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Synthesis and Hydrolysis of Cationic Palladium(II) 2,6-Diacetylpyridine Dimethyl Ketal Complexes. Cyclopalladation of 2,6-Diacetylpyridine. Palladium-Catalyzed Synthesis of a 1,5-Benzodiazepine†

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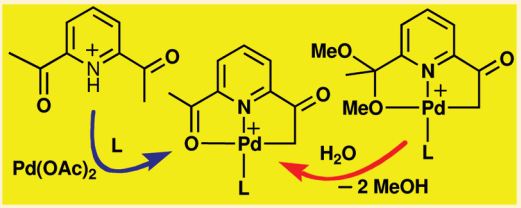
Supporting Information

ABSTRACT: The complex $[Pd(O^1,N^1,C^1\text{-L})(OClO_3)]$ (L = monoanionic ligand resulting from deprotonation of the acetyl group of the dimethyl monoketal of 2,6-diacetylpyridine) reacts with neutral ligands L^1 (phosphines, isocyanides, CO, N-donor ligands) to give the complexes $[Pd(O^1,N^1,C^1\text{-L})L^1]ClO_4$, $[Pd(N^1,C^1\text{-L})L^1_2]ClO_4$, and $[Pd(C^1\text{-L})L^1_3]ClO_4$. The complex $[Pd(N^1,C^1\text{-L})(pda)]ClO_4$ (pda = $NH_2C_6H_4NH_2$-2) can be used as a catalyst for the synthesis of 2′,2′,4′-trimethyl-2′,3′-dihydro-1*H*-1′,5′-benzodiazepine (Bzdiaz) from pda and acetone. The intermediate $[Pd(O^1,N^1,C^1\text{-L})(Bzdiaz)]ClO_4$ has been isolated from an acetone solution of $[Pd(N^1,C^1\text{-L})(pda)]ClO_4$. The ligand L in some of the above complexes hydrolyzes to give $[Pd(O^1,N^1,C^1\text{-L}')L^1]ClO_4$ (L′ = monoanionic ligand resulting from the deprotonation of one acetyl group of 2,6-diacetylpyridine, L^1 = MeCN, ^{t}BuNC). These complexes are best prepared by reacting L^1 with $[Pd(O^1,N^1,C^1\text{-L}')(NCMe)]ClO_4$, which, in turn, can be obtained from 2,6-diacetylpyridinium perchlorate and $Pd(OAc)_2$ in MeCN. When THF is used as solvent, $[Pd(O^1,N^1,C^1\text{-L}')(OH_2)]ClO_4$ can be isolated. The crystal structures of $[Pd(O^1,N^1,C^1\text{-L}')(NCMe)]ClO_4$ and $[Pd(O^1,N^1,C^1\text{-L})(CNXy)]ClO_4$ have been determined.



INTRODUCTION

Pd(II) ketonyl compounds of the type $[Pd]CH_2C(O)R$[1−3] are interesting because of their stability, reactivity, and role as intermediates in organic synthesis.[4] We have reported the synthesis and/or reactivity of ketonyl derivatives of other metals, such as Pt,[2,5] Au,[6,7] Hg,[3,5] and Tl.[7,8] In this context, we have recently described various attempts to prepare Pd(II) ketonyl complexes derived from 2,6-diacetylpyridine (dap; Scheme 1).[9] However, they were unsuccessful, likely because of the low nucleophilicity of this ligand, owing to the electron-withdrawing nature of the two acetyl groups. It was only after the ketalization of one these groups that metalation of the other could be achieved. Both processes occurred when a MeOH solution of $PdCl_2$ and dap was refluxed, which allowed the isolation of the pincer complex $[Pd(O^1,N^1,C^1\text{-L})Cl]$ (**1**; Scheme 1),[9] where L is the monoanionic ligand resulting from deprotonation of the acetyl methyl group in the monoketal of 2,6-diacetylpyridine.

From complex **1** we have isolated some homologues[9] and the first family of Pd(IV) pincer complexes $[Pd(O^1,N^1,C^1\text{-L})X_3]$ (X = Cl, Br,[10] I;[11] Scheme 1). Recently, we have reported the first oxidative addition of an aryl halide to a palladium(II) complex, which led to the synthesis of the Pd(IV) complex $[Pd(O^1,N^1,C^1\text{-L})(C,O\text{-}C_6H_4CO_2\text{-}2)I]$ (Scheme 1).[12] The latter and the Pd(II) derivatives $[Pd(O^1,N^1,C^1\text{-L})(OAc)]$,[12] $[Pd(O^1,N^1,C^1\text{-L})(OClO_3)]$ (**2**; Scheme 1), and $[Pd(O^1,N^1,C^1\text{-L}')(NCMe)]ClO_4$ (**3**; L′ = monoanionic ligand resulting from the deprotonation of one acetyl group of 2,6-diacetylpyridine; Scheme 1) were shown to be precatalysts for some room-temperature Heck-type reactions.[13] The study of these reactions allowed us to provide the first clear evidence of a Pd(II)/Pd(IV) catalytic cycle,[12,13] kinetic data proving that **3** was the best precatalyst, and a method for the isolation of complex **3** from the catalytic mixture. This surprised us because, as mentioned above, we unfruitfully attempted to prepare homologues of **3** directly from palladium salts and dap (Scheme 1).

The above results showed the great promise of the pincer complexes containing the ligands L and L′ and, at the same time, the need for further work to prepare and study the reactivity of derivatives **1**−**3**. In this paper, we report (1) the preparation of a family of cationic derivatives of **2**, some of which hydrolyze to give **3**-type complexes, and (2) a direct synthesis of **3** from dap, its reactivity, and its X-ray crystal structure.

RESULTS AND DISCUSSION

Synthesis of Cationic Complexes from $[Pd(O^1,N^1,C^1\text{-L})(OClO_3)]$ (2). In the course of the study of the Heck olefination of 2-iodobenzoic acid in acetone using **2** as precatalyst,[13] we observed the formation of the cationic

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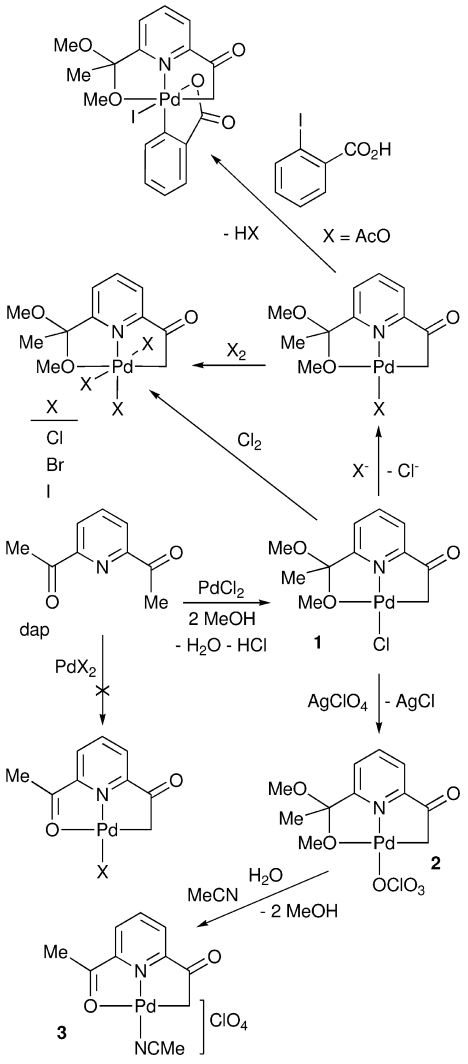
Scheme 1

