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Cyclopalladated Complexes Derived from Phenylacetone Oxime. Insertion Reactions of Carbon Monoxide, Isocyanides, and Alkynes. Novel Amidines of the Isoquinoline Series

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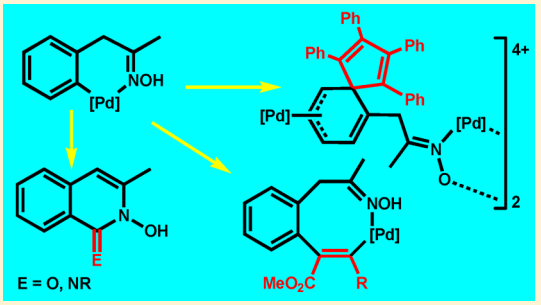
Supporting Information

ABSTRACT: Neutral and cationic six-membered *C,N*-palladacycles with the core "Pd{*C,N*-C_6H_4{$CH_2C(Me)$=NOH}-2}" have been obtained by oxidative addition of the oxime BrC_6H_4{$CH_2C(Me)$=NOH}-2 to "$Pd(dba)_2$" (dba = dibenzylideneacetone) in the presence of mono- or bidentate ligands. The oximato complex $[Pd\{\mu\text{-}C,N,O\text{-}C_6H_4\{CH_2C(Me)=NO\}\text{-}2\}(PTol_3)]_2$ forms after dehydrobromination of the appropriate oxime complex with K^{t}BuO, while the pincer derivative $[Pd\{C,N,N'\text{-}C_6H_4\{CH_2C(Me)=NOCH_2py\}\text{-}2\}Br]$ results by attack of an *in situ* generated oximato complex to $BrCH_2py{\cdot}HBr$. Insertion of CO or RNC in some of the palladacycles causes a depalladation/coupling process, giving 1,2-dihydro-1-oxo-2-hydroxy-3-methylisoquinoline or 1,2-dihydro-1-imino(R)-2-hydroxy-3-methylisoquinoline, respectively, while the insertion of alkynes produces eight-membered alkenyl(oxime) palladacycles "Pd{*C,N*-C(R′)=C(R)C_6H_4{$CH_2C(Me)$=NOH}-2}". When using diphenylacetylene, a dimeric tetranuclear complex $[\{Pd(tbbpy)\}_2\{\mu\text{-}N,O\text{-}\{\eta^3\text{-}C_6H_4(C_4Ph_4)\{CH_2C(Me)=NO\}\}\}]_2^{4+}$ forms instead, in which a π-allyl-coordinated oximato, bearing a spirocyclic substituent, acts as the bridging ligand. The crystal structures of the oxime and of each type of complexes have been determined.



INTRODUCTION

The interest of aryl-palladium complexes in themselves or in organic synthesis is of general knowledge. In particular, the group of ortho-functionalized aryl complexes have the additional attraction of affording, in some cases, cyclopalladated complexes[1,2] displaying numerous and interesting applications in catalytic[3] and stoichiometric synthesis of organic compounds.[4]

Catalytic C−C or C−heteroatom coupling reactions usually take place after reacting aryl palladium complexes with nucleophiles. Sometimes, the coupling reaction's product forms, along with Pd(0), after coordination of the nucleophile to Pd;[5,6] other times, before decomposition, the nucleophile inserts into the Pd−C_{aryl} bond.[7] Insertion of CO or isocyanides into the Pd−C_{aryl} bond of aryl palladium complexes is known to produce the corresponding benzoyl[8] or iminobenzoyl[9,10] complexes. Transition-metal-catalyzed carbonylations have been used to prepare carboxylic acids, esters, amides, heterocycles, etc.[11] Similarly, palladium-catalyzed reactions involving isocyanides afford nitrogen-containing organic compounds,[12] and insertions of alkynes into the aryl−Pd bond have found applications in the synthesis of cyclic species.[13]

Our main research line is the study of ortho-substituted aryl palladium complexes as catalysts[2,14,15] or their reactivity toward unsaturated reagents, mainly, CO, RNC,[2,16,17] and alkynes[2,15,18] but also with carbodiimides,[19] isothiocyanates,[20] olefins,[16,21] nitriles,[22] or allenes.[23,24] In some cases we have also studied sequential insertions of two or three of these reagents.[25−27] From these studies we have isolated interesting palladium complexes and organic compounds.[2,15,17,20,21,24,26,28−30] We have synthesized the first family of palladacycles derived from methyl aryl ketone oximes,[31,32] of which only a few derivatives were known.[33] We carried out the first study of the reactivity of this type of complexes, which was surprisingly unexplored in view of their versatile and efficient use as precatalysts in C−C coupling processes.[34]

In this paper we describe the synthesis of cyclopalladated derivatives of phenylacetone oxime, which are the first six-membered cyclometalated complexes of any metal derived from an oxime (Chart 1). Their reactivity toward CO or isocyanides has allowed the synthesis of 1-oxo- and 1-imino-substituted 1,2-dihydro-2-hydroxyisoquinoline derivatives. Many compounds containing the isoquinoline core have been shown to display biological and pharmacological activity,[35] and, in particular, some 2-hydroxyisoquinolones are antidepressant and tranquilizer agents.[36] As far as we are aware, 1-(alkyl- or aryl-imino)-

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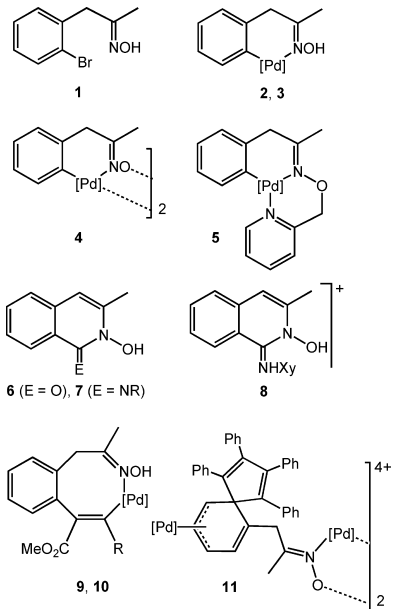
Chart 1



1,2-dihydro-2-hydroxyisoquinolines, i.e., amidine compounds derived from isoquinoline, are unknown.

In addition, a *C,N,N′*-pincer complex forms by reaction with 2-bromomethylpyridine, and alkynes insert into the Pd−C bond, leading to stable eight-membered alkenyl(oxime) palladacycles. When diphenylacetylene is used, a dimeric tetranuclear complex bearing an oximato ligand with a spirocyclic substituent is isolated. The various types of compounds prepared are depicted in Chart 1.

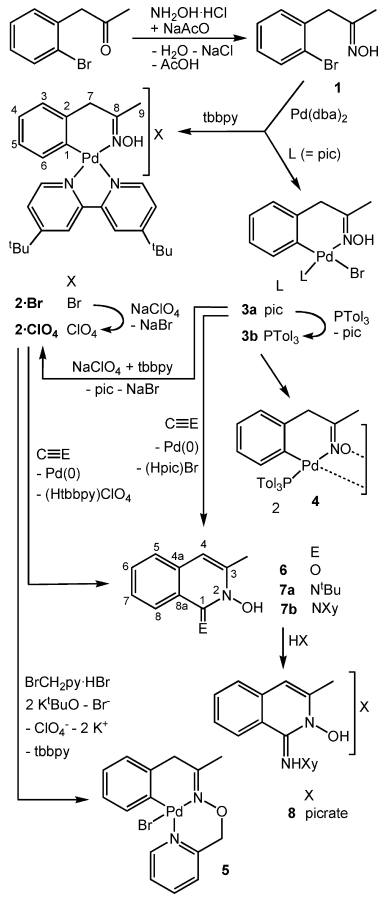
RESULTS AND DISCUSSION

Synthesis. The oxime $BrC_6H_4\{CH_2C(Me)=NOH\}$-2 (**1**) was recently reported and used in the first step of the synthesis of benzoimidazolylmethylpyrimidineamine derivatives, analogues of serine/threonine PAK1 inhibitors.[37] It was characterized only by its ESI-MS. The method we report here (Scheme 1) allows a much shorter reaction time and a nearly quantitative yield. We decided to use this bromo-substituted oxime to prepare orthopalladated phenylacetone oxime complexes by oxidative addition to $[Pd_2(dba)_3]\cdot$dba ("Pd(dba)$_2$", dba = dibenzylideneacetone) only after various failed attempts to orthometalate the unsubstituted oxime $C_6H_5\{CH_2C(Me)=NOH\}$-2 by reacting it with $Li_2[PdCl_4]$ in MeOH or with $Pd(OAc)_2$ in MeCN in the presence or not of triflic acid.

The reaction of "Pd(dba)$_2$" with **1** (1:1, in toluene at 65 °C, 4 h under nitrogen) gave, instead of the expected complex $[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}(\mu\text{-}Br)]_2$, a mixture that we could not separate. However, when the same reaction was carried out in the presence of 1 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbpy), $[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}(tbbpy)]Br$ (**2·Br**) could be obtained in 53% yield (Scheme 1).

Quantitative replacement of bromide by perchlorate in **2·Br** to give $[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}(tbbpy)]ClO_4$ (**2·ClO$_4$**) was achieved by reacting it with excess $NaClO_4\cdot H_2O$ in acetone. The reaction of "Pd(dba)$_2$" with **1** and 4-methylpyridine (pic) (1:1:2, in THF, at 45 °C) did not give a cationic complex analogous to **2·Br**; the neutral complex *SP-4-4*-$[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}Br(pic)]$ (**3a**) was obtained instead (63% yield), showing that the coordination of bromide is preferred to that of pic. The yield did not improve but decreased when the stoichiometric amount of pic was used. Complex **2·ClO$_4$** could also be prepared by reacting **3a** with tbbpy (1:1) and excess $NaClO_4\cdot H_2O$ in acetone. We attribute the moderate yields achieved in the isolation of complexes **2·Br** and **3a** to the fact that oxidative addition reactions to Pd(0) species are commonly accompanied by more or less abundant decomposition to Pd(0).[28] Additionally, recrystallization was required to remove small amounts of $[PdBr_2(pic)_2]$ and $[PdBr_2(tbbpy)]$, respectively. Complex *SP-4-4*-$[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}Br(PTol_3)]$ (Tol = C_6H_4Me-4, **3b**) was obtained by replacing the pic ligand in **3a** with $PTol_3$.

Scheme 1



The reaction of complex **2·ClO$_4$** or **2·Br** with K^{t}BuO, which we did under various reaction conditions with the purpose of preparing the zwitterionic oximato complex $[Pd\{C,N\text{-}C_6H_4\{CH_2C(Me)=NO\}\text{-}2\}(tbbpy)]$, homologous to those derived from the oximes of acetophenone and *p*-nitroacetophenone,[32] gave a complex mixture from which we could not isolate any pure species. In spite of the fact that dinuclear bridging oximato complexes $[Pd\{\mu\text{-}C,N,O\text{-}C_6H_4\{C(R)=NO\}\text{-}2\}(L)]_2$ (R = Me, L = XyNC, ^{t}BuNC, $PTol_3$; R = NH_2, L = $PTol_3$), derived from the above-mentioned oximes or benzamidoxime,[38] were isolated in good yield, the reaction of **3a** with K^{t}BuO produced a mixture, probably because of the ability of the oximato ligand to displace both the bromo and the picoline ligand. In fact, **3b** reacted with K^{t}BuO to give the pure oximato complex $[Pd\{\mu\text{-}C,N,O\text{-}C_6H_4\{CH_2C(Me)=NO\}\text{-}2\}$-

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$(PTol_3)]_2$ (**4**). After removing the insoluble KBr by filtration and concentrating the resulting solution, **4** precipitated in 57% yield upon the addition of pentane. A second crop of **4** was obtained by concentrating the mother liquor to dryness, making a total yield of 79%.

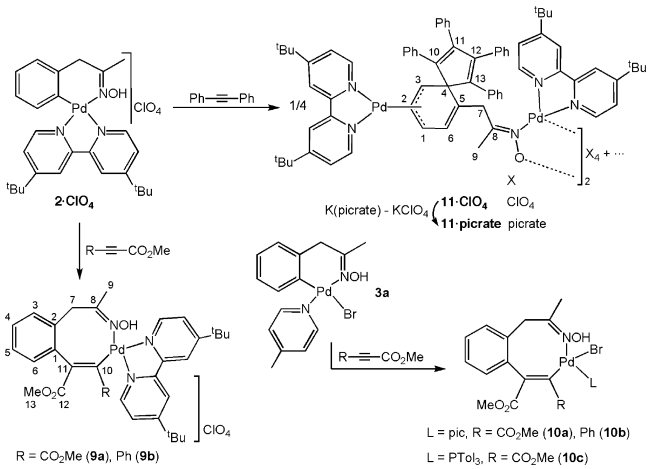
We have previously shown that pincer complexes containing the *C,N,N′*-oxime ether ligand *C,N,N′*-$C_6H_4\{C(Me)=NOCH_2(C_5H_4N\text{-}2)\}$-2 can be prepared by reacting the appropriate oxime palladacyclic complex with K^{t}BuO and XCH_2py-2 (X = Cl, Br),[31] which, in turn, forms by dehydrohalogenation of the commercial reagent XCH_2py·HX with K^{t}BuO. The pincer ligand forms by attack of the generated oximato function on the reagent's methylene group. Similarly, the reaction of **3a** with $BrCH_2$py·HBr and K^{t}BuO (1:1:2, in CH_2Cl_2, 2 h) allowed the synthesis of $[Pd\{C,N,N'\text{-}C_6H_4\{CH_2C(Me)=NOCH_2(C_5H_4N\text{-}2)\}\text{-}2\}Br]$ (**5**, Scheme 1), which was isolated in 55% yield upon precipitation with Et_2O. **5** could also be obtained using **2·ClO$_4$** instead of **3a**, but in this case the yield was somewhat lower.

