ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Synthesis of Arylpalladium(II) Complexes Derived from Benzyl Alcohol, Reactivity toward Alkyl Halides, and Synthesis of Dinuclear Arylpalladium(II) Complexes

María-José Fernández-Rodríguez, Eloísa Martínez-Viviente,* and José Vicente

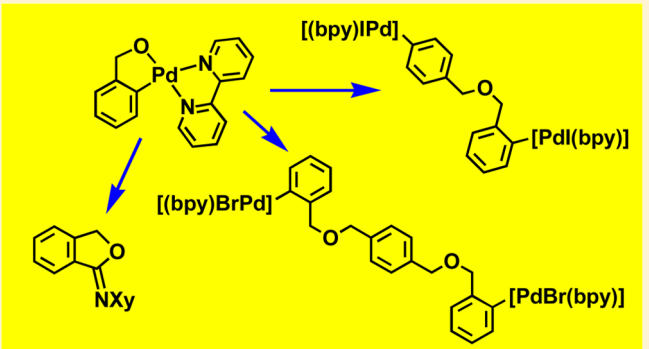
Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, 30071, Murcia, Spain

Peter G. Jones*

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023, Braunschweig, Germany

Supporting Information

ABSTRACT: The aryl palladium complexes [PdI-($C_6H_4CH_2OH$-2)(N^N)] (N^N = bpy = 2,2′-bipyridyl (**1a**), tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine (**1b**), tmeda = *N,N,N′,N′*-tetramethylethylenediamine (**1c**)) were synthesized by oxidative addition of 2-iodobenzyl alcohol to one equivalent of "[$Pd(dba)_2$]" (dba = dibenzylideneacetone) in the presence of the N^N ligands. By reaction of **1a** with three equivalents of XyNC (Xy = 2,6-dimethylphenyl) the insertion complex *trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}$(CNXy)_2$] (**2**) was formed. The reaction of **1a** with KO^{t}Bu resulted in the formation of the chelate complex [Pd(κ^2-*C,O*-$C_6H_4CH_2O$-2)(bpy)] (**3**), which crystallizes as pairs of molecules bridged by hydrogen bonds to water of crystallization. Complex **3** reacts with XyNC, forming the cyclic imidate *N*-(2,6-dimethylphenyl)-2-benzofuran-1(3*H*)-imine (**4**). By reaction of **3** with various primary alkyl halides RCH_2X, the complexes [PdX($C_6H_4CH_2OCH_2$R-2)(bpy)] (X = I, R = H (**5a**), X = Br, R = Ph (**5b**), *p*-$C_6H_4CH_2Br$ (**5c**), *p*-C_6H_4Br (**5d**), and *p*-C_6H_4I (**5e**)) were obtained. When the reaction of **3** with *p*-$C_6H_4(CH_2Br)_2$ was carried out in a 2:1 ratio, the dinuclear arylpalladium complex [{(bpy)BrPd($C_6H_4CH_2OCH_2$-2)}$_2$(C_6H_4-1,4)] (**6**) formed. An halide exchange reaction on **5e**, using AgOTf and an excess of NaI, afforded [PdI{$C_6H_4(CH_2OCH_2(C_6H_4I$-4))-2}(bpy)] (**5f**), which by oxidative addition to [$Pd(dba)_2$] in the presence of bpy formed another dinuclear arylpalladium complex, [(bpy)IPd($C_6H_4CH_2$-2)O($CH_2C_6H_4$-4)PdI(bpy)] (**7**). All the complexes have been extensively characterized by NMR spectroscopy. The crystal structures of **1a**, **3**·H_2O, and **5e** were determined by X-ray diffraction studies.



INTRODUCTION

Pd(II) aryl complexes have acquired a great relevance in organometallic chemistry, because of their involvement in carbon−carbon and carbon−heteroatom bond-forming reactions of great synthetic importance.[1] We have been especially interested in the synthesis of *ortho*-substituted arylpalladium complexes,[2−8] as the substituent in *ortho* position may participate in the reactions with unsaturated organic molecules, forming new ligands and/or organic compounds.[2−6,8−15] Very often, the *ortho* substitution also results in the formation of cyclopalladated complexes.[2,3,6−8,10,12−15]

Within this line of research, our group has previously reported on the synthesis and reactivity of *ortho*-palladated phenol derivatives.[5,12−14,16] Their reactions with CO, isocyanides, alkenes, alkynes, and allenes did not involve the interaction with the OH group in *ortho* position.[5,16] The electron-donating ability of this group, however, played a crucial role in the reactivity toward nitriles,[12,14] carbodiimides,[13,14] and isothiocyanates,[14] which afforded the first examples of the insertion of these molecules into a C−M bond of a late transition metal. In view of these results, we decided to extend our research to *ortho*-palladated hydroxymethylphenyl complexes, to investigate how the methylene link in the alcoholic substituent would affect the reactivity of the complexes. 2-Hydroxymethylphenyl palladium complexes with a dppf ligand (dppf = 1,1′-bis(diphenylphosphino)ferrocene) have been used as catalysts to build end-functionalized polyacetylenes.[17] There has also been a report on oxapalladacycles derived from 2-hydroxymethylbenzene[18] and their use as

Received: April 13, 2015

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

precatalysts in Heck and cross-coupling reactions.[19] However, the reactivity of these complexes toward unsaturated molecules has not been systematically investigated. In this paper we report our first results in this area, which involve the synthesis of a family of Pd complexes derived from benzyl alcohol, one of them a chelate complex resulting from the deprotonation of the alcohol. This chelate complex has shown an interesting chemistry toward alkyl halides, involving the nucleophilic attack of the coordinated oxygen on the alkyl group and resulting in the opening of the chelate ring and the formation of new aryl palladium complexes with larger substituents on the aryl ring. We have found no precedent in the literature for this type of reactivity in a *C,O*-cyclometalated aryl group coordinated to a late transition metal. The reaction works very well for a variety of primary alkyl halides and can be a useful chemical tool to build ligands on a pre-existing complex, as in **6** and **7**.

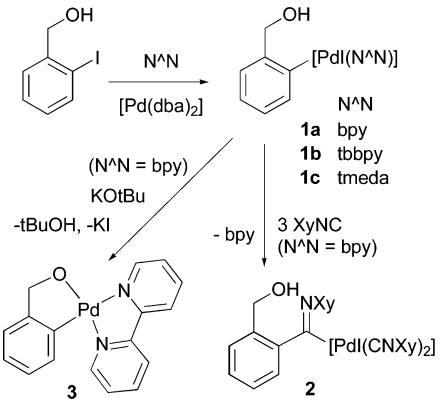
Dinuclear Pd complexes have attracted considerable interest in the literature. There are examples where the two [Pd] moieties are attached to the same aryl ring,[19−24] as well as examples where the two Pd atoms are linked by other ligands.[8,23,25−33] These dinuclear complexes have in some cases been used as catalysts, e.g., for Heck,[28] Hartwig−Buchwald,[32] Hiyama,[33] and Suzuki−Miyaura reactions.[25,31] The presence of two Pd atoms can improve the efficiency and selectivity of a catalyst, promote reactions that are difficult to achieve with a mononuclear complex, and result in the formation of unexpected compounds.[30,31] The dinuclear complexes that we report in this paper are quite novel in that they are bis(arylpalladium) complexes, for which there are very few precedents in the literature.[8,23,26,29] Moreover, they are the first examples where the aryl groups are *ortho*-substituted. Their reactivity in insertion[8] or coupling[26] reactions can afford interesting and novel compounds, and we plan to pursue this subject.

We also report in this paper the result of the reactions with XyNC of the complexes derived from benzyl alcohol, where a previously unknown cyclic imidate has been isolated and characterized. Five-membered cyclic imidates are of interest because they are expected to have potential bioactivities similar to those of their structurally similar isoindolin-1-one counterparts.[34]

RESULTS AND DISCUSSION

Synthesis of [PdI($C_6H_4CH_2OH$-2)(N^N)] (N^N = bpy (1a), tbbpy (1b), tmeda (1c)). Complexes **1a−c** were obtained by oxidative addition of 2-iodobenzyl alcohol to one equivalent of [Pd(dba)$_2$] in the presence of bpy, tbbpy, and tmeda (Scheme 1). We have similarly prepared the related complex [PdI($C_6H_4CH_2OH$-2}(PPh_3)$_2$] (**I**) (see the Supporting Information), which had already been prepared using [Pd(PPh_3)$_4$] as the oxidative addition substrate.[18] In the synthesis of **1b** (N^N = tbbpy) and **1c** (N^N = tmeda) the reactants were used in stoichiometric amounts, while in the synthesis of **1a** (N^N = bpy) and **I** 50% excess alcohol was used to obtain either a better yield (**1a**) or a clean product (**I**). Complexes **1b,c** decompose in solution to form [PdI$_2$(N^N)] (N^N = tbbpy, tmeda), which are identified by their characteristic ^{1}H NMR resonances at 9.84 ppm (dd) for [PdI$_2$(tbbpy)] (which also has a characteristic red color) or 2.95 ppm (s) for [PdI$_2$(tmeda)]. Attempts to prepare complexes similar to **1a−c** with a Br ligand instead of I, starting from 2-bromobenzyl alcohol, were unsuccessful.

