **6a1** (Figure 4), **8a**·CH_2Cl_2 (Figure 5), **9a1** (Figure 6), and **13** (Figure 7) have been determined by X-ray diffraction studies, offering the first structural data for each of the various types of complexes here described since no derivatives of these pincer ligands have been reported so far for any metal. In all cases the palladium atom is in a slightly distorted square-planar environment.

In the pincer ligands, the five-membered palladacycles are planar, the highest mean deviation from the plane in all complexes being 0.0434 Å (in **5a3**), while the six-membered palladacycle adopts an envelope conformation except in complex **9a1**, which displays a boat−boat conformation in both six-membered metallacycles.

The Pd(1)−C(1), Pd(1)−N(1), N(1)−O(1), and N(1)=C(7) bond distances in our complexes are within the values found in the few other crystal structures of palladacycles derived from aryloximes.[43] As expected, the formation of the O(1)−C(9) bond causes an appreciable weakening of the N−O bond (N(1)−O(1) bond distance within 1.3987(15) and 1.4116(19) Å) compared to that in the only cyclopalladated aryloximato complex reported so far (1.301(2) Å).[13]

In complex **8a**·CH_2Cl_2 the two half-molecules are oriented anti with respect to each other, allowing some interaction between both palladiums since the Pd(1)−Pd(2) bond

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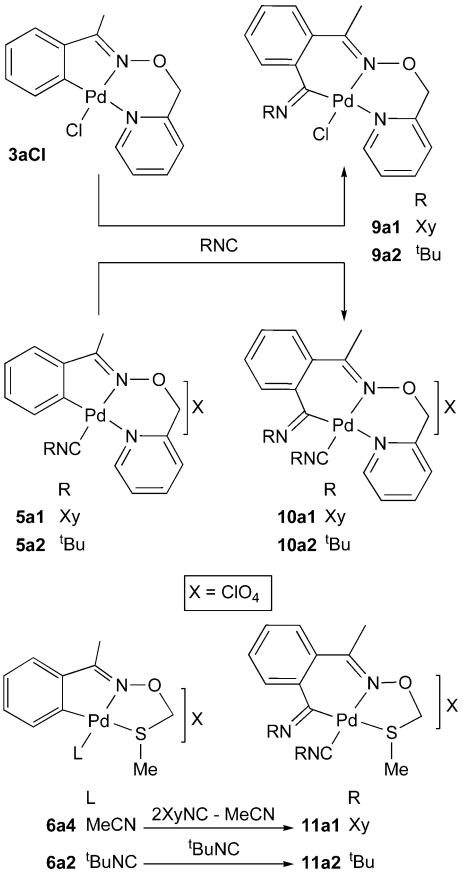
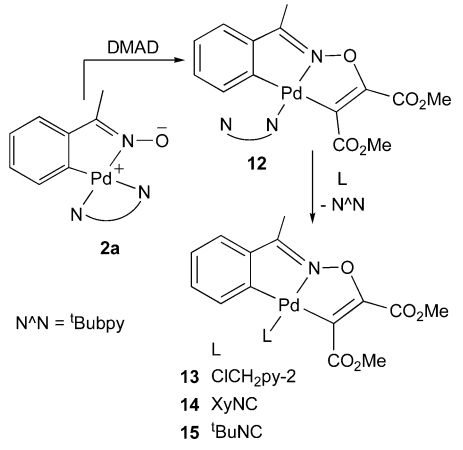
Scheme 3



Scheme 4



distance, 3.0428(3) Å), is shorter than twice the van der Waals radius of palladium (1.63 Å). In the only compounds related to **8a**·CH_2Cl_2, two non-organometallic trifluoroacetato complexes, the Pd(1)···Pd(2) distances are 3.165 and 3.412 Å, too long for any bonding or attractive interaction between the two metal atoms.[44] In **9a1** the xylyl group in the iminobenzoyl fragment is folded toward the chloro ligand, thus avoiding contact with the H^6 proton.

With the exception of **3aBr** and **9a1**, the complexes display intermolecular nonclassical C−H···O hydrogen bonds (see Figures 2, 4, 5, and 7) with the involvement of one OMe group (**3bCl**) or the counteranions, and additionally, **3bCl** shows

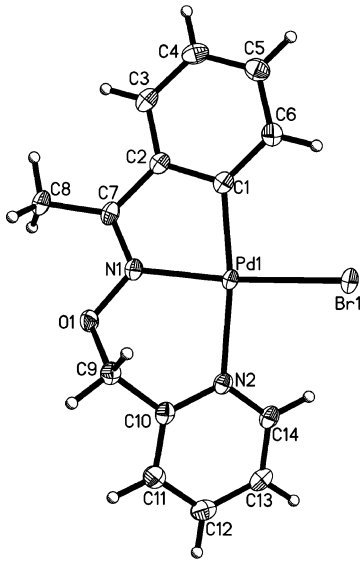


Figure 1. Thermal ellipsoid representation plot (50% probability) of complex **3aBr**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.9961(18), Pd(1)−N(1) 2.0034(14), Pd(1)−N(2) 2.1506(15), Pd(1)−Br(1) 2.4184(3), C(2)−C(7) 1.461(3), N(1)−C(7) 1.292(2), N(1)−O(1) 1.3990(19), C(9)−O(1) 1.447(2), C(9)−C(10) 1.504(2), N(2)−C(10) 1.351(2); C(1)−Pd(1)−N(1) 79.74(7), N(1)−Pd(1)−N(2) 91.51(6), C(1)−Pd(1)−Br(1) 94.89(5), N(2)−Pd(1)−Br(1) 93.98(4), N(1)−C(7)−C(2) 111.46(15), C(7)−N(1)−O(1) 115.67(14), N(1)−O(1)−C(9) 108.84(12), O(1)−C(9)−C(10) 112.83(14).

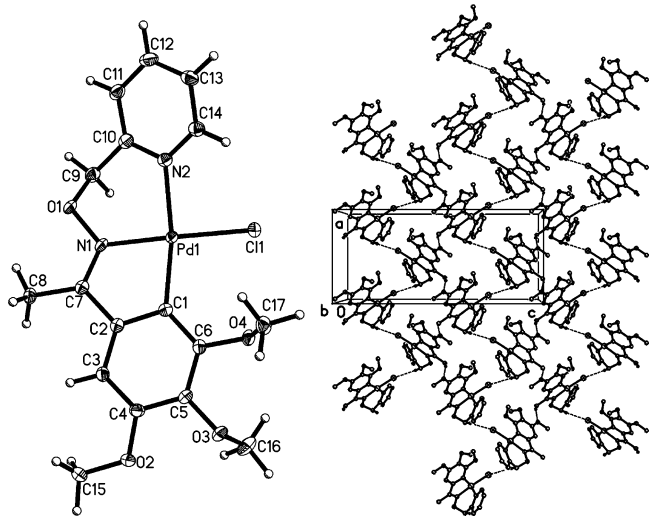


Figure 2. Left: Thermal ellipsoid representation plot (50% probability) of complex **3bCl**. Right: Intermolecular C−H···O and C−H···Cl bonds in **3bCl** giving layers parallel to the *ac* plane. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 2.024(2), Pd(1)−N(1) 1.9923(17), Pd(1)−N(2) 2.1483(18), Pd(1)−Cl(1) 2.3031(5), C(2)−C(7) 1.465(3), N(1)−C(7) 1.290(3), N(1)−O(1) 1.405(2), O(1)−C(9) 1.441(3), C(9)−C(10) 1.504(3), N(2)−C(10) 1.347(3); N(1)−Pd(1)−C(1) 79.51(8), N(1)−Pd(1)−N(2) 91.17(7), C(1)−Pd(1)−Cl(1) 99.79(6), N(2)−Pd(1)−Cl(1) 90.10(5), N(1)−C(7)−C(2) 111.90(18), C(7)−N(1)−O(1) 115.52(17), N(1)−O(1)−C(9) 109.40(15), O(1)−C(9)−C(10) 112.11(18).

nonclassical C−H···Cl hydrogen bonds. A 3D network results in the case of **5a3**, and layers parallel to the *bc* plane form in **13**.

NMR Spectroscopy. Because of their low solubility in $CDCl_3$, the NMR spectra of complexes **5a4**, **6a1**, **6a2** (^{13}C),

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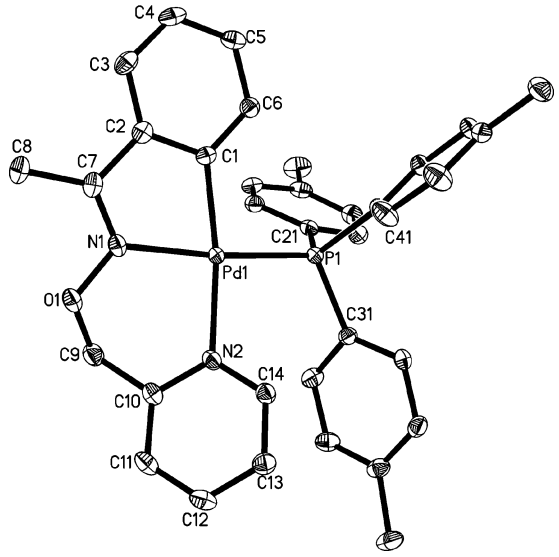

Figure 3. Thermal ellipsoid representation plot (50% probability) of the cation of complex **5a3** (40%). Hydrogen atoms and the ClO_4 anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 2.015(2), Pd(1)−N(1) 2.0429(17), Pd(1)−N(2) 2.1425(17), Pd(1)−P(1) 2.2716(5), C(2)−C(7) 1.469(3), N(1)−C(7) 1.285(3), N(1)−O(1) 1.402(2), O(1)−C(9) 1.455(3), C(9)−C(10) 1.505(3), N(2)−C(10) 1.353(3); C(1)−Pd(1)−N(1) 79.72(8), N(1)−Pd(1)−N(2) 88.47(7), C(1)−Pd(1)−P(1) 93.83(6), N(2)−Pd(1)−P(1) 99.27(5), N(1)−C(7)−C(2) 112.14(18), C(7)−N(1)−O(1) 116.44(16), N(1)−O(1)−C(9) 108.46(15), O(1)−C(9)−C(10) 111.46(17).

