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The First Complexes with Two Metallacycles Fused Around a Common Aryl Substituent: "Akimbo" Complexes

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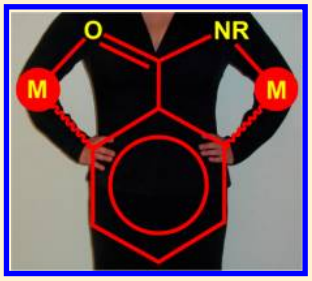
Supporting Information

ABSTRACT: Following the reaction sequence i) oxidative addition of $RNHC(O)C_6H_3I_2$-2,6 (R = Me, Tol) to $[Pd_2(dba)_3]\cdot dba$ in the presence of chelating ligands N^N or XyNC (Xy = $C_6H_3Me_2$-2,6), ii) treatment of the resulting complexes with TlTfO or Tl(acac) (acac = acetylacetonato), and iii) insertion of unsaturated molecules (CO, XyNC, $MeO_2CC{\equiv}CCO_2Me$, $MeC(O)CH{=}CH_2$) into one of the Pd−C_{aryl} bonds of the resulting complexes allowed the synthesis of aryldipalladated complexes containing the ligands L1 = μ-*C,C*-$\{C_6H_3C(O)NHR\}$-2,6, L2 = μ-*C,C*-$\{C_6H_3C(O)NHMe\}(C{=}NXy)_2$-2,6, L3 = μ-*C,O,C*-$\{C_6H_3C(O)NHMe\}$-2,6, L4 = μ-*C,O,C,N*-$\{C_6H_3C(O)NR\}$-2,6, L6 = μ-*C,N,C,O*-$\{C_6H_3C(O)NR\}$-2-(C=O)-6, L7 = μ-*C,N,C,O*-$\{C_6H_3C(O)NR\}$-2-$\{C(CO_2Me){=}C(CO_2Me)\}$-6, L8 = μ-*C,N,C,O*-$\{C_6H_3C(O)NR\}$-2-(C=NXy)-6 and two arylmonopalladated complexes with the ligands L5 = *C,O*-$\{C_6H_4C(O)NHMe\}$-2 and L9 = *C,N*-$\{C_6H_3C(O)NTol\}$-2-$\{CH{=}CHC(O)Me\}$-6. The complex with the ligand L7 inserted CO into the second Pd−C_{aryl} bond to give an L10-Pd_2 complex (L10 = μ-*C,N,C,O*-$\{C_6H_3C(O)NTol\}(C{=}O)$-2-$\{C(CO_2Me){=}C(CO_2Me)\}$-6. The dipalladated species display a different environment for each palladium atom and represent the first systems containing two 5 + 5, 5 + 6, 5 + 7, or 6 + 7-membered palladacycles condensed over the central benzamide group. The two arms of the ligands L4 and L6-L8 and L10 are "akimbo", and we coin this name both for the ligands and for the dimetallic complexes bearing them. The crystal structure of a $[\{Pd(N^N)\}_2L6]^+$ complex has been determined.



INTRODUCTION

Arylpalladium complexes have attracted great interest over the last decades mainly because they are involved in many important palladium-catalyzed organic reactions.[1]

We are currently studying the synthesis of ortho-functionalized aryl metal complexes and their reactivity toward unsaturated molecules, for example isocyanides,[2−4] CO,[4−6] alkynes,[6−8] alkenes,[9,10] allenes,[9,11] carbodiimides,[12,13] isothiocyanates,[5,12] nitriles,[12,14] and cyanamides.[12] These reactions are of interest because they are involved in the synthesis of new cyclometalated or pincer palladium complexes and in many stoichiometric and catalytic palladium-mediated organic transformations.[2,5,7,10,15,16]

A few years ago we started exploring the possibility of synthesizing polypalladated aryl derivatives with organic substituents ortho to each palladium atom, in the hope that they could open the way to the palladium-catalyzed syntheses of polycyclic organic compounds. So far, we have reported a few tripalladated[17,18] and dipalladated[17,19] aryl complexes, some of them bearing the palladium moieties in meta position to each other. The latter belong to a rather large family of symmetrical complexes[20,21] with both palladium atoms in identical environments. Only one such complex, [μ-[2-[4,6-bis(1*H*-pyrazol-1-ylmethyl)-2-pyrimidinyl]-1,3-phenylene]]dichloro dipalladium,[21] has been said to display both palladium atoms coordinated to the same aryl ligand and sharing a single substituent, which we call an "akimbo" complex. It was obtained, along with the monopalladated derivative, from the reaction of bis(pyrazolylmethyl)pyrimidine with $Li_2[PdCl_4]$, but the mixture could not be resolved and the dipalladated complex was identified only by a peak in its FAB-MS spectrum corresponding to the loss of HCl.

This work reports the synthesis of the first "akimbo" complexes, which we have prepared from 2,6-diiodobenzamides. In addition, the insertion of unsaturated molecules into the Pd−C_{aryl} bonds in these complexes has allowed the expansion of one or both palladacycles, giving rise to systems containing three condensed 6+5+6, 6+5+7, or 6+6+7-membered C^O^N^C "akimbo" complexes. Related to them is a complex resulting from the 3-fold cyclopalladation of a single benzene ring.[22]

RESULTS AND DISCUSSION

Synthesis. The new benzamides $RNHC(O)C_6H_3I_2$-2,6 (R = Me (**A1**), Tol (**A2**)) were isolated in yields of over 75% from the reaction of $HO_2CC_6H_3I_2$-2,6 with $SOCl_2$, and the appropriate amine RNH_2, following a procedure previously described for other amides.[23]

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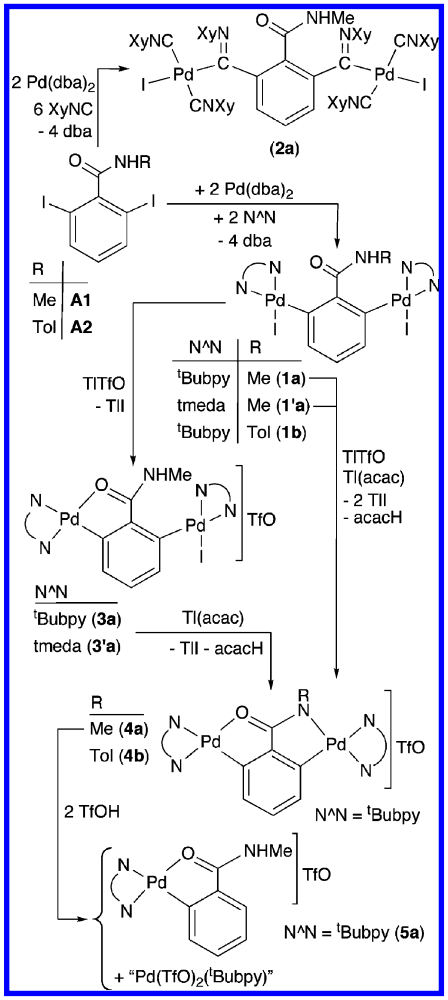
Dipalladated aryl derivatives of the type [{PdI(N^N)}$_2$L1] (Scheme 1. L1, see Chart 1, N^N = 4,4′-di-*tert*-butyl-2,2′-

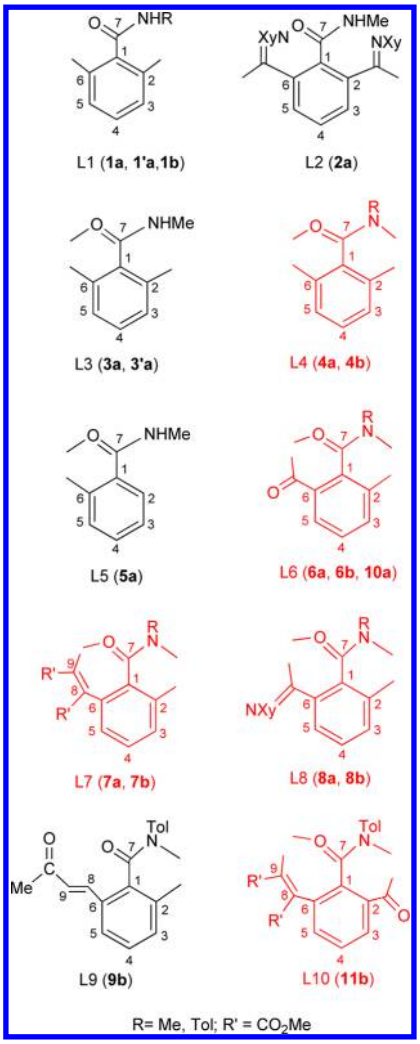
Scheme 1



bipyridine (^{t}Bubpy), R = Me (**1a**), C_6H_4Me-4 (Tol) (**1b**); N^N = tetramethylethylenediamine (tmeda), R = Me (**1′a**)) were obtained by oxidative addition of the appropriate diiodobenzamide to "Pd(dba)$_2$" ([Pd$_2$(dba)$_3$]·dba; dba = dibenzylideneacetone) in the presence of an excess of N^N. While complexes **1b·H$_2$O** and **1′a** were prepared in good yields at room temperature, to isolate pure compound **1a** it was necessary to heat the reaction mixture to 50 °C. Otherwise, it was contaminated with a complex that was difficult to remove. A small amount of this compound could be isolated from the solution obtained by washing the impure compound with Et$_2$O, and its elemental analyses and ^{1}H NMR spectrum[24] suggest it to be [PdI{C$_6$H$_3$}{C(O)NHMe}-2-I-6}^{t}Bubpy] (Chart 2). When **A1** and excess XyNC (Xy = C$_6$H$_3$Me$_2$-2,6), instead of the N^N ligands, were used, the oxidative addition reaction and the insertion of one XyNC molecule in each Pd–C bond took place, to give complex [{PdI(CNXy)$_2$}$_2$L2] (**2a**) (Scheme 1. L2, see Chart 1).

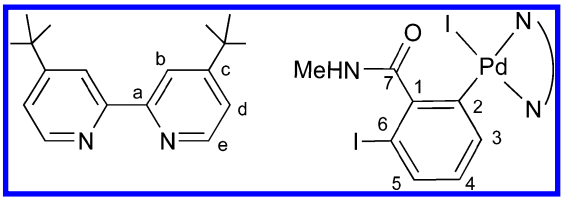
Treatment of complexes **1a** and **1′a** with two equiv of TlTfO caused the removal of only one of the iodo ligands, together with coordination of the amide oxygen to one of the palladium atoms, to give the five-membered palladacyclic complexes [{Pd$_2$I(N^N)$_2$}L3]TfO (Scheme 1. L3, see Chart 1, N^N = ^{t}Bubpy (**3a**), tmeda (**3′a**)), which were isolated in *ca.* 90%

Chart 1. Ligands L1–L10 Present in Complexes 1–11, Showing the Numbering Scheme[a]



[a]"Akimbo" ligands are shown in red.