Complex **3a** was reacted with CO with the purpose of preparing the corresponding benzoyl derivative, but it must be unstable and, after spontaneous depalladation, an isocarbostyril compound, namely, 1,2-dihydro-2-hydroxy-3-methylisoquinolone (**6**), formed in 84% yield along with the equimolar amount of pic·HBr (Scheme 1). Similarly, the reaction of **2·Br** with CO, under the same reaction conditions, gave **6** and [tbbpyH]Br, although in this case the yield was lower. The reactions with CO were carried out in a Carius tube, using a $CHCl_3$ solution of the palladium complex and a 1.4 bar pressure of CO, and the insoluble ammonium salts were removed upon extraction of the reaction mixture with Et_2O. The synthesis of **6** by treating 2-methyl-1-indanone with *n*-butyl nitrite and HCl (1:1:1, 4 days in toluene, 68% yield) or by ozonization of 3-methylisoquinoline-2-oxide (CH_2Cl_2, 0 °C, 15% yield) was previously reported.[39] Some 2-hydroxy-3-alkylisocarbostyrils have gained relevance because of their antidepressant and tranquilizing activity.[36]

We could not isolate any adduct or iminobenzoyl complexes by reacting our aryloxime complexes with isocyanides, at difference with what we observed with other oxime Pd(II) complexes.[32,38] However, when **2·ClO$_4$** was reacted with 2 equiv of RNC (R = ^{t}Bu, Xy, room temperature), compounds 1,2-dihydro-1-imino(R)-2-hydroxy-3-methyl-isoquinoline (R = ^{t}Bu (**7a**), Xy (**7b**), Scheme 1) were isolated, probably by decomposition of the expected iminobenzoyl complexes. Using 1 equiv of isocyanide caused in both cases a significant yield decrease. Compounds **7** were also obtained when **3a** was used instead of **2·ClO$_4$**, but some additional impurities made the purification process difficult. Although the insertion process is known to be facilitated when the aryl carbon bonded to Pd and the isocyanide carbon bear higher negative and positive charge, respectively,[10,20] we have not found significant differences within all these reactions in spite of the starting complex being cationic or neutral and the Xy and ^{t}Bu groups in the isocyanide having opposite electronic effect. After various failed attempts to grow single crystals of compounds **7**, we reacted **7b** with picric acid (1:1, CH_2Cl_2, 30 min at room temperature). The picrate salt **8** was isolated by precipitation with Et_2O, but the crystals we were able to grow were too small for an X-ray diffraction study. Although cyclic amidine derivatives related to isoquinoline are known,[20,40,41] some of them displaying anti-inflammatory, analgesic, or antihypertensive properties, the amidines **7** and the amidinium salt **8**, derived from 1,2-dihydro-2-hydroxy-3-methylisoquinoline, are the first such compounds bearing an OH group on the endocyclic nitrogen. The preparation of compounds **6**–**8** shows, for the first time, the direct participation of cyclopalladated oximes in organic synthesis, although they have been used as a source of palladium nanoparticles that act as catalysts in many coupling reactions.[5]

We have also studied the reaction of **2·ClO$_4$** or **3a** with alkynes. With dimethyl acetylenedicarboxylate we obtained the alkenyl complexes $[Pd\{C,N\text{-}C(CO_2Me)=C(CO_2Me)\text{-}C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}(tbbpy)]ClO_4$ (**9a**) and *SP-4*-[Pd{*C,N*-$C(CO_2Me)=C(CO_2Me)C_6H_4\{CH_2C(Me)=NOH\}$-2}Br(pic)] (**10a**) (Scheme 2), respectively. The

Scheme 2



reactions with **2·ClO$_4$** required a large excess of alkyne, while with **3a** they were complete in a shorter time using 1 equiv of alkyne, which may be attributed to the higher negative charge on the aryl carbon attached to Pd in the neutral complex **3a**, although the bulkier tbbpy ligand in **2·ClO$_4$** could also impose more difficulty in the coordination of the alkyne to Pd, previous to the migratory insertion. The reaction of **10a** with an equimolar amount of $PTol_3$ (in CH_2Cl_2, 4 h) causes the replacement of the pic ligand by $PTol_3$ to give *SP-4-4*-[Pd{*C,N*-$C(CO_2Me)=C(CO_2Me)C_6H_4\{CH_2C(Me)=NOH\}$-2}Br-$(PTol_3)]$ (**10c**), which was isolated in 72% yield. Dehydrobromination of **10c** with K^{t}BuO (1:1, 4 h in CH_2Cl_2) was attempted with the aim to prepare the corresponding oximato complex $[Pd\{\{\mu\text{-}C,N,O\text{-}C(CO_2Me)=C(CO_2Me)C_6H_4\text{-}\{CH_2C(Me)=NO\}\text{-}2\}(PTol_3)\}]_2$, but a complex mixture formed instead, from which we could not separate or identify any species. **10b** was isolated in 80% yield from **3a** and methyl phenylpropiolate, but we could not obtain pure $[Pd\{C,N\text{-}C(CO_2Me)=C(Ph)C_6H_4\{CH_2C(Me)=NOH\}\text{-}2\}(tbbpy)]\text{-}ClO_4$ (**9b**) from the same alkyne and **2·ClO$_4$**. When the reaction time was prolonged and/or a large excess of alkyne was used, mixtures of **9b** with some polyinsertion species were isolated. We have tentatively assigned the resonances attributable to **9b** from a recrystallized mixture.[42]

The reaction of **2·ClO$_4$** with 1 or 2 equiv of diphenylacetylene at room temperature was shown by ^{1}H NMR to occur at a low extent. When we forced the reaction conditions (1:3, $CHCl_3$, 48 h, 60 °C), the insoluble product $[\{Pd(tbbpy)\}_2\{\mu\text{-}N,O\text{-}\{\eta^3\text{-}C_6H_4(C_4Ph_4)\{CH_2C(Me)=NO\}\}\}]_2(ClO_4)_4$ (**11·ClO$_4$**, Scheme 2) formed, containing an η^3-allyl-bridging

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oximato ligand with a spirocyclic moiety, which we isolated in 42% yield and identified by its elemental analyses, HRMS (ESI + and ESI−), and NMR spectra. The reaction is rather complex, as proved by the presence of several unidentified species in the ^{1}H NMR spectrum of the mother liquor from which **11·ClO$_4$** precipitated. The complex is also scarcely soluble in CH_2Cl_2 and acetone, and, although it decomposes on standing in DMSO or CD_3CN, we could measure its NMR spectra in CD_3CN after a short acquisition time. After various failed attempts to grow single crystals of **11·ClO$_4$** in order to ascertain the proposed structure, we tried to synthesize **11·TfO** from [Pd{*C*,*N*-C$_6$H$_4$\{CH$_2$C(Me)=NOH\}-2}(tbbpy)]TfO (prepared, in turn, from **2·Br**, AgOTf, and tbbpy) and diphenylacetylene, but a complex mixture was obtained that we could not separate. We also attempted the reaction of **2·ClO$_4$** with 4-BrC$_6$H$_4$C≡CC$_6$H$_4$Br-4, which allowed the synthesis of the complex analogous to **11·ClO$_4$** (by NMR) in 11% yield, but it was still less soluble. The reaction of **2·ClO$_4$** with potassium picrate (5-fold excess, acetone, 4 h at room temperature) did not produce complete replacement of perchlorate by picrate (elemental analyses and IR spectrum), and longer reaction times led to decomposition. The reaction produced a mixture that analyzes as **11·ClO$_4$** + 3 **11·picrate**, from which we could grow single crystals of **11·picrate** suitable, in spite of many disorder problems, for its crystal structure to be measured. In addition, repeated recrystallization of the above-mentioned mixture from $CHCl_3$ and Et_2O allowed the isolation of a small crop of pure **11·picrate**, which we used for analytical and spectroscopic measurements.

Palladium complexes containing π-allyl spirocyclic ligands of the type found in complex **11·ClO$_4$** are known to form from the insertion of two molecules of alkyne into the Pd−C bond, followed by cyclization of the resulting butadienyl moiety.[18,25,43,44] We assume that complex **11·ClO$_4$** forms through a sequential di-insertion/cyclization reaction (giving intermediates **A** and **B**, Scheme 3) followed by the acid/base reaction **B** + **2·ClO$_4$** → C$_6$H$_5$CH$_2$C(Me)=NOH + 1/2 **11·ClO$_4$**.

The molar conductivities of complexes **11** (**11·picrate**, 210 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$; **11·ClO$_4$**, 283 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$; approximately 5 × 10^{-4} mol·L^{-1}) in acetone solutions are well below that found for a 3:1 electrolyte (446 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$).[45] We are not aware of data of molar conductivities of 1:4 electrolytes in acetone but reasonably should be greater. We attribute the low value for **11** to the reduced mobility of the cation, because of its extremely big size, and to some type of ions' association.

The behavior of our six-membered aryloxime palladacycles toward alkynes, described above, differs from that of the five-membered analogues derived from acetophenone oxime or 3,4,5-trimethoxy acetophenone oxime, which did not react with dimethylacetylene dicarboxylate or led to complex mixtures when the reaction conditions were forced.

Attempts to insert XyNC or CO into the Pd−C bond of the alkenyl complex **9a** were unfruitful. In both cases mixtures were obtained that we could not separate, likely containing various polyinsertion products in view of the many CO$_2$*Me* resonances in their ^{1}H NMR spectra.

X-ray Crystal Structures. The crystal structures of the oxime **1** (Figure 1) and of complexes **2·Br** (Figure 2), **3a** (Figure 3), **5** (Figure 4), **9a** (Figure 5), **10a** (Figure 6), and **11·picrate** (Figure 7) have been determined by X-ray diffraction studies. Details on crystal data, data collection, and refinements are summarized in the Supporting Information.

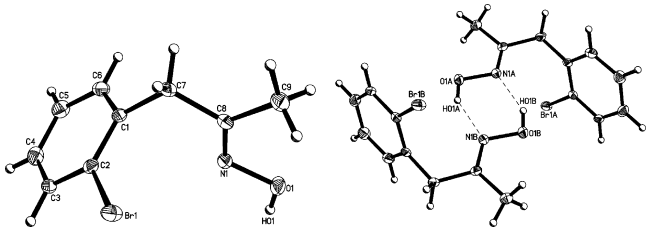


Figure 1. Left: Thermal ellipsoid representation plot (50% probability) of compound **1**. Selected bond lengths (Å) and angles (deg): N(1)−C(8) 1.276(3), N(1)−O(1) 1.415(2); C(8)−N(1)−O(1) 112.37(15), N(1)−C(8)−C(9) 125.16(18), N(1)−C(8)−C(7) 117.21(17), C(9)−C(8)−C(7) 117.61(18). Right: Dimer formed in **1** through O−H···N hydrogen bonds.