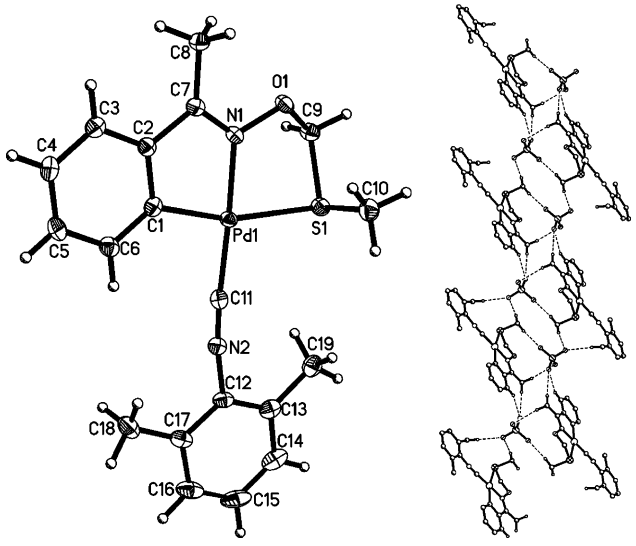

Figure 4. Left: Thermal ellipsoid representation plot (50% probability) of the cation of complex **6a1**. The ClO_4 anion is omitted for clarity. Right: The molecules are arranged into ribbons parallel to (1 0 −1) by C−H···O(ClO_4) interactions. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 1.9391(19), Pd(1)−N(1) 1.9960(15), Pd(1)−C(1) 2.0127(18), Pd(1)−S(1) 2.4072(5), C(2)−C(7) 1.473(2), N(1)−C(7) 1.288(2), N(1)−O(1) 1.4116(19), O(1)−C(9) 1.420(2), S(1)−C(9) 1.8227(19); C(11)−Pd(1)−C(1) 96.99(8), N(1)−Pd(1)−C(1) 80.05(7), C(11)−Pd(1)−S(1) 99.48(5), N(1)−Pd(1)−S(1) 83.45(5), N(1)−C(7)−C(2) 110.90(16), C(7)−N(1)−O(1) 117.02(15), N(1)−O(1)−C(9) 109.72(13), O(1)−C(9)−S(1) 114.39(12).

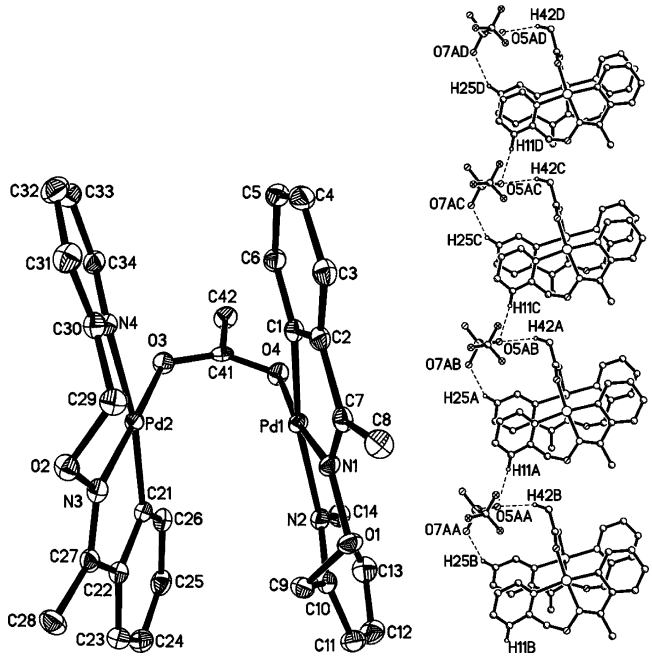

Figure 5. Left: Thermal ellipsoid representation plot (50% probability) of the cation of complex **8a**·CH_2Cl_2. Hydrogen atoms, the TfO anion, and the solvent are omitted for clarity. Right: Two oxygens of the triflate anions join the molecules by C−H···O into layers parallel to the *a* axis. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2) 3.0428(3), Pd(1)−C(1) 1.9847(18), Pd(1)−N(1) 1.9882(15), Pd(1)−O(4) 2.0491(13), Pd(1)−N(2) 2.1364(15), C(2)−C(7) 1.466(2), N(1)−C(7) 1.294(2), O(1)−N(1) 1.4056(18), O(1)−C(9) 1.446(2), C(9)−C(10) 1.510(3), N(2)−C(10) 1.349(2), Pd(2)−C(21) 1.9807(18), Pd(2)−N(3) 1.9835(15), Pd(2)−O(3) 2.0533(13), Pd(2)−N(4) 2.1275(15), C(22)−C(27) 1.463(3), N(3)−C(27) 1.295(2), O(2)−N(3) 1.3987(19), O(2)−C(29) 1.442(2), C(29)−C(30) 1.513(3), N(4)−C(30) 1.348(2); C(1)−Pd(1)−N(1) 79.93(7), C(1)−Pd(1)−O(4) 94.75(6), N(1)−Pd(1)−N(2) 92.60(6), O(4)−Pd(1)−N(2) 91.92(6), C(1)−Pd(1)−Pd(2) 87.82(5), C(21)−Pd(2)−N(3) 80.39(7), C(21)−Pd(2)−O(3) 94.95(7), N(3)−Pd(2)−N(4) 92.81(6), O(3)−Pd(2)−N(4) 91.37(6).

and **6a4** were measured in CD_3CN. The ^1H and ^{13}C methyl nuclei of the SMe group in complex **6a3** (2.01 and 15.8 ppm, respectively) are shielded with respect to those in **4** and in the remaining complexes **6** (2.50−2.68 and 16.4−16.9 ppm, respectively). This is probably caused by the aryl groups of the phosphine ligand. The singlet observed at room temperature for the methylene protons (H^9, Chart 1; 4.58−5.46 ppm) changes to an AB system when the temperature is lowered. The methoxy aryl substituents in complexes **3bCl** and **3bBr** must be responsible for the shielding of the C^1 and C^2 resonances with respect to those in the "**a**" derivatives bearing the unsubstituted arene ($\Delta\delta \approx 20$ and 5 ppm, respectively), as found previously when comparing the spectra of **1a** and **1b**.[13]

In the iminobenzoyl complexes **9**−**11**, the isocyanide insertion into the Pd−C_{aryl} bond produces a marked shielding of the C resonances in the resulting six-membered palladacycle, with respect to their precursor complexes ($\Delta\delta$ (ppm) = 20−22 (C^1), 9−16 (C^2), and 10−17 (C^7)). At room or lower temperature, the C═NXy methyl groups give two separate resonances in **9a1**, while at 55 °C only one resonance is observed. However, only below −30 °C do the spectra of complexes **10a1** and **11a1** show two Me(Xy) resonances,

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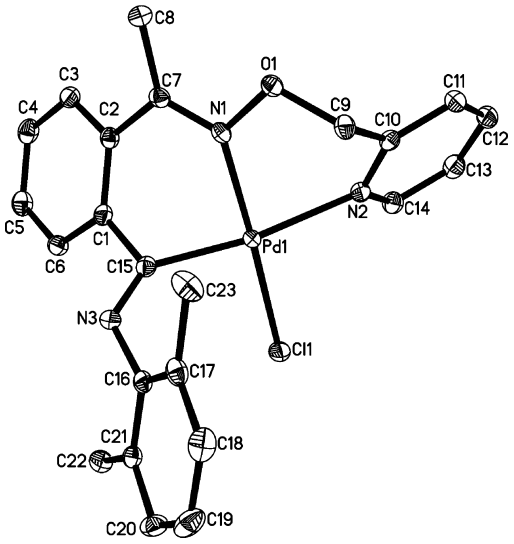
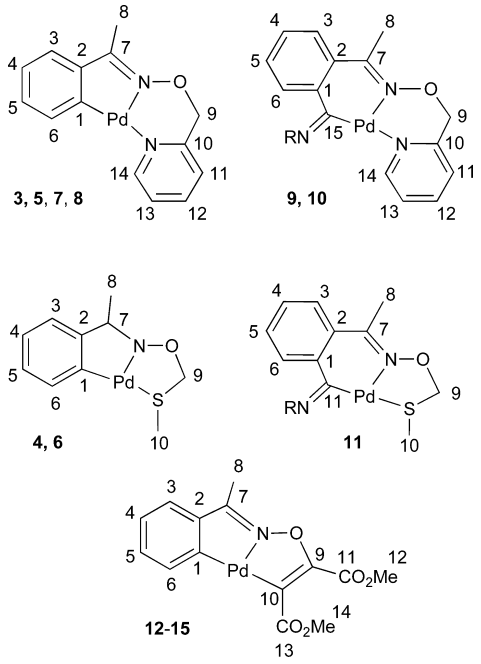


Figure 6. Thermal ellipsoid representation plot (50% probability) of complex **9a1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(15) 1.9617(19), Pd(1)−N(1) 2.0491(15), Pd(1)−N(2) 2.1738(15), Pd(1)−Cl(1) 2.3037(5), C(15)−N(3) 1.261(2), C(2)−C(7) 1.484(3), N(1)−C(7) 1.288(2), N(1)−O(1) 1.4156(19), O(1)−C(9) 1.442(2), C(9)−C(10) 1.507(3), N(2)−C(10) 1.349(2); C(15)−Pd(1)−N(1) 86.03(7), N(1)−Pd(1)−N(2) 86.78(6), C(15)−Pd(1)−Cl(1) 91.93(5), N(2)−Pd(1)−Cl(1) 95.01(4), C(1)−C(15)−Pd(1) 107.93(12), N(1)−C(7)−C(2) 116.85(16), C(7)−N(1)−O(1) 112.38(15), N(1)−O(1)−C(9) 111.67(13), O(1)−C(9)−C(10) 112.73(15).

suggesting that the isocyanide ligand exerts less congestion at the iminoacyl Xy group than the chloro ligand in complex **9a1**.

