Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2016, **45**, 820

Reactivity towards nitriles, cyanamides, and carbodiimides of palladium complexes derived from benzyl alcohol. Synthesis of a mixed Pd_2Ag complex†

María-José Fernández-Rodríguez,[a] Eloísa Martínez-Viviente,*[a] José Vicente[a] and Peter G. Jones[b]

The chelate complex [Pd(κ^2-*C*,*O*-$C_6H_4CH_2O$-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*-C_6H_4\{$CH_2OC(=NX)Y$\}-2}(bpy)](OTf), where X = H, Y = Me (**1**), NMe_2 (**2a**), NEt_2 (**2b**), X = R, Y = NHR (R = ^{i}Pr (**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*-C_6H_4\{$CH_2OC(=NTol)NTol$\}-2}(bpy)] (**4**). Complexes **3b** and **4** can be interconverted by deprotonation (**3b** + KO^{t}Bu) 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 Ag_2Pd 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 [PdI($C_6H_4CH_2OH$-2)(bpy)] (**I**) reacts with ^{i}PrN=C=N^{i}Pr in the presence of TlOTf, instead of AgOTf, a *ca.* 1 : 1 mixture of **3a** and [Pd{κ^2-*O*,*N*-OCH_2\{C_6H_4\{$C(=NH^iPr)N^iPr$\}-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**·2.5$CHCl_3$·0.5Et_2O have been determined by X-ray diffraction studies.

Received 14th September 2015,
Accepted 23rd November 2015

DOI: 10.1039/c5dt03597j

www.rsc.org/dalton

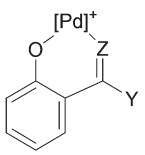
Introduction

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 compounds.[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]

[a]*Grupo de Química Organometálica, Dpto. de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain. E-mail: jvs1@um.es, eloisamv@um.es; http://www.um.es/gqo/*
[b]*Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: p.jones@tu-bs.de*

†Electronic supplementary information (ESI) available: NMR data table of complexes **1–6**, extended comments on the NMR data, X-ray crystallographic data, structure refinement details, CIF files for compounds **2a**, **3a**, **5**, **III**, and **IV**. CCDC 1424207–1424211. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03597j



Y	Z
NHR	NR
NHR	S
R	NH
NR_2	NH

[Pd] = [Pd(N^N)]
N^N = bpy, tmeda

Chart 1

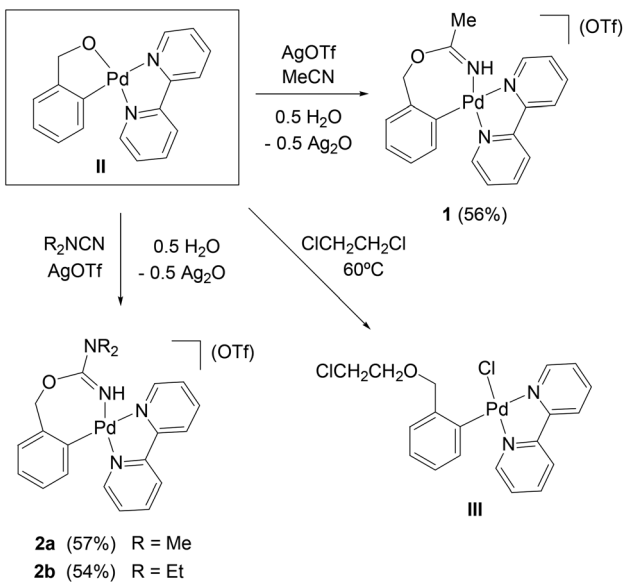
the addition of the O–H group to one of the C═N bonds of the substrate, together with the coordination of the other N to the Pd atom, was an alternative reaction to the insertion.[11]

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 complexes[15] 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 work[14] we synthesized the complex [PdI($C_6H_4CH_2OH$-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 XyNC gave a clean insertion product, *trans*-[PdI{C(═NXy)$C_6H_4CH_2OH$-2}$(CNXy)_2$].[14] By deprotonation of complex **I** we prepared the chelate complex [Pd{κ^2-*C*,*O*-$C_6H_4(CH_2O)$-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{κ^2-*C*,*N*-C_6H_4\{CH_2OC-(═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 Pd_2Ag complex, which has been characterized by X-ray crystallography. Other heterometallic Pd_2Ag[18] or Pd_2Ag_2 [19] 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{κ^2-*C*,*O*-$C_6H_4CH_2O$-2}(bpy)] (**II**) reacts with acetonitrile and AgOTf (1 : 5 : 1 molar ratio, CH_2Cl_2), in the presence of residual water, to form [Pd{κ^2-*C*,*N*-C_6H_4\{CH_2OC(═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 $R_2NC{\equiv}N$ (R = Me, Et) and AgOTf to form [Pd{κ^2-*C*,*N*-C_6H_4\{CH_2OC(═NH)NR_2}-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 TlOTf, 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 C_3–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-(C_6H_4Y-2)(tmeda)] (Y = OH, NH_2, 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 NH_2 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 CH_2 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{$C_6H_4(CH_2OCH_2CH_2Cl)$-2}-(bpy)] (**III**), which is the result of the nucleophilic attack of the oxygen in **II** at a CH_2 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]

