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Synthesis of 1,2-Dihydroquinazolinium-4-yl Palladium Complexes through a Cyclization Reaction

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The reaction of *trans*-[PdI{C(=NXy)$C_6H_4NH_2$-2}$(CNXy)_2$] (**1**, Xy = $C_6H_3Me_2$-2,6) with HO_3SCF_3 (HOTf) and RC(O)R′ affords 1,2-dihydro-3-xylylquinazolinium-4-yl complexes *trans*-[PdI{C=N(Xy)C(R)(R′)NHC_6H_4-2}$(CNXy)_2$]OTf (R = Me, R′ = Me (**2a**), Ph (**2b**), $CH_2C(O)Me$ (**2c**), H (**2d**), R = H, R′ = H (**2e**), CH=CH_2 (**2f**), Ph (**2g**), C_6H_4Me-4 (To) (**2h**), {Fe(C_5H_4)(C_5H_5)} (Fc) (**2i**)). In the absence of a carbonyl compound, the reaction of **1** with HOTf yields complex *SP-4-4*-[PdI{*C,N*-C(=NHXy)$C_6H_4NH_2$-2}CNXy]OTf (**3**), which reacts with PPh_3 to give *SP-4-3*-[PdI{C(=NHXy)$C_6H_4NH_2$-2}(CNXy)(PPh_3)]OTf (**4**). In turn, **4** reacts with RC(O)R′ to give complexes *SP-4-3*-[PdI{C=N(Xy)C(R)(R′)NHC_6H_4-2}(CNXy)(PPh_3)]OTf (R = R′ = Me (**2′a**), R = H, R′ = CH(Me)(Ph) (**2′b**), To (**2′c**)). A possible intermediate in the cyclization process, *trans*-[PdI{C(=NXy)C_6H_4N=CHTo-2}$(CNXy)_2$] (**6**), has been prepared by reacting IC_6H_4N=CHTo-2, $[Pd_2(dba)_3]\cdot$dba ("Pd$(dba)_2$") (dba = dibenzylideneacetone) with N^N (to give [PdI(C_6H_4-N=CHTo-2)(N^N)] (N^N^ = 2,2′-bipyridine (bpy, **5a**), 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbp, **5b**)) and XyNC. The crystal structures of complexes **2i**, **2′a**, **3**, and **6** have been determined, and the electrochemical behavior of **2i** has been studied.

Introduction

We are studying the synthesis and reactivity of *ortho*-functionalized aryl metal complexes. In particular, insertion reactions of isocyanides into the Pd−C bond have allowed us to prepare a variety of iminobenzoyl palladium complexes (I; Scheme 1)[1−6] as well as some heterocycles (for example, II).[3,7] Additionally, sometimes metalated heterocycles (for example III) form after an intramolecular process.[6,8]

We have decided to study the reactivity of our ortho-functionalized iminobenzoyl complexes I with the hope that interesting results could arise due to the modified reactivity imposed by the metal center on both the X and −C=NR groups (Scheme 1) or to their joint reactivity favored by their vicinity. This paper describes the first results of this novel approach, namely, the synthesis of a family of 1,2-dihydro-3-xylylbenzoquinazolinium-4-yl palladium complexes (IV; Scheme 1) by reacting 2-aminoxylyliminobenzoyl palladium complexes (I, R = Xy, X = NH_2) with carbonyl compounds (aldehydes or ketones) and an acid. A different method described recently by us gave the first two 1,2-dihydroquinazolinium-4-yl complexes;[6] however it lacks the applicability of the present method.

Quinazoline-based structures have attracted considerable attention over the years since they are present in many natural or synthetic products with interesting pharmacological antitumor, antidepressant, anti-inflammatory, or antimalaria properties.[9,10]

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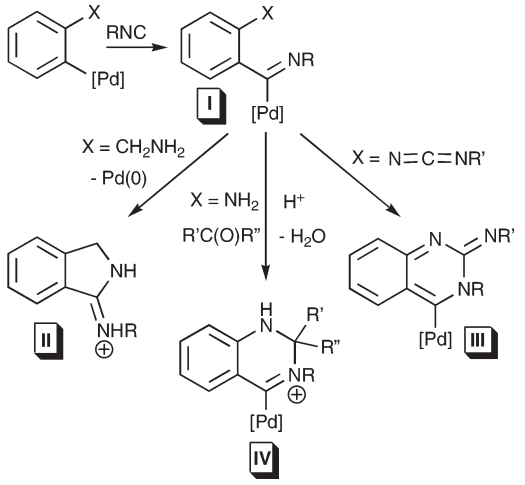
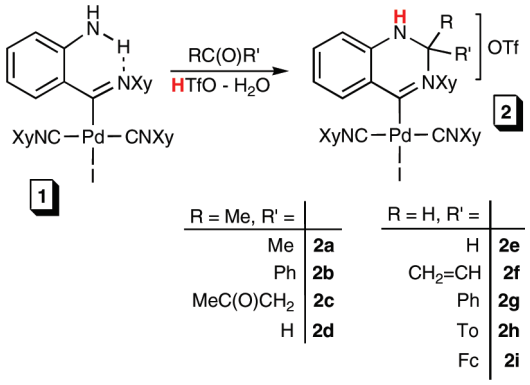
Scheme 1. Cyclization Reactions from *ortho*-Substituted Iminoacyl Palladium Complexes



Scheme 2

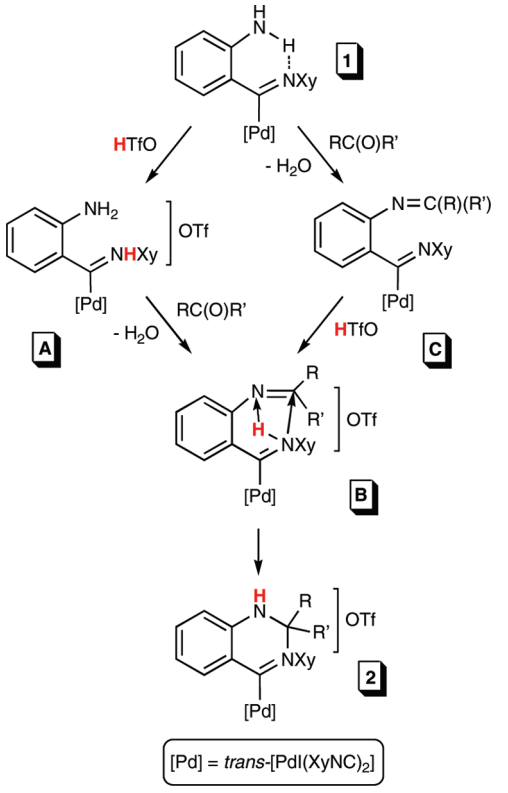


Nonmetalated 1,2-dihydroquinazolinium derivatives have been prepared through a variety of methods with the participation, in some cases, of Li or Grignard derivatives.[10,11] The method reported herein could open ways for the stoichiometric or catalytic synthesis of dihydroquinazoline derivatives, which could also form by depalladation of our complexes.

Results and Discussion

Synthesis and Reaction Pathway. While studying the reactivity of different iminobenzoyl palladium complexes toward a variety of reagents, we found that protonation of *trans*-[PdI{C(=NXy)$C_6H_4NH_2$-2}$(CNXy)_2$][1] (**1**, Scheme 2) with HOTf (OTf = O_3SCF_3) in acetone afforded *trans*-[PdI{C=N(Xy)$CMe_2NHC_6H_4$-2}$(CNXy)_2$]OTf (**2a**). The scope of this reaction is quite general because similar complexes [PdI{C=N(Xy)C(R)(R′)NHC_6H_4-2}$(CNXy)_2$]OTf (R = Me, R′ = Ph (**2b**), $CH_2C(O)Me$ (**2c**), H (**2d**), R = H, R′ = H (**2e**), $CH=CH_2$ (**2f**), Ph (**2g**), C_6H_4Me-4 (To) (**2h**), {$Fe(C_5H_4)(C_5H_5)$} (Fc) (**2i**)) could be obtained when **1** was reacted with HOTf and different carbonyl compounds RC(O)R′ in CH_2Cl_2 or using the carbonyl compound as solvent (**2b**, **2c**). In general, the isolation of complexes **2** was achieved by adding cold Et_2O to the concentrated reaction mixture and stirring the suspension in a cold bath because otherwise oily materials tend to form.

Scheme 3



The synthesis of the first 1,2-dihydroquinazolinium-4-yl (in what follows DHQ) metal complexes, namely, *trans*-[PdI_2-{C=N(Xy)C(Me){$CH_2C(O)Me$}NHC_6H_4-2}(CNXy)L] (L = PPh_3, CNXy), was recently reported by us through an intramolecular process that lacks the wide applicability of the method we report here.[6]

In search of the reaction pathway leading to complexes **2**, we have considered (Scheme 3) protonation followed by a condensation reaction (**1** → **A** → **B** → **2**) and the opposite sequence (**1** → **C** → **B** → **2**). With this purpose, the reaction of **1** with triflic acid in CH_2Cl_2 was studied. Although protonation of other palladium iminoacyl complexes has been previously found to give readily the corresponding iminium-benzoyl species,[6,12] the expected complex **A** ([Pd] = [PdI$(CNXy)_2$], Scheme 4) was not isolated. Instead, the reaction led to precipitation of the chelate complex *SP-4-4*-[PdI{*C,N*-C(=NHXy)$C_6H_4NH_2$-2}CNXy]OTf (**3**), resulting after protonation of the iminobenzoyl nitrogen atom and XyNC replacement. Probably, the protonation of the iminoacyl group gives **A** by splitting the intramolecular N−H···N hydrogen bond present in **1**,[1] which allows the displacement of one of the XyNC ligands by the NH_2 group favored by the chelate effect and the insolubility of **3**. From the reaction of **3** with excess XyNC (1:1.2) in CH_2Cl_2 we could not isolate

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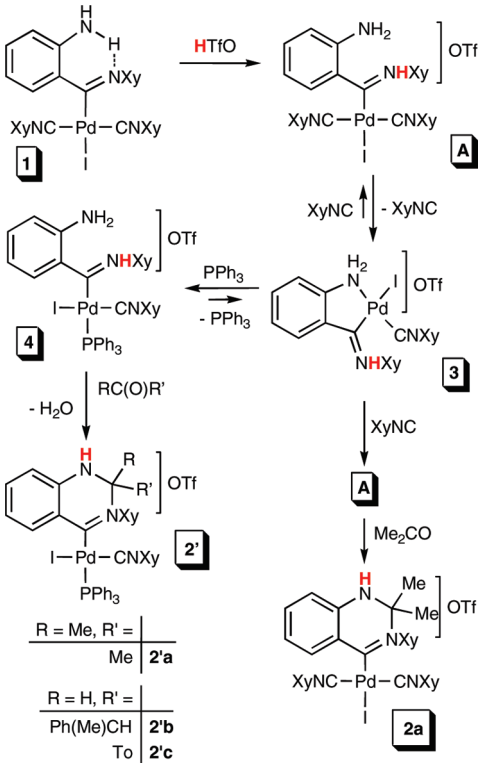
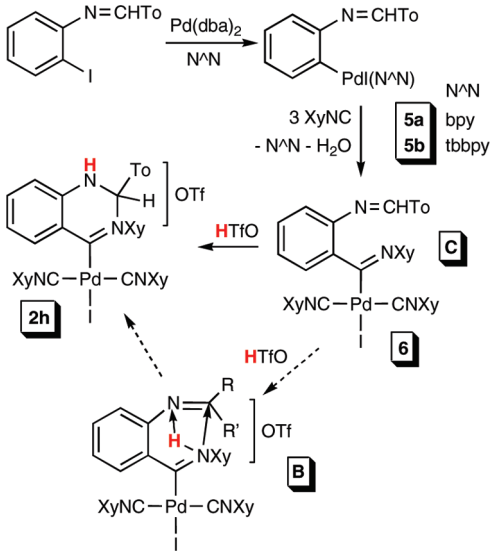
Scheme 4



complex **A**; a mixture formed instead, which, upon recrystallization, gave **3** as the only identified product. However, this reaction in acetone gives, probably through **A**, complex **2a** (Scheme 4) although in lower yield than starting from **1**. Likely, in acetone some side products are also formed. The reaction of **1** with HOTf and acetophenone or acetylacetone gives, along with **2b** or **2c**, appreciable amounts of complex **3**, even when the ketones are used as solvents. The reaction of **1** with HOTf and benzophenone (1:1:10, in CH_2Cl_2, 3.5 h) gave 70% yield of complex **3**, while only traces of the expected complex *trans*-[PdI{C=N(Xy)CPh_2NHC_6H_4-2}(CNXy)$_2$]OTf could be observed in the ^{1}H NMR spectrum of the mother liquor. This suggests that for bulky ketones a slow condensation reaction (**A** → **B**, Scheme 3) allows the chelation reaction (**A** → **3**, Scheme 4) to take place. In these cases, the reaction workup is not as straigthforward and the yield of complexes **2b** and **2c** is low.

