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820Reactivity towards nitriles, cyanamides, and
carbodiimides of palladium complexes derived
from benzyl alcohol. Synthesis of a mixed Pd₂Ag
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The chelate complex [Pd(κ^2 -C,O-C₆H₄CH₂O-2)(bpy)] (**II**) reacts with acetonitrile, cyanamides, or carbodiimides, in the presence of AgOTf (1 : 5 : 1 molar ratio) and residual water, to form complexes [Pd(κ^2 -C, N-C₆H₄{CH₂OC(=NX)Y}-2)(bpy)](OTf), where X = H, Y = Me (**1**), NMe₂ (**2a**), NEt₂ (**2b**), X = R, Y = NHR (R = ⁱPr (**3a**), Tol (**3b**)), as a result of the insertion of the unsaturated reagent into the O–Pd bond of **II** and the protonation of one of the N atoms. In the absence of AgOTf the reaction of **II** with TolN=C=NTol (Tol = *p*-Tolyl) results in the formation of the neutral complex [Pd(κ^2 -C,N-C₆H₄{CH₂OC(=NTol)NTol}-2)(bpy)] (**4**). Complexes **3b** and **4** can be interconverted by deprotonation (**3b** + KO^tBu) or protonation (**4** + KOTf + HOTf) reactions. When the reaction of **II** with TolN=C=NTol in the presence of AgOTf is carried out in a 1 : 1 : 1 stoichiometric ratio, or for a short period of time, a mixture of **3b** and a mixed heterometallic Ag₂Pd complex **5** is obtained (**5** = [Ag(N-**4**)₂](OTf)). Complex **5** is the major product when the AgOTf is added before the carbodiimide, and the reaction is stopped immediately. **5** can also be obtained by reaction of **4** with 0.5 equiv. of AgOTf. When complex [PdII(C₆H₄CH₂OH-2)(bpy)] (**I**) reacts with ⁱPrN=C=NⁱPr in the presence of TlOTf, instead of AgOTf, a ca. 1 : 1 mixture of **3a** and [Pd(κ^2 -O, N-OCH₂{C₆H₄{C(=NHⁱPr)NⁱPr}-2})(bpy)](OTf) (**6**) forms. Complex **6** is the result of the insertion of the carbodiimide into the C–Pd bond. Complexes **1–6** have been extensively characterized by NMR spectroscopy, and the crystal structures of **2a**, **3a**, and **5**·2.5CHCl₃·0.5Et₂O have been determined by X-ray diffraction studies.

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Introduction

The importance of Pd(II) aryl complexes in organometallic chemistry derives mainly from their involvement in carbon–carbon and carbon–heteroatom bond-forming reactions.¹ Their reactivity with unsaturated molecules often results in the insertion of these molecules into the aryl–Pd bonds, forming new ligands or, after decomposition reactions, organic com-

pounds.² A valuable synthetic tool that we have extensively explored is the incorporation of a substituent at the *ortho* position of the aryl group,^{3–7} as this substituent can become involved in the reactivity with the Pd centre and the organic substrate in many interesting ways.^{3–6,8–12} Very often, the *ortho*-substitution also results in the formation of cyclopalladated complexes.^{3,4,7,9,10–12}

Following this line of research, our group has previously investigated the reactivity of *ortho*-palladated phenol derivatives.^{6,10–13} Their reactions with CO, isocyanides, alkenes, alkynes, and allenes did not involve the OH group in the *ortho* position.^{6,13} In contrast, the electron-donating ability of this group played a crucial role in the reactivity towards nitriles,^{10,12} carbodiimides,^{11,12} cyanamides,¹² and isothiocyanates,¹² which afforded the first examples of the insertion^{10–12} of these molecules into a C–M bond of a late transition metal. These insertion reactions occurred together with the deprotonation and coordination of the hydroxyl oxygen to Pd, forming 6-membered chelate rings (Chart 1).^{10–12} With carbodiimides,¹¹

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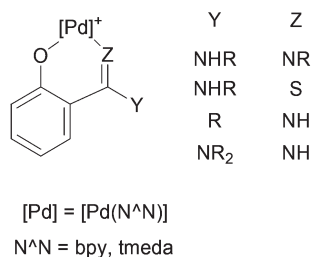


Chart 1

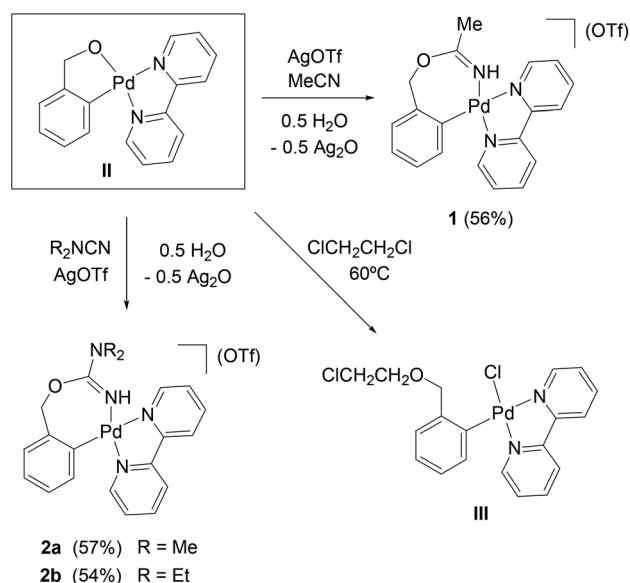
the addition of the O–H group to one of the C=N bonds of the substrate, together with the coordination of the other N to the Pd atom, was an alternative reaction to the insertion.¹¹

We have recently extended this research to *ortho*-palladated hydroxymethylphenyl complexes,¹⁴ where the methylene link in the alcoholic substituent might significantly influence the reactivity towards unsaturated molecules. There are very few reports of 2-hydroxymethylphenyl palladium complexes¹⁵ or oxapalladacycles derived from them.¹⁶ These compounds have been used as precatalysts in Heck and cross-coupling reactions,¹⁷ but their reactivity towards unsaturated molecules had not been systematically investigated, with a single report on a reaction of a palladacycle with *tert*-butyl isocyanide, yielding an imidate, while the reaction of the same compound with maleic anhydride resulted in the coordination of the olefin to the Pd(II) centre.¹⁶ In our recent work¹⁴ we synthesized the complex [PdI(C₆H₄CH₂OH-2)(bpy)] (**I**) and investigated its reactivity towards alkynes, alkenes, nitriles, cyanamides, allenes, and carbon monoxide, which did not result in clean insertion (C–Pd bond) or addition (O–H bond) reactions.¹⁴ Only the reaction of **I** with X_yNC gave a clean insertion product, *trans*-[PdI{C(=NX_y)C₆H₄CH₂OH-2}(CNX_y)₂].¹⁴ By deprotonation of complex **I** we prepared the chelate complex [Pd{κ²-C,O-C₆H₄(CH₂O)-2}(bpy)] (**II**), which displayed an interesting reactivity towards primary alkyl halides, *via* a nucleophilic attack of the coordinated oxygen at the alkyl group of the halide.¹⁴ We have now extended our research to the chelate complex **II**, which, in the presence of AgOTf, reacts with acetonitrile, cyanamides, and carbodiimides to give novel complexes containing a [Pd{κ²-C,N-C₆H₄{CH₂OC(=NX)Y}-2}] chelate ring, resulting, unexpectedly, from insertion reactions of the C≡N or C=N bonds into the O–Pd bond of **II**. We have not found examples for such a chelate structure with any metal. The Ag⁺ cations play a key role in these reactions, which is also an interesting observation. An insertion reaction of a carbodiimide into the aryl–Pd bond of **I** is also described, as is a mixed-metal Pd₂Ag complex, which has been characterized by X-ray crystallography. Other heterometallic Pd₂Ag¹⁸ or Pd₂Ag₂¹⁹ complexes have been described in the literature, but their structures differ greatly from the one reported in this work. Thus, the reactivity that we report in this paper differs greatly from the reactions described for complexes **I** and **II** in our previous work.¹⁴