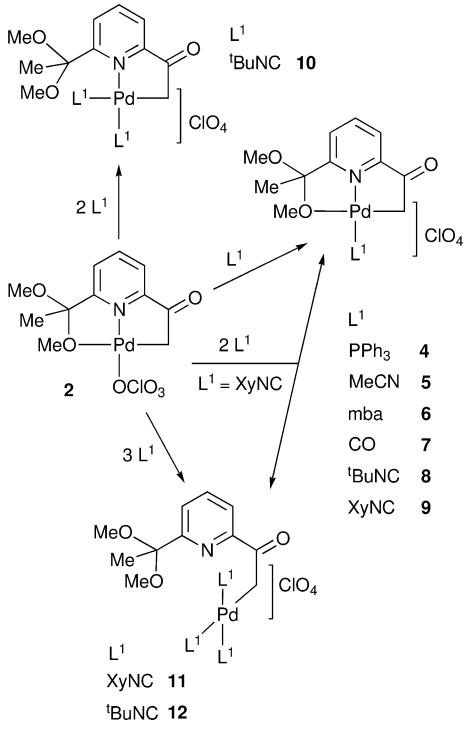


solvento complex $[Pd(O^1,N^1,C^1\text{-}L)(S)]ClO_4$ (S = acetone; L = monoanionic ligand resulting from deprotonation of the acetyl group of the dimethyl monoketal of 2,6-diacetylpyridine) and its slow hydrolysis to give MeOH and $[Pd(O^1,N^1,C^1\text{-}L')(S)]ClO_4$ (L′ = monoanionic ligand resulting from the deprotonation of one acetyl group of 2,6-diacetylpyridine). From the mixture resulting at the end of the catalytic reaction we isolated $[Pd(O^1,N^1,C^1\text{-}L')(NCMe)]ClO_4$ (**3**) upon adding MeCN. As we did not observe this hydrolysis in solutions of the complex $[Pd(O^1,N^1,C^1\text{-}L)Cl]$ (**1**; Scheme 1) and its neutral homologues,[9] we concluded that the hydrolysis of $[Pd(O^1,N^1,C^1\text{-}L)(S)]ClO_4$ in acetone occurred because of its cationic nature: i.e., the increase in the acidic character of the metal center favored the hydrolysis (see below). This explains that our previous attempts to prepare cationic complexes from **1** gave products that decomposed very easily at room temperature.

Therefore, to prepare the desired cationic complexes, we reacted P-, N- or C-donor neutral ligands with $CHCl_3$ or CH_2Cl_2 solutions of **2** at short reaction times and temperatures around 0 °C, in order to slow down the hydrolysis. The greater stability of the cationic complexes resulting from **2** and primary amines ($H_2NCH_2C_6H_4OMe$-4 = mba; *o*-phenylendiamine = pda) or 1 equiv of XyNC allowed us to perform the reaction at room temperature.

Monodentate ligands L^1 reacted with **2**, affording the complexes $[Pd(O^1,N^1,C^1\text{-}L)L^1]ClO_4$ (L^1 = PPh_3 (**4**), MeCN (**5**), mba (**6**), CO (**7**), ^{t}BuNC (**8**), XyNC (**9**; Xy = $C_6H_3Me_2$-2,6); Scheme 2). One equivalent of L^1 was used to prepare **4**, **6**,

Scheme 2



8, or **9**. Dissolving solid **2** in MeCN or bubbling CO for 15 min through a $CHCl_3$ solution of **2** sufficed to prepare **5** or **7**, respectively.

The reaction of **2** with 2 equiv of RNC afforded $[Pd(N^1,C^1\text{-}L)(CN^tBu)_2]ClO_4$ (**10**) or equimolecular amounts of **9** and $[Pd(C^1\text{-}L)(CNXy)_3]ClO_4$ (**11**); however, when 3 equiv of RNC was used, only the complex $[Pd(C^1\text{-}L)(CNR)_3]ClO_4$ (R = Xy (**11**), ^{t}Bu (**12**)) was obtained. We have reported that **1** reacts with isocyanides, giving at low temperature neutral complexes resulting from coordination and insertion of RNC into the Pd−C bond. When the temperature was raised, a tautomerization process from *β*-ketoimine to *β*-ketoenamine took place.[9] This represents a significant difference with respect to the reactions with **2**, which we attribute to the reinforcement of the C−Pd bond in the cationic complexes preventing the insertion reaction. Recently, a similar behavior has been reported in the migratory insertion of allyl groups across the Pd−C bond in Pd(II) isocyanide complexes.[14] One equivalent of the bidentate ligand L^2 gave the complexes $[Pd(N^1,C^1\text{-}L)L^2]ClO_4$ (L^2 = bis(diphenylphosphino)methane = dppm (**13**), 4,4′-di-*tert*-butyl-2,2′-bipyridine = dbbpy (**14**), *o*-phenylendiamine = pda (**15**); Scheme 3). When a 2:1 molar ratio of **2** and dppm was used, the dinuclear complex $[Pd_2(O^1,N^1,C^1\text{-}L)_2(\mu\text{-dppm})](ClO_4)_2$ (**16**) was obtained.

Reactivity of Cationic Complexes. Most of these cationic complexes are stable at room temperature in the solid state (exceptions are complexes **7**, **11**, and **12**, which have to be stored at approximately −30 °C) but, with the exception of **6** and **15**, they hydrolyze or/and decompose in open-air solutions. In most cases this transformation affords an

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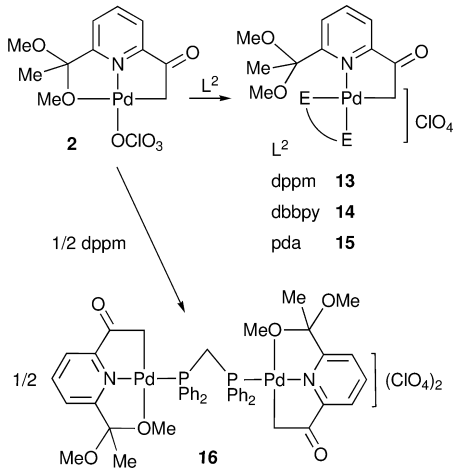
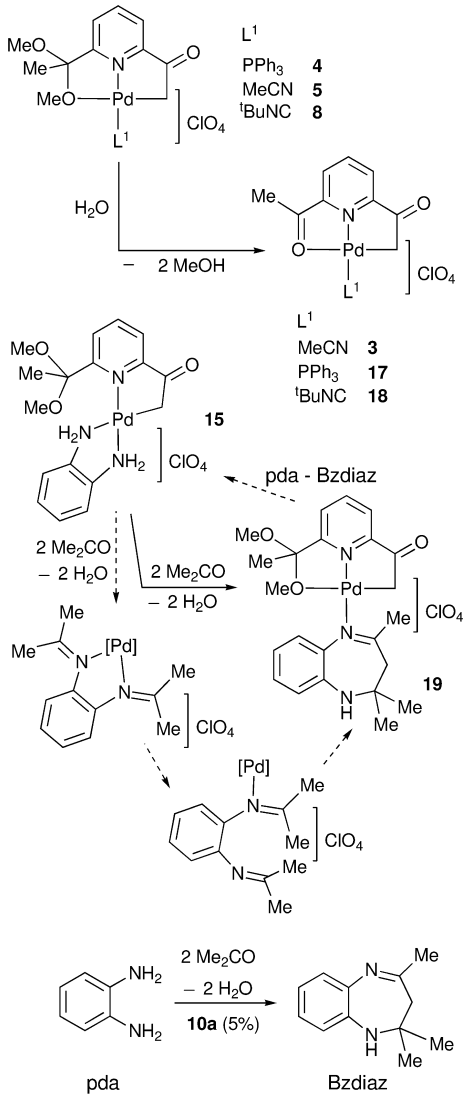
Scheme 3



Scheme 4



irresolvable mixture of products but, in some cases, clean and slow hydrolysis of the cationic complex was observed. Thus, when a solution of **4** in $CHCl_3$ was stirred in the open air for 24 h at room temperature, the complex $[Pd(O^1,N^1,C^1\text{-}L')(PPh_3)]ClO_4$ (**17**; Scheme 4) was quantitatively isolated as a stable compound in the solid state and in solution. Similarly, a solution of **5** in $CHCl_3$ led after 15 days at room temperature to **3** (95% yield). In solution, the carbonyl complex **7** hydrolyzes, loses CO, and decomposes, giving Pd metal. The hydrolysis of **8** was followed by ^1H NMR in $CDCl_3$. After 3 days, only **18** was detected, but it could not be isolated analytically pure from the reaction mixture.

