Synthesis, Structure, Reactivity, and Catalytic Activity of *C,N*- and *C,N,N*-Orthopalladated Iminophosphoranes

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The orthopalladated complexes $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2{=}NPh\text{-}\kappa\text{-}C,N)]_2$ (**1**) and $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)Cl]$ (**11**) have been obtained by reaction of $Pd(OAc)_2$ (OAc = acetate) with the iminophosphoranes $Ph_3P{=}NPh$ and $Ph_3P{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4$, respectively, in the presence of excess LiCl. Complex **11** has been characterised by X-ray diffraction methods. The orthoplatinated derivative $[Pt(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)Cl]$ (**12**) can be obtained by reaction of $[PtCl_2(NCPh)_2]$ with $Ph_3P{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4$ in refluxing 2-methoxyethanol. Complex **1** shows the typical reactivity of *C,N*-orthopalladated complexes, while complex **11** shows that the *C,N,N*-orthometallated ligand is strongly bonded to the Pd atom and cannot be easily displaced. The catalytic activity of the complexes $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2{=}NPh\text{-}\kappa\text{-}C,N)]_2$ (**1**), $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}NPh\text{-}\kappa\text{-}C,N)(Cl)(py)]$ (**4**), $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)Cl]$ (**11**) and $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)(NCMe)]ClO_4$ (**13**) in the Mizoroki–Heck (MH) reaction between methyl acrylate and different haloarenes has been examined. All complexes behave as moderate to good catalysts, yielding turnover numbers (TON) up to 526000. Their role as catalysts or precatalysts and the formation of nanoparticles is also discussed.

Introduction

Iminophosphoranes (phosphane imines) are compounds of general structure $R_3P{=}NR'$ (R, R′ = alkyl, aryl, acyl, etc). They show notable analogies with the phosphorus ylides $R_3P{=}CR'(R'')$,[1] and also have numerous applications in organic chemistry (e.g. the aza-Wittig reaction), either as neutral or as anionic reagents.[1–3] In addition, the bonding properties of these compounds as ligands towards transition metals are still attracting the interest of chemists,[4–28] for several reasons: their ability to form and to stabilize carbene complexes,[5,8] the easy modulation of the electronic and steric properties of different types of catalysts (for instance, in oligo- and polymerisation of ethylene,[4,6,23] hydrogen-transfer processes,[9,10] etc.), their applications in enantioselective synthesis and catalysis (allylic substitution),[25,26] the synthesis of alkaline earth organometallic complexes,[7] and, in general, due to their versatility. In this context, we have recently reported some aspects of the chemistry of the α-stabilized iminophosphoranes $Ph_3P{=}NCN$, $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$, which can behave as monodentate, bridging bidentate or chelate bidentate ligands towards Pd^{II} and Pt^{II} complexes using different donor atoms.[29,30]

However, the synthesis of orthometallated aryl complexes derived from iminophosphoranes is still scarcely represented, as well as the properties of the resulting complexes (reactivity, catalytic performance),[31–36] although very recently relevant contributions have appeared in the literature.[37,38]

With the aim of expanding the scope of this type of orthometallated derivatives, and also to gain more insight into their chemical behaviour, we have studied the reactivity of several iminophosphoranes towards Pd^{II} and Pt^{II} metallating reagents. In addition, we have also studied the reactivity of the resulting orthopalladated complexes towards different neutral and anionic ligands. We also report their behaviour as catalysts in specific C–C couplings such as the MH reaction, a field in which the application of orthopalladated complexes is in continuous growth.[39–44]

Results and Discussion

Synthesis of Orthometallated Iminophosphorane Complexes

The reactivity of different iminophosphoranes, such as $Ph_3P{=}NPh$, $Ph_3P{=}NCN$,[45] $Ph_3P{=}NC(O)CH_2Cl$, $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$[46] and $Ph_3P{=}N{-}N{\equiv}C$[47] towards some standard metallating Pd^{II} and Pt^{II} reagents has been studied. The reaction of $Pd(OAc)_2$ (OAc = acetate) with