The room-temperature ^{1}H NMR spectra of **11a2** and **12** show only one resonance of 18 H for both *tert*-buthyl groups at 1.57 and 1.37 ppm, respectively. In **11a2**, this suggests an interchange between the coordinated and inserted isocyanides,

Chart 1. Atom Numbering Used in the NMR Assignments



which at −60 °C is slow on the NMR time scale, showing two resonances at 1.59 and 1.61 ppm. In the case of complex **12**, whatever the coordination mode of the ^{t}Bubpy ligand, the NMR is indicative of a fluxional process interchanging the relative position of the two halves of the ligand. While the ^{1}H NMR spectra of the isocyanide complexes **14** and **15** show the CO_2Me protons very close together at around 3.75 ppm or accidentally coinciding, respectively, in those of their homologues with nitrogen donor ligands, **12** and **13**, one of such resonances remains unaltered, while the other one is appreciably shielded (Δ = 0.35 ppm), which could be attributed

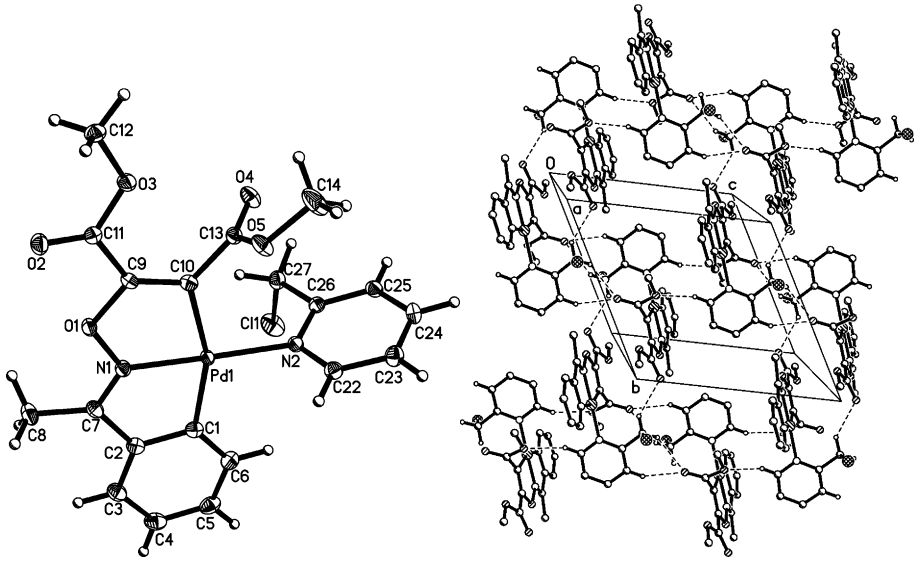


Figure 7. Left: Thermal ellipsoid representation plot (50% probability) of complex **13**. Right: Layers parallel to the *bc* plane resulting from intermolecular C−H···O hydrogen bonds. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 2.0485(18), Pd(1)−N(1) 1.9390(14), Pd(1)−C(10) 2.0623(17), Pd(1)−N(2) 2.0489(14), C(9)−C(10) 1.332(2), C(9)−O(1) 1.418(2), N(1)−O(1) 1.4044(18), C(7)−N(1) 1.296(2), C(2)−C(7) 1.478(2), C(1)−C(2) 1.423(3); N(1)−Pd(1)−C(1) 80.18(7), C(1)−Pd(1)−N(2) 102.62(6), N(1)−Pd(1)−C(10) 79.70(6), N(2)−Pd(1)−C(10) 97.55(6), N(1)−O(1)−C(9) 108.32(12), C(10)−C(9)−O(1) 121.65(15), C(9)−C(10)−Pd(1) 110.84(12), C(7)−N(1)−Pd(1) 122.27(12), N(1)−C(7)−C(2) 110.82(15), C(1)−C(2)−C(7) 116.17(15), C(2)−C(1)−Pd(1) 110.31(12).

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to the anisotropic effect of the aromatic rings of the ^{t}Bubpy or $ClCH_2$py-2 ligands coordinated in cis position with respect to one of the $C(CO_2Me)$ fragments.

CONCLUSION

We report a chelate-to-pincer complex conversion process using a new strategy, which consists in the generation of a coordinating side arm in the chelating ligand by attacking it with a ligand. Both the chelating and the added ligands must remain bonded in such a manner as to permit the coordination of a donor atom of the added ligand. The chosen processes to illustrate this method have been (1) the reaction between a cyclopalladated oxime complex and a halomethylene derivative XCH_2E (X = Cl, Br, E = py-2, SMe) and a base and (2) the reaction between DMAD and an oximato complex. Some of the resulting oxime ether pincer complexes insert isocyanides in the Pd−C bond.

EXPERIMENTAL SECTION

General Procedures. When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded in Bruker Avance, 200, 300, or 400 MHz, NMR spectrometers. The NMR assignments were performed with the help of APT, HMQC, and HMBC experiments. The atom numbering used in NMR assignments is shown in Chart 1. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate Mass TOF LC/MS spectrometer. $ClCH_2SMe$, $PTol_3$, ^{t}BuNC, XyNC, AgTfO (Fluka), $(ClCH_2$pyH-2)Cl (Lancaster), $(BrCH_2$pyH-2)Br, ^{t}Bubpy, K^{t}BuO, $AgClO_4$, AgAcO (Aldrich), NaAcO (Sigma), MeCN (Carlo Erba), and dimethyl acetylenedicarboxylate (DMAD, Alfa Aesar) were obtained from commercial sources. The syntheses of complexes **1a**, **1b**, and **2a** were recently reported by us.[13]

X-ray Crystallography. Compounds **3aBr**, **3bCl**, **5a3**, **6a1**, **8a1**·CH_2Cl_2, **9a1**, and **13** were measured on a Bruker Smart APEX machine at 100 K. Data were collected using monochromated Mo Kα radiation in ω scan mode. The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl groups were refined using rigid groups (AFIX 137), and the other hydrogens were refined using a riding model. Further details on crystal data, data collection, and refinements are summarized in the Supporting Information.

Synthesis of [Pd{*C,N,N*′-Ar^R\{C(Me)═NOCH$_2$(C$_5$H$_4$N)-2\}-2}X] (Ar^R = C$_6$H$_4$, X = Cl (3aCl), Br (3aBr); Ar^R = C$_6$H(OMe)$_3$-4,5,6, X = Cl (3bCl), Br (3bBr)). To a suspension containing K^{t}BuO (for **3aCl**, 298 mg, 2.52 mmol; for **3aBr**, 263 mg, 2.23 mmol; for **3bCl**, 98 mg, 0.83 mmol; for **3aBr**, 88 mg, 0.75 mmol) and $(XCH_2$pyH-2)X (for **3aCl**, X = Cl, 206 mg, 1.26 mmol; for **3aBr**, X = Br, 281 mg, 1.10 mmol; for **3bCl**, X = Cl, 67 mg, 0.41 mmol; for **3bBr**, X = Br, 281 mg, 1.10 mmol) in CH_2Cl_2 (for **3aCl**, **3aBr**, 20; for **3bCl**, **3bBr**, 10 mL) was added complex **1a** (for **3aCl**, 346 mg, 0.63 mmol; for **3aBr**, 299 mg, 0.54 mmol) or **1b** (for **3bCl**, 146 mg, 0.20 mmol; for **3bBr**, 135 mg, 0.18 mmol). The resulting suspension was stirred for 2.5 (**3bCl**, **3bBr**), 3 (**3aCl**), or 4.5 (**3aBr**) h and filtered through a short pad of Celite, the solution was concentrated under vacuum to 1 (**3aCl**, **3bCl**) or 2 mL (**3aBr**, **3bBr**), and Et_2O (15 mL) was added. For **3aCl** and **3bCl** the suspension was filtered and the solid was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven (70 °C, 15 (**3aCl**) or 5 h (**3bCl**), to give pale tan colored solids. A second crop of **3aCl** was obtained by concentrating the mother liquor almost to dryness, stirring the residue with Et_2O (15 mL), filtering the suspension, washing the solid with Et_2O (3 × 2 mL), and drying it as above. For **3aBr** and **3bBr**,[41] the suspension was filtered, and the solid collected was reacted with NaBr (for **3aBr**, 450 mg, 4.37 mmol; for **3bBr**, 250 mg, 2.43 mmol) in acetone (for **3aBr**, 35; for **3bBr**, 15 mL) overnight. The solvent was removed under vacuum, CH_2Cl_2 (20 mL) was added, and the suspension was filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (3 × 3 mL) and dried by suction to give a pale yellow solid. **3aBr** was additionally recrystallized from CH_2Cl_2/Et_2O and dried, first by suction and then in a vacuum oven (70 °C, 5 h).

3aCl: Yield: 413 mg, 1.13 mmol, 90%. Mp: 245 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.35 (s, 3 H, Me), 5.18 (s, 2 H, CH_2), 7.07 (td, 1 H, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.11 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.18 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.42 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.46 (ddd, 2 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.88 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.01 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 9.45 (d, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz); (400 MHz, $CDCl_3$, −60 °C): δ 2.42 (s, 3 H, Me), 5.24 (AB system, 2 H, CH_2, ν_A = 5.21, ν_B = 5.27, J_{AB} = 13 Hz), 7.17 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 7.14 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.27 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.53−7.57 (m, 2 H, H^{11+13}), 7.98−8.01 (m, 2 H, H^{6+12}), 9.38 (d, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 11.8 (Me^8), 76.4 (C^9), 124.7 (C^4), 125.1 (C^{11+13}), 126.1 (C^3), 129.6 (C^5), 136.1 (C^6), 139.1 (C^{12}), 141.3 (C^2), 151.8 (C^{10}), 152.3 (C^{14}), 154.3 (C^1), 171.1 (C^7). Anal. Calcd for $C_{14}H_{13}ClN_2OPd$: C, 45.80; H, 3.57; N, 7.63. Found: C, 45.58; H, 3.54; N, 7.58.

3aBr: Yield: 275 mg, 0.67 mmol, 62%. Mp: 220 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.35 (s, 3 H, Me), 5.19 (s, 2 H, CH_2), 7.02−7.10 (m, 2 H), 7.16−7.22 (m, 1 H, H$^{3\text{ or }5}$), 7.42−7.46 (m, 2 H, H^{11+13}), 7.89 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.24−8.30 (m, 1 H, H$^{4\text{ or }6}$), 9.56−9.58 (m, 1 H, H^{14}); (400 MHz, $CDCl_3$, −60 °C): δ 2.43 (s, 3 H, Me), 5.26 (AB system, 2 H, CH_2, ν_A = 5.22, ν_B = 5.30, J_{AB} = 14 Hz), 7.10−7.16 (m, 2 H), 7.27−7.29 (m, 1 H, H$^{3\text{ or }5}$), 7.51−7.56 (m, 2 H, H^{11+13}), 8.00 ("t", 1 H, H^{12}, $^3J_{HH}$ = 8 Hz), 8.23−8.27 (m, 1 H, H$^{4\text{ or }6}$), 9.51 ("d", 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 11.9 (Me^8), 76.6 (C^9), 124.6 (CH, Ar), 125.1 (C^{13}), 125.2 (C^{11}), 126.2 (C$^{3\text{ or }5}$), 129.9 (CH, Ar), 139.0 (C$^{4\text{ or }6}$), 139.1 (C^{12}), 141.6 (C^2), 152.0 (C^{10}), 153.6 (C^1), 153.9 (C^{14}), 170.9 (C^7). Anal. Calcd for $C_{14}H_{13}BrN_2OPd$: C, 40.86; H, 3.18; N, 6.81. Found: C, 40.71; H, 3.17; N, 6.78. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into a solution of **3aBr** in CH_2Cl_2.