Complex **15** is insoluble in CH_2Cl_2 or $CHCl_3$. When a solution of **15** in acetone was stirred for 4 days at room temperature, condensation of the amine ligand with the solvent occurred, to give a good yield (85%) of the complex $[Pd(O^1,N^1,C^1\text{-}L)(Bzdiaz)]ClO_4$ (**19**; Bzdiaz = 2′,2′,4′-trimethyl-2′,3′-dihydro-1*H*-1′,5′-benzodiazepine coordinated through N5′; Scheme 4), which is stable in the solid state and does not hydrolyze in open air solutions. This cyclization reaction probably occurs through a double condensation of acetone with the diamine followed by an aldol-like addition (Scheme 4). As far as we know, only a few 1,5-benzodiazepine complexes have been reported,[15−17] some of which have been used as catalysts in ethylene oligomerization and polymerization.[17] Only one is a palladium complex,[15] and all have been obtained by reacting a metal complex with Bzdiaz. Therefore, **19** represents the first example of a 1,5-benzodiazepine complex obtained by attack of a ketone at the coordinated diamine. We have reported a similar condensation process in the reaction of $[Au(NH{=}CMe_2)_2]^+$ with NH_3 and acetone.[18]

We have studied the use of complex **15** as a catalyst in the reaction of pda with acetone. Thus, an acetone solution of pda, in the presence of 5% of **15**, gave a 96% yield of Bzdiaz, after 5 days at room temperature (Scheme 4). We have carried out various experiments trying to optimize this process. However, although lower concentrations of catalyst (1 or 5 mol %) at 50 °C improved the rate of the reaction, the 1,5-benzodiazepine was obtained along with an unidentified by-product. The room-temperature reaction with 1% catalyst gave only 5% conversion after 22 h. In the absence of catalyst, the reaction afforded only traces of Bzdiaz after 24 h and, after 10 days, a mixture, the major component of which was Bzdiaz. It is reasonable to assume that the catalytic cycle is closed when **19** reacts with pda to give **15** (Scheme 4) and Bzdiaz. The most general method for the synthesis of 1,5-benzodiazepines involves condensation of *o*-phenylenediamine with α,β-unsaturated carbonyl compounds, β-halo ketones, or ketones. Many catalysts have been reported in the literature for this reaction.[19] Antineuroinflammatory effects as well as anxiolytic and cytotoxic against human cancer activities have been reported for 1,5-benzodiazepines.[20]

We have described the synthesis of stable neutral complexes containing the $[Pd](O^1,N^1,C^1\text{-L})$, $[Pd](N^1,C^1\text{-L})$, and $[Pd](C^1\text{-L})$ moieties.[9] However, all attempts to isolate the corresponding complexes with the hydrolyzed L′ ligand by reacting the stable O^1,N^1,C^1-L′ complexes with neutral ligands were unfruitful. Thus, the reaction of a $CDCl_3$ solution of **18** with 1 equiv of ^{t}BuNC did not afford the corresponding *cis*-$[Pd(N^1,C^1\text{-L}')(CN^tBu)_2]ClO_4$ complex but metallic palladium and a complex mixture of products in which free 2,6-diacetylpyridine was identified. The same result was obtained when **3** (Scheme 4) was reacted with 1 equiv of bpy (2,2′-bipyridine) or dbbpy or with 2 equiv of ^{t}BuNC.

Hydrolysis (deprotection) of ketals and acetals takes place by reacting them with acids.[21] Some metal salts or complexes have also been used,[22] the metal playing the role of a Lewis acid.

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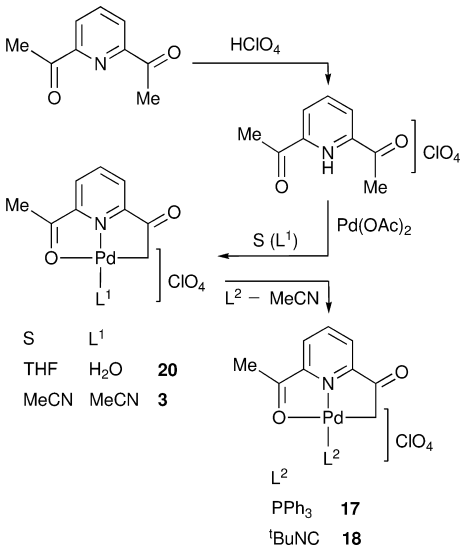
Therefore, we assume that the cationic nature of complexes **4**, **5**, and **8** converts their metal center in a stronger acid than in their neutral precursors facilitating the hydrolysis, as mentioned above. We are not aware of any article reporting the hydrolysis of a complex with a ketal or acetal ligand. However, several works report the hydrolysis of cyclopalladated and -platinated imines.[23]

The hydrolysis of the cationic complexes **4**, **5**, and **8** is a slow process (Scheme 4). In the case of **5**, we have found that the amount of water (present in the solvent or added) does not affect the rate of hydrolysis, being 14% after 14 h in acetone solution. In contrast, if 10% $HClO_4$ is added instead of water, a quantitative yield of **3** was obtained after 40 min (see the Experimental Section). This could mean that, although Pd(II) activates the C−O(Me)Pd bond, a strong acid catalyst is required to achieve a reasonable rate of hydrolysis.

The Palladation of dap. Synthesis of 3 and Related Complexes. Once we realized that complexes **3** and **17**, resulting from the hydrolysis of the cationic ketal derivatives, were stable and isolable, we planned to retry the palladation of dap. As we were aware that the low nucleophilicity of dap prevents it from coordinating to Pd, which is essential to assist palladation, we decided to attempt the reaction between 2,6-diacetylpyridinium perchlorate, $(Hdap)ClO_4$, and $Pd(OAc)_2$ in a weakly coordinating solvent, S. This way, we would generate dap along with a highly electrophilic palladium compound ("$Pd(OAc)(ClO_4)(S)_n$"), potentially capable of coordinating dap and deprotonating it with its basic acetato ligand. Fortunately, our expectation was met when we reacted a THF suspension of $(Hdap)ClO_4$ with 1 equiv of $Pd(OAc)_2$ and obtained $[Pd(O^1,N^1,C^1\text{-}L')(OH_2)]ClO_4$ (**20**; Scheme 5) in almost quantitative yield (98%). Complex **20** can be stored in the solid state at 4 °C under N_2 but decomposes at room temperature in the solid state or in acetone solution. When this reaction was carried out in MeCN, complex **3** was isolated in 94% yield. The same synthetic strategy has been recently applied to prepare ortho-palladated primary and secondary amines, which had been previously obtained by less direct methods or in lower yields.[24]

Scheme 5



Complex **3**, which is stable in the solid state and in solution, is the best precursor for the synthesis of other palladated derivatives of 2,6-diacetylpyridine. Thus, the best way to prepare **17**, first obtained from **4** (Scheme 4), is the reaction of **3** with PPh_3 (Scheme 5). The reaction of **3** with ^{t}BuNC (1:1) was the only way we found to isolate pure complex **18** (98% yield), because the hydrolysis of **8** led to a mixture from which we could not separate **18**.

Crystal Structures. The crystal structures of complexes **3** (Figure 1) and **9** (Figure 2) have been determined by X-ray diffraction (Table 1, Supporting Information). Both show a nearly square-planar coordination around the palladium atom (mean deviation from the coordination plane: 0.0313 and 0.0292 Å for **3** and **9**, respectively). In complex **3**, the py ring and the palladacycles PdNCCO and PdNCCC are almost coplanar (the angles between the mean planes are 2.9 and 5.0°, respectively), suggesting some electronic delocalization involving the pyC(Me)CO groups. The molecules are connected by Pd···Pd (3.2179(3) Å) contacts (van der Waals radii of Pd: 2.05 Å),[25] giving dimers with an inversion center. These dimers are connected through nonclassical hydrogen-bonding interactions C(11)−H(11A)···O(1), giving chains along the *c* axis. Anions and cations are connected by two C−H···O hydrogen bonds, giving altogether a complex 3D network. Both C−O distances are significantly different (1.207(3) and 1.232(2) Å), being longer, as expected, than the C−O(Pd) distance. The electronic delocalization involving the pyC(Me)CO group forces the Pd−O bond distance (2.2711(14) Å) to be longer than in **9** (2.2028(14) Å), in which, as expected, the PdNCCO ring is not planar (Figure 2), the O(1) and C(8) atoms being −0.3286 and +0.2157 Å, respectively, out of the plane formed by the pyridyl ring and the palladium atom (mean deviation 0.0385 Å). In **9**, the XyNC ligand and the pyridine ring are almost coplanar (subtended angle 11.3°). Anions and cations are connected by two C−H···O_4 hydrogen bonds, giving centrosymmetric dimers. The cations are also interconnected by a C(9)−

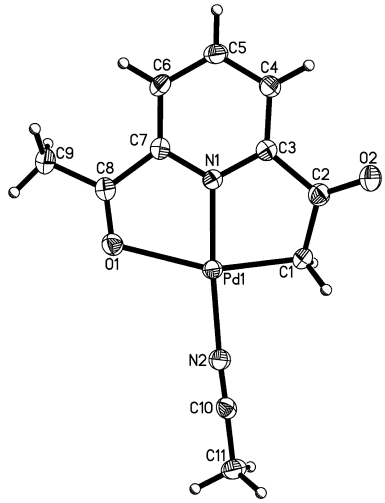


Figure 1. Ellipsoid representation of **3** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)−N(1) = 1.9705(16), Pd(1)−N(2) = 2.0072(17), Pd(1)−C(1) = 2.012(2), Pd(1)−O(1) = 2.2711(14), Pd(1)−Pd(1)#1 = 3.2179(3), N(1)−C(7) = 1.343(2), C(7)−C(8) = 1.501(3), O(1)−C(8) = 1.232(2), O(2)−C(2) = 1.207(3); N(1)−Pd(1)−C(1) = 83.25(7), N(2)−Pd(1)−C(1) = 91.95(8), N(2)−Pd(1)−O(1) = 108.39(6), N(1)−Pd(1)−O(1) = 76.08(6), C(8)−O(1)−Pd(1) = 111.55(12), O(1)−C(8)−C(7) = 118.22(17), N(1)−C(7)−C(8) = 113.47(17), C(7)−N(1)−Pd(1) = 120.35(13).

