Reactivity towards nitriles, cyanamides, and carbodiimides of palladium complexes derived from benzyl alcohol. Synthesis of a mixed Pd$_2$Ag complex†

Maria-José Fernández-Rodríguez,* Eloisa Martinez-Viviente,* José Vicente* and Peter G. Jones*

The chelate complex [Pd(x$_2$-C$_6$H$_4$CH$_2$O-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(x$_2$-C$_6$H$_4$(CH$_2$OC(-NX)Y)-2)(bpy)][OTf], where X = H, Y = Me (I), NMe$_2$ (2a), NE$_2$(2b), X = R, Y = NhR (R = 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=NTol (Tol = p-Toly1) results in the formation of the neutral complex [Pd(x$_2$-C$_6$H$_4$(CH$_2$OC(-NTol)INTol)-2)(bpy)] (4). Complexes 3b and 4 can be interconverted by deprotonation (3b + KO'Bu) or protonation (4 + KOTf + HOTf) reactions. When the reaction of II with TolN=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$_2$Pd complex 5 is obtained (5 = [Ag(N–4)$^2_2$(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 [Pd(C$_6$H$_4$CH$_2$OH-2)(bpy)] (I) reacts with 1′PrN$_2$=C=NTol in the presence of TIOTf, instead of AgOTf, a ca. 1 : 1 mixture of 3a and [Pd(x$_2$-O,N-OCH$_2$(C$_6$H$_4$(C=NH(Pr)NPr)-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 5.2.5CHCl$_3$·0.5Et$_2$O have been determined by X-ray diffraction studies.

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.⁵,¹⁰–¹³ Their reactions with CO, isocyanides, alkenes, alkynes, and allenes did not involve the OH group in the ortho position.⁶,¹¹ 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 insertion¹⁰–¹² 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...
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.\textsuperscript{11}

We have recently extended this research to \textit{ortho}-palladated hydroxymethylphenyl complexes,\textsuperscript{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\textsuperscript{15} or oxapalladacycles derived from them.\textsuperscript{16} These compounds have been used as precatalysts in Heck and cross-coupling reactions,\textsuperscript{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.\textsuperscript{16} In our recent work\textsuperscript{14} we synthesized the complex [Pd\{\(\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{OH}-2\}\text{(bpy)}\] (I) and investigated its reactivity towards alkynes, alkene, cyanamides, cyanides, allenes, and carbon monoxide, which did not result in clean insertion (C←Pd bond) or addition (O←H bond) reactions.\textsuperscript{14} Only the reaction of I with XyNC gave a clean insertion product, \textit{trans}-[Pd\{\(\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{OH}-2\}\text{(CNXy)}\] ,\textsuperscript{14} By deprotonation of complex I we prepared the chelate complex [Pd\{\(\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{OH}-2\}\text{(bpy)}\] (II), which displayed an interesting reactivity towards primary alkyl halides, \textit{via} a nucleophilic attack of the coordinated oxygen at the alkyl group of the halide.\textsuperscript{14} We have now extended our research to the chelate complex II, which, in the presence of AgOTf, reacts with acetonitrile and cyanamides, and carbodiimides to give novel complexes containing a [Pd\{\(\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{OH}-2\}\text{(CNXy)}\] 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\textsuperscript{+} 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 complex\textsuperscript{18} or Pd\_2Ag\textsuperscript{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.\textsuperscript{14}
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 \([\text{PdCl(C}_6\text{H}_4\text{Y}-2)(\text{tmeda})]\) \((Y = \text{OH}, \text{NH}_2)\), 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 \([\text{PdCl(C}_6\text{H}_4(\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl})-2})(\text{bpy})]\) \((\text{III})\), 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 \((R = ^1\text{Pr}, \text{Tol})\) and AgOTf \((1:5:1 \text{ molar ratio, } \text{CH}_2\text{Cl}_2)\) in the presence of residual water, to form \([\text{Pd}[k^2-C_5\text{N}-\text{C}_6\text{H}_4(\text{CH}_2\text{OC}(-=\text{NR})\text{NHR})-2-](\text{bpy})][\text{OTf}]\) \((R = ^1\text{Pr} \text{(3a), Tol (3b), Scheme 2})\) 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 \(^1\text{PrN} = \text{C} = \text{N}^1\text{Pr}\) there was no reaction, whereas with TolN = C = NTol the reaction in the absence of AgOTf resulted in the formation of \([\text{Pd}[k^2-C_5\text{N}-\text{C}_6\text{H}_4(\text{CH}_2\text{OC}(-=\text{NTol})\text{N}[\text{NTol}]-2)(\text{bpy})]]\) \((4\text{, Scheme 2})\), 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\(_2\)O.