Chart 2. Numbering Scheme Used in the NMR Assignment of the Resonances of ^{t}Bubpy Ligand and [PdI{C$_6$H$_3$}{C(O)NHMe}-2-I-6}^{t}Bubpy]



yield. The reaction of **1b** with two equiv of TlTfO gave a mixture containing the corresponding complex **3b** along with some impurities that we could neither identify nor remove. Surprisingly, elimination of both iodo ligands from complexes **1** could not be achieved, even when the reaction was carried out using an even larger excess of TlOTf (2.5:1) at 60 °C for 1 h. Probably, the equilibrium **1** ⇆ [{Pd$_2$I(N^N)$_2$}L3]$^+$ + I$^-$ (Scheme 2), involving decoordination/recoordination of I$^-$ caused by the amide oxygen coordination (see below), allows the precipitation of TlI. However, the second iodo ligand does not participate in a similar equilibrium because of the poor donor ability of the NHMe group.

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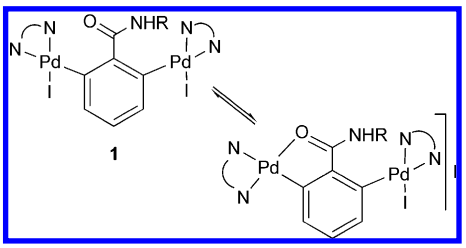
Scheme 2



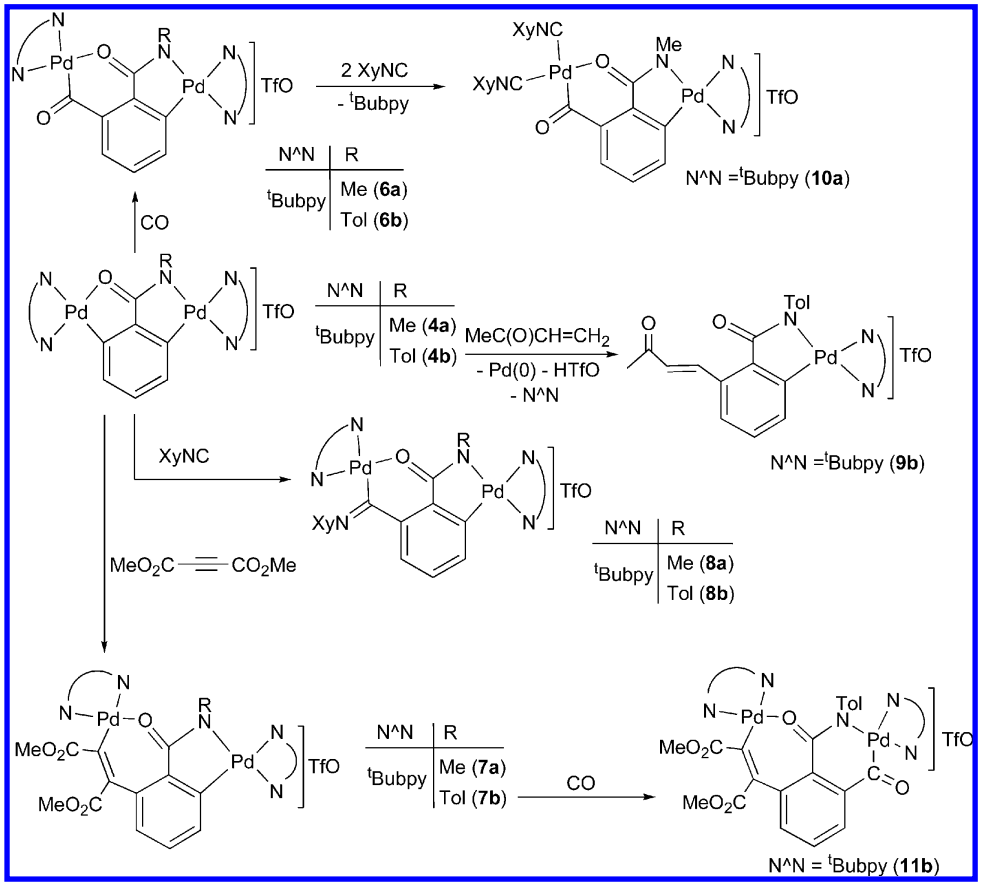
Surprisingly, when **1a** was reacted with one equiv of TlTfO a product **X** was isolated from the reaction mixture, the elemental analyses and IR spectrum of which coincided with that of **3a**, while its ^{1}H NMR spectrum showed two singlets corresponding to the ^{t}Bu protons instead of the four singlets observed in **3a**. The explanation for these apparently incongruent data was that **X** contained **3a** contaminated with **1a**. When **X** was dissolved, the amount of I^-, generated from the traces of **1a** through the above-mentioned equilibrium, is enough to react with **3a**, triggering the fast equilibrium **3a** + I^- ⇆ **1a** + TfO^- thus making both ^{t}Bubpy ligands equivalent. Indeed, the low temperature (−55 °C) ^{1}H NMR spectrum of **X** is identical to that of **3a**, probably favored by the low solubility of **1** at low temperature. Also, the ^{1}H NMR spectrum of a mixture of **3a** with traces of NaI is the same as that of **X**.

Removal of both iodo ligands from complexes **1** could be achieved by reacting them with TlTfO and a base, for example Tl(acac), in 1:1:1 molar ratio. In this way, the benzamidato group, a strong donor, displaced the other iodo ligand, allowing its removal as TlI, to give [{Pd(^{t}Bubpy)}$_2$L4]TfO (Scheme 1; L4, see Chart 1, R = Me (**4a**, 88%), Tol (**4b**, 93%)). Complex **4a** could also be obtained (92%) by reacting **3a** with one equiv of Tl(acac). Complexes **4** are the first "akimbo" complexes of any metal. Various dinuclear palladium complexes bearing bridging amidinato ligands *N,O*-R′C(O)NR ligands,[25] have been reported but, in contrast to **4**, in none of them are the two Pd atoms coordinated to the R′ group.

The isolation of **4a** gave us the opportunity to treat it with TfOH in a new attempt to synthesize the dicationic complex [{Pd(N^N)}$_2${μ-*C,O,N,C*-C$_6$H$_3$C(O)NHMe-2,6}](TfO)$_2$, which, as mentioned above, could not be obtained from **1a** and excess of TlTfO (1:2). However, the addition of TfOH to **4a** (1:1) produced an orange solution containing the monopalladated complex [Pd(L5)(^{t}Bubpy)]TfO (**5a**) (Scheme 1. L5, see Chart 1) along with some impurities that we could not identify. Complex **5a** results from the protonation of both the amide nitrogen and the C2 carbon in **4a**, with concomitant depalladation, and could be isolated pure when two equiv of TfOH were used (1:2). After removing a small amount of Pd(0), complex **5a** precipitated (56% yield) upon concentrating the CH_2Cl_2 solution, while some "Pd(TfO)$_2$(^{t}Bubpy)" species that we could not identify remained in the red solution.

Only a few mononuclear cyclopalladated derivatives of benzamides ArC(=O)NRR′ (Ar = C$_6$H$_4$OMe-3, R = Me, R′ = Ph, C$_6$H$_4$Me-2; Ar = C$_6$H$_3$(OMe)$_2$-3,4, R = Me, R′ = Ph;[26] Ar = C$_6$H$_2$(OMe)$_3$-2,3,4, R = H, R′ = ^{t}Bu);[16] Ar = Ph, R = H, R′ = Me, Ph)[27] have been isolated. In all of them, the *O*-coordination of the amide group was assumed[27] or established by X-ray diffraction.[16,28] We have reported the only cationic

Scheme 3



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complex homologous to **5a**, [Pd(L′5)(bpy)]TfO (where L′5 is an aryl ligand similar to L5; bpy =2,2′-bipyridine).[16] When R = H, the reactions of benzamides or ortho-halobenzamides with a Pd(II) or Pd(0) complex, respectively, in the presence of a base have been proposed to occur through the intermediacy of a monopalladacyclic benzamidato complex.[29] However when the R′ group contains a donor atom (P,[30] S[31]) in the appropriate position, a pincer benzamidato complex could be isolated.

Insertion Reactions. The synthesis of akimbo complexes **4** offers the first opportunity to study whether unsaturated molecules display different tendencies to insert into their two Pd−C_{aryl} bonds. Complexes **4** react with excess CO or $MeO_2CC{\equiv}CCO_2Me$ (DMAD) or with one equiv of XyNC to produce good yields of monoinsertion products [{Pd-(^{t}Bubpy)}$_2$L]TfO (Scheme 3) where L = L6, (Chart 1, R = Me (**6a**), Tol (**6b**)), L7 (Chart 1, R = Me (**7a**), Tol (**7b**)), L8 (Scheme 3, Chart 1, R = Me (**8a**), Tol (**8b**)), respectively. When the reactions with DMAD were carried out in 1:1 molar ratio, variable amounts of the unreacted cyclometalated complexes **4** were recovered. No reaction was observed between complexes **4** and RC≡CR (R = Me, Et), even if an excess of the alkyne was used, while the reaction of **4a·H_2O** with PhC≡CH (1:1 or 1:5 molar ratios) led to mixtures of unidentified products.

Partial depalladation occurred in the reaction of complex **4b** with methyl vinyl ketone (MVK; 1:2), which afforded for the first time a Heck reaction product in the form of a cyclopalladated complex [{Pd(^{t}Bubpy)(CNXy)$_2$}L9]TfO (Scheme 3, L9, see Chart 1 (**9b**)), which was isolated in moderate yield. When the reaction was carried out using equimolar amounts of the reagents, a mixture formed containing **4b** and **9b** among other unidentified products.