The reaction of **3** with PPh_3 (1:1.2, CH_2Cl_2) afforded the **A**-type complex *SP-4-3*-[PdI{C(=NHXy)$C_6H_4NH_2$-2}(CNXy)(PPh_3)]OTf (**4**, Scheme 4). Although this complex was characterized by elemental analyses and ^{1}H NMR, neither its ^{13}C NMR spectrum nor its crystal structure could be obtained because it slowly decomposes back to **3**. In fact, crystals of **3** suitable for an X-ray diffraction study were

Scheme 5



obtained when we attempted to grow single crystals of **4**. Therefore, in solution it behaves as we assume for its homologue **A**, although more slowly. The decomposition of **4** into **3** is favored by the chelate effect and the strong transphobic effect[1,4,13] between the iminiumbenzoyl and PPh_3 ligands.[14] In agreement with our expectations, **4** reacted with RC(O)R′ to give *SP-4-3*-[PdI{C=N(Xy)C(R)(R′)NHC_6H_4-2}(CNXy)(PPh_3)]OTf (R = R′ = Me (**2′a**), R = H, R′ = CH(Me)Ph (**2′b**), To (**2′c**)), and **3** reacted with PPh_3 in acetone to afford **2′a**. Therefore, complex **4** is an isolated complex of type **A** that behaves as an intermediate in the synthesis of DHQ complexes.

We have also considered the reverse reaction pathway **1** → **C** → **B** → **2** (Scheme 3), involving condensation of **1** with RC(O)R′ followed by the protonation and cyclization processes. Complex **1** did not react with acetone or ToCHO even by refluxing the mixture in the presence of molecular sieves, and when 0.1 equiv of HOTf was added to catalyze the process, only a 10:1 **1**:**2a** or **1**:**2h** mixture, respectively, was isolated. However, we have independently prepared the **C**-type complex with R = H, R′ = To (Scheme 5). Thus, the reaction of IC_6H_4N=CHTo-2 with Pd(dba)$_2$ and N^N (1:1:1) afforded [PdI(C_6H_4N=CHTo-2)(N^N)] (N^N = bpy (**5a**), tbbpy (**5b**)), which, in turn, reacted with XyNC (1:3) to yield *trans*-[PdI{C(=NXy)C_6H_4N=CHTo-2}(CNXy)$_2$] (**6**, Scheme 2). The **C**-type complex **6** reacted inmediately with HOTf to give complex **2h**.

Since both the reaction of **4** with acetone and that of **6** with HOTf produced **2′a** and **2h**, respectively, we believe that both reaction pathways (**1** → **A** → **B** → **2** and **1** → **C** → **B** → **2**) could be involved in the cyclization process. Although we have not detected intermediate **C** from **1**, its formation in trace amounts cannot be discharged, and its fast reaction with acid could give the DHQ complexes.

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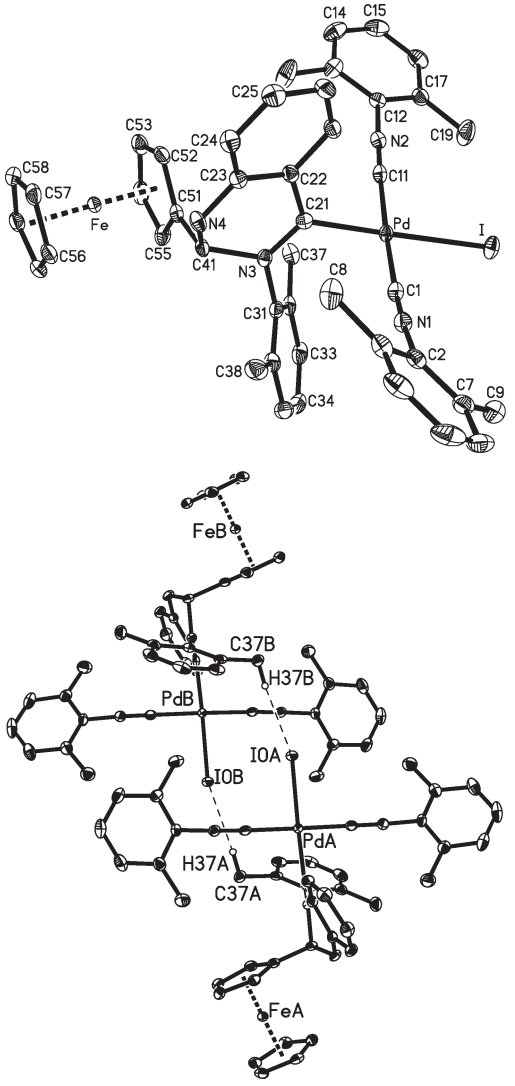


Figure 1. (Top) Crystal structure of the cation of **2i**·$CHCl_3$. The thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(1) 1.965(2), Pd−C(11) 1.967(2), Pd−C(21) 2.0311(19), Pd−I 2.6421(3), C(21)−C(22) 1.441(3), C(22)−C(23) 1.418(3), N(3)−C(21) 1.310(3), N(3)−C(31) 1.452(2), N(3)−C(41) 1.513(2), N(4)−C(23) 1.358(3), N(4)−C(41) 1.434(3); C(1)−Pd−C(21) 87.41(8), C(11)−Pd−C(21) 92.71(7), C(1)−Pd−I 91.15(6), C(11)−Pd−I 88.48(6). (Bottom) Packing diagram: C(37)−H(37) 0.98, H(37)···I#1 3.09, C(37)···I#1 3.914, C(37)−H(37)−I#1 142.1. Hydrogen atoms, except H(37), are omitted for clarity.

Crystal Structures. The crystal structures of complexes **2i**·$CHCl_3$ (Figure 1), **2′a**·H_2O (Figure 2), **3**·CH_2Cl_2 (Figure 3), and **6** (Figure 4) have been determined by X-ray diffraction. Those of **2f**, **2h**, and **5a** will be published elsewhere. The palladium atom in all of them is in a distorted square-planar environment. In complexes **2i** and **2′a** (in what follows complexes **2**) the heterocycle adopts a boat conformation with C(22) and C(41) out of the plane formed by the four other atoms. The C(22)−C(21)−N(3) plane is almost perpendicular to both the coordination and the C(31)→C(36) xylyl planes (torsion angles 79.4°, 72.1° (**2i**), 94.4°, 98° (**2′a**)). The molecules of **2i**·$CHCl_3$ pack into dimers (Figure 3) due to C(37)−H(37C)···I#1 hydrogen bonds. Complex **3** shows D−H···O_{OTf} hydrogen bond interactions, where D is C(28), C(7), N(1), and N(2).

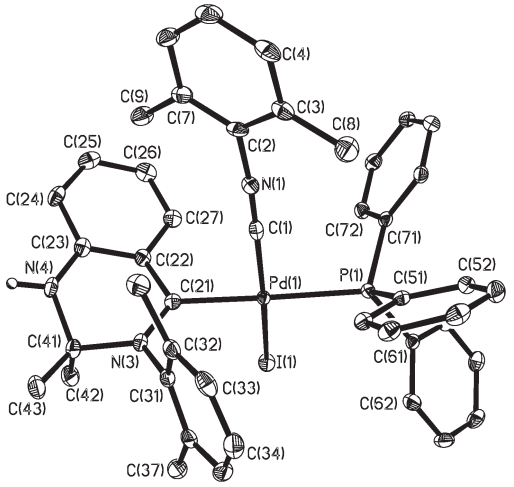


Figure 2. Crystal structure of the cation of **2′a**·H_2O. The thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(1) 1.967(3), Pd−C(21) 2.053(2), Pd−P 2.3456(6), Pd−I 2.5983(2), C(21)−C(22) 1.443(3), C(22)−C(23) 1.419(3), N(3)−C(21) 1.315(3), N(3)−C(31) 1.459(3), N(3)−C(41) 1.531(3), N(4)−C(23) 1.360(3), N(4)−C(41) 1.452(3); C(1)−Pd−C(21) 89.50(9), C(1)−Pd−P(1) 89.36(7), P−Pd−I 93.478(16), C(21)−Pd−I 87.47(6).

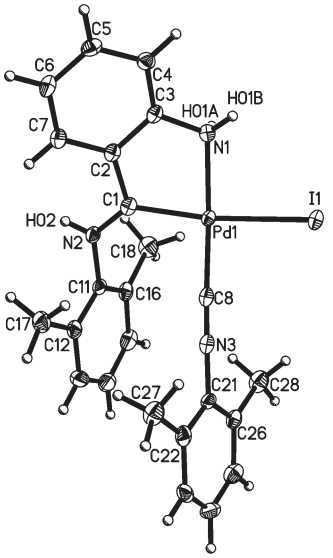


Figure 3. Crystal structure of the cation of **3**·CH_2Cl_2. The thermal ellipsoids are displayed at 50% probability. Solvent is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(1) 2.009(3), Pd−C(8) 1.930(3), Pd−N(1) 2.073(3), Pd−I 2.6391(3), C(1)−N(2) 1.282(4); C(1)−Pd−C(8) 97.04(12), C(1)−Pd−N(1) 80.73(11), C(8)−Pd−I 90.12(9), N(1)−Pd−I 91.92(7).

The common DHQ skeleton in complexes **2** (Figures 1 and 2) shows similar bond distances and angles. The Pd−C(21) bond distance in **2i** (2.0311(19) Å) < **2′a** (2.053(2) Å) shows the *trans* influence sequence I < PPh_3. The Pd−C(1) bond length in **3** (2.009(3)) is significantly shorter than the above C(DHQ)−Pd distances probably due to the chelating nature of the orthoamino-iminiumacyl ligand. The stereochemistry in **2′a**, in spite of the great C/P transphobia[1,4,13] between the DHQ and PPh_3 ligands,[14] is probably due to steric reasons.