By deprotonation of the ionic complex 3b with KO\(^i\)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 \((R = ^1\text{Pr})\) with KO\(^i\)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\(_2\)Ag\(_{18}\) or Pd\(_2\)Ag\(_{19}\) complexes found in
the literature. With the carbodiimide \(^{1}\)PrN\(=\)C\(=\)N’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 \(\Pi\) 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 \(\Pi\) on a [Ag(TolN\(=\)C\(=\)NTol)] \(^{-}\) 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 \(\Pi\), 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\(_2\)Cl\(_2\), 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 \(\Pi\) 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 \(\Pi\)) 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 [PdII(C\(_6\)H\(_4\)CH\(_2\)OH-2)[bpy]] \(^{1}\) (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 \(^{3}\)PrN\(=\)C\(=\)N’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[x\(^2\)-O,N-OCH\(_2\)(C\(_6\)H\(_4\)(C\(=\)N’Pr)[NHPr]=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 4V, 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.\(^{1}\) 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 cyamidates, 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.\(^{1}\) together with a more extended discussion.

For the complexes 1–5, the insertion of the organic molecules (MeC\(=\)N\(_2\)R\(_2\)NC\(=\)N\(_2\), 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\(_2\)OH 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 \(\phi\)-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\(^{1}\)). For \(3a, b\) and 6, the position of the proton at the uncoordinated N is also confirmed by the \(^{1}\)H-NOE 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 (\(\delta\) 8.45 ppm) than in \(2a, b\) (\(\delta\) 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...
cytans, 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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 13C 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 Pd₂Ag 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 13C NMR resonances is observed. One of the tolyl groups (the one closer to the Ag) again shows strongly broadened 1H and 13C 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=O stretching vibrations from the 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.
other Ag-N bond distances reported in the literature for compounds with a N-Ag-N moiety.\textsuperscript{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°).\textsuperscript{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$_2$N(2)--C(8) (1.343(4) Å, 2a), Pr$_2$N(2)--C(8) (1.346(2) Å, 3a), and TolN(1)--C(7), TolN(3)--C(37) (1.31(4) and 1.322(10) Å, 5) are much shorter than the C-N bonds (Me-N, 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; 1.305(4) 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).\textsuperscript{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 carboximidates and cyanamides into the C-Pd bond, or the addition of carboximidates to the O-H bond, of ortho-palladated phenol derivatives.\textsuperscript{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$_3$O chelate) towards nitriles, cyanamides and carboximidates. With the chelate complex we have obtained novel neutral or ionic complexes containing a 7-membered κ$^2$-C$_3$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$_2$Ag complex has also been synthesized. Starting from the non-chelate complex, we have achieved the insertion of a carboximide 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. $5 \times 10^{-4}$ M solutions in acetonitrile, 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$_2$Cl$_2$ and Et$_2$O were distilled before use. [Pd(II)]$_2$(C$_8$H$_8$CH$_2$OH-2)[bpy] (I),\textsuperscript{14} [Pd(κ$^2$-C$_3$O-C$_8$H$_8$CH$_2$OH-2)[bpy]] (II),\textsuperscript{14} and [Pd(dba)$_2$]$_2$\textsuperscript{25} were prepared.
Synthesis of [Pd(κ²-C₅N-C₄H₄(CH₂OC(=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-C₅N-C₄H₄(CH₂OC)](bpy) (II) (100 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) under N₂. 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 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 1 as a pale yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 85 mg (56%). Mp: 99 °C. Anal. Calcd for C₂₁H₁₉F₃N₄O₄PdS: C, 42.58; H, 2.92; N, 7.19; S, 5.42. Single crystals of 1 were grown by liquid diffusion of Et₂O into a solution of 2a in CH₂Cl₂.