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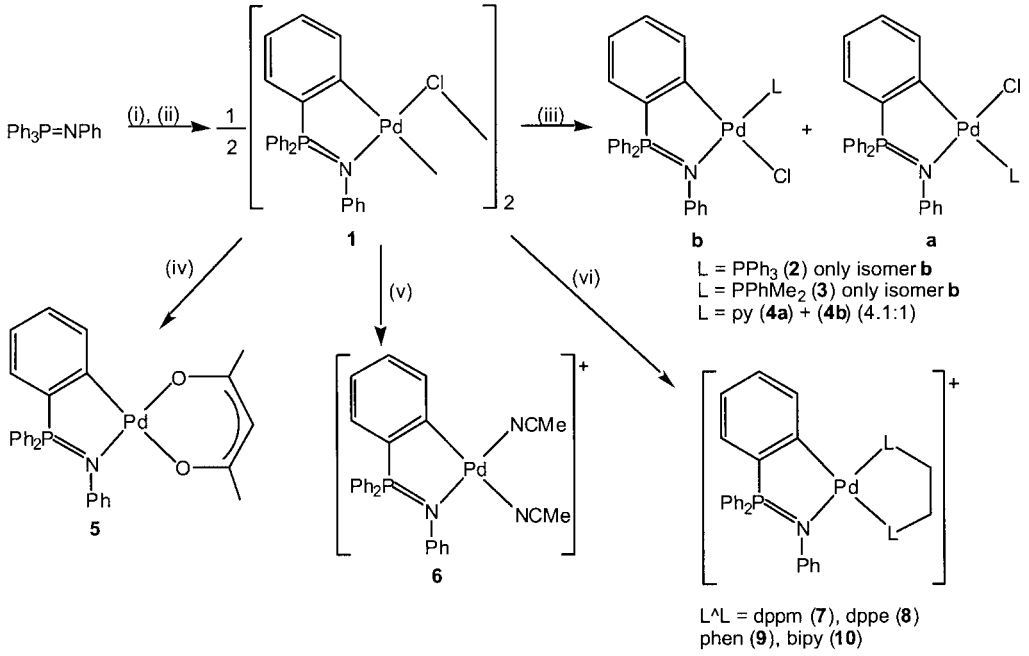
Ph_3P=NPh (1:1 molar ratio) in refluxing CH_2Cl_2, followed by evaporation to dryness and treatment of the residue with excess LiCl in MeOH, gives the orthometallated dimer $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}NPh\text{-}\kappa\text{-}C,N)(\mu\text{-}Cl)]_2$ (**1**) in very good yield (see Scheme 1). It has been previously reported that complexes related to **1**, but with different aryl substituents, can be obtained from the reaction of $Na_2[PdCl_4]$[36] or $Pd(OAc)_2$[37] and the corresponding iminophosphoranes in moderate to good yields (56–97%). The synthesis of **1** has been reported very recently[38] from the reaction of $[o\text{-}C_6H_4\text{-}PPh_2NPh)Li]_2{\cdot}OEt_2$ with $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene). However, this process gives a mixture of **1** and the bis-aryl derivative, from which **1** is isolated in very poor yield (14%). As expected, **1** can also be obtained from the reaction of $Li_2[PdCl_4]$ and Ph_3P=NPh, but this reaction gives a mixture of **1** and the N-bonded derivative $[Cl_2Pd\{N(=PPh_3)Ph\}_2]$ from which **1** could not be separated in pure form. Thus, the preparation described here seems to be the most convenient method for the synthesis of **1**. In order to obtain the corresponding Pt^{II} derivative, two different procedures were checked. The first one involves the direct orthometallation of the substrate by reaction with $[PtCl_2(NCPh)_2]$ in refluxing 2-methoxyethanol, a method successfully applied in the synthesis of cycloplatinated complexes derived from phosphonium salts.[48,49] The second one is the reaction of the substrate with the dimer $[Pt(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in refluxing chloroform.[50] However, neither of the two methods gives the expected orthoplatinated dimer: in the first case, complete reduction to black Pt^0 was observed, while in the second case a complex mixture of unidentified products was obtained.

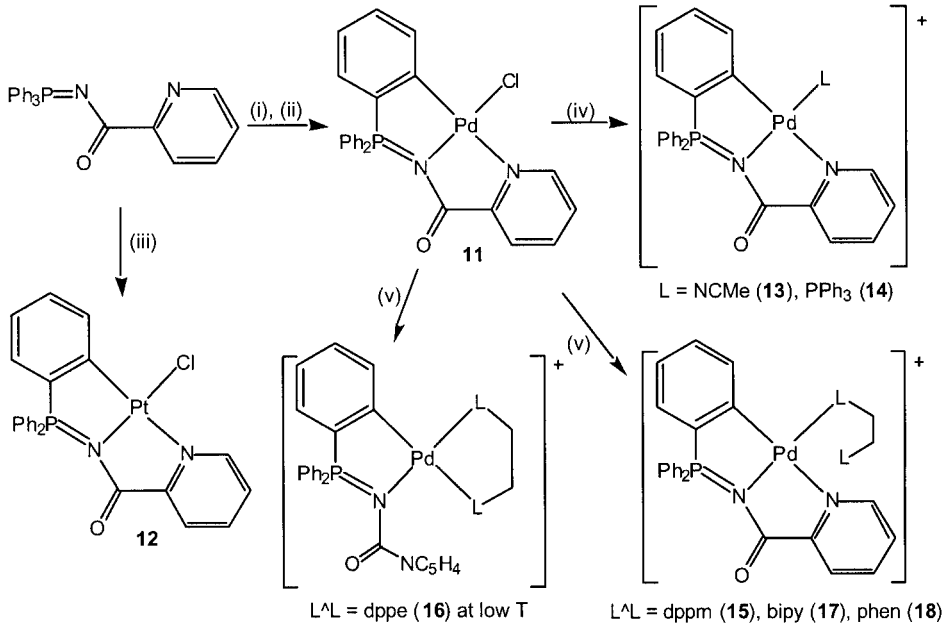
We attempted a similar reaction with the other α-stabilized iminophosphoranes. The reaction of $Pd(OAc)_2$ with Ph_3P=N-C(O)-2-NC_5H_4 and with LiCl, performed under the same experimental conditions as those reported for **1**, gives the orthometallated monomer $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)(Cl)]$ (**11**) in good yield (see Scheme 2). As described for **1**, the reaction of $Li_2[PdCl_4]$ with Ph_3P=N-C(O)-2-NC_5H_4 gives a mixture of **11** and the coordination product $[Cl_2Pd\{N(=PPh_3)C(O)\text{-}2\text{-}NC_5H_4\}]$, already described by us,[30] and from which **11** could not be cleanly separated. On the other hand, the analogous Pt^{II} complex $[Pt(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N)(Cl)]$ (**12**) can be easily obtained in moderate yield by reaction of $[PtCl_2(NCPh)_2]$ with Ph_3P=N-C(O)-2-NC_5H_4 (1:1 molar ratio) in refluxing 2-methoxyethanol for 8 h. It is worthwhile to note that the previous reactivity of the iminophosphorane Ph_3P=N-C(O)-2-NC_5H_4 towards different Pd^{II} and Pt^{II} precursors[30] never resulted in a metallated compound. The obvious difference in reactivity with that reported here comes from the reaction conditions: the processes performed at room temperature or at a low reflux temperature (CH_2Cl_2/acetone) give coordination compounds,[30] while those performed in harsh conditions (refluxing 2-methoxyethanol) give the metallated derivatives.