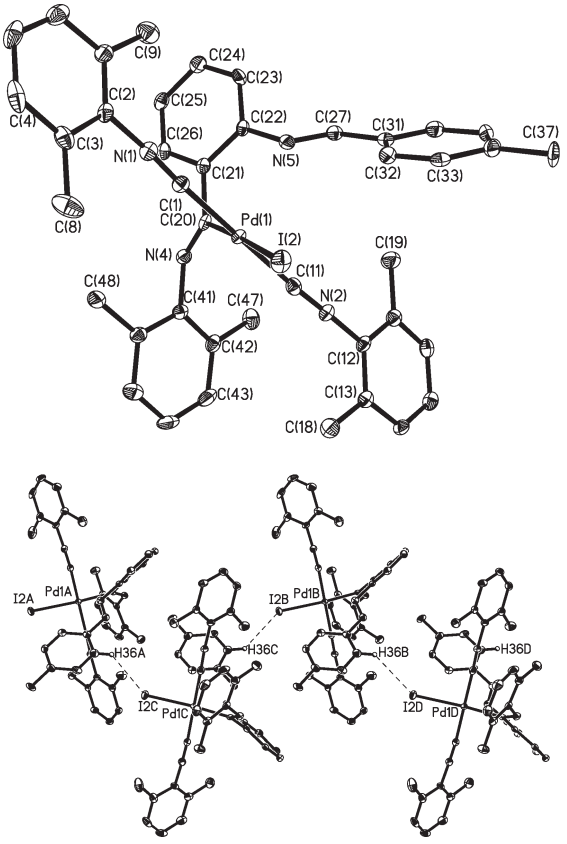


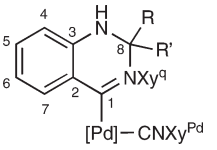
Figure 4. (Top) Crystal structure of complex **6**. The thermal ellipsoids are displayed at 50% probability. Selected bond lengths (Å) and angles (deg): Pd−C(1) 1.977(3), Pd−C(11) 1.972(3), Pd−C(20) 2.050(3), Pd−I(2) 2.7164(3), C(20)−N(4) 1.263(4), N(4)−C(41) 1.414(4), C(20)−C(21) 1.493(4), N(5)−C(27) 1.281(4); C(1)−Pd−C(20) 89.04(11), C(1)−Pd−I(2) 88.58(9), C(11)−Pd−C(20) 90.67(12), C(11)−Pd(1)−I(2) 91.70(9). (Bottom) Packing diagram. C(36)−H(36) 0.95, H(36)···I(2)#13.13, C(36)···I(2)#1 3.861(3); C(36)−H(36)−I(2)#1 135.2.

However, in **3** the isocyanide ligand is *trans* to the NH_2 group due to great C/C transphobia and because steric repulsions are much less important than in **2′a**. The two pairs of distances C(22)−C(21), Pd−C(21) and C(21)−N(3), N(3)−C(31) in **2i** (1.441(3), 2.0311(19) and 1.310(3), 1.452(2) Å, respectively) are shorter and longer, respectively, than those in its parent complex **1** (1.486(5), 2.059(4) and 1.264(5), 1.417(5) Å, respectively).[1] Both observations suggest a migration of π-electron density from the Xy−N=C-(21) fragment to the C−C−Pd moiety due to the cyclization process. In general, the C(22)−C(21) bond lengths are shorter and the pair of bond distances N(3)−C(21), N(3)−C(31) are longer in complexes **2** than in other palladium xylyliminobenzoyl complexes:[1,2,4,15] 1.441(3)−1.449(3) Å vs 1.476−1.512 Å, 1.310(3)−1.318(3) Å vs 1.251−1.283 Å, and 1.454-(3)−1.459(3) Å vs 1.392−1.453 Å, respectively.

The structure of complex **6** (Figure 4) shows in its fragment Xy−N=C(C)−Pd, the Pd−C, C=N, and C−C bond distances (2.050(3), 1.263(4), 1.493(4) Å, respectively), similar to those in **1** (2.059(4), 1.264(5), 1.486(5) Å),[1] while the Xy−N length is shorter in **6** (1.414(4) Å vs 1.452(2) Å) probably due to the XyN···H hydrogen bond in **1**. Additionally, the iminoacyl C=N bond distance in **6** (1.263(4) Å) is shorter than that in the imino C=N group (1.281(4) Å), which in turn is similar to that of the iminiumacyl C=N bond in **3** (1.282(4) Å) or even shorter than that in complexes **2** (1.315(3) Å (**2′a**), 1.310(3) Å (**2i**)). The molecules of **6** (Figure 4) pack into chains along the *b* axis due to intermolecular C(36)−H(36)···I(2)#1 hydrogen bonds in which the tolyl group is involved.

(15) *Cambridge Structural Database, versión 5.30*; Cambridge Crystallographic Data Centre: Cambridge, U.K., November 2008; www.ccdc.cam.ac.uk

Chart 1



Comparison of the Pd−I bonds in all these complexes suggests the *trans* influence of the ligands to follow the series DHQ (2.6421(3) Å (**2i**)) ∼ iminiumacyl (2.6391(3) Å (**3**)) > XyNC (2.5983(2) Å (**2′a**)). The neutral nature of **6** can be responsible for its long Pd−I bond distance (2.7164(3) Å) compared to that in the other cationic complexes because all have a carbon donor ligands *trans* to I.

IR and NMR Spectra. Complexes **2a**−**i** show in their IR spectra a single ν(C≡N) band indicating the mutually *trans* disposition of the two XyNC ligands in the solid state, as has been established in the X-ray diffraction studies of complexes **2f**, **2h**, and **2i**. Some NMR data also confirm this disposition in solution (see below).

The NMR spectra of **2a** and **2e** (R = R′ = Me, H, respectively) show, as expected, single resonances for the R substituents and the methyls in the xylyl groups Xy−N=C (Xy^q) and Xy−NCPd (Xy^{Pd}; see Chart 1). The same is observed in the room-temperature ^{1}H and ^{13}C NMR spectra of complexes **2b** and **2c**, showing that rotation around the Pd−C^1, N−Xy^{Pd}, and N−Xy^q bonds is fast enough at room temperature to allow the observed equivalence of methyl groups, in spite of R ≠ R′. In solutions of **2b** at −40 °C the Xy^q methyl protons become inequivalent, but the Xy^{Pd} methyl protons remain isochronous. However, at −60 °C the Xy methyl protons appear as singlets of 6H:6H (Xy^{Pd}) and 3H:3H (Xy^q) intensities. This is also the pattern observed for the Xy methyl resonances in the spectra of **2c** at −40 °C and in those of the remaining complexes **2** at room temperature. The differences observed should be attributed to electronic rather than steric effects in view of the bulkier substituents in **2b** (R = Me, R′ = Ph) than in **2g** (R = H, R′ = Ph) or in **2c** (R = Me, R′ = $CH_2C(O)Me$) than in **2f** (R = H, R′ = $CH{=}CH_2$).

We assume complexes **2′a**−**c** to have in solution the same geometry as that determined for **2′a** in the solid state by X-ray crystallography on the basis of the similar position of the ^{31}P NMR resonances (14.4−15.1 ppm) and the J_{PC^1} values (152−153 Hz). In **2′a**, with R = R′ = Me, the Xy^{Pd} methyl protons are equivalent, while the Xy^q ones are not, which suggests that fast rotation around the N−Xy^{Pd} bond occurs, while rotation around N−Xy^q and Pd−C^1 bonds is slow on the NMR time scale. This is also observed in **2′b** and **2′c**. Thus, two stereoisomers of **2′c** are observed due to the slow rotation around the Pd−C^1 on the NMR time scale and the different nature of the two ligands *cis* to the iminobenzoyl group, I and XyNC (*cis* effect). Both factors and the chirality

of the C*HPh(Me) (R′) carbon explain the formation of four stereoisomers of **2′b**, which requires that the chirality of the C*RR′ carbon is not fully determined by that of the CHPh(Me) group; that is, the diastereoisomeric excess (de) induced on the CRR′ group by the chirality of the R′ group (ketone chirality effect) is < 100%. According to ^{1}H and ^{31}P NMR spectra, the *cis* effect is quite important because it induces a 6:1 molar ratio of stereoisomers in **2′c** (71% de). The four stereoisomers in **2′b** form in 12:4:3:1 molar ratios. The 12:3 = 4:1 (60% de) molar ratios can be related with one of the two effects, while the other must be responsible for the 12:4 = 3:1 molar ratios (50% de). It is reasonable to assume that the greater diastereoisomeric ratio is related to the *cis* effect, while the second one is due to the ketone chirality effect.

Iminoacyl complexes of the type [Pd]{C(=NXy)Ar}[6] show the resonance due to the carbon atom bonded to Pd at 170−180 ppm (including complex **6**, 176.4 ppm; Scheme 5). Formation of the DHQ ring results in an appreciable deshielding of this nucleus (199.1−205.4 ppm in **2**, **2′**; not observed in **3**). Such deshielding is even greater in the DHQ complexes *trans*-[PdI$_2${C=N(Xy)C(Me){CH$_2$C(O)Me}NHC$_6$H$_4$-2}(L)] (L = CNXy, 219.2 ppm; PPh$_3$ 221.4 ppm), previously reported by us,[6] probably due to the replacement of XyNC by the more electronegative iodo ligand. The resonance due to the XyN≡*C*−Pd carbon around 135 ppm is observed only in some cases.[16]

In the ^{1}H NMR spectra of the iminiumbenzoyl complexes **3** and **4** the δ(NH) resonances follow the order δ(XyNH) (11.42−12.53 ppm) > δ(Pd−NH$_2$) (**3**, 7.56 ppm) > δ(NH$_2$) (**4**, 6.07 ppm). The increase in the shielding constant is parallel to the decrease of the formal charge at N. Complex **4** is rather insoluble in CDCl$_3$ and scarcely stable in solution, which prevented registering its ^{13}C NMR spectrum or growing a single crystal to determine its structure. The ^{1}H and ^{31}P NMR spectra of **4** in CDCl$_3$ were very poorly resolved. Although they improve when measured in CD$_3$CN, the resonances are broad at room temperature and even at −40 °C. The significant difference between δ(^{31}P) in **4** and in complexes **2′** (23.5 vs 14.4−15.1 ppm) could be due to the solvent (CD$_3$CN in **4** and CDCl$_3$ in **2′**) or to the steric conditions imposed by the heterocyclic ring, which certainly stresses the coordination plane of palladium. Other factors are equal or similar: the *trans* influences of DHQ and iminiumacyl ligands (see above) and the nature of the *cis* ligands.

Electrochemical Study. The voltammogram of **2i** shows the redox process to be reversible. The oxidation potential of this complex, 200 mV higher than that of ferrocene, is in agreement with the electron-withdrawing ability of the palladated 1,2-dihydroquinazolinium substituent of the ferrocene moiety and shows an efficient electronic communication between the iminoacyl nitrogen, in which the positive charge of the substituent is mainly localized, and the iron center.

Conclusion and Prospects

A general method for the synthesis of 1,2-dihydro-3-xylylquinazolinium-4-yl (DHQ) palladium complexes involving the reaction between an orthoamino-iminoacyl palladium complex, a carbonyl compound, and an acid is reported. Some of the probable intermediates have been isolated and their reactivity studied, showing them to behave as expected in the proposed reaction pathway. Thus, the synthesis of some orthoamino-iminiumacyl complexes has allowed us to prove that they react with carbonyl compounds to give DHQ palladium complexes. Alternatively, we have prepared an orthoimino-iminoacyl complex and reacted it with an acid to give a DHQ palladium complex. Experiments will be carried out (1) to prepare oligomers and dendrimers by choosing the appropriate carbonyl compounds and (2) to prepare mono- or poly-1,2-dihydro-3-(*R*)-quinazolinium-4-yl derivatives by depalladation.