Synthesis of [Pd(κ²-C₅N-C₄H₄(CH₂OC(=NH)Ne)-2)(bpy)](OTf) (2b)

Diethylcyanamide (133 mg, 1.35 mmol) and AgOTf (69 mg, 0.27 mmol) were added to a solution of II (100 mg, 0.27 mmol) in CH₂Cl₂ (20 mL) under N₂. 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. 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 2b as a pale yellow solid, which is soluble in CH₂Cl₂, CHCl₃, and acetone. Yield: 100 mg (54%). Mp: 104 °C. Anal. Calcd for C₂₁H₁₉F₃N₄O₄PdS: C, 44.95; H, 4.22; N, 8.85; S, 4.89.
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 acetonitrile. Yield: 104 mg (60%). Mp: 195 °C. λmax (acetone): 140\(\Omega^{-1}\) cm\(^{-1}\) mol\(^{-1}\). IR (cm\(^{-1}\)): \(\nu(S=O)\) 1028, 1276, \(\nu(C=N)\) 1611, \(\nu(NH)\) 3354. \(^1\)H NMR (400 MHz, CDCl3): 8.68 (dd, 2\(\lambda_{HH}\) = 5 Hz, 2\(\lambda_{HH}\) = 1 Hz, 1H, H16’ bpy), 8.52 (dd, 2\(\lambda_{HH}\) = 5 Hz, 2\(\lambda_{HH}\) = 1 Hz, 1H, H6 bpy), 8.40 (d, 2\(\lambda_{HH}\) = 8 Hz, 1H, H13 bpy), 8.35 (d, 2\(\lambda_{HH}\) = 8 Hz, 1H, H13’ bpy), 8.16 (td, 2\(\lambda_{HH}\) = 8 Hz, 1H, H14 bpy), 8.15 (td, 2\(\lambda_{HH}\) = 8 Hz, 2\(\lambda_{HH}\) = 2 Hz, 1H, H14’ bpy), 7.82 (ddd, 2\(\lambda_{HH}\) = 8 Hz, 2\(\lambda_{HH}\) = 5 Hz, 2\(\lambda_{HH}\) = 1 Hz, 1H, H15’ bpy), 7.44 (ddd, 2\(\lambda_{HH}\) = 8 Hz, 5\(\lambda_{HH}\) = 5 Hz, 1\(\lambda_{HH}\) = 1 Hz, H15’ bpy), 7.39 (ddd, 2\(\lambda_{HH}\) = 7 Hz, 5\(\lambda_{HH}\) = 1 Hz, 1H, H6 aryl), 7.26 (td, 2\(\lambda_{HH}\) = 7 Hz, 2\(\lambda_{HH}\) = 2 Hz, 1H, H5 aryl), 7.07 (td, 2\(\lambda_{HH}\) = 7 Hz, 2\(\lambda_{HH}\) = 1 Hz, 1H, H4 aryl), 7.03 (dd, 2\(\lambda_{HH}\) = 7 Hz, 2\(\lambda_{HH}\) = 2 Hz, 1H, H3 aryl), 6.65 (A part of AB system, 2\(\lambda_{HH}\) = 11 Hz, 1H, CH1), 5.57 (2\(\lambda_{HH}\) = 7 Hz, 1H, NH1), 5.12 (B part of AB system, 2\(\lambda_{HH}\) = 11 Hz, 1H, CH3), 3.89 (d, 2\(\lambda_{HH}\) = 7 Hz, 2\(\lambda_{HH}\) = 6 Hz, 1H, CH2, 2\(\lambda_{HH}\) = 3 ppm), 3.78 (sept, 2\(\lambda_{HH}\) = 6 Hz, 1H, CH2, 2\(\lambda_{HH}\) = 1 ppm), 1.35 (2\(\lambda_{HH}\) = 6 Hz, 3H, Me2 Pr’), 1.28 (d, 2\(\lambda_{HH}\) = 6 Hz, 3H, Me2 Pr’), 1.14 (d, 2\(\lambda_{HH}\) = 6 Hz, 3H, Me2 Pr’), 0.70 (d, 2\(\lambda_{HH}\) = 6 Hz, 3H, Me2 Pr’), 13C\(^{1}\)H NMR (100.6 MHz, CDCl3): 156.9 (C12 bpy), 156.3 (C13 bpy), 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), 128.8 (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, \(\nu(CF)\) = 320 Hz, OTf), 74.3 (CH2), 51.0 (CH2 Pr’), 45.4 (CH2 Pr’), 26.0 (Me2 Pr’), 23.7 (Me Pr’), 23.1 (Me Pr’), 22.0 (1C, Me Pr’), Anal. Calcd for C\(_{31}\)H\(_{22}\)F\(_{2}\)N\(_{2}\)O\(_{4}\)PdS: C, 51.77; H, 4.00; N, 8.35; S, 4.59. Found: C, 51.60; H, 4.20; 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\(^{2+}\)-2,3-C\(_{2}\)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 CH2Cl2 (20 mL) under N\(_{2}\). The mixture was stirred for 3 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 3b as a red solid, which is soluble in CH2Cl2, CHCl3, and acetonitrile, and partially soluble in Et2O. Yield: 130 mg (81%). Starting from 3b; KOtBu (27 mg, 0.24 mmol) was added to a solution of 3b (60 mg, 0.08 mmol) in CH2Cl2 (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\(^{-1}\)): \(\nu(C=N)\) 1660. \(^1\)H NMR (400 MHz, CDCl3): 8.45 (d, \(\lambda_{HH}\) = 5 Hz, 1H, H16’ bpy), 8.39 (d, \(\lambda_{HH}\) = 5 Hz, 1H, H16 bpy), 8.06 (d, \(\lambda_{HH}\) = 8 Hz, 1H, H13 bpy), 8.02 (d, \(\lambda_{HH}\) = 8 Hz, 1H, H13’ bpy), 7.96 (t, \(\lambda_{HH}\) = 8 Hz, 1H, H14’ bpy), 7.91 (t, \(\lambda_{HH}\) = 8 Hz, 1H, H14’ bpy), 7. A part of AB system, 8.01 (d, \(\lambda_{HH}\) = 8 Hz, 2H, o-H Tol), 7.70 (d, \(\lambda_{HH}\) = 7 Hz, 1H, H6 aryl), 7.39–7.30 (m, 2H, H15, 15’ bpy), 7.03 (t, \(\lambda_{HH}\) = 7 Hz, 1H, H5 aryl), 7.00–6.95 (br m, 4H, o-H Tol), 6.93 (t, \(\lambda_{HH}\) = 7 Hz, 1H, H4 aryl), 6.85 (8 part of AB system, \(\lambda_{HH}\) = 8 Hz, 2H, m-H