Results and discussion

Reactions with nitriles and cyanamides

The chelate complex [Pd{κ²-C,O-C₆H₄CH₂O-2}(bpy)] (**II**) reacts with acetonitrile and AgOTf (1 : 5 : 1 molar ratio, CH₂Cl₂), in the presence of residual water, to form [Pd{κ²-C,N-C₆H₄{CH₂OC(=NH)Me}-2}(bpy)](OTf) (**1**, Scheme 1), the result of the insertion of the nitrile into the O–Pd bond of **II**, and the protonation of the N by the residual water. Complex **II** reacts similarly with the cyanamides R₂NC≡N (R = Me, Et) and AgOTf to form [Pd{κ²-C,N-C₆H₄{CH₂OC(=NH)NR₂}-2}(bpy)](OTf) (R = Me (**2a**), Et (**2b**), Scheme 1). The presence of Ag⁺ is a requirement in these reactions (otherwise there is no reaction or, with TfOTf, mixtures of compounds are obtained). There are two possible explanations for this: either the Ag⁺ forms *in situ* a complex with the ligands, increasing the electrophilicity of the unsaturated carbon atom, and thus favouring the nucleophilic attack of the O atom of **II**; or the Ag⁺ coordinates to the O atom, activating the O–Pd bond in **II** and favouring the coordination of the ligands to Pd, which would in turn activate them towards the nucleophilic attack of the O. In any case, this influence of added Ag⁺ on the reactivity of an aryl-palladium complex (without halide or pseudohalide ligands), towards unsaturated molecules, controlling the site of the insertion reaction, can be a very useful synthetic tool. Although nucleophilic reactions at coordinated nitriles have been thoroughly investigated,²⁰ the reactions reported here show the interesting feature that the initially uncoordinated nitrile or cyanamide is activated *in situ* by one of the two proposed mechanisms (coordination to Ag⁺ or to the Pd centre) and then attacked by an (initially) chelating O atom. Seven-membered C₃–Pd–N=C–O chelate rings such as those resulting in these reactions (in **1** and **2a,b**) have not been described before for any metal.



Scheme 1



We have not been able to achieve the insertion of nitriles or cyanamides into the C–Pd bond of complexes **I** or **II**. This negative result contrasts with the successful insertion reactions that we observed with the related complexes [PdI(C₆H₄Y-2)(tmeda)] (Y = OH, NH₂, N[^]N = tmeda, bpy, tbbpy), and a wide variety of nitriles^{10,12} and cyanamides.¹² In those reactions we proposed that the electron-donating OH or NH₂ group in *ortho* position would play a key role in the mechanism, *via* delocalization of a negative charge on the aryl *ipso* carbon.^{10,12} That mechanistic proposal would be now supported by the failure of these insertion reactions with the complexes **I** and **II**, for which the CH₂ link between the OH function and the aryl ring prevents the delocalization of electron density.

In one of our attempts to react complex **II** with nitriles, we used 1,2-dichloroethane as solvent and heated to 60 °C. We obtained then the complex [PdCl{C₆H₄(CH₂OCH₂CH₂Cl)-2-(bpy)}] (**III**), which is the result of the nucleophilic attack of the oxygen in **II** at a CH₂ group of the 1,2-dichloroethane solvent. Complex **III** has been characterized by X-ray diffraction studies (see the ESI†), but we have not been able to purify and fully characterize it. We have described similar reactions of **II** with alkyl halides (bromides and iodides) in a previous paper.¹⁴

Reactions with carbodiimides

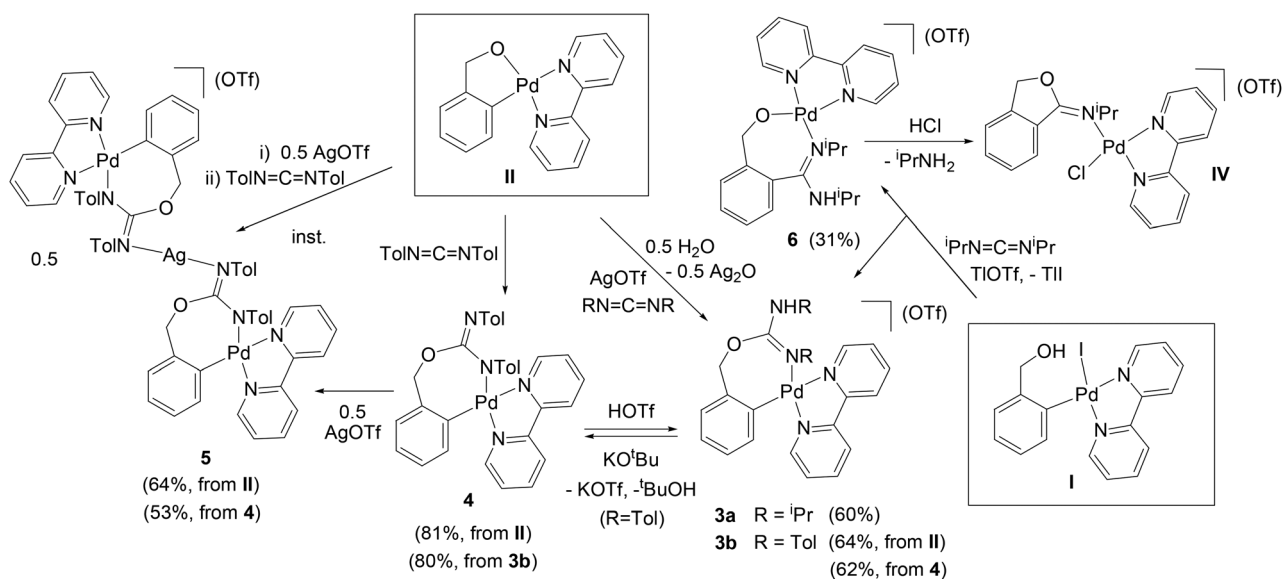
Complex **II** reacts with the carbodiimides RN=C=NR (R = ⁱPr, Tol) and AgOTf (1 : 5 : 1 molar ratio, CH₂Cl₂) in the presence of residual water, to form [Pd{κ²-C,N-C₆H₄{CH₂OC(=NR)NHR}-2-(bpy)}](OTf) (R = ⁱPr (**3a**), Tol (**3b**), Scheme 2) which, similarly to **1** and **2a,b**, are the result of the insertion of the organic products into the O–Pd bond of **II**.