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 Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded in Varian 300 or 400 NMR spectrometers. The NMR assignments were performed, in some cases, with the help of APT, HMQC, and HMBC experiments. Chart 1 gives the atom numbering used in NMR assignments. HOTf, XyNC, bpy, tbbp, and ToCHO were purchased from Fluka. [Pd$_2$(dba)$_3$]·dba ("Pd(dba)$_2$")[18] was prepared as reported in the literature. Although the synthesis of *trans*-[Pd{C(=NXy)C$_6$H$_4$NH$_2$-2}I(CNXy)$_2$] (**1**) in two steps was previously reported by us,[1] we describe here a more straigtforward method giving a higher yield. The solvents were distilled before use.

X-ray Crystallography. Compounds **2i**·CHCl$_3$, **2′a**·H$_2$O, **3**·CH$_2$Cl$_2$, and **6** were measured on a Bruker Smart APEX machine. 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. Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. The NH and NH$_2$ were refined as free with SADI in NH$_2$ compounds, the methyl groups were refined using a rigid groups, and the other hydrogens were refined using a riding mode. *Special features*: For **2′a**·H$_2$O the water hydrogens were refined as free. Further details on crystal data, data collection, and refinements are summarized in the Supporting Information.

Cyclic Voltammetry. The electrochemical experiment was performed at 298 K with a potentiostat/galvanostat AUTOLAB-100 (Echo-Chemie, Utrecht) using a one-compartment three-electrode system with a glassy carbon electrode as the working electrode (Metrohm, 2 mm of diameter). A Ag/AgCl/KCl (saturated) electrode was the reference and a glassy carbon bar was the auxiliary electrode. A 2.5 mM solution of **2i** in acetonitrile with 0.4 M anhydrous lithium perchlorate as supporting electrolyte and 1.5 M AcOH were purged with pure argon prior to use, and the cyclic voltammogram was obtained at 100 mV s^{-1}. The value of the reduction potential is referenced to the redox couple [Fe(C$_5$H$_5$)$_2$]$^{+/0}$ (E_0^{red} = 300 mV).

Synthesis of *trans*-[PdI{C(=NXy)C$_6$H$_4$NH$_2$-2}(CNXy)$_2$] (1).[1] To a suspension of "Pd(dba)$_2$" (2.0 g, 3.48 mmol) in toluene

(16) Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. *Organometallics* **2005**, *24*, 5634. Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. *Organometallics* **2004**, *23*, 4871.

(17) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 6193. Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 2051. Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Aullón, G.; Bautista, D. *Organometallics* **2007**, *26*, 6155. Vicente, J.; Chicote, M. T.; Vicente-Hernández, I.; Bautista, D. *Inorg. Chem.* **2008**, *47*, 9592.

(18) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

(50 mL) under a nitrogen atmosphere were successively added XyNC (1.37 g, 10.43 mmol) and $IC_6H_4NH_2$-2 (761.8 mg, 3.48 mmol) with a 15 min interval. The suspension was stirred for 6.5 h, the solvent was removed under vacuum, and the residue was stirred with CH_2Cl_2 (30 mL). The suspension was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum to ca. 3 mL. Upon the addition of cold Et_2O (30 mL, 0 °C), a precipitate formed, which was filtered off, washed with Et_2O (3 × 3 mL), and suction dried to give **1** (1.574 g, 2.19 mmol, 63%).

Synthesis of *trans*-[PdI{C═N(Xy)CMe$_2$NHC$_6$H$_4$-2}(CNXy)$_2$]-TfO (2a). To a solution of **1** (150 mg, 0.21 mmol) in acetone (15 mL) was added HOTf (18.5 μL, 0.21 mmol). The reaction mixture was stirred for 2 h and concentrated under vacuum to 1 mL, and Et_2O (20 mL) was added. A suspension formed, which was filtered, and the solid collected was dried first by suction and then in an oven at 70 °C for 4 h to give **2a** as a lemon-yellow solid. Yield: 151.6 mg, 0.17 mmol, 80%. Dec pt: 208 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.65 (s, 6 H, Me, CMe_2), 2.26 (s, 12 H, Me, Xy^{Pd}), 2.28 (s, 6 H, Me, Xy^q), 6.97 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.14 (d, 4 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.20 (d, 2 H, *meta*-Xy^q, $^3J_{HH}$ = 8 Hz), 7.29−7.38 (m, 3 H, *para*-Xy^{q+Pd}), 7.39 (d, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.54 (dd, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz), 8.22 (dd, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.29 (s br, 1 H, NH). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ 18.6 (Me, Xy^{Pd}), 19.8 (Me, Xy^q), 24.9 (CMe_2), 77.2 (C^8), 117.8 (C^4), 118.5 (C^6), 120.6 (q, TfO, $^1J_{CF}$ = 320 Hz), 124.4 (*ipso*-C, Xy^{Pd}), 125.4 (C^2), 128.6 (*meta*-CH, Xy^{Pd}), 129.7 (*meta*-Xy^q), 129.8 (*para*-Xy^q), 131.3 (*para*-Xy^{Pd}), 134.5 (*ortho*-C, Xy^q), 135.5 (*C*≡NXy^{Pd}), 135.5 (C^7), 136.2 (*ortho*-C, Xy^{Pd}), 138.4 (C^5), 141.6 (*ipso*-C, Xy^q), 142.5 (C^3), 202.1 (C^1). IR (Nujol, cm^{-1}): ν(C≡N) 2199. Anal. Calcd for $C_{37}H_{38}F_3IN_4O_3PdS$: C, 48.88; H, 4.21; N, 6.16; S, 3.53. Found: C, 49.05; H, 4.23; N, 6.06; S, 3.35.

Synthesis of *trans*-[PdI{C═N(Xy)C(Me)(Ph)NHC$_6$H$_4$-2}-(CNXy)$_2$]OTf (2b). To a solution of **1** (120 mg, 0.17 mmol) in acetophenone (2 mL) was added HOTf (15 μL, 0.17 mmol), and the reaction mixture was stirred for 2.5 h. Upon the addition of cold Et_2O (40 mL, 0 °C) to the resulting solution, a suspension formed, which was filtered. The solid collected was recrystallized from CH_2Cl_2 (1 mL) and *n*-pentane (20 mL) at 0 °C, washed with cold pentane (3 × 5 mL, 0 °C), and dried in an oven at 70 °C for 4 h to give **2b**·2H_2O as a yellow solid. Yield: 74.2 mg, 0.07 mmol, 44%). Dec pt: 141 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.58 (br, 2 H, H_2O), 2.00 (s, 3 H, Me), 2.22 (s, 12 H, Me, Xy^{Pd}), 2.24 (s, 6 H, Me, Xy^q), 6.95 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.07−7.15 (m, 9 H), 7.24−7.34 (m, 3 H), 7.49−7.56 (m, 4 H), 8.17 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.95 ppm (s br, 1 H, N*H*). ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C, TMS): δ 2.00 (s, 3 H, Me), 2.19 (s, 3 H, Me, Xy^q), 2.22 (s, 12 H, Me, Xy^{Pd}), 2.26 (s, 3 H, Me, Xy^q), 6.99 (t, 1 H, H^6, $^3J_{HH}$ = 7 Hz), 7.09−7.20 (m, 9 H), 7.28−7.40 (m, 3 H), 7.46−7.51 (m, 3 H), 7.57 (dt, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.20 (d, 1 H, H^7, $^3J_{HH}$ = 7 Hz), 8.77 (s br, 1 H, N*H*). ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C, TMS): δ 2.00 (s, 3 H, Me), 2.20 (s, 3 H, Me, Xy^a), 2.21 (s, 6 H, Me, Xy^{Pd}), 2.22 (s, 6 H, Me, Xy^{Pd}), 2.27 (s, 3 H, Me, Xy^a), 7.00 (t, 1 H, H^6, $^3J_{HH}$ = 8 Hz), 7.10−7.24 (m, 9 H), 7.30−7.41 (m, 3 H), 7.43−7.51 (m, 3 H), 7.59 (t, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 8.21 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz), 8.72 (s br, 1 H, N*H*). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2, 25 °C, TMS): δ 18.8 (Me, Xy^{Pd}), 20.9 (Me, Xy^q), 25.5 (Me), 83.2 (C^8), 117.6 (C^4), 120.4 (C^6), 124.9 (*ipso*-C, Xy^{Pd}), 126.2 (C^2), 127.5 (*ortho*-Ph), 128.3 (*meta*-Ph), 128.9 (*meta*-Xy^{Pd}), 129.7 (*para*-Ph), 130.0 (*para*-Xy^q), 130.1 (*meta*-Xy^q), 131.6 (*para*-Xy^{Pd}), 135.4 (*ortho*-Xy^q), 136.2 (C^7), 136.7 (*ortho*-Xy^{Pd}), 138.4 (*ipso*-Ph), 139.1 (C^5), 142.7 (*ipso*-Xy^q), 143.1 (C^3), 205.4 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3218, ν(C≡N) 2197, ν(C═N + C═C) 1615, 1532. Λ_M = 157 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{42}H_{44}F_3IN_4O_5PdS$: C, 50.09; H, 4.40; N, 5.56; S, 3.18. Found: C, 49.81; H, 4.03; N, 5.81; S, 3.36.

Synthesis of *trans*-[PdI{C═N(Xy)C(Me){CH$_2$C(O)Me}NH-C$_6$H$_4$-2}(CNXy)$_2$]OTf (2c). To a suspension of **1** (150 mg, 0.21 mmol) in acetylacetone (2 mL) was added HOTf (19 μL, 2.2 mmol). A solution formed immediately, which was stirred for 2.5 h. Upon the addition of Et_2O (25 mL) an oily material formed, which was converted into a solid by stirring it with a 1:10 mixture of CH_2Cl_2 and Et_2O (3 × 22 mL). The solid was treated with CH_2Cl_2 (10 mL), the resulting suspension was filtered, the solution was concentrated under vacuum (2 mL), cold Et_2O (20 mL, 0 °C) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 5 mL) and dried in an oven at 70 °C for 8 h to give **2c** as a lemon-yellow solid. Yield: 70.3 mg, 0.07 mmol, 36%. Mp: 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.79 (s, 3 H, Me), 1.83 (s, 3 H, Me), 2.28 (s, 12 H, Me, Xy^{Pd}), 2.32 (s, 6 H, Me, Xy^q), 3.15 (s br, 2 H, CH_2), 7.04 (t, 1 H, H^6, $^3J_{HH}$ = 7 Hz), 7.14 (d, 4 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz,), 7.19 (d, 2 H, meta-Xy^q, $^3J_{HH}$ = 8 Hz,), 7.29−7.40 (m, 4 H), 7.58 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 8.23 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz), 8.32 (s br, 1 H, N*H*); (400 MHz, $CDCl_3$, −40 °C, TMS): δ 1.78 (s, 3 H, Me), 1.84 (s, 3 H, Me), 2.25 (s, 9 H, Me, Xy^q + Xy^{Pd}), 2.30 (s, 6 H, Me, Xy^{Pd}), 2.37 (s, 3 H, Me, Xy^q), 3.16 (AB system, 2H, CH_2, ν_A = 3.26, ν_B = 3.05, J_{AB} = 15 Hz), 7.08 (t, 1 H, $^3J_{HH}$ = 7 Hz), 7.17−7.25 (m, 6 H), 7.34−7.42 (m, 4 H), 7.62 (t, 1 H, $^3J_{HH}$ = 8 Hz), 8.25 (overlapped d+br s, 2 H, NH + H^7). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ 17.9 (Me, Xy^{Pd}), 20.0 (Me, Xy^q), 22.9 (Me), 31.3 (C(O)*Me*), 78.6 (C^8), 117.8 (C^4), 120.1 (C^6), 125.8 (C^2), 128.6 (*meta*-CH, Xy^{Pd}), 129.9 (br, *meta*-Xy^q), 130.1 (*para*-Xy^q), 131.3 (*para*-Xy^{Pd}), 135.6 (C^7), 136.2 (*ortho*-Xy^{Pd}), 138.6 (C^5), 141.3 (C^3), 141.7 (*ipso*-Xy^q), 203.7 (C^1), 204.0 (CO). IR (Nujol, cm^{-1}): ν(NH) = 3219, ν(C≡N) 2194, ν(C═O), ν(C═N + C═C) 1720, 1616, 1533. Λ_M = 140 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{39}H_{40}F_3IN_4O_4PdS$: C, 49.25; H, 4.24; N, 5.89; S, 3.37. Found: C, 48.83; H, 3.86; N, 5.84; S, 3.29.