3bCl: Yield: 130 mg, 0.284 mmol, 71%. Mp: 187 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.32 (s, 3 H, Me), 3.84 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 5.18 (s, 2 H, CH_2), 6.69 (s, 1 H, H^3), 7.39 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.49 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.88 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 9.82 (dd, 1 H, H^{14}, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz); (400 MHz, $CDCl_3$, −60 °C): δ 2.41 (s, 3 H, Me), 3.90 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 5.25 (AB system, 2 H, CH_2, ν_A = 5.20, ν_B = 5.30, J_{AB} = 13 Hz), 6.74 (s, 1 H, H^3), 7.51 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.58 (t, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz), 7.99 (t, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz), 9.59 (d, 1 H, H^{14}, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 12.4 (Me^8), 56.3 (OMe), 60.9 (OMe), 62.0 (OMe), 76.2 (C^9), 107.3 (C^3), 124.7 (C^{11}), 124.9 (C^{13}, 136.8 (C$^{1\text{ or }2}$), 136.9 (C$^{1\text{ or }2}$), 139.0 (C^{12}), 144.9 (C, Ar), 151.25 (C, Ar, or C^{10}), 151.29 (C, Ar or C^{10}), 151.8 (C^{14}), 159.5 (C, Ar), 170.9 (C^7). Anal. Calcd for $C_{17}H_{19}ClN_2O_4Pd$: C, 44.66; H, 4.19; N, 6.13. Found: C, 44.28; H, 4.11; N, 5.95. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into a solution of **3bCl** in CH_2Cl_2.

3bBr: Yield: 103 mg, 0.21 mmol, 56%. Mp: 197 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.32 (s, 3 H, Me), 3.84 (s, 3 H, OMe), 3.91 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 5.20 (s, 2 H, CH_2), 6.69 (s, 1 H, H^3), 7.39 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.47 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.88 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 9.82 (ddd, 1 H, H^{14}, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz); (400 MHz, $CDCl_3$, −55 °C): δ 2.41 (s, 3 H, Me), 3.90 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 5.28 (AB system, 2 H, CH_2, ν_A = 5.20, ν_B = 5.35, J_{AB} = 14 Hz), 6.75 (s, 1 H, H^3), 7.51 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.55 ("t", 1 H, H^{13}, $^3J_{HH} \approx {}^3J_{HH} \approx$ 7 Hz), 7.99 (t, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz), 9.71 (d, 1 H, H^{14}, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} (NMR

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(75 MHz, $CDCl_3$, 25 °C): δ 12.5 (Me^8), 56.4 (OMe), 60.9 (OMe), 62.1 (OMe), 76.5 (C^9), 107.4 (C^3), 124.8 ($C^{11\ or\ 13}$), 125.1 ($C^{11\ or\ 13}$), 136.7 (C^1), 137.1 (C^2), 139.0 (C^{12}), 144.5 (C, Ar), 151.4 (C, Ar), 151.6 (C^{10}), 153.5 (C^{14}), 159.2 (C, Ar), 170.7 (C^7). Anal. Calcd for $C_{17}H_{19}BrN_2O_4Pd$: C, 40.70; H, 3.82; N, 5.58. Found: C, 40.36; H, 3.87; N, 5.49.

Synthesis of [Pd{*C,N,S*-C_6H_4{C(Me)═NOCH$_2$SMe}-2}Cl] (4a). To a suspension containing K^{t}BuO (46 mg, 0.39 mmol) and complex **1a** (107 mg, 0.19 mmol) in CH_2Cl_2 (8 mL) was added $ClCH_2SMe$ (41 μL, 0.40 mmol). The resulting suspension was stirred for 18 h and filtered through a short pad of Celite, the solution was concentrated under vacuum (1 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven (70 °C, 15 h), to give **4a**·0.3H_2O as a light brown solid. Yield: 90 mg, 0.26 mmol, 68%. Mp: 196 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.57 (s, 0.6 H, H_2O), 2.27 (s, 3 H, Me^8), 2.54 (s, 3 H, MeS), 5.10 (s, 2 H, CH_2), 7.03 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.08 (td, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.16 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.76 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, solvent, $CDCl_3$, 25 °C): δ 12.4 (Me^8), 16.4 (Me^{10}), 78.1 (C^9), 125.3 (C^4), 126.7 (C^3), 130.8 (C^5), 134.0 (C^6), 144.9 (C^2), 155.7 (C^1), 170.2 (C^7). Anal. Calcd for $C_{10}H_{12.6}ClNO_{1.3}PdS$: C, 35.17; H, 3.72; N, 4.10; S, 9.39. Found: C, 35.00; H, 3.44; N, 4.21; S, 9.51.

Synthesis of [Pd{*C,N,N′*-C_6H_4{C(Me)═NOCH$_2$(C_5H_4N-2)}-2}L]ClO_4 (L = XyNC (5a1), ^{t}BuNC (5a2), $PTol_3$ (5a3), MeCN (5a4)). A mixture containing $AgClO_4$ (for **5a1**, 70 mg, 0.33 mmol; for **5a2**, 181 mg, 0.85 mmol; for **5a4**, 78 mg, 0.37 mmol) or $NaClO_4·H_2O$ (for **5a3**, 25 mg, 0.18 mmol), complex **3aCl** (for **5a1**, 114 mg, 0.31 mmol; for **5a2**, 307 mg, 0.84 mmol; for **5a3**, 51 mg, 0.12 mmol; for **5a4**, 134 mg, 0.37 mmol), and the appropriate ligand (for **5a1**, XyNC, 41 mg, 0.31 mmol; for **5a2**, ^{t}BuNC, 97 μL, 0.86 mmol; for **5a3**, $PTol_3$, 38 mg, 0.13 mmol; for **5a4**, MeCN, 3 mL, 57.3 mmol) in acetone (for **5a1** and **5a2**, 20 mL; for **5a3**, 10 mL) or in CH_2Cl_2 (for **5a4**, 5 mL) was stirred for 40 min (**5a4**), 2 h (**5a1**, **5a3**), or 4 h (**5a2**) protected from light and then filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), Et_2O (20 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven at 75 °C for 5 h, to give the title compound as an off-white solid.

5a1: Yield: 134 mg, 0.24 mmol, 77%. Mp: 243 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.54 (s, 3 H, Me^8), 2.58 (s, 6 H, Me, Xy), 5.32 (s, 2 H, CH_2), 7.17 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.28 (td, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.30 (m, 2 H, *meta*-CH, Xy), 7.43 (dd, 1 H, *para*-CH, Xy, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz), 7.46 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.45 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.66 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz), 7.76 (ddd, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz), 8.18 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.76 (ddd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz).$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): δ 12.5 (Me^8), 19.2 (Me, Xy), 77.2 (C^9), 125.6 (m, *ipso*-C, Xy), 126.8 (C^{13}), 126.9 (C^4), 127.8 (C^{11}), 128.96 (C^3), 129.02 (*meta*-C, Xy), 131.6 (*para*-C, Xy), 131.8 (C^5), 136.6 (*ortho*-C, Xy), 137.9 (C^6), 141.8 (C^2),142.0 (C^{12}), 143.5 (1:1:1, t, C≡N, $^1J_{CN}$ = 22 Hz), 152.6 (C^{10}), 153.2 (C^1), 153.9 (C^{14}), 175.8 (C^7). IR (cm^{-1}): ν(C≡N) 2185, ν(ClO) 1090, δ(OClO) 622. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 134. Anal. Calcd for $C_{23}H_{22}ClN_3O_5Pd$: C, 49.13; H, 3.94; N, 7.47. Found: C, 49.01; H, 3.90; N, 7.53.

5a2: Yield: 354 mg, 0.69 mmol, 82%. Mp: 154 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.75 (s, 9 H, ^{t}Bu), 2.47 (s, 3 H, Me^8), 5.24 (s, 2 H, CH_2), 7.20 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.26 (td, 1 H, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.32 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.41 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.71−7.75 (m, 2 H, H^{11+13}), 8.15 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.62 (ddd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): δ 12.4 (Me^8), 30.1 (Me, ^{t}Bu), 60.7 (CMe_3), 77.1 (C^9), 126.7 (C^4), 127.0 (C^{13}), 127.6 (C^{11}), 128.7 (C^3), 130.5 (1:1:1, t, C≡N, $^1J_{CN}$ = 19 Hz), 131.7 (C^5), 137.5 (C^6), 141.7 (C^{12}), 141.9 (C^2), 152.4 (C^{10}), 152.8 (C^1), 153.8 (C^{14}), 175.3 (C^7). IR (cm^{-1}): ν(C≡N) 2223, ν(ClO) 1091, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 129. Anal. Calcd for $C_{19}H_{22}ClN_3O_5Pd$: C, 44.38; H, 4.31; N, 8.17. Found: C, 44.68; H, 4.35; N, 8.25.