Synthesis of [Pd\(^{2+}\)-2,3-C\(_{2}\)N-C\(_{6}\)H\(_{4}\)(CH\(_{2}\)OC(=NTOl)NHTol)-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 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 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 acetonitrile. This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.
TolB), 6.70 (d, J_{HH} = 7 Hz, 1H, H3), 5.02 and 4.73 (br) (AB system, J_{HH} = 14 Hz, 2H, CH₂), 2.27 (s, 3H, Me TolB), 2.16 (s, 3H, Me TolB), 1.54 (s, 2H, H₂O), 13C (¹H) NMR (150.9 MHz, CDCl₃, 213 K): 155.7 (C=O), 155.2 (C₁₂ bpy), 153.1 (C₁₂' bpy), 125.1 (CH₁₆ bpy), 149.6 (C₁ ary1), 149.3 (CH₁₆' bpy), 147.9 (i-C TolB), 146.4 (t-C TolB), 140.7 (C₂ aryl), 139.1 (CH₁₄ bpy), 138.8 (CH₁₄ bpy), 136.2 (CH₆ aryl), 129.5 (p-C TolB), 128.9 (2C, m-CH TolB), 128.92 (p-C TolB), 128.91 (2C, m-CH TolB), 127.0 (CH₁₅' bpy), 126.9 (CH₅ ary1), 126.7 (CH₁₅ bpy), 124.9 (CH₃ aryl), 124.6 (2C, o-CH TolB), 123.5 (CH₄ aryl), 122.7 (2C, o-CH TolB), 122.1 (CH₁₃ bpy), 121.6 (CH₁₃' bpy), 71.2 (CH₂), 21.1 (Me), 21.0 (Me TolB). Anal. Calcd for C₅₇H₆₄N₂O₇Pd (4H₂O): C, 63.11; H, 4.96; N, 9.20. Found: C, 63.25; H, 4.68; N, 9.27.