Synthesis of *trans*-[PdI{C═N(Xy)CH(Me)NHC$_6$H$_4$-2}(CN-Xy)$_2$]OTf (2d). To a solution of **1** (150 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) were successively added acetaldehyde (100 μL, 1.77 mmol) and HOTf (19 μL, 0.22 mmol). The reaction mixture was stirred for 2 h and concentrated under vacuum (1 mL). Upon the addition of Et_2O (20 mL), a suspension formed, which was filtered. The solid collected was suction dried to give **2d** as a yellow solid. Yield: 166.3 mg, 0.19 mmol, 89%. Dec pt: 199 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.55 (d, 3 H, $^3J_{HH}$ = 6 Hz, CH*Me*), 2.23 (s, 3 H, Me, Xy^q), 2.26 (s, 6 H, Me, Xy^{Pd}), 2.28 (s, 6 H, Me, Xy^{Pd}), 2.35 (s, 3 H, Me, Xy^q), 5.28 (q, 1 H, $^3J_{HH}$ = 6 Hz, C*H*Me), 6.96 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.11−7.17 (m, 5 H), 7.24−7.38 (m, 5 H), 7.52 (ddd, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.10 (s br, 1 H, NH), 8.16 (dd, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR(75.5 MHz, $CDCl_3$, 25 °C, TMS): δ 17.3 (Me), 18.6 (Me, Xy^{Pd}), 18.7 (Me, Xy^{q+Pd}), 19.4 (Me, Xy^q), 71.0 (N_2CHMe), 117.3 (C^4), 119.6 (C^5), 124.1 (C^2), 128.6 (meta-Xy^{Pd}), 129.4 (*meta*-Xy^q), 129.9 (*meta*-Xy^q), 130.1 (*para*-Xy^q), 131.3 (*para*-Xy^{Pd}), 131.4 (*para*-Xy^{Pd}), 133.5 (*ortho*-Xy^q), 134.1 (*ortho*-Xy^q), 136.0 (*ortho*-Xy^{Pd}), 136.1 (C^7), 136.5 (*ortho*-Xy^{Pd}), 138.6 (C^6), 141.8 (*ipso*-Xy^q), 143.9 (C^3), 203.3 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3237, ν(C≡N) 2194, ν(C═N + C═C) 1615, 1526. Λ_M = 146 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{36}H_{36}F_3IN_4O_3PdS$: C, 48.30; H, 4.05; N, 6.26; S, 3.58. Found: C, 48.07; H, 3.81; N, 6.20; S, 3.48.

Synthesis of *trans*-[PdI{C═N(Xy)CH$_2$NHC$_6$H$_4$-2}(CNXy)$_2$]-OTf (2e). To a solution of **1** (120 mg, 0.17 mmol) in CH_2Cl_2 (20 mL) were successively added *para*-formaldehyde (5 mg, 0.17 mmol) and HOTf (15 μL, 0.17 mmol). The reaction mixture was stirred for 3 h and filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), Et_2O (20 mL) was added, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and dried in an oven at 70 °C for 4 h to give **2e**·H_2O as a deep yellow solid. Yield: 108.2 mg, 0.12 mmol, 74%. Dec pt: 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS):

δ 1.56 (br, 2 H, H_2O), 2.28 (s, 12 H, Me, Xy^{Pd}), 2.29 (s, 6 H, Me, Xy^{q}), 5.13 (d, 2 H, CH_2, $^3J_{HH}$ = 2 Hz), 6.98 (apparent dt, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.14−7.21 (m, 7 H), 7.29−7.37 (m, 3 H), 7.52 (ddd, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.85 (s br, 1 H, NH), 8.17 (dd, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR(100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.5 (Me, Xy^{q}), 18.6 (Me, Xy^{Pd}), 63.6 (N_2CH_2), 117.0 (C^4), 119.9 (C^6), 124.4 (br, *ipso*-C, Xy^{Pd}), 124.6 (C^2), 128.6 (*meta*-Xy^{Pd}), 129.6 (*meta*-Xy^{q}), 130.3 (*para*-Xy^{q}), 131.4 (*para*-Xy^{Pd}), 133.2 (*ortho*-Xy^{q}), 134.5 (br, *C*≡N), 136.3 (*ortho*-Xy^{Pd}), 136.5 (C^7), 138.6 (C^5), 142.9 (*ipso*-Xy^{q}), 144.4 (C^3), 204.0 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3214, ν(C≡N) 2202, ν(C=N + C=C) 1615, 1568, 1531. Λ_M = 157 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{35}H_{36}F_3IN_4O_4PdS$: C, 46.76; H, 4.04; N, 6.23; S, 3.57. Found: C, 47.13; H, 3.68; N, 6.25; S, 3.62.

Synthesis of *trans*-[PdI{C=N(Xy)CH(CH=CH$_2$)NHC$_6$H$_4$-2}(CNXy)$_2$]OTf (2f). To a solution of **1** (200 mg, 0.28 mmol) in CH_2Cl_2 (20 mL) were successively added acrolein (25 μL, 0.34 mmol) and HOTf (25 μL, 0.29 mmol). After 5 h of stirring, the solution was concentrated under vacuum (1 mL) and cold Et_2O (0 °C, 25 mL) was added. The suspension was filtered and the solid collected was recrystallized from CH_2Cl_2 (1 mL) and Et_2O (0 °C, 20 mL) and dried in an oven at 70 °C for 8 h to give **2f** as a lemon-yellow solid. Yield: 203.6 mg, 0.22 mmol, 81%. Mp: 154 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 2.21 (s, 6 H, Me, Xy^{Pd}), 2.22 (s, 3 H, Me, Xy^{q}), 2.34 (s, 6 H, Me, Xy^{Pd}), 2.41 (s, 3 H, Me, Xy^{q}), 5.33 (d, 1 H, CH=CH_2, $^3J_{HH}$ = 10 Hz), 5.56 (d, 1 H, CH=CH_2, $^3J_{HH}$ = 17 Hz), 5.67 (dd, 1 H, CHN_2, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 3 Hz), 6.09 (ddd, 1 H, C*H*=CH_2, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 7 Hz), 6.95 (ddd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 1 Hz), 7.06 (d br, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.15 (m, 4 H), 7.24−7.35 (m, 5 H), 7.53 (ddd, 1 H, H^5 $^3J_{HH}$ = 9 Hz, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.13 (dd, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.21 (d br, 1 H, NH, $^3J_{HH}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.5 (Me, Xy^{Pd}), 18.7 (Me, Xy^{q}), 18.8 (Me, Xy^{Pd}), 19.9 (Me, Xy^{q}), 75.9 (C^8), 117.2 (C^4), 119.5 (C^6), 120.6 (OTF, $^1J_{CF}$ = 319.7 Hz), 123.4 (CH_2), 123.5 (C^2), 124.5 (br, *ipso*-Xy^{Pd}), 128.5 (*meta*-Xy^{Pd}), 128.7 (*meta*-Xy^{Pd}), 129.2 (*C*H=CH_2), 129.5 (*meta*-Xy^{q}), 129.8 (*meta*-Xy^{q}), 130.0 (*para*-Xy^{q}), 131.3 (*para*-Xy^{Pd}), 131.4 (*para*-Xy^{Pd}), 133.3 (*ortho*-Xy^{q}), 134.1 (*ortho*-Xy^{q}), 136.0 (*ortho*-Xy^{Pd}), 136.4 (C^7), 136.6 (*ortho*-Xy^{Pd}), 138.8 (C^5), 142.6 (*ipso*-Xy^{q}), 142.9 (C^3), 203.0 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3218, ν(C≡N) 2199, ν(C=N + C=C) 1614, 1531. Λ_M = 144 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{37}H_{36}F_3IN_4O_3PdS$: C, 48.99; H, 4.00; N, 6.18; S, 3.53. Found: C, 48.69; H, 3.66; N, 6.08; S, 3.40. Crystals of **2f**·0.5Et_2O suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of the complex in $CHCl_3$.

Synthesis of *trans*-[PdI{C=N(Xy)CH(Ph)NHC$_6$H$_4$-2}(CNXy)$_2$]OTf (2g). To a solution of **1** (120 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) were successively added benzaldehyde (17 μL, 0.17 mmol) and HOTf (15 μL, 0.17 mmol). The reaction mixture was stirred for 2 h and concentrated under vacuum to dryness, and the residue was stirred with cold Et_2O (0 °C, 20 mL). The suspension was filtered, and the filtrate was concentrated under vacuum (10 mL). Upon cooling at 0 °C, a suspension formed, which was filtered, and the solid collected was washed with cold Et_2O (0 °C, 3 × 3 mL) and dried by suction to give **2g**·H_2O as a lemon-yellow solid. Yield: 120.3 mg, 0.13 mmol, 75%). Mp: 119 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.58 (br, 2 H, H_2O), 1.74 (s, 3 H, Me, Xy^{q}), 2.17 (s, 6 H, Me, Xy^{Pd}), 2.32 (s, 6 H, Me, Xy^{Pd}), 2.35 (s, 3 H, Me, Xy^{q}), 6.38 (d, 1 H, CHN_2, $^3J_{HH}$ = 4 Hz), 6.92 (apparent t, 1 H, H^6, $^3J_{HH}$ = 7.3 Hz), 7.06−7.35 (m, 15 H), 7.55 (apparent dt, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.11 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz), 8.32 (d br, 1 H, NH, $^3J_{HH}$ = 4 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ 18.3 (Me, Xy^{q}), 18.4 (Me, Xy^{Pd}), 18.9 (Me, Xy^{q}), 19.0 (Me, Xy^{Pd}), 77.2 (C^8), 116.5 (C^4), 118.9 (C^6), 121.0 (C^2), 127.0 (*ortho*-Ph), 128.5 (*meta*-Xy^{Pd}), 128.6 (*meta*-Xy^{Pd}), 129.1 (*meta*-Ph), 129.7 (*meta*-Xy^{q}), 129.8 (*para*-Xy^{q}), 129.9 (*meta*-Xy^{q}), 130.5 (*para*-Ph), 131.2 (*para*-Xy^{Pd}), 131.4 (*para*-Xy^{Pd}), 132.6 (*ortho*-Xy^{q})], 134.8 (*ortho*-Xy^{q}), 136.0 (*ortho*-Xy^{Pd}), 136.7 [C^7 + *ortho*-Xy^{Pd}), 137.0 (*ipso*-Ph), 139.3 (C^5), 142.0 (*ipso*-Xy^{q}), 143.1 (C^3), 203.1 (C^1). IR (Nujol, cm^{-1}): ν(C≡N) 2197, ν(C=N + C=C) 1615, 1538, 1527. Λ_M = 143 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{41}H_{40}F_3IN_4O_4PdS$: C, 50.50; H, 4.13; N, 5.75; S, 3.29. Found: C, 50.37; H, 3.73; N, 5.71; S, 3.21.