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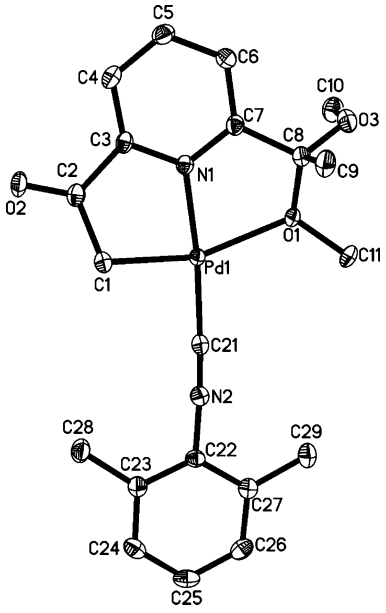


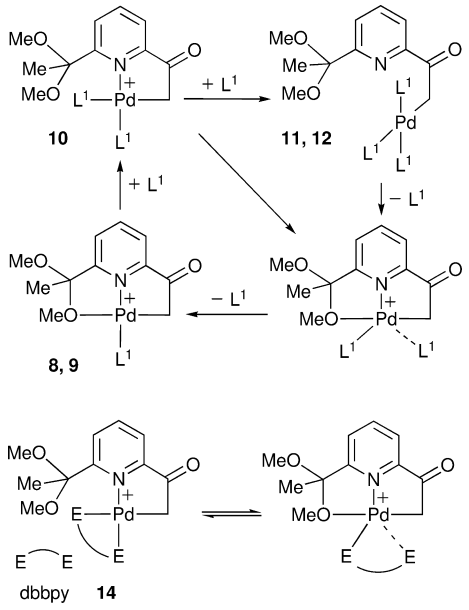
Figure 2. Ellipsoid representation of **9** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(21) = 1.937(2), Pd(1)−N(1) = 1.9939(17), Pd(1)−C(1) = 2.016(2), Pd(1)−O(1) = 2.2028(14), N(1)−C(7) = 1.336(3), C(7)−C(8) = 1.527(3), O(1)−C(8) = 1.461(2), O(2)−C(2) = 1.213(2); C(21)−Pd(1)−C(1) = 91.24(8), N(1)−Pd(1)−C(1) = 83.42(8), N(1)−Pd(1)−O(1) = 76.22(6), C(21)−Pd(1)−O(1) = 109.18(7), C(8)−O(1)−Pd(1) = 112.24(11), O(1)−C(8)−C(7) = 105.21(16), N(1)−C(7)−C(8) = 116.37(18), C(7)−N(1)−Pd(1) = 120.76(14).

H(9A)···O(3) hydrogen bond, giving another centrosymmetric dimer. All these nonclassical hydrogen bonds produce a double chain. The Pd−N(1) bond distance is longer in **9** (1.9939 (17) Å) than in **3** (1.9705(16) Å), showing the greater trans influence of the C- with respect to the N-donor ligand.

Spectroscopic Properties. The low stability of some complexes in solution prevented us from recording their $^{13}C\{^1H\}$ NMR spectra. The CH_2 and MeO protons in those complexes in which the ketal group is coordinated, **4**−**9**, **16**, and **19**, are equivalent at room temperature because of a fast exchange between both MeO groups.[9−12] This equivalence is maintained in the other complexes in which the ketal group is not coordinated. The isocyanides in complexes **10**−**12** are equivalent probably because the neutral ligands are involved in dissociation/reassociation processes, as shown in Scheme 6. The exchange of RNC ligands can be slowed down at −60 °C to see two types of isocyanides in the expected 1:1 (**10**) or 2:1 molar ratio (**11**, **12**). At this temperature, **10** gives two broad MeO resonances and a singlet for the CH_2 protons, **11** shows a singlet for the MeO and another for the CH_2 protons, and **12** has a broad resonance including the MeO and CH_2 protons. Similarly, in the ^1H NMR spectrum of **14** at room temperature, the CH_2 group gives a broad resonance and each of the ^{t}Bu and MeO protons shows a singlet, which suggests the existence of the fast equilibrium shown in Scheme 6. At −60 °C they resolve into two doublets (CH_2) and two pairs of singlets (^{t}Bu and MeO).

The IR spectra of all complexes show an absorption in the region 1652−1723 cm^{-1} corresponding to ν(CO) of the L or L′ ligands. Complexes with L′ ligands show also a band at lower frequency (range 1636−1705 cm^{-1}) assignable to ν(CO) of the coordinated carbonyl group; these data are in agreement with those obtained in the X-ray diffraction study of **3** (see above). The band due to ν(C≡O) in the carbonyl complex **7** appears at 2136 cm^{-1}, only slightly below that in free CO (2143 cm^{-1}), as a result of the decreased π-donor ability of the palladium atom in a cationic complex.[26]

Scheme 6



CONCLUSION

Solutions of the complex [Pd(O^1,N^1,C^1-L)($OClO_3$)], where L is the monoanionic ligand resulting from deprotonation of the acetyl group of the dimethyl monoketal of 2,6-diacetylpyridine, have been used as starting material for the synthesis of cationic dimethyl ketal complexes with the L ligand acting as pincer, chelate (N^1,C^1-L), or terminal (C^1-L). The complex [Pd(N^1,C^1-L)(*N*,*N*-$NH_2C_6H_4NH_2$-2)]ClO_4, which reacts with acetone to afford a 1,5-benzodiazepine complex resulting from the condensation of *o*-phenylenediamine with two molecules of acetone, is a catalyst for the synthesis of 1,5-benzodiazepine from *o*-phenylenediamine in acetone. Some of these cationic complexes hydrolyze spontaneously to give MeOH and the corresponding complexes with the pincer O^1,N^1,C^1-L′ ligand (L′ = monoanionic ligand resulting from deprotonation of one acetyl group of 2,6-diacetylpyridine). The complex [Pd(O^1,N^1,C^1-L′)(NCMe)]ClO_4, which can also be prepared by metalation of 2,6-diacetylpyridine, provides another way to prepare other complexes with the L′ ligand.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded on Bruker AC 200 and Avance 300 and 400 spectrometers. Chemical shifts were referenced to TMS (^1H, ^{13}C) or H_3PO_4 (^{31}P). When needed, NMR assignments were performed with the help of APT, HMQC, and HMBC experiments. Chart 1 shows the atom numbering used in NMR assignments. The complex [Pd(O^1,N^1,C^1-L)Cl] (**1**) was prepared as reported

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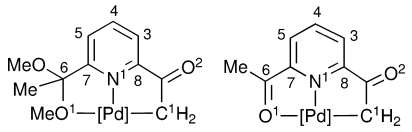
Chart 1



previously.[9] $CHCl_3$ or CH_2Cl_2 solutions of $[Pd(O^1,N^1,C^1\text{-L})(OClO_3)]$ (**2**)[13] were obtained by reacting **1** with excess $AgClO_4$.

Synthesis of (Hdap)ClO_4. To a solution of 2,6-diacetylpyridine (1.95 g, 11.95 mmol) in Et_2O (40 mL) was slowly added $HClO_4$ (70%, 1.54 mL, 17.92 mmol), and when the hot reaction mixture reached room temperature, it was filtered. The solid was washed with Et_2O and then recrystallized in acetone (6 mL)/Et_2O (30 mL) to give (Hdap)ClO_4 as a colorless solid. Yield: 97%. Mp: 121−122 °C. IR (cm^{-1}): ν(C═O) 1723, ν(C═N) 1617, ν(N−H) 3234, 3205, 3186, ν(Cl−O) 1081. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.10 (m, 1H, *p*-H), 8.95 (m, 2H, *m*-H), 2.93 (s, 6H, 2 Me). ^{1}H NMR (300 MHz, MeCN-d_3): δ 11.15 (br, 1H, NH), 9.14 (t, 1H, *p*-H, $^2J_{HH}$ = 7.8 Hz), 8.83 (d, 2H, *m*-H, $^2J_{HH}$ = 7.8 Hz), 2.87 (s, 6H, Me). ^{13}C NMR (75.45 MHz, MeCN-d_3): δ 190.9 (s, CO), 153.5 (s, *p*-C), 143.2 (s, *o*-C), 131.3 (s, *m*-C), 26.6 (s, Me). Anal. Calcd for $C_9H_{10}NO_6Cl$: C, 41.00; H, 3.82; N, 5.31. Found: C, 41.07; H, 3.96; N, 5.67.