Scheme 1



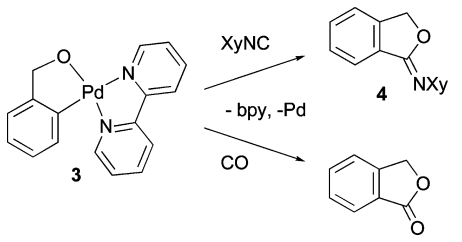
Reactivity of [PdI($C_6H_4CH_2OH$-2)(bpy)] (1a). We have investigated the reactivity of complex **1a** toward unsaturated molecules such as alkynes, alkenes, nitriles, cyanamides, allenes, and carbon monoxide, with and without the addition of TlOTf, but we were not able to obtain clean insertion (C−Pd bond) or addition (O−H bond) products, in contrast to our previous observations with *ortho*-palladated phenol derivatives.[5,16] We had already proposed that the OH group directly bonded to the aryl ligand played a crucial role in the insertion reactions with nitriles,[12,14] carbodiimides,[13,14] and isothiocyanates,[14] via a resonance form that locates the negative charge on the *ipso* carbon.[12,14] It now seems that the methylene link is detrimental even in the reactions with other molecules such as alkynes, alkenes, and CO, where the OH group did not seem to be involved.[5,16] We have been successful only in the reaction of **1a** with three equivalents of XyNC (Xy = 2,6-dimethylphenyl), which, when carried out in cold THF, instantaneously formed the insertion complex *trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}(CNXy)$_2$] (**2**, Scheme 1), which had to be isolated immediately to avoid decomposition. Complex **2** is the result of the insertion of one isocyanide molecule into the C−Pd bond and the displacement of the bpy ligand by two other molecules. The compound is stable in the solid state, but it decomposes in solution to form [Pd_2I_2(CNXy)$_2$], which is easily identified by its ^{1}H NMR resonance at 2.53 ppm. Pd complexes similar to **2**, with other functional groups in the aryl ring, have been previously prepared in a similar manner, mainly by our research group.[5,6,8,10,11,35] We have also described a few dinuclear analogues, prepared by oxidative addition[22] or by a double insertion reaction.[8,24]

The reaction of complex **1a** with KO^{t}Bu resulted in the abstraction of the alcoholic proton and the coordination of the oxygen to Pd, displacing the iodo ligand and forming the neutral chelate complex [Pd{κ^2-*C,O*-$C_6H_4(CH_2O)$-2}(bpy)] (**3**, Scheme 1), which crystallizes as a dinuclear aqua-bridged species (see below).

Reactions of [Pd(κ^2-*C,O*-$C_6H_4CH_2O$-2)(bpy)] (3) with XyNC and CO. The reaction of **3** with XyNC resulted in the formation of *N*-(2,6-dimethylphenyl)-2-benzofuran-1(3*H*)-imine (**4**) (Scheme 2), which was isolated as a yellowish oil and characterized by NMR spectroscopy and high-resolution mass spectroscopy (see the Experimental Section). The cyclic imidate **4** had not been described before, although the related compound with a ^{t}Bu group instead of Xy had been prepared by reaction of a dimeric oxapalladacycle phosphine complex with ^{t}BuNC.[18] The synthesis of other five-membered imidates by Pd-catalyzed reaction of 2-bromobenzyl alcohol and several

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

Scheme 2



isocyanides (not XyNC)[36] or by other, unrelated methods[37] has also been reported. The reaction of **3** with CO resulted in the decomposition of the complex to give 1(3*H*)-isobenzofuranone (phthalide) (Scheme 2). Both cyclic compounds reasonably form through a XyCN or CO insertion reaction into the C−Pd bond followed by a C−O coupling reaction. A CO insertion into the O−Pd bond would also be possible.[38]

Reactions of [Pd(κ^2-*C,O*-$C_6H_4CH_2O$-2)(bpy)] (3) with Alkyl Halides. By reaction of complex **3** with an excess of various primary alkyl halides of general formula RCH_2X (X = Br, I), the complexes $[PdX(C_6H_4CH_2OCH_2R\text{-}2)(bpy)]$ (X = I, R = H (**5a**), X = Br, R = Ph (**5b**), *p*-$C_6H_4CH_2Br$ (**5c**), *p*-C_6H_4Br (**5d**), and *p*-C_6H_4I (**5e**)) were obtained (Scheme 3). These complexes result from the nucleophilic attack of the coordinated oxygen in **3** at the alkyl group of the halide, followed by the coordination of the halide to the Pd atom and the opening of the chelate ring. We have found no precedent for this type of reaction in an arylpalladium complex. A 5-fold excess of RCH_2X was enough for the synthesis of **5d,e** in good yield, while for **5a−c** a 10-fold excess was required (see the Experimental Section).[39] Similar reactions with PhI or ^{i}PrI did not result in the formation of analogous complexes, suggesting that the success of the nucleophilic substitution requires a primary halide as substrate.

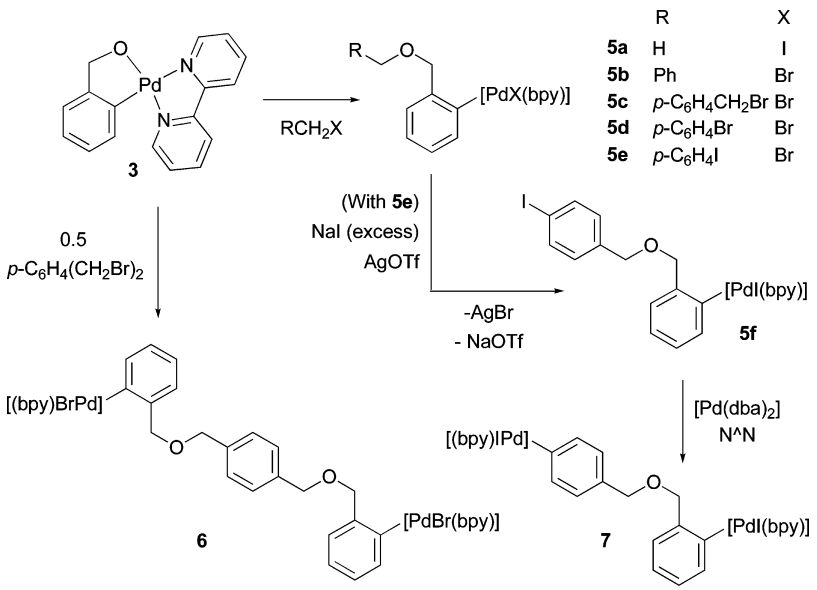
Synthesis of Dinuclear Palladium Complexes. When the reaction of **3** with *p*-$C_6H_4(CH_2Br)_2$ was carried out in a 2:1 ratio, we obtained the dinuclear Pd complex $[\{(bpy)BrPd(C_6H_4CH_2OCH_2\text{-}2)\}_2(C_6H_4\text{-}1,4)]$ (**6**, Scheme 3), which is the result of the nucleophilic attack of **3** on *both* methylene groups of the substrate.

We also attempted to prepare a dinuclear complex by oxidative addition of the C−X bond in **5d** (X = Br) or **5e** (X = I) to $[Pd(dba)_2]$ in the presence of bpy. However, with **5d** (X = Br) there was no oxidative addition, and with **5e** (X = I) we obtained a mixture of two complexes, probably as a consequence of the partial substitution by I of the Br ligand attached to Pd. We decided then to fully replace this Br ligand by I before the oxidative addition, by reaction of **5e** with AgOTf and a large excess of NaI, obtaining complex $[PdI\{C_6H_4(CH_2OCH_2(C_6H_4I\text{-}4))\text{-}2\}(bpy)]$ (**5f**, Scheme 3). By reaction of **5f** with $[Pd(dba)_2]$ and bpy (1:1:1 ratio) we cleanly obtained the dinuclear Pd complex $[(bpy)IPd(C_6H_4CH_2\text{-}2)O(CH_2C_6H_4\text{-}4)PdI(bpy)]$ (**7**, Scheme 3). Similarly to **6**, complex **7** shows a bridging organic chain with two aryl−Pd bonds, although now only one of them is *ortho*-substituted.

NMR and IR Data. All the complexes reported in this paper were extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^{1}H and ^{13}C resonances. To facilitate comparison, the data are collected in Table S.1 in the Supporting Information, together with a more extended discussion. We also include the data of complex **I**, which had been reported but not fully assigned.[18]

The methylenic protons of the CH_2OH groups are diastereotopic in complexes **1a−c** but equivalent in complex **I**, which has a symmetry plane. In the chelate complex **3** the methylenic protons are also equivalent, an indication that the molecule has a symmetry plane in solution (even in the solid state the molecule is almost planar, as shown by the X-ray structure below). The OH proton of **I** is strongly shifted to lower frequency (0.02 ppm) with respect to **1a−c** (2.66−3.00 ppm), as a consequence of the anisotropic effect of the PPh_3 ligands. Another peculiarity of complex **I** is the shift of the aryl *ipso* carbon to higher frequency (158.6 ppm) with respect to the complexes with N,N-donor ligands, **1a−c** (143.7−146.3 ppm). A similar trend has been observed previously by some of us for other aryl palladium complexes[3,21] and cannot be explained in terms of simplistic resonance or induction effects,

Scheme 3



DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

as ^{13}C chemical shifts are mainly determined by the paramagnetic contribution to the shielding constant.[40] A single ^{31}P resonance for the PPh_3 complex **I** (at 22.6 ppm) confirms the *trans* geometry of the complex.