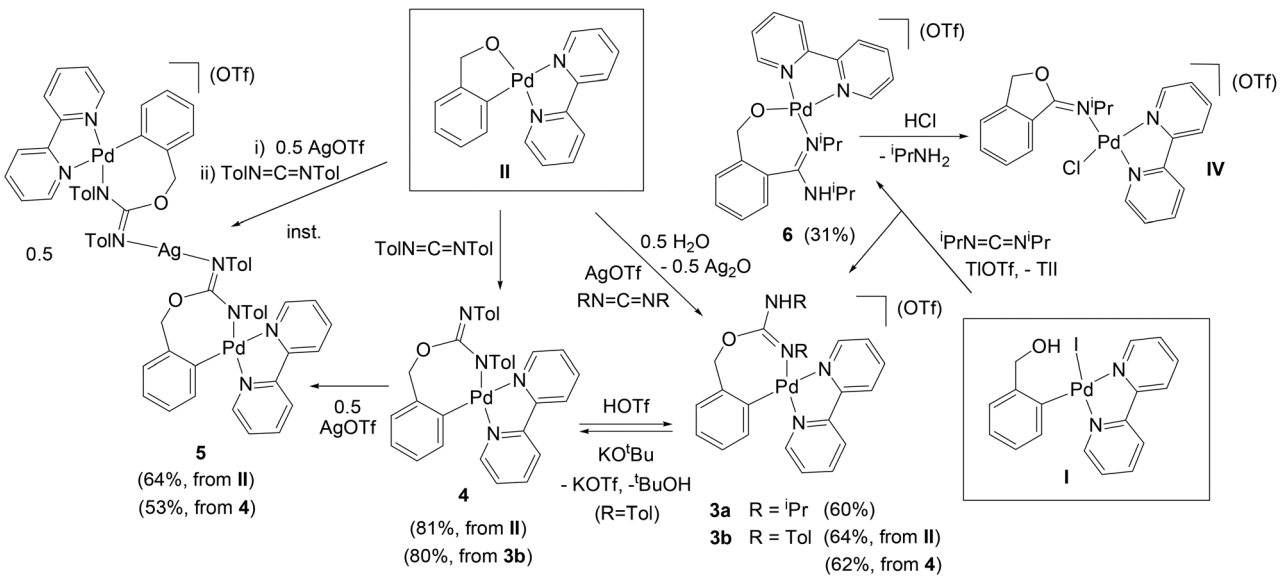
Reactions with carbodiimides

Complex **II** reacts with the carbodiimides RN=C=NR (R = ^{i}Pr, Tol) and AgOTf (1 : 5 : 1 molar ratio, CH_2Cl_2) in the presence of residual water, to form [Pd{κ^2-*C*,*N*-C_6H_4{$CH_2OC(=NR)NHR$}-2}-(bpy)](OTf) (R = ^{i}Pr (**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 ^{i}PrN=C=N^{i}Pr there was no reaction, whereas with TolN=C=NTol the reaction in the absence of AgOTf resulted in the formation of [Pd{κ^2-*C*,*N*-C_6H_4{CH_2OC-(=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 Et_2O.

By deprotonation of the ionic complex **3b** with KO^{t}Bu, 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 = ^{i}Pr) with KO^{t}Bu 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 Pd_2Ag[18] or Pd_2Ag_2 [19] complexes found in



Scheme 2

the literature. With the carbodiimide ^{i}PrN=C=N^{i}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 TolN=C=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 TolN=C=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 $[Ag(TolN{=}C{=}NTol)_2]^+$ 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 TolN=C=NTol, only **3b** is detected, while the same reaction with only one equivalent of TolN=C=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 TolN=C=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-hydroxymethylphenyl Pd complex [PdI($C_6H_4CH_2OH$-2)(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}PrN=C=N^{i}Pr in the presence of TlOTf, 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 [Pd{κ^2-*O*,*N*-OCH$_2${C$_6$H$_4${C(=N^{i}Pr)NH^{i}Pr}-2}}(bpy)](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 TolN=C=NTol and TlOTf 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 TlOTf, 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 ^{1}H 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 (MeC≡N, R$_2$NC≡N, or RN=C=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 ^{1}H,^{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 ^{1}H-NOESY and ^{1}H,^{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 R$_2$N–C=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 ^{1}H 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 ^{1}H resonances, and also of the ^{1}H resonances of the more external tolyl group. These resonances sharpen at low temperature, but the ^{1}H 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 ^{1}H and ^{13}C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened ^{1}H 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** = [Ag(*N*-**4**)$_2$](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 for the stronger *trans* influence of the aryl ligand with respect to N-donor ligands.