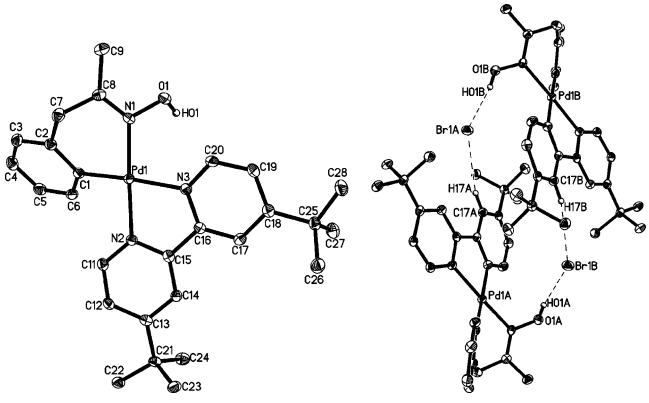
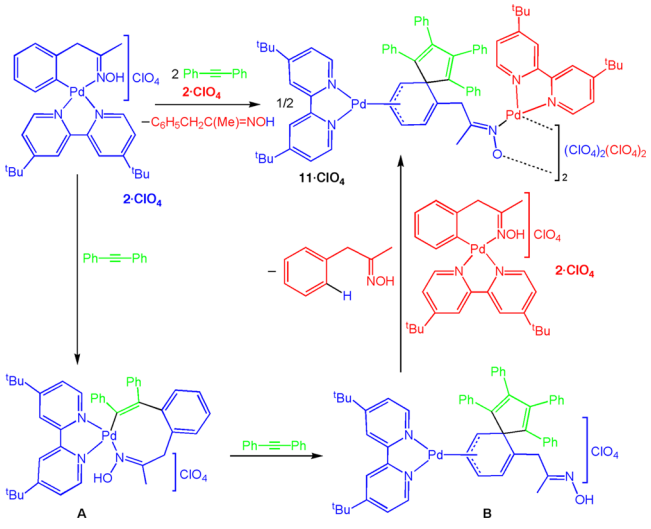


Figure 2. Left: Thermal ellipsoid representation plot (50% probability) of the cation of complex **2·Br**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.994(2), Pd(1)−N(1) 2.013(2), Pd(1)−N(2) 2.0462(19), Pd(1)−N(3) 2.1144(19), N(1)−C(8) 1.280(3), N(1)−O(1) 1.399(3); C(1)−Pd(1)−N(1) 84.66(8), C(1)−Pd(1)−N(2) 97.83(8), N(1)−Pd(1)−N(2) 177.41(8), C(1)−Pd(1)−N(3) 175.46(8), N(1)−Pd(1)−N(3) 98.98(7), N(2)−Pd(1)−N(3) 78.50(7), C(8)−N(1)−O(1) 114.59(19), C(8)−N(1)−Pd(1) 126.00(16), O(1)−N(1)−Pd(1) 119.04(14), C(8)−C(7)−C(2)-110.57(19). Right: Dimers formed in **2·Br** through O−H···Br and C−H···Br hydrogen bonds.

Scheme 3



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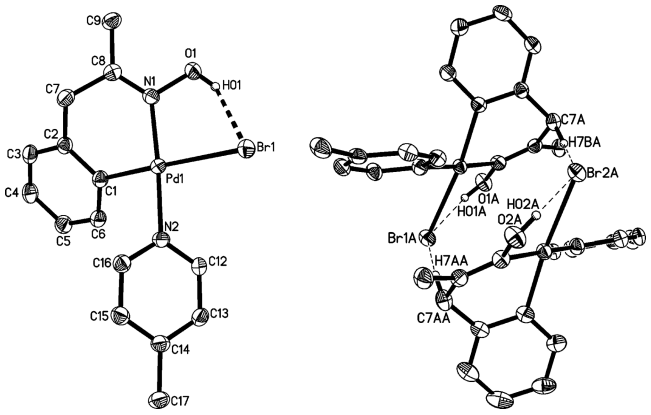

Figure 3. Left: Thermal ellipsoid representation plot (50% probability) of complex **3a**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.994(3), Pd(1)−N(1) 2.029(3), Pd(1)−N(2) 2.050(3), Pd(1)−Br(1) 2.5836(9), N(1)−C(8) 1.282(4), N(1)−O(1) 1.409(4); C(1)−Pd(1)−N(1) 87.42(13), C(1)−Pd(1)−N(2) 89.17(13), N(1)−Pd(1)−Br(1) 91.01(9), N(2)−Pd(1)−Br(1) 92.54(8), C(8)−N(1)−O(1) 114.8(3), C(8)−N(1)−Pd(1) 127.9(2), O(1)−N(1)−Pd(1) 117.29(19), C(8)−C(7)−C(2) 113.5(3). Right: Dimers formed in **3a** through O−H···Br and C−H···Br hydrogen bonds.

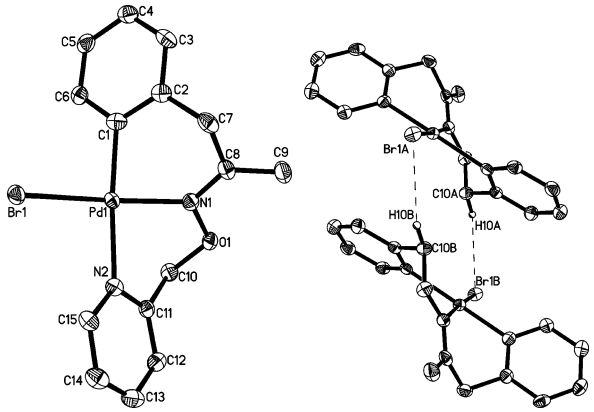

Figure 4. Left: Thermal ellipsoid representation plot (50% probability) of complex **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 1.995(3), Pd(1)−N(1) 2.036(2), Pd(1)−N(2) 2.151(3), Pd(1)−Br(1)-2.4249(8), N(1)−C(8) 1.278(4), N(1)−O(1) 1.421(3); C(1)−Pd(1)−N(1) 86.40(12), N(1)−Pd(1)−N(2) 88.16(10), C(1)−Pd(1)−Br(1) 91.94(10), N(2)−Pd(1)−Br(1) 93.64(7), C(8)−N(1)−O(1) 113.6(2), C(8)−C(7)−C(2) 111.4(3), N(1)−C(8)−C(9) 124.9(3), N(1)−C(8)−C(7) 116.1(3), C(9)−C(8)−C(7) 119.0(3). Right: Dimers formed in **5** through C−H···Br hydrogen bonds.

In complexes **2·Br**, **3a**, **5**, **9a**, and **10a** the palladium atom is in a square planar environment, slightly distorted mainly because of the small bite of the tbbpy ligand (N(2)−Pd(1)−N(3) in deg: 78.50(7) in **2·Br**, 80.11(8) in **9a**) and, second, because of that of the more flexible six-membered oxime palladacycle C(1)−Pd(1)−N(1) (in deg: 84.66(8) in **2·Br**, 87.42(13) in **3a**, 86.40(12) in **5**, or C(10)−Pd(1)−N(1): 86.05(9) in **9a**, 86.51(9) in **10a**). The N(1)−Pd(1)−N(2) bond angle in the pincer complex **5** is 88.16(10)°. The Pd−C and Pd−N bond distances in the oxime palladacycle (in the ranges 1.994(2)−2.011(3) and 2.010(2)−2.036(2) Å, respectively) are similar to those found in the few other crystal structures of aryloxime palladacycles previously reported.[46] Compared to the analogous parameters in the free oxime **1**, the C(8)═N(1) bond distances are similar (1.276(3)−1.284(3) vs 1.276(3) Å), while the N(1)−O(1) bond distances are somewhat shorter (1.396(3)−1.409(4) vs 1.415(2) Å). In the alkenyl(oxime) palladacycles **9a** and **10a**, the C(10)−C(11) bond distance (1.344(4) and 1.335(4) Å) is normal for a $C(sp^2)-C(sp^2)$ double bond.[47]

In the oxime **1**, the skeleton C(7)−C(8)−C(9)−N(1)−O(1) is essentially planar and the phenyl ring is almost perpendicular to that plane (torsion angle 73.59°). The six-membered oxime palladacycles (Pd(1)−C(1)−C(2)−C(7)−C(8)−N(1) in complexes **2·Br**, **3a**, and **5** and Pd(1)−N(1)−O(1)−C(10)−C(11)−N(2) in **5**) adopt a twist boat conformation. In complexes **9a** and **10a**, the eight-membered ring Pd(1)−C(10)−C(11)−C(2)−C(7)−C(8)−N(1) adopts an almost twist-boat conformation, although the usual designations of cyclooctane conformations are not strictly applicable.[48] The structures of complexes **3a** and **10a** reveal the existence of intramolecular O−H···Br hydrogen bonds; additionally, the structures of compounds **1**−**3** and **5** show the presence of dimers formed by hydrogen bonding: OH···N in **1**, O−H···Br and C−H···Br in **2·Br** with participation of an aromatic CH of the tbbpy ligand, O−H···Br and C−H···Br in **3a** with participation of the methylene group, and C−H···Br in **5** with participation of the methylene group. In complex **9a**, chains along the *c* axis form by C−H···O hydrogen bonding with the involvement of an aromatic CH group of the tbbpy ligand and a CO_2Me group, while in **10a** layers parallel to the *bc* plane form through various C−H···O and C−H···Br hydrogen bonds in which the oxime Me group, an aromatic CH and the Me group in the picoline ligand, and oxygen atoms from the CO_2Me groups participate.

In the crystal structure of **11·picrate**, the two monomeric units display only slightly different parameters. The central six-membered ring Pd(3)−O(3)−N(5)−Pd(4)−O(4)−N(6) adopts a slightly twisted boat conformation. Within the bridging oximato-palladium moieties, the Pd−N bond distances are similar to those found in the remaining complexes, while the C═N (1.291(4), 1.292(4) Å) are longer and N−O (1.365(3), 1.374(3) Å) shorter. The parameters within the Pd(*π*-allyl) fragment are similar to those found in complexes containing this subunit.[25,44]

NMR Spectra. In complexes **2**, **3**, **5**, and **9**−**11** the Me9 proton resonance appears in the range 2.14−2.81 ppm, while in the organic compounds **7** and **8** this resonance is at 2.55−2.81 ppm, obviously deshielded with respect to the oxime **1** (1.85 ppm) and in the oximato complex **4** at 1.16 ppm, appreciably shielded probably because of both the anisotropic effect of one of the tolyl rings and the neighbor oximato oxygen. This latter contribution could explain the shielding on the CH_2 resonance in **4**, at 3.48 ppm, with respect to that in the remaining complexes, in the range 3.67−3.95 ppm. This resonance is observed as an AB system in the room-temperature spectra of all complexes, except in **2** and **3b**, which display a broad singlet, suggesting they are fluxional in $CDCl_3$ solution at room temperature. In fact, in the low-temperature (−58 °C) spectra of complexes **2**, the expected AB system is observed. Additionally, the room-temperature ^1H NMR spectrum of **2·Br** shows, unlike **2·ClO$_4$**, a single resonance for each type of tbbpy proton in spite of its two halves being inequivalent in the solid state. At −58 °C, the decoordination/rotation/recoordination of the tbbpy ligand that makes equal its two halves is

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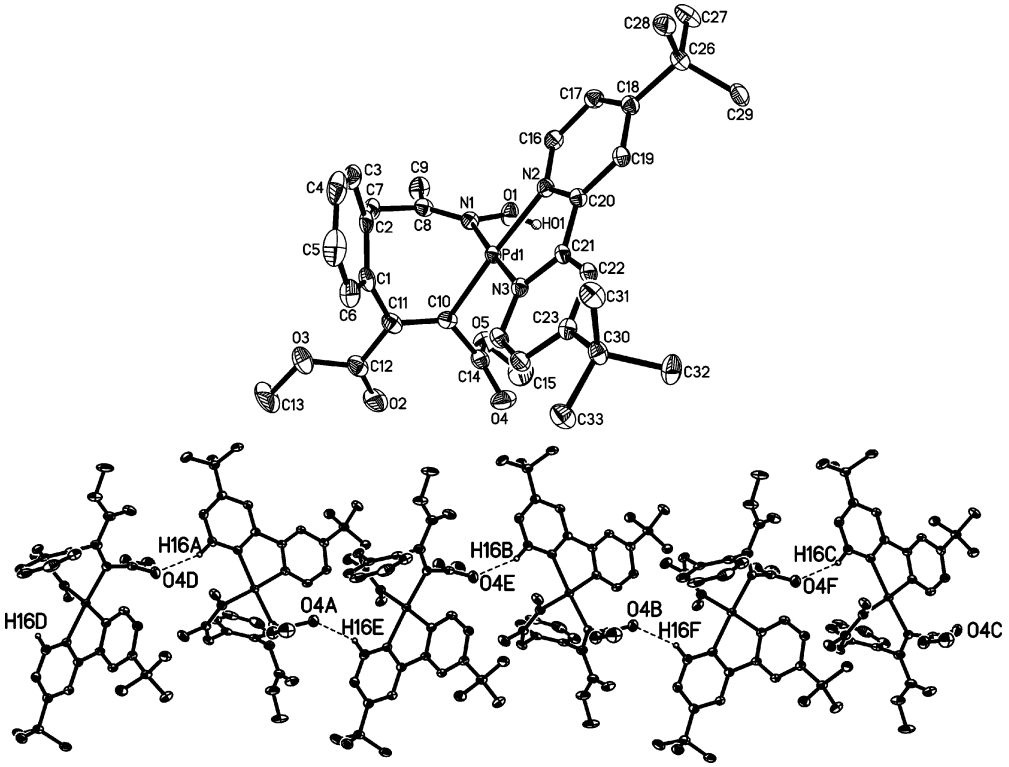