Synthesis of [Ag(N₄)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 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. A₅ (acetone): 122 Ω cm² mol⁻¹. IR (cm⁻¹): 2 v(S=O) 1032, 1262, v(C=N) 1609, 1H NMR (600 MHz, CDCl₃): 8.85 (d, JHH = 5 Hz, 1H, H16' bpy), 8.52 (d, JHH = 5 Hz, 1H, H16 bpy), 8.10-8.06 (m, 2H, H13', 14' bpy), 8.04 (d, JHH = 8, 1H, H13 bpy), 8.00 (td, JHH = 8 Hz, JHF = 1 Hz, 1H, H14 bpy), 7.71 (td, JHH = 6 Hz, JHF = 1 Hz, 1H, H15 bpy), 7.57-7.53 (m, 2H, H15 bpy, H6 aryl), 7.43 (d, JHH = 8 Hz, JHF = 1 Hz, 1H, H4 aryl), 7.32 (td, JHH = 8 Hz, JHF = 1 Hz, H₅ aryl), 6.39 (d, JHH = 9 Hz, 1H, NH), 4.57 and 3.84 (AB system, JHH = 10 Hz, 2H, CH₂), 4.25 (sept, JHH = 6 Hz, 1H, CH₂Pr), 3.55 (dspt, JHH = 9 Hz, JHF = 6 Hz, 1H, CH₂Pr), 1.65 and 1.54 (d, JHH = 6 Hz, 3H, Me Pr), 1.40 and 1.04 (d, JHH = 6 Hz, 3H, Me Pr)³³. C (¹H) NMR (150.9 MHz, CDCl₃): 162.0 (C=N), 155.7 (C₁₂ bpy), 154.8 (C₁₃ bpy), 152.2 (CH₂ bpy), 148.1 (CH₁₆' bpy), 146.0 (C₂ aryl), 140.6 (CH₁₄' bpy), 140.1 (CH₁₄ bpy), 134.2 (C₁ ary1), 131.3 (C₄ ary1), 130.8 (C₃ 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, JCF = 321 Hz, OTf), 69.9 (CH₂), 50.7 (CH₂Pr), 48.9 (CH₂Pr), 33.1 (CH₂), 21.2 (CH₄).
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-Rodriguez 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. Sureka, 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. Canoves, F. Visentin, C. Santo, C. Levi and A. Dolmella, Organometallics, 2007, 26, 5590–5601; K. J. Cavell and D. S. McGuinness, 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. Suzuki, 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. Ramirez 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. Ramirez 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, 2003, 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-Llamos, Comments Inorg. Chem., 2007, 28, 39–72.

8 J. Vicente, J. A. Abad, R. Berge, M. C. Ramirez de Arellano, E. Martinez-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. Martinez-Viviente and P. G. Jones, Organometallics, 2003, 22, 1967–1978.

9 J. Vicente, I. Saura-Llamos, 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-Llamos, 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-Rodriguez, E. Martínez-Viviente, J. Vicente and P. G. Jones, Organometallics, 2015, 34, 3282–3291.

15 M. Shiotsuki, A. Nakagawa, J. Rodriguez-Castañon, N. Onishii, 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. Pomeiro, 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.