When these reactions were performed in the absence of AgOTf, however, the results differed for the two carbodiimides

investigated. With ⁱPrN=C=NⁱPr there was no reaction, whereas with TolN=C=NTol the reaction in the absence of AgOTf resulted in the formation of [Pd{κ²-C,N-C₆H₄{CH₂OC(=NTol)NTol}-2-(bpy)}] (**4**, Scheme 2), which is the conjugate base of **3b**. These results suggest that the TolN=C=NTol is the only reactant investigated in this work that is electrophilic enough to undergo nucleophilic attack by the O atom in **II**, without the need of activation by Ag⁺. Complex **4** has a characteristic red color, and it forms after only 5 min in the reaction with either one equivalent or excess of the carbodiimide. It is partially soluble in Et₂O.

By deprotonation of the ionic complex **3b** with KO^tBu, it is possible to obtain the neutral complex **4** and, *vice versa*, by reaction of **4** with KOTf and HOTf complex **3b** is obtained. In this reaction it is necessary to add the KOTf first and then the HOTf after a few minutes, as otherwise a different product forms, which could not be characterized. Thus, the K⁺ ion seems to stabilize the reaction intermediate, probably by coordinating to the O atom. The deprotonation of the ionic complex **3a** (R = ⁱPr) with KO^tBu gives a red neutral complex similar to **4**, but it re-protonates very easily, so that it could not be characterized. Clearly, the Tol groups in **4** play a very important role in the stability of this complex, most probably through resonance effects.

Curiously, when the reaction of **II** with AgOTf and a 5-fold excess of TolN=C=NTol was stopped after only 2 hours, or when it was performed in a *ca.* 1 : 1 : 1 stoichiometric ratio (overnight), a mixture of **3b** and a different product formed (in *ca.* 1.9 : 1 or 1.4 : 1 ratio, respectively). This product was identified by X-ray crystallography (see below) as an ionic trinuclear complex consisting of two molecules of **4** coordinated through N to one atom of Ag (complex **5** = [Ag(N-**4**)₂](OTf), Scheme 2). The structure of **5** differs greatly from other heterometallic Pd₂Ag¹⁸ or Pd₂Ag₂¹⁹ complexes found in



Scheme 2



the literature. With the carbodiimide $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ we did not observe a similar reactivity. The formation of complex **5** is favoured by a shorter reaction time and a smaller amount of carbodiimide, and we have also observed that it is strongly influenced by the order of addition of the reactants. Thus, in the reactions of **II** with one equivalent of $\text{ToIN}=\text{C}=\text{NTol}$ and AgOTf , if the carbodiimide is added first and then the AgOTf , the major product is **3b** (even if the reaction is stopped immediately), although it forms together with a variable amount of **5** (between *ca.* 5–10%). In contrast, if AgOTf is added first, followed by one equivalent of $\text{ToIN}=\text{C}=\text{NTol}$, and the reaction is stopped immediately, the trinuclear complex **5** is the major product, with only *ca.* 20% of **3b** (this amount increases if a longer reaction time is allowed). Complex **5** can then be separated from **3b** by exploiting differences in solubility (see the Experimental section). From these observations we suggest that the trinuclear complex **5** forms by the nucleophilic attack of **II** on a $[\text{Ag}(\text{ToIN}=\text{C}=\text{NTol})_2]^+$ intermediate, and then it reacts with residual water, losing the Ag atom and forming two molecules of **3b**. This “decomposition” to **3b** would be favoured by an excess of carbodiimide, which would coordinate to the Ag facilitating the rupture of **5** (in an overnight reaction with a 5-fold excess of $\text{ToIN}=\text{C}=\text{NTol}$, only **3b** is detected, while the same reaction with only one equivalent of $\text{ToIN}=\text{C}=\text{NTol}$ gives a mixture of **3b** and **5** in *ca.* 1:0.8 ratio). In contrast, when the carbodiimide is added before the AgOTf , it would immediately react with **II**, forming, presumably, first the neutral complex **4** and then, upon addition of the AgOTf , the ionic complex **3b**, so that **5** would only be a minor product. We have tried to obtain complex **5** by reaction of **4** with 0.5 equivalents of AgOTf and, after 2 hours in CH_2Cl_2 , the major product of this reaction was indeed the trinuclear complex **5**, together with *ca.* 20% of **3b**. Thus, it seems that complex **4** can be transformed in the presence of AgOTf to both **3b** or **5**, and the favoured product is determined by the reaction conditions. To summarize: to obtain **3b** the best method is the reaction of **II** with AgOTf and $\text{ToIN}=\text{C}=\text{NTol}$ in a 1:1:5 ratio overnight (the order of addition of the reactants is not important), while for **5** the best method is to carry out the reaction in a 1:0.8:1 stoichiometric ratio (better than the theoretical 1:0.5:1 ratio), adding the AgOTf (to a solution of **II**) before the carbodiimide, and stopping the reaction immediately by evaporation of the solvent. **5** then needs to be separated from **3b** by solubility difference (see the Experimental section).

Complexes **3a,b** also form in the reaction of the 2-hydroxy-methylphenyl Pd complex $[\text{PdI}(\text{C}_6\text{H}_4\text{CH}_2\text{OH}-2)(\text{bpy})]$ (**I**) with the corresponding carbodiimides and AgOTf , but with a much lower yield and purity, so that these reactions have not been pursued. Additionally, when complex **I** reacts with $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ in the presence of TIOTf , instead of AgOTf , a *ca.* 1:1 mixture of two complexes forms: one is again **3a** (which is now the result of the addition of the OH group to the carbodiimide and the coordination of one of the N atoms to Pd) and the other is $[\text{Pd}\{\kappa^2\text{-O}, N\text{-OCH}_2\{\text{C}_6\text{H}_4\{\text{C}(=\text{N}^i\text{Pr})\text{NH}^i\text{Pr}-2\}\}(\text{bpy})\}(\text{OTf})]$ (**6**, Scheme 2), which is the result of the insertion of the

carbodiimide into the C–Pd bond. We have not been able to obtain complex **6** independently of **3a**, even by varying the amount of carbodiimide or the reaction time, but we have been able to separate it from **3a** by preparative TLC on alumina (see the Experimental section). Additionally, from a CDCl_3 solution of **6** we obtained single crystals, the X-ray structure of which showed them to be the unexpected complex **IV**, apparently formed by reaction of **6** with the residual HCl of the deuterated solvent (the attack of HCl on **6** would promote the intramolecular attack of the O on the C=N group of the inserted carbodiimide, the breaking of the C–N and Pd–N bonds and the formation of a new Pd–N bond). Unfortunately, despite much effort we have not been able to reproduce the synthesis of this complex, but we include the X-ray data in the ESI.† Finally, the reaction of **I** with $\text{ToIN}=\text{C}=\text{NTol}$ and TIOTf instead of AgOTf resulted in the formation of a complex that is probably an insertion product similar to **6** but that was not pure enough to be characterized. The (relatively) cleaner reactivity of the carbodiimides with **I** and TIOTf , compared to the similar reactions with acetonitrile and cyanamides, which gave intractable mixtures, is probably attributable to a combination of electronic and steric effects. The greater steric hindrance in the carbodiimides, together with their appreciable dipole moments,²¹ would favour one (or two) major reaction pathways while hindering other secondary reactions.