Some attempts to prepare complexes resulting from a second insertion reaction were attempted starting from **6a** or **7b**. However, **6a** reacted with two equiv of XyNC to give the substitution product [{Pd$_2$(^{t}Bubpy)(CNXy)$_2$}L6]TfO (Scheme 3. L6, see Chart 1, (**10a**)). Using equimolar amounts of the reagents, a mixture formed containing equimolar amounts of **6a** and **10a**. In contrast, when a solution of complex **7b** was stirred in a CO atmosphere for 6 h, insertion of CO into the TolNPd−C bond produced the complex [{Pd(^{t}Bubpy)}$_2$L10]TfO (Scheme 3, L10, see Chart 1 (**11b**)), which was isolated in moderate yield.

All insertion reactions, with the exception of that leading to **11b**, occurred into the C^6−Pd bond. This selectivity could be favored by the weaker Pd−O bond in complexes **4** compared to Pd−N, facilitating the coordination of the unsaturated molecule, prior to its migratory insertion. The weaker CO−Pd bond in **4b** with respect to that in **4a**, associated with the higher electron-withdrawing ability of Tol compared to Me, may favor in the former the coordination of the alkyne. This must be the reason why the reaction **4b** → **7b** requires less excess of alkyne and less time to complete than the analogous reaction **4a** → **7a** (1:2, 24 h vs 1:5, 48 h). When both reactions were carried out at 80 °C, mixtures of unidentified products formed, regardless of the molar ratio of the reagents.

It is noteworthy that the same type of CO insertion that afforded **11b** from **7b** did not occur starting from **4b**, to give **6b**. It is possible that the electron withdrawing −C(CO_2Me)=C(CO_2Me)− group favors the resonance form [Pd]O−C(Ar)=N(R)[Pd] weakening the N−Pd bond and facilitating the coordination of the second molecule of CO and, correspondingly, its insertion into the C^2−Pd bond.

Crystal Structures. The crystal structure of **6b·0.36H_2O** (Figure 1) shows the two condensed palladacycles resulting

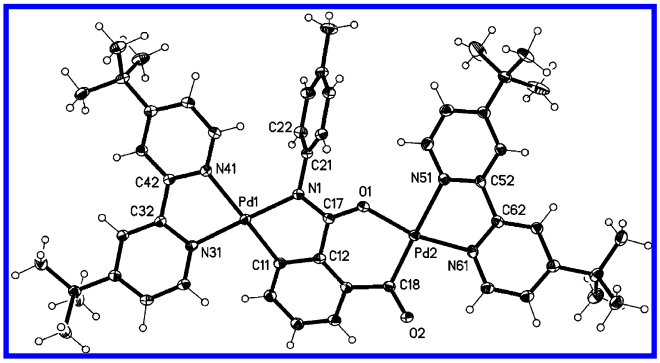

Figure 1. Crystal structure of the cation of **6b·0.36H_2O**. The anion and the solvent are omitted for clarity. The thermal ellipsoids are displayed at 50% probability. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) 1.997(4), Pd(1)−N(1) 2.019(3), Pd(1)−N(31) 2.059(3), Pd(1)−N(41) 2.146(3), Pd(2)−C(18) 1.970(4), Pd(2)−O(1) 2.011(3), Pd(2)−N(61) 2.059(3), Pd(2)−N(51) 2.162(3), O(1)−C(17) 1.271(5), C(13)−C(18) 1.519(6), O(2)−C(18) 1.208(5), N(1)−C(17) 1.324(5), N(31)−Pd(1)−N(41) 77.85(12), C(11)−Pd(1)−N(1) 79.45(15), N(51)−Pd(2)−N(61) 77.94(13), C(18)−Pd(2)−O(1) 94.20(14), C(17)−N(1)−Pd(1) 116.5(3), O(1)−C(17)−N(1) 122.0(3), C(17)−O(1)−Pd(2) 129.1(3), C(13)−C(18)−Pd(2) 119.4(3).

from the insertion of CO into the C−Pd bond of the *C,O*-ring in its precursor. The longer Pd(1)−N(41) and Pd(2)−N(51) bond distances (2.146(3) and 2.162(3) Å, respectively) compared to Pd(1)−N(31) and Pd(2)−N(61) (2.059(3) and 2.059(3) Å, respectively), are consistent with the greater *trans influence* of carbon- with respect to nitrogen- or oxygen-donor ligands. The seventeen atoms comprising the four palladacycles are roughly in a plane (mean deviation 0.15 Å), with respect to which the C(11)−C(16) and C(21)−C(26) aryl groups are rotated by 18.6 and 72.4°, respectively.

The number of structurally characterized benzamido or benzamidato complexes of palladium is rather limited. In fact, only one crystal structure has been reported of a mononuclear *C,N*-benzamidato complex[32] and five complexes containing *C*-monocoordinated[33] or *C,O*-chelating benzamide ligands.[16,26] the later being trifluoroacetato-bridged dimeric complexes.[26] The structure of **6b·0.36H_2O** shows for the first time a benzamidato ligand acting, simultaneously, as chelating and bridging in a monomeric dipalladated complex.

The crystal structure of **7b** was also measured and the connectivity of the cation could be established unambiguously, proving that insertion of DMAD occurs also into the C−Pd bond of the *C,O*-ring. However, it was impossible to refine it satisfactorily (wR2 about 35%) even after measuring various crystals which all presented the same problems, i.e. i) the structure is very large, consisting of two independent molecules, ii) some butyl groups are disordered, iii) the −CO_2Me groups have high thermal parameters, and iv) one of the two triflate anions is badly disordered.

NMR Spectra. The NMR resonances were assigned based on APT, HMBC, and HMQC experiments carried out for complexes **5a**, **6b**, **8b**, **9b**, and **11b.** Complex **2a** decomposed upon standing in solution, which impeded the measurement of its ^{13}C NMR spectrum. The C^2 resonances are not observed in the ^{13}C NMR spectra of complexes **8**. A sample of complex **11b**

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was prepared using ^{13}CO in order to assign its NMR spectra unambiguously. The inequivalence of the two halves of the N^N ligands is shown by the duplication of some of the resonances, although some others accidentally coincide. However, the spectra of **1a** does not show such duplication, indicating the interchange of positions of the two nitrogens. This process could be facilitated by the fast equilibrium **1a** ⇆ $[\{Pd_2I(^tBubpy)_2\}L3]^+ + I^-$ (Scheme 2), which could occur through a planar trigonal intermediate $[\{Pd_2I(^tBubpy)_2\}L1]I$ in which the interchange would take place. Such equivalence is not observed in the case of **1b**, probably because of the poorer donor ability of the carbonyl amide group caused by the electron-withdrawing nature of the Tol group.

Replacement of the iodine atoms in **A1** and **A2** by two $PdI(^tBubpy)$ groups in complexes **1a,b** causes a marked deshielding of the C^{2+6} resonance (from ∼92 to ∼149 ppm, $\Delta\delta \approx 57$ ppm), but the C^7 resonance changes only slightly ($\Delta\delta$ = 3 ppm). The behavior of these complexes in solution differs from that of the homologous **1′a** which, at room temperature, displays very broad ^{13}C NMR resonances suggesting a fluxional process. At −50 °C, the C^2 and C^6 nuclei are inequivalent (150.2 and 155.7 ppm, respectively) and, along with C^7 (180.1 ppm), more deshielded than those in **1a,b**. The low temperature spectrum of **1′a** is very similar to those of complexes **3** in which the amide oxygen is coordinated to palladium. This suggests that in complex **1′a** the equilibrium **1′a** ⇆ $[\{Pd_2I(tmeda)_2\}L3]^+ + I^-$ (Scheme 2) at low temperature is displaced toward the right.

Compared to **3**, complexes **4** bearing anionic amide ligands show the C^7 resonance further deshielded (up to $\Delta\delta$ = 10 ppm), while the C^2 and C^6 resonances are shielded (approximately 10 ppm), which could be attributed to the electron delocalization in complexes **4** allowed by the planarity of the palladacycles.

Based on NMR correlation experiments, we can assess that the insertion of CO, DMAD, or XyNC occurs in the C^6−Pd (Chart 1) bond of complexes **4** to give complexes **6**−**8**, respectively which was confirmed for **6b** in the solid state by its crystal structure (see above).

In complexes **6**−**8** and **10a** the C^2 and C^6 resonances appear in the ranges 131.0−133.6 and 150.6−159.3 ppm, respectively, while **11b** shows these resonances at 132.2 and 138.3 ppm, respectively, the former appearing in the APT spectrum of a sample prepared from ^{13}CO as a doublet ($^1J_{CC}$ = 64 Hz) with inverted polarity, which is indicative of C^2 being contiguous to the inserted ^{13}CO.[34] The $-C(CO_2Me)=CCO_2Me$ group in **11b** seems to withdraw electron density from the acyl group, causing both the higher shielding of C^6 with respect to its precursor **7b** and the large shift of the ν(C=O) band in **11b** (1819 cm^{-1}) compared to that in the other acyl complexes (**6** and **10a**, *ca.* 1645 cm^{-1}).

The NMR correlation experiments did not unambiguously determine which of the ^{t}Bubpy ligands in **6a** is replaced by two XyNC ligands to give **10a**, but we tentatively assign it the structure depicted in Scheme 3, based on our assumption that in this way the substitution is facilitated by the weaker Pd−O bond.

IR Spectra. The variable position of the NH stretching bands, appearing in the in the range 3219−3347 cm^{-1} in the IR spectra of benzamides **A1,2** and benzamido complexes **1**−**3** and **5**, could be associated with the participation of the NH group in intermolecular hydrogen bonding to the C=O group (**1**) or the triflato anion (**3**, **5**). Coordination of the benzamide oxygen to Pd causes the ν(CO) band to shift from 1643 (**1a**) to 1631 cm^{-1} in **1′a** or to 1615−1598 cm^{-1} in the remaining complexes, as previously found in other benzamido complexes.[16,35] The ν(C≡N) and ν(C=N) bands in the isocyanide (**2a**, **10a**) and in the iminobenzoyl (**2a**, **8**) complexes appear in the ranges 2170−2184 and 1642−1662 cm^{-1}, respectively and the $\nu_{asym}(CO_2)$ in complexes with inserted DMAD (**7**, **11b**) at 1702−1722 cm^{-1}. The ν(C=O) band in complex **11b** (1819 cm^{-1}) was unambiguously assigned to the benzoyl ν(C=O) since it shifts to 1778 cm^{-1} when the spectrum is measured on a sample prepared using labeled ^{13}CO.