In the tbbpy (complex **1b**) and bpy ligands (complexes **1a**, **5a**−**f**, **6**, and **7**), the *ortho* hydrogen atoms of the pyridyl ring *cis* to the aryl group (H16 in our numbering system) are strongly shielded (7.33−7.69 ppm) with respect to those of the pyridyl ring *trans* to aryl (H16′, 9.33−9.66 ppm). This is a common observation in aryl palladium complexes[3,21,24] and is a consequence of the anisotropic effect of the aryl group on the closest hydrogen of the bpy or tbbpy ligand. For the chelate complex **3**, in contrast, this effect is not observed (δ = 9.03 ppm for H16′ and 9.18 ppm for H16), because the aryl group is forced to be almost coplanar with the bpy ligand.

In the tmeda complex (**1c**) the presence of four ^{1}H and ^{13}C resonances for the Me groups of the tmeda indicates that the rotation around the Ar−Pd bond is hindered by the presence of the CH_2OH substituent in *ortho* position.

For the dinuclear complex **6** we expected that both halves of the molecule would be equivalent in solution, but this is not the case, as we observe two sets of ^{1}H and ^{13}C resonances that are almost coincident, with a few exceptions in the ^{1}H spectrum (see the Supporting Information). The molecule seems to be too bulky to adopt a completely symmetric structure in solution. The four central C_6H_4 protons appear as a single sharp doublet with J = 4 Hz. Most probably these protons form an AA′BB′ system (as in **5c**−**f**) where A and B are isochronous (but not equivalent, so that they are coupled with each other). The *p*-[PdI(bpy)] fragment in **7** hinders the rotation of the C_6H_4 group, so that the two *ortho* protons and the two *meta* protons are not equivalent, and they form an ABMN system, i.e., four (slightly broad) doublets with $^{3}J_{AB} = {}^{3}J_{MN}$ = 8 Hz.

The structure of the cyclic imidate **4** is confirmed by the $^{1}H,^{13}C$-HMBC spectrum, where the expected two- and three-bond $^{1}H,^{13}C$ correlations are observed. In the IR spectrum, the C═N band appears at 1693 cm^{-1}.

Finally, for complex **2**, resulting from the reaction of **1a** with XyNC, we have no ^{13}C NMR data, as the complex decomposes too rapidly in solution. In the ^{1}H NMR spectrum we observe the expected 1:2 Me resonances corresponding, respectively, to the inserted and the two (equivalent) coordinated XyNC groups. These groups give characteristic IR bands at 2182 cm^{-1} for the coordinated C≡NXy groups and at 1606 cm^{-1} for the inserted C═NXy group.

X-ray Structure Determinations. The crystal structures of the complexes **1a** (Figure 1), **3**·H_2O (Figures 2 and 3), and **5e** (Figure 4) were determined by X-ray diffraction studies (see Table S.2 for experimental details). The three structures show somewhat distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are 0.05 Å for **1a**, 0.08 Å for **3**·H_2O, and 0.04 Å for **5e**. For **3**·H_2O, the distortion arises from the steric pressure between the two ligands, which are forced to be approximately coplanar with a short contact H6···H26 2.14 Å; N21 lies 0.34 Å out of the plane of Pd and the other three ligand donor atoms. The lesser distortion for the other two structures might be a consequence of the chelating nature of the bpy ligand. The Pd−C bond distances are very similar for the three complexes (2.003(2) Å for **1a**, 1.9968(17) Å for **3**·H_2O, and 1.9903(19) Å for **5e**) and in the range expected for Pd−C bonds *trans* to a N-donor ligand.[3,21] The Pd−N bond distances follow the expected order of *trans* influence:[41] Pd−N

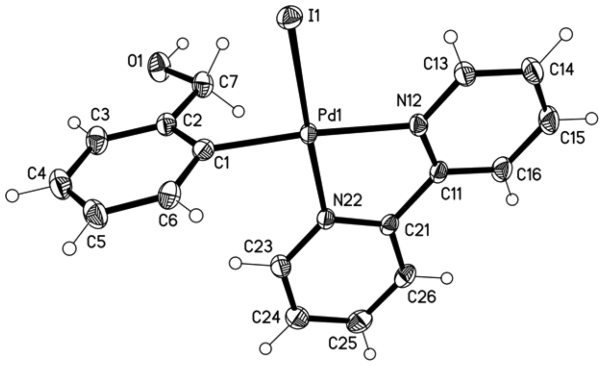


Figure 1. Thermal ellipsoid plot (50% probability level) of **1a**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.003(2), Pd(1)−N(12) = 2.1364(16), Pd(1)−N(22) = 2.0649(16), Pd(1)−I(1) = 2.5810(2), C(7)−O(1) = 1.423(2), C(2)−C(7) = 1.505(3), C(1)−C(2) = 1.399(3); C(1)−Pd(1)−N(22) = 93.36(7), C(1)−Pd(1)−I(1) = 88.53(5), N(12)−Pd(1)−N(22) = 78.80(6), N(12)−Pd(1)−I(1) = 99.48(5), C(1)−Pd(1)−N(12) = 171.18(7), N(22)−Pd(1)−I(1) = 177.02(5), C(2)−C(7)−O(1) = 110.69(17), C(1)−C(2)−C(7) = 119.46(18), C(2)−C(1)−Pd(1) = 119.08(15).

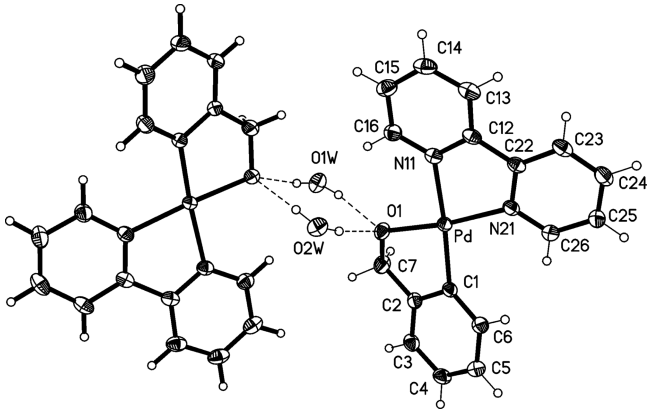


Figure 2. Thermal ellipsoid plot (50% probability level) of **3**·H_2O; two adjacent molecules of **3** are connected by two water molecules, each of which lies on a 2-fold axis. Only the asymmetric unit is numbered. Selected bond lengths (Å) and angles (deg): Pd−O(1) = 1.9916(12), Pd−C(1) = 1.9968(17), Pd−N(21) = 2.0379(15), Pd−N(11) = 2.1039(15), C(7)−O(1) = 1.419(2), C(2)−C(7) = 1.498(3), C(1)−C(2) = 1.409(2); C(1)−Pd-N(21) = 103.50(6), O(1)−Pd-C(1) = 82.54(6), O(1)−Pd−N(11) = 95.34(6), N(21)−Pd−N(11) = 79.21(6), C(1)−Pd−N(11) = 173.15(6), O(1)−Pd−N(21) = 172.22(6), C(7)−O(1)−Pd = 111.32(10), O(1)−C(7)−C(2) = 109.73(15), C(1)−C(2)−C(7) = 115.65(15), C(2)−C(1)−Pd = 111.49(12).

trans to aryl (2.1364(16) Å in **1a**, 2.1039(15) Å in **3**·H_2O, and 2.1362(17) Å in **5e**) > Pd−N *trans* to I (2.0649(16) Å in **1a**) > Pd−N *trans* to Br (2.0563(17) Å in **5e**) > Pd−N *trans* to O (2.0379(15) Å in **3**·H_2O). From the three Pd−N bond distances *trans* to aryl we can observe that in the chelate complex **3**·H_2O the *trans* influence of the aryl ligand is lower than for **1a** and **5e**.

The five-membered chelate ring in **3**·H_2O displays an approximate envelope conformation, whereby the Pd atom lies 0.55 Å out of the plane of the other four atoms (mean deviation 0.08 Å); the aryl ring is forced to an angle of only 26° with the plane defined by the bpy fragment, as opposed to the almost perpendicular disposition in **1a** (88°) and **5e** (87°). Within the chelate ring, the O−Pd bond distance is 1.9916(12)

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

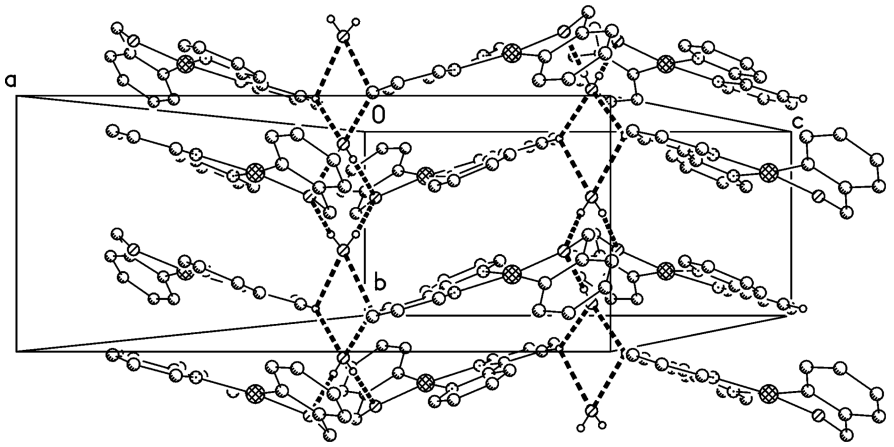


Figure 3. Packing diagram of $3{\cdot}H_2O$ viewed perpendicular to the *bc* plane. Hydrogen bonds O−H···O and C−H−O are drawn as dashed bonds. Adjacent chains of molecules overlap in this view direction, but are not connected.