NMR and IR data

All the complexes reported in this paper have been extensively studied by NMR spectroscopy (1D and 2D experiments), allowing an almost full assignment of the ^1H and ^{13}C resonances. To facilitate comparison, the data are collected in Table S.1 in the ESI,† together with a more extended discussion.

For the complexes **1–5**, the insertion of the organic molecules ($\text{MeC}\equiv\text{N}$, $\text{R}_2\text{NC}\equiv\text{N}$, or $\text{RN}=\text{C}=\text{NR}$) into the O–Pd bond, and not the C–Pd bond, is confirmed by the three-bond correlation between the inserted iminic C=N carbon and the methylenic CH_2OH protons, observed in the ^1H , ^{13}C -HMBC spectra. For complex **6**, in contrast, a three-bond correlation between the iminic C=N carbon and the *o*-H of the aryl ligand is observed. Other NOE and correlation data confirm these structures and allow the assignment of the different groups within the molecules (see the ESI†). For **3a,b** and **6**, the position of the proton at the uncoordinated N is also confirmed by the ^1H -NOESY and ^1H , ^{13}C -HMBC spectra, and is similar to that observed in the related complexes resulting from the reaction of carbodiimides with *ortho*-palladated phenol derivatives.^{11,12} The C=NH proton in complex **1** resonates at much higher frequency (δ 8.45 ppm) than in **2a,b** (δ 4.81 and 4.76 ppm), for which the partial release of the lone pair from the NR_2 group results in a resonance form with a negative charge at the NH group. This electronic delocalization along the $\text{R}_2\text{N}-\text{C}=\text{NH}$ bonds in **2a,b** is confirmed by the X-ray diffraction study of **2a**, which shows a shortening of the single N–C bond and a lengthening of the double C=N bond, relative to other values (see below). In the complexes derived from



cyanamides, the three C=NH ^1H NMR chemical shifts are rather similar: δ 5.57 ppm for **3a**, 6.49 ppm for **3b** and 6.39 ppm for **6**.

The neutral complex **4** shows a fluxional behaviour within the chelate ring, which results in the broadening of one of the methylenic ^1H resonances, and also of the ^1H resonances of the more external tolyl group. These resonances sharpen at low temperature, but the ^1H chemical shifts do not change significantly, so that the room temperature data are given in Table S.1† and in the Experimental section. The ^{13}C NMR data, however, are given for 213 K, because at room temperature the S/N ratio of some resonances is too low.

In the mixed trinuclear Pd_2Ag complex **5**, the two halves of the molecule are equivalent in solution (not in the solid state, see below), as only one set of ^1H and ^{13}C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened ^1H and ^{13}C resonances, indicating that the rotation around that Tol-N bond is hindered by the steric crowding in the molecule.

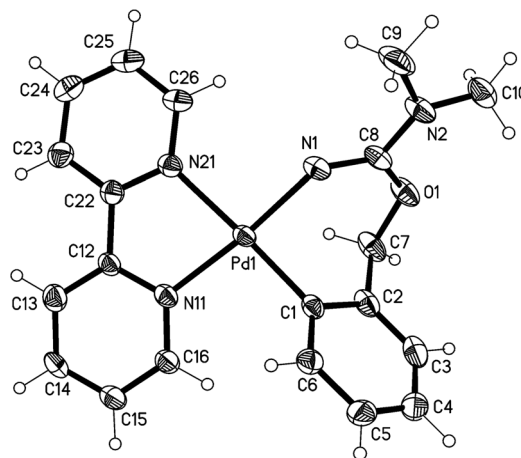
The IR bands of the C=N bonds in **1**, **2a,b**, **3a,b**, and **6** all appear in the range 1599–1635 cm^{-1} . For complex **4**, where the C=N bond is uncoordinated, the corresponding IR band appears at higher frequency, 1660 cm^{-1} . In the related complex **5** ($5 = [\text{Ag}(\text{N-4})_2](\text{OTf})$), however, the coordination of the C=N bond to Ag shifts the IR band again to lower frequency, 1600 cm^{-1} . The IR bands of the N–H bonds in **1**, **2a,b**, **3a,b**, and **6** are observed in the range 3213–3401 cm^{-1} .

X-ray structure determinations

The crystal structures of the complexes **2a** (Fig. 1), **3a** (Fig. 2), and **5** (Fig. 3; only one of the two independent cations is shown), have been determined by X-ray diffraction studies (see Table S.2† for Experimental details). The crystal structures of **III** and **IV** are described in the ESI† together with details of disordered solvent and anions.

The structures of **2a**, **3a**, and **5** show somewhat distorted square planar coordination around the Pd atoms. Mean deviations from the best plane through Pd and the four donor atoms are 0.01 Å for **2a**, 0.02 Å for **3a**, and 0.03 (Pd1), 0.14 (Pd2), 0.04 (Pd1'), and 0.01 (Pd2') Å for **5**. The PdN2C2 chelate rings are all essentially planar and also coplanar with the Pd coordination planes (maximum interplanar angle 8°). The seven-membered rings in **2a** and **3a** have similar conformations, with the five atoms, Pd, N1, O1, C7, and C8 approximately coplanar, and C1 and C2 lying out of the plane to the same side. For **5**, however, all four seven-membered rings have a different form in which C1, C2, N1, and C7 are coplanar, with Pd, O1, and C8 lying out of the plane to the same side.

The Pd–C bond distances for **2a** and **3a** are 1.981(3) Å and 1.9716(15) Å, respectively, both in the range expected for aryl ligands *trans* to N (*ca.* 1.97–2.00 Å).^{4,11,14,22} The two Pd–C bond distances for **5** are slightly longer, 2.014(7) Å for Pd(1)–C(1) and 2.009 Å for Pd(2)–C(31). The Pd–N (*trans* to aryl) bond distances are very similar for the three complexes (between 2.115(5) and 2.118(2) Å), and they are longer than the Pd–N (*trans* to N) bond distances (in the range 2.026(2)–2.070(5) Å), as expected





according to literature procedures. Other products were obtained from commercial sources and used without further purifications.

Synthesis of $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_4\{\text{CH}_2\text{OC(=NH)Me}\}\text{-2}\}(\text{bpy})](\text{OTf})$ (**1**)