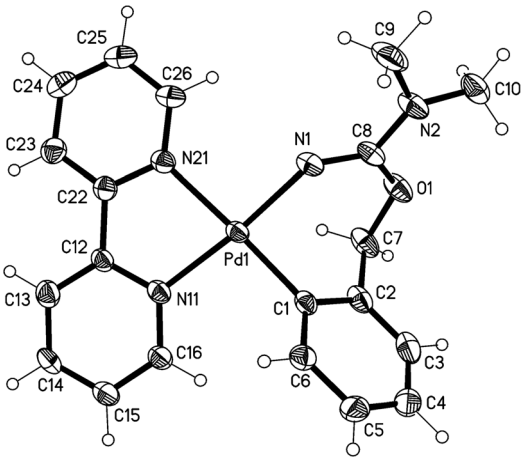


Fig. 1 Thermal ellipsoid plot (50% probability level) of the cation of **2a**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) = 1.981(3), Pd(1)–N(1) = 2.026(2), Pd(1)–N(11) = 2.051(2), Pd(1)–N(21) = 2.118(2), O(1)–C(7) = 1.462(4), O(1)–C(8) = 1.334(4), C(8)–N(1) = 1.305(4), C(8)–N(2) = 1.343(4), C(9)–N(2) = 1.450(4), C(10)–N(2) = 1.462(4); C(1)–Pd(1)–N(1) = 87.22(11), C(1)–Pd(1)–N(11) = 97.84(10), N(1)–Pd(1)–N(21) = 95.85(10), N(11)–Pd(1)–N(21) = 79.20(10), N(1)–Pd(1)–N(11) = 174.20(9), C(1)–Pd(1)–N(21) = 176.21(9), C(7)–O(1)–C(8) = 120.0(2), O(1)–C(8)–N(1) = 124.7(3), O(1)–C(8)–N(2) = 112.2(3), N(1)–C(8)–N(2) = 123.1(3), C(8)–N(1)–Pd(1) = 136.3(2).

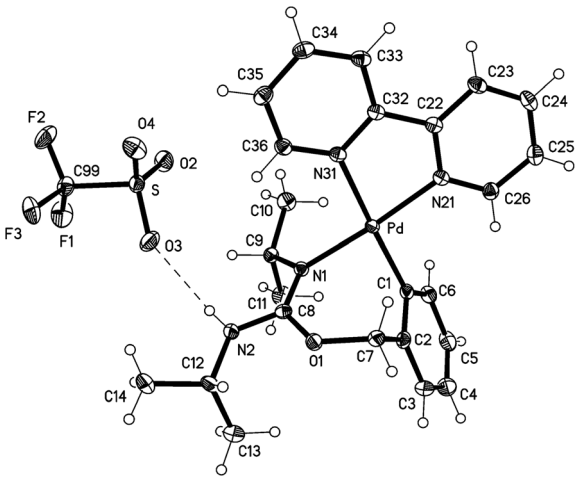


Fig. 2 Thermal ellipsoid plot (50% probability level) of **3a**. Selected bond lengths (Å) and angles (°): Pd–C(1) = 1.9716(15), Pd–N(1) = 2.0313(13), Pd–N(21) = 2.0331(13), Pd–N(31) = 2.1157(12), O(1)–C(7) = 1.4567(19), O(1)–C(8) = 1.3350(19), C(8)–N(1) = 1.3054(18), C(8)–N(2) = 1.346(2), C(9)–N(1) = 1.494(2), C(12)–N(2) = 1.4658(19); C(1)–Pd–N(1) = 84.69(6), C(1)–Pd–N(21) = 98.38(6), N(1)–Pd–N(31) = 97.75(5), N(21)–Pd–N(31) = 79.53(5), N(1)–Pd–N(21) = 175.14(5), C(1)–Pd–N(31) = 174.44(6), C(7)–O(1)–C(8) = 123.79(12), O(1)–C(8)–N(1) = 125.21(14), O(1)–C(8)–N(2) = 111.20(13), N(1)–C(8)–N(2) = 123.58(16), C(8)–N(1)–Pd = 125.84(12).

The X-ray diffraction study of **5** (Fig. 3) confirms the structure proposed for this compound, consisting of two molecules of **4** coordinated *via* nitrogen to a silver atom. The two Ag–N bond lengths are 2.121(5) and 2.128(4) Å, similar to