Synthesis of [Pd(O^1,N^1,C^1-L')(NCMe)]ClO_4 (3). *Method a.* To a solution of (Hdap)ClO_4 (894.2 mg, 3.39 mmol) in MeCN (40 mL) was added $Pd(OAc)_2$ (761.5 mg; 3.39 mmol). The resulting solution was stirred for 40 min and then concentrated to dryness. The resulting oil was dissolved in acetone (20 mL) and the solution concentrated to dryness; this process was carried out twice. The resulting solid was stirred with Et_2O (2 × 40 mL) in a water/ice bath until a suspension formed. It was filtered under N_2 and the resulting solid was washed with Et_2O and dried under a N_2 stream, giving an orange solid that was recrystallized in MeCN/Et_2O to give **3** as a spectroscopically pure solid.[13] Yield: 94%.

Method b. To a solution of **5** (51.1 mg, 0.12 mmol) in acetone (5 mL) was added an aqueous solution of $HClO_4$ (11.64 mol L^{-1}, 1 μL, 0,012 mmol). The mixture was stirred for 40 min and then concentrated (1 mL). Addition of Et_2O (5 mL) gave a suspension that was filtered, and the solid was washed with Et_2O and air-dried to give **3** as an orange solid. Yield: 94%.

Synthesis of [Pd(O^1,N^1,C^1-L)(PPh_3)]ClO_4 (4). To a cold solution of **2** (from 0.05 mmol of **1** and 0.16 mmol of $AgClO_4$ in 5 mL of $CHCl_3$, at 0 °C) was added PPh_3 (13.9 mg; 0.05 mmol). The reaction mixture was stirred for 40 min and concentrated (to 1 mL). Addition of Et_2O (5 mL) gave a suspension that was filtered, and the solid was washed with Et_2O and air-dried to give **4** as a pale yellow solid. Yield: 89%. Mp: 115−116 °C. IR (cm^{-1}): ν(C═O) 1699, ν(C═N) 1600, ν(Cl−O) 1094. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 7.94 (m, 1 H, H3), 7.84 (m, 1 H, H5), 7.78−7.68 (m, 6 H, PPh_3), 7.62−7.50 (m, 9 H, PPh_3), 3.19 (d, 2 H, CH_2, $^3J_{HP}$ = 4 Hz), 3.05 (s, 6 H, OMe), 1.88 (s, 3 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 200.8 (s, CO), 157.1 (s, C7), 150.8 (d, $^3J_{CP}$ = 2 Hz, C8), 142.5 (s, C4), 134.0 (d, $^2J_{CP}$ = 13 Hz, *o*-CH, PPh_3), 132.1 (d, $^4J_{CP}$ = 3 Hz, *p*-CH, PPh_3), 129.5 (d, $^3J_{CP}$ = 11 Hz, *m*-CH, PPh_3), 127.5 (d, $^1J_{CP}$ = 51.5 Hz, C_{ipso}), 127.3 (d, $^4J_{CP}$ = 3 Hz, C5), 124.2 (s, C3), 109.2 (s, C6), 52.5 (s, OMe), 41.1 (d, $^2J_{CP,cis}$ = 5.3 Hz, CH_2), 25.2 (s, Me). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ 30.85. Anal. Calcd for $C_{29}H_{29}NO_7ClPPd$: C, 51.50; H, 4.32; N, 2.07. Found: C, 51.15; H, 4.45; N, 2.36.

Synthesis of [Pd(O^1,N^1,C^1-L)(NCMe)]ClO_4 (5). A solution of **2** (from 0.08 mmol of **1** and 0.31 mmol of $AgClO_4$ in 4 mL of $CHCl_3$) was concentrated to dryness, and the resulting solid was dissolved in MeCN (1 mL). After 5 min of stirring, the solution was concentrated to dryness. The residue was vigorously stirred in Et_2O (5 mL), the resulting suspension was filtered, and the solid was washed with Et_2O and air-dried to give **5** as a pale yellow solid. Yield: 88%. Mp: 126−127 °C. IR (cm^{-1}): ν(C≡N) 2295, ν(C═O) 1703, ν(C═N) 1600, ν(Cl−O) 1091. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.35 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 7.86 (dd, 1 H, H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.77 (dd, 1 H, H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.58 (s, 2 H, CH_2), 3.49 (s, 6 H, OMe), 2.54 (br, 3 H, MeCN), 1.82 (s, 3H, Me). ^{13}C NMR (50.30 MHz, $CDCl_3$): δ 200.9 (s, CO), 158.6 (s, C7), 151.8 (s, C8), 142.6 (s, C4), 127.7 (s, C5), 124.4 (s, C3), 123.3 (br, MeCN), 107.9 (s, C6), 52.8 (s, OMe), 35.7 (s, CH_2), 25.0 (s, Me), 3.5 (s, $NCCH_3$). Anal. Calcd for $C_{13}H_{17}N_2O_7ClPd$: C, 34.30; H, 3.76; N, 6.15. Found: C, 34.22; H, 3.80; N, 6.05.

Synthesis of [Pd(O^1,N^1,C^1-L)($NH_2CH_2C_6H_4OMe$-4)]ClO_4 (6). To a solution of **2** (from 0.26 mmol of **1** and 0.51 mmol of $AgClO_4$ in 10 mL of CH_2Cl_2) was added *p*-methoxybenzylamine (33.4 μL; 0.26 mmol) to give an orange solution that was stirred for 30 min. Concentration (2 mL) and addition of Et_2O (15 mL) gave a suspension; the solid was filtered off, washed with Et_2O, and air-dried to give **6** as a pale orange solid. Yield: 138.1 mg, 97%. Mp: 125−126 °C. IR (cm^{-1}): ν(N−H) 3247, ν(C═O) 1694, ν(C═N) 1610, ν(Cl−O) 1030. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 7.80 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.61 (m, 3 H), 6.90 (m, 2 H), 3.87 (m, 2 H, NH_2), 3.78 (s, 3 H, MeO), 3.69 (m, 2 H, CH_2), 3.38 (s, 2 H, CH_2Pd), 3.18 (s, 6 H, OMe), 1.65 (s, 3 H, Me). ^{1}H NMR (200 MHz, acetone-d_6): δ 8.42 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 7.91 (dd, 1 H, H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.86 (dd, 1 H, H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.70 (m, 2 H, *o*-amine), 6.98 (m, 2 H, *m*-amine), 4.31 (br, 2 H, NH_2), 3.96 (m, 2 H, CH_2), 3.79 (s, 3 H, MeO), 3.45 (s, 2 H, CH_2Pd), 3.27 (s, 6 H, OMe), 1.72 (s, 3 H, Me). ^{13}C{^{1}H} NMR (75.45 MHz, acetone-d_6): δ 202.7 (C2), 160.8 (*C*OMe), 159.0 (C7), 153.2 (C8), 142.8 (C4), 131.9 (*o*-CH), 131.6 (*C*−CH_2), 128.3 (C3), 124.4 (C5), 115.0 (*m*-CH), 108.8 (C6), 55.7 (*p*-OMe), 52.5 (OMe), 49.4 (CH_2NH_2), 34.0 (CH_2Pd), 25.1 (Me). Anal. Calcd for $C_{19}H_{25}N_2O_8ClPd$: C, 41.39; H, 4.57; N, 5.08. Found: C, 41.45; H, 4.64; N, 5.06.

Synthesis of [Pd(O^1,N^1,C^1-L)(CO)]ClO_4 (7). After CO was bubbled into a solution of **2** (from 0.18 mmol of **1** and 0.55 mmol of $AgClO_4$ in 3 mL of $CHCl_3$) for 15 min, colorless needles crystallized. The solid was filtered off, washed with $CHCl_3$, and air-dried to give **7**. Yield: 78%. Mp: 119−120 °C. IR (cm^{-1}): ν(C≡O) 2136, ν(C═O) 1709, ν(C═N) 1599. ^{1}H NMR (200 MHz, acetone-d_6): δ 8.62 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.14 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.10 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 4.04 (s, 2H, CH_2), 3.65 (s, 6H, OMe), 1.90 (s, 3H, Me). Anal. Calcd for $C_{12}H_{14}NO_8ClPd$: C, 32.60; H, 3.19; N, 3.17. Found: C, 32.41; H, 3.05; N, 3.20.