5a3·H_2O: Yield: 78 mg, 0.104 mmol, 84%. Mp: > 200 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.73 (br s, 2 H, H_2O), 2.36 (s, 9 H, Me, $PTol_3$), 2.50 (s, 3 H, Me^8), 5.47 (s, 2 H, CH_2), 6.50 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HP}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 6.63 (td, 1 H, $H^{4\ or\ 5}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.94 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.05 (dd, 1 H, $H^{4\ or\ 5}$, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.19 (m, 6 H, *meta*-CH, $PTol_3$), 7.34 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.53 (m, 6 H, *ortho*-CH, $PTol_3$), 7.68 (d, 1 H, H^{14}, $^3J_{HH}$ = 6 Hz), 7.73 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.85 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz); (400 MHz, $CDCl_3$, −60 °C): δ 2.28 (br s, 2 H, H_2O), 2.40 (br s, 9 H, Me, $PTol_3$), 2.55 (s, 3 H, Me^8), 5.47 (AB system, 2 H, CH_2, ν_A = 5.40, ν_B = 5.55, J_{AB} = 14 Hz), 6.49 ("t", 1 H, H^6, $^3J_{HP} \approx {}^3J_{HH}$ = 7 Hz), 6.69 (t, 1 H, $H^{4\ or\ 5}$, $^3J_{HH}$ = 7 Hz), 6.98 ("t", 1 H, H^{13}, $^3J_{HH} \approx {}^3J_{HH} \approx$ 7 Hz), 7.12 (t, 1 H, $H^{4\ or\ 5}$, $^3J_{HH}$ = 7 Hz), 7.24 (vbr s, 6 H, *meta*-CH, $PTol_3$), 7.41 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.53−8.04 (vbr s, 6 H, *ortho*-CH, $PTol_3$), 7.64 (d, 1 H, H^{14}, $^3J_{HH}$ = 6 Hz), 7.80 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.93 (t, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 12.4 (Me^8), 21.4 (Me, $PTol_3$), 77.3 (C^9), 124.9 (C^{13}), 125.3 (d, *ipso*-C, $PTol_3$, $^1J_{CP}$ = 53 Hz), 125.7 ($C^{4\ or\ 5}$), 126.9 (C^{11}), 127.6 (C^3), 129.88 (d, *meta*-CH, $PTol_3$, $^3J_{CP}$ = 12 Hz), 129.90 ($C^{4\ or\ 5}$), 134.8 (d, *ortho*-CH, $PTol_3$, $^2J_{CP}$ = 13 Hz), 138.3 (d, C^6, $^3J_{CP}$ = 11 Hz), 140.2 (C^{12}), 142.6 (d, *para*-C, $PTol_3$, $^4J_{CP}$ = 2 Hz), 142.8 (C^2), 152.2 (d, C^{14}, $^3J_{CP}$ = 3 Hz), 152.56 ($C^{1\ or\ 10}$), 152.61 ($C^{1\ or\ 10}$), 171.7 (C^7). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 25 °C): δ 40.45. IR (cm^{-1}): ν(ClO) 1093, δ(OClO) 622. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 124. Anal. Calcd for $C_{35}H_{36}ClN_2O_6PPd$: C, 56.19; H, 4.82; N, 3.72. Found: C, 55.97; H, 4.99; N, 3.82. HRMS (ESI+, *m/z*): calcd for $C_{35}H_{34}N_2OPPd$ $[M]^+$ 636.1468, found 636.1474, error = 0.94 ppm. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into a solution of **5a3** in CH_2Cl_2.

5a4: Yield: 153 mg, 0.324 mmol, 89%. Mp: 180 °C (dec). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 1.97 (s, 3 H, MeCN), 2.42 (s, 3 H, Me^8), 5.23 (s, 2 H, CH_2), 7.21 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.25 (td, 1 H, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.37 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.41 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.65 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.69 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 8.13 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.71 (d, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ. 1.8 (Me, CH_3CN), 12.6 (Me^8), 77.2 (C^9), 118.3 (CH_3CN), 126.9 (C^{13}), 127.1 (C^4), 127.4 (C^{11}), 128.8 (C^3), 131.4 (C^5), 134.9 (C^6), 141.9 (C^{12}), 142.3 (C^2), 152.6 (C^{14}), 152.9 (C^{10}), 154.4 (C^1), 177.1 (C^7). IR (cm^{-1}): ν(C≡N) 2326, ν(ClO) 1093, δ(OClO) 624. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 130. Anal. Calcd for $C_{16}H_{16}ClN_3O_5Pd$: C, 40.70; H, 3.42; N, 8.90. Found: C, 40.74; H, 3.44; N, 8.82.

Synthesis of [Pd{*C,N,S*-C_6H_4{C(Me)═NOCH$_2$SMe}-2}L]ClO_4 (L = XyNC (6a1), ^{t}BuNC (6a2), $PTol_3$ (6a3), MeCN (6a4)). Complex **4a** (for **6a1**, 102 mg, 0.30 mmol; for **6a2**, 101 mg, 0.30 mmol; for **6a3**, 99 mg, 0.30 mmol; for **6a4**, 95 mg, 0.28 mmol) was added to a solution containing $AgClO_4$ (97%, for **6a1**, 66 mg, 0.31 mmol; for **6a2** and **6a3**, 65 mg, 0.30 mmol; for **6a4**, 61 mg, 0.29 mmol) and the appropriate ligand (for **6a1**, XyNC, 40 mg, 0.31 mmol; for **6a2**, ^{t}BuNC, 35 μL, 0.31 mmol; for **6a3**, $PTol_3$, 90 mg, 0.30 mmol; for **6a4**, MeCN, 2 mL, 38.2 mmol) in acetone (for **6a1** and **6a2**, 10 mL; for **6a3**, 20 mL; for **6a4**, 8 mL). The resulting suspension was stirred protected from light for 0.5 (**6a3**), 1.5 (**6a1**, **10a4**), or 3 h (**6a2**). For **6a1** and **6a2** the suspension was filtered through a short pad of Celite and concentrated under vacuum (2 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried by suction to give a pale orange (**6a1**) or yellow (**6a2**) solid. For **6a3** and **6a4** the reaction mixture was concentrated to dryness, CH_2Cl_2 (10 mL) was added, and the suspension was filtered through a short pad of Celite. The solution was concentrated (1 mL), Et_2O (15 mL) was added, and the suspension was stirred (for **6a3**, 30 min in an ice/water bath) and filtered. The solid collected was washed wit Et_2O (3 × 2 mL), and **6a3** was additionally recrystallized from CH_2Cl_2/Et_2O and dried, first by suction and then in a vacuum oven (**6a3**: 80 °C, 5 h; **6a4**: 65 °C, 15 h), to give **6a3**·H_2O or **6a4** as pale tan solids.

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6a1: Yield: 144 mg, 0.27 mmol, 89%. Mp: 132 °C (dec). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 2.48 (s, 3 H, Me^8), 2.52 (s, 6 H, Me, Xy), 2.61 (s, 3 H, Me^{10}), 5.28 (br s, 2 H, CH_2), 7.27 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.31 (m, 2 H, *meta*-CH, Xy), 7.32 (td, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.43 (t, 1 H, *para*-CH, Xy, $^3J_{HH}$ = 8 Hz), 7.46 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.49 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ 13.3 (Me^8), 16.8 (Me^{10}), 19.0 (Me, Xy), 79.7 (C^9), 126.6 (m, *ipso*-C, Xy), 127.8 (C^4), 129.4 (*meta*-C, Xy), 130.4 (C^3), 132.0 (*para*-C, Xy), 133.4 (C^5), 137.2 (*ortho*-C, Xy), 137.9 (C^6), 142.6 (m, C≡N), 147.1 (C^2), 156.6 (C^1), 176.3 (C^7). IR (cm^{-1}): ν(C≡N) 2184, ν(ClO) 1097, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 132. Anal. Calcd for $C_{19}H_{21}ClN_2O_5PdS$: C, 42.95; H, 3.98; N, 5.27; S, 6.04. Found: C, 43.08; H, 4.00; N, 5.27; S, 5.95. Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a solution of **6a1** in acetone.

6a2: Yield: 136 mg, 0.29 mmol, 94%. Mp: 142 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.71 (s, 9 H, ^{t}Bu), 2.48 (s, 3 H, Me^8), 2.68 (s, 3 H, Me^{10}), 5.28 (vbr s, 2 H, CH_2), 7.17−7.31 (m, 4 H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ 12.9 (Me^8), 16.9 (Me^{10}), 30.0 (Me, ^{t}Bu), 60.0 ($C(Me)_3$), 79.0 (C^9), 126.8 (C, Ar), 128.9 (C, Ar), 132.5 (C, Ar), 135.8 (C, Ar), 145.6 (C^2), 155.3 (C^1), 174.5 (C^7). IR (cm^{-1}): ν(C≡N) 2216, ν(ClO) 1091, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 140. Anal. Calcd for $C_{15}H_{21}ClN_2O_5PdS$: C, 37.28; H, 4.38; N, 5.80; S, 6.64. Found: C, 37.36; H, 4.54; N, 5.69; S, 6.41.

6a3·H_2O: Yield: 142 mg, 0.20 mmol, 67%. Mp: 187 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.63 (br s, 2 H, H_2O), 2.01 (s, 3 H, MeS), 2.41 (s, 9 H, Me, $PTol_3$), 2.50 (s, 3 H, Me^8), 5.27 (br s, 2 H, CH_2), 6.42 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HP}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 6.73 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.09 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.29−7.26 (m, 7 H, H^6 + *meta*-CH, $PTol_3$), 7.52 (m, 6 H, *ortho*-CH, $PTol_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 12.7 (Me^8), 15.8 (Me^{10}), 21.4 (Me, $PTol_3$), 78.7 (d, C^9, $^3J_{CP}$ = 3 Hz), 125.9 (d, *ipso*-C, $PTol_3$, $^1J_{CP}$ = 55 Hz), 126.1 (C^4), 128.4 (C^3), 129.9 (d, *meta*-C, $PTol_3$, $^3J_{CP}$ = 12 Hz), 131.3 (C^5), 134.2 (d, *ortho*-C, $PTol_3$, $^2J_{CP}$ = 13 Hz), 137.6 (d, C^6, $^3J_{CP}$ = 10 Hz), 142.7 (d, *para*-C, $^4J_{CP}$ = 2 Hz), 146.8 (C^2), 156.1 (C^1), 173.0 (C^7). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, 25 °C): δ 36.21. IR (cm^{-1}): ν(ClO) 1095, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 134. Anal. Calcd for $C_{31}H_{35}ClNO_6PSPd$: C, 51.53; H, 4.88; N, 1.94; S, 4.44. Found: C, 51.41; H, 4.83; N, 1.97; S, 4.36.

6a4: Yield: 100 mg, 0.23 mmol, 80%. Mp: 173 °C (dec). ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 1.97 (s, 3 H, MeCN), 2.40 (s, 3 H, Me^8), 2.58 (s, 3 H, Me^{10}), 5.14 (s, 2 H, CH_2), 7.22−7.30 (m, 3 H, Ar), 7.34−7.36 (m, 1 H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ 1.8 (Me, MeCN), 13.2 (Me^8), 16.5 (Me^{10}), 78.8 (C^9), 127.6 (C, Ar), 129.4 (C, Ar), 132.5 (C, Ar), 133.7 (C, Ar), 146.2 (C^2), 155.8 (C^1), 176.0 (C^7), MeCN resonance not observed. IR (cm^{-1}): ν(C≡N) 2331, ν(ClO) 1088, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 140. Anal. Calcd for $C_{12}H_{15}ClN_2O_5PdS$: C, 32.67; H, 3.43; N, 6.35; S, 7.27. Found: C, 32.72; H, 3.27; N, 6.29; S, 6.99.