Attempted orthometallation reactions involving the iminophosphoranes $Ph_3P{=}NC{\equiv}N$, $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NN{\equiv}C$ using the methods described above were not successful. In the case of Pd, mixtures of the corresponding *cis*- and *trans*-$[Cl_2Pd(N\text{-ligand})_2]$ derivatives were obtained;[29,30] in the case of platinum only decomposition to black Pt^0 was observed. Due to the lack of reactivity of these iminophosphoranes, they were not further investigated.

Complex **1** has been characterised previously and its structure is shown in Scheme 1.[38] Complexes **11** and **12**



Scheme 1. (i) $Pd(OAc)_2$, reflux, CH_2Cl_2; (ii) LiCl, room temp., MeOH; (iii) L, CH_2Cl_2, room temp.; (iv) Tl(acac), – TlCl, CH_2Cl_2, room temp.; (v) $AgClO_4$, – AgCl, NCMe, room temp.; (vi) $AgClO_4$, – AgCl, L, acetone, room temp.



Scheme 2. (i) $Pd(OAc)_2$, reflux, CH_2Cl_2; (ii) LiCl, room temp., MeOH; (iii) $[PtCl_2(NCPh)_2]$, 2-methoxyethanol, reflux; (iv) $AgClO_4$, – AgCl, L, NCMe or acetone, room temp.; v) $AgClO_4$, – AgCl, L, acetone, room temp.

give satisfactory elemental analyses, and their mass spectra show the expected molecular peaks with the correct isotopic distribution. The IR spectra of **11** and **12** show sharp absorptions due to the ν_{CO} stretch at 1644 (**11**) and 1646 (**12**) cm^{-1}, shifted to higher frequencies with respect to the corresponding absorption in the free ligand, and also show two strong bands due to the ν_{PN} stretch at 1332 (**11**) and 1330 (**12**) cm^{-1}, while in the free ligand this absorption appears at 1366 cm^{-1}.[46] These two facts indicate that the iminic N-atom is coordinated to the metal centre.[30] The ^1H NMR spectra of **11** and **12** show similar patterns, and unambiguously reveal the presence of the cyclometallated $[M(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-})]$ unit. Thus, four different signals assigned to the protons of the C_6H_4 unit can be observed at δ = 7.00, 7.13, 7.28 and 8.10 ppm in complex **11** and at δ = 6.95, 7.05, 7.23 and 8.02 ppm in **12**, with the signal at δ = 8.02 ppm showing ^{195}Pt satellites, as well as signals corresponding to the pyridine group. Moreover, the N-bonding of the pyridine ring can be inferred from the shift to low field of the resonance attributed to the H_α proton (δ = 8.97 ppm in **11**; δ = 9.17 ppm in **12**) with respect to its position in the free ligand (δ = 8.69 ppm),[46] and from the presence, in **12**, of ^{195}Pt satellites for the multiplet at δ = 9.17 ppm ($^3J_{Pt,H} \approx 20$ Hz). These IR and ^1H NMR spectroscopic data are in good agreement with the structure proposed in Scheme 2 for **11** and **12**, in which the orthometallated iminophosphorane acts as a *C*,*N*,*N*-terdentate ligand. The $^{31}P\{^1H\}$ NMR spectra of **11** and **12** show singlet signals at δ = 51.88 ppm in both cases (the signal of **12** shows the expected ^{195}Pt satellites), and these signals are strongly deshielded with respect to their position, not only in the free ligand (δ = 23.89 ppm) but also in the *N*,*N*-bonded complexes ($\delta \approx$ 34 ppm).[30] The position of this resonance is similar to that found in other recently described cyclopalladated derivatives in which the metallated iminophosphorane behaves as a *C*,*N*-chelating group.[37] Finally, the $^{13}C\{^1H\}$ NMR spectrum of **11** shows signals corresponding to the presence of all the expected functional groups, and confirms the structure proposed in Scheme 2. The orthometallated carbon atom C_1-Pd appears at δ = 153.19 ppm.