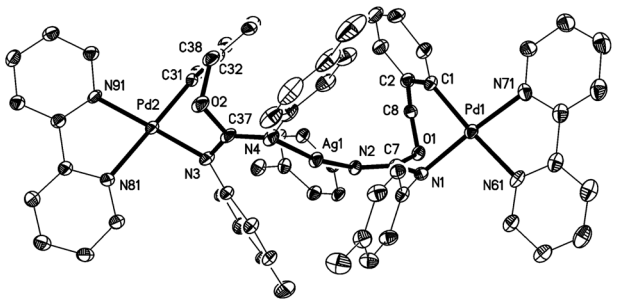


Fig. 3 Thermal ellipsoid plot (50% probability level) of one of the two independent cations of **5**. Selected bond lengths (Å) and angles (°): Ag(1)–N(4) = 2.121(5), Ag(1)–N(2) = 2.128(4), Pd(1)–C(1) = 2.014(7), Pd(1)–N(1) = 2.044(5), Pd(1)–N(71) = 2.070(5), Pd(1)–N(61) = 2.115(5), Pd(2)–C(31) = 2.009(6), Pd(2)–N(91) = 2.045(5), Pd(2)–N(3) = 2.054(6), Pd(2)–N(81) = 2.117(6), O(1)–C(8) = 1.439(8), O(1)–C(7) = 1.368(7), N(1)–C(7) = 1.341(8), N(1)–C(11) = 1.422(8), N(2)–C(7) = 1.292(8), N(2)–C(21) = 1.418(8), O(2)–C(38) = 1.456(9), O(2)–C(37) = 1.390(7), N(3)–C(37) = 1.322(10), N(3)–C(41) = 1.416(8), N(4)–C(37) = 1.310(9), N(4)–C(51) = 1.415(10); N(4)–Ag(1)–N(2) = 167.5(2), C(1)–Pd(1)–N(1) = 88.7(2), C(1)–Pd(1)–N(71) = 96.5(3), N(1)–Pd(1)–N(61) = 95.7(2), N(71)–Pd(1)–N(61) = 78.5(2), N(1)–Pd(1)–N(71) = 171.9(2), C(1)–Pd(1)–N(61) = 173.1(2), C(31)–Pd(2)–N(91) = 97.9(2), C(31)–Pd(2)–N(3) = 86.4(3), N(91)–Pd(2)–N(81) = 79.7(2), N(3)–Pd(2)–N(81) = 97.5(2), N(91)–Pd(2)–N(3) = 168.8(2), C(31)–Pd(2)–N(81) = 171.3(3), C(7)–O(1)–C(8) = 112.9(4), O(1)–C(7)–N(1) = 111.4(5), O(1)–C(7)–N(2) = 122.1(6), N(1)–C(7)–N(2) = 126.4(6), C(7)–N(2)–Ag(1) = 120.8(4), C(37)–O(2)–C(38) = 112.0(5), O(2)–C(37)–N(3) = 112.2(6), O(2)–C(37)–N(4) = 119.7(7), N(3)–C(37)–N(4) = 128.1(6), C(37)–N(4)–Ag(1) = 120.1(4).

other Ag–N bond distances reported in the literature for compounds with a N–Ag–N moiety.[23] The N(2)–Ag(1)–N(4) angle of 167.5(2)° departs significantly from linearity, but is still close to those found in the literature (between 168 and 179°).[23]

For the three structures we can suggest electronic delocalization along the N–C═N group, as a shortening of the single N–C bond and a lengthening of the double C═N bond is observed when compared with other bonds in the same or other molecules. Thus, the "single" bonds Me_2N(2)–C(8) (1.343(4) Å, **2a**), ^{i}PrN(2)–C(8) (1.346(2) Å, **3a**), and TolN(1)–C(7), TolN(3)–C(37) (1.341(8) and 1.322(10) Å, **5**) are much shorter than the C–N bonds (Me–N, ^{i}Pr–N and Tol–N) in the same complexes, which measure between 1.415(10) and 1.494(2) Å. The corresponding "double" bonds C(8)═N(1) (1.305(4) Å, **2a**; 1.3054(18) Å, **3a**), and C(7)═N(2), C(37)═N(4) (1.292(8), and 1.310(9) Å, **5**) are longer than the mean value in imines (1.279 Å).[24] This C═N bond lengthening can be attributed to both the electronic delocalization along the N–C–N bonds and the coordination of the iminic nitrogen to Pd (in **2a**, **3a**) or Ag (in **5**) (although it is interesting to note that the coordination of N(1) and N(3) to Pd in **5** does not cause a significant lengthening of the corresponding C–N single bonds (1.341(8) and 1.322(10) Å) with respect to the values for the (uncoordinated) C(8)–N(2) bonds in **2a** (1.343(4) Å) and **3a** (1.346(2) Å)). Our group has previously observed a similar electronic delocalization along the N–C–N bonds for complexes resulting from the insertion of carbodiimides and cyanamides into the C–Pd bond, or the addition of carbodiimides to the O–H bond, of *ortho*-palladated phenol derivatives.[12] It is also interesting to note that in the trinuclear complex **5** the electronic delocalization in one of the N–C═N moieties is much greater than in the other (bond lengths in N(1)–C(7)═N(2) are 1.292(8) and 1.341(8) Å while for N(3)–C(37)–N(4) the two bond lengths are more similar, 1.310(9) and 1.322(10) Å).

The structure of **3a** shows a classical hydrogen bond between the NH proton of the complex and an oxygen atom of the triflate, with an O(3)···H–N(2) distance of 2.22(2) Å.

Conclusions

We have investigated the reactivity of two Pd complexes derived from benzyl alcohol (one of them a κ^2-*C*,*O* chelate) towards nitriles, cyanamides and carbodiimides. With the chelate complex we have obtained novel neutral or ionic complexes containing a 7-membered κ^2-*C*,*N* chelate ring, resulting from the insertion of the organic molecules into the O–Pd bond. The presence of AgOTf was necessary for most of these reactions. A novel heterometallic bis-chelate Pd_2Ag complex has also been synthesized. Starting from the non-chelate complex, we have achieved the insertion of a carbodiimide into the aryl–Pd bond. All the new compounds have been extensively characterized by NMR spectroscopy, and three of them, including the mixed-metal complex, by X-ray crystallography.

Experimental

The ^{1}H and ^{13}C resonances were assigned with the help of 2D NMR experiments measured in Bruker Avance 400 and 600 MHz spectrometers (see Chart 2 for the numbering system). Molar conductivities were measured for *ca.* 5×10^{-4} M solutions in acetone, using a CRISON micro CM2200 conductivity meter. Infrared spectra were recorded using a Perkin Elmer Spectrum 100 spectrophotometer, and C, H, N, and S elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Melting points were determined on a Reichert apparatus and are uncorrected. Unless otherwise specified, all experiments were conducted under N_2 atmosphere using Schlenk techniques. CH_2Cl_2 and Et_2O were distilled before use. [PdI($C_6H_4CH_2$OH-2)(bpy)] (**I**),[14] [Pd(κ^2-*C*,*O*-$C_6H_4CH_2$O-2)(bpy)] (**II**),[14] and [Pd(dba)$_2$][25] were prepared