Synthesis of [Pd(O^1,N^1,C^1-L)(CN^tBu)]ClO_4 (8). To a cold solution of **2** (from 0.15 mmol of **1** and 0.58 mmol of $AgClO_4$ in 5 mL of $CHCl_3$, at 0 °C) was added ^{t}BuNC (645 μL, 226.2 mM solution, 0.15 mmol). The solution was stirred for 20 min at 0 °C and then concentrated to dryness. The residue was stirred in Et_2O (10 mL) at 0 °C for 15 min and then filtered off. The solid was washed with Et_2O and air-dried to give **8** as a pale yellow solid. Yield: 89%. Mp: 114−115 °C. IR (cm^{-1}): ν(C≡N) 2213, ν(C═O) 1705, ν(C═N) 1600, ν(Cl−O) 1093. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (t, 1 H, H4, $^3J_{HH}$ = 7.6 Hz), 7.94 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.83 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 3.55 (s, 2 H, CH_2), 3.52 (s, 6 H, OMe), 1.84 (s, 3 H, Me), 1.62 (s, 9 H, ^{t}Bu). Anal. Calcd for $C_{16}H_{23}N_2O_7ClPd$: C, 38.65; H, 4.66; N, 5.63. Found: C, 38.97; H, 4.61; N, 5.61.

Synthesis of [Pd(O^1,N^1,C^1-L)(CNXy)]ClO_4 (9). To a solution of **2** (from 0.01 mmol of **1** and 0.3 mmol of $AgClO_4$ in 3 mL of $CHCl_3$) was added a solution of XyNC (13.0 mg, 0.01 mmol) in $CHCl_3$ (1 mL). The reaction mixture was stirred for 2 h and then concentrated (2 mL). The resulting solid was washed with $CHCl_3$ and air-dried to give **9** as a colorless solid. Yield: 88%. Mp: 210−211 °C. IR (cm^{-1}): ν(C≡N) 2194, ν(C═O) 1703, ν(C═N) 1601, ν(Cl−O) 1080. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.59 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.12 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.08 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.44 (m, 1 H, *p*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 7.29 (m, 2 H, *m*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 3.78 (s, 2 H, CH_2), 3.66 (s, 6 H, OMe), 2.52 (s, 6 H, Me, Xy), 1.93 (s, 3 H, Me). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.41 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.02 (dd, 1 H,

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H5 or H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.87 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.35 (m, 1 H, *p*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 7.24 (m, 2 H, *m*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 3.73 (s, 2 H, CH_2), 3.56 (s, 6 H, OMe), 2.48 (s, 6 H, Me, Xy), 1.88 (s, 3 H, Me). ^{1}H NMR (200 MHz, MeCN-d_3): δ 8.37 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 7.97 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.89 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.40 (m, 1 H, *p*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 7.28 (d, 2 H, *m*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 3.65 (s, 2 H, CH_2), 3.50 (s, 6 H, OMe), 2.48 (s, 6 H, Me, Xy), 1.80 (s, 3 H, Me). Anal. Calcd for $C_{20}H_{23}N_2O_7ClPd$: C, 44.05; H, 4.25; N, 5.14. Found: C, 44.02; H, 4.21; N, 5.15. Single crystals were obtained by slow evaporation of the solvent of a solution of **9** in CD_2Cl_2.

Synthesis of *cis*-[Pd(N^1,C^1-L)(CN^{t}Bu)$_2$]ClO$_4$ (10). To a cold solution of **2** (from 0.23 mmol of **1** and 0.92 mmol of $AgClO_4$ in 7 mL of CH_2Cl_2, at 0 °C) was added ^{t}BuNC (2 mL, 226.2 mM, 0.46 mmol). The resulting solution was concentrated (2 mL, 0 °C), and Et_2O (7 mL) was added. The mixture was vigorously stirred at 0 °C for 15 min, and the solid was filtered off, washed with Et_2O, and dried under N_2 to give **10** as a colorless solid. Yield: 98%. Mp: 95−96 °C. IR (cm^{-1}): ν(C≡N) 2242, 2214, ν(C═O) 1677, ν(C═N) 1602, ν(Cl−O) 1093. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.30 (br, 1 H, H4), 7.96 (d, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz), 7.88 (d, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz), 3.00−3.80 (br, 8 H, CH_2 + 2 MeO), 1.78 (br, 3 H, Me), 1.61 (br, 18 H, 2 ^{t}Bu). ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ 8.38 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.08 (d, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz), 8.00 (d, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz), 3.39 (br, 3 H, MeO), 3.28 (br, 3 H, MeO), 3.21 (s, 2 H, CH_2), 1.73 (s, 3 H, Me), 1.70 (s, 9 H, ^{t}Bu), 1.65 (s, 9 H, ^{t}Bu). Anal. Calcd for $C_{21}H_{32}N_3O_7ClPd$: C, 43.46; H, 5.56; N, 7.24. Found: C, 43.21; H, 5.88; N, 7.31.

Synthesis of [Pd(C^1-L)(CNXy)$_3$]ClO$_4$·H$_2$O (11). To a cold solution of **2** (from 0.06 mmol of **1** and 0.19 mmol of $AgClO_4$ in 3 mL of $CHCl_3$, at 0 °C) was added a cold solution of XyNC (25.2 mg, 0.19 mmol) in $CHCl_3$ (1 mL, at 0 °C). The resulting solution was stirred for 20 min and concentrated to dryness at 0 °C, and the solid was dissolved in CH_2Cl_2 (1 mL). Addition of Et_2O (5 mL) gave a suspension that was stored at −33 °C for 2 h. The solid was filtered off, washed with Et_2O, and air-dried to give **11** as a pale yellow solid. Yield: 95%. Mp: 75−76 °C. IR (cm^{-1}): ν(C≡N) 2196, 2184 (sh), ν(C═O) 1660, ν(C═N) 1581, ν(Cl−O) 1091. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95−7.81 (m, 3 H, H3 + H4 + H5), 7.35 (t, 1 H, *p*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 7.20 (d, 2 H, *m*-H, Xy, $^3J_{HH}$ = 7.6 Hz), 3.64 (s, 2 H, CH_2), 3.08 (s, 6 H, OMe), 2.46 (s, 18 H, Me, Xy), 1.65 (br, 1 H, H_2O), 1.55 (s, 3 H, Me). ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ 7.98 (d, 1 H, H5 or H3, $^3J_{HH}$ = 7.6 Hz), 7.93 (t, 1 H, H4, $^3J_{HH}$ = 7.6 Hz), 7.88 (d, 1 H, H3 or H5, $^3J_{HH}$ = 7.6 Hz), 7.44−7.41 (m, 3 H, *p*-H, Xy), 7.30−7.22 (m, 6 H, *m*-H, Xy), 3.66 (s, 2 H, CH_2), 3.06 (s, 6 H, OMe), 2.50 (s, 12 H, Me, Xy), 2.49 (s, 6 H, Me, Xy), 1.51 (s, 3 H, Me). Anal. Calcd for $C_{38}H_{41}N_4O_7ClPd·H_2O$: C, 55.28; H, 5.25; N, 6.79. Found: C, 55.20; H, 5.15; N, 6.70.

Synthesis of [Pd(C^1-L)(CN^{t}Bu)$_3$]ClO$_4$ (12). To a cold solution of **2** (from 0.14 mmol of **1** and 0.55 mmol of $AgClO_4$ in 6 mL of $CHCl_3$, at 0 °C) was added ^{t}BuNC (36.8 mg, 0.44 mmol); the solution was stirred for 20 min and then concentrated to dryness. The residue was crystallized in CH_2Cl_2/*n*-pentane and then filtered. The solid was washed with *n*-pentane and air-dried to give **12** as a colorless solid. Yield: 94%. Mp: 104−105 °C. IR (cm^{-1}): ν(C≡N) 2222, ν(C═O) 1659, ν(C═N) 1581, ν(Cl−O) 1092. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.00−7.80 (m, 3 H, H3 + H4 + H5), 3.20 (s, 6 H, OMe), 3.14 (s, 2 H, CH_2), 1.70 (s, 3 H, Me), 1.59 (s, 27 H, ^{t}Bu). ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ 8.04−7.86 (m, 3 H, H3 + H4 + H5), 3.21 (br, 8 H, OMe + CH_2), 1.73 (s, 3 H, Me), 1.63 (s, 18 H, ^{t}Bu), 1.62 (s, 9 H, ^{t}Bu). Anal. Calcd for $C_{26}H_{41}N_4O_7ClPd$: C, 47.07; H, 6.23; N, 8.44. Found: C, 46.97; H, 6.27; N, 8.47.