In summary, the standard methods of C–H bond activation to give orthometallated complexes of Pd^{II} and Pt^{II} can be applied successfully to iminophosphorane ligands to afford cyclopalladated and cycloplatinated complexes. The crystal structure of **11** has been determined by X-ray diffraction methods and provides additional structural information.

X-ray Structure of Complex 11

Crystals of **11** of adequate quality for X-ray purposes were grown by slow vapour diffusion of Et_2O into a CH_2Cl_2 solution of the crude complex at room temperature. A drawing of the organometallic complex is shown in Figure 1. The parameters concerning the data collection and refinement are collected in Table 1, and selected bond lengths and angles are given in Table 2.

The Pd atom is located in a slightly distorted square-planar environment and is surrounded by the metallated carbon atom C(7), the chlorine atom Cl(1) and the two N atoms of the iminophosphorane ligand, the iminic N atom, N(1), and the pyridinic N atom, N(2). Thus, the metallated iminophosphorane behaves as a *C*,*N*,*N*-terdentate ligand, in good agreement with the NMR spectroscopic data, forming two fused, five membered rings. The bite angles of the two chelating moieties are 87.24(9)° [C(7)–Pd(1)–N(1)] and 79.40(8)° [N(1)–Pd(1)–N(2)], and the sum of the bond

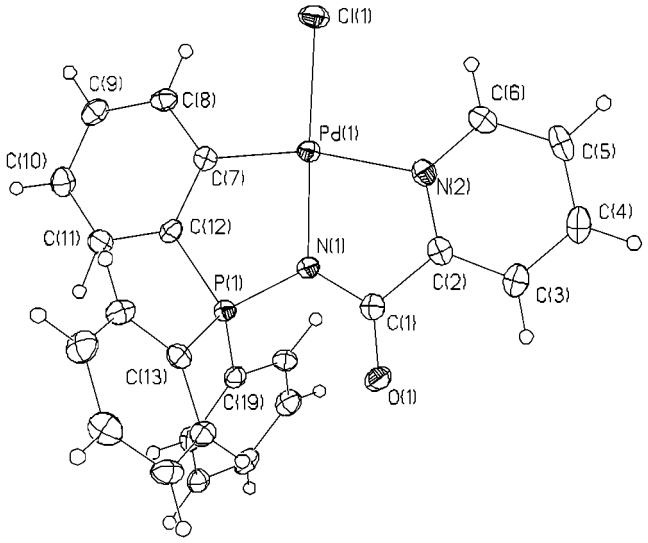


Figure 1. Thermal ellipsoid plot of [Pd(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)Cl] (**11**). Non-hydrogen atoms are drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for complex **11**.

Formula	$C_{24}H_{18}ClN_2OPPd$
Formula mass	523.22
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	9.9726(6)
b [Å]	11.4926(7)
c [Å]	18.6220(11)
β [°]	101.033(1)
V [Å^3]	2094.8(2)
Z	4
D_c [Mg m^{-3}]	1.659
μ [mm^{-1}]	1.109
Refl. collected	18137
Unique reflections	4791, R_{int} = 0.0391
Data/restr./param.	4791/0/271
R_1 [$I > 2\sigma(I)$]	0.0300
wR_2 [$I > 2\sigma(I)$]	0.0660
Goodness of fit	1.042
T [K]	100(2)
λ(Mo-K_α) [Å]	0.71073

Table 2. Selected bond lengths [Å] and angles [°] for complex **11**.

Pd(1)–C(7)	1.976(3)	Pd(1)–N(1)	1.997(2)
Pd(1)–N(2)	2.120(2)	Pd(1)–Cl(1)	2.3039(7)
P(1)–N(1)	1.649(2)	P(1)–C(12)	1.777(3)
P(1)–C(13)	1.788(3)	P(1)–C(19)	1.796(3)
C(1)–O(1)	1.227(3)	N(1)–C(1)	1.362(3)
N(2)–C(6)	1.335(3)	N(2)–C(2)	1.347(3)
C(1)–C(2)	1.506(4)	C(7)–C(8)	1.403(3)
C(7)–C(12)	1.416(3)	C(8)–C(9)	1.382(4)
C(9)–C(10)	1.388(4)	C(10)–C(11)	1.383(4)
C(11)–C(12)	1.395(4)		
C(7)–Pd(1)–N(1)	87.24(9)	C(7)–Pd(1)–N(2)	166.54(9)
N(1)–Pd(1)–N(2)	79.40(8)	C(7)–Pd(1)–Cl(1)	96.06(8)
N(1)–Pd(1)–Cl(1)	175.83(6)	N(2)–Pd(1)–Cl(1)	97.35(6)
N(1)–P(1)–C(12)	100.49(11)	C(1)–N(1)–P(1)	122.96(18)
C(1)–N(1)–Pd(1)	118.70(17)	P(1)–N(1)–Pd(1)	117.10(11)
O(1)–C(1)–N(1)	125.2(2)	O(1)–C(1)–C(2)	122.5(2)
N(1)–C(1)–C(2)	112.3(2)		