Synthesis of [Pd{*C,N,N*′-C_6H_4{C(Me)=NOCH$_2$(C_5H_4N-2)}-2}-(OAc)] (7a). To a solution of **3aCl** (155 mg, 0.42 mmol) in CH_2Cl_2 (15 mL) was added AgAcO (72 mg, 0.43 mmol). The suspension was stirred for 15 h protected from light and then filtered through a short pad of Celite. The solution was concentrated under vacuum (1 mL), and Et_2O (15 mL) was added. The suspension was filtered, and the solid collected was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven (70 °C, 15 h), to give **7a**·0.3H_2O as a pale yellow solid. Yield: 153 mg, 0.39 mmol, 92%. Mp: >140 °C (dec). ^{1}H NMR (400 MHz,$CDCl_3$, 25 °C): δ 1.95 (vbr s, 0.6 H, H_2O), 2.28 (s, 3 H, Me, AcO), 2.33 (s, 3 H, Me^8), 5.17 (s, 2 H, CH_2), 7.07 (td, 1 H, $H^{4\text{ or }5}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.13 (td, 1 H, $H^{4\text{ or }5}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.18 (dd, 1 H, $H^{3\text{ or }6}$, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.26 (d, 1 H, $H^{3\text{ or }6}$, $^3J_{HH}$ = 7 Hz), 7.43 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.47 (m, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.89 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.75 (dd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 11.7 (Me^8), 24.4 (Me, AcO), 75.9 (C^9), 124.6 ($C^{4\text{ or }5}$), 125.1 (C^{11+13}), 125.7 ($C^{3\text{ or }6}$), 129.7 ($C^{4\text{ or }5}$), 133.1 ($C^{3\text{ or }6}$), 139.0 (C^{12}), 141.2 (C^2), 150.7 (C^{14}), 151.9 (C^{10}), 154.3 (C^1), 171.3 (C^7), 177.7 (CO_2). IR (cm^{-1}): $\nu_{asym}(CO_2)$ 1622. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 130. Anal. Calcd for $C_{16}H_{16.6}N_2O_{2.3}Pd$: C, 48.52; H, 4.48; N, 7.07. Found: C, 48.23; H, 4.21; N, 7.22.

Synthesis of [{Pd{*C,N,N*′-C_6H_4{C(Me)=NOCH$_2$(C_5H_4N-2)}-2}$_2$(μ-OAc)]TfO (8a). To a suspension of AgTfO (99%; 44 mg, 0.17 mmol) and AgAcO (99%; 28 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) was added complex **3aCl** (122 mg, 0.33 mmol). The suspension was stirred for 45 min protected from light and then filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), Et_2O (10 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 4 mL) and dried, first by suction and then in a vacuum oven (75 °C, 5h), to give **8a** as a pale yellow solid. Yield: 133 mg, 0.15 mmol, 92%. Mp: 184 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.44 (s, 3 H, Me^8), 2.44 (s, 3 H, Me, AcO), 4.58 (s, 2 H, CH_2), 6.28 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 6.35 (d, 1 H, H^6, $^3J_{HH}$ = 7 Hz), 6.74 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 7.12 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.21 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.42 (m, 1 H, H^{13}), 7.79 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.49 (d, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 12.4 (Me^8), 25.6 (Me, OAc), 75.6 (C^9), 121.1 (q, CF_3, J_{CF} = 321 Hz), 124.7 (C^{13}), 125.1 (C^4), 125.7 (C^{11}), 126.6 (C^3), 128.6 (C^5), 133.0 (C^6), 139.4 (C^{12}), 140.6 (C^2), 148.7 (C^{14}), 151.9 (C^{10}), 154.0 (C^1), 173.2 (C^7), 183.0 (CO_2). $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$, 25 °C): δ −78.8 (TfO). IR (cm^{-1}): $\nu_{asym}(CO_2)$ 1551, ν(S=O, TfO) 1029. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 127. Anal. Calcd for $C_{31}H_{29}F_3N_4O_7Pd_2S$: C, 42.73; H, 3.35; N, 6.43; S, 3.68. Found: C, 42.40; H, 3.06; N, 6.65; S, 3.20. Crystals suitable for an X-ray diffraction study were grown by slow difussion of Et_2O into a solution of **8a** in CH_2Cl_2.

Synthesis of [Pd{*C,N,N*′-C(=NR)C_6H_4{C(Me)=NOCH$_2$(C_5H_4N-2)}-2}Cl] (R = Xy (9a1), ^{t}Bu (9a2)). To a solution of **3aCl** (for **9a1**, 63 mg, 0.17 mmol; for **9a2**, 123 mg, 0.34 mmol) in CH_2Cl_2 (**9a1**, 7 mL) or $CHCl_3$ (**9a2**, 7 mL) was added the appropriate isocyanide (for **9a1**, XyNC, 31 mg, 0.24 mmol; for **9a2**, ^{t}BuNC, 65 μL, 0.58 mmol). The solution was stirred for 2 (**9a1**) or 20 h (**9a2**) and concentrated under vacuum (1 mL). Upon addition of Et_2O (15 mL) a suspension formed, which was filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried, first by suction and then in a vacuum oven (75 °C, 5 h), to give **9a1**·0.3H_2O or **9a2** as a yellow solid.

9a1·0.3H_2O: Yield: 77 mg, 0.39 mmol, 92%. Mp: 210 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.59 (s, 0.6 H, H_2O), 2.39 (vbr s, 3 H, Me, Xy), 2.45 (s, 3 H, Me^8), 2.49 (vbr s, 3 H, Me, Xy), 5.51 (AB system, 2 H, CH_2, ν_A = 6.00, ν_B = 5.03, J_{AB} = 13 Hz), 6.91 (t, 1 H, *para*-CH, Xy, $^3J_{HH}$ = 7 Hz), 7.04 (vbr m, 2 H, *meta*-CH, Xy), 7.31−7.35 (m, 2 H, H^{11+13}), 7.40 (ddd, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.44 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.49 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.64 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.76 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.70 (m, 1 H, H^{14}). (400 MHz, $CDCl_3$, 55 °C): δ 1.45 (s, 0.6 H, H_2O), 2.42 (vbr s, 6 H, Me, Xy), 2.43 (s, 3 H, Me^8), 5.01, 6.00 (two vbr s, 2 H, CH_2), 6.88 (t, 1 H, *para*-CH, Xy, $^3J_{HH}$ = 7 Hz), 7.02 (d, 2 H, *meta*-CH, Xy, $^3J_{HH}$ = 7 Hz), 7.28−7.32 (m, 2 H, H^{11+13}), 7.37 (ddd, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.42 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.47 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.63 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.73 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.72 (ddd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 15.3 (Me^8), 19.4 (br s, Me, Xy), 75.6 (C^9), 122.8 (*para*-CH, Xy), 123.6 (br s, *ortho*-C, Xy), 124.0 (C^{11}), 125.3 (C^{13}), 125.5 (C^6), 127.4 (br s, *meta*-CH, Xy), 128.1 (C^3), 128.7 (C^4), 129.4 (br s, *ortho*-C, Xy), 132.0 (C^2), 132.7 (C^5), 134.4 (C^1), 138.9 (C^{12}), 148.9 (*ipso*-C, Xy), 150.4 (C^{14}), 152.6 (C^{10}), 156.7 (C^7), 178.4 (C=NXy). IR (cm^{-1}): ν(C=NXy) 1652. Anal. Calcd for $C_{23}H_{22.6}ClNO_{3.3}Pd$: C, 54.84; H, 4.52; N, 8.34. Found: C, 54.37; H, 4.16; N, 8.19. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into a solution of **9a1** in CH_2Cl_2.

9a2: Yield: 80 mg, 0.18 mmol, 53%. Mp: 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.84 (s, 9 H, Me, ^{t}Bu), 2.34 (s, 3 H, Me^8), 5.57 (AB system, 2 H, CH_2, ν_A = 6.10, ν_B = 5.05, J_{AB} = 13 Hz), 7.25−

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7.30 (m, 3 H, CH, Ar and/or py-2), 7.38−7.43 (m, 3 H, CH, Ar and/or py-2), 7.82 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.82 (dd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): δ 14.8 (Me^8), 32.3 (Me, ^{t}Bu), 56.8 (CMe_3), 76.0 (C^9), 124.3 (CH, Ar or py-2), 124.5 (CH, Ar or py-2), 125.4 (C^{13}), 127.3 (CH, Ar or py-2), 127.5 (CH, Ar or py-2), 131.8 (C^2), 132.7 (CH, Ar or py-2), 134.5 (C^1), 138.8 (C^{12}), 150.2 (C^{14}), 153.2 (C^{10}), 156.4 (C^7), 169.0 (C═N^{t}Bu). IR (cm^{-1}): ν(C═N^{t}Bu) 1625. Anal. Calcd for $C_{19}H_{22}ClN_3OPd$: C, 50.68; H, 4.92; N, 9.23. Found: C, 50.35; H, 4.98; N, 9.24.

Synthesis of [Pd{*C,N,N′*-C(═NR)C_6H_4{C(Me)═NOCH$_2$(C_5H_4N-2)}-2}(CNR)]ClO_4 (R= Xy (10a1), ^{t}Bu (10a2)). A mixture containing the appropriate complex **5** (for **10a1**: **5a1**, 110 mg, 0.20 mmol; for **10a2**: **5a2**, 15 mg, 0.22 mmol) and RNC (for **10a1**: R = Xy, 32 mg, 0.24 mmol; for **10a2**: R = ^{t}Bu, 28 μL, 0.25 mmol) in $CHCl_3$ (10 mL) was stirred for 2.5 or 4.5 h (**10a2**) and then filtered through a short pad of Celite. The solution was concentrated under vacuum (3 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 2 mL) and dried by suction. **10a1** was recrystallized from CH_2Cl_2/Et_2O and **10a1** and **10a2** were additionally dried in a vacuum oven (70 °C, 10 h) to give **10a1**·0.3H_2O or **10a2** as pale yellow solids.