EXPERIMENTAL SECTION

General Procedures. When not stated, the reactions were carried out at room temperature without precautions to exclude light or atmospheric oxygen or moisture. NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers, at 298 K, unless otherwise stated. Chemical shifts are referred to internal TMS (^1H and $^{13}C\{^1H\}$). The assignments of the ^1H and $^{13}C\{^1H\}$ NMR spectra were made with the help of APT, HMBC, and HMQC experiments. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass TOF LC/MS. Molar conductivities were measured on about 5×10^{-4} mol·L^{-1} acetone solutions with a Crison Micro CM2200 conductimeter. Synthesis grade solvents were obtained from commercial sources. Toluene, CH_2Cl_2, and THF were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technology, Inc. CO (Air Products); TfOH, XyNC (Xy = $C_6H_3Me_2$-2,6, xylyl), tmeda (*N,N,N′,N′*-tetramethylethylenediamine), $SOCl_2$, MVK (methyl vinyl ketone) (Fluka), $MeNH_2$ (33 wt % in abs EtOH), ^{t}Bubpy (4,4′-*tert*-butyl-2,2′-bipyridine) (Aldrich), $TolNH_2$ (Merck), and DMAD (DiMethyl Acetylene Dicarboxylate) (Alfa Aesar) were obtained from commercial sources. TlTfO was prepared by reacting of Tl_2CO_3 (Fluka) with TfOH (1:2) in water and recrystallized from acetone/Et_2O. The compounds $[Pd_2(dba)_3]$·dba (dba = dibenzylideneacetone),[36] Tl(acac) (acacH = acetylacetone),[37] and 2,6-diiodobenzoic acid[38] were prepared according to published procedures. All other reagents were obtained from commercial sources and used without further purification.

Synthesis of $RNHC(O)C_6H_3I_2$-2,6 (R = Me (A1), Tol (A2)). $SOCl_2$ (for **A1**: 2.80 mL, 38.7 mmol; for **A2:** 2.18 mL, 30.8 mmol) was added dropwise under nitrogen to a stirred solution of $HO_2CC_6H_3I_2$-2,6 (for **A1**: 804.0 mg, 2.50 mmol; for **A2**: 639 mg, 1.70 mmol) in CH_2Cl_2 (20 mL). The solution was refluxed for 3 (**A1**) or 4 h (**A2**), cooled to room temperature, and concentrated under vacuum to give a pale yellow oil. Ethyl acetate (for **A1**: 3 mL; for **A2**: 2 mL) and a solution of the appropriate amine (for **A1**: $MeNH_2$, 3.8 mL, 30.10 mmol; for **A2**: $TolNH_2$, 1.47 g, 13.70 mmol) in MeOH (for **A1**: 5 mL) or CH_2Cl_2 (for **A2**: 2 mL) were successively added dropwise. After 5 min of stirring, the mixture was treated with an aqueous solution of K_2CO_3 (for **A1**: 500.0 mg/80 mL; for **A2**: 400.0 mg/60 mL) and stirred for 5 min. For **A1**, the suspension was filtered, and the solid was washed with water (2 × 5 mL) and vacuum-dried to give a white powder. For **A2**, the solvent was poured off, the residue was washed with water (3 × 10 mL), and the suspension was filtered. After air drying the solid, it was stirred in n-hexane, the suspension was filtered, and the solid was dissolved in CH_2Cl_2 (30 mL), filtered through anhydrous $MgSO_4$, and concentrated to 2 mL. Upon the addition of n-hexane (30 mL) a suspension formed, which was filtered; the solid was vacuum-dried to give a white powder.

A1: Yield: 613.0 mg, 74%. Mp: 241 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 8 Hz), 6.73 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 5.61 (br, 1 H, NH), 3.05 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$): δ 170.5 (C^7), 147.4 (C^1), 138.9 (C^{3+5}),

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131.7 (C^4), 92.2 (C^{2+6}), 26.7 (Me). IR (cm^{-1}): ν(NH), 3258; ν(CO), 1650. Anal. Calcd for $C_8H_7I_2NO$: C, 24.83; H, 1.82; N, 3.62. Found: C, 25.05; H, 1.61; N, 3.56.

A2: Yield: 715.2 mg, 90%. Mp: 259 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 8 Hz), 7.52 (d, 2 H, *o*-CH, Tol, $^3J_{HH}$ = 8 Hz), 7.21 (d, 2 H, *m*-CH, Tol, $^3J_{HH}$ = 8 Hz), 6.78 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 2.36 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$): δ 167.6 (C^7), 147.0 (C^1), 139.0 (C^{3+5}), 135.1 (*p*-C, Tol), 134.4 (*i*-C, Tol), 132.0 (C^4), 129.7 (*m*-C, Tol), 120.7 (*o*-C, Tol), 92.3 (C^{2+6}), 21.0 (Me). IR (cm^{-1}): ν(NH), 3252; ν(CO), 1656. Anal. Calcd for $C_{14}H_{11}I_2NO$: C, 36.31; H, 2.39; N, 3.02. Found: C, 36.05; H, 2.23; N, 3.23.

Synthesis of [{PdI(N^N)}$_2$L1] (N^N = ^{t}Bubpy, L1 = *μ-C,C*-{$C_6H_3C(O)NHR$}-2,6, R = Me (1a), Tol (1b); N^N = tmeda, R = Me, (1′a)). A suspension containing $Pd(dba)_2$ (for **1a**: 646.4 mg, 1.12 mmol; for **1b**: 1.5 g, 2.66 mmol; for **1′a**: 743 mg, 1.29 mmol), the appropriate N^N ligand (for **1a**: ^{t}Bubpy, 805.0 mg, 3 mmol; for **1b**: 950.0 mg, 3.54 mmol; for **1′a**: tmeda, 311 μL, 2.07 mmol), and the appropriate compound **A** (for **1a**: **A1**, 145.0 mg, 0.37 mmol; for **1b**: **A2**, 410.0 mg, 0.88 mmol; for **1′a**: **A1**, 200.0 mg, 0.52 mmol) in dry toluene (20 mL) was stirred under nitrogen atmosphere for 5 h or heated in a Carius tube at 50 °C for 4 h (**1a**). The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (20 mL) and filtered through Celite. The filtrate was concentrated under vacuum to 2 mL, the residue was stirred for 10 min with Et_2O (25 mL, for **1b** in an ice/water bath) or n-hexane (**1a**, 30 mL), and the suspension was filtered. The solid collected was washed with hot n-hexane (10 × 15 mL) and dried under vacuum to give an orange solid. In the case of **1b**, the hydrate **1b·H$_2$O** was obtained in spite of drying the solid in a vacuum oven at 60 °C for 14 h. **1′a** was recrystallized from CH_2Cl_2/Et_2O (2:25 mL) and dried by suction.

1a: Yield: 363.0 mg, 85%. Mp: 171 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (br, 4 H, H^b), 7.93 (br, 4 H, H^e), 7.47 (dd, 4 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.26 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 7 Hz), 6.70 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 2.75 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 1.40 (br, 36 H, CMe_3). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$): δ 173.0 (C^7), 163.1–162.6 (C^c), 148.9 (C^{2+6}), 132.6 (C^{3+5}), 126.5 (C^4), 123.8 (br, C^d), 118.2 (br,C^e), 35.4 (CMe_3), 30.3 (CMe_3), 26.3 (Me). IR (cm^{-1}): ν(NH), 3233; ν(CO), 1643. Anal. Calcd for $C_{44}H_{55}I_2N_5OPd_2$: C, 46.50; H, 4.88; N, 6.16. Found: C, 46.23; H, 4.76; N, 5.78.

1b·H$_2$O: Yield: 865.0 mg, 80%. Mp: 228 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (br, 3 H, NH + H^b), 7.85 (br, 6 H, H^b + H^e), 7.55 (d, 2 H, Tol, $^3J_{HH}$ = 8 Hz), 7.43 (dd, 4 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.34 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 8 Hz), 6.82 (d, 2 H, Tol, $^3J_{HH}$ = 8 Hz), 6.70 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 2.11 (s, 3 H, Me, Tol), 1.73 (s, 2 H, H_2O), 1.39 (s, 18 H, CMe_3), 1.32 (s, 18 H, CMe_3). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$): δ 169.3 (C^7), 162.7 (C^c), 155.3 (C^a), 154.1 (C^a), 152.3 (C^b), 150.6 (C^b), 147.9 (C^{2+6}), 145.4 (C^1), 137.2 (*i*-C, Tol), 133.7 (C^{3+5}), 131.5 (*p*-C, Tol), 128.5 (*m*-C, Tol), 126.0 (C^4), 123.9 (C^d), 123.4 (C^d), 119.1 (*o*-C, Tol), 118.0 (C^e), 117.7 (C^e), 35.3 (CMe_3), 30.3 (CMe_3), 30.2 (CMe_3), 20.6 (Me, Tol). IR (cm^{-1}): ν(NH), 3305; ν(CO), 1661. Anal. Calcd for $C_{50}H_{61}I_2N_5O_2Pd_2$: C, 48.80; H, 5.00; N, 5.69. Found: C, 48.50; H, 4.76; N, 5.55.

1′a: Yield: 366.0 mg, 85%. Mp: 140 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$, −50 °C): δ 6.91 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 7 Hz), 6.67 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 3.14 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 2.76 (br, 8 H, CH_2, tmeda), 2.62 (br, 24 H, Me, tmeda). $^{13}C\{^1H\}$ NMR APT (100 MHz, $CDCl_3$): δ 128.1 (C^{3+5}), 61.8 (CH_2), 52.7 (Me, tmeda), 26.9 (Me). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$, −50 °C): δ 180.1 (C^7), 155.7 (C^6), 150.2 (C^2), 144.2 (C^1), 129.4 (C^4), 125.8 (C^{3+5}), 64.8 (CH_2), 62.0 (CH_2), 58.2 (CH_2), 57.0 (CH_2), 54.0–45.0 (Me, tmeda), 27.7 (Me). IR (cm^{-1}): ν(NH), 3218; ν(CO), 1631. Anal. Calcd for $C_{20}H_{39}I_2N_5OPd_2$: C, 28.87; H, 4.72; N, 8.42. Found: C, 28.73; H, 4.90; N, 8.40.