Acetonitrile (55 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of $[\text{Pd}(\kappa^2\text{-C,O-C}_6\text{H}_4\text{CH}_2\text{O-2})(\text{bpy})]$ (**II**)¹⁴ (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2 . The mixture was stirred in the dark for 16 h at room temperature (the colour darkened and a precipitate formed). It was then filtered over Celite and the resulting yellow solution was concentrated *in vacuo* to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried *in vacuo* to give **1** as a yellow solid, which is soluble in CH_2Cl_2 , CHCl_3 , and acetone. Yield: 85 mg (56%). Mp: 99 °C. Λ_{M} (acetone): $115 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{S=O})$ 1029, 1279, $\nu(\text{C=N})$ 1635, $\nu(\text{NH})$ 3213. ^1H NMR (400 MHz, CDCl_3): 8.89 (ddd, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 2$ Hz, $^5J_{\text{HH}} = 1$ Hz, 1H, H16' bpy), 8.45 (br s, 1H, NH), 8.37 (ddd, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 2$ Hz, $^5J_{\text{HH}} = 1$ Hz, 1H, H16 bpy), 8.25 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13 bpy), 8.17 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13' bpy), 8.11 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 2$ Hz, 1H, H14' bpy), 8.07 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 2$ Hz, 1H, H14 bpy), 7.82 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15' bpy), 7.43 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15 bpy), 7.31–7.27 (m, 1H, H5 aryl), 7.22 (d, $^3J_{\text{HH}} = 7$ Hz, 1H, H6 aryl), 7.15–7.11 (m, 2H, H3,4 aryl), 6.60 and 5.05 (AB system, $^2J_{\text{HH}} = 11$ Hz, 2H, CH_2), 2.30 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): 175.1 (C=NH), 157.0 (C12 bpy), 152.6 (C12' bpy), 152.0 (C1 aryl), 151.9 (CH16 bpy), 151.0 (CH16' bpy), 140.09 and 140.06 (CH14, 14' bpy), 139.4 (C2 aryl), 134.7 (CH6 aryl), 130.6 (CH5 aryl), 128.3 (CH15' bpy), 127.6 (CH3 aryl), 126.7 (CH15 bpy), 125.4 (CH4 aryl), 123.0 (CH13 bpy), 122.1 (CH13' bpy), 121.0 (q, $^1J_{\text{CF}} = 320$ Hz, OTf), 72.2 (CH_2), 23.6 (Me). Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}_3\text{O}_4\text{PdS}$: C, 42.91; H, 3.24; N, 7.51; S, 5.73. Found: C, 42.58; H, 2.92; N, 7.19; S, 5.42.

Synthesis of $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_4\{\text{CH}_2\text{OC(=NH)NMe}_2\}\text{-2}\}(\text{bpy})](\text{OTf})$ (**2a**)

Dimethylcyanamide (95 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of **II**¹⁴ (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2 . The mixture was stirred in the dark for 16 h at room temperature (the color darkened and a precipitate formed). It was then filtered over Celite and the resulting pale yellow solution was concentrated *in vacuo* to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried *in vacuo* to give **2a** as a pale yellow solid, which is soluble in CH_2Cl_2 , CHCl_3 , and acetone. Yield: 91 mg (57%). Mp: 182 °C (dec). Λ_{M} (acetone): $125 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{S=O})$ 1029, 1275, $\nu(\text{C=N})$ 1602, $\nu(\text{NH})$ 3306. ^1H NMR (600 MHz, CDCl_3): 8.65 (ddd, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 2$ Hz, $^5J_{\text{HH}} = 1$ Hz, 1H, H16' bpy), 8.42 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13 bpy), 8.35 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13' bpy), 8.32 (ddd, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 2$ Hz, $^5J_{\text{HH}} = 1$ Hz, 1H, H16 bpy), 8.14 (td, $^3J_{\text{HH}} =$

8 Hz, $^4J_{\text{HH}} = 2$ Hz, 1H, H14 bpy), 8.08 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 2$ Hz, 1H, H14' bpy), 7.79 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15' bpy), 7.39 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15 bpy), 7.29–7.26 (m, 2H, H5,6 aryl), 7.16–7.10 (m, 2H, H3,4 aryl), 6.62 and 5.10 (AB system, $^2J_{\text{HH}} = 11$ Hz, 2H, CH_2), 4.81 (s, 1H, NH), 3.00 (s, 6H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, CDCl_3): 161.3 (C=NH), 157.0 (C12 bpy), 153.13 and 153.11 (C12' bpy and C1 aryl), 151.6 (CH16 bpy), 149.1 (CH16' bpy), 140.5 (CH14' bpy), 140.3 (CH14 bpy), 139.3 (C2 aryl), 134.9 (CH6 aryl), 130.3 (CH5 aryl), 127.9 (CH15' bpy), 127.6 (CH3 aryl), 126.7 (CH15 bpy), 125.1 (CH4 aryl), 123.8 (CH13 bpy), 123.0 (CH13' bpy), 121.0 (q, $^1J_{\text{CF}} = 320$ Hz, OTf), 73.2 (CH_2), 38.0 (Me). Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{N}_4\text{O}_4\text{PdS}$: C, 42.83; H, 3.59; N, 9.51; S, 5.44. Found: C, 42.81; H, 3.60; N, 9.43; S, 5.12. Single crystals of **2a** were grown by liquid diffusion of Et_2O into a solution of **2a** in CH_2Cl_2 .

Synthesis of $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_4\{\text{CH}_2\text{OC(=NH)NET}_2\}\text{-2}\}(\text{bpy})](\text{OTf})$ (**2b**)

Diethylcyanamide (133 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of **II**¹⁴ (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2 . The mixture was stirred in the dark for 16 h at room temperature (the color darkened and a precipitate formed). It was then filtered over Celite and the resulting pale yellow solution was concentrated *in vacuo* to a volume of ca. 1 mL. Et_2O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et_2O (3×5 mL), and dried *in vacuo* to give **2b** as a pale yellow solid, which is soluble in CH_2Cl_2 , CHCl_3 , and acetone. Yield: 100 mg (54%). Mp: 104 °C. Λ_{M} (acetone): $123 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{S=O})$ 1030, 1277, $\nu(\text{C=N})$ 1599, $\nu(\text{NH})$ 3321. ^1H NMR (400 MHz, CDCl_3): 8.58 (dd, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H16' bpy), 8.44 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13 bpy), 8.39 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H13' bpy), 8.32 (dd, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H16 bpy), 8.15 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H14 bpy), 8.13 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H14' bpy), 7.78 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15' bpy), 7.39 (ddd, $^3J_{\text{HH}} = 8$ Hz, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15 bpy), 7.29–7.26 (m, 2H, H5,6 aryl), 7.14–7.12 (m, 2H, H3,4 aryl), 6.66 and 5.11 (AB system, $^2J_{\text{HH}} = 11$ Hz, 2H, CH_2O), 4.76 (s, 1H, NH), 3.33 (m, 4H, CH_2CH_3), 1.13 (t, $^3J_{\text{HH}} = 7$ Hz, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): 160.2 (C=NH), 157.0 (C12 bpy), 153.2 (C12' bpy), 153.0 (C1 aryl), 151.6 (CH16 bpy), 148.9 (CH16' bpy), 140.6 (CH14' bpy), 140.3 (CH14 bpy), 139.1 (C2 aryl), 134.9 (CH6 aryl), 130.2 (CH5 aryl), 127.7 (CH15' bpy), 127.4 (CH3 aryl), 126.7 (CH15 bpy), 125.0 (CH4 aryl), 123.9 (CH13 bpy), 123.2 (CH13' bpy), 121.0 (q, $^1J_{\text{CF}} = 321$ Hz, OTf), 73.1 (CH_2O), 43.3 (CH_2CH_3), 13.6 (CH_2CH_3). Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{F}_3\text{N}_4\text{O}_4\text{PdS}$: C, 44.78; H, 4.08; N, 9.08; S, 5.20. Found: C, 44.95; H, 4.22; N, 8.85; S, 4.89.