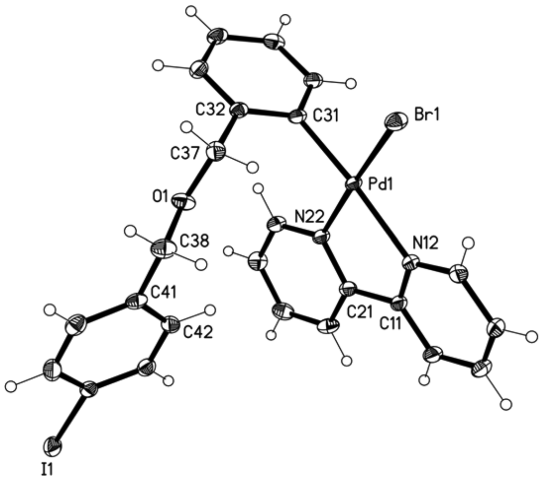


Figure 4. Thermal ellipsoid plot (50% probability level) of **5e**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(31) = 1.9903(19), Pd(1)−N(22) = 2.0563(17), Pd(1)−N(12) = 2.1362(17), Pd(1)−Br(1) = 2.4226(3), C(44)−I(1) = 2.097(2), C(37)−O(1) = 1.432(2), C(38)−O(1) = 1.423(2), C(31)−C(32) = 1.398(3), C(32)−C(37) = 1.498(3), C(38)−C(41) = 1.501(3); C(31)−Pd(1)−N(22) = 93.59(7), C(31)−Pd(1)−Br(1) = 90.12(6), N(12)−Pd(1)−Br(1) = 97.49(5), N(22)−Pd(1)−N(12) = 78.86(7), C(31)−Pd(1)−N(12) = 172.34(7), N(22)−Pd(1)−Br(1) = 174.97(5), C(32)−C(37)−O(1) = 108.19(16), C(37)−O(1)−C(38) = 110.84(15), O(1)−C(38)−C(41) = 108.10(16).

Å, slightly shorter than the O−Pd distance (2.048(3) Å) found in a related 2-hydroxymethylphenyl chelate complex that is a dimer with a PPh_3 ligand *trans* to O and two Pd−O bridges.[18] The C−O bond distance in $3{\cdot}H_2O$ (1.419(2) Å) is slightly shorter than the C−O bond distances in **1a** (1.423(2) Å) and **5e** (1.432(2) and 1.423(2) Å), and the Ar−CH_2 bond distances are similar (all in the range 1.498−1.505 Å), indicating that the formation of the chelate ring does not involve a weakening of the bonds within the ring.

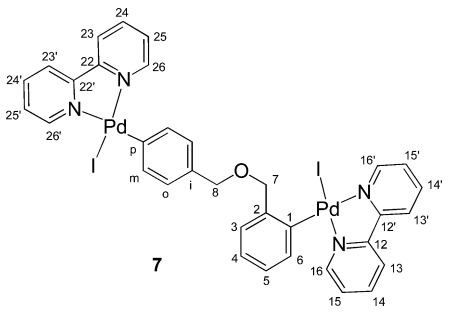
The packing of **1a** involves O−H···I hydrogen bonds that connect the molecules via the *n* glide planes. The chelate complex $3{\cdot}H_2O$ (Figure 2) crystallizes with two molecules of water, both lying with the oxygen atom on a crystallographic 2-fold axis, which are hydrogen-bonded to the oxygen in the chelate ring, forming dimeric units $(3{\cdot}H_2O)_2$ bridged by two water molecules. The central ring belongs to the graph set $R_4^2(8)$. The $(3{\cdot}H_2O)_2$ dimers are further connected by three-center interactions H23···O1W,O2W to form ribbons of molecules parallel to the short *b* axis (Figure 3).

Conclusion. We have synthesized new aryl Pd complexes derived from benzyl alcohol, one of them a chelate complex resulting from the deprotonation of the alcohol. The reactivity of these complexes toward XyNC has resulted in an insertion complex and a cyclic imidate. The chelate complex reacts with primary alkyl halides via a nucleophilic attack of the coordinated oxygen on the alkyl group, resulting in the opening of the chelate ring and the formation of new aryl palladium complexes with larger substituents on the aryl ring. Two novel dinuclear bis(arylpalladium) complexes have been prepared, either by reaction with an alkyl dihalide or by a secondary oxidative addition to one of the new complexes.

EXPERIMENTAL SECTION

The ^1H and ^{13}C resonances were assigned with the help of 2D NMR experiments (see Chart 1 for the numbering system). All experiments

Chart 1



were conducted under a N_2 atmosphere using Schlenk techniques. THF, CH_2Cl_2, hexane, and Et_2O were distilled before use. [Pd(dba)$_2$][42] and *trans,trans*-2,5-distyryl-1,4-dibromobenzene were prepared according to literature procedures. TlOTf was prepared by reaction of Tl_2CO_3 and triflic acid (1:2) in water and recrystallized from acetone/Et_2O.

Synthesis of [PdI($C_6H_4CH_2OH$-2)(bpy)] (1a). 2-Iodobenzyl alcohol (183 mg, 0.782 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and bpy (81.4 mg, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for ca. 90 min until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Et_2O (20 mL) was added, and the resulting pale pink suspension was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **1a** as a pale reddish solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 124 mg (48%). Mp: 229 °C dec. IR (cm^{-1}): ν(OH) 3430. ^{1}H NMR (600 MHz, CD_2Cl_2): 9.46 (ddd, 1H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1, H16′ bpy), 8.06–8.02 (m, 2H, H13,13′ bpy), 7.98 (td, 1H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, H14′ bpy), 7.94 (td, 1H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, H14 bpy), 7.53 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 1H, H15′ bpy), 7.39–7.36 (m, 1H, H6 aryl), 7.33 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, H16 bpy), 7.27–7.23 (m, 1H, H15 bpy), 7.13–7.10 (m, 1H, H3 aryl), 6.93–6.89 (m, 2H, H5,H4 aryl), 4.99 (dd, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 3 Hz, 1H, CH_2), 4.48 (dd, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 10 Hz, 1H, CH_2), 2.66 (dd, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 3 Hz, 1H, OH). ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2): 156.6 (C12 bpy), 154.4 (C12′ bpy), 153.1 (CH16′ bpy), 150.4 (CH16 bpy), 146.3 (C1 aryl), 145.4 (C2 aryl), 139.6 (CH14 bpy), 139.5 (CH14′ bpy), 136.6 (CH6 aryl), 128.8 (CH3 aryl), 127.6 (CH15′ bpy), 127.2 (CH15 bpy), 126.8 (CH5 aryl), 124.3 (CH4 aryl), 122.8 (CH13 bpy), 122.4 (CH13′ bpy), 68.7 (CH_2). Anal. Calcd for $C_{17}H_{15}IN_2OPd$: C, 41.11; H, 3.04; N, 5.64. Found: C, 40.98; H, 3.06; N, 5.70. Single crystals of **1a** were grown by liquid diffusion of Et_2O into a solution of **1a** in CH_2Cl_2.

Synthesis of [PdI($C_6H_4CH_2OH$-2)(tbbpy)] (1b). 2-Iodobenzyl alcohol (122 mg, 0.521 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and tbbpy (140 mg, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for 2 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Warm hexane (20 mL) was added, and the resulting yellow suspension was filtered off, washed with warm hexane (3 × 5 mL), and dried in vacuo to give **1b** as a pale yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, acetone, and Et_2O (partially). Yield: 133 mg (42%). Mp: 217 °C dec. IR (cm^{-1}): ν(OH) 3490. ^{1}H NMR (400 MHz, $CDCl_3$): 9.46 (d, $^3J_{HH}$ = 6 Hz, 1H, H16′ tbbpy), 7.98 (s, 1H, H13 tbbpy), 7.97 (s, 1H, H13′ tbbpy), 7.53 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1H, H15′ tbbpy), 7.50 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 1H, H6 aryl), 7.33 (d, $^3J_{HH}$ = 6 Hz, 1H, H16 tbbpy), 7.28 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 2H, H15 tbbpy), 7.20 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 1H, H3 aryl), 7.02–6.93 (m, 2H, H5,H4 aryl), 5.21 (dd, $^3J_{HH}$ = 12 Hz, $^4J_{HH}$ = 3 Hz, 1H, CH_2), 4.66 (app t, J_{HH} = 10 Hz, 1H, CH_2), 2.92–2.86 (m, 1H, OH), 1.43 (s, 9H, ^{t}Bu′ tbbpy), 1.38 (s, 9H, ^{t}Bu tbbpy). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 163.62 (C14 tbbpy), 163.58 (C14′ tbbpy), 156.2 (C12 tbbpy), 154.0 (C12′ tbbpy), 152.6 (CH16′ tbbpy), 149.7 (CH16 tbbpy), 146.3 (C1 aryl), 144.8 (C2 aryl), 136.2 (CH6 aryl), 128.6 (CH3 aryl), 126.6 (CH5 aryl), 124.2 (CH15′ tbbpy), 123.93 (CH4 aryl), 123.91 (CH15 tbbpy), 118.7 (CH13 tbbpy), 118.2 (CH13′ tbbpy), 68.8 (CH_2), 35.74 (CMe_3 tbbpy), 35.70 (CMe_3′ tbbpy), 30.6 (CMe_3′ tbbpy), 30.5 (CMe_3 tbbpy). Anal. Calcd for $C_{25}H_{31}IN_2OPd$: C, 49.32; H, 5.13; N, 4.60. Found: C, 49.43; H, 5.11; N, 4.68.