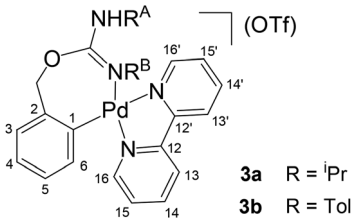


Chart 2

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

Synthesis of [Pd{κ²-*C*,*N*-C_6H_4{$CH_2OC(=NH)Me$}-2}(bpy)](OTf) (1)

Acetonitrile (55 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of [Pd(κ²-*C*,*O*-$C_6H_4CH_2O$-2)(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 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S=O) 1029, 1279, ν(C=N) 1635, ν(NH) 3213. ^{1}H NMR (400 MHz, $CDCl_3$): 8.89 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.45 (br s, 1H, NH), 8.37 (ddd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1, 1H, H16 bpy), 8.25 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.17 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.11 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14′ bpy), 8.07 (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 Hz, 1H, H15′ bpy), 7.43 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.31–7.27 (m, 1H, H5 aryl), 7.22 (d, $^3J_{HH}$ = 7 Hz, 1H, H6 aryl), 7.15–7.11 (m, 2H, H3,4 aryl), 6.60 and 5.05 (AB system, $^2J_{HH}$ = 11 Hz, 2H, CH_2), 2.30 (s, 3H, Me). $^{13}C\{^1H\}$ 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, $^1J_{CF}$ = 320 Hz, OTf), 72.2 (CH_2), 23.6 (Me). Anal. Calcd for $C_{20}H_{18}F_3N_3O_4PdS$: 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 [Pd{κ²-*C*,*N*-C_6H_4{$CH_2OC(=NH)NMe_2$}-2}(bpy)](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 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S=O) 1029, 1275, ν(C=N) 1602, ν(NH) 3306. ^{1}H NMR (600 MHz, $CDCl_3$): 8.65 (ddd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.42 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.35 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.32 (ddd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz, 1H, H16 bpy), 8.14 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14 bpy), 8.08 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, H14′ bpy), 7.79 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15′ bpy), 7.39 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 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, $^2J_{HH}$ = 11 Hz, 2H, CH_2), 4.81 (s, 1H, NH), 3.00 (s, 6H, Me). $^{13}C\{^1H\}$ 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, $^1J_{CF}$ = 320 Hz, OTf), 73.2 (CH_2), 38.0 (Me). Anal. Calcd for $C_{21}H_{21}F_3N_4O_4PdS$: 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 [Pd{κ²-*C*,*N*-C_6H_4{$CH_2OC(=NH)NEt_2$}-2}(bpy)](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 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S=O) 1030, 1277, ν(C=N) 1599, ν(NH) 3321. ^{1}H NMR (400 MHz, $CDCl_3$): 8.58 (dd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H16′ bpy), 8.44 (d, $^3J_{HH}$ = 8 Hz, 1H, H13 bpy), 8.39 (d, $^3J_{HH}$ = 8 Hz, 1H, H13′ bpy), 8.32 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H16 bpy), 8.15 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H14 bpy), 8.13 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H14′ bpy), 7.78 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15′ bpy), 7.39 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 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, $^2J_{HH}$ = 11 Hz, 2H, CH_2O), 4.76 (s, 1H, NH), 3.33 (m, 4H, CH_2CH_3), 1.13 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ 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, $^1J_{CF}$ = 321 Hz, OTf), 73.1 (CH_2O), 43.3 (CH_2CH_3), 13.6 (CH_2CH_3). Anal. Calcd for $C_{23}H_{25}F_3N_4O_4PdS$: 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 [Pd{κ²-*C*,*N*-C_6H_4{$CH_2OC(=N^iPr)NH^iPr$}-2}(bpy)](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. 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 **3a** as a pale yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 104 mg (60%). Mp: 195 °C. Λ_M (acetone): 140 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S═O) 1028, 1276, ν(C═N) 1611, ν(NH) 3354. ^{1}H NMR (400 MHz, $CDCl_3$): 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, CH_2), 5.57 (d, $^3J_{HH}$ = 7 Hz, 1H, NH), 5.12 (B part of AB system, $^2J_{HH}$ = 11 Hz, 1H, CH_2), 3.89 (dsept, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, 1H, CH $^iPr^A$), 3.78 (sept, $^3J_{HH}$ = 6 Hz, 1H, CH $^iPr^B$), 1.55 (d, $^3J_{HH}$ = 6 Hz, 3H, Me $^iPr^B$), 1.28 (d, $^3J_{HH}$ = 6 Hz, 3H, Me $^iPr^A$), 1.14 (d, $^3J_{HH}$ = 6 Hz, 3H, Me $^iPr^A$), 0.70 (d, $^3J_{HH}$ = 6 Hz, 3H, Me of $^iPr^B$). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): 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 (CH_2), 51.0 (CH $^iPr^B$), 45.4 (CH $^iPr^A$), 26.0 (Me $^iPr^B$), 23.7 (Me $^iPr^A$), 23.1 (Me $^iPr^A$), 22.0 (1C, Me $^iPr^B$). Anal. Calcd for $C_{25}H_{29}F_3N_4O_4PdS$: 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 Et_2O into a solution of **3a** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*,*N*-C$_6$H$_4${CH$_2$OC(═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 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. 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 **3b** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, 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 CH_2Cl_2 (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 CH_2Cl_2 (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. 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 **3b** as a yellow solid. Yield: 46 mg (62%). Mp: 182 °C. Λ_M (acetone): 125 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S═O) 1030, 1259, ν(C═N) 1600, ν(NH) 3401. ^{1}H NMR (600 MHz, $CDCl_3$): 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, CH_2), 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, CH_2), 2.31 (s, 3H, Me Tol^A), 2.29 (s, 3H, Me Tol^B). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): 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 (CH_2), 21.14 (Me Tol^B), 21.11 (Me Tol^A). The OTf carbon is not observed. Anal. Calcd for $C_{33}H_{29}F_3N_4O_4PdS$: 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*-C$_6$H$_4${CH$_2$OC(═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 CH_2Cl_2 (20 mL) under N_2. 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 Et_2O (15 mL) was added to precipitate a solid, which was filtered off, washed with cold Et_2O (3 × 5 mL), and dried *in vacuo* to give **4** as a red solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone, and partially soluble in Et_2O. Yield: 130 mg (81%). Starting from **3b**; KO^{t}Bu (27 mg, 0.24 mmol) was added to a solution of **3b** (60 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) under N_2. 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}): ν(C═N) 1660. ^{1}H NMR (400 MHz, $CDCl_3$): 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, $^3J_{HH}$ = 7 Hz, 1H, H3), 5.02 and 4.73 (br) (AB system, $^2J_{HH}$ = 14 Hz, 2H, CH_2), 2.27 (s, 3H, Me Tol^A), 2.16 (s, 3H, Me Tol^B), 1.54 (s, 2H, H_2O). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 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 (CH_2), 21.1 (Me Tol^A), 21.0 (Me Tol^B). Anal. Calcd for $C_{32}H_{30}N_4O_2Pd$ (**4**·H_2O): C, 63.11; H, 4.96; N, 9.20. Found: C, 63.25; H, 4.68; N, 9.27.