Synthesis of $[\text{Pd}\{\kappa^2\text{-C,N-C}_6\text{H}_4\{\text{CH}_2\text{OC(=N}^i\text{Pr)NH}^i\text{Pr}\}\text{-2}\}(\text{bpy})](\text{OTf})$ (**3a**)

1,3-Diisopropylcarbodiimide (170 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of **II**¹⁴ (100 mg, 0.27 mmol) in CH_2Cl_2 (20 mL) under N_2 . The mixture was



stirred in the dark for 16 h at room temperature. It was then filtered over Celite and the resulting yellow solution was concentrated *in vacuo* to a volume of *ca.* 1 mL. Et₂O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give **3a** as a pale yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 104 mg (60%). Mp: 195 °C. Λ_M (acetone): 140 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm⁻¹): $\nu(\text{S=O})$ 1028, 1276, $\nu(\text{C=N})$ 1611, $\nu(\text{NH})$ 3354. ¹H NMR (400 MHz, CDCl₃): 8.68 (dd, ³J_{HH} = 5 Hz, ⁴J_{HH} = 1 Hz, 1H, H16' bpy), 8.52 (dd, ³J_{HH} = 5 Hz, ⁴J_{HH} = 1 Hz, 1H, H16 bpy), 8.40 (d, ³J_{HH} = 8 Hz, 1H, H13 bpy), 8.35 (d, ³J_{HH} = 8 Hz, 1H, H13' bpy), 8.16 (td, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 1H, H14 bpy), 8.15 (td, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 1H, H14' bpy), 7.82 (ddd, ³J_{HH} = 8 Hz, ³J_{HH} = 5 Hz, ⁴J_{HH} = 1, 1H, H15' bpy), 7.44 (ddd, ³J_{HH} = 8 Hz, ³J_{HH} = 5 Hz, ⁴J_{HH} = 1, 1H, H15 bpy), 7.39 (dd, ³J_{HH} = 7 Hz, ⁴J_{HH} = 1 Hz, 1H, H6 aryl), 7.26 (td, ³J_{HH} = 7 Hz, ⁴J_{HH} = 2 Hz, 1H, H5 aryl), 7.07 (td, ³J_{HH} = 7 Hz, ⁴J_{HH} = 1 Hz, 1H, H4 aryl), 7.03 (dd, ³J_{HH} = 7 Hz, ⁴J_{HH} = 2 Hz, 1H, H3 aryl), 6.65 (A part of AB system, ²J_{HH} = 11 Hz, 1H, CH₂), 5.57 (d, ³J_{HH} = 7 Hz, 1H, NH), 5.12 (B part of AB system, ²J_{HH} = 11 Hz, 1H, CH₂), 3.89 (dsept, ³J_{HH} = 7 Hz, ³J_{HH} = 6 Hz, 1H, CH ¹Pr^B), 3.78 (sept, ³J_{HH} = 6 Hz, 1H, CH ¹Pr^B), 1.55 (d, ³J_{HH} = 6 Hz, 3H, Me ¹Pr^B), 1.28 (d, ³J_{HH} = 6 Hz, 3H, Me ¹Pr^A), 1.14 (d, ³J_{HH} = 6 Hz, 3H, Me ¹Pr^A), 0.70 (d, ³J_{HH} = 6 Hz, 3H, Me of ¹Pr^B). ¹³C {¹H} NMR (100.6 MHz, CDCl₃): 156.9 (C12 bpy), 156.3 (C=N), 153.6 (C1 aryl), 153.1 (C12' bpy), 151.7 (CH16 bpy), 150.8 (CH16' bpy), 140.4 (CH14' bpy), 140.3 (CH14 bpy), 138.3 (C2 aryl), 134.4 (CH6 aryl), 129.8 (CH5 aryl), 128.2 (CH15' bpy), 127.4 (CH3 aryl), 126.9 (CH15 bpy), 124.7 (CH4 aryl), 123.5 (CH13 bpy), 122.7 (CH13' bpy), 121.1 (q, ¹J_{CF} = 320 Hz, OTf), 74.3 (CH₂), 51.0 (CH ¹Pr^B), 45.4 (CH ¹Pr^A), 26.0 (Me ¹Pr^B), 23.7 (Me ¹Pr^A), 23.1 (Me ¹Pr^A), 22.0 (1C, Me ¹Pr^B). Anal. Calcd for C₂₅H₂₉F₃N₄O₄PdS: C, 46.55; H, 4.53; N, 8.69; S, 4.97. Found: C, 46.67; H, 4.40; N, 8.37; S, 4.59. Single crystals of **3a** were grown by liquid diffusion of Et₂O into a solution of **3a** in CH₂Cl₂.

Synthesis of [Pd{ κ^2 -C,N-C₆H₄{CH₂OC(=NTol)NHTol}-2}(bpy)] (OTf) (**3b**)

Starting from II.¹⁴ 1,3-Di-*p*-tolylcarbodiimide (300 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of **II**¹⁴ (100 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) under N₂. The mixture was stirred in the dark for 16 h at room temperature. It was then filtered over Celite and the resulting yellow solution was concentrated *in vacuo* to a volume of *ca.* 1 mL. Et₂O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give **3b** as a yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 128 mg (64%). Starting from **4**; KOTf (190 mg, 1.0 mmol) was added to a solution of **4** (60 mg, 0.10 mmol) in commercial CH₂Cl₂ (20 mL) and in an open flask. The mixture was stirred for 20 min at room temperature, with no change in the yellow color. Then a solution of HOTf in commercial CH₂Cl₂ (15 mg, 0.10 mmol, in 2 mL) was added dropwise (whereupon the color changed from yellow to red). After the addition the mixture was filtered over Celite and the resulting yellow solution was concentrated *in vacuo* to a

volume of *ca.* 1 mL. Et₂O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give **3b** as a yellow solid. Yield: 46 mg (62%). Mp: 182 °C. Λ_M (acetone): 125 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm⁻¹): $\nu(\text{S=O})$ 1030, 1259, $\nu(\text{C=N})$ 1600, $\nu(\text{NH})$ 3401. ¹H NMR (600 MHz, CDCl₃): 8.61 (d, ³J_{HH} = 5 Hz, 1H, H16' bpy), 8.54 (d, ³J_{HH} = 8 Hz, 1H, H13 bpy), 8.50 (d, ³J_{HH} = 8 Hz, 1H, H13' bpy), 8.31 (d, ³J_{HH} = 5 Hz, 1H, H16 bpy), 8.18 (t, ³J_{HH} = 8 Hz, 1H, H14 bpy), 8.14 (t, ³J_{HH} = 8 Hz, 1H, H14' bpy), 7.69 (dd, ³J_{HH} = 8 Hz, ³J_{HH} = 5, 1H, H15' bpy), 7.50 (d, ³J_{HH} = 7 Hz, 1H, H6 aryl), 7.44 (td, ³J_{HH} = 7 Hz, ⁴J_{HH} = 2 Hz, 1H, H5 aryl), 7.39 (dd, ³J_{HH} = 8 Hz, ³J_{HH} = 5 Hz, 1H, H15 bpy), 7.29 (part A of AB system, ³J_{HH} = 8 Hz, 2H, *o*-H Tol^B), 7.22 (part A of AB system, ²J_{HH} = 11 Hz, 1H, CH₂), 7.20 (part B of AB system, ³J_{HH} = 8 Hz, 2H, *m*-H Tol^B), 7.22–7.18 (m, 2, H3,4 aryl), 7.09 (part A of AB system, ³J_{HH} = 8 Hz, 2H, *m*-H Tol^A), 6.85 (part B of AB system, ³J_{HH} = 8 Hz, 2H, *o*-H Tol^A), 6.49 (s, 1H, NH), 5.27 (part B of AB system, ²J_{HH} = 11 Hz, 1H, CH₂), 2.31 (s, 3H, Me Tol^A), 2.29 (s, 3H, Me Tol^B). ¹³C {¹H} NMR (150.9 MHz, CDCl₃): 156.9 (C12 bpy), 156.5 (C=N), 153.7 (C1 aryl), 153.4 (C12' bpy), 151.6 (CH16 bpy), 149.3 (CH16' bpy), 141.8 (*i*-C Tol^B), 141.0 (2C, CH14, 14' bpy), 137.9 (C2 aryl), 137.4 (*p*-C Tol^B), 136.2 (*p*-C Tol^A), 134.2 (CH6 aryl), 133.4 (*i*-C Tol^A), 131.3 (2C, *m*-CH Tol^B), 131.2 (CH5 aryl), 129.9 (2C, *m*-CH Tol^A), 127.9 (CH3 aryl), 127.5 (CH15' bpy), 126.9 (CH15 bpy), 125.9 (2C, *o*-CH Tol^B), 125.6 (CH4 aryl), 124.5 (CH13 bpy), 123.9 (2C, *o*-CH Tol^A), 123.8 (CH13' bpy), 74.2 (CH₂), 21.14 (Me Tol^B), 21.11 (Me Tol^A). The OTf carbon is not observed. Anal. Calcd for C₃₃H₂₉F₃N₄O₄PdS: C, 53.48; H, 3.94; N, 7.56; S, 4.33. Found: C, 53.12; H, 3.64; N, 7.52; S, 4.09.