angles around the Pd(1) atom is 360.05(9)°. The molecule deviates only slightly from planarity: for instance, the maximum deviations found in the best least-square planes defined by [C(7)–C(12)–P(1)–N(1)–Pd(1)] and [Pd(1)–N(1)–C(1)–C(2)–N(2)] are only 0.09 Å and 0.02 Å, respectively. The dihedral angle between these two planes is 4.5°. The Pd(1)–C(7) bond length [1.976(3) Å] is statistically identical or slightly longer than those found in the related complex [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4Me-4′)-2}(μ-OAc)]$_2$ [1.964(3) Å and 1.959(3) Å], and is shorter than that found in [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4Me-4′)-2}(tmeda)]ClO_4 [2.019(3) Å] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[37] The Pd–N(iminic) bond length [Pd(1)–N(1) = 1.997(2) Å] is shorter than those found in the aforementioned related complexes [2.050(2), 2.051(2) and 2.055(2) Å], probably reflecting the low *trans* influence of the chlorine ligand. The Pd–N(pyridine) bond length [Pd–N(2) = 2.120(2) Å] is similar to those found in related arrangements (pyridine *trans* to aryl carbon).[51,52] This distance is longer than those found in related Pd^{II} complexes in which the pyridine fragment is *trans* to an atom with a smaller *trans* influence; for instance, the Pd–N(py) bond length in [Pd($C_6H_4CH_2NMe_2$)(Ph_3PNC(O)-2-NC_5H_4)]ClO_4 is 2.056(3) Å, and in this complex the pyridine is *trans* to the aminic N atom of the NMe_2 group.[30]

The P(1)–N(1) bond length [1.649(2) Å] is longer than those reported in all related complexes. The complex [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4Me-4′)-2}(μ-OAc)]$_2$ shows P–N bond length values of 1.605(2) Å and 1.610(2) Å, while that found in [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4Me-4′)-2}(tmeda)]ClO_4 is 1.607(3) Å.[37] This clear elongation of the P–N bond in **11** is due to two main facts: the coordination of the N atom and the presence of the carbonyl group, which delocalizes the charge density through the P-N-C-O system. As a comparison, the P–N bond length in [Pd($C_6H_4CH_2NMe_2$)(Ph_3PNC(O)-2-NC_5H_4)]ClO_4 is 1.624(4) Å,[30] and in this complex the iminophosphorane bonds to the palladium through the pyridine N-atom and the carbonyl oxygen, leaving the -N=P fragment uncoordinated. The delocalisation of the charge density is also reflected in the short value of the N(1)–C(1) bond length [1.362(3) Å], which is similar, within experimental error, to that found in Ph_3P=NC(O)Ph [1.353(5) Å].[53,54] Finally, the environment around the P atom is tetrahedral, with P–C bond lengths similar to those found in related complexes.[30,37]

Reactivity of Orthometallated Iminophosphorane Complexes

The reactivity of complexes **1** and **11** was examined in order to check the stability of the metallated chelating (**1**) or pincer (**11**) ligands. The main results are resumed in Scheme 1 and 2, respectively. Thus, the dinuclear complex **1** reacts with neutral monodentate ligands L (L = PPh_3, $PPhMe_2$ or pyridine) to give the corresponding mononuclear derivatives **2**, **3** and **4**, respectively, as a result of the cleavage of the chloride bridging system. The NMR spectra