Synthesis of [Ag(*N*-4)$_2$](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 CH_2Cl_2 (20 mL) under N_2, followed by 1,3-di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol). The solvent was immediately evaporated *in vacuo* and 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 a mixture of **5** and **3b** in *ca.* 1 : 0.2 ratio. Yield, 192 mg. This solid was dissolved in CH_2Cl_2 (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 Et_2O (7 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 pure **5** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, 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 CH_2Cl_2 (20 mL) under N_2. 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*. Et_2O (15 mL) was added to precipitate a solid which was filtered off, washed with Et_2O (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 CH_2Cl_2 (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 Et_2O (3 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 pure **5** as a yellow solid. Yield: 38 mg (53%). Mp: 159 °C. Λ_M (acetone): 148 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(S═O) 1030, 1272, ν(C═N) 1600. ^{1}H NMR (600 MHz, $CDCl_3$): 8.35 (d, $^3J_{HH}$ = 5 Hz, 2H, H16 bpy), 8.33 (d, $^3J_{HH}$ = 8 Hz, 2H, H13 bpy), 8.28 (d, $^3J_{HH}$ = 8 Hz, 2H, H13′ bpy), 8.13 (d, $^3J_{HH}$ = 5 Hz, 2H, H16′ bpy), 8.10 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 2H, H14 bpy), 8.00 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 2H, H14′ bpy), 7.84 (d, $^3J_{HH}$ = 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, $^3J_{HH}$ = 7 Hz, 2H, H4 aryl), 7.00 (A part of AB system, $^3J_{HH}$ = 7 Hz, 4H, *m*-H Tol^B), 6.95–6.75 (br, 4H, *o*-H Tol^A), 6.66 (d, $^3J_{HH}$ = 7 Hz, 2H, H3 aryl), 6.13 (B part of AB system br, $^3J_{HH}$ = 7 Hz, 4H, *o*-H Tol^B), 4.88 and 4.19 (AB system, $^2J_{HH}$ = 12 Hz, 2H, CH_2), 2.37 (s, 6H, Me Tol^B), 2.04 (s, 6H, Me Tol^A). The *m*-H Tol^A protons are not observed. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 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, $^1J_{CF}$ = 321 Hz, OTf), 72.9 (2C, CH_2), 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 $C_{65}H_{56}AgF_3N_8O_5Pd_2S$: 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**·2.5$CHCl_3$·0.5Et_2O were grown by liquid diffusion of Et_2O into a solution of **5** in $CHCl_3$.