Figure 5. Top: Thermal ellipsoid representation plot (50% probability) of the cation of complex **9a**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(10) 2.000(2), Pd(1)−N(1) 2.010(2), Pd(1)−N(3) 2.0190(19), Pd(1)−N(2) 2.074(2), N(1)−C(8) 1.284(3), N(1)−O(1) 1.396(3); C(10)−Pd(1)−N(1) 85.05(9), C(10)−Pd(1)−N(3) 98.04(9), N(1)−Pd(1)−N(2) 96.84(8), N(3)−Pd(1)−N(2) 80.11(8), C(8)−N(1)−O(1) 112.3(2), C(8)−N(1)−Pd(1) 130.66(19), O(1)−N(1)−Pd(1) 116.94(15), C(8)−C(7)−C(2) 124.9(2). Bottom: Chain along the *c* axis in **9a** formed through C−H···O hydrogen bonds.

slow on the NMR time scale. The different behavior of **2·Br** with respect to **2·ClO$_4$** can be explained assuming that the bromide counterion intervenes in the above-mentioned fluxional process, binding to Pd and favoring the decoordination of the tbbpy, which does not occur with the weak donor perchlorate ion. This difference also explains the differences in molar conductivity within these complexes. Thus, the molar conductivity in acetone solution of **2·Br** (56 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) is rather below the value of **2·ClO$_4$** (140 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$), which is in the range expected for 1:1 electrolytes.[45] The OH resonance, absent in the NMR spectrum of **4**, appears as a singlet at 9.38−11.78 ppm in the spectra of complexes **2**, **3**, **9**, and **10**. This resonance, which is deshielded with respect to that in the free oxime **1** (8.35 ppm), appears in the range found for other aryloxime palladium complexes. Compounds **6**−**8** show this resonance between 7.22 and 10.30 ppm. In all the oxime compounds **2**−**10** the position of the OH resonance cannot be rationalized unless the participation of this group in more or less strong hydrogen bonding is admitted. Compounds of the type of **7** have no precedent in the literature. We have assigned the structure of these amidine compounds derived from 1,2-dihydro-2-hydroxy-3-methylisoquinoline based on their ^{1}H, ^{13}C, HMBC, HMQC, and NOESY NMR spectra. The latter show correlation between H8 and the ^{t}Bu (**7a**) or Xy (**7b**, **8**) methyl protons, proving that, in all cases, the iminobenzoyl compound forms as the *E* isomer. The H8 resonance in the ^{1}H NMR spectrum of **7a** (8.17 ppm, R = ^{t}Bu) is similar to that found for the analogous proton in the isoquinolone **6** (8.34 ppm) and in other cyclic amidines and lactams. Its deshielding with respect to the normal position for aryl proton resonances has been attributed to the anisotropic effect of the exocyclic C═O or C═N double bond.[20,40] This resonance appears in **7b** and **8** at 7.12 and 7.17−7.24 ppm, respectively. The shielding of this resonance compared to its homologue in **7a** could be a consequence of the anisotropic effect of the Xy group in these *E* isomers, as has been previously reported in other cyclic amidines and amidinium salts.[20] Although the smaller steric hindrance acts generally in favor of the *Z* isomers, in **7a** and **7b** the *E* disposition could be preferred since it allows the formation of an intramolecular O−H···NR (R = ^{t}Bu, Xy) hydrogen bond. Although this type of interaction cannot be invoked in **8**, the protonated form of **7b**, its NOESY spectrum proves it to be also the *E* isomer. We expected this would be the most likely result of the protonation of *E*-**7b** because, being that *E*-**8** is expected to form initially, its isomerization into *Z*-**8** would be difficult in view of the partial double-bond character of the C−N bond, restricting its rotation.

The structure of the alkenyl complex **10b** has been unequivocally established by means of HMBC and HMQC experiments. The HMBC spectrum shows correlation between the C11 and both H6 and the Me protons of the CO_2Me group and also between C10 and the phenyl protons, while no correlation is observed between C10 and H6. These data prove that the insertion of methyl phenylpropiolate into the Pd−C bond occurs in the expected manner according to various studies on the factors, electronic and steric, governing the regiochemistry of the insertion of alkynes into the Pd−C bond,[20,49] and to the empirical scale proposed for the tendency of the CR′ moiety of an alkyne RC≡CR′ to be attached to C_{Pd}.[23,30]

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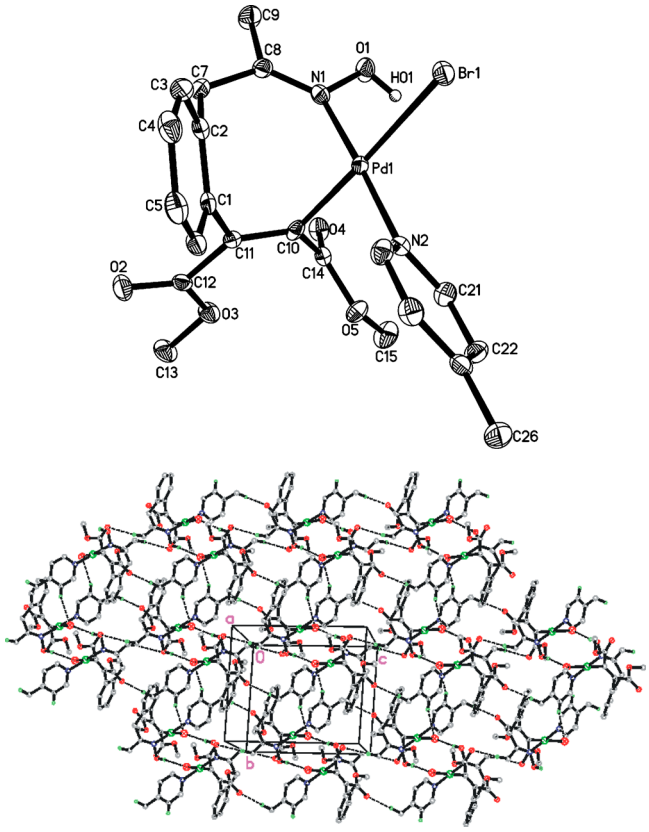

Figure 6. Top: Thermal ellipsoid representation plot (50% probability) for complex **10a**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(10) 2.011(3), Pd(1)−N(1) 2.017(2), Pd(1)−N(2) 2.040(2), Pd(1)−Br(1) 2.5335(6), N(1)−C(8) 1.276(3), N(1)−O(1), 1.405(3); C(10)−Pd(1)−N(1) 86.51(9), C(10)−Pd(1)−N(2) 91.33(9), N(1)−Pd(1)−Br(1) 91.32(6), N(2)−Pd(1)−Br(1) 90.84(6), C(8)−N(1)−O(1) 113.3(2), O(1)−N(1)−Pd(1) 114.37(15), C(8)−C(7)−C(2) 124.7(2). Bottom: Layers parallel to the *bc* plane in **10a** formed through C−H···O and C−H···Br hydrogen bonds.

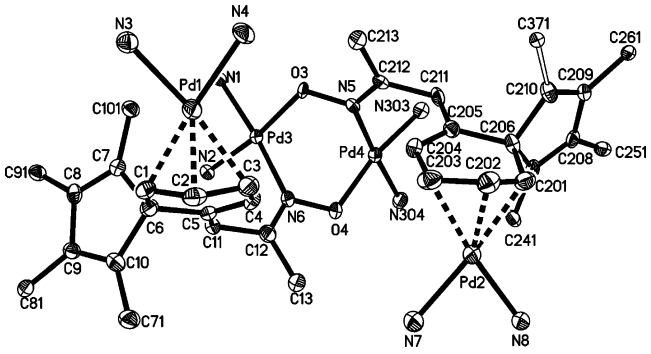

Figure 7. Thermal ellipsoid representation plot (50% probability) for the cation of **11·picrate**. For simplicity, the hydrogen atoms are omitted as well as the four tbbpy ligands and the eight phenyl substituents on the tetraphenylbutadienyl spirane, with the exception of their nitrogen [N(1)−N(4), N(7), N(8), N(303), and N(304)] and *ipso*-carbon [C(71), C881), C(91), C(101), C(241), C(251), C(261), and C(371)] atoms, respectively. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 2.141(4), Pd(1)−C(2) 2.063(4), Pd(1)−C(3) 2.182(4), Pd(1)−N(3) 2.106(3), Pd(1)−N(4) 2.101(3), Pd(2)−C(201) 2.140(4), Pd(2)−C(202) 2.074(4), Pd(2)−C(203) 2.158(4), Pd(2)−N(7) 2.102(3), Pd(2)−N(8) 2.100(3), Pd(3)−O(3) 1.987(2), Pd(3)−N(1) 2.000(3), Pd(3)−N(2) 2.000(3), Pd(3)−N(6) 2.013(3), Pd(4)−O(4) 1.984(2), Pd(4)−N(304) 2.002(3), Pd(4)−N(303) 2.012(3), Pd(4)−N(5) 2.019(3), O(3)−N(5) 1.365(3), O(4)−N(6) 1.374(3); C(2)−Pd(1)−N(4) 136.80(13), C(2)−Pd(1)−N(3) 132.06(13), N(4)−Pd(1)−N(3) 77.66(12), C(2)−Pd(1)−C(1) 39.01(13), N(4)−Pd(1)−C(1) 175.58(13), N(3)−Pd(1)−C(1) 106.43(13), C(2)−Pd(1)−C(3) 38.72(14), N(4)−Pd(1)−C(3) 109.47(13), N(3)−Pd(1)−C(3) 170.77(13), C(1)−Pd(1)−C(3) 66.29(14), C(202)−Pd(2)−N(8) 134.18(13), C(202)−Pd(2)−N(7) 137.33(14), N(8)−Pd(2)−N(7) 77.92(12), C(202)−Pd(2)−C(201) 38.51(13), N(8)−Pd(2)−C(201) 107.63(13), N(7)−Pd(2)−C(201) 174.43(14), C(202)−Pd(2)−C(203) 38.60(14), N(8)−Pd(2)−C(203) 172.75(13), N(7)−Pd(2)−C(203) 108.46(14), C(201)−Pd(2)−C(203) 66.04(14), O(3)−Pd(3)−N(2) 171.69(11), O(3)−Pd(3)−N(1) 90.76(11), N(2)−Pd(3)−N(1) 80.93(12), O(3)−Pd(3)−N(6) 91.92(10), N(2)−Pd(3)−N(6) 96.36(11), N(1)−Pd(3)−N(6) 173.53(11), O(4)−Pd(4)−N(304) 89.53(11), O(4)−Pd(4)−N(303) 169.56(11), N(304)−Pd(4)−N(303) 80.75(12), O(4)−Pd(4)−N(5) 91.86(10), N(304)−Pd(4)−N(5) 176.18(11), N(303)−Pd(4)−N(5) 97.60(12).

The $^{13}C\{^1H\}$ NMR spectra of all complexes show the expected resonances, although in a few cases some quaternary carbon nuclei were not observed (see Experimental Section). In complexes **2**, **3**, **5**, **9**, and **10** the Me (C9), CH_2 (C7), and C═NO (C8) nuclei give a resonance at 17.9−20.7, 41.4−46.8, and 162.3−169.8 ppm, respectively, while in the oximato complex **4** the C9 and C8 resonances are appreciably shielded (at 16.4 and 150.8 ppm, respectively), probably by the above-mentioned reasons. In complexes **9** and **10**, the alkenyl carbon nuclei C10 and C11 appear at 166.3−174.8 and 130.3−133.7 ppm, respectively.

IR Spectra. In the IR spectra of compounds **1**, **2·ClO$_4$**, **3**, and **6**−**10**, the ν(OH) mode is observed as a broad band in the wide range of 3155−3282 cm^{-1}, which could be justified by the participation of the OH group in hydrogen bonding, as above-mentioned in the discussion of the NMR spectra. This band is absent in the spectra of **4** and **5** and is not observed in the spectrum of **2·Br**. In that of **8**, a broad band centered at 3335 cm^{-1} must include the ν(OH) and ν(NH) absorptions. The ν(C═NO) band is present in all compounds between 1556 and 1616 cm^{-1}, and in some cases it is impossible to assign it unequivocally because of the presence of one or two additional bands in the same region attributable to C═C or C═NR or to aromatic CC and CN stretching modes. Bands at around 1100 and 620 cm^{-1} are observed in the spectra of complexes **2·ClO$_4$**, **9**, and **11·ClO$_4$** assignable to the ν(ClO) and δ(OClO) modes. The bands ν_{asym} and $\nu_{sym}(NO_2)$ characteristic of nitroaromatic groups, expected to appear in the spectra of **8** and **11·picrate** between 1510−1495 and 1345−1320 cm^{-1}, respectively, cannot be assigned because of the presence of various other bands in the same regions. The $\nu_{asym}(CO_2)$ corresponding to the methoxycarbonyl groups in complexes **9** and **10** appear at around 1715−1720 cm^{-1}.