of **2** and **3** display a single set of signals in each case, which shows that these complexes are obtained as a single isomer. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows the presence of two doublet signals ($^3J_{P,P}$ = 4.7 Hz), which suggests the *trans* location of the iminic nitrogen and the PPh_3 ligand. The *cis* arrangement of the metallated carbon and the phosphane ligand is in good agreement with the *transphobia* between these ligands.[37,55–57] However, the NMR spectra of complex **4** show the presence of a mixture of isomers **a** and **b** (see Scheme 1) in a molar ratio **4a:4b** of 4.1:1. This fact is worthy of note, since the typical reactivity of *C*,*N*-cyclopalladated halide-bridged dimers towards neutral ligands L (L = phosphanes, pyridines, etc.) always gives a single isomer in which the incoming ligand is coordinated *trans* to the nitrogen atom.[58–60] Moreover, the major isomer **4a** has been characterised as that containing the pyridine ligand *cis* with respect to the iminic nitrogen, that is, to the NPh group. This assignment of structures **4a** and **4b** has been carried out by comparison of the chemical shifts of the H_6 proton of the C_6H_4 group (*ortho* to the metallated position) in the two isomers. Thus, the major isomer **4a** shows the signal corresponding to H_6 at δ = 8.30 ppm, while the minor isomer **4b** shows the corresponding signal at δ = 6.30 ppm. This clear upfield shift can be due to the anisotropic shielding undergone by H_6, which is promoted by the *cis* pyridine ligand in **4b**.[58] In line with this, a mutual anisotropic shielding between the phenyl and pyridine rings in complex **4a** should be possible and, in fact, the chemical shifts of the *ortho* protons of both rings in **4a** are found at higher field than the corresponding ones in **4b** [NPh: δ = 6.79 ppm (**4a**) and δ = 7.13 ppm (**4b**), $\Delta\delta$ = 0.34 ppm; py: δ = 8.52 ppm (**4a**) and δ = 8.90 ppm (**4b**), $\Delta\delta$ = 0.38 ppm]. Obviously, the free rotation of both rings − the pyridine around the Pd–N bond and the phenyl around the N–C bond − gives less-effective shielding (about 0.3–0.4 ppm) than in the case of the fixed orthometallated ring (2 ppm). A similar behaviour is observed in the $^{13}C\{^1H\}$ NMR spectrum of the mixture **4a/4b** (see Experimental Section).

The treatment of **1** with Tl(acac) (acac = acetylacetonate; CH_2Cl_2, 1:2 molar ratio) gives the *O*,*O*′-acac derivative [Pd(C_6H_4-2-PPh_2=NPh)(acac-O,O′)] (**5**), while the reaction of **1** with $AgClO_4$ (1:2 molar ratio) in acetonitrile gives the bis-solvate [Pd(C_6H_4-2-PPh_2=NPh)$(NCMe)_2$]ClO_4 (**6**). The two complexes show correct elemental analyses and mass spectra. Key spectroscopic parameters for **5** are the presence of two strong absorptions attributed to the *O*,*O*′-bonded acac ligand in the IR spectrum (1582, 1515 cm^{-1}) and the presence of the typical signals in the ^1H [δ = 1.74 and 2.06 ppm (CH_3); δ = 5.35 ppm (CH)] and $^{13}C\{^1H\}$ NMR spectra [δ = 27.14 and 27.31 ppm (CH_3); δ = 99.75 ppm (CH); δ = 185.42 and 187.92 ppm (CO)].[61] In the same way, the observation of two absorptions at 2321 and 2291 cm^{-1} in the IR spectrum, and two signals at δ = 2.26 and 2.50 ppm in the ^1H NMR spectrum of **6** suggest the presence of bonded acetonitrile. In these two cases, the presence of the cyclopalladated unit is confirmed through the observation of its characteristic absorptions (IR, ν_{PN}) and resonances in the NMR spectra.

Complex **1** reacts with $AgClO_4$ (1:2 molar ratio) in acetone to give, after filtration of the AgCl, solutions containing the solvated species [Pd(C_6H_4-2-PPh_2=NPh)$(S)_x$]ClO_4 (S = solvent; x = 2). The treatment of these freshly prepared solutions with bidentate ligands L_2 (1:1 molar ratio) gives the cationic complexes [Pd(C_6H_4-2-PPh_2=NPh)(L_2)]ClO_4 [L_2 = $Ph_2PCH_2PPh_2$ (**7**), $Ph_2PCH_2CH_2PPh_2$ (**8**), 1,10-phenanthroline (**9**), 2,2′-bipyridine (**10**)]. We have not observed the displacement of the metallated unit, nor the decoordination of the iminic nitrogen, even if the reactions are performed in presence of an excess of incoming ligand L_2. Compounds **7**–**10** show correct elemental analyses and mass spectra, and their IR spectra show in all cases the presence of a strong absorption in the range 1260–1290 cm^{-1}, assigned to the ν_{PN} stretch, which suggest that the iminic N-atom is bonded to the metal centre. The chelate coordination of the L_2 ligands is clearly inferred from their NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows three signals, one at low field (δ = 48.38 ppm) attributed to the P atom in the metallated ring, and two at high field (δ = –10.60 and –34.16 ppm) characteristic of the *P*,*P*′-chelating dppm.[62] From the analysis of the $^{31}P\{^1H\}$ NMR spectrum of **8** the *P*,*P*′-bonding mode of the dppe is also evident since it shows three low-field signals, one corresponding to the iminophosphorane (δ = 45.31 ppm) and the other two to the dppe ligand (δ = 43.81 and 58.85 ppm).[63] In the case of complex **9** the ^1H NMR spectrum shows, in addition to the signals assigned to the NPh, PPh_2 and C_6H_4 protons, eight sharp peaks attributed to the phen ligand, and this fact clearly reveals the inequivalence of the two halves of the phen ligand due to its *N*,*N*′-bonding to the metal centre. Moreover, the complete attribution of all resonances of the phen ligand can be done unambiguously since one of the *ortho* protons is shifted to high field (δ = 8.00 ppm) with respect to the other (δ = 9.22 ppm) due to the anisotropic shielding exerted by the NPh ring.