Synthesis of [Pd{κ^2-*O*,*N*-OCH$_2${C$_6$H$_4${C(═N^{i}Pr)NH^{i}Pr}-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-($C_6H_4CH_2$OH-2)(bpy)] (**I**)[14] (100 mg, 0.20 mmol) in CH_2Cl_2 (20 mL) under N_2. 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. 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 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 Et_2O (15 mL) resulted in the formation of a precipitate, which was filtered off, thoroughly washed with Et_2O (3 × 5 mL), and dried *in vacuo* to give **6** as a yellow solid, which is soluble in CH_2Cl_2, $CHCl_3$, and acetone. Yield: 54 mg (31%). Mp: 177 °C. Λ_M (acetone): 122 Ω^1 cm^2 mol^{-1}. IR (cm^{-1}): ν(S═O) 1032, 1262, ν(C═N) 1609, ν(NH) 3318. ^{1}H NMR (600 MHz, $CDCl_3$): 8.85 (d, $^3J_{HH}$ = 5 Hz, 1H, H16′ bpy), 8.52 (d, $^3J_{HH}$ = 5 Hz, 1H, H16 bpy), 8.10–8.06 (m, 2H, H13′, 14′ bpy), 8.04 (d, $^3J_{HH}$ = 8, 1H, H13 bpy), 8.00 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H14 bpy), 7.71 (td, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, H15 bpy), 7.57–7.53 (m, 2H, H15′ bpy, H6 aryl), 7.43 (d, $^3J_{HH}$ = 8 Hz, 1H, H3 aryl), 7.40 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H4 aryl), 7.32 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1H, H5 aryl), 6.39 (d, $^3J_{HH}$ = 9 Hz, 1H, NH), 4.57 and 3.84 (AB system, $^2J_{HH}$ = 10 Hz, 2H, CH_2), 4.25 (sept, $^3J_{HH}$ = 6 Hz, 1H, CH ^{i}Pr^B), 3.55 (dsept, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, 1H, CH ^{i}Pr^A), 1.65 and 1.54 (d, $^3J_{HH}$ = 6 Hz, 3H, Me ^{i}Pr^B), 1.40 and 1.04 (d, $^3J_{HH}$ = 6 Hz, 3H, Me ^{i}Pr^A). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): 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, $^1J_{CF}$ = 321 Hz, OTf), 69.9 (CH_2), 50.7 (CH ^{i}Pr^B), 48.9 (CH

$^{i}Pr^{A}$), 25.2 (Me $^{i}Pr^{A}$), 24.9 (Me $^{i}Pr^{B}$), 23.1 (Me $^{i}Pr^{A}$), 22.4 (1C, Me $^{i}Pr^{B}$). Anal. Calcd for $C_{25}H_{29}F_3N_4O_4PdS$: 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.

Acknowledgements

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

References

1 J. Tsuji, *Palladium Reagents and Catalysis: Innovations in Organic Synthesis*, John Wiley & Sons, Chichester, UK, 1995; N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483; J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1998, **37**, 2047–2067; J. P. Wolfe, S. Wagaw, J.-F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805–818; A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176–4211; A. R. Muci and S. L. Buchwald, *Top. Curr. Chem.*, 2002, **219**, 131–209; G. Zeni and R. C. Larock, *Chem. Rev.*, 2004, **104**, 2285–2309; R. B. Bedford, C. S. J. Cazin and D. Holder, *Coord. Chem. Rev.*, 2004, **2004**, 2283–2321; R. C. Larock and G. Zeni, *Chem. Rev.*, 2006, **106**, 4644–4680; S. L. Buchwald, C. Mauger, G. Mignani and U. Scholz, *Adv. Synth. Catal.*, 2006, **348**, 23–39; J. P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651–2710; R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874–922; M. A. Fernández-Rodríguez and J. F. Hartwig, *J. Org. Chem.*, 2009, **74**, 1663–1672; N. Selander and K. J. Szabo, *Chem. Rev.*, 2011, **111**, 2048–2076; J. Le Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170–1214; D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27–50; C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215–1292.

2 J. Spencer, M. Pfeffer, N. Kyritsakas and J. Fischer, *Organometallics*, 1995, **14**, 2214–2224; M. Catellani, E. Motti and S. Ghelli, *Chem. Commun.*, 2000, 2003–2004; K. R. Reddy, K. Surekha, G.-H. Lee, S.-M. Peng and S.-T. Liu, *Organometallics*, 2001, **20**, 5557–5563; C. Sirlin, J. Chengebroyen, R. Konrath, G. Ebeling, I. Raad, J. Dupont, M. Paschaki, F. KotzybaHibert, C. HarfMonteil and M. Pfeffer, *Eur. J. Org. Chem.*, 2004, 1724–1731; L. Canovese, F. Visentin, C. Santo, C. Levi and A. Dolmella, *Organometallics*, 2007, **26**, 5590–5601; K. J. Cavell and D. S. McGuinnes, in *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and M. P. Mingos, Pergamon Press, Oxford, UK, 2007, vol. 8, pp. 197–268; T. Bai, L. Q. Xue, P. Xue, J. Zhu, H. H. Y. Sung, S. M. Ma, I. D. Wiliams, Z. Y. Lin and G. C. Jia, *Organometallics*, 2008, **27**, 2614–2626; Y. Suzaki, M. Shirokawa, T. Yagyu and K. Osakada, *Eur. J. Inorg. Chem.*, 2015, **2015**, 421–429.

3 J. Vicente, J. A. Abad, K. F. Shaw, J. Gil-Rubio, M. C. Ramírez de Arellano and P. G. Jones, *Organometallics*, 1997, **16**, 4557–4566; J. Vicente, J.-A. Abad, J. López-Serrano, P. G. Jones, C. Nájera and L. Botella-Segura, *Organometallics*, 2005, **24**, 5044–5057; J. Vicente, M. T. Chicote, A. J. Martínez-Martínez, P. G. Jones and D. Bautista, *Organometallics*, 2008, **27**, 3254–3271; J. Vicente, M. T. Chicote, A. J. Martínez-Martínez and D. Bautista, *Organometallics*, 2009, **28**, 5915–5924; J. Vicente, P. González-Herrero, R. Frutos-Pedreño, M. T. Chicote, P. G. Jones and D. Bautista, *Organometallics*, 2011, **30**, 1079–1093; J. Vicente, J. A. Abad, R. M. López-Nicolás and P. G. Jones, *Organometallics*, 2011, **30**, 4983–4998; R. Frutos-Pedreño, P. González-Herrero, J. Vicente and P. G. Jones, *Organometallics*, 2013, **32**, 4664–4676; R. Frutos-Pedreño, P. González-Herrero, J. Vicente and P. G. Jones, *Organometallics*, 2013, **32**, 1892–1904.