HRMS Spectra. The HRMS (ESI+) spectra were measured for the isoquinoline derivatives **7** and, for **8** and **11**, both the ESI+ and the ESI− spectra. In the ESI+ of complexes **11** the peaks assigned to the dipalladated species $[C_{73}H_{77}N_5OPd_2]^{2+}$ (M^{2+}) and $[M - H^+]^+$ were isotopically resolved and their isotopic resolution is in good agreement with the theoretical distribution.

■ CONCLUSION

We report the synthesis of the first cyclometalated phenylacetone oxime complexes, inaccessible by the usual orthometalation reactions, by oxidative addition of $C_6H_4Br\{CH_2C$-

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(Me)=NOH}-2 to a Pd(0) complex. Their reactivity toward CO, isocyanides, and alkynes allowed the synthesis of 1,2-dihydro-1-oxo-2-hydroxy-3-methylisoquinoline, 1,2-dihydro-1-imino(R)-2-hydroxy-3-methylisoquinolines, i.e., novel amidines of the isoquinoline series, neutral and cationic eight-membered alkenyl(oxime) palladacycles, or tetrapalladated species containing a π-allyl-bridging coordinated oximato ligand bearing a spirocyclic substituent. These results are the first obtained starting from cyclopalladated oximes. Deprotonation with K^{t}BuO led to an oximato complex or, in the presence of $BrCH_2py$, a *C,N,N′*-oxime ether pincer complex.

EXPERIMENTAL SECTION

General Procedures. When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points are uncorrected. IR spectra were recorded using Nujol mulls between polyethylene sheets. NMR spectra were recorded in 200, 300, 400, or 600 MHz NMR spectrometers. The NMR assignments were performed, in some cases, with the help of APT, HMQC, and HMBC experiments. The atom-numbering scheme used in the Experimental Section is shown in **2·Br** for the aryl oxime ligands in complexes **2**−**5** and for compounds **6**−**8** (Scheme 1); complexes **9** and **11** (Scheme 2) show the numbering scheme used for the alkenyl oxime and the π-allyl(bridging oximato) ligands in complexes **9**−**11**, respectively. The tbbpy and pic nuclei are numbered separately according to the usual rules. $Pd(OAc)_2$, $C_6H_4Br\{CH_2C(O)Me\}$-2, $H_2NOH{\cdot}HCl$, XyNC (Xy = $C_6H_3Me_2$-2,6 = xylyl), $NaClO_4{\cdot}H_2O$, TfOH (TfO = CF_3SO_3 = triflate), AgOTf, tbbpy (4,4′-di-*tert*-butyl-2,2′-bipyridine), methyl phenylpropiolato, K^{t}BuO (95%), C_2Ph_2, $BrCH_2py{\cdot}HBr$, NaOAc MeCN, dimethyl acetylenedicarboxylate (DMAD), ^{t}BuNC, 4-methylpyridine, KOH, anhydrous $MgSO_4$, and picric acid were obtained from commercial sources. $[Pd_2(dba)_3]{\cdot}dba$ ("$Pd(dba)_2$", dba = dibenzylideneacetone) was prepared as previously reported.[50] K(picrate) was prepared by adding an EtOH solution (1 M) of KOH to another containing an equimolar amount of picric acid in acetone. The suspension was filtered, and the solid collected was washed successively with a 1:1 mixture of acetone/Et_2O (3 × 3 mL) and Et_2O (3 × 3 mL) and dried by suction to give a deep yellow solid. The synthesis of the oxime $C_6H_4Br\{CH_2C(Me)=NOH\}$-2 (**1**) was previously reported,[37] but the ESI-MS was the only information available. We have improved its synthesis, providing shorter reaction time and somewhat higher yield, and fully characterized it including its crystal structure.

X-ray Crystallography. All diffraction measurements were carried out at 100 K. Data were collected using monochromated Mo Kα radiation in ω scan and compounds **3a**, **5**, and **9a** in ω and ϕ scans. The structures were solved by direct methods. All atoms were refined anisotropically on F^2. The OH hydrogens were refined as free, the methyl hydrogen atoms using a rigid group, and the other hydrogens using a riding mode. *Special features:* for **9a**, the perchlorate anion is disordered over two positions, 53:47%; for **11·picrate**, three of the ^{t}Bu groups of the tbbpy ligands are disordered over two positions, ca. 58:42% and 72:28%, 61:39%. One phenyl ligand is disordered over two positions, ca. 64:36%. Some of the NO_2 groups of the picrate anions are disordered over two positions. There was a solitary peak of 4.49 e·Å^3 at 1.80 Å of an oxygen that was interpreted as an oxygen of half water. Its H's were not located so they were not included in the refinement. There is a poorly resolved region of residual electron density. This could not be adequately modeled and so was "removed" using the program SQUEEZE, which is part of the PLATON system. The void volume per cell was 3283.8 Å^3, with a void electron count per cell of 655. This additional solvent was not taken into account when calculating derived parameters such as the formula weight, because the nature of the solvent was uncertain. Further details on crystal data, data collection, and refinements are summarized in Table 1 in the Supporting Information.

Synthesis of $C_6H_4Br\{CH_2C(Me)=NOH\}$-2 (1). To a solution of $H_2NOH{\cdot}HCl$ (1.70 g, 24.46 mmol) and $NaOAc{\cdot}3H_2O$ (5.56 g, 40.86 mmol) in water (13 mL) were added $C_6H_4Br\{CH_2C(O)Me\}$-2 (1 mL, 6.58 mmol) and EtOH (10 mL). The resulting suspension was heated at 75 °C for 5 h, allowed to cool at room temperature, stirred in an ice/water bath for 15 min, and filtered. The solid collected was washed with cold water (3 × 5 mL, 0 °C), dried by suction, and dissolved in Et_2O. The solution was dried over anhydrous $MgSO_4$ and concentrated under vacuum (5 mL), and pentane (30 mL) was added. The suspension was filtered, and the solid collected was washed with pentane and dried by suction to give **1** as a white solid (1.47 g, 6.44 mmol, 98%). Mp: 125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.86 (s, 3 H, Me), 3,67 (s, 2 H, CH_2), 7.11 (ddd, 1H, H4, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.21−7.28 (m, 2 H, H5+H6), 7.56 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.35 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 13.5 (Me), 41.7 (C7), 124.9 (C1 or C2), 127.5 (C5), 128.4 (C4), 130.8 (C6), 132.9 (C3), 136.3 (C1 or C2), 156.5 (C8). IR (cm^{-1}): ν(OH), 3243. Anal. Calcd for $C_9H_{10}BrNO$: C, 47.39; H, 4.42; N, 6.14. Found: C, 47.28; H, 4.59; N, 6.08. Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a solution of **1** in a mixture of $CHCl_3$, Et_2O, and *n*-hexane.

Synthesis of [Pd{*C,N*-$C_6H_4\{CH_2C(Me)=NOH\}$-2}(tbbpy)]Br (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, 2·Br). A Carius tube was charged under a nitrogen atmosphere with solid "$Pd(dba)_2$" (505 mg, 0.88 mmol), **1** (200 mg, 0.88 mmol), tbbpy (235 mg, 0.88 mmol), and dry toluene (20 mL). The mixture was stirred at room temperature for 15 min and then heated at 65 °C for 4 h. The resulting greenish suspension was filtered through a short pad of Celite. The solid plus Celite mixture was dried by suction for 2 h and stirred with CH_2Cl_2 (30 mL) for 10 min. The suspension was filtered, the filtrate was concentrated under vacuum to dryness, and the residue was dissolved in CH_2Cl_2 (5 mL). Et_2O (12 mL) was slowly added until the solution became cloudy, and the suspension was filtered rapidly at this point. On stirring the filtrate for an additional 30 min, a suspension formed, which was filtered. The solid collected was washed with Et_2O (3 × 3 mL), recrystallized from CH_2Cl_2/Et_2O, and dried, first by suction and then in a vacuum oven (5 h, 75 °C), to give **2·Br** as a pale yellow solid (282 mg, 0.47 mmol, 53%). Mp: 199 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.42 (s, 18 H, Me, ^{t}Bu), 2.34 (s, 3 H, Me9), 3.83 (br s, 2 H, C7), 6.95 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.02 (td, 1 H, H4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.07 (td, 1 H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.49 (m, 2 H, H5 + H5′, tbbpy), 7.51 (dd, 1 H, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.01 (d, 2 H, H3+H3′, tbbpy, $^4J_{HH}$ = 2 Hz), 8.88 (vbr s, 2 H, H6+H6′, tbbpy), 11.78 (br s, 1H, OH). ^{1}H NMR ($CDCl_3$, 400 MHz, −58 °C): δ 1.427 (s, 9 H, Me, ^{t}Bu), 1.432 (s, 9 H, Me, ^{t}Bu), 2.34 (s, 3 H, Me9), 3.88 (AB system, 2 H, CH_2, ν_A = 4.22, ν_B = 3.54, J_{AB} = 15 Hz), 7.03 (d, 1 H, H3, $^3J_{HH}$ = 7 Hz), 7.07 (t, 1 H, H4, $^3J_{HH}$ = 7 Hz), 7.13 (t, 1 H, H5, $^3J_{HH}$ = 7 Hz), 7.47 (br d, 1 H, H5 or C5′, tbbpy, $^3J_{HH}$ = 6 Hz), 7.52 (vbr s, 1 H, H5 or H5′, tbbpy), 7.57 (d, 1 H, H6, $^3J_{HH}$ = 7 Hz), 8.02 (br s, 1 H, H3 or H3′, tbbpy), 8.04 (br s, 1 H, H3 or H3′, tbbpy), 8.58 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 9.14 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 11.59 (br s, 1H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 18.8 (Me9), 30.2 (Me, ^{t}Bu), 35.4 ($C(Me)_3$), 46.6 (CH_2), 118.6 (C3+C3′, tbbpy), 123.6 (C5+C5′, tbbpy), 124.2 (C4), 125.3 (C3), 126.4 (C5), 135.6 (C6), 136.7 (C2), 151.5 (C6+C6′, tbbpy), 151.9 (C1), 154.5 (br, C2+C2′, tbbpy), 163.9 (C4+C4′, tbbpy), 166.0 (C8). IR (cm^{-1}): ν(OH), not observed; ν(C=NO), 1615. Λ_M ($\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$): 56 ($2.8 \times 10^{-4}$ M, in acetone). Anal. Calcd for $C_{27}H_{34}BrN_3OPd$: C, 53.79; H, 5.68; N, 6.97. Found: C, 53.58; H, 5.75; N, 6.67. Crystals of **2·Br** suitable for an X-ray diffraction study were grown by the liquid diffusion method from acetone/Et_2O.

Synthesis of [Pd{*C,N*-$C_6H_4\{CH_2C(Me)=NOH\}$-2}(tbbpy)]ClO_4 (2·ClO_4). To a suspension of **2·Br** (103 mg, 0.17 mmol) in acetone (25 mL) was added $NaClO_4{\cdot}H_2O$ (148 mg, 1.05 mmol), and the reaction mixture was stirred for 4 h. The suspension was concentrated under vacuum to dryness, the residue was stirred with CH_2Cl_2 (20 mL), and the suspension was filtered through a short pad of Celite. The filtrate was concentrated (2 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried by suction to give **2·ClO_4** as a white solid (98 mg, 0.16 mmol, 92%). Mp: 194 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25

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°C): δ 1.42 (s, 9 H, Me, ^{t}Bu), 1.43 (s, 9 H, Me, ^{t}Bu), 2.34 (s, 3 H, Me9), 3.88 (br s, 2 H, C7H$_2$), 6.98 (dd, 1 H, H3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.04 (td, 1 H, H4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.09 (td, 1 H, H5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.40 (dd, 1 H, H6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.41 (dd, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.62 (dd, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 8.04 (d, 2 H, H3+H3′, tbbpy, $^4J_{HH}$ = 2 Hz), 8.47 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 8.95 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 10.06 (br s, 1H, OH). ^{1}H NMR (CDCl$_3$, 400 MHz, −58 °C): δ 1.42 (s, 9 H, Me, ^{t}Bu), 1.44 (s, 9 H, Me, ^{t}Bu), 2.34 (s, 3 H, Me9), 3.93 (AB system, 2 H, C7H$_2$, ν_A = 4.27, ν_B = 3.59, J_{AB} = 16 Hz), 7,06−7,15 (m, 3 H, H3+H4+H5), 7.42 (d, H6, $^3J_{HH}$ = 7 Hz), 7.48 (dd, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.53 (br d, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 4 Hz), 8.06 (br s, 2 H, H3+H3′, tbbpy), 8.46 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 8.92 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 10.12 (br s, 1H, OH). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 18.4 (Me9), 30.2 (Me, ^{t}Bu), 35.6 (*C*Me$_3$), 46.4 (C7), 118.6 (C3 or C3′, tbbpy), 119.2 (C3 or C3′, tbbpy), 123.4 (C5 or C5′, tbbpy), 124.3 (C5 or C5′, tbbpy), 124.6 (C4), 125.6 (C3), 126.6 (C5), 135.4 (C6), 136.2 (C2), 150.8 (C6 or C6′, tbbpy), 151.4 (C1), 151.8 (C6 or C6′, tbbpy), 153.0 (C2 or C2′, tbbpy), 156.9 (C2 or C2′, tbbpy), 164.4 (C4 or C4′, tbbpy), 164.7 (C2 or C2′, tbbpy), 167.6 (C8). IR (cm^{-1}): ν(OH), 3172; ν(C═NO), 1619; δ(OClO), 624. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 140 (5.3 × 10^{-4} M, in acetone). Anal. Calcd for C$_{27}$H$_{34}$ClN$_3$O$_5$Pd: C, 52.10; H, 5.51; N, 6.75. Found: C, 51.88; H, 5.36; N, 6.57.