Synthesis of *trans*-[PdI{C=N(Xy)CH(To)NHC$_6$H$_4$-2}(CNXy)$_2$]OTf (2h). To a solution of **1** (150 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) were successively added ToCHO (To = C_6H_4Me-4, 25 μL, 0.21 mmol) and HOTf (18.5 μL, 0.21 mmol). The resulting suspension was stirred for 2 h and filtered through a short pad of Celite. The filtrate was concentrated under vacuum to 1 mL and cooled at 0 °C, and cold Et_2O (20 mL, 0 °C) was added. The suspension was filtered, and the solid collected was recrystallized from CH_2Cl_2/Et_2O and dried first by suction and then in an oven at 70 °C for 8 h to give **2h** as a deep yellow solid. Yield: 116.4 mg, 0.12 mmol, 57%. Dec pt: 209 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.78 (s, 3 H, Me, Xy^{q}), 2.17 (s, 6 H, Me, Xy^{Pd}), 2.27 (s, 3 H, Me, To), 2.33 (s, 6 H, Me, Xy^{Pd}), 2.34 (s, 3 H, Me, Xy^{q}), 6.32 (d, 1 H, C*H*To, $^3J_{HH}$ = 4 Hz), 6.90 (dt, 1 H, H6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 6.98 (d, 2 H, *meta*-To, $^3J_{HH}$ = 8 Hz), 7.06 (d, 1H, *meta*-Xy^{q}, $^3J_{HH}$ = 8 Hz), 7.09−7.17 (m, 7 H, *meta*-Xy^{Pd} + *ortho*-To + *meta*-Xy^{q}), 7.20 (d, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 7.27−7.35 (m, 3 H, *para*-Xy^{q+Pd}), 7.53 (dt, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.11 (dd, 1 H, H^7, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.25 (d br, 1 H, NH, $^3J_{HH}$ = 4 Hz). $^{13}C\{^1H\}$ (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.3 (Me, Xy^{q}), 18.4 (Me, Xy^{Pd}), 19.0 (Me, Xy^{Pd}), 19.1 (Me, Xy^{q}), 21.2 (Me, To), 77.2 (C^8), 116.6 (C^4), 118.8 (C^6), 120.5 (q, OTf, $^1J_{CF}$ = 320 Hz), 122.0 (C^2), 124.4 (*ipso*-Xy^{Pd}), 124.6 (*ipso*-Xy^{Pd}), 126.9 (*ortho*-To), 128.5 (*meta*-Xy^{Pd}), 128.6 (*meta*-Xy^{Pd}), 129.6 (*meta*-To), 129.7 (*meta*-Xy^{q}), 129.8 (*para*-Xy^{q}), 129.9 (*meta*-Xy^{q}), 131.2 (*para*-Xy^{Pd}), 131.3 (*para*-Xy^{Pd}), 132.6 (*ortho*-Xy^{q}), 134.1 (*ipso*-To), 134.8 (*ortho*-Xy^{q}), 135.5 (C≡N), 135.6 (C≡N), 135.9 (*ortho*-Xy^{Pd}), 136.6 (C^7), 136.7 (*ortho*-Xy^{Pd}), 139.2 (C^5), 140.6 (*para*-To), 143.0 (*ipso*-Xy^{q}), 143.2 (C^3), 202.7 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3212, ν(C≡N) 2197, ν(C=N + C=C) 1615, 1590, 1539. Λ_M = 143 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{42}H_{40}F_3IN_4O_3PdS$: C, 51.94; H, 4.15; N, 5.77; S, 3.30. Found: C, 52.10; H, 4.15; N, 5.70; S, 3.29.

Synthesis of *trans*-[PdI{C=N(Xy)CH{*C*-Fe(C$_5$H$_4$)(C$_5$H$_5$)}NHC$_6$H$_4$-2}(CNXy)$_2$]OTf (2i). To a solution of **1** (200 mg, 0.28 mmol) in CH_2Cl_2 (20 mL) were successively added ferrocenyl carboxaldehyde (59.5 mg, 0.28 mmol) and HOTf (24.5 μL, 0.28 mmol). The reaction mixture was stirred for 2.5 h and filtered through a short pad of Celite. The solution was concentrated under vacuum (2 mL), and cold Et_2O (0 °C, 30 mL) was added. The resulting suspension was filtered, and the solid collected was washed with Et_2O (3 × 5 mL) and dried in an oven at 70 °C for 4 h to give **2i** as an orange solid. Yield: 235.2 mg, 0.22 mmol, 80%. Dec pt: 191 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.95 (s, 3 H, Me, Xy^{q}), 2.13 (s, 6 H, Me, Xy^{Pd}), 2.28 (s, 3 H, Me, Xy^{q}), 2.32 (s, 6 H, Me, Xy^{Pd}), 3.94 (s br, 1 H, C_5H_4), 4.00 (s br, 1 H, C_5H_4), 4.04 (s br, 1 H, C_5H_4), 4.15 (s br, 1 H, C_5H_4), 4.38 (s, 5 H, Cp), 5.96 (d, 1 H, CHN_2, $^3J_{HH}$ = 4 Hz), 6.94 (apparent t, 1 H, H^6, $^3J_{HH}$ = 8 Hz), 7.12 (m, 6 H, *meta*-Xy^{q+Pd}), 7.29 (m, 3 H, *para*-Xy^{q+Pd}), 7.40 (d, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.59 (apparent dt, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.07 (dd, 1 H, H^7, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.28 (s br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 18.3 (Me, Xy^{Pd}), 18.4 (Me, Xy^{q}), 19.2 (Me, Xy^{Pd}), 19.8 (Me, Xy^{q}), 65.2 (CH, C_5H_4), 68.7 (CH, C_5H_4), 69.5 (CH, C_5H_4), 69.9 (CH, Cp), 74.6 (C^8), 85.2 (C, C_5H_4), 116.7 (C^4), 118.9 (C^5), 122.4 (C^2), 124.4 (*ipso*-Xy^{Pd}), 124.6 (*ipso*-Xy^{Pd}), 128.4 (*meta*-Xy^{Pd}), 128.5 (*meta*-Xy^{Pd}), 129.5 (*meta*-Xy^{q}), 129.6 (*para*-Xy^{q}), 129.7 (*meta*-Xy^{q}), 131.1 (*para*-Xy^{Pd}), 131.3 (*para*-Xy^{Pd}), 132.7 (*ortho*-Xy^{q}), 134.8 (*ortho*-Xy^{q}), 136.0 (*ortho*-Xy^{Pd}), 136.3 (C^7), 136.8 (*ortho*-Xy^{Pd}), 138.7 (C^6), 142.0 (C^3), 143.0 (*ipso*-Xy^{q}), 199.9 (C^1). IR (Nujol, cm^{-1}): ν(NH) 3322, ν(C≡N) 2198, ν(C=N + C=C) 1614, 1525. Λ_M = 141 Ω^{-1} cm^2 mol^{-1}.

Anal. Calcd for $C_{45}H_{37}F_3FeIN_4O_3SPd$: C, 50.99; H, 3.52; N, 5.29; S, 3.02. Found: C, 50.86; H, 3.93; N, 5.33; S, 2.79.

Synthesis of *SP-4-3*-[PdI{C=N(Xy)CMe$_2$NHC$_6$H$_4$-2}(CNXy)(PPh$_3$)]OTf (2′a). A suspension of **4** (120 mg, 0.12 mmol) in acetone (10 mL) was stirred for 30 min. The resulting solution was concentrated under vacuum (1 mL), and Et_2O (20 mL) was added to precipitate a lemon-yellow solid, which was filtered off and dried by suction to give **2′a**·H_2O. Yield: 107.5 mg, 0.10 mmol, 87%. Dec pt: 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.46 (s, 6 H, Me, Xy^{Pd}), 1.51 (s, 3 H, CMe$_2$), 1.63 (br, H_2O), 1.71 (s, 3 H, CMe$_2$), 1.88 (s, 3 H, Me, Xy^q), 2.73 (s, 3 H, Me, Xy^q), 6.91 (m, 3 H), 7.14 (m, 2 H), 7.24−7.48 (m, 19 H), 7.86 (s br, 1 H, NH), 8.38 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 17.5 (Me, Xy^{Pd}), 19.3 (Me, Xy^q), 22.6 (Me, Xy^q), 24.5 (Me) 24.9 (Me), 75.6 (d, N$_2$*C*Me$_2$, $^4J_{CP}$ = 5 Hz), 117.5 (C^4), 118.3 (C^6), 120.7 (q, OTf, $^1J_{CF}$ = 320 Hz), 124.2 (s br, *ipso*-Xy^{Pd}), 127.0 (d, C^2, $^3J_{CP}$ = 3 Hz), 128.2 (*meta*-Xy^{Pd}), 128.6 (d, *meta*-PPh$_3$, $^3J_{CP}$ = 11 Hz), 129.1 (*meta*-Xy^q), 130.1 (*para*-Xy^q), 130.5 (d, *ipso*-PPh$_3$, $^1J_{CP}$ = 46 Hz), 130.7 (*para*-Xy^{Pd}), 131.3 (d, *para*-PPh$_3$, $^4J_{CP}$ = 2 Hz, 134.1 (d, *ortho*-PPh$_3$, $^2J_{CP}$ = 11 Hz), 135.0 (*ortho*-Xy^{Pd}), 136.2 (*ortho*-Xy^q), 136.6 (C^7), 136.7 (*ortho*-Xy^q), 138.1 (C^5), 141.0 (d, *ipso*-Xy^q, $^4J_{CP}$ = 4 Hz), 142.6 (d, C^3, $^4J_{CP}$ = 3 Hz), 204.8 (d, C^1, J_{CP} = 153 Hz). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$, 25 °C, TMS): δ 14.4. IR (Nujol, cm^{-1}): ν(NH) 3521, 3462, ν(C≡N) 2181, ν(C=N + C=C) 1612, 1568, 1526. Λ_M = 154 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{46}H_{46}F_3IN_3O_4PPdS$: C, 52.21; H, 4.38; N, 3.97; S, 3.03. Found: C, 51.81; H, 4.30; N, 3.91; S, 2.84.