Synthesis of [*trans*-{PdI(CNXy)$_2$}$_2$L2] (L2 = *μ-C,C*-{$C_6H_3C(O)NHMe$}(C═NXy)$_2$-2,6 (2a)). A suspension containing $Pd(dba)_2$ (297.2 mg, 0.52 mmol), XyNC (237.4 mg, 1.81 mmol), and **A1** (100 mg, 0.26 mmol) in dry toluene (20 mL) was stirred for 15 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (20 mL). The suspension was filtered through Celite, the filtrate was concentrated to 2 mL, Et_2O (25 mL) was added, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and dried, first by suction and then in an oven at 60 °C for 24 h, to give **2a** as a yellow powder. Yield: 163.0 mg, 45%. Mp: 179 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 8 Hz), 7.47 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.19 (t, 4 H, *p*-CH, Xy, $^3J_{HH}$ = 8 Hz), 7.03 (d, 8 H, *m*-CH, Xy, $^3J_{HH}$ = 8 Hz), 6.84 (s, 6 H, CH, Xy), 6.65 (q, 1 H, NH, $^3J_{HH}$ = 5 Hz), 2.95 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 2.21 (s, 24 H, Me, Xy), 2.17 (s, 12 H, Me, Xy). IR (cm^{-1}): ν(NH), 3347; ν(C≡N), 2184, 2175; ν(C═N), 1662; ν(CO), 1636. Anal. Calcd for $C_{62}H_{61}I_2N_7OPd_2$: C, 53.70; H, 4.43; N, 7.07. Found: C, 53.87; H, 4.74; N, 7.06.

Synthesis of [{Pd$_2$I(N^N)$_2$}L3]TfO (L3 = *μ-C,O,C*-{$C_6H_3C(O)NHMe$}-2,6, N^N = ^{t}Bubpy (3a), tmeda (3′a)). To a solution of the appropriate compound **1** (for **3a**: **1a**, 300.0 mg, 0.26 mmol; for **3′a**: **1c**, 200.0 mg, 0.26 mmol) in dry CH_2Cl_2 (15 mL) was added TlTfO (for **3a**: 233.3 mg, 0.66 mmol; for **3′a**: 170.0 mg, 0.48 mmol). The resulting suspension was stirred for 30 min and filtered through Celite. The solution was concentrated to 2 mL, Et_2O (25 mL) was added, and the suspension was filtered. The solid was suction dried to give the appropriate compound **3** as an orange powder.

3a: Yield: 272.0 mg, 89%. Mp: 202 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (q, 1 H, NH, $^3J_{HH}$ = 5 Hz), 9.47 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.90 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.70 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.16 (s, br, 2 H, H^b), 8.09 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.05 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.72 (m, 2 H, H^d), 7.58 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.54 (d, 1 H, $H^{3\text{ or }5}$, $^3J_{HH}$ = 8 Hz), 7.37 (dd, 1H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.06 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 6.95 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 6.89 (d, 1 H, $H^{3\text{ or }5}$, $^3J_{HH}$ = 8 Hz), 3.07 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 1.50 (s, 9 H, CMe_3), 1.48 (s, 9 H, CMe_3), 1.47 (s, 9 H, CMe_3), 1.38 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ NMR APT (100 MHz, $CDCl_3$): δ 180.6 (C^7), 164.7 (C^c), 164.5 (C^c), 164.3 (C^c), 157.2 (C^6), 156.7 (C^a), 155.8 (C^a), 154.1 (C^a), 152.9 (C^a), 152.2 (C^e), 151.2 (C^e), 149.9 (C^2), 149.0 (C^e), 148.4 (C^e), 144.2 (C^1), 133.3 ($C^{3\text{ or }5}$), 130.3 ($C^{3\text{ or }5}$), 126.9 (C^4), 124.6 (C^d), 124.4 (C^d), 124.3 (C^d), 124.2 (C^d), 120.4 (C^b), 119.2 (C^b), 119.1 (C^b), 118.9 (C^b), 35.9 (CMe_3), 35.8 (CMe_3), 35.6 (CMe_3), 30.4 (CMe_3), 30.3 (CMe_3), 30.3 (CMe_3), 30.1 (CMe_3), 27.3 (Me). IR (cm^{-1}): ν(NH), 3233; ν(CO), 1611. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 132. Anal. Calcd for $C_{45}H_{55}F_3IN_5O_4Pd_2S$: C, 46.64; H, 4.78; N, 6.04; S, 2.77. Found: C, 46.61; H, 4.88; N, 5.93; S, 2.45.

3′a: Yield: 186.0 mg, 91%. Mp: 138 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.26 (q, 1 H, NH, $^3J_{HH}$ = 5 Hz), 7.38 (d, 1 H, $CH^{3\text{ or }5}$, $^3J_{HH}$ = 8 Hz), 6.80 (t, 1 H, C^4, $^3J_{HH}$ = 8 Hz), 6.52 (d, 1 H, $CH^{3\text{ or }5}$, $^3J_{HH}$ = 8 Hz), 3.16 (d, 3 H, Me, $^3J_{HH}$ = 5 Hz), 2.94 (s, br, 5 H, Me + CH_2, tmeda), 2.90 (s, br, 5 H, Me + CH_2, tmeda), 2.75 (s, br, 13 H, 3 Me + 2 CH_2, tmeda), 2.69 (s, br, 3 H, Me, tmeda), 2.31 (s, 3 H, Me, tmeda), 2.18 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ NMR APT (75 MHz, $CDCl_3$): δ 180.7 (C^7), 154.8 (C^6), 150.4 (C^2), 144.6 (C^1), 133.8 ($C^{3\text{ or }5}$), 129.3 (C^4), 126.1 ($C^{3\text{ or }5}$), 65.2 (CH_2), 62.3 (CH_2), 58.6 (CH_2), 57.4 (CH_2), 51.9 (Me, tmeda), 51.7 (Me, tmeda), 50.7 (Me, tmeda), 50.6 (Me, tmeda), 49.6 (Me, tmeda), 49.1 (Me, tmeda), 48.2 (Me, tmeda), 47.8 (Me, tmeda), 26.9 (Me). IR (cm^{-1}): ν(NH), 3219; ν(CO), 1598. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 129.4. Anal. Calcd for $C_{21}H_{39}F_3IN_5O_4Pd_2S$: C, 29.52; H, 4.60; N, 8.20; S, 3.75. Found: C, 29.14; H, 4.36; N, 8.04; S, 3.54.

Synthesis of [{Pd(^{t}Bubpy)}$_2$L4]TfO (L4 = *μ-C,O,C,N*-{$C_6H_3C(O)NMe$}-2,6 (4a)). To a solution of **3a** (72.0 mg, 0.06 mmol) in acetone (20 mL) was added Tl(acac) (37.7 mg, 0.12 mmol). The resulting suspension was stirred for 45 min, and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (25 mL), and the suspension was filtered through Celite. The solution was concentrated to 1 mL, Et_2O (25 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (2 × 5 mL) and dried first by suction and then in a vacuum oven at 80 °C for 4 h to give **4a·H$_2$O** as a yellow powder. Yield: 58.0 mg, 92%. Mp: 210 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, 1H, H^e, $^3J_{HH}$ = 6 Hz), 8.82 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.81 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.67 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.15 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.12 (s, br, 2 H, H^b), 8.09 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.75 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.64 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.60 (dd, 2 H, H^d,

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$^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 6.91 (d, 1 H, H$^{3\text{ or }5}$, $^3J_{HH}$ = 7 Hz), 6.84 (d, 1 H, H$^{3\text{ or }5}$, $^3J_{HH}$ = 7 Hz), 6.80 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 3.16 (s, 3 H, Me), 1.57 (s, 2 H, H_2O), 1.478−1.47 (s, br, 36 H, CMe_3). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 190.9 (C^7), 164.7 (C^c), 164.6 (C^c), 164.5 (C^c), 162.5 (C^1), 157.0 (C^a), 156.4 (C^a), 154.5 (C^a), 153.1 (C^a), 152.1 (C^e), 151.2 (C^e), 149.6 (C^e), 148.6 (C^e), 143.4 (C$^{2\text{ or }6}$), 141.9 (C$^{2\text{ or }6}$), 127.1 (C$^{3\text{ or }5}$), 126.2 (C^4), 125.9 (C$^{3\text{ or }5}$), 124.2 (C^d), 123.8 (C^d), 123.7 (C^d), 120.0 (C^b), 119.8 (C^b), 119.2 (C^b), 118.7 (C^b), 35.8−35.7 (CMe_3), 34.3 (Me), 30.4−30.2 (CMe_3). IR (cm^{-1}): ν(CO), 1611. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 123. Anal. Calcd for $C_{45}H_{56}F_3N_5O_5Pd_2S$: C, 51.53; H, 5.38; N, 6.68; S, 3.06. Found: C, 51.45; H, 5.36; N, 6.58; S, 2.74.

Synthesis of [{Pd(t Bubpy)}$_2$L4]TfO (L4 = *μ-C,O,C,N*-{C$_6$H$_3$C(O)NTol}-2,6 (4b)). To a solution of **1b·H$_2$O** (243.0 mg, 0.20 mmol) in acetone (20 mL) was added TlTfO (70.8 mg, 0.20 mmol) and Tl(acac) (60.8 mg, 0.20 mmol). The resulting suspension was stirred for 1 h and filtered through Celite. The solution was concentrated to 1 mL, Et_2O (25 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (2 × 5 mL) and dried, first by suction and then in an oven at 80 °C for 4 h, to give **4b·H$_2$O** as a yellow powder. Yield: 210.0 mg, 93%. Mp: 217 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (d, 1H, H^e, $^3J_{HH}$ = 6 Hz), 8.88 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.36 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.13 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.10 (br, 1 H, H^b), 8.07 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.05 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.67 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.64 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.52 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.38 (d, 2 H, *o*-CH, Tol, $^3J_{HH}$ = 8 Hz), 7.24 (d, 2 H, *m*-CH, Tol, $^3J_{HH}$ = 8 Hz), 7.10 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.02−6.91 (various m, 3 H, H^{3+4+5}), 6.72 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 2.45 (s, 3 H, Me, Tol), 1.59 (s, 2 H, H_2O), 1.49 (s, 9 H, CMe_3), 1.48 (s, 9 H, CMe_3), 1.44 (s, 9 H, CMe_3), 1.38 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 189.5 (C^7), 164.9 (C^c), 164.9 (C^c), 164.8 (C^c), 164.3 (C^c), 162.8 (C^1), 157.0 (C^a), 156.5 (C^a), 154.5 (C^a), 153.0 (C^a), 152.2 (C^e), 151.3 (C^e), 148.9 (C^e), 148.6 (C^e), 143.4 (C$^{2\text{ or }}$6), 142.7 (C$^{2\text{ or }6}$), 142.2 (*i*-C, Tol), 135.0 (*p*-C, Tol), 129.5 (*m*-C, Tol), 127.3 (C$^{3\text{ or }5}$), 127.2 (C$^{3\text{ or }5+4}$), 126.3 (*o*-C, Tol), 124.0 (C^d), 123.8 (C^d), 122.9 (C^d), 120.2 (C^b), 120.0 (C^b), 119.0 (C^b), 118.7 (C^b), 35.8 (CMe_3), 35.5 (CMe_3), 30.3 (CMe_3), 30.2 (CMe_3), 21.3 (Me, Tol). IR (cm^{-1}): ν(CO), 1614. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 127. Anal. Calcd for $C_{51}H_{60}F_3N_5O_5Pd_2S$: C, 54.45; H, 5.38; N, 6.28; S, 2.85. Found: C, 54.30; H, 5.52; N, 6.17; S, 2.77.