Synthesis of *SP-4-4*-[Pd{*C,N*-C$_6$H$_4${CH$_2$C(Me)═NOH}-2}Br(pic)] (pic = γ-picoline, 3a). A Carius tube was charged, under a nitrogen atmosphere, with solid "Pd(dba)$_2$" (642 mg, 1.12 mmol) and **1** (254 mg, 1.11 mmol). pic (225 μL, 2.27 mmol) and THF (15 mL) were successively added. The reaction mixture was stirred at room temperature for 30 min, then heated at 45 °C for 1 h, and filtered through a short pad of Celite, and the solution was concentrated under vacuum to dryness. The residue was stirred with Et$_2$O (8 mL) in an ice/water bath and filtered. The solid collected was washed with cold Et$_2$O (4 × 3 mL, 4 °C), dried by suction, and recrystallized from CH$_2$Cl$_2$/Et$_2$O to give **3a** as a white solid (302 mg, 0.71 mmol, 63%), which was dried, first by suction and then in a vacuum oven (85 °C, 5h). Mp: 162 °C (dec). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 2.23 (s, 3 H, Me, pic), 2.40 (s, 3 H, Me9), 3.86 (s, 2 H, C7), 6.33 (m, 1 H, Ar), 6.70−6.76 (m, 1 H, Ar), 6.95 (m, 2 H, Ar), 7.14 (m, 2 H, H3, pic), 8.58 (m, 2 H, H2, pic), 9.38 (s, 1 H, OH). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 18.2 (Me9), 21.2 (Me, pic), 46.2 (CH$_2$), 124.6 (C, Ar), 125.6 (C, Ar), 125.9 (C3, pic), 126.4 (C, Ar), 134.7 (C1 or C2), 134.8 (C, Ar), 145.3 (C1 or C2), 150.2 (C4, pic), 152.9 (C2, pic), 162.3 (C8). IR (cm^{-1}): ν(OH), 3175; ν(C═NO), 1616. Anal. Calcd for C$_{15}$H$_{17}$BrN$_2$OPd: C, 42.13; H, 4.01; N, 6.55. Found: C, 42.23; H, 3.96; N, 6.32. Crystals of **3a** suitable for an X-ray diffraction study were grown by the liquid diffusion method from CHCl$_3$/*n*-hexane.

Synthesis of *SP-4-4*-[Pd{*C,N*-C$_6$H$_4${CH$_2$C(Me)═NOH}-2}Br(PTol$_3$)] (Tol = C$_6$H$_4$Me-4, 3b). Solid PTol$_3$ (69 mg, 0.23 mmol) was added to a solution of **3a** (91 mg, 0.21 mmol) in CH$_2$Cl$_2$ (5 mL). The solution was stirred for 1 h and concentrated under vacuum (1 mL), pentane (15 mL) was added, and the suspension was filtered. The solid collected was washed with pentane (2 × 3 mL) and dried by suction to give **3b** as a yellow solid (116 mg, 0.18 mmol, 85%). Mp: 220 °C (dec). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 2.22 (s, 3 H, Me9), 2.34 (s, 9 H, Me, Tol), 3.82 (s, 2 H, C7), 6.33 (t, 1 H, H5, $^3J_{HH}$ = 7 Hz), 6.62 ("t", 1 H, H6, $^3J_{HH} \approx {}^4J_{HP}$ = 7 Hz), 6.73 (t, 1 H, H4, $^3J_{HH}$ = 7 Hz), 6.87 (dd, 1 H, H3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.11 (m, 6 H, *meta*-Tol), 7.43 (m, 6 H, *ortho*-Tol), 9.66 (d, 1 H, OH, $^4J_{HP}$ = 2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 17.8 (Me9), 22.3 (Me, Tol), 46.7 (C7), 123.6 (C4), 125.5 (d, C5, $^4J_{CP}$ = 5 Hz), 126.5 (C3), 127.9 (d, *ipso*-Tol, $^1J_{CP}$ = 53 Hz), 128.6 (d, *meta*-Tol, $^3J_{CP}$ = 11 Hz), 134.7 (d, *ortho*-Tol, $^2J_{CP}$ = 12 Hz), 136.2 (C2), 137.9 (d, C6, $^3J_{CP}$ = 13 Hz), 140.6 (d, *para*-Tol, $^4J_{CP}$ = 2 Hz), 150.5 (d, C1, $^2J_{CP}$ = 2 Hz), 161.6 (C8). ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, 25 °C): δ 33.3. IR (cm^{-1}): ν(OH), 3155; ν(C═NO), 1597. Anal. Calcd for C$_{30}$H$_{31}$BrNOPPd: C, 56.40; H, 4.89; N, 2.19. Found: C, 56.44; H, 4.99; N, 2.07.

Synthesis of [Pd{μ-*C,N,O*-C$_6$H$_4${CH$_2$C(Me)═NO}-2}(PTol$_3$)]$_2$ (4). Solid K^{t}BuO (15 mg, 0.13 mmol) was added to a solution of **3b** (70 mg, 0.11 mmol) in CH$_2$Cl$_2$ (5 mL). The suspension was stirred for 4 h, filtered through a short pad of Celite, and concentrated under vacuum (1 mL), and pentane (20 mL) was added. Partial concentration of the solution (10 mL) under vacuum produced a suspension, which was filtered while cold. The solid collected was dried by suction to give **4**·H$_2$O as a white solid (35 mg, 0.061 mmol, 55%). Concentration of the filtrate to dryness gave a second crop of the same product (14 mg, 0.024 mmol; total yield 77%). Mp: 232 °C (dec). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 1.16 (s, 3 H, Me9), 1.67 (s, 2 H, H$_2$O), 2.22 (s, 9 H, Me, Tol), 3.48 (AB system, 2 H, C7, ν_A = 4.05, ν_B = 2.91, J_{AB} = 15 Hz), 6.32−6.38 (m, 1 H, Ar), 6.61−6.65 (m, 1 H, Ar), 6.71 (m, 6 H, *meta*-Tol), 6.76−6.79 (m, 2 H, Ar), 7.18 (m, 6 H, *ortho*-Tol). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz, 25 °C): δ 16.4 (Me9), 21.3 (Me, Tol), 46.5 (C7), 122.0 (C4), 124.0 (C5), 124.7 (C3), 128.2 (d, *ipso*-C, Tol, $^1J_{CP}$ = 45 Hz), 128.4 (d, *meta*-Tol, $^3J_{CP}$ = 11 Hz), 134.8 (d, *ortho*-Tol, $^2J_{CP}$ = 13 Hz), 136.2 (C2), 139.4 (*para*-Tol), 140.3 (d, C6, J_{CP} = 12 Hz), 140.9 (C1 or C2), 150.8 (C8). ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, 25 °C): δ 30.2. IR (cm^{-1}): ν(C═NO), 1598. Anal. Calcd for C$_{30}$H$_{32}$NO$_2$PPd: C, 62.56; H, 5.60; N, 2.43. Found: C, 62.40; H, 5.37; N, 2.36.

Synthesis of [Pd{*C,N,N*′-C$_6$H$_4${CH$_2$C(Me)═NOCH$_2$(C$_5$H$_4$N-2)}-2}Br] (5). To a suspension containing K^{t}BuO (64.2 mg, 0.54 mmol) and BrCH$_2$py·HBr (70 mg, 0.27 mmol) in CH$_2$Cl$_2$ (20 mL) was added complex **3a** (113 mg, 0.26 mmol). The suspension was stirred for 2.5 h and filtered through a short pad of Celite, the solution was concentrated under vacuum to 5 mL, and Et$_2$O (15 mL) was added. The resulting suspension was filtered, and the solid was washed with Et$_2$O (3 × 3 mL) and dried, first by suction and then in a vacuum oven at 80 °C for 5 h to give **5** as a pale yellow solid (62 mg, 0.15 mmol, 55%). Mp: > 230 °C (dec). ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): δ 2.22 (s, 3 H, Me9), 3.87 (s, 2 H, C7), 5.46 (s, 2 H, C*H*$_2$py), 6.89−6.98 (m, 3 H, Ar), 7.38 (d, 1 H, H3, py, $^3J_{HH}$ = 8 Hz), 7.44 (ddd, 1 H, H5, py, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz), 7.87 (td, 1 H, H4, py, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.92 (m, 1 H, Ar), 9.24 (dd, 1 H, H6, py, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz, 25 °C): δ 18.7 (Me9), 46.8 (C7), 75.1 (*C*H$_2$-py), 124.17 (C3, py), 124.21 (C, Ar), 125.2 (C5, py), 125.4 (C, Ar), 126.4 (C3), 133.1 (C1 or C2), 138.9 (C4, py), 139.7 (C1 or C2), 140.8 (C, Ar), 152.9 (C6, py), 153.5 (C2, py), 162.3 (C8). IR (cm^{-1}): ν(C═NO) + (ν(CC) + ν(CN))$_{aromatic}$, 1601, 1569, 1558. Anal. Calcd for C$_{15}$H$_{15}$BrN$_2$OPd: C, 42.33; H, 3.55; N, 6.58. Found: C, 42.27; H, 3.38; N, 6.65. Crystals of **5** suitable for an X-ray diffraction study were grown by the liquid diffusion method from CDCl$_3$/Et$_2$O.

Synthesis of 1,2-Dihydro-1-oxo-2-hydroxy-3-methylisoquinoline (6). A solution of **3a** (71.4 mg, 0.17 mmol) in CHCl$_3$ (8 mL) was stirred for 5 h in a Carius tube under a CO pressure of 1.4 bar. The resulting suspension was filtered through a short pad of Celite to remove some Pd(0), and the solution was concentrated under vacuum to dryness to give a 1:1 mixture (84% yield) of **6** and [picH]Br. A sample of pure **6**, used for its characterization by ^{1}H NMR, was obtained by extracting the mixture with Et$_2$O and concentrating the extract to dryness. ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 2.55 (d, 3 H, Me9, $^4J_{HH}$ = 1 Hz), 6.47 (s, 1 H, H4), 7.46 (ddd, 1H, H6 or H7, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.52 (d, 1H, H5, $^3J_{HH}$ = 8 Hz), 7,63 (ddd, 1H, H6 or H7, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.34 (ddd, 1H, H8, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, $^4J_{HH}$ = 1 Hz), 10.30 (vbr s, OH).

Synthesis of 1,2-Dihydro-1-imino(R)-2-hydroxy-3-methylisoquinoline (R = ^{t}Bu (7a), Xy (7b)). ^{t}BuNC (for **7a**, 75 μL, 0.65 mmol) or XyNC (for **7b**, 69 mg, 0.53 mmol) was added to a solution of **2**·ClO$_4$ (for **7a**, 200 mg, 0.32 mmol; for **7b**, 166 mg, 0.28 mmol) in CH$_2$Cl$_2$ (20 mL). The resulting solution was stirred for 40 (**7a**) or 48 h (**7b**) and concentrated under vacuum to ca. 4 mL. Pentane (20 mL) was added, and the resulting suspension was filtered. The solid was dissolved in CH$_2$Cl$_2$ (1 mL), pentane (10 mL) was added, and the suspension was filtered. After repeating this two more times, the

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combined filtrates were concentrated to dryness, the residue was extracted with pentane (4 × 4 mL), and the combined extracts were concentrated under vacuum to dryness. For **7a**, the yellowish oil obtained was chromatographed on a silica column using a 4:1 EtOAc/Et_2O mixture as the eluent. The solution was concentrated to dryness, and the residue was dissolved in CH_2Cl_2 and washed with H_2O (3 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness. The residue was extracted with pentane (3 × 3 mL), and the extracts were concentrated under vacuum to dryness to give **7a** as an off-white solid (70 mg, 0.30 mmol, 95%). For **7b**, the residue was chromatographed on a silica column using a 2:1 acetone/*n*-hexane mixture as the eluent. The solution was concentrated to dryness to give **7b** as a pale yellow solid (54.2 mg, 0.19 mmol, 74%).