Synthesis of [Pd(N^1,C^1-L)(dppm)]ClO$_4$·0.75H$_2$O (13). A mixture of a cold solution of **2** (from 0.10 mmol of **1** and 0.31 mmol of $AgClO_4$ in 6 mL of CH_2Cl_2, at 0 °C) and dppm (39.4 mg; 0.10 mmol) was stirred for 30 min and then concentrated to 1 mL. Addition of Et_2O (5 mL) led to a suspension that was filtered, and the solid was washed with Et_2O and air-dried to give **13** as a pale orange solid. Yield: 89%. Mp: 172−173 °C. IR (cm^{-1}): ν(C═O) 1652, ν(C═N) 1599, ν(Cl−O) 1094. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.05−7.98 (m, 2 H, H5 + H3), 7.70−7.35 (m, 20 H, dppm), 4.43 (dd, 2 H, CH_2, dppm, $^2J_{HP}$ = 12.4 Hz, $^2J_{HP}$ = 7.2 Hz), 3.32 (dd, 2 H, CH_2, $^3J_{HP,cis}$ = 1.6 Hz, $^3J_{HP,trans}$ = 12 Hz), 2.81 (s, 6 H, OMe), 1.58 (s, 1.5 H, H_2O), 1.39 (s, 3 H, Me). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ −2.83 (d, $^2J_{PP}$ = 206.4 Hz), −27.65 (d, $^2J_{PP}$ = 206.4 Hz). Anal. Calcd for $C_{36}H_{36}NO_7ClPPd·0.75H_2O$: C, 53.25; H, 4.65; N, 1.72. Found: C, 53.11; H, 4.66; N, 1.64.

Synthesis of [Pd(N^1,C^1-L)(dbbpy)]ClO$_4$·0.5H$_2$O (14). To a solution of **2** (from 0.08 mmol of **1** and 0.30 mmol of $AgClO_4$ in 8 mL of $CHCl_3$) was added dbbpy (4,4′-di-*tert*-butyl-2,2′-bipyridine, 20.1 mg, 0.08 mmol). The resulting solution was stirred at 0 °C for 30 min and then concentrated to 1 mL. Addition of Et_2O (3 mL) and *n*-pentane (5 mL) gave a suspension; the solid was filtered off, washed with *n*-pentane, and air-dried to give **14** as a yellow solid. Yield: 85%. Mp: 258 °C dec. IR (cm^{-1}): ν(C═O) 1673, ν(C═N) 1614, 1547, ν(Cl−O) 1081. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (br, 2 H, ^{t}bpy), 8.23 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.17 (br, 2 H, ^{t}bpy), 7.90 (br, 2 H, H3 + H5), 7.62 (dd, 2 H, ^{t}bpy, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.6 Hz), 3.70 (br, 2 H, CH_2), 3.16 (s, 6 H, OMe), 1.82 (s, 3 H, Me), 1.59 (br, 1 H, H_2O), 1.46 (s, 18 H, ^{t}Bu). ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ 8.58 (d, 1H, ^{t}bpy, $^3J_{HH}$ = 5 Hz), 8.37 (t, 1H, H4, $^3J_{HH}$ = 8 Hz), 8.22 (br, 1 H, ^{t}bpy), 8.17 (br, 1 H, ^{t}bpy), 8.08 (d, 1 H, ^{t}bpy, $^3J_{HH}$ = 5 Hz), 7.98 (d, 1 H, H5 or H3, $^3J_{HH}$ = 8 Hz), 7.95 (d, 1 H, H3 or H5, $^3J_{HH}$ = 8 Hz), 7.68 (m, 2 H, ^{t}bpy), 4.36 (d, 1 H, CH_2, $^1J_{HH}$ = 6.4 Hz), 3.36 (s, 3 H, MeO), 3.08 (d, 1 H, CH_2, $^1J_{HH}$ = 6.4 Hz), 3.07 (s, 3 H, MeO), 1.81 (s, 3 H, Me), 1.51 (s, 9 H, ^{t}Bu), 1.46 (s, 9 H, ^{t}Bu). Anal. Calcd for $C_{29}H_{38}N_3O_7ClPd·0.5H_2O$: C, 50.37; H, 5.68; N, 6.08. Found: C, 50.12; H, 5.85; N, 5.88.

Synthesis of [Pd(N^1,C^1-L)(*N*,*N*-NH$_2$C$_6$H$_4$NH$_2$-2)]ClO$_4$·0.5H$_2$O (15). To a solution of **2** (from 0.39 mmol of **1** and 0.80 mmol of $AgClO_4$ in 10 mL of CH_2Cl_2) was added *o*-phenylidenediamine (42.3 mg; 0.39 mmol); the reaction mixture was stirred for 5 min and then concentrated to 2 mL. Upon the addition of Et_2O (8 mL) the suspension that formed was filtered, and the solid was washed with Et_2O and air-dried to give **15** as a pale yellow solid. Yield: 201.7 mg, 97%. Mp: 175 °C dec. IR (cm^{-1}): ν(N−H) 3302, ν(C═O) 1654, ν(C═N) 1601, ν(Cl−O) 1076. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.34 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 8.13 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.91 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.49 (m, 2 H), 7.32−7.30 (m, 2 H), 6.67 (br, 2 H, NH_2), 5.81 (br, 2 H, NH_2), 3.38 (s, 6 H, OMe), 3.29 (s, 2 H, CH_2), 2.84 (s, 1 H, H_2O), 2.13 (s, 3 H, Me). Anal. Calcd for $C_{17}H_{22}N_3O_7ClPd·0.5H_2O$: C, 38.43; H, 4.36; N, 7.91. Found: C, 38.50; H, 4.33; N, 7.91.

Synthesis of [Pd$_2$(O^1,N^1,C^1-L)$_2$(μ-dppm)](ClO$_4$)$_2$ (16). To a solution of **2** (from 0.24 mmol of **1** and 0.52 mmol of $AgClO_4$ in 5 mL of CH_2Cl_2) was added dppm (46.7 mg, 0.12 mmol). The mixture was stirred for 4 h and then concentrated to 1 mL. Addition of Et_2O (6 mL) gave an oil that was vigorously stirred in a water/ice bath. The resulting suspension was filtered and the solid washed with Et_2O and air-dried to give **16** as an orange solid. Yield: 98%. Mp: 167−168 °C. IR (cm^{-1}): ν(C═O) 1698, ν(C═N) 1600, ν(Cl−O) 1094. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (t, 2 H, H4, $^3J_{HH}$ = 8 Hz), 7.90−7.80 (m, 10 H, H5 or H3 and 8 H, dppm), 7.75 (dd, 2 H, H3 or H5, $^3J_{HH}$ = 8 Hz), 7.42−7.35 (m, 12 H, dppm), 3.96 (t, 2 H, CH_2, dppm, $^2J_{HP}$ = 10.8 Hz), 3.34 (d, 4 H, CH_2, $^3J_{HP}$ = 3.6 Hz), 3.05 (s, 12 H, OMe), 1.82 (s, 6 H, Me). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ 19.46 (s). Anal. Calcd for $C_{47}H_{50}N_2O_{14}Cl_2P_2Pd_2$: C, 46.55; H, 4.16; N, 2.31. Found: C, 46.17; H, 4.56; N, 2.47.

Synthesis of [Pd(O^1,N^1,C^1-L′)(PPh$_3$)]ClO$_4$·H$_2$O (17). *Method a.* To a solution of **3** (61.2 mg; 0.15 mmol) in acetone (12 mL) was added PPh_3 (39.3 mg; 0.15 mmol). The solution was stirred for 15 min and then concentrated to 2 mL. Addition of Et_2O (10 mL) gave a suspension that was stirred in an ice/water bath for 10 min. The resulting suspension was filtered and the solid washed with Et_2O and air-dried to give **17** as an orange solid. Yield: 83%.