In summary, the reactivity of **1** in cleavage reactions with neutral ligands (**2**–**4**) or substitution reactions of the halide bridging system by anionic (**5**) or neutral ligands (**6**–**10**) shows that the five-membered orthometallated iminophosphorane is quite stable, and behaves similarly to other *C*,*N*-orthometallated complexes derived from different amines. However, the reactivity of complex **11**, which contains a *C*,*N*,*N*-terdentate ligand reveals some noteworthy differences.

The reaction of **11** with $AgClO_4$ (1:1 molar ratio) in NCMe gives the solvate derivative [Pd(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)(NCMe)]ClO_4 (**13**). The presence of bonded NCMe is inferred from the observation of an absorption in the IR spectrum at 2328 cm^{-1} (ν_{CN}) and a signal at δ = 2.79 ppm in the ^1H NMR spectrum. A comparison of the spectral parameters of **13** with those of **11** suggests that the metallated iminophosphorane still behaves as a *C*,*N*,*N*-terdentate ligand. The complex [Pd(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)(PPh_3)]ClO_4 (**14**) can be obtained in the same way by treatment of **11** with $AgClO_4$ and PPh_3 (1:1:1 molar ratio) in acetone. The characterisation of **14** is straightforward from its $^{31}P\{^1H\}$ NMR spec-

trum, which shows the presence of coordinated PPh_3 (δ = 39.34 ppm), and from its ^1H NMR spectrum, which shows all expected signals for the proposed stoichiometry. It is noteworthy that complex **14** is also obtained when the reaction is performed in the presence of an excess of PPh_3 (1:1:2 molar ratio), thus showing that the displacement of the N-bonded pyridine group does not take place under these conditions.

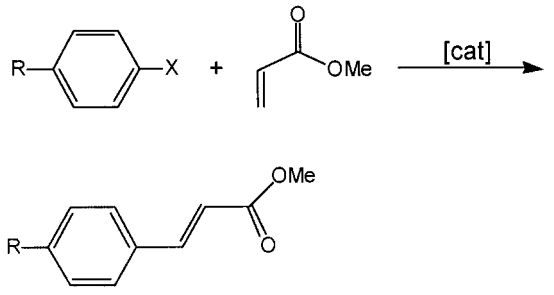
In order to check the strength of the pyridine fragment (usually a ligand easily removable from the metal coordination sphere) and the stability of the terdentate bonding mode κ-C,N,N of the metallated iminophosphorane, we investigated the reactivity of **11** towards several bidentate ligands, which usually act as chelating ligands. Complex **11** does not react with Tl(acac) under the usual experimental conditions (room temperature, 1:1 molar ratio), and unchanged **11** can be recovered at the end of the reaction. However, the reaction of **11** with $AgClO_4$ and $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) (1:1:1 molar ratio) in acetone gives complexes of stoichiometry $[Pd(C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4)(L\text{-}L)]ClO_4$ [L-L = dppm (**15**), dppe (**16**), bipy (**17**), phen (**18**)], in keeping with their elemental analyses and mass spectra. The IR spectra of **15**–**18** show the absorption due to the ν_{PN} stretch in the range 1330–1340 cm^{-1}, thereby suggesting that the Pd–N(imine) bond is still present. The NMR spectra of **15** are temperature independent and show clearly that the metallating ligand is terdentate κ-C,N,N: the $^{31}P\{^1H\}$ NMR spectrum shows three well-defined signals at δ = 49.14 ($N{=}PPh_2$), 27.05 (dppm, $Pd\text{-}PPh_2$) and –24.75 ppm (dppm, free PPh_2). The observation of only one signal at high field (δ = –24.75 ppm) is diagnostic for the presence of monodentate P-dppm.[62] The formation of a four-membered metallacycle (*P*,*P*′-dppm) at the expense of the loss of the more stable five-membered ring by cleavage of the Pd–N(py) bond is probably not an energetically favourable process. In contrast to this, the NMR spectra of **16** are temperature dependent. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows only a sharp singlet peak at δ = 47.28 ppm, assigned to the metallated $C_6H_4\text{-}2\text{-}PPh_2{=}N$ unit. On cooling ($CDCl_3$, 233 K) two new signals appear and an AMX spin system is observed. At this temperature, the chemical shift of the iminophosphorane appears at virtually the same position (δ = 47.84 ppm), as a doublet of doublets, and the signals attributed to the dppe ligand appear at δ = 41.38 (dd) and 58.21 ppm (d), clearly showing its *P*,*P*′-chelating mode.[50,63] The cleavage of the Pd–N(py) bond at low temperature is also inferred from the position of the *ortho* proton of the pyridine group, which appears in the ^1H NMR spectrum at δ = 8.72 ppm, that is, shifted to high field with respect to its position in **11**. All these facts suggest that the metallated $C_6H_4\text{-}2\text{-}PPh_2{=}N$ unit behaves statically on the NMR timescale in the range of temperatures measured, while the pyridine and dppe groups are involved into a series of dynamic process of coordination–decoordination, with the two processes being more or less equally favourable at room temperature. This process is stopped at low temperature, with *P*,*P*′-chelation of the dppe ligand.