10a1·0.3H_2O: Yield: 124 mg, 0.18 mmol, 91%. Mp: 194 °C (dec). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.7−2.7 (vbr s, 6 H, Me, Xy^{im}), 2.10 (s, 6 H, Me, Xy^{Pd}), 2.60 (s, 3 H, Me^8), 5.64 (br s, 2 H, CH_2), 6.4−7.4 (vbr s, 2 H, *meta*-Xy^{im}), 6.88 (t, 1 H, *para*-Xy^{im}, $^3J_{HH}$ = 7 Hz), 7.12 (d, 2 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.31 (t, 1 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.58 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz), 7.59−7.68 (m, 4 H, Ar), 7.89 (ddd, H^{11}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz), 8.05 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.29 (ddd, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz). (400 MHz, $CDCl_3$, 55 °C): δ 2.10 (s, 6 H, Me, Xy^{Pd}), 2.24 (br s, 6 H, Me, Xy^{im}), 2.60 (s, 3 H, Me^8), 5.63 (s, 2 H, CH_2), 6.87 (br m, 3 H, *meta*-Xy^{im} + *para*-Xy^{im}), 7.10 (d, 2 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.28 (t, 1 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.56 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.57−7.67 (m, 4 H, Ar), 7.85 ("d", H^{11}, $^3J_{HH}$ = 8 Hz), 8.02 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.30 ("d", 1 H, H^{14}, $^3J_{HH}$ = 5 Hz); (400 MHz, $CDCl_3$, −30 °C): δ 1.94 (s, 3 H, Me, Xy^{im}), 2.11 (s, 6 H, Me, Xy^{Pd}), 2.55 (s, 3 H, Me, Xy^{im}), 2.62 (s, 3 H, Me^8), 5.68 (AB system, 2 H, CH_2, ν_A = 5.73, ν_B = 5.62, J_{AB} = 14 Hz), 6.56 (d, 1 H, *meta*-Xy^{im}, $^3J_{HH}$ = 7 Hz), 6.94 (t, 1 H, *para*-Xy^{im}, $^3J_{HH}$ = 7 Hz), 7.17 (d, 2 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.23 (d, 1 H, *meta*-Xy^{im}, $^3J_{HH}$ = 7 Hz), 7.36 (t, 1 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.60 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.65−7.68 (m, 4 H, Ar), 7.96 ("d", H^{11}, $^3J_{HH}$ = 8 Hz), 8.09 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.27 ("d", 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 15.9 (Me^8), 18.7 (Me, Xy^{Pd}), 18.9 (br, Me, Xy^{im}), 76.0 (C^9), 124.1 (*para*-C, Xy^{im}), 124.6 (br, *ipso*-C, Xy^{Pd}), 126.1 (br, *ortho*-C, Xy^{im}), 126.4 ($C^{3,\,4,\,5\ or\ 6}$), 126.9 (C^{13}), 127.1 (C^{11}), 128.2 (*meta*-C, Xy^{Pd}), 129.6 (C, Ar), 130.7 (C, Ar), 130.8 (*para*-C, Xy^{Pd}), 131.7 (C^2), 132.5 (C^1), 133.4 (C, Ar), 135.5 (*ortho*-C, Xy^{Pd}), 138.5 (m, C≡N), 141.3 (C^{12}), 150.4 (*ipso*-C, Xy^{im}), 150.5 (C^{14}), 153.0 (C^{10}), 159.8 (C^7), 174.8 (C═NXy), *meta*-C, Xy^{im} not observed. IR (cm^{-1}): ν(C≡N) 2198, ν(C═NXy) 1630. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 121. Anal. Calcd for $C_{32}H_{31.6}ClN_4O_{5.3}Pd$: C, 55.00; H, 4.56; N, 8.02. Found: C, 54.60; H, 4.81; N, 7.94.

10a2: Yield: 129 mg, 0.22 mmol, 97%. Mp: 139 °C (dec). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.60 (s, 9 H, Me, ^{t}Bu), 1.67 (s, 9 H, Me, ^{t}Bu), 2.42 (s, 3 H, Me^8), 5.54 (AB system, 2 H, CH_2, ν_A = 5.73, ν_B = 5.35, J_{AB} = 14 Hz), 7.09 (d, 1 H, H^6, $^3J_{HH}$ = 7.5 Hz), 7.41−7.45 (m, 2 H, H^{3+4}), 7.47−7.53 (m, 1 H, H^5), 7.74 (d, 1 H, H^{11}, $^3J_{HH}$ = 8 Hz), 7.78 (ddd, 1 H, H^{13}, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 8.04 (td, 1 H, H^{12}, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.39 (d, 1 H, H^{14}, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 15.1 (Me^8), 29.8 (Me, $^tBu^{Pd}$), 31.1 (Me, $^tBu^{im}$), 56.6 (CMe_3), 59.8 (CMe_3), 76.1 (C^9), 124.1 (C^6), 126.8 (C^{11}), 127.2 (C^{13}), 128.5 (C^3), 129.0 (C^4), 131.2 (C^2), 133.1 (C^5), 133.8 (C^1), 140.8 (C^{12}), 150.7 (C^{14}), 153.0 (C^{10}), 158.7 (C^7), 164.0 (C═N^{t}Bu). IR (cm^{-1}): ν(C≡N) 2210, ν(ClO) 1092, ν(OClO) 625. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 134. Anal. Calcd for $C_{24}H_{31}ClN_4O_5Pd$: C, 48.25; H, 5.23; N, 9.38. Found: C, 48.23; H, 5.17; N, 9.47.

Synthesis of [Pd{*C,N,S*-C(═Xy)C_6H_4{C(Me)═NOCH$_2$SMe}-2}(CNXy)]ClO_4 (11a1). A solution of XyNC (69 mg, 0.53 mmol) in CH_2Cl_2 (9 mL) was slowly added to another of complex **6a4** (110 mg, 0.25 mmol) in the same solvent (10 mL), and the mixture was stirred for 5 h and then filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), and Et_2O (20 mL) was added. The suspension was stirred in an ice/water bath for 15 min and filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried, first by suction and then under vacuum, to give **11a1** as a yellow solid. Yield: 151 mg, 0.23 mmol, 91%. Mp: 161 °C (dec). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.13 (s, 6 H, Me, Xy^{Pd}), 2.16 (br s, 6 H, Me, Xy^{im}), 2.50 (s, 3 H, Me^{10}), 2.92 (s, 3 H, Me^8), 4.7−5.4 (br s, 2 H, CH_2), 6.7−7.0 (vbr s, 1 H, *meta*-Xy^{im}), 6.87 (br "t", 1 H, *para*-Xy^{im}, $^3J_{HH}$ = 7 Hz), 7.12 (d, 2 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.15−7.30 (vbr s, 1 H, *meta*-Xy^{im}), 7.30 (t, 1 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.62 (td, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.70 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.75 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.96 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 16.46 (Me^8), 16.53 (Me^{10}), 18.5 (Me, Xy^{Pd}), 19.0 (br, Me, Xy^{im}), 75.0 (C^9), 124.3 (CH, Xy^{im}), 124.8 (br, *ipso*-C, Xy^{Pd}), 126.6 (br, Xy^{im}), 127.1 (C^6, Ar), 128.0 (br, Xy^{im}), 128.2 (*meta*-C, Xy^{Pd}), 128.6 (br, Xy^{im}), 130.2 (C^4, Ar), 130.5 (C^3), 130.7 (*para*-C, Xy^{Pd}), 130.9 (C^2, Ar), 133.8 (C^5, Ar), 134.2 (C^1), 135.0 (*ortho*-C, Xy^{Pd}), 138.2 (m, C≡N or *ipso*-C(Xy^{im})), 150.5 (C, Xy^{im}), 167.8 (C^7), 174.3 (C═NXy). IR (cm^{-1}): ν(C≡N) 2198, ν(C═NXy) 1636. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 136. Anal. Calcd for $C_{28}H_{30}ClN_3O_5PdS$: C, 50.77; H, 4.56; N, 6.34; S, 4.84. Found: C, 50.69; H, 4.48; N, 6.40; S, 4.55.

Synthesis of [Pd{*C,N,S*-C(N═^{t}Bu)C_6H_4{C(Me)═NOCH$_2$SMe}-2}CN^{t}Bu]ClO_4 (11a2). To a solution of **6a2** (102 mg, 0.21 mmol) in CH_2Cl_2 (5 mL) was added ^{t}BuNC (26 μL, 0.23 mmol). After 1.5 h of stirring the solvent was removed under vacuum, and the residue was stirred with *n*-pentane (12 mL). The suspension was filtered, and the solid was washed with pentane (3 × 3 mL) and dried, first by suction and then in a vacuum oven (60 °C, 10 h), to give **11a2** as a yellow solid. Yield: 95 mg, 0.168 mmol, 79%. Mp: 92 °C (dec). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.57 (s, 18 H, Me, ^{t}Bu) 2.52 (s, 3 H, Me^{10}), 2.73 (s, 3 H, Me^8), 5.04 (br AB system, 2 H, CH_2, ν_A = 4.88, ν_B = 5.18, J_{AB} = 10 Hz), 7.17 (d, 1 H, H^6, $^3J_{HH}$ = 7 Hz), 7.45 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.55 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.72 (d, 1 H, H^3, $^3J_{HH}$ = 8 Hz). $^3C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 15.5 (Me^8), 17.2 (Me^{10}), 29.8 (Me, ^{t}Bu), 31.1 (Me, ^{t}Bu), 56.6 (CMe_3), 59.6 (CMe_3), 75.7 (C^9), 124.7 (C^6), 128.7 (C^4), 129.4 (C^3), 130.4 (C^2), 133.5 (C^5), 135.0 (C^1), 161.1 (C═N^{t}Bu), 166.1 (C^7). IR (cm^{-1}): ν(C≡N) 2210, ν(ClO) 1090, δ(OClO) 623. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 127. Anal. Calcd for $C_{20}H_{30}ClN_3O_5PdS$: C, 42.41; H, 5.34; N, 7.42; S, 5.66. Found: C, C, 42.53; H, 5.06; N, 7.43; S, 5.80.