Method b. A solution of **4** (10.0 mg; 0.02 mmol) in $CHCl_3$ (2 mL) was stirred for 24 h and then concentrated (1 mL). Addition of Et_2O

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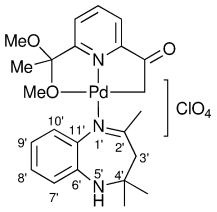
(4 mL) gave a suspension that was stirred in a cool bath (0 °C) for 10 min. The resulting suspension was filtered and the solid washed with Et_2O and air-dried to give **17** as an orange solid. Yield: 93%. Mp: 161−162 °C. IR (cm^{-1}): ν(C═O) 1708, 1636, ν(C═N) 1595, ν(Cl−O) 1095. ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (m, 1 H, H5), 8.52 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 8.12 (m, 1 H, H3), 7.65−7.49 (m, 15H, PPh_3), 3.17 (d, 2 H, CH_2, $^3J_{HP}$ = 3.6 Hz), 3.07 (s, 3H, Me), 1.78 (s, 2 H, H_2O). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 206.5 (s, C6), 200.5 (s, C2), 151.0 (d, C8, $^3J_{CP}$ = 2 Hz), 150.8 (d, C7, $^3J_{CP}$ = 2 Hz), 143.4 (s, C4), 133.9 (d, *o*-CH, PPh_3, $^2J_{CP}$ = 12.7 Hz), 132.4 (s, C3), 131.9 (d, *p*-CH, PPh_3, $^4J_{CP}$ = 2.4 Hz), 129.4 (d, *m*-CH, PPh_3, $^3J_{CP}$ = 11.4 Hz), 128.3 (d, C_{ipso}, PPh_3, $^1J_{CP}$ = 52.2 Hz), 127.9 (s, C5), 40.6 (d, CH_2, $^2J_{CP,cis}$= 4.8 Hz), 26.6 (s, Me). $^{31}P\{^1H\}$ NMR (162.29 MHz, $CDCl_3$): δ 29.92 (s, PPh_3). Anal. Calcd for $C_{27}H_{23}NO_6ClPPd{\cdot}H_2O$: C, 50.02; H, 3.89; N, 2.16. Found: C, 50.04; H, 3.60; N, 2.29.

Synthesis of [Pd(*O*^{1},*N*^{1},*C*^{1}-L′)(CN^{t}Bu)]ClO$_4$ (18). To a solution of **3** (338.0 mg; 0.83 mmol) in MeCN (10 mL) was added ^{t}BuNC (93.4 μL; 0.83 mmol). The reaction mixture was stirred for 15 min and concentrated to dryness. The residue was dissolved in CH_2Cl_2 (4 mL), and Et_2O (8 mL) was added. The resulting suspension was stirred at 0 °C for 30 min, and the solid was filtered off, washed with Et_2O, and air-dried. The resulting solid was treated with CH_2Cl_2 (10 mL) and filtered through Celite. The filtrate was concentrated (2 mL), and Et_2O (10 mL) was added. The suspension was filtered, and the solid was washed with Et_2O and air-dried to give **18** as a yellow solid. Yield: 332.4 mg, 89%. Mp: 206 °C dec. IR (cm^{-1}): ν(C≡N) 2218, ν(C═O) 1703, 1635, ν(C═N) 1596, ν(Cl−O) 1086. ^1H NMR (400 MHz, acetone-d_6): δ 8.86 (dd, 1 H, H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz), 8.74 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 8.28 (dd, 1 H, H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz), 3.69 (s, 2 H, CH_2), 3.09 (s, 3H, Me), 1.67 (br, 9H, ^{t}Bu). ^1H NMR (200 MHz, $CDCl_3$): δ 8.67 (dd, 1 H, H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 8.53 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 8.12 (dd, 1 H, H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 3.61 (s, 2 H, CH_2), 3.04 (s, 3H, Me), 1.61 (br, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75.45 MHz, acetone-d_6): δ 200.4 (s, C6), 152.9 (s, C8), 152.5 (s, C7), 144.6 (s, C4), 132.7 (s, C3), 128.6 (s, C5), 35.0 (s, CH_2), 29.9 (s, $C(CH_3)_3$), 26.5 (s, Me). Anal. Calcd for $C_{14}H_{17}N_2O_6ClPd$: C, 37.27; H, 3.80; N, 6.21. Found: C, 37.00; H, 3.84; N, 6.22.



19

Synthesis of [Pd(*O*^{1},*N*^{1},*C*^{1}-L)(Bzdiaz)]ClO$_4$ (19). A suspension of **15** (164.0 mg, 0.31 mmol) in acetone (25 mL) was stirred for 4 days and then concentrated to dryness. The residue was dissolved in CH_2Cl_2 (2 mL), and Et_2O (10 mL) was added. The solid was filtered off, washed with Et_2O, and air-dried to give **19** as a yellow solid. Yield: 160.3 mg, 85%. Mp: 134−135 °C. IR (cm^{-1}): ν(N−H) 3322, ν(C═O) 1698, ν(C═N) 1621, 1599, ν(Cl−O) 1079. ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (t, 1 H, H4, $^3J_{HH}$ = 8 Hz), 7.90 (dd, 1 H, H10′, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.84 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.74 (dd, 1 H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.25−7.15 (m, 2 H, H8′ + H9′), 6.98 (dd, 1 H, H7′, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 3.51 (br, 1 H, NH), 3.44 (s, 2 H, CH_2), 3.23 (s, 6 H, MeO), 3.10 (s, 3 H, *Me*C2′), 2.44 (s, 2 H, H3′), 1.75 (s, 3 H, Me), 1.40 (s, 6 H, *Me*C4′). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$): δ 201.7 (C2), 186.1 (C2′), 158.2 (C7), 152.1 (C8), 142.0 (C4), 139.3 (C11′), 138.9 (C6′), 129.1 (C9′), 127.3 (C5), 127.0 (C10′), 124.0 (C3), 123.7 (C7′), 123.2 (C8′), 108.1 (C6), 70.5 (C4′), 52.4 (OMe), 46.0 (C3′), 33.7 (CH_2), 32.6 (N═C*Me*), 30.0 (C*Me*$_2$), 25.0 (Me). Anal. Calcd for $C_{23}H_{30}N_3O_7ClPd$: C, 45.86; H, 5.02; N, 6.98. Found: C, 45.41; H, 5.39; N, 6.94.

Pd-Catalyzed Synthesis of 2′,2′,4′-Trimethyl-2′,3′-dihydro-1*H*-1′,5′-benzodiazepine. To a solution of complex **15** (17.5 mg, 0.03 mmol) in acetone (15 mL) was added *o*-phenylenediamine (72.5 mg, 0.67 mmol). The mixture was stirred at room temperature for 5 days, the solvent was evaporated, and Et_2O was added (10 mL). The suspension was filtered through a Celite plug, and the filtrate was concentrated to dryness to give the spectroscopically pure 1,5-benzodiazepine as a colorless solid. Yield: 96%. TON: 21. ^1H NMR (200 MHz, $CDCl_3$):[27] δ 7.14−6.69 (m, 4 H, Ar), 3.02 (br, 1 H, NH), 2.34 (s, 3 H, Me), 2.20 (s, 2 H, CH_2), 1.31, (s, 6 H, 2 Me). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.23; H, 8.72; N, 14.66.

Synthesis of [Pd(*O*^{1},*N*^{1},*C*^{1}-L′)(OH$_2$)]ClO$_4$ (20). To a suspension of (Hdap)ClO_4 (610.3 mg; 2.31 mmol) in THF (18 mL) was added $Pd(OAc)_2$ (519.7 mg; 2.31 mmol), and the mixture was stirred for 30 min to give a suspension (A) and an oil. The suspension A was decanted, and the oil was vigorously stirred with Et_2O (3 × 20 mL) for 20 min. The resulting solid was filtered off and dried with a N_2 stream to give orange **20**. The suspension A was concentrated to dryness, and the residue was ground with Et_2O (20 mL) for 10 min and filtered off under N_2 to get a second crop of **20**. Yield: 98%. Mp: 260 °C dec. IR (cm^{-1}): ν(H_2O) 3371, ν(C═O) 1721 (sh), 1705, ν(C═N) 1570, ν(Cl−O) 1089. ^1H NMR (200 MHz, acetone-d_6): δ 8.82 (dd, 1 H, H5 or H3, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz), 8.68 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 8.15 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz), 3.66 (s, 2 H, CH_2), 3.07 (s, 3 H, Me), 3.05 (br, 2 H, H_2O). Anal. Calcd for $C_9H_{10}NO_7ClPd$: C, 28.00; H, 2.61; N, 3.63. Found: 27.76; H, 2.75; N, 3.56.

X-ray Structure Determinations. Complexes **3** and **9** were measured on a Bruker Smart APEX machine. The data were collected using monochromated Mo Kα radiation in ω-scan. The structures were solved by direct methods. All of the non-hydrogen atoms were refined anisotropically on F^2. The methyl groups were refined using rigid groups and the other hydrogens in the riding mode.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and Table 1, giving crystal data for compounds **3** and **9**. 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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