Synthesis of [PdI($C_6H_4CH_2OH$-2)(tmeda)] (1c). 2-Iodobenzyl alcohol (122 mg, 0.521 mmol) was added to a suspension of [Pd(dba)$_2$] (300 mg, 0.521 mmol) and tmeda (78.2 μL, 0.521 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for 4 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the reddish solution was evaporated to dryness. Et_2O (20 mL) was added, and the resulting pale pink suspension was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **1c** as an orange solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 140 mg (59%). Mp: 105 °C. IR (cm^{-1}): ν(OH) 3305. ^{1}H NMR (400 MHz, $CDCl_3$): 7.29 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 1H, H6 aryl), 7.11 (dd, $^3J_{HH}$ = 7, $^4J_{HH}$ = 2 Hz, 1H, H3 aryl), 6.93–6.84 (m, 2H, H5,H4 aryl), 5.43 (dd, $^3J_{HH}$ = 11 Hz, $^4J_{HH}$ = 3 Hz, 1H, CH_2), 4.68 (app t, J_{HH} = 11 Hz, 1H, CH_2), 3.00 (dd, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 3 Hz, 1H, OH), 2.95–2.86 (m, 1H, CH_2 tmeda), 2.75–2.45 (several m, 3H, CH_2 tmeda), 2.72, 2.69, 2.48, and 2.12 (s, 3H, Me tmeda). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 145.0 (C2 aryl), 143.7 (C1 aryl), 135.6 (CH6 aryl), 128.4 (CH3 aryl), 126.2 (CH5 aryl), 123.7 (CH4 aryl), 69.1 (CH_2), 62.4 (CH_2 tmeda), 58.5 (CH_2 tmeda), 51.2 and 50.7 (Me tmeda), 49.0 (2C, Me tmeda). Anal. Calcd for $C_{13}H_{23}IN_2OPd$: C, 34.19; H, 5.08; N, 6.13. Found: C, 34.54; H, 5.02; N, 5.94.

Synthesis of *trans*-[PdI{C(=NXy)($C_6H_4CH_2OH$-2)}(CNXy)$_2$] (2). XyNC (159 mg, 1.21 mmol) was added to a solution of **1a** (200 mg, 0.403 mmol) in dry degassed THF (20 mL), under N_2 and in an ice bath. The solvent was immediately evaporated in vacuo, and Et_2O (20 mL) was added under N_2, forming a yellow suspension, which was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **2** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 147 mg (50%). Mp: 130 °C. IR (cm^{-1}): ν(OH) 3311, ν(C≡N) 2182, ν(C=N) 1606. ^{1}H NMR (300 MHz, $CDCl_3$): 8.56 (d, $^3J_{HH}$ = 8 Hz, 1H, aryl), 7.56–7.48 (m, 1H, aryl), 7.41–7.37 (m, 2H, aryl), 7.26–7.18 (m, 2H, Xy^{co}), 7.06 (d, $^3J_{HH}$ = 8 Hz, 4H, Xy^{co}), 6.95 (br s, 3H, Xy^{in}), 5.12 (t, $^3J_{HH}$ = 7 Hz, 1H, OH), 4.70 (2, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 2.192 (s, 6H, Me Xy^{in}), 2.186 (s, 12H, Me Xy^{co}). No ^{13}C NMR data are available because the complex decomposes rapidly in solution. Anal. Calcd for $C_{34}H_{34}IN_3OPd$: C, 55.64; H, 4.67; N, 5.72. Found: C, 55.57; H, 4.80; N, 5.64.

Synthesis of [Pd(κ^2-*C,O*-$C_6H_4CH_2O$-2)(bpy)] (3). KO^{t}Bu (361 mg, 3.22 mmol) was added to a solution of **1a** (400 mg, 0.805 mmol) in CH_2Cl_2 (20 mL) under N_2, whereby the color changed from reddish to yellow. The mixture was stirred for 15 min at room temperature and then filtered over Celite. The resulting yellow solution was evaporated to dryness, and Et_2O (20 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **3** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 227 mg (77%). Mp: 129 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): 9.18 (d, $^3J_{HH}$ = 5 Hz, 1H, H16 bpy), 9.03 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.08–7.96 (m, 4H, H13,13′,14,14′ bpy), 7.59–7.52 (m, 2H, H15,15′ bpy), 7.23–7.19 (m, 1H, H6 aryl), 7.04–6.97 (m, 3H, H3,4,5 aryl), 5.21 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): 166.2 (C2 aryl), 156.6 (C12 bpy), 153.4 (C12′ bpy), 152.0 (CH16 bpy), 151.0 (C1 aryl), 149.9 (CH16′ bpy), 138.8 (CH14′ bpy), 138.1 (CH14 bpy), 131.7 (CH6), 126.6 (CH15 bpy), 126.3 (CH15′ bpy), 124.0 (CH4 aryl), 123.6 (CH5 aryl), 122.5 (CH13 bpy), 121.1 (CH13′ bpy), 119.1 (CH3 aryl), 78.4 (CH_2). Anal. Calcd for $C_{17}H_{14}N_2OPd$: C, 55.37; H, 3.83; N, 7.60. Found: C, 55.12; H, 3.74; N, 7.43. Single crystals of **3**·H_2O were grown by liquid diffusion of hexane into a solution of **3** in CH_2Cl_2.

Synthesis of *N*-(2,6-Dimethylphenyl)-2-benzofuran-1(3*H*)-imine (4). XyNC (35.6 mg, 0.271 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in THF (20 mL) under N_2. The mixture was stirred for 2 h in an ice bath, whereby the color changed from yellow to black. It was then filtered over $MgSO_4$, and the resulting yellow solution was evaporated to dryness, leaving a yellow oil. This oil was washed with cold hexane (10 mL), to eliminate the bpy ligand, and then dried in vacuo to give **4** as a yellow oil, which is soluble in Et_2O, CH_2Cl_2, $CHCl_3$, and acetone. Yield: 29.0 mg (45%). IR (cm^{-1}): ν(C=N) 1693. Mp: 129 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, $^3J_{HH}$ = 7 Hz, 1H, H7), 7.59 (t, $^3J_{HH}$ = 7 Hz, 1H, H5), 7.53 (t, $^3J_{HH}$ = 7 Hz, 1H, H6), 7.41 (d, $^3J_{HH}$ = 7 Hz, 1H, H4), 7.05 (d, $^3J_{HH}$ = 7 Hz, 2H, *m*-H Xy), 6.93 (7, $^3J_{HH}$ = 7 Hz, 1H, *p*-H Xy), 5.31 (s, 2H, CH_2), 2.16 (s, 6H, Me Xy). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 158.1 (C=N), 145.4 (*i*-C Xy), 143.9 (C3), 132.1 (CH5), 129.9 (C8), 128.9 (CH6), 128.4 (2C, *o*-C Xy), 127.8 (2C, m-CH^{Xy}), 124.4 (CH7), 123.3 (*p*-CH Xy), 121.7 (CH4), 72.6 (CH_2), 18.5 (2C, Me Xy). HR ESI+ TOF MS: calcd for $C_{16}H_{15}NO$, m/z 238.1226, found 238.1226, Δ = 0.00 ppm.

Reaction of 3 with CO. CO was bubbled for 5 min through a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL), whereby extensive decomposition was observed. The mixture was stirred for 1 h in a CO atmosphere. Then it was filtered over $MgSO_4$, and the resulting yellow solution was evaporated to dryness, whereby a reddish color appeared in the residue. This residue was extracted with cold

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX–XXX

Et_2O (10 mL), and the resulting yellowish solution was filtered over Celite and then dried in vacuo to give a solid (45 mg), which is shown by ^1H NMR spectroscopy to be a clean mixture of 1(3*H*)-isobenzofuranone (phthalide) and bpy in a 1:1 ratio. ^1H NMR (400 MHz, $CDCl_3$): 8.69 (d, $^3J_{HH}$ = 5 Hz, 2H, bpy), 8.40 (d, $^3J_{HH}$ = 8 Hz, 2H, bpy), 7.94 (d, $^3J_{HH}$ = 8 Hz, 1H, phthalide), 7.83 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 2H, bpy), 7.69 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, phthalide), 7.54 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, phthalide), 7.50 (dt, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, phthalide), 7.32 (ddd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 2H, bpy), 5.33 (s, 2H, phthalide).

Synthesis of [PdI($C_6H_4CH_2OMe$-2)(bpy)] (5a). MeI (169 μL, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred in the dark for 4 h at room temperature, whereby the yellow color darkened. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **5a** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 101 mg (73%). Mp: 202 °C. ^1H NMR (400 MHz, $CDCl_3$): 9.66 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.09−8.04 (m, 2H, H13,13′ bpy), 8.01 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14′ bpy), 7.98 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.57 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15′ bpy), 7.53 (ddd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16 bpy), 7.50−7.45 (m, 1H, H6 aryl), 7.32 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.26−7.22 (m, 1H, H3 aryl), 7.02−6.95 (m, 2H, H4,5 aryl), 5.00 and 4.77 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2), 3.32 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 155.9 (C12 bpy), 153.9 (C12′ bpy), 153.2 (CH16′ bpy), 150.6 (CH16 bpy), 145.3 (C1 aryl), 142.2 (C2 aryl)), 138.74 (CH14′ bpy), 138.69 (CH14 bpy), 136.1 (CH6 aryl)), 127.08 (CH3 aryl)), 127.05 (CH15′ bpy), 126.6 (CH15 bpy), 126.3 (CH5 aryl)), 123.8 (CH4 aryl)), 121.9 (CH13 bpy), 121.6 (CH13′ bpy), 78.5 (CH_2), 58.5 (Me). Anal. Calcd for $C_{18}H_{17}IN_2OPd$: C, 42.34; H, 3.36; N, 5.49. Found: C, 41.97; H, 3.23; N, 5.53.