Synthesis of [Pd{ κ^2 -C,N-C₆H₄{CH₂OC(=NTol)NTol}-2}(bpy)] (**4**)

Starting from II.¹⁴ 1,3-Di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol) was added to a solution of **II**¹⁴ (100 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) under N₂. The mixture was stirred for 5 min at room temperature, with a change in color from yellow to red. Then it was filtered over Celite and the resulting red solution was concentrated to dryness *in vacuo*. Cold Et₂O (15 mL) was added to precipitate a solid, which was filtered off, washed with cold Et₂O (3 × 5 mL), and dried *in vacuo* to give **4** as a red solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone, and partially soluble in Et₂O. Yield: 130 mg (81%). Starting from **3b**; KO^tBu (27 mg, 0.24 mmol) was added to a solution of **3b** (60 mg, 0.08 mmol) in CH₂Cl₂ (20 mL) under N₂. The mixture was stirred for 10 min at room temperature, with a change in color from yellow to red. Work-up as in the previous reaction gave **4** as a red solid. Yield: 38 mg, 80%. Mp: 96 °C. IR (cm⁻¹): $\nu(\text{C=N})$ 1660. ¹H NMR (400 MHz, CDCl₃): 8.45 (d, ³J_{HH} = 5 Hz, 1H, H16 bpy), 8.39 (d, ³J_{HH} = 5 Hz, 1H, H16' bpy), 8.06 (d, ³J_{HH} = 8 Hz, 1H, H13 bpy), 8.02 (d, ³J_{HH} = 8 Hz, 1H, H13' bpy), 7.96 (t, ³J_{HH} = 8 Hz, 1H, H14 bpy), 7.91 (t, ³J_{HH} = 8 Hz, 1H, H14' bpy), 7.9 (A part of AB system, ³J_{HH} = 8 Hz, 2H, *o*-H Tol^B), 7.70 (d, ³J_{HH} = 7 Hz, 1H, H6 aryl), 7.39–7.30 (m, 2H, H15, 15' bpy), 7.03 (t, ³J_{HH} = 7 Hz, 1H, H5 aryl), 7.00–6.95 (br m, 4H, *o,m*-H Tol^A), 6.93 (t, ³J_{HH} = 7 Hz, 1H, H4 aryl), 6.85 (B part of AB system, ³J_{HH} = 8 Hz, 2H, *m*-H



Tol^B), 6.70 (d, $^3J_{\text{HH}} = 7$ Hz, 1H, H3), 5.02 and 4.73 (br) (AB system, $^2J_{\text{HH}} = 14$ Hz, 2H, CH₂), 2.27 (s, 3H, Me Tol^A), 2.16 (s, 3H, Me Tol^B), 1.54 (s, 2H, H₂O). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, CDCl₃, 213 K): 155.7 (C=N), 155.2 (C12 bpy), 153.1 (C12' bpy), 152.1 (CH16 bpy), 149.6 (C1 aryl), 149.3 (CH16' bpy), 147.9 (i-C Tol^A), 146.4 (i-C Tol^B), 140.7 (C2 aryl), 139.1 (CH14' bpy), 138.8 (CH14 bpy), 136.2 (CH6 aryl), 129.5 (*p*-C Tol^B), 128.97 (2C, *m*-CH Tol^A), 128.92 (*p*-C Tol^A), 128.91 (2C, *m*-CH Tol^B), 127.0 (CH15' bpy), 126.9 (CH5 aryl), 126.7 (CH15 bpy), 124.9 (CH3 aryl), 124.6 (2C, *o*-CH Tol^B), 123.5 (CH4 aryl), 122.7 (2C, *o*-CH Tol^A), 122.1 (CH13 bpy), 121.6 (CH13' bpy), 71.2 (CH₂), 21.1 (Me Tol^A), 21.0 (Me Tol^B). Anal. Calcd for C₃₂H₃₀N₄O₂Pd (4·H₂O): C, 63.11; H, 4.96; N, 9.20. Found: C, 63.25; H, 4.68; N, 9.27.

Synthesis of [Ag(*N*-4)](OTf) (5)

Starting from II. ¹⁴ AgOTf (57 mg, 0.22 mmol) was added to a solution of II ¹⁴ (100 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) under N₂, followed by 1,3-di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol). The solvent was immediately evaporated *in vacuo* and Et₂O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give a mixture of 5 and 3b in *ca.* 1 : 0.2 ratio. Yield, 192 mg. This solid was dissolved in CH₂Cl₂ (20 mL) and the resulting solution was filtered over Celite. The yellow solution was then concentrated *in vacuo* to a volume of *ca.* 1 mL. A small amount of Et₂O (7 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give pure 5 as a yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 124 mg (64%). Starting from 4; AgOTf (13 mg, 0.05 mmol) was added to a solution of 4 (60 mg, 0.10 mmol) in CH₂Cl₂ (20 mL) under N₂. The mixture was stirred for 2 h at room temperature, with a change in color from red to yellow. Then it was filtered over Celite, and the resulting yellow solution was evaporated to dryness *in vacuo*. Et₂O (15 mL) was added to precipitate a solid which was filtered off, washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give a mixture of 5 and 3b in *ca.* 1 : 0.2 ratio. Yield: 71 mg. This solid was dissolved in CH₂Cl₂ (20 mL) and the resulting solution was filtered over Celite. The yellow solution was then concentrated *in vacuo* to a volume of *ca.* 0.5 mL. A small amount of Et₂O (3 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give pure 5 as a yellow solid. Yield: 38 mg (53%). Mp: 159 °C. Λ_{M} (acetone): 148 Ω⁻¹ cm² mol⁻¹. IR (cm⁻¹): $\nu(\text{S=O})$ 1030, 1272, $\nu(\text{C=N})$ 1600. ¹H NMR (600 MHz, CDCl₃): 8.35 (d, $^3J_{\text{HH}} = 5$ Hz, 2H, H16 bpy), 8.33 (d, $^3J_{\text{HH}} = 8$ Hz, 2H, H13 bpy), 8.28 (d, $^3J_{\text{HH}} = 8$ Hz, 2H, H13' bpy), 8.13 (d, $^3J_{\text{HH}} = 5$ Hz, 2H, H16' bpy), 8.10 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 2H, H14 bpy), 8.00 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 2H, H14' bpy), 7.84 (d, $^3J_{\text{HH}} = 7$ Hz, 2H, H6 aryl), 7.39–7.33 (m, 4H, H15 bpy, H5 aryl), 7.33–7.30 (m, 1H, H15' bpy), 7.17 (t, $^3J_{\text{HH}} = 7$ Hz, 2H, H4 aryl), 7.00 (A part of AB system, $^3J_{\text{HH}} = 7$ Hz, 4H, *m*-H Tol^B), 6.95–6.75 (br, 4H, *o*-H Tol^A), 6.66 (d, $^3J_{\text{HH}} = 7$ Hz, 2H, H3 aryl), 6.13 (B part of AB system br, $^3J_{\text{HH}} = 7$ Hz, 4H, *o*-H Tol^B), 4.88 and 4.19 (AB system, $^2J_{\text{HH}} = 12$ Hz, 2H, CH₂), 2.37 (s, 6H,