7a. Mp: 80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.42 (s, 9 H, Me, ^{t}Bu), 2.66 (d, 3 H, Me9, $^4J_{HH}$ = 1 Hz), 6,68 (br s, 1 H, H4), 7.22 (s, 1H, OH), 7.44−7.52 (m, 2 H, H6+H7), 7.62 (m, 1 H, H5), 8.17 (m, 1 H, H8). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 18.6 (Me), 31.7 (Me, ^{t}Bu), 56.9 (*C*Me$_3$), 115.3 (C4), 123.2 (C8a), 125.8 (C7), 126.0 (C5+C8), 128.3 (C6), 130.0 (C4a), 143.4 (C3), 149.9 (C1). IR (cm^{-1}): ν(OH), 3232; ν(CC$_{arom}$ + C═N^{t}Bu), 1556, 1495. HRMS (ESI+, *m*/*z*): found 231.1498, calcd for $C_{14}H_{18}N_2O$ $[M + H]^+$ 231.1492. Error: 2.47 ppm.

7b. Mp: 147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.17 (s, 6 H, Me, Xy), 2.73 (d, 3 H, Me9, $^4J_{HH}$ = 0.4 Hz), 7.02 (br s, 1 H, H4), 7.05 (ddd, 1 H, H7, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.12 (m, 1 H, H8), 7.16 (m, 2 H, *meta*-Xy), 7.22 (m, 1 H, *para*-Xy), 7.40 (ddd, 1 H, H6, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.58 (br d, 1 H, H5, $^3J_{HH}$ = 8.0 Hz), 9.43 (br s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 18.4 (Me), 18.6 (Me, Xy), 111.1 (C4), 117.1 (C8a), 121.7 (C8), 125.9 (C7), 126.5 (C5), 127.4 (*para*-C, Xy), 128.6 (C6), 128.7 (*meta*-C, Xy), 130.7 (C4a), 136.3 (*ortho*-C, Xy), 137.3 (*ipso*-C, Xy), 142.6 (C3), 145.9 (C1). IR (cm^{-1}): ν(OH), 3157; ν(CC$_{arom}$ + C═NXy), 1567, 1516. HRMS (ESI+, *m*/*z*): found 279.1501, calcd for $C_{18}H_{18}N_2O$ $[M + H]^+$ 279.1492. Error: 3.23 ppm.

Synthesis of [1,2-Dihydro-1-xylyliminium-2-hydroxy-3-methylisoquinoline]picrate (8). Picric acid (27 mg, 0.12 mmol) was added to a solution of **7b** (32 mg, 0.12 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred for 30 min and concentrated under vacuum to ca. 1 mL, and Et_2O (12 mL) was added. The resulting suspension was filtered, and the solid collected was washed with Et_2O (3 × 2 mL) and dried, first by suction and then in a vacuum oven (5 h, 75 °C), to give **8** (45 mg, 0.09 mmol, 77%) as a yellow solid. Mp: 181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.15 (s, 6 H, Me, Xy), 2.81 (s, 3 H, Me9), 7.07 (s, 1 H, H4), 7.17−7.24 (m, 4 H, H8 + Ar + *meta*-Xy), 7.31 (dd, 1 H, *para*-Xy, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz), 7.66−7.71 (m, 2 H, Ar), 8.88 (s, 2 H, picrate), 8,99 (br s, 1 H, NH), 9.59 (vbr s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 17.9 (Me), 18.2 (Me, Xy), 112.2 (C4), 117.1 (C8a), 124.3 (C5, C6, C7 or C8), 126.0 (C, picrate), 127.2 (C5, C6, C7, or C8), 127.7 (C5, C6, C7, or C8), 129.2 (*para*-C, Xy), 129.4 (*meta*-C, Xy), 130.3 (C, picrate), 133.4 (C5, C6, C7, or C8), 134.6 (*ipso*-C, Xy), 135.8 (C4a), 135.9 (*ortho*-C, Xy), 141.4 (*ortho*-C, picrate), 142.0 (C3), 149.5 (C1), 160,3 (C, picrate). Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 64 ($5.03 \times 10^{-4}$ M in acetone). IR (cm^{-1}): ν(OH + NH), 3335 br. HRMS (ESI+, *m*/*z*): found 279.1499, calcd for $C_{18}H_{19}N_2O$ $[M]^+$ 279.1492. Error: 2.45 ppm. HRMS (ESI−, *m*/*z*): found 227.9904, calcd for $C_6H_2N_3O_7$ (picrate) 227.9898. Error: 2.57 ppm.

Synthesis of [Pd{*C,N*-C(CO$_2$Me)═C(CO$_2$Me)C$_6$H$_4$\{CH$_2$C(Me)═NOH\}-2}(tbbpy)]ClO$_4$ (9a). Dimethyl acetylenedicarboxylate (200 μL, 1.59 mmol) was added to a solution of **2·ClO$_4$** (112 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 40 h and filtered through a short pad of Celite, the filtrate was concentrated under vacuum (2 mL), Et_2O (20 mL) was added, and the resulting suspension was filtered. The solid collected was washed with Et_2O (3 × 3 mL), recrystallized from $CHCl_3$/pentane, and dried, first by suction and then in a vacuum oven (80 °C, 5 h), to give **9a** as a pale yellow solid (126 mg, 0.16 mmol, 92%). Mp: 179 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.36 (s, 9 H, Me, ^{t}Bu), 1.40 (s, 9 H, Me, ^{t}Bu), 2.38 (s, 3 H, Me9), 3.75 (s, 3 H, CO_2Me), 3.80 (AB system, 2 H, C7, ν_A = 3.87, ν_B = 3.72, J_{AB} = 19 Hz), 3.88 (s, 3 H, CO_2Me), 6.97−7.01 (m, 2 H, H5+H6), 7.06 (m, 1 H, H4), 7.22 ("d", 1 H, H3), 7.46 (dd, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.50 (dd, 1 H, H5 or H5′, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.80 (d, 1 H, H3 or H3′, tbbpy, $^4J_{HH}$ = 2 Hz), 7.81 (d, 1 H, H3 or H3′, tbbpy, $^4J_{HH}$ = 2 Hz), 8.16 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 8.64 (d, 1 H, H6 or H6′, tbbpy, $^3J_{HH}$ = 6 Hz), 10,05 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 20.5 (Me9), 30.1 (Me, ^{t}Bu), 35.6 (*C*(Me)$_3$), 35.7 (*C*(Me)$_3$), 42.0 (C7), 52.1 (CO_2*Me*), 52.3 (CO_2*Me*), 118.8 (C3 or C3′, tbbpy), 119.0 (C3 or C3′, tbbpy), 123.8 (C5 or C5′, tbbpy), 124.6 (C5 or C5′, tbbpy), 127.5 (C5), 127.7 (C4), 128.0 (C6), 131.2 (C3), 131.6 (C11), 133.6 (C2), 142.6 (C1), 149.5 (C6 or C6′, tbbpy), 152.1 (C6 or C6′, tbbpy), 153.0 (C2 or C2′, tbbpy), 156.0 (C2 or C2′, tbbpy), 161.4 (C12 or C14), 164.8 (C4 or C4′, tbbpy), 164.9 (C4 or C4′, tbbpy), 169.0 (C10−Pd), 169.8 (C8), 170.8 (C12 or C14). Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 134 ($4.5 \times 10^{-4}$ M in acetone). IR (cm^{-1}): ν(OH), 3282; ν(CO), 1713; ν(ClO) 1098; δ(OClO), 625. Anal. Calcd for $C_{33}H_{40}ClN_3O_9Pd$: C, 51.84; H, 5.27; N, 5.50. Found: C, 51.55; H, 5.22; N, 5.50. Crystals of **9a** suitable for an X-ray diffraction study were grown by the liquid diffusion method from $CDCl_3$ and pentane.

Synthesis of *SP-4-4*-[Pd{*C,N*-C(R)═C(CO$_2$Me)C$_6$H$_4$\{CH$_2$C(Me)═NOH\}-2}Br(pic)] (R = CO$_2$Me (10a), Ph (10b)). The appropriate alkyne (for **10a**, DMAD, 35 μL, 0.28 mmol; for **10b**, methyl phenylpropiolate, 41 μL, 0.27 mmol) was added to a solution of complex **3a** (for **10a**, 118 mg, 0.28 mmol; for **10b**, 115 mg, 0.27 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred for 6 h. The solution was filtered through a short pad of Celite and concentrated under vacuum (4−5 mL), Et_2O (20 mL) was added, and the resulting suspension was filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried, first by suction and then in a vacuum oven (**10a**, 55 °C, 10 h; **10b**, 75 °C, 5 h), to give the title complex as a pale yellow solid.

10a. Yield: 132 mg, 0.23 mmol, 84%. Mp: 184 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.22 (s, 3 H, Me9), 2.34 (s, 3 H, Me, pic), 3.63 (s, 3 H, CO_2Me), 3.70 (AB system, 2 H, C7, ν_A = 3.84, ν_B = 3.55, J_{AB} = 18 Hz), 3.84 (s, 3 H, CO_2Me), 7.05 (d, 2 H, H3, pic), 7.10 (d, 1 H, H6, $^3J_{HH}$ = 8 Hz), 7.39 (td, 1 H, H5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.42 (m, 1 H, H3), 7.47 (ddd, 1 H, H4, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 8.14 (d, 2 H, H2, pic), 8.39 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 20.7 (Me9), 21.1 (Me, pic), 41.4 (C7), 51.9 (C15), 52.0 (C13), 125.6 (C3, pic), 127.1 (C5), 128.4 (C4), 128.6 (C6), 131.7 (C3), 131.8 (C11), 134.8 (C2), 141.9 (C1), 150.3 (C4, pic), 152.0 (C2, pic), 160.8 (C12), 166.3 (C10), 169.1 (C8), 170.0 (C14). IR (cm^{-1}): ν(OH), 3198; ν(CO), 1713, 1701. Anal. Calcd for $C_{21}H_{23}BrN_2O_5Pd$: C, 44.27; H, 4.07; N, 4.92. Found: C, 43.98; H, 3.84; N, 4.86. Crystals of **10a** suitable for an X-ray diffraction study were grown by the liquid diffusion method from $CDCl_3$ and Et_2O.

10b. Yield: 127 mg, 0.22 mmol, 80%. Mp: 173 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 2.29 (s, 3 H, Me9), 2.33 (s, 3 H, Me, pic), 3.42 (s, 3 H, CO_2Me), 3.77 (AB system, 2 H, C7, ν_A = 3.96, ν_B = 3.57, J_{AB} = 17 Hz), 6.96 (d, 2 H, H3, pic), 6.98 (m, 2 H, *ortho*-Ph), 7.27−7.30 (m, 3 H, *meta*- + *para*-Ph), 7.31−7.33 (m, 1 H, H6), 7.42−7.44 (m, 1 H, H3), 7.45−7.48 (m, 2 H, H4+H5), 7.82 (d, 2 H, H2, pic), 8.74 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 25 °C): δ 20.6 (Me9), 21.0 (Me, pic), 41.4 (C7), 51.2 (C13), 125.4 (C3, pic), 126.0 (*ortho*-CH, Ph), 126.4 (*para*-C, Ph), 127.1 (C5), 128.0 (C4 + *meta*-C, Ph), 129.2 (C6), 130.3 (C11), 131.4 (C3), 134.6 (C2), 142.2 (C1), 143.0 (*ipso*-C, Ph) 149.8 (C4, pic), 151.6 (C2, pic), 162.3 (C12), 168.4 (C8), 174.8 (C10). IR (cm^{-1}): ν(OH), 3223; ν(CO), 1720. Anal. Calcd for $C_{25}H_{25}BrN_2O_3Pd$: C, 51.09; H, 4.29; N, 4.77. Found: C, 50.88; H, 4.22; N, 4.73.