Synthesis of *SP-4-3*-[PdI{C=N(Xy)CH{CH(Me)(Ph)}NHC$_6$H$_4$-2}(CNXy)(PPh$_3$)]OTf (2′b). To a suspension of **4** (150 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was added CH(Me)(Ph)CHO (21 μL, 0.15 mmol). After 1 h of stirring, the resulting mixture was filtered though anhydrous $MgSO_4$ and concentrated under vacuum to 0.5 mL, and cold *n*-pentane (20 mL, 0 °C) was added. A suspension formed, which was stirred for 15 min at 0 °C and filtered. The solid collected was stirred with cold Et_2O (0 °C, 5 mL) for 15 min, filtered off, and dried in an oven under vacuum at 70 °C for 10 h to give **2′b**·H_2O as a yellow solid. Yield: 98.5 mg, 0.09 mmol, 52%. Mp: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): Major isomer, δ 1.38 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 1.43 (s, 6 H, Me, Xy^{Pd}), 1.60 (br, 2 H, H_2O), 2.05 (s, 3 H, Me, Xy^q), 2.27 (s, 3 H, Me, Xy^q), 5.51 (apparent quint, 1 H, C*H*Me, $^3J_{HH}$ = 7 Hz), 5.59 (apparent t, 1 H, CHN$_2$, $^3J_{HH}$ = 5 Hz), 6.85−7.03 (various m, 5 H), 7.10−7.45 (various m, 24 H), 7.63 (d br, 1 H, NH, $^3J_{HH}$ = 5 Hz), 8.52 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, TMS): major isomer, δ 17.4 (Me, Xy^{Pd}), 18.3 (Me, Xy^q), 19.1 (CH*Me*Ph), 22.7 (Me, Xy^q), 44.6 (*C*HMePh), 78.1 (d, C^8, $^4J_{CP}$ = 5 Hz), 116.4 (C^4), 118.1 (C^6), 120.6 (q, TfO, $^1J_{CF}$ = 321 Hz), 124.1 (*ipso*-Xy^{Pd}), 125.3 (d, C^2, $^3J_{CP}$ = 4 Hz), 127.2 (*para*-Ph), 128.1 (*meta*-Xy^{Pd} or *ortho*- or *meta*-Ph), 128.2 (*meta*-Xy^{Pd} or *ortho*- or *meta*-Ph), 128.6 (d, *meta*-PPh$_3$, $^3J_{CP}$ = 11 Hz), 128.8 (*ortho*- or *meta*-Ph), 129.0 (CH-Xy^q or *para*-Xy^{Pd}), 129.8 (CH-Xy^q or *para*-Xy^{Pd}), 129.9 (d, *ipso*-PPh$_3$, $^1J_{CP}$ = 46 Hz), 130.4 (CH-Xy^q or *para*-Xy^{Pd}), 130.7 (CH-Xy^q or *para*-Xy^{Pd}), 131.3 (d, *para*-PPh$_3$, $^4J_{CP}$ = 2 Hz), 134.0 (d, *ortho*-PPh$_3$, $^2J_{CP}$ = 11 Hz), 134.8 (*ortho*-Xy^q), 134.9 (*ortho*-Xy^{Pd}), 135.5 (*ortho*-Xy^q), 137.5 (C^7), 139.7 (C^5), 140.6 (*ipso*-Ph), 141.0 (d, *ipso*-Xy^q, $^4J_{CP}$ = 4 Hz), 145.6 (d, C^3, $^4J_{CP}$ = 3 Hz), 208.7 (d, C^1, $^2J_{CP}$ = 152 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): major isomer, δ 15.1. IR (Nujol, cm^{-1}): ν(NH) 3223, ν(C≡N) 2184, ν(C=N + C=C) 1614, 1586, 1531. Λ_M = 111 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{52}H_{50}F_3IN_3O_4PPdS_2$: C, 55.06; H, 4.44; N, 3.70; S, 2.83. Found: C, 54.91; H, 4.16; N, 3.84; S, 2.73.

Synthesis of *SP-4-3*-[PdI{C=N(Xy)CH(To)NHC$_6$H$_4$-2}(CNXy)(PPh$_3$)]OTf (2′c). To a suspension of **4** (100 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added ToCHO (To = C_6H_4Me-4, 12 μL, 0.1 mmol). The resulting suspension was stirred for 1.5 h and filtered though Celite. The solution was concentrated under vacuum (1 mL), and *n*-pentane (20 mL) was added. The resulting suspension was filtered, and the solid collected was dried first by suction an then in an oven under vacuum at 60 °C for 4 h to give **2′c** as a yellow solid. Yield: 86.4 mg, 0.0784 mmol, 78%. Dec pt: 190 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): major isomer, δ 1.52 (s, 6 H, Me, Xy^{Pd}), 1.96 (s, 3 H, Me, Xy^q), 2.23 (s, 3 H, Me, To), 2.27 (s, 3 H, Me, Xy^q), 6.21 (d, 1 H, CH, $^3J_{HH}$ = 5 Hz), 6.84 (t, 1 H, $^3J_{HH}$ = 8 Hz), 6.90−6.96 (m, 3H), 7.05 (d, 2H, $^3J_{HH}$ = 8 Hz), 7.10−7.17 (m, 2H), 7.16−7.46 (various m, 20 H), 7.86 (d br, 1H, NH, $^3J_{HH}$ = 5 Hz), 8.45 (d, 1H H^7, $^3J_{HH}$ = 8 Hz); minor isomer, δ 1.59 (s, 6 H, Me, Xy^{Pd}), 1.99 (s, 3 H, Me, Xy^q), 2.19 (s, 3 H, Me, To), 2.60 (s, 3 H, Me, Xy^q), 5.88 (d, 1 H, CH, $^3J_{HH}$ = 2 Hz), 7.67 (s br, 1H, NH), 8.35 (d, 1H H^7, $^3J_{HH}$ = 8 Hz), the remaining resonances are obscured by those of the major isomer. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): Major isomer, δ 17.5 (Me, Xy^{Pd}), 18.5 (Me, Xy^q), 21.2 (Me, To), 22.0 (Me, Xy^q), 76.6 (C^8), 116.2 (C^4), 117.7 (C^6), 120.6 (q, TfO, $^1J_{CF}$ = 320 Hz), 123.8 (d, C^2, $^3J_{CP}$ = 4 Hz), 124.2 (*ipso*-Xy^{Pd}), 127.0 (*ortho*-To), 128.3 (*meta*-Xy^{Pd}), 128.6 (d, *meta*-PPh$_3$, $^3J_{CP}$ = 11 Hz), 129.3 (CH, Xy$^{q\ or\ Pd}$), 129.4 (*meta*-To + CH-Xy$^{q\ or\ Pd}$), 130.0 (d, *ipso*-PPh$_3$, $^1J_{CP}$ = 47 Hz), 130.4 (CH, Xy$^{q\ or\ Pd}$), 130.8 (CH, Xy$^{q\ or\ Pd}$), 131.3 (d, *para*-PPh$_3$, $^4J_{CP}$ = 2 Hz), 134.0 (d, *ortho*-PPh$_3$, $^2J_{CP}$ = 11 Hz), 135.0 (*ortho*-Xy^{Pd}), 135.8 (*ortho*-Xy^q), 136.1 (*ortho*-Xy^q), 137.4 (C^7), 139.6 (C^5), 139.9 (*para*-To), 140.7 (d, *ipso*-Xy^q, $^4J_{CP}$ = 4 Hz), 144.8 (d, C^3, $^4J_{CP}$ = 3 Hz), 207.4 (d, C^1, $^2J_{CP}$ = 152 Hz); minor isomer, δ = 17.8 (Me, Xy^{Pd}), 20.1 (Me, Xy^q), 21.1 (Me, To), 22.7 (Me, Xy^q), 116.7 (C^4), 119.0 (C^6), 127.9 (*ortho*-To), 128.4 (CH), 129.0 (CH), 129.2 (CH), 130.0 (CH), 130.1 (d, *ipso*-PPh$_3$, $^1J_{CP}$ = 45 Hz), 134.1 (d, *ortho*-PPh$_3$, $^2J_{CP}$ = 12 Hz), 134.4 (C-Xy$^{q\ or\ Pd}$), 135.2 (C-Xy), 135.9 (C-Xy), 137.3 (C^7), 138.3 (C^5), 140.6 (C-Xy), 139.9 (*para*-To), 140.7 (d, *ipso*-Xy^q, $^4J_{CP}$ = 4 Hz), 144.8 (d, C^3, $^4J_{CP}$ = 3 Hz), 207.4 (d, C^1, $^2J_{CP}$ = 152 Hz), the remaining resonances are obscured by those of the major isomer. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): Major isomer, δ 14.6 (br); minor isomer 12.5 (br). IR (Nujol, cm^{-1}): ν(NH) 3243, ν(C≡N) 2190, ν(C=N + C=C) 1616, 1589, 1537. Λ_M = 110 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{51}H_{46}F_3IN_3O_3PPdS$: C, 55.57; H, 4.21; N, 3.81; S, 2.91. Found: C, 55.17; H, 4.02; N, 3.85; S, 2.63.

Synthesis of *SP-4-4*-[PdI{*C,N*-C(=NHXy)C$_6$H$_4$NH$_2$}CNXy]OTf (3). To a solution of **1** (120 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) was added HOTf (15 μL, 0,17 mmol). The reaction mixture was stirred for 5 h, the resulting suspension was filtered, and the solid collected was washed with CH_2Cl_2 (3 × 5 mL) and dried, first by suction and then in an oven at 70 °C for 4 h to give **3** as a pale yellow solid. Yield: 83.6 mg, 0.11 mmol, 68%. Dec pt: 226 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ 2.29 (s, 6 H, Me, Xy^q), 2.55 (s, 6 H, Me, Xy^{Pd}), 6.70 (t, 1 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.08 (d, 2 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.19 (d, 2 H, *meta*-Xy^q, $^3J_{HH}$ = 8 Hz), 7.32 (t, 1 H, *para*-Xy^q, $^3J_{HH}$ = 8 Hz), 7.56 (br s, 2H, NH$_2$), 7.61 (t, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 7.82 (d, 1 H, H^7, $^3J_{HH}$ = 8 Hz), 7.89 (td, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz) 8.46 (d, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 12.53 (br s, 1 H, =NH). ^{13}C{^{1}H} (100.8 MHz, [D$_6$]acetone, 25 °C, TMS): δ 18.6 (Me, Xy^q), 18.9 (Me, Xy^{Pd}), 122.0 (q, OTf, J_{CF} = 321 Hz), 126.0 (C^4), 126.8 (*ipso*-Xy^q), 127.6 (C^7), 128.9 (*meta*-Xy^q), 129.5 (*meta*-Xy^{Pd}), 129.6 (C^5), 130.8 (*para*-Xy^{Pd}), 131.0 (*para*-Xy^q), 135.1 (*ortho*-Xy^{q+Pd}), 137.8 (C^6), 140.5 (C^3), 141.5 (*ipso*-Xy^{Pd}), 151.6 (C^2). IR (Nujol, cm^{-1}): ν(NH) 3211, 3187, 3150, 3075, ν(C≡N) 2207, ν(C=N + C=C) 1591, 1571. Λ_M = 144 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{25}H_{25}F_3IN_3O_3PdS$: C, 40.69; H, 3.42; N, 5.69; S, 4.35. Found: C, 40.61; H, 3.46; N, 5.62; S, 4.38. Crystals of **3**·CH_2Cl_2 suitable for an X-ray diffraction study were obtained by slow evaporation of a solution of complex **4** in CH_2Cl_2.