Synthesis of [PdBr($C_6H_4CH_2OCH_2Ph$-2)(bpy)] (5b). $PhCH_2Br$ (322 μL, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to dryness. Cold Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with cold Et_2O (3 × 5 mL), and dried in vacuo to give **5b** as a pale yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone and partially soluble in Et_2O. Yield: 122 mg (83%). Mp: 171 °C. ^1H NMR (400 MHz, $CDCl_3$): 9.43 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.06−7.99 (m, 2H, H14′,13′ bpy), 7.97 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 7.88 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.69 (ddd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 2 Hz, 1H, H16 bpy), 7.62−7.57 (m, 1H, H15′ bpy), 7.53−7.47 (m, 1H, H6 aryl), 7.32−7.27 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.12−7.05 (m, 5H, Ph), 7.05−6.98 (m, 2H, H4,5 aryl), 5.31 and 4.89 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.56 and 4.52 (AB system, $^2J_{HH}$ = 12 Hz, 2H, CH_2-8). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 155.9 (C12 bpy), 153.7 (C12′ bpy), 151.7 (CH16 bpy), 150.9 (CH16′ bpy), 149.7 (C1 aryl), 141.9 (C2 aryl), 139.2 (*i*-C Ph), 138.9 (CH14′ bpy), 138.4 (CH14 bpy), 135.0 (CH6 aryl), 128.13 (CH3 aryl), 128.12 (2C, *m*-CH Ph), 127.7 (2C, *o*-CH Ph), 127.1 (*p*-CH Ph), 126.74 (CH15′ bpy), 126.71 (CH5 aryl), 126.6 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.3 (CH13′ bpy), 76.0 (CH_2-7), 72.6 (CH_2-8). Anal. Calcd for $C_{24}H_{21}BrN_2OPd$: C, 53.40; H, 3.92; N, 5.19. Found: C, 53.65; H, 4.04; N, 5.42.

Synthesis of [PdBr{$C_6H_4(CH_2OCH_2(C_6H_4CH_2Br$-4))-2}(bpy)] (5c). *p*-Xylylene dibromide (715 mg, 2.71 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature, whereby the color changed from yellow to orange. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **5c** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 104 mg (61%). Mp: 103 °C dec. ^1H NMR (400 MHz, $CDCl_3$): 9.39 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.03−7.99 (m, 2H, H14′,13′ bpy), 7.94 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 7.85 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.62 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1, 1H, H16 bpy), 7.59−7.54 (m, 1H, H15′ bpy), 7.53−7.48 (m, 1H, H6 aryl), 7.32−7.27 (m, 1H, H3 aryl), 7.14 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.07 (A part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *m*-H C_6H_4), 7.01 (B part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *o*-H C_6H_4), 7.03−6.99 (m, 2H, H4,5 aryl), 5.28 and 4.85 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.53 (s, 2H, CH_2-8), 4.41 (s, 2H, CH_2Br). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 155.7 (C12 bpy), 153.7 (C12′ bpy), 151.4 (CH16 bpy), 150.7 (CH16′ bpy), 150.2 (C1 aryl), 141.8 (C2 aryl), 139.7 (*i*-C $C_6H_4CH_2Br$), 139.0 (CH14′ bpy), 138.5 (CH14 bpy), 136.3 (*p*-C $C_6H_4CH_2Br$), 135.0 (CH6 aryl), 128.8 (2C, *m*-CH $C_6H_4CH_2Br$), 128.1 (CH3 aryl), 127.8 (2C, *o*-CH $C_6H_4CH_2Br$), 126.8 (CH5 aryl), 126.7 (CH15′ bpy), 126.5 (CH15 bpy), 123.8 (CH4 aryl), 122.0 (CH13 bpy), 121.6 (CH13′ bpy), 76.2 (CH_2-7), 72.0 (CH_2-8), 34.0 (CH_2Br). Anal. Calcd for $C_{25}H_{22}Br_2N_2OPd$: C, 47.46; H, 3.50; N, 4.43. Found: C, 47.47; H, 3.78; N, 4.30.

Synthesis of [PdBr{$C_6H_4(CH_2OCH_2(C_6H_4Br$-4))-2}(bpy)] (5d). 4-Bromobenzyl bromide (340 mg, 1.36 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature, whereby the color changed from yellow to orange. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **5d** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 145 mg (87%). Mp: 185 °C. ^1H NMR (300 MHz, $CDCl_3$): 9.39 (d, $^3J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.05−8.01 (m, 2H, H13′,14′ bpy), 7.98 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 7.89 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.62 (d, $^3J_{HH}$ = 6 Hz, 1H, H16 bpy), 7.61−7.53 (m, 1H, H15′ bpy), 7.51−7.46 (m, 1H, H6 aryl), 7.26−7.21 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.11 (A part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *m*-H C_6H_4Br), 7.04−6.98 (m, 2H, H4,5 aryl), 6.95 (B part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *o*-H C_6H_4Br), 5.28 and 4.85 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.52 and 4.46 (AB system, $^2J_{HH}$ = 12 Hz, 2H, CH_2-8). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): 155.8 (C12 bpy), 153.6 (C12′ bpy), 151.5 (CH16 bpy), 150.8 (CH16′ bpy), 149.9 (C1 aryl), 141.6 (C2 aryl), 139.0 (CH14′ bpy), 138.4 (CH14 bpy), 138.2 (*i*-C C_6H_4Br), 135.0 (CH6 aryl), 131.1 (2C, *m*-CH C_6H_4Br), 129.5 (2C, *o*-CH C_6H_4Br), 128.1 (CH3 aryl), 126.82 (CH5 aryl), 126.76 (CH15′ bpy), 126.5 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.5 (CH13′ bpy), 120.8 (*p*-C C_6H_4Br), 76.1 (CH_2-7), 71.8 (CH_2-8). Anal. Calcd for $C_{24}H_{20}Br_2N_2OPd$: C, 46.59; H, 3.26; N, 4.53. Found: C, 46.51; H, 3.23; N, 4.36.

Synthesis of [PdBr{$C_6H_4(CH_2OCH_2(C_6H_4I$-4))-2}(bpy)] (5e). 4-Iodobenzyl bromide (404 mg, 1.36 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **5e** as a pale yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 167 mg (93%). Mp: 173 °C. ^1H NMR (400 MHz, $CDCl_3$): 9.40 (d, $^3J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.05−8.01 (m, 2H, H13′,14′ bpy), 7.97 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 7.89 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.62 (d, $^3J_{HH}$ = 6 Hz, 1H, H16 bpy), 7.58 (td, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 3 Hz, 1H, H15′ bpy), 7.51−7.46 (m, 1H, H6 aryl), 7.30 (A part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *m*-H C_6H_4I), 7.25−7.20 (m, 1H, H3 aryl), 7.17 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.04−6.98 (m, 2H, H4,5 aryl), 6.81 (B part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *o*-H C_6H_4I), 4.84 and 5.28 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.51 and 4.46 (AB system, $^2J_{HH}$ = 12 Hz, 2H, CH_2-8). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): 155.8 (C12 bpy), 153.6 (C12′ bpy), 151.5 (CH16 bpy), 150.8 (CH16′ bpy), 150.0 (C1 aryl), 141.7 (C2

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

aryl), 138.99 (CH14′ bpy), 138.96 (*i*-C C_6H_4I), 138.4 (CH14 bpy), 137.1 (2C, *m*-CH C_6H_4I), 135.0 (CH6 aryl), 129.7 (2C, *o*-CH C_6H_4I), 128.1 (CH3 aryl), 126.83 (CH5 aryl), 126.76 (CH15′ bpy), 126.5 (CH15 bpy), 123.9 (CH4 aryl), 121.8 (CH13 bpy), 121.5 (CH13′ bpy), 92.5 (*p*-C C_6H_4I), 76.1 (CH_2-7), 71.9 (CH_2-8). Anal. Calcd for $C_{24}H_{20}BrIN_2OPd$: C, 43.30; H, 3.03; N, 4.21. Found: C, 43.41; H, 3.03; N, 4.42. Single crystals of **5e** were grown by liquid diffusion of Et_2O into a solution of **5e** in CH_2Cl_2.