Synthesis of [Pd{*C,N,C′*-C_6H_4{C(Me)═NOC(CO$_2$Me)═C-(CO$_2$Me)}-2}(^{t}Bubpy)] (12). To a solution of **2a** (114 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) was added dimethyl acetylenedicarboxylate (36 μL, 0.29 mmol). The resulting solution was stirred for 1.5 h and filtered through a short pad of Celite, the solution was concentrated under vacuum (1 mL), and a mixture of Et_2O and *n*-pentane (1:3, 20 mL) was added. The suspension was filtered, and the solid was washed successively with the same solvent mixture (3 × 3 mL) and with Et_2O (3 mL) to give **12** (131 mg, 0.20 mmol, 71%). Mp: 167 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.37 (s, 18 H, Me, ^{t}Bu), 2.24 (s, 3 H, Me^8), 3.47 (s, 3 H, CO_2Me), 3.77 (s, 3 H, CO_2Me), 6.11−6.15 (m, 1 H, $H^{4,\,5\ or\ 6}$), 6.78−6.83 (m, 2 H, $H^{4,\,5\ and/or\ 6}$), 6.84−6.87 (m, 1 H, H^3), 7.30 (dd, 2 H, H^{18}, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 8.64 (d, 1 H, H^{19}, ^{t}Bubpy, $^3J_{HH}$ = 6 Hz), 8.66 (d, 2 H, H^{16}, ^{t}Bubpy, $^4J_{HH}$ = 2 Hz). $^3C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 11.7 (Me^8), 30.3 (Me, ^{t}Bu), 35.3 (CMe_3), 50.7 (CO_2Me), 52.2 (CO_2Me), 121.2 (C^{18}), 121.8 (C^{16}), 123.8 ($C^{4,\,5\ or\ 6}$), 125.4 (C^3), 130.4 ($C^{4,\,5\ or\ 6}$), 132.8 ($C^{4,\,5\ or\ 6}$), 144.0 ($C^{9\ or\ 10}$), 147.8 (C^2), 150.0 (C^{19}), 152.0 ($C^{9\ or\ 10}$), 157.6 (C^{15}), 157.9 (CO_2Me), 161.4 (C^{17}), 163.8 (C^1), 169.4 (C^7), 173.3 (CO_2Me). IR (cm^{-1}): ν(C═O) 1718, 1688. Anal. Calcd for $C_{32}H_{37}N_3O_5Pd$: C, 59.13; H, 5.74; N, 6.46. Found: 59.01; H, 5.79; N, 6.42.

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Synthesis of [Pd{*C,N,C′*-C_6H_4{C(Me)=NOC(CO_2Me)=C-(CO_2Me)}-2}(L)] (L = $ClCH_2$py-2 (13), XyNC (14), ^{t}BuNC (15)). To a solution of **2a** (for **13**, 160 mg, 0.32 mmol; for **14**, 102 mg, 0.20 mmol; for **15**, 124 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was added dimethyl acetylenedicarboxylate (for **13**, 40 μL, 0.32 mmol; for **14**, 26 μL, 0.21 mmol; for **15**, 32 μL, 0.26 mmol). The resulting solution was stirred for 1 h, and the appropriate ligand was then added (for **13**, $ClCH_2$py-2 prepared *in situ* from ($ClCH_2$pyH-2)Cl (66 mg, 0.4 mmol) and K^{t}BuO (44 mg, 0.37 mmol) in CH_2Cl_2 (5 mL); for **14**, CNXy, 27 mg, 0.21 mmol; for **15**, ^{t}BuNC, 56 μL, 0.50 mmol). After 1.5 or 2 h (**15**) of stirring, the reaction mixture was filtered through a short pad of Celite. For **13**, the solution was concentrated under vacuum (1 mL), Et_2O (15 mL) was added, and the suspension was filtered to remove some impurities. The filtrate was concentrated to dryness, the residue was dissolved in CH_2Cl_2 (2 mL), and a mixture of Et_2O/*n*-pentane (1:3, 20 mL) was added. The suspension was filtered, and the solid collected was successively washed with the same mixture of solvents (3 × 3 mL) and with Et_2O (3 mL). For **14** and **15**, the solution was concentrated (0.5−1 mL), Et_2O (15 mL) was added, the suspension was filtered, and the solid collected was washed with Et_2O (3 × 2 mL). The yellow compounds were all dried by suction, and **15** was additionally dried under vacuum.

13: Yield: 83 mg, 0.16 mmol, 52%. Mp: 163 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.36 (s, 3 H, Me^8), 3.36 (s, 3 H, CO_2Me), 3.75 (s, 3 H, CO_2Me), 5.21 (AB system, 2 H, CH_2, ν_A = 5.20, ν_B = 5.23, J_{AB} = 14 Hz), 6.25−6.29 (m, 1 H, H$^{4\text{ or }6}$), 6.94−7.01 (m, 2 H, H$^{5+4\text{ or }6}$), 7.03−7.07 (m, 1 H, H^3), 7.37 (ddd, 1 H, H^{18}, py-2, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.85 (d, 1 H, H^{16}, py-2, $^3J_{HH}$ = 8 Hz), 7.92 (td, 1 H, H^{17}, py-2, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.81 (d, 1 H, H^{19}, $^3J_{HH}$ = 6 Hz). ^{3}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 12.0 (Me^8), 46.0 (CH_2), 50.8 (CO_2*Me*), 52.1 (CO_2*Me*), 123.8 (C^{18}), 124.6 (C^{16}), 124.7 (C$^{4\text{ or }6}$), 126.3 (C^3), 131.0 (C^5), 132.7 (C$^{4\text{ or }6}$), 138.0 (C^{17}), 145.0 (C$^{9\text{ or }10}$), 148.7 (C^2), 150.1 (C$^{9\text{ or }10}$), 151.3 (C^{19}), 157.5 (C^{15}), 157.7 (CO_2Me), 164.2 (C^1), 170.2 (C^7), 173.0 (CO_2Me). IR (cm^{-1}): ν(C=O) 1721, 1702. Anal. Calcd for $C_{20}H_{19}ClN_2O_5Pd$: C, 47.17; H, 3.76; N, 5.50. Found: C, 46.83; H, 3.79; N, 5.35. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of *n*-pentane into a solution of **13** in acetone.

14: Yield: 70 mg, 0.14 mmol, 68%. Mp: 165 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.37 (s, 3 H, Me^8), 2.48 (s, 6 H, Me, Xy), 3.73 (s, 3 H, CO_2Me), 3.77 (s, 3 H, CO_2Me), 7.03 (m, 1 H, H^4), 7.07−7.12 (m, 2 H, H^{3+5}), 7.16 (d, 2 H, *meta*-Xy, $^3J_{HH}$ = 8 Hz), 7.25−7.29 (m, 1 H, *para*-Xy), 7.31 (d, 1 H, H^6, $^3J_{HH}$ = 7/7.1 Hz). ^{3}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 11.9 (Me^8), 18.8 (Me, Xy), 51.4 (CO_2*Me*), 52.3 (CO_2*Me*), 125.0 (C^{4}H), 126.5 (*ipso*-C, Xy), 127.1 (C^3), 128.1 (*meta*-CH, Xy), 129.7 (*para*-CH, Xy), 131.9 (C^5), 135.4 (*ortho*-C, Xy), 136.9 (C^6), 147.5 (C$^{9\text{ or }10}$), 147.9 (C$^{9\text{ or }10}$), 148.8 (C^2), 158.1 (CO_2Me), 163.2 (C^1), 172.1 (C^7), 174.2 (CO_2Me). IR (cm^{-1}): ν(C≡N) 2172; ν(C=O) 1715, 1691. Anal. Calcd for $C_{22}H_{22}N_2O_5Pd$: C, 53.87; H, 4.32; N, 5.46. Found: C, 53.90; H, 4.46; N, 5.33.

15: Yield: 71 mg, 0.15 mmol, 63%. Mp: 153 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.58 (s, 9 H, Me, ^{t}Bu), 2.33 (s, 3 H, Me^8), 3.76 (s, 6 H, CO_2Me), 6.98−7.04 (m, 2 H, H^{3+4}), 7.08 (td, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.14 (d, 1 H, H^6, $^3J_{HH}$ = 7 Hz). ^{3}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 11.8 (Me^8), 30.3 (Me, ^{t}Bu), 51.1 (CO_2*Me*), 52.1 (CO_2*Me*), 58.0 (*C*Me$_3$), 124.7 (C^4), 126.8 (C^3), 131.7 (C^5), 134.3 (1:1:1, t, C≡N, $^1J_{CN}$ = 17 Hz), 136.5 (C^6), 147.0 (C$^{9\text{ or }10}$), 148.2 (C$^{9\text{ or }10}$), 148.8 (C^2), 158.0 (CO_2Me), 163.2 (C^1), 171.6 (C^7), 173.9 (CO_2Me). IR (cm^{-1}): ν(C≡N) 2195; ν(C=O) 1716, 1704. Anal. Calcd for $C_{19}H_{22}N_2O_5Pd$: C, 49.10.87; H, 4.77; N, 6.03. Found: C, 48,82; H, 4.53; N, 5.74.

X-ray Structure Determinations of Complexes 3aBr, 3bCl, 5a3, 6a1, 8a·CH_2Cl_2, 9a1, and 13. All complexes were measured on a Bruker Smart APEX machine at 100 K. Data were collected using monochromated Mo Kα radiation in ω-scan mode. The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl groups were refined using rigid groups (AFIX 137), and the others were refined using a riding model.

Crystallography data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 891028 (**3aBr**), 891029 (**3bCl**), 891030 (**5a3**), 891031 (**6a1**), 891032 (**8a**·CH_2Cl_2) 891033 (**9a1**), and 891968 (**13**). Copies of these data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk; or http://www.ccdc.cam.ac.hk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and tables giving crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(42) HRMS (ESI+, *m*/*z*): calcd for $C_{17}H_{21}N_2O_4$ ($[M]^+$ + 2 H^+) 317.1501, found 317.1506. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): 2.32 (s, 3 H, Me), 3.85 (s, 3 H, OMe^4), 3.88 (s, 6 H, OMe^{3+5}), 5.39 (s, 2 H, CH_2), 6.87 (s, 2 H, H^{2+6}, Ar), 7.21 (m, 1 H, py), 7.42 (d, 1 H, py, $^3J_{HH}$ = 8 Hz), 7.70 (td, 1 H, py, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.59 (m, 1 H, py). $^{13}C\{^1H\}$-APT NMR (75 MHz, $CDCl_3$, 25 °C): 13.1 (Me), 56.1(OMe^{3+5}), 60.8 (OMe^4), 76.6 (CH_2), 103.5 (CH^{2+6}, Ar), 121.6 (CH, py), 12.3 (CH, py), 131.9 (C), 136.5 (CH, py), 139.1 (C), 149.1 (CH, py), 153.0 (C^{3+5}), 155.2 (C), 158.4 (C).

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