Synthesis of *SP-4-4*-[Pd{*C,N*-C(CO$_2$Me)═C(CO$_2$Me)-C$_6$H$_4$\{CH$_2$C(Me)═NOH\}-2}Br(PTol$_3$)] (10c). Solid $PTol_3$ (56.2 mg, 0.18 mmol) was added to a solution of **10a** (105 mg, 0.18 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred for 4 h. The solution was concentrated under vacuum (1 mL), pentane (15 mL) was added, and the suspension was filtered. The solid collected was dissolved in CH_2Cl_2 (1 mL), *n*-hexane (10 mL) was added, and the solution was kept at 4 °C overnight. The resulting suspension was

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filtered, and the solid collected was dried by suction to give **10c** as a pale yellow solid (63 mg, 0.08 mmol, 45%). Concentration of the filtrate to dryness gave a second crop of the same compound (38 mg, 0.05 mmol; total yield 72%). Mp: 193 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.18 (s, 3 H, Me9), 2.36 (s, 9 H, Me, Tol), 3.56 (s, 3 H, CO_2Me), 3.59 (s, 3 H, CO_2Me), 3.64 (AB system, 2 H, C7, ν_A = 3.80, ν_B = 3.48, J_{AB} = 18 Hz), 5.77 (dd, 1 H, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.07 (td, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.12 (m, 6 H, *meta*-Tol), 7.25 (m, 6 H, *ortho*-Tol) 7.35 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.40 (td, 1 H, H4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 9.05 (d, 1 H, OH, $^4J_{HP}$ = 2 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 19.9 (4, Me9, $^4J_{CP}$ = 2 Hz), 21.5 (Me, Tol), 41.3 (C7), 51.6 (CO_2Me), 51.7 (CO_2Me), 126.9 (d, *ipso*-C, Tol, $^1J_{CP}$ = 56 Hz), 127.3 (C4 or C6), 127.7 (C4 or C6), 128.5 (d, *meta*-Tol, $^3J_{CP}$ = 12 Hz),131.4 (C3), 133.7 (d, C11), 133.8 (C2), 135.1 (d, *ortho*-Tol, $^2J_{CP}$ = 11 Hz), 140.9 (d, *para*-Tol, $^4J_{CP}$ = 2 Hz), 142.8 (C1), 162.7 (C12), 166.7 (d, C8, $^3J_{CP}$ = 3 Hz), 169.4 (d, C14, $^3J_{CP}$ = 4 Hz), 170.6 (C10). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 25 °C): δ 20.1. IR (cm^{-1}): ν(OH), 3233; ν(CO), 1712, 1702. Anal. Calcd for $C_{36}H_{37}BrNO_5Pd$: C, 55.37; H, 4.78; N, 1.79. Found: C, 55.31; H, 4.84; N, 1.71.

Synthesis of [{Pd(tbbpy)}$_2${μ-*N,O*-{η^3-$C_6H_4(C_4Ph_4)$}{CH_2C(Me)=NO}}]$_2$ (ClO_4)$_4$ (11·ClO_4). To a solution of **2**·ClO_4 (328 mg, 0.53 mmol) in $CHCl_3$ (15 mL) was added diphenyl acetylene (288 mg, 1.58 mmol), and the solution was heated in a Carius tube at 60 °C for 48 h. The resulting suspension was filtered, the solid collected was washed with $CHCl_3$ (3 × 3 mL), dried by suction, and dissolved in acetone (35 mL), and the solution was filtered through a short pad of Celite. The solution was concentrated under vacuum (5 mL), Et_2O (15 mL) was added, and the suspension was filtered. The solid collected was washed with Et_2O (3 × 3 mL) and dried, first by suction and then in a vacuum oven (80 °C, 5 h), to give **11**·ClO_4 as a pale yellow solid (160 mg, 0.06 mmol, 42%). Mp: >250 °C (dec). ^{1}H NMR (CD_3CN, 600 MHz, 25 °C): δ 1.22 (s, 9 H, Me, ^{t}Bu), 1.26 (s, 9 H, Me, ^{t}Bu), 1.34 (s, 9 H, Me, ^{t}Bu), 1.50 (s, 9 H, Me, ^{t}Bu), 2.14 (s, 3 H, Me9), 3.95 (AB part of an ABX system, 2 H, C7, ν_A = 4.48, ν_B = 3.41, J_{AB} = 19 Hz, J_{AX} = 2 Hz, J_{BX} = 0 Hz), 5.45 (dd, 1 H, H3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 5.54 (td, 1 H, H1, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 5.94 (m, 2 H, Ph), 6.11 (m, 1 H, Ph), 6.15 (m, 3 H, H6 + Ph), 6.43 (t, 1 H, H2, $^3J_{HH}$ = 6 Hz), 6.77 (m, 2 H, Ph), 6.89 (m, 2 H, Ph), 7.05 (m, 1 H, Ph), 7.09 (m, 2 H, Ph), 7.16 (m, 2 H, Ph), 7.26 (dd, 1 H, H5–H5‴, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.41–7.44 (m, 3 H, Ph), 7.46–7.49 (m, 6 H (4 Ph + 2 H5–H5‴, tbbpy)), 7.64 (dd, 1 H, H5–H5‴, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.97 (d, 1 H, H3–H3‴, $^4J_{HH}$ = 2 Hz), 8.02 (d, 1 H, H6–H6‴, $^3J_{HH}$ = 6 Hz), 8.07 (d, 1 H, H3–H3‴, $^4J_{HH}$ = 2 Hz), 8.09 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz), 8.16 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 8.20 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 8.25 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz), 8,95 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} NMR (CD_3CN, 100 MHz, 25 °C): δ 8.8 (Me9), 30.20 (Me, ^{t}Bu), 30.23 (Me, ^{t}Bu), 30.28 (Me, ^{t}Bu), 30.6 (Me, ^{t}Bu), 36.4 (CMe_3), 36.79 (CMe_3), 36.86 (CMe_3), 36.90 (CMe_3), 40.2 (C7), 66.4 (C1), 72.5 (C4), 81.8 (C3), 105.3 (C2), 120.5 (C3–C3‴, tbbpy), 121.3 (C3–C3‴, tbbpy), 121.6 (C3–C3‴, tbbpy), 122.5 (C3–C3‴, tbbpy), 123.9 (C5–C5‴, tbbpy), 124.9 (C5–C5‴, tbbpy), 125.0 (C5–C5‴, tbbpy), 126.7 (C5–C5‴, tbbpy), 127.4 (C6), 128.1 (C, Ph), 128.2 (C, Ph), 128.4 (C, Ph), 128.67 (C, Ph), 128.73 (C, Ph), 129.0 (C, Ph), 129.2 (C, Ph), 130.2 (C, Ph), 130.4 (C, Ph), 130.7 (C, Ph), 131.2 (C, Ph), 132.9 (C5), 135.7 (*ipso*-C, Ph), 135.8 (*ipso*-C, Ph), 136.1 (*ipso*-C, Ph), 136.2 (*ipso*-C, Ph), 143.3 (C10+C13), 148.0 (C11 or C12), 148.4 (C11 or C12), 149.7 (C6–C6‴, tbbpy), 152.0 (C6–C6‴, tbbpy), 154.29 (C6–C6‴, tbbpy), 154.33 (C6–C6‴, tbbpy), 154.5 (C2–C2‴, tbbpy), 155.6 (C2–C2‴, tbbpy), 155.9 (C2–C2‴, tbbpy), 156.7 (C2–C2‴, tbbpy), 161.1 (C8), 165.0 (C4–C4‴, tbbpy), 166.6 (C4–C4‴, tbbpy), 168.1 (C4–C4‴, tbbpy), 168.2 (C4–C4‴, tbbpy). Λ_M (Ω^{-1}·cm^2·mol^{-1}): 283 (1.0 × 10^{-4} M, in acetone). IR (cm^{-1}): ν(C=N), 1616; ν(ClO), 1095; δ(OClO). 624. Anal. Calcd for $C_{146}H_{154}N_{10}Cl_4O_{18}Pd_4$: C, 60.38; H, 5.34; N, 4.82. Found: C, 60.09; H, 5.47; N, 5.06. HRMS (ESI+, *m*/*z*): calcd for the monomer $[C_{73}H_{77}N_5OPd_2]^{2+}$ (M^{2+}) 626.7118, found 626.7122; Error = 0.64 ppm. Calcd for $[M - H^+]^+$ 1252.4174, found 1252.4143. Error = 2.48 ppm. (ESI–, *m*/*z*): calcd for ClO_4^- 98.9491, found 98.9493. Error = 2.32 ppm.

Synthesis of [{Pd(tbbpy)}$_2${μ-*N,O*-{η^3-$C_6H_4(C_4Ph_4)$}{CH_2C(Me)=NO}}]$_2$(picrate)$_4$ (11·picrate). To a suspension of **11**·ClO_4 (102.0 mg, 0.04 mmol) in acetone (50 mL) was added excess potassium picrate (198 mg, 0.74 mmol). The solution was stirred for 4 h and concentrated under vacuum to dryness. The residue was stirred with CH_2Cl_2 (25 mL), and the suspension was filtered through a short pad of Celite. The solution was concentrated under vacuum to 2 mL, Et_2O (15 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (3 × 3 mL) and dried, first by suction and then in a vacuum oven (80 °C, 5h), to give a 1:3 mixture of **11**·ClO_4 and **11**·**picrate** (109 mg), which was recrystallized repeatedly from $CHCl_3$ and Et_2O, giving a small crop of pure **11**·**picrate**. Single crystals of this complex suitable for an X-ray structure determination were grown from the above-mentioned 1:3 mixture by the liquid diffusion method using CH_2Cl_2 and Et_2O. Mp: 160 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.12 (s, 9 H, Me, ^{t}Bu), 1.16 (s, 9 H, Me, ^{t}Bu), 1.21 (s, 9 H, Me, ^{t}Bu), 1.37 (s, 9 H, Me, ^{t}Bu), 1.83 (s, 3 H, Me9), 3.86 (AB system, 2 H, C7, ν_A = 4.43, ν_B = 3.29, J_{AB} = 19 Hz), 5.15 (dd, 1 H, H3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 5.88 (t, 1 H, H1, $^3J_{HH}$ = 6 Hz), 6.09–6.15 (m, 3 H, H6 + Ph), 6.27 (m, 3 H, Ph), 6.42 (t, 1 H, H2, $^3J_{HH}$ = 6 Hz), 6.56 (m, 2 H, Ph), 6.94 (m, 2 H, Ph), 7.00 (m, 2 H, Ph), 7.04 (dd, 1 H, H5–H5‴, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.11 (m, 2 H, Ph), 7.16 (m, 2 H, Ph), 7.25–7.30 (m, 4 H, Ph), 7.48 (m, 3 H, tbbpy), 7.52 (dd, 1 H, H5–H5‴, tbbpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.73 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz), 7.85 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 7.94 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 8.33 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz), 8.34 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 8.51 (d, 1 H, H3–H3‴, tbbpy, $^4J_{HH}$ = 2 Hz), 8.65 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz), 8.66 (s, 4 H, *meta*-picrate), 9.21 (d, 1 H, H6–H6‴, tbbpy, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 17.8 (Me9), 29.79 (Me, ^{t}Bu), 29.81 (Me, ^{t}Bu), 30.0 (Me, ^{t}Bu), 30.1 (Me, ^{t}Bu), 35.5 (CMe_3), 35.8 (CMe_3), 36.0 (CMe_3), 39.3 (C7), 66.9 (C1), 71.3 (C4), 79.7 (C3), 104.4 (C2), 118.5 (C3–C3‴, tbbpy), 118.8 (C3–C3‴), 120.4 (C3–C3‴, tbbpy), 121.8 (C3–C3‴, tbbpy), 122.3 (C5–C5‴, tbbpy), 124.8 (C5–C5‴, tbbpy), 125.1 (C5–C5‴, tbbpy), 125.28 (C6), 125.33 (*ipso*-C or *para*-C, picrate), 125.9 (C5–C5‴, tbbpy), 126.1 (*meta*-C, picrate), 127.3 (C, Ph), 127.7 (C, Ph), 128.0 (C, Ph), 128.1 (C, Ph), 128.3 (C, Ph), 128.4 (C, Ph), 129.2 (C, Ph), 129.5 (C, Ph), 129.7 (C, Ph), 129.8 (C, Ph), 133.5 (C5), 133.8 (*ipso*-C, Ph), 134.1 (*ipso*-C, Ph), 134.3 (*ipso*-C, Ph), 134.6 (*ipso*-C, Ph), 142.1 (C10 and/or C13), 142.2 (*ortho*-C, picrate), 146.8 (C11 or C12), 147.1 (C11 or 12), 150.3 (C6–C6‴, tbbpy), 151.0 (C6–C6‴, tbbpy), 152.8 (C6–C6‴, tbbpy), 153.6 (C2–C2‴, tbbpy), 153.6 (C2–C2‴, tbbpy), 153.8 (C6–C6‴), 154.4 (C2–C2‴), 155.8 (C2–C2‴), 158.7 (C8), 162.0 (*ipso*-C or *para*-C, picrate), 163.6 (C4–C4‴, tbbpy), 165.1 (C4–C4‴, tbbpy), 166.8 (C4–C4‴, tbbpy), 167.1 (C4–4‴, tbbpy). Λ_M (Ω^{-1}·cm^2·mol^{-1}): 210 (1.8 × 10^{-4} M in acetone). IR (cm^{-1}): ν(C=N), 1634. Anal. Calcd for $C_{170}H_{162}N_{22}O_{30}Pd_4$: C, 59.72; H, 4.78; N, 9.01. Found: C, 59.44; H, 4.75; N, 8.71. HRMS (ESI+, *m*/*z*): calcd for the monomer $[C_{73}H_{77}N_5OPd_2]^{2+}$ (M^{2+}) 626.7118, found 626.7137. Error = 3.03 ppm. Calcd for $[M - H^+]^+$ 1252.4174, found 1252.4203. Error = 2.32 ppm. (ESI–, *m*/*z*): calcd for $(C_6H_2N_3O_7)^-$, picrate, 227.9898, found 227.9900. Error = 0.95 ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Combined CIF file and a table giving crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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