Synthesis of [PdI{$C_6H_4(CH_2OCH_2(C_6H_4I$-4))-2}(bpy)] (5f). AgOTf (38.5 mg, 0.150 mmol) and an excess of NaI (2250 mg, 15.0 mmol) were added to a solution of **5e** (100 mg, 0.150 mmol) in CH_2Cl_2 (20 mL) under N_2. A suspension formed immediately, which was stirred for 1 h at room temperature. Then it was filtered over $MgSO_4$, and the resulting orange solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (25 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **5f** as an orange solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 51.0 mg (48%). Mp: 145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 9.61 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, $^5J_{HH}$ = 2 Hz, 1H, H16′ bpy), 8.04−8.00 (m, 2H, H13′,14′ bpy), 7.97−7.85 (m, 2H, H13,14 bpy), 7.58−7.52 (m, 1H, H15′ bpy), 7.50−7.42 (m, 2H, H6 aryl, H16 bpy), 7.28 (A part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *m*-H C_6H_4I), 7.25−7.17 (m, 2H, H3 aryl, H15 bpy), 7.01−6.95 (m, 2H, H4,H5 aryl), 6.79 (B part of AB system, $^3J_{HH}$ = 8 Hz, 2H, *o*-H C_6H_4I), 5.14 and 4.79 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.49 and 4.44 (AB system, $^2J_{HH}$ = 12 Hz, 2H, CH_2-8). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): 155.6 (C12 bpy), 153.6 (C12′ bpy), 153.1 (CH16′ bpy), 150.5 (CH16 bpy), 146.8 (C1 aryl), 142.0 (C2 aryl), 139.0 (*i*-C C_6H_4I), 138.7 (CH14′ bpy), 138.4 (CH14 bpy), 137.1 (2C, *m*-CH C_6H_4I), 136.3 (CH6 aryl), 129.7 (2C, *o*-CH C_6H_4I), 128.0 (CH3 aryl), 127.0 (CH15′ bpy), 126.7 (CH5 aryl), 126.4 (CH15 bpy), 123.7 (CH4 aryl), 121.7 (CH13 bpy), 121.6 (CH13′ bpy), 92.5 (*p*-C C_6H_4I), 77.1 (CH_2-7), 71.9 (CH_2-8). Anal. Calcd for $C_{24}H_{20}I_2N_2OPd$: C, 40.45; H, 2.83; N, 3.93. Found: C, 40.20; H, 2.68; N, 4.00.

Synthesis of [{(bpy)BrPd($C_6H_4CH_2OCH_2$-2)}$_2$(C_6H_4-1,4)] (6). *p*-Xylylene dibromide (35.9 mg, 0.136 mmol) was added to a solution of **3** (100 mg, 0.271 mmol) in CH_2Cl_2 (20 mL) under N_2. The mixture was stirred for 4 h at room temperature with no significant change in color. It was then filtered over Celite, and the resulting yellow solution was concentrated in vacuo to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried in vacuo to give **6** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 115 mg (85%). Mp: 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 9.36−9.33 (m, 2H, H16′,16′ bpy), 8.06−8.03 (m, 2H, H14′,13′ bpy), 8.00−7.97 (m, 3H, H13′,13,13 bpy), 7.89 and 7.88 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14,14′ bpy), 7.78 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 7.58−7.53 (m, 3H, H16,16,15′ bpy), 7.53−7.48 (m, 3H, H6,6 aryl and H15′ bpy), 7.28−7.24 (m, 1H, H3 aryl), 7.23−7.19 (m, 1H, H3 aryl), 7.17−7.11 (m, 2H, H15,15 bpy), 7.06−6.98 (m, 4H, H5,5,4,4), 6.77 (d, $^3J_{HH}$ = 4 Hz, 4H, C_6H_4), 5.20 and 4.87 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 5.20 and 4.80 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.45−4.37 (m, 4H, CH_2-8, CH_2-8). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): 155.96 and 155.93 (C12 bpy), 153.79 and 153.71 (C12′ bpy), 151.32 and 151.30 (CH16 bpy), 150.58 and 150.57 (CH16′ bpy), 149.99 and 149.96 (C1 aryl), 142.05 and 142.01 (C2 aryl), 139.23 and 139.16 (CH14′ bpy), 138.74 and 138.66 (CH14 bpy), 137.76 and 137.75 (*i*-C C_6H_4), 135.23 and 135.20 (CH6 aryl), 128.08 and 128.01 (CH3 aryl), 127.40 and 127.35 (2C, CH C_6H_4), 126.75 and 126.69 (CH5 aryl), 126.66 and 126.62 (CH15′ bpy), 126.53 and 126.49 (CH15 bpy), 123.81 and 123.77 (CH4 aryl), 122.39 and 122.32 (CH13 bpy), 121.91 and 121.85 (CH13′ bpy), 75.78 and 75.63 (CH_2-7), 72.41 and 72.30 (CH_2-8). Anal. Calcd for $C_{42}H_{36}Br_2N_4O_2Pd_2$: C, 50.37; H, 3.62; N, 5.59. Found: C, 50.03; H, 3.50; N, 5.62.

Synthesis of [(bpy)IPd($C_6H_4CH_2$-2)O($CH_2C_6H_4$-4)PdI(bpy)] (7). **5f** (71.0 mg, 0.100 mmol) was added to a suspension of [Pd(dba)$_2$] (57.6 mg, 0.100 mmol) and bpy (15.6 mg, 0.100 mmol) in dry degassed toluene (20 mL) under N_2. The resulting mixture was stirred in an ice bath for ca. 2.5 h until the dark red color of [Pd(dba)$_2$] was no longer observed. The brownish suspension was then concentrated in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered over Celite, and the orange solution was evaporated to dryness. Et_2O (20 mL) was added, and the resulting orange suspension was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give **7** as an orange solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 55.0 mg (56%). Mp: 153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 9.61 and 9.57 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1, 1H, H16′,26′ bpy), 8.17−8.02 (several m, 4H, H13,13′,23,23′ bpy), 8.02−7.92 (several m, 4H, H14′,24′ and H14 or H24 bpy), 7.87 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H24 or H14 bpy), 7.59−7.53 (m, 2H, H6 aryl and H15′ or 25′ bpy), 7.48−7.36 (m, 3H, H16,26, H25′or 15′ bpy), 7.35 (ddd, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 or 25 bpy), 7.21 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 1H, H3 aryl), 7.11 (ddd, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H25 or 15 bpy), 7.02 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 1H, H5 aryl), 6.96 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, H4 aryl), 7.03 and 6.85 (br, A part of AB system, 1H, $^3J_{HH}$ = 8 Hz, *m*-H C_6H_4[Pd]), 6.57 and 6.42 (br, B part of AB system, 1H, $^3J_{HH}$ = 8 Hz, *o*-H C_6H_4[Pd]), 5.22 and 4.62 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-7), 4.48 and 4.40 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2-8). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): 155.7 and 155.2 (C12,22 bpy), 154.5 and 153.9 (C12′,22′ bpy), 153.0 and 152.4 (C16′,26′ bpy), 150.6 and 150.0 (CH16,26 bpy), 148.8 (C1 aryl), 143.9 (*p*-C C_6H_4[Pd]), 142.3 (C2 aryl), 138.89, 138.86, 138.8, and 138.5 (CH14,14′,24,24′ bpy), 136.3 (CH6 aryl), 135.8 and 135.6 (*m*-CH C_6H_4[Pd]), 133.8 (*i*-C C_6H_4[Pd]), 128.6 (CH3 aryl), 126.94, 126.92, and 126.86 (CH15′,25′ and CH5 bpy), 126.5 and 126.4 (*o*-CH C_6H_4[Pd]), 126.4 and 125.9 (CH15,25 bpy), 123.4 (CH4 aryl), 122.9, 122.4, 122.0, and 121.7 (CH13,13′,23,23′ bpy), 77.6 (CH_2-7), 72.6 (CH_2-8). Anal. Calcd for $C_{34}H_{28}I_2N_4OPd_2$: C, 41.87; H, 2.89; N, 5.74. Found: C, 41.80; H, 3.23; N, 5.53.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis of complex **I**. NMR data tables of complexes **1a−c**, **I**, **3**, **5a−f**, **6**, and **7**. Extended comments on the NMR data. X-ray crystallographic data, structure refinement details, and CIF files for compounds **1a**, **3**·H_2O, and **5e**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00309.

■ AUTHOR INFORMATION

Corresponding Authors

*Correspondence regarding the synthesis and properties of compounds: eloisamv@um.es (E. Martínez-Viviente). Web: http://www.um.es/gqo/.

*Correspondence regarding the X-ray diffraction studies: p.jones@tu-bs.de (P. G. Jones).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Ministerio de Educación y Ciencia (Spain), FEDER (Project CTQ2011-24016), and Fundación Séneca (04539/GERM/06) for financial support. M.J.F.-R. is grateful to the Ministerio de Educación y Ciencia (Spain) for a grant.

■ REFERENCES

(1) Tsuji, J. *Palladium Reagents and Catalysts*. Wiley: Chichester, U.K., 1995. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2047−2067. Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818. Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211. Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131−209. Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285−2309.

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *2004*, 2283−2321. Larock, R. C.; Zeni, G. *Chem. Rev.* **2006**, *106*, 4644−4680. Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz, U. *Adv. Synth. Catal.* **2006**, *348*, 23−39. Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651−2710. Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874−922. Fernández-Rodríguez, M. A.; Hartwig, J. F. *J. Org. Chem.* **2009**, *74*, 1663−1672. Selander, N.; Szabo, K. J. *Chem. Rev.* **2011**, *111*, 2048−2076. Le Bras, J.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170−1214. Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27−50. Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215−1292.

(2) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557−4566.

(3) Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752−760.

(4) Vicente, J.; Abad, J. A.; López-Peláez, B.; Martínez-Viviente, E. *Organometallics* **2002**, *21*, 58−67. Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, *23*, 4711−4722.

(5) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Förtsch, W.; Jones, P. G. *Organometallics* **2004**, *23*, 4414−4429.