Synthesis of [PdL5(t Bubpy)]TfO (L5 = *C,O*-{C$_6$H$_4$C(O)NMe}-2 (5a)). To a solution of **4a·H$_2$O** (100.0 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added TfOH (17 μL, 0.19 mmol). The reaction mixture was stirred for 2 h and filtered through Celite. Upon concentrating the orange solution to 5 mL, a pale-yellow solid appeared. The suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and dried, first by suction and then in an oven at 55 °C for 10 h, to give **5a·H$_2$O** as a pale yellow powder. Yield: 36.0 mg, 56%. Mp: 218 °C (dec). ^{1}H NMR (400 MHz, d_6-dmso): δ 9.57 (br, 1 H, NH), 8.60 (s, br, 2 H, H^d), 8.52 (br, 2 H, H^e), 7.75 (br, 2 H, H^b), 7.51 (d, 1 H, H^2, $^3J_{HH}$ = 7 Hz), 7.35 (d, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.30 (t, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.19 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 3.31 (br, 2 H, H_2O), 2.96 (d, 3 H, Me, $^3J_{HH}$ = 4 Hz), 1.43 (s, 18 H, CMe_3). $^{13}C\{^1H\}$ NMR APT (100 MHz, d_6-dmso): δ 177.4 (C^7), 165.1 (C^c), 151.4 (C^6), 141.2 (C^1), 131.8 (C^5), 131.5 (C^4), 126.3 (C^2), 125.2 (C^3), 124.1 (C^b), 123.8 (C^e), 122.3 (C^a), 121.4 (C^d), 35.8 (CMe_3), 29.9 (CMe_3), 26.6 (Me). IR (cm^{-1}): ν(NH), 3301; ν(CO), 1607. Λ_M (Ω^{-1}·cm^2·mol^{-1}): not soluble in acetone. Anal. Calcd for $C_{27}H_{34}F_3N_3O_5PdS$: C, 47.97; H, 5.07; N, 6.22; S, 4.74. Found: C, 48.11; H, 4.90; N, 6.03; S, 4.76.

Synthesis of [{Pd(t Bubpy)}$_2$L6]TfO (L6 = *μ-C,N,C,O*-{C$_6$H$_3$C(O)NR}-2-(C═O)-6, R = Me (6a), Tol (6b)]. A solution of the appropriate complex **4** (**4a·H$_2$O**, 500.0 mg, 0.48 mmol; **4b·H$_2$O**, 105.0 mg, 0.09 mmol) in CH_2Cl_2 (15 mL) was stirred under a CO atmosphere for 1 or 2 h, respectively. The suspension was filtered through Celite, the yellow solution was concentrated to 1 mL, and Et_2O (25 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and dried, first by suction and then under vacuum at 55 °C for 10 h to give a yellow (**6a·H$_2$O**) or orange (**6b·H$_2$O**) powder.

6a·H$_2$O: Yield: 493.0 mg, 95 Mp: 228 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.07 (d, 2 H, H^e, $^3J_{HH}$ = 6 Hz), 8.87−8.83 (m, 2 H, H^e), 8.07 (br, 1 H, H^b), 8.05 (br, 1 H, H^b), 8.01 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.00 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.92 (d, 1 H, H^d, $^3J_{HH}$ = 6 Hz), 7.81 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.63−7.61 (m, 2 H, H^d), 7.34 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.21 (d, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.09 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 3.60 (s, 3 H, Me), 1.57 (s, 2 H, H_2O), 1.50 (s, 9 H, CMe_3), 1.49 (s, 9 H, CMe_3), 1.46 (s, 9 H, CMe_3), 1.45 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 218.6 (C═O), 175.7 (C^7), 164.8 (C^c), 164.5 (C^c), 164.4 (C^c), 164.2 (C^c), 156.3 (C^a), 155.2 (C^a), 154.2 (C^a), 153.7 (C^6), 152.6 (C^a), 151.5 (C^e), 150.6 (C^e), 150.2 (C^e), 147.6 (C^e), 143.2 (C^1), 135.6 (C^3), 131.6 (C^2), 130.2 (C^4), 124.9 (C^d), 124.1 (C^d), 124.0 (C^d), 123.3 (C^d), 121.3 (C^5), 119.8 (C^b), 119.0 (C^b), 118.9 (C^b), 118.1 (C^b), 37.0 (Me), 35.7 (CMe_3), 35.5 (CMe_3), 30.3 (CMe_3). IR (cm^{-1}): ν(CO), 1643, 1612. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 126. Anal. Calcd for $C_{46}H_{56}F_3N_5O_6Pd_2S$: C, 51.31; H, 5.24; N, 6.50; S, 2.98. Found: C, 51.13; H, 4.86; N, 6.40; S, 3.19.

6b·H$_2$O: Yield: 97.0 mg, 93%. Mp: 225 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.95 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.16 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.15 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.01 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.97 (s, br, 1 H, H^b), 7.73 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 7.70 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.63 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.50 (m, 2 H, H^{3+5}), 7.43, 7.41 (AÁXX́ system, 4 H, CH, Tol, J_{AX} = 8 Hz), 7.34 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.18 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.14 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 6.80 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 2.57 (s, 3 H, Me, Tol), 1.56 (s, 2 H, H_2O), 1.50 (s, 9 H, CMe_3), 1.45 (s, 9 H, CMe_3), 1.42 (s, 9 H, CMe_3), 1.40 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 216.8 (C═O), 176.2 (C^7), 165.2 (C^c), 164.8 (C^c), 164.6 (C^c), 164.5 (C^c), 156.5 (C^a), 155.1 (C^a), 154.8 (C^a), 154.2 (C^6), 152.8 (C^a), 151.9 (C^e), 150.1 (C^e), 149.0 (C^e), 147.3 (C^e), 143.9 (*i*-C, Tol), 142.9 (C^1), 136.1 (C^3), 136.0 (*p*-C, Tol), 132.1 (C^2), 131.5 (C^4), 129.9 (*m*-C, Tol), 127.0 (*o*-C, Tol), 124.3 (C^d), 123.4 (C^d), 123.0 (C^d), 122.7 (C^d), 122.0 (C^5), 120.3 (C^b), 119.3 (C^b), 119.1 (C^b), 118.2 (C^b), 35.8 (CMe_3), 35.6 (CMe_3), 35.5 (CMe_3), 30.3 (CMe_3), 30.2 (CMe_3), 21.3 (Me, Tol). Single crystals of **6b·0.36H$_2$O** suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **6b** in CH_2Cl_2. IR (cm^{-1}): ν(CO), 1648, 1614. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 128. Anal. Calcd for $C_{52}H_{60}F_3N_5O_6Pd_2S$: C, 54.17; H, 5.25; N, 6.07; S, 2.78. Found: C, 54.30; H, 5.15; N, 6.16; S, 2.50.

Synthesis of [{Pd(t Bubpy)}$_2$L7]TfO (L7 = *μ-C,N,C,O*-{C$_6$H$_3$C(O)NR}-2-{C(CO$_2$Me)═C(CO$_2$Me)}-6, R = Me (7a), Tol (7b)). To a solution of the appropriate complex **4** (**4a·H$_2$O**, 62 mg, 0.06 mmol; **4b·H$_2$O**, 100.0 mg, 0.09 mmol) in CH_2Cl_2 (20 mL) was added $MeO_2CC{\equiv}CCO_2Me$ (for **7a**: 37 μL, 0.30 mmol; for **7b**: 22 μL, 0.18 mmol). The reaction mixture was stirred for 48 or 24 h, respectively, filtered through Celite, and concentrated to 1 mL. Et_2O (25 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (2 × 5 mL) and suction dried to give **7a·H$_2$O** or **7b·2H$_2$O** as a yellow powder.

7a·H$_2$O: Yield: 44.0 mg, 62%. Mp: 195 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.89 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.84 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.41 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.12 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.02 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.95 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.93 (br, 2 H, H^{b+d}), 7.64 (d, 1 H, H^d, $^3J_{HH}$ = 6 Hz), 7.51 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.42 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz), 6.92 (m, 2 H, H^{3+5}), 6.76 (br, t, 1 H, H^4), 3.84 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 3.45 (s, 3 H, Me), 1.69 (s, 2 H, H_2O), 1.43 (s, 9 H, CMe_3), 1.42 (s, 9 H, CMe_3), 1.38 (s, 9 H, CMe_3), 1.37 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 182.2 (C^7), 172.2 (CO$_2$), 165.5 (C^c), 164.9 (C^c), 164.7 (C^c + CO$_2$), 163.9 (C^c), 156.2 (C^a), 156.0 (C^{a+9}), 155.0 (C^e), 154.7 (C^a), 153.2 (C^a), 152.1 (C^6), 151.9 (C^e), 149.9 (C^e), 147.6 (C^e), 141.0 (C^1), 135.2 (C^8), 131.5 (C^2), 131.3 (C$^{3\text{ or }5}$), 128.3 (C$^{3\text{ or }5}$), 127.5 (C^4), 124.5 (C^d), 124.4 (C^d), 124.1 (C^d), 123.9 (C^d), 120.9 (C^b), 119.6 (C^b), 119.3 (C^b), 118.7 (C^b), 52.1 (OMe), 52.0 (OMe), 37.1 (Me), 35.8−35.7 (CMe_3), 30.4 (CMe_3), 30.3 (CMe_3), 30.2 (CMe_3), 30.1 (CMe_3). IR (cm^{-1}): ν(CO, CO$_2$Me), 1722; ν(CO), 1615. Λ_M (Ω^{-1}·cm^2·mol^{-1}):

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131.2. Anal. Calcd for $C_{51}H_{62}F_3N_5O_9Pd_2S$: C, 51.43; H, 5.25; N, 5.88; S, 2.69. Found: C, 51.32; H, 5.06; N, 6.05; S, 2.43.