4 J. Vicente, J. A. Abad, E. Martínez-Viviente, M. C. Ramírez de Arellano and P. G. Jones, *Organometallics*, 2000, **19**, 752–760.

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

6 J. Vicente, J. A. Abad, M. J. López-Sáez, W. Förtsch and P. G. Jones, *Organometallics*, 2004, **23**, 4414–4429.

7 J. Vicente and I. Saura-Llamas, *Comments Inorg. Chem.*, 2007, **28**, 39–72.

8 J. Vicente, J. A. Abad, R. Bergs, M. C. Ramirez de Arellano, E. Martínez-Viviente and P. G. Jones, *Organometallics*, 2000, **19**, 5597–5607; J. Vicente, J. A. Abad, E. Martinez-Viviente and P. G. Jones, *Organometallics*, 2002, **21**, 4454–4467; J. Vicente, J. A. Abad, E. Martínez-Viviente and P. G. Jones, *Organometallics*, 2003, **22**, 1967–1978.

9 J. Vicente, I. Saura-Llamas, C. Grünwald, C. Alcaraz, P. G. Jones and D. Bautista, *Organometallics*, 2002, **21**, 3587–3595; M. J. Oliva-Madrid, J.-A. García-López, I. Saura-Llamas, D. Bautista and J. Vicente, *Organometallics*, 2014, **33**, 6420–6430.

10 J. Vicente, J. A. Abad, M. J. López-Sáez and P. G. Jones, *Angew. Chem., Int. Ed.*, 2005, **44**, 6001–6004.

11 J. Vicente, J. A. Abad, M. J. López-Sáez and P. G. Jones, *Organometallics*, 2006, **25**, 1851–1853.

12 J. Vicente, J. A. Abad, M. J. López-Sáez, P. G. Jones and D. Bautista, *Chem. – Eur. J.*, 2010, **16**, 661–676.

13 J. Vicente, J. A. Abad, M. J. López-Sáez and P. G. Jones, *Organometallics*, 2010, **29**, 409–416.

14 M. J. Fernández-Rodríguez, E. Martínez-Viviente, J. Vicente and P. G. Jones, *Organometallics*, 2015, **34**, 3282–3291.

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

16 C. Fernández-Rivas, D. J. Cárdenas, B. Martín-Matute, A. Monge, E. Gutiérrez-Puebla and A. M. Echavarren, *Organometallics*, 2001, **20**, 2998–3006.

17 M. P. Muñoz, B. Martín-Matute, C. Fernández-Rivas, D. J. Cárdenas and A. M. Echavarren, *Adv. Synth. Catal.*, 2001, **343**, 338–342.
18 I. Meana, P. Espinet and A. C. Albéniz, *Organometallics*, 2014, **33**, 1–7; T. Nakajima, M. Tsuji, N. Hamada, Y. Fukushima, B. Kure and T. Tanase, *J. Organomet. Chem.*, 2014, **768**, 61–67.
19 K. Umakoshi, Y. Yamauchi, K. Nakamiya, T. Kojima, M. Yamasaki, H. Kawano and M. Onishi, *Inorg. Chem.*, 2003, **42**, 3907–3916; J. Forniés, A. Martín, V. Sicilia and M. Martín, *Chem. – Eur. J.*, 2003, **9**, 3427–3435; I. Ara, J. Forniés, R. Lasheras, A. Martín and V. Sicilia, *Eur. J. Inorg. Chem.*, 2006, 948–657; K. Umakoshi, T. Kojima, Y. Arikawa and M. Onishi, *Chem. – Eur. J.*, 2006, **12**, 5094–5104.
20 R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, 1996, **147**, 299–338; V. Y. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771–1802.
21 P. H. Mogul, R. N. Kniseley and V. A. Fassel, *Spectrosc. Lett.*, 1977, **10**, 959–970.
22 J. Vicente, R. V. Shenoy, E. Martínez-Viviente and P. G. Jones, *Organometallics*, 2009, **28**, 6101–6108.
23 P. Majumdar, K. K. Kamar, A. Castineiras and S. Goswami, *Chem. Commun.*, 2001, 1292–1293; J. Dinda, S. Jasimuddin, G. Mostafa, C.-H. Hung and C. Shinha, *Polyhedron*, 2004, **23**, 793–800; C. L. Chen, H. Y. Tan, J. H. Yao, Y. Q. Wan and C. Y. Su, *Inorg. Chem.*, 2005, **44**, 8510–8520; F. Bélanger-Gariépy and A. L. Beauchamp, *J. Am. Chem. Soc.*, 1980, **102**, 3461–3464.
24 F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, L. Brammer and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19.
25 Y. Takahashi, S. Ito, S. Sakai and Y. Ishii, *J. Chem. Soc., Chem. Commun.*, 1970, 1065–1066; R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, 1985.