Me Tol^B), 2.04 (s, 6H, Me Tol^A). The *m*-H Tol^A protons are not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl₃): 162.2 (2C, C=N), 156.5 (2C, C12 bpy), 153.7 (2C, C12' bpy), 152.4 (2C, CH16 bpy), 150.0 (2C, C1 aryl), 149.0 (2C, CH16' bpy), 146.4 (2C, i-C Tol^B), 143.6 (2C, i-C Tol^A), 139.9 (2C, CH14' bpy), 139.8 (2C, CH14 bpy), 138.9 (2C, C2 aryl), 136.1 (2C, CH6 aryl), 132.5 (2C, *p*-C Tol^A), 131.3 (2C, *p*-C Tol^B), 129.7 (4C, br, *m*-CH Tol^A), 128.7 (4C, *m*-CH Tol^B), 127.2 (2C, CH5 aryl), 126.9 (2C, CH15' bpy), 126.8 (2C, CH15 bpy), 126.6 (2C, CH3 aryl), 124.2 (4C, *o*-CH Tol^B), 124.1 (2C, CH4 aryl), 123.4 (2C, CH13 bpy), 122.7 (2C, CH13' bpy), 119.9 (q, $^1J_{\text{CF}} = 321$ Hz, OTf), 72.9 (2C, CH₂), 21.2 (2C, Me Tol^B), 21.0 (2C, Me Tol^A). The *o*-CH Tol^A and OTf carbons are not observed. Anal. Calcd for C₆₅H₅₆AgF₃N₈O₅Pd₂S: C, 54.25; H, 3.92; N, 7.79; S, 2.23. Found: C, 54.11; H, 3.81; N, 7.86; S, 2.07. Single crystals of 5·2.5CHCl₃·0.5Et₂O were grown by liquid diffusion of Et₂O into a solution of 5 in CHCl₃.

Synthesis of [Pd{κ²-*O*,*N*-OCH₂{C₆H₄{C(=NⁱPr)NHⁱPr}-2}}(bpy)](OTf) (6)

1,3-Diisopropylcarbodiimide (252 mg, 2.0 mmol) and TlOTf (70 mg, 0.20 mmol) were added to a solution of [PdI-(C₆H₄CH₂OH-2)(bpy)] (I) ¹⁴ (100 mg, 0.20 mmol) in CH₂Cl₂ (20 mL) under N₂. The mixture was stirred for 16 h at room temperature. It was then filtered over Celite and the resulting yellow solution was concentrated *in vacuo* to a volume of *ca.* 1 mL. Et₂O (15 mL) was added to precipitate a solid, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give a mixture of 3a and 6 in a 1 : 1.3 ratio. Yield: 97 mg. The products were separated by preparative TLC on alumina using acetone as eluent. The band with *R*_f = 0.48 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and addition of Et₂O (15 mL) resulted in the formation of a precipitate, which was filtered off, thoroughly washed with Et₂O (3 × 5 mL), and dried *in vacuo* to give 6 as a yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 54 mg (31%). Mp: 177 °C. Λ_{M} (acetone): 122 Ω⁻¹ cm² mol⁻¹. IR (cm⁻¹): $\nu(\text{S=O})$ 1032, 1262, $\nu(\text{C=N})$ 1609, $\nu(\text{NH})$ 3318. ¹H NMR (600 MHz, CDCl₃): 8.85 (d, $^3J_{\text{HH}} = 5$ Hz, 1H, H16' bpy), 8.52 (d, $^3J_{\text{HH}} = 5$ Hz, 1H, H16 bpy), 8.10–8.06 (m, 2H, H13', 14' bpy), 8.04 (d, $^3J_{\text{HH}} = 8$, 1H, H13 bpy), 8.00 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H14 bpy), 7.71 (td, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H15 bpy), 7.57–7.53 (m, 2H, H15' bpy, H6 aryl), 7.43 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, H3 aryl), 7.40 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H4 aryl), 7.32 (td, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1$ Hz, 1H, H5 aryl), 6.39 (d, $^3J_{\text{HH}} = 9$ Hz, 1H, NH), 4.57 and 3.84 (AB system, $^2J_{\text{HH}} = 10$ Hz, 2H, CH₂), 4.25 (sept, $^3J_{\text{HH}} = 6$ Hz, 1H, CH ⁱPr^B), 3.55 (dsept, $^3J_{\text{HH}} = 9$ Hz, $^3J_{\text{HH}} = 6$ Hz, 1H, CH ⁱPr^A), 1.65 and 1.54 (d, $^3J_{\text{HH}} = 6$ Hz, 3H, Me ⁱPr^B), 1.40 and 1.04 (d, $^3J_{\text{HH}} = 6$ Hz, 3H, Me ⁱPr^A). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, CDCl₃): 162.0 (C=N), 155.7 (C12' bpy), 154.8 (C12 bpy), 152.2 (CH16 bpy), 148.1 (CH16' bpy), 146.0 (C2 aryl), 140.6 (CH14' bpy), 140.1 (CH14 bpy), 134.2 (C1 aryl), 131.3 (CH4 aryl), 130.8 (CH3 aryl), 128.4 (CH15 bpy), 128.0 (CH6 aryl), 127.9 (CH5 aryl), 126.1 (CH15' bpy), 122.8 (CH13 bpy), 122.4 (CH13' bpy), 121.2 (q, $^1J_{\text{CF}} = 321$ Hz, OTf), 69.9 (CH₂), 50.7 (CH ⁱPr^B), 48.9 (CH



ⁱPr^A), 25.2 (Me ⁱPr^A), 24.9 (Me ⁱPr^B), 23.1 (Me ⁱPr^A), 22.4 (1C, Me ⁱPr^B). Anal. Calcd for C₂₅H₂₉F₃N₄O₄PdS: C, 46.55; H, 4.53; N, 8.69; S, 4.97. Found: C, 46.38; H, 4.80; N, 8.54; S, 4.98.

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