7b·2H$_2$O: Yield: 102.0 mg, 88%. Mp: 214 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.91 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.05 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.02 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.92 (br, 2 H, H^b), 7.77 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.73 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 7.41 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.30 (d, 2 H, Tol, $^3J_{HH}$ = 8 Hz), 7.26−7.13 (m, 7 H, 2 CH, Tol, 2 H^d, H^{3+54+5}), 6.90 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 3.81 (s, 3 H, OMe), 3.71 (s, 3 H, OMe), 2.45 (s, 3 H, Me, Tol), 1.58 (s, 4 H, H_2O), 1.47 (s, 9 H, CMe_3), 1.38 (s, 27 H, CMe_3). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 181.7 (C^7), 172.4 (CO_2), 165.4 (C^c), 165.0 (C^c), 164.9 (C^c), 164.3 (C^c), 164.1 (CO_2), 156.8 (C^9), 156.3 (C^a), 156.0 (C^a), 154.9 (C^e), 154.7 (C^a), 153.1 (C^a), 152.6 (C^e), 150.6 (C^6), 149.0 (C^e), 147.9 (C^e), 143.8 (*i*-C, Tol), 140.1 (C^1), 136.9 (C^8), 135.9 (*p*-C, Tol), 131.2 (C$^{3\text{ or }5}$), 131.0 (C^2), 129.1 (C$^{3\text{ or }5}$), 128.7 (C^4), 124.6 (C^d), 123.9 (C^d), 123.4 (C^d), 123.0 (C^d), 120.0 (C^b), 119.4 (C^b), 119.0 (C^b), 118.8 (C^b), 52.0 (OMe), 35.8 (CMe_3), 35.7 (CMe_3), 35.6 (CMe_3), 35.5 (CMe_3), 30.2 (CMe_3), 30.1 (CMe_3), 21.2 (Me, Tol). IR (cm^{-1}): ν(CO, CO_2Me), 1702; ν(CO), 1615. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 130. Anal. Calcd for $C_{57}H_{68}F_3N_5O_{10}Pd_2S$: C, 53.27; H, 5.33; N, 5.45; S, 2.50. Found: C, 53.36; H, 5.26; N, 5.45; S, 2.30.

Synthesis of [{Pd(t Bubpy)}$_2$L8]TfO (L8 = *C,N,C,O*-{C$_6$H$_3$C(O)NR}-2-(C═NXy)-6, R = Me (8a), Tol (8b)). To a solution of the appropriate complex **4** (**4a·H$_2$O**: 250.0 mg, 0.24 mmol; **4b·H$_2$O**: 216.0 mg, 0.19 mmol) in CH_2Cl_2 (20 mL) was added XyNC (for **8a**: 31.8 mg, 0.24 mmol; for **8b**: 25.6 mg, 0.19 mmol). The reaction mixture was stirred for 30 min or 1 h, respectively, and filtered through Celite, and the solution was concentrated to 1 mL. Et_2O (for **8a**, 25 mL) or n-hexane (for **8b**, 25 mL) was added; the suspension was filtered. The solid was washed with Et_2O (**8a**, 2 × 5 mL) or n-hexane (**8b**, 2 × 5 mL) and suction dried to give **8a·H$_2$O** or **8b·2H$_2$O** as an orange powder.

8a·H$_2$O: Yield: 200.0 mg, 71%. Mp: 210 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (m, 2 H, H^e, $^3J_{HH}$ = 6 Hz), 8.76 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.16 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.13 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.92 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.84 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.81 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.78 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.64 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.18 (d, 2 H, H^{3+5}, $^3J_{HH}$ = 7 Hz), 7.12 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 6.88 (d, 2 H, *m*-CH, Xy, $^3J_{HH}$ = 7 Hz), 6.69 (t, 1 H, *p*-CH, Xy, $^3J_{HH}$ = 7 Hz), 3.56 (s, 3 H, Me), 2.57 (br, 6 H, Me, Xy), 1.58 (s, 2 H, H_2O), 1.49 (s, 18 H, CMe_3), 1.44 (s, 9 H, CMe_3), 1.36 (s, 9 H, CMe_3). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 179.2 (C^7), 164.8 (C^c), 163.8 (C^c), 156.5 (C^a), 155.2 (C^a), 154.6 (C^a), 152.6 (C^a), 152.5 (C^e), 152.0 (C^e), 151.7 (C^6), 150.1 (C^e), 147.9 (o-C, Xy), 147.5 (C^e), 142.8 (C^1), 138.3 (C=NXy), 132.3 (C^3), 130.3 (C^4), 128.1 (*m*-C, Xy), 127.3 (*i*-C, Xy), 124.4 (C^d), 124.2 (C^d), 124.1 (C^d), 124.0 (C^d), 122.7 (*p*-C, Xy), 122.2 (C^5), 120.0 (C^b), 119.4 (C^b), 118.7 (C^b), 118.2 (C^b), 36.8 (Me), 35.7 (CMe_3), 35.5 (CMe_3), 30.4 (CMe_3), 30.3 (CMe_3), 30.1 (CMe_3), 19.9 (Me, Xy). IR (cm^{-1}): ν(CO), 1612. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 121. Anal. Calcd for $C_{54}H_{65}F_3N_6O_5Pd_2S$: C, 54.96; H, 5.55; N, 7.12; S, 2.72. Found: C, 54.62; H, 5.39; N, 7.01; S, 3.06.

8b·2H$_2$O: Yield: 223.0 mg, 92%. Mp: 216 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.12 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 8.10 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.87 (s, br, 1 H, H^b), 7.82 (s, br, 1 H, H^b), 7.70 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.66 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 7.43 (d, 2 H, *o*-CH, Tol, $^3J_{HH}$ = 8 Hz), 7.36 (d, 2 H, *m*-CH, Tol, $^3J_{HH}$ = 8 Hz), 7.28 (d, 1 H, H^3, $^3J_{HH}$ = 8 Hz), 7.23 (d, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 7.19−7.12 (m, 4 H, 2 H^d, H^e, H^4), 6.88 (d, 2 H, *m*-CH, Xy, $^3J_{HH}$ = 8 Hz), 6.77 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 6.69 (t, 1 H, *p*-CH, Xy, $^3J_{HH}$ = 8 Hz), 2.55 (s, 9 H, Me, Xy, Tol), 1.58 (s, 4 H, H_2O), 1.49 (s, 9 H, CMe_3), 1.40 (s, 9 H, CMe_3), 1.39 (s, 9 H, CMe_3), 1.35 (s, 9 H, CMe_3). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 178.7 (C^7), 165.0 (C^c), 164.6 (C^c), 164.5 (C^c), 163.9 (C^c), 156.5 (C^a), 155.0 (C^a), 154.7 (C^a), 152.6 (C^a), 152.3 (C^e), 152.0 (C^e), 151.9 (C^6), 149.1 (C^e), 148.0 (*o*-C, Xy), 147.0 (C^e), 143.9 (*i*-C, Tol), 142.2 (C^1), 139.0 (C=NXy), 135.7 (*p*-C, Tol), 132.6 (C^3), 131.2 (C^4), 129.7 (*m*-C, Tol), 128.1 (*m*-C, Xy), 127.1 (*i*-C, Xy), 126.9 (*o*-C, Tol), 124.1 (C^d), 123.1 (C^d), 123.0 (C^d), 122.7 (*p*-C, Xy), 122.2 (C^d), 121.7 (C^5), 120.2 (C^b), 119.1 (C^b), 118.8 (C^b), 118.2 (C^b), 35.8 (CMe_3), 35.6 (CMe_3), 35.5 (CMe_3), 30.3 (CMe_3), 30.2 (CMe_3), 30.1 (CMe_3), 21.3 (Me, Tol), 19.8 (Me, Xy). IR (cm^{-1}): ν(CO), 1613. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 133.4. Anal. Calcd for $C_{60}H_{71}F_3N_6O_6Pd_2S$: C, 56.56; H, 5.62; N, 6.60; S, 2.52. Found: C, 56.36; H, 5.80; N, 6.50; S, 2.22.

Synthesis of [Pd(L9)(t Bubpy)] (L9 = *C,N*-{C$_6$H$_3$C(O)NTol}-2-{CH═CHC(O)Me}-6 (9b)). To a solution of **4b·H$_2$O** (100.0 mg, 0.09 mmol) in CH_2Cl_2 (15 mL) was added MeC(O)CH═CH_2 (14.6 μL, 0.18 mmol). The reaction mixture was stirred for 2 h and filtered through a short pad of $MgSO_4$. The solution was concentrated to 1 mL and Et_2O (25 mL) was added. The suspension was filtered, and the solid was recrystallized from CH_2Cl_2/pentane (1:25 mL) and suction dried to give **9b·1.5H$_2$O** as a yellow powder. Yield: 26 mg, 43%. Mp: 193 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.61 (d, 1 H, H^9, $^3J_{HH}$ = 17 Hz), 9.03 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 7.94 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.93 (d, 1 H, H^b, $^4J_{HH}$ = 2 Hz), 7.61 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.38 (m, 3 H, Tol + H^5, $^3J_{HH}$ = 8 Hz), 7.29 (d, 1 H, H^3, $^3J_{HH}$ = 8 Hz), 7.18 (d, 2 H, Tol, $^3J_{HH}$ = 8 Hz), 7.12 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.07 (dd, 1 H, H^d, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 6.62 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 6.51 (d, 1 H, H^8, $^3J_{HH}$ = 17 Hz), 2.44 (s, 3 H, Me), 2.37 (s, 3 H, Me, Tol), 1.57 (s, 3 H, H_2O), 1.47 (s, 9 H, CMe_3), 1.36 (s, 9 H, CMe_3). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 201.3 (C═O), 179.6 (C^7), 163.6 (C^c), 163.3 (C^c), 156.3 (C^a), 154.6 (C^a), 152.1 (C^e), 151.4 (C^6), 149.7 (C^e), 146.1 (*i*-C, Tol), 144.5 (C^9), 141.5 (C^1), 134.5 (C^2), 134.1 (*p*-C, Tol), 132.9 (C^3), 129.7 (*m*-C, Tol), 128.9 (C^8), 128.2 (*o*-C, Tol), 127.7 (C^4), 123.6 (C^d), 123.4 (C^5), 122.7 (C^d), 119.2 (C^b), 118.1 (C^b), 35.6 (CMe_3), 35.3 (CMe_3), 30.3 (CMe_3), 25.9 (Me), 21.2 (Me, Tol). IR (cm^{-1}): ν(CO), 1665, 1615. Anal. Calcd for $C_{36}H_{42}N_3O_{3.5}Pd$: C, 63.67; H, 6.23; N, 6.19. Found: C, 63.47; H, 6.18; N, 6.23.