Synthesis of *SP-4-3*-[PdI{C(=NHXy)C$_6$H$_4$NH$_2$-2}(CNXy)(PPh$_3$)]OTf (4). To a suspension of **3** (167.0 mg, 0.23 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (71.2 mg, 0.27 mmol, 20% excess). After 1.5 h of stirring the resulting solution was concentrated under vacuum (1 mL) and Et_2O (20 mL) was added. The resulting suspension was filtered, and the solid collected was washed with Et_2O (3 × 5 mL) and dried under vacuum for 2 h to

give **4** as a lemon yellow solid. Yield: 170.7 mg, 0.17 mmol, 75%. Dec pt: 161 °C. ^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ 2.13 (s, 6 H, Me, Xy^{Pd}), 2.15 (s, 3 H, Me, Xy^q), 2.43 (s, 3 H, Me, Xy^q), 5.23 (d, 1 H, $^3J_{HH}$ = 8 Hz), 5.71 (t, 1 H, $^3J_{HH}$ = 8 Hz), 6.07 (s br, 2 H, NH_2), 6.73 (d, 1 H, $^3J_{HH}$ = 8 Hz), 6.98−7.03 (m, 1 H), 7.05−7.07 (d, 2 H, $^3J_{HH}$ = 8 Hz), 7.10−7.14 (m, 2 H), 7.22−7.26 (m, 2 H), 7.43−7.62 (m, 15 H, PPh_3), 11.42 (s br, 1 H, NH).; (400 MHz, $CDCl_3$, −40 °C, TMS): δ 1.92 (s, 6 H, Me, Xy^{Pd}), 2.14 (s br, 3 H, Me, Xy^q), 2.19 (s br, 3 H, Me, Xy^q), 5.12 (d, 1 H, $^3J_{HH}$ = 8 Hz), 5.68 (t, 1 H, $^3J_{HH}$ = 8 Hz), 5.84 (s br, 2 H, NH_2), 6.69 (d, 1 H, $^3J_{HH}$ = 8 Hz), 6.84 (s br, 1 H), 6.92 (d, 1 H, $^3J_{HH}$ = 8 Hz), 6.96 (d, 2 H, $^3J_{HH}$ = 8 Hz), 3 H), 7.01−7.06 (m, 2 H), 7.17 (t, 1 H, $^3J_{HH}$ = 8 Hz), 7.41−7.72 (m, 15 H, PPh_3), 12.14 (s br, 1 H, NH). $^{31}P\{^1H\}$ NMR (162.3 MHz, CD_3CN, 25 °C, TMS): δ 22.3 (br); (162.3 MHz, $CHCl_3$, −40 °C, TMS): δ 23.5 (s). IR (Nujol, cm^{-1}): ν(NH) 3414, 3328, ν(C≡N) 2195, 2181, ν(C=N + C=C) 1604, 1536, 1531. Anal. Calcd for $C_{43}H_{40}F_3IN_3O_3PPdS$: C, 51.64; H, 4.03; N, 4.20; S, 3.21. Found: C, 51.50; H, 4.03; N, 4.17; S, 3.01.

Synthesis of [PdI(C_6H_4N=CHTo-2)(N^N)] [N^N^ = bpy (5a), tbbpy (5b)]. Synthesis of IC_6H_4N=CHTo-2. To a solution of $IC_6H_4NH_2$-2 (2 g, 9.13 mmol) in toluene (30 mL) were added ToCHO (To = C_6H_4Me-4, 1.1 mL, 9.30 mmol) and 4 Å molecular sieves. The reaction mixture was refluxed for 3 h and filtered. The filtrate was concentrated under vacuum to dryness to give an oily material, which was dissolved in *n*-pentane (15 mL) and cooled at −33 °C. The resulting suspension was filtered, the solid was washed with cold *n*-pentane (3 × 5 mL, −33 °C), and dried by suction to give the title compound as a pale tan solid. Yield: 2.02 g, 6.30 mmol, 82%. Mp: 53 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 2.40 (s, 3 H, Me), 6.88 (dt, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.96 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.27 (d, 2 H, *meta*-To, $^3J_{HH}$ = 8 Hz), 7.33 (dt, 1H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.84 (d, 2 H, *ortho*-To, $^3J_{HH}$ = 8 Hz), 7.87 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.23 (s, 1 H, C*H*To). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, 25 °C, TMS): δ 21.7 (Me), 94.8 (C^1), 118.4 (C^3), 126.8 (C^5), 129.1 (*ortho*-To), 129.3 (C^4), 129.5 (*meta*-To), 133.2 (*ipso*-To), 138.9 (C^6), 142.2 (*para*-To), 153.1 (C^2), 160.7 (CH=N). IR (Nujol): ν(C=N + C=C) 1623, 1609. Anal. Calcd for $C_{14}H_{12}IN$: C, 52.36; H, 3.77; N, 4.36. Found: C, 52.18; H, 3.71; N, 4.33.

Synthesis of 5a and 5b. To a suspension of "Pd(dba)$_2$" (for **5a**: 750 mg, 1.30 mmol; for **5b**: 500 mg, 0.87 mmol) in toluene (20 mL) under a nitrogen atmosphere were added the appropriate bidentate ligand (**5a**, bpy, 203.7 mg, 1.30 mmol; **5b**, tbbpy, 233.4 mg, 0.87 mmol) and IC_6H_4N=CHTo-2 (for **5a**: 418.9 mg, 1.30 mmol; for **5b**: 279.2 mg, 0.87 mmol) with a 10 min interval. The reaction mixture was stirred for 3 (**5a**) or 1.5 (**5b**) h, and the solvent was removed under vacuum to dryness. The residue was stirred with CH_2Cl_2 (20 mL), the suspension was filtered through Celite, and the filtrate was concentrated to ca. 5 mL (**5a**) or to dryness (**5b**). In the case of **5a** Et_2O (20 mL) was added, the suspension was filtered, and the solid collected was washed with Et_2O (3 × 3 mL) and dried by suction to give a yellow solid. For **5b**, cold Et_2O (0 °C, 10 mL) and *n*-hexane (0 °C, 30 mL) were added to precipitate **5b** along with some dba. The crude product was refluxed in *n*-hexane (4 × 20 mL) for 15 min, and the suspension was filtered while hot. The yellow solid collected was washed with *n*-hexane (3 × 5 mL) and dried by suction to give a yellow product. **5a**: Yield: 533.8 mg, 0.91 mmol, 70%. Mp: 192 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 2.28 (s, 3 H, Me), 6.87 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.90 (dt, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.00 (dt, 1 H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.07 (d, 2 H, *meta*-To, $^3J_{HH}$ = 8 Hz), 7.27 (ddd, 1 H, bpy, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.40 (ddd, 1 H, bpy, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.61 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.62 (d, 2 H, *ortho*-To, $^3J_{HH}$ = 8 Hz), 7.81 (dd, 1 H, bpy, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.89 (m, 2 H, bpy), 8.00 (m, 2 H, bpy), 9.05 (s, 1 H, C*H*To), 9.55 (dd, 1 H, bpy, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 25 °C, TMS): δ 21.5 (Me), 120.3 (C^3), 121.6 (CH^{bpy}), 121.9 (CH^{bpy}), 123.5 (C^5), 124.2 (C^4), 126.4 (CH^{bpy}), 126.5 (CH^{bpy}), 128.5 (*ortho*-To), 129.1 (*meta*-To), 134.5 (*ipso*-To), 137.0 (C^1), 138.3 (CH^{bpy}), 138.4 (CH^{bpy}), 139.0 (C^6), 140.6 (*para*-To), 150.3 (CH^{bpy}), 152.9 (CH^{bpy}), 153.0 (C^{bpy}), 155.6 (C^{bpy}), 155.9 (C^2), 160.4 (C*H*To). IR (Nujol, cm^{-1}): ν(C=N + C=C) 1623, 1602, 1562. Anal. Calcd for $C_{24}H_{20}IN_3Pd$: C, 49.38; H, 3.45; N, 7.20. Found: C, 49.13; H, 3.36; N, 7.04.

5b: Yield: 187.3 mg, 0.27 mmol, 31%. Mp: 181 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.36 (s, 9 H, ^{t}Bu), 1.40 (s, 9 H, ^{t}Bu), 2.30 (s, 3 H, Me), 6.87 (m, 2 H, H^{6+5}), 7.00 (dt, 1 H, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.08 (d, 2 H, *meta*-To, $^3J_{HH}$ = 8 Hz), 7.32 (dd, 1 H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.45 (dd, 1 H, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.63 (d, 2 H, *ortho*-To, $^3J_{HH}$ = 8 Hz), 7.64 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.73 (d, 1 H, tbbpy, $^3J_{HH}$ = 6 Hz), 7.87−7.88 (m, 2 H, tbbpy), 9.25 (s, 1 H, C*H*To), 9.51 (d, 1 H, tbbpy, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): δ 21.5 (Me), 30.2 (Me, ^{t}Bu), 30.3 (Me, ^{t}Bu), 35.3 (CMe_3), 35.4 (CMe_3), 117.8 (CH^{tbbpy}), 118.1 (CH^{tbbpy}), 121.0 ($C^{6\text{ or }5}$), 123.4 ($C^{6\text{ or }5}$), 123.7 (CH^{tbbpy}), 123.8 (CH^{tbbpy}), 124.0 (C^4), 128.5 (*ortho*-CH, To), 129.0 (*meta*-CH, To), 134.6 (*ipso*-C, To), 137.3 (C^1), 139.3 (C^3), 140.4 (*para*-C, To), 149.9 (CH^{tbbpy}), 152.7 (CH^{tbbpy}), 154.0 (C^{tbbpy}), 155.6 (C^{tbbpy}), 155.8 (C^2), 160.5 (C*H*To), 162.8 (C^{ttbbpy}), 162.9 (C^{tbbpy}). IR (Nujol, cm^{-1}): ν(C=N + C=C 1614, 1564, 1546). Anal. Calcd for $C_{32}H_{36}IN_3Pd$: C, 55.22; H, 5.21; N, 6.04. Found: C, 55.77; H, 4.94; N, 5.84.

Synthesis of *trans*-[PdI{C(=NXy)C_6H_4N=CHTo-2}(CN-Xy)$_2$] (6). To a solution of **5a** (200 mg, 0.34 mmol) in CH_2Cl_2 (20 mL) was added XyNC (224.7 mg, 1.71 mmol). After 3 h of stirring, the solution was concentrated under vacuum to ca. 1 mL, Et_2O (20 mL) was added, the suspension was filtered, and the solid collected was recrystallized from CH_2Cl_2/Et_2O (15 mL/50 mL) and dried first by suction and then in an oven at 70 °C for 8 h to give **6**·H_2O as a yellow solid. Yield: 201.9 mg, 0.24 mmol, 71%. Dec pt: 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, −20 °C, TMS): δ 1.55 (s, 2 H, H_2O), 1.95 (s, 12 H, Me, Xy^{Pd}), 2.09 (s, 6 H, Me, Xy^q), 2.32 (s, 3 H, Me, To), 6.79 (d, 2H, *meta*-Xy^q, $^3J_{HH}$ = 7 Hz), 6.85 (t, 1 H, *para*-Xy^q, $^3J_{HH}$ = 7 Hz), 7.00 (d, 4 H, *meta*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.07 (d, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.18 (t, 2 H, *para*-Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.25−7.29 (m, 3 H, H^6 + *meta*-To), 7.48 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.73 (d, 1 H, H^7, $^3J_{HH}$ = 7 Hz), 8.23 (d, 2 H, *ortho*-To, $^3J_{HH}$ = 8 Hz), 8.47 (s, 1 H, C*H*To). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$, −20 °C, TMS): δ 18.4 (Me, Xy^{Pd}), 18.8 (Me, Xy^q), 21.7 (Me, To), 119.3 (C^4), 123.0 (*para*-Xy^q), 125.2 (*ipso*-Xy^{Pd}), 125.3 (C^6), 125.5 (C^7), 126.8 (*ortho*-Xy^q), 127.6 (*meta*-Xy^{Pd}), 127.7 (*meta*-Xy^q), 129.3 (*meta*-To), 129.5 (*para*-Xy^{Pd}), 130.0 (*ortho*-To), 130.6 (C^5), 132.5 (*ipso*-To), 135.5 (*ortho*-Xy^{Pd}), 139.1 (C^2), 142.1 (*para*-To), 143.1 (C≡N), 151.2 (*ipso*-Xy^q), 151.6 (C^3), 160.8 (C*H*To), 176.4 (C^1). IR (Nujol, cm^{-1}): ν(C≡N) 2177, 2147. Anal. Calcd for $C_{41}H_{41}IN_4OPd$: C, 58.69; H, 4.93; N, 6.68. Found: C, 58.82; H, 5.05; N, 6.78. Crystals of **6** suitable for an X-ray diffraction study were obtained by the liquid diffusion method from CH_2Cl_2/Et_2O.

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Supporting Information Available: Cyclic voltammogram of **2i**, details on crystal data, data collection, and refinements, listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and CIF files for compounds **2i**, **2′a**, **3**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.