(6) Vicente, J.; Abad, J.-A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044−5057. Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254−3271. Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Bautista, D. *Organometallics* **2009**, *28*, 5915−5924. Vicente, J.; González-Herrero, P.; Frutos-Pedreño, R.; Chicote, M. T.; Jones, P. G.; Bautista, D. *Organometallics* **2011**, *30*, 1079−1093. Frutos-Pedreño, R.; González-Herrero, P.; Vicente, J.; Jones, P. G. *Organometallics* **2013**, *32*, 4664−4676. Frutos-Pedreño, R.; González-Herrero, P.; Vicente, J.; Jones, P. G. *Organometallics* **2013**, *32*, 1892−1904.

(7) Vicente, J.; Saura-Llamas, I. *Comments Inorg. Chem.* **2007**, *28*, 39−72.

(8) Vicente, J.; Abad, J. A.; López-Nicolás, R. M.; Jones, P. G. *Organometallics* **2011**, *30*, 4983−4998.

(9) Vicente, J.; Abad, J. A.; Bergs, R.; Ramirez de Arellano, M. C.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2000**, *19*, 5597−5607.

(10) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587−3595.

(11) Vicente, J.; Abad, J. A.; Martinez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454−4467. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2003**, *22*, 1967−1978.

(12) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 6001−6004.

(13) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2006**, *25*, 1851−1853.

(14) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G.; Bautista, D. *Chem.—Eur. J.* **2010**, *16*, 661−676.

(15) Oliva-Madrid, M. J.; García-López, J.-A.; Saura-Llamas, I.; Bautista, D.; Vicente, J. *Organometallics* **2014**, *33*, 6420−6430.

(16) Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2010**, *29*, 409−416.

(17) Shiotsuki, M.; Nakagawa, A.; Rodriguez Castañon, J.; Onishi, N.; Kobayashi, T.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5549−5556. Rodriguez Castañon, J.; Kuwata, K.; Shiotsuki, M.; Sanda, F. *Chem.—Eur. J.* **2012**, *18*, 14085−14093.

(18) Fernández-Rivas, C.; Cárdenas, D. J.; Martín-Matute, B.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998−3006.

(19) Muñoz, M. P.; Martín-Matute, B.; Fernández-Rivas, C.; Cárdenas, D. J.; Echavarren, A. M. *Adv. Syn. Catal.* **2001**, *343*, 338−342.

(20) Trofimenko, S. *Inorg. Chem.* **1973**, *12*, 1215−1221. Nanda, K. K.; Nag, K.; Venkatsubramanian, K.; Paul, P. *Inorg. Chim. Acta* **1992**, *196*, 195−199. Macdonald, P. M.; Hunter, A. D.; Lesley, G.; Li, J. *Solid State Nucl. Magn. Reson.* **1993**, *2*, 47−55. Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269−5282. Carina, R. F.; Williams, A. F.; Bernardinelli, G. *J. Organomet. Chem.* **1997**, *548*, 45−48. El Hatimi, A.; Gómez, M.; Jansat, S.; Muller, G.; Fontbardia, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1998**, 4229−4236. de Geest, D. J.; O'Keefe, B. J.; Steel, P. J. *J. Organomet. Chem.* **1999**, *579*, 97−105. Vicente, J.; Lyakhovych, M.; Bautista, D.; Jones, P. G. *Organometallics* **2001**, *20*, 4695−4699. Bedford, R. B.; Blake, M. E.; Coles, S. J.; Hursthouse, M. B.; Scully, P. N. *Dalton Trans.* **2003**, 2805−2807. Slater, J. W.; Rourke, J. P. *J. Organomet. Chem.* **2003**, *688*, 112−120. Vicente, J.; Martínez-Viviente, E.; Fernández-Rodríguez, M. J.; Jones, P. G. *Organometallics* **2009**, *28*, 5845−5847. Liu, B. B.; Wang, X. R.; Guo, Z. F.; Lu, Z. L. *Inorg. Chem. Commun.* **2010**, *13*, 814−817. Fernandez, A.; Lopez-Torres, M.; Castro-Juiz, S.; Merino, M.; Vázquez-García, D.; Vila, J. M.; Fernández, J. J. *Organometallics* **2011**, *30*, 386−395. Vicente, J.; Shenoy, R. V.; Martínez-Viviente, E.; Jones, P. G. *Inorg. Chem.* **2011**, *50*, 7189−7194. Micutz, M.; Ilis, M.; Staicu, T.; Dumitrascu, F.; Pasuk, I.; Molard, Y.; Roisnel, T.; Circu, V. *Dalton Trans.* **2014**, *43*, 1151−1161.

(21) Vicente, J.; Shenoy, R. V.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2009**, *28*, 6101−6108.

(22) Chicote, M. T.; Vicente-Hernández, I.; Jones, P. G.; Vicente, J. *Organometallics* **2012**, *31*, 6252−6261.

(23) Fu, H.; Song, Q.; Li, J.; Zhang, Z.; Li, X.; Zhan, H.; Cheng, Y. *J. Coord. Chem.* **2014**, *67*, 482−494.

(24) Fernández-Rodríguez, M. J.; Martínez-Viviente, E.; Vicente, J.; Jones, P. G. *Organometallics* **2015**, *34*, 2240−2254.

(25) Mazet, C.; Gade, L. H. *Organometallics* **2001**, *20*, 4144−4146.

(26) Suzaki, Y.; Osakada, K. *Organometallics* **2003**, *22*, 2193−2195.

(27) Houjou, H.; Schneider, N.; Nagawa, Y.; Kanesato, M.; Ruppert, R.; Hiratani, K. *Eur. J. Inorg. Chem.* **2004**, 4216−4222. Ganesamoorthy, C.; Baladrishna, M. S.; Mague, J. T.; Tuononen, H. M. *Inorg. Chem.* **2008**, *47*, 7035−7047. Valdés, H.; Poyatos, M.; Peris, E. *Organometallics* **2013**, *32*, 6445−6451.

(28) Zanardi, A.; Mata, J. A.; Peris, E. *Organometallics* **2009**, *28*, 1480−1483. Prabhu, R. N.; Ramesh, R. *Tetrahedron Lett.* **2012**, *53*, 5961−5965. Ma, M.-T.; Lu, J.-M. *Appl. Organomet. Chem.* **2012**, *26*, 175−179. Kalhapure, R. S.; Govender, T.; Akamanchi, K. G. *Synth. Commun.* **2014**, *44*, 337−3345.

(29) Altman, M.; Zenkina, O. V.; Ichiki, T.; Iron, M. A.; Evmenenko, G.; Dutta, P.; Van der Boom, M. E. *Chem. Matter.* **2009**, *21*, 4676−4684.

(30) Ohno, K.; Arima, K.; Tanaka, S.; Yamagata, T.; Tsurugi, H.; Mashima, K. *Organometallics* **2009**, *28*, 3256−3263.

(31) Tsukada, N.; Abe, T.; Inoue, Y. *Helv. Chim. Acta* **2013**, *96*, 1093−1102.

(32) Yang, J.; Li, P.; Zhang, Y.; Wang, L. *J. Organomet. Chem.* **2014**, *766*, 73−78.

(33) Yang, J.; Li, P.; Zhang, Y.; Wang, L. *Dalton Trans.* **2014**, *43*, 7166−7175.

(34) Yu, Y.; Deck, J. A.; Hunsaker, L. A.; Deck, L. M.; Royer, R. E.; Goldberg, E.; Jagt, D. L. V. *Biochem. Pharmacol.* **2001**, *62*, 81−89. Mehta, S.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2012**, *77*, 10938−10944.

(35) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. *Organometallics* **2001**, *20*, 2704−2715. Vicente, J.; Abad, J. A.; Frankland, A. D.; Lopez-Serrano, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272−282. Canovese, L.; Visentin, F.; Santo, C.; Levi, C.; Dolmella, A. *Organometallics* **2007**, *26*, 5590−5601.

(36) Saluste, C. G.; Crumpler, S.; Furber, M.; Whitby, R. J. *Tetrahedron Lett.* **2004**, *45*, 6995−6996.

(37) Stirling, C. J. M. *J. Chem. Soc.* **1960**, 255−262. Tam, J. N. S.; Mojelsky, T.; Hanaya, K.; Chow, Y. L. *Tetrahedron* **1975**, *31*, 1123−1128. Koseki, Y.; Nagasaka, T. *Chem. Pharm. Bull.* **1995**, *43*, 1604−1606. Ma, S.; H, X. *J. Org. Chem.* **2002**, *67*, 6575−6578. Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 9625−9631. Ma, S.; Gu, Z.; Yu, Z. *J. Org. Chem.* **2005**, *70*, 6291−6294. Esmaeili, A. A.; Zendegani, H. *Tetrahedron* **2005**, *61*, 4031−4034. Tang, Y.; Li, C. *Tetrahedron Lett.* **2006**, *47*, 3823−3825. Xiong, T.; Zhang, Q.; Zhang, Z.; Liu, Q. *J. Org. Chem.* **2007**, *72*, 8005−8009.

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX

(38) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686−1687. Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182−2188.
(39) A reviewer has suggested that a more polar solvent, such as acetone, could enhance the reactivity and decrease the amount of substrate required in these reactions.
(40) Martínez-Viviente, E.; Pregosin, P. S.; Tschoerner, M. *Magn. Reson. Chem.* **2000**, *38*, 23−28.
(41) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005.
(42) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065−1066. Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

DOI: 10.1021/acs.organomet.5b00309
Organometallics XXXX, XXX, XXX−XXX