Synthesis of [{Pd$_2$(t Bubpy)(CNXy)$_2$}L6]TfO (L6 = *μ-C,N,C,O*-{C$_6$H$_3$C(O)NMe}-2-(C═O)-6 (10a)). To a solution of **6a·H$_2$O** (125.0 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) was added XyNC (31 mg, 0.24 mmol). The reaction mixture was stirred for 30 min and filtered through Celite. The solution was concentrated to 1 mL, Et_2O (25 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (3 × 5 mL) and suction dried to give **10a·H$_2$O** as a yellow powder. Yield: 104.0 mg, 81%. Mp: 213 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.81 (d, 1 H, H^e, $^3J_{HH}$ = 6 Hz), 8.05 (br, 2 H, H^b), 7.81 (d, br, 1 H, H^d, $^3J_{HH}$ = 6 Hz), 7.61 (d, br, 1 H, H^d, $^3J_{HH}$ = 6 Hz), 7.54 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.37 (m, 4 H, H^5 + CH, Xy), 7.24 (m, 3 H, CH, Xy), 7.14 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 3.67 (s, 3 H, Me), 2.53 (s, 6 H, Me, Xy), 7.51 (s, 6 H, Me, Xy), 1.59 (s, 2 H, H_2O), 1.46 (s, 18 H, CMe_3). ^{13}C{^{1}H} APT NMR (100 MHz, $CDCl_3$): 217.8 (C═O), 177.1 (C^7), 165.2 (C^c), 164.5 (C^c), 155.2 (C^a), 153.9 (C^6), 152.7 (C^a), 150.2 (C^e), 147.5 (C^e), 143.2 (C^1), 140.4 (C^3), 135.8 (*o*-C, Xy), 135.6 (*o*-C, Xy), 133.5 (C^2), 131.5 (C^4), 131.1 (*p*-C, Xy), 130.9 (*p*-C, Xy), 128.4 (*m*-C, Xy), 128.1 (*m*-C, Xy), 124.1 (C^d), 123.4 (C^d), 122.5 (C^5), 119.1 (C^b), 118.3 (C^b), 40.2 (Me), 35.7 (CMe_3), 35.6 (CMe_3), 30.4 (CMe_3), 30.3 (CMe_3), 18.8 (Me, Xy). IR (cm^{-1}): ν(C≡N), 2170; ν(CO), 1643, 1612. Λ_M (Ω^{-1}·cm^2·mol^{-1}): 134.2. Anal. Calcd for $C_{46}H_{50}F_3N_5O_6Pd_2S$: C, 51.60; H, 4.71; N, 6.54; S, 2.99. Found: C, 51.92; H, 4.56; N, 6.89; S, 2.60.

Synthesis of [{Pd(t Bubpy)}$_2$L10]TfO (L10 = *μ-C,N,C,O*-{C$_6$H$_3$C(O)NTol}(C═O)-2-{C(CO$_2$Me)═C(CO$_2$Me)}-6 (11b)). A solution containing **7b·2H$_2$O** (72.0 mg, 0.06 mmol) in CH_2Cl_2 (15 mL) was stirred under a CO atmosphere for 6 h. The resulting suspension was filtered through Celite, the solution was concentrated to 1 mL, and Et_2O (25 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **11b·H$_2$O** as a yellow powder. Yield: 42.0 mg, 58%. Mp: 226 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (d, 4 H, H^e, $^3J_{HH}$ = 6 Hz), 8.81 (d, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 8.12 (s, 4 H, H^b), 7.70 (m, 5 H, 4 H^d + H^3), 7.61 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.19 (d, 2 H, *o*-CH, Tol, $^3J_{HH}$ = 8 Hz), 6.98 (d, 2 H, *m*-CH, Tol, $^3J_{HH}$ = 8 Hz), 3.88 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 2.27 (s, 3 H, Me, Tol), 1.58 (s, 2 H, H_2O), 1.44 (s, 36 H, CMe_3). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 213.6 (C═O), 173.5 (CO_2), 166.8 (C^7), 164.9 (C^c), 163.4 (CO_2), 154.2 (C^a), 148.5 (C^e), 145.3 (C^9), 140.1 (C^8), 138.3 (C^6), 137.9 (*p*-C, Tol), 136.2

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(C^5), 134.3 (C^4), 132.2 (C^2), 129.7 (C^1), 129.4 (*o*-C, Tol), 128.7 (*i*-C, Tol), 125.9 (*m*-C, Tol), 123.8 (C^d), 123.2 (C^3), 118.8 (C^b), 52.5 (O*Me*), 52.4 (O*Me*), 35.6 (CMe_3), 30.3 (CMe_3), 21.2 (Me, Tol). $^{13}C\{^1H\}$ APT NMR of complex **11** prepared using ^{13}CO (100 MHz, $CDCl_3$): δ 213.6 (C═O), 173.5 (CO_2), 166.8 (C^7), 164.9 (C^c), 163.4 (CO_2), 154.2 (C^a), 148.5 (C^e), 145.3 (C^9), 140.1 (C^8), 138.3 (d, C^6, $^3J_{CC}$ = 5 Hz), 137.9 (*p*-C, Tol), 136.2 (C^5), 134.2 (d, C^4, $^3J_{CC}$ = 5 Hz), 132.2 (d, C^2, $^1J_{CC}$ = 64 Hz), 129.7 (d, C^1, $^2J_{CC}$ = 3 Hz), 129.4 (*o*-C, Tol), 128.7 (*i*-C, Tol), 125.9 (*m*-C, Tol), 123.8 (C^d), 123.2 (d, C^3, $^2J_{CC}$ = 3 Hz), 118.8 (C^b), 52.5 (O*Me*), 52.4 (O*Me*), 35.6 (CMe_3), 30.3 (CMe_3), 21.2 (Me, Tol). IR (cm^{-1}): ν(C═O), 1819 (the sample prepared with ^{13}CO shows this band at 1778 cm^{-1}); $\nu_{assym}(CO_2)$, 1721, 1709; ν(C═OPd), 1615. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 129.5. Anal. Calcd for $C_{58}H_{66}F_3N_5O_{10}Pd_2S$: C, 53.79; H, 5.14; N, 5.41; S, 2.48. Found: C, 53.50; H, 4.98; N, 5.29; S, 2.40.

X-ray Crystallography. Numerical details of crystal data, data collection, and refinement are summarized in Table 1. The data for **6b·0.36H_2O** were recorded at 100 K on an Oxford Diffraction Nova diffractometer using mirror-focused Cu-*Kα* radiation in *ω*-scan mode. Absorption corrections were based on indexed faces. The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Treatment of hydrogen atoms: methyls as rigid groups allowed to rotated but not tip, other H using a riding model starting from calculated positions. *Special features of refinement:* The butyl group C57−60 is rotationally disordered over two positions. The triflate is also slightly disordered, with a small but definite (7% occupation) second site. A single significant peak of residual electron density was arbitrarily identified as a partially occupied water molecule and refined accordingly (but without hydrogens). An alternative would be the use of SQUEEZE to remove the unwanted electron density.[39] A major problem is the large difference peak of ca. 6 e/Å^3 near Pd2. This could conceivably be due to disorder, although no obvious model suggests itself, or twinning (although all reflections seemed to be well indexed), or residual absorption errors. A variety of data reduction and absorption correction options were used, but the peak remained.

Table 1. Crystal Data and Structure Refinement of Complex 6b·0.36H_2O

parameters	remarks
complex	**6b**·0.36H_2O
formula	$C_{52}H_{58.72}F_3N_5O_{5.36}Pd_2S$
fw	1141.38
temperature (K)	100(2)
crystal system	triclinic
space group	P(−1)
a (Å)	10.8315(5)
b (Å)	11.6081(5)
c (Å)	19.9343(8)
α (deg)	83.369(4)
β (deg)	89.530(4)
γ (deg)	86.773(4)
volume (Å^3)	2485.67(19)
Z	2
ρ_{calcd} (Mg m^{-3})	1.525
μ (Cu K_α) (mm^{-1})	6.765
F(000)	1167
crystal size (mm)	0.25 × 0.06 × 0.06
θ range (deg)	3.84 to 75.87
no. of rflns coll	66629
no. of indep rflns/R_{int}	10316/0.0373
transmission	0.687 and 0.244
restraints/parameters	81/674
goodness-of-fit on F^2	1.030
*R*1 ($I > 2\sigma(I)$)	0.0498
*wR*2 (all reflns)	0.1214
largest diff. peak/hole (e.Å^{-3})	6.213/−1.500

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for compound **6b·0.36H_2O**. 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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(24) [PdI{C_6H_3}{C(O)NHMe}-2-I-6}{^{t}Bubpy] (see Chart 2). Anal. Calcd for $C_{26}H_{28}I_2N_3OPd$: C, 41.16; H, 3.72; N, 5.54. Found: C, 41.43; H, 3.96; N, 5.19. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.42 (d, 1 H, H^e, $^3J_{HH}$ = 5.7 Hz), 7.93 (d, 1 H, H^b, $^4J_{HH}$ = 1.5 Hz), 7.92 (d, 1 H, H^b, $^4J_{HH}$ = 2.1 Hz), 7.60 (d, 1 H, H^e, $^3J_{HH}$ = 5.7 Hz), 7.51 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.9 Hz), 7.48 (dd, 1 H, H^d, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.1 Hz), 7.45 (dd, 1 H, H3 or H5, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.9 Hz), 7.38 (dd, 1 H, H^d, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.1 Hz), 6.68 (t, 1 H, H4, $^3J_{HH}$ = 7.8 Hz), 6.48 (q, 1 H, NH, $^3J_{HH}$ = 4.9 Hz), 2.92 (d, 3 H, Me, $^3J_{HH}$ = 4.9 Hz), 1.43 (s, 9 H, *t*-Bu), 1.37 (s, 9 H, *t*-Bu).
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(39) A referee recommended this option, but we can see little advantage in it.