The ^1H NMR spectra of **17** and **18** are temperature independent from 298 to 213 K (CD_2Cl_2) and show some noteworthy features. The first is the equivalence of the two rings of the bipy or phen ligands, inferred from the presence of a set of only four resonances (see Experimental Section), which do not split on cooling. This equivalence can be explained by assuming that they are bonded to the metal centre through only one nitrogen atom and that there is a rapid exchange of the N-bonded atoms, which can not be stopped at low temperature. This fast exchange can be easily rationalised through either a dissociative mechanism of the Pd–N bond or through a fluxional process, which could be a "single oscillatory motion of the potentially bidentate ligand via a trigonal-bipyramidal transition state". Similar proposals have been reported for related systems.[50,63] Whatever the mechanism, the coordination of the N-N ligands seems to occur in a plane normal to the molecular plane. This fact is clearly reflected in the anisotropic shielding undergone not only by the H_6 proton of the metallated C_6H_4 group (*ortho* to the palladated position), but also by the *ortho* proton of the pyridine fragment (H_α). These two protons appear strongly shifted to high field with respect to their positions in any other derivative. For instance, H_6 (C_6H_4) appears at δ = 6.33 (**17**) or 5.85 ppm (**18**) while in **11** its chemical shift is δ = 8.10 ppm; H_α (py) appears at δ = 7.95 (**17**) or 7.29 ppm (**18**) and at δ = 8.97 ppm in **11**.

In summary, the reactivity of **11** shows that the bonding of the terdentate ligand $[C_6H_4\text{-}2\text{-}PPh_2{=}N\text{-}C(O)\text{-}2\text{-}NC_5H_4\text{-}\kappa\text{-}C,N,N]$ to the Pd atom is remarkably stable. The decoordination of the pyridine fragment is not achieved upon treatment with classical chelating ligands (dppm, phen, bipy) and even in the presence of strongly chelating groups (dppe) only a competitive dynamic process is observed. These facts, together with the stability shown by the *C*,*N*-metallated complexes **1**–**10**, prompted us to study the plausible applications of this type of complex in catalytic processes.

Catalityc Activity of Orthometallated Complexes: Their Role as Precatalysts and the Formation of Nanoparticles in Mizoroki–Heck Processes

Four different complexes were selected in order to check the catalytic activity of orthopalladated iminophosphoranes. Complexes **1** and **4** are representative of complexes with the metallated $Ph_3P{=}NPh$ ligand, one neutral and one cationic, and both of them with available coordination sites. In the same way, **11** and **13** are representative examples of complexes with the metallated $Ph_3P{=}NC(O)$-2-py ligand, and with the same characteristics. The selected catalytic process is the C–C Mizoroki–Heck (MH) coupling between aryl halides and methyl acrylate, due to the exceptional activity shown by C,X-cyclopalladated complexes in this type of reaction (not limited to the MH reaction, but also applied to Suzuki, Stille, etc.),[39–44,50,64–69] and the wide interest in C–C Heck or Heck-type couplings.[70–77]



R = H, X = I; R = CHO, X = Br; R = CN, X = Br
[cat] = complex **1**, **4**, **11** or **13**

Conditions:
aryl halide (1.13 mmol); methyl acrylate (1.35 mmol);
DMF (15 mL), NEt_3 (1.13 mmol); reflux 24 h.

Table 3. Catalytic results in the MH reaction performed with catalysts **1**, **4**, **11** and **13**.

Entry	Catalyst	Substrate	Solvent	Yield [%]	TON
1	**1** (1%)	IPh	DMF	92.1	92
2	**1** (0.1%)	IPh	DMF	72.0	720
3	**1** (0.001%)	IPh	DMF	86.0	86000
4	**1** (0.0001%)	IPh	DMF	43.4	434000
5	**4** (1%)	IPh	DMF	64.9	65
6	**4** (0.1%)	IPh	DMF	57.8	578
7	**4** (0.001%)	IPh	DMF	52.0	52000
8	**4** (0.0001%)	IPh	DMF	52.6	526000
9	**11** (1%)	IPh	DMF	80.0	80
10	**11** (0.1%)	IPh	DMF	78.6	786
11	**11** (0.0001%)	IPh	DMF	11.4	114000
12	**13** (1%)	IPh	DMF	72.1	72
13	**13** (0.1%)	IPh	DMF	58.7	587
14	**13** (0.0001%)	IPh	DMF	45.6	456000
15	**1** (1%)	IPh	DMA	27.2	27
16	**4** (1%)	IPh	DMA	42.6	43
17	**11** (1%)	IPh	DMA	20.7	21
18	**13** (1%)	IPh	DMA	6.2	6
19	**1** (1%)	*p*-BrC_6H_4CHO	DMF	8.9	9
20	**4** (1%)	*p*-BrC_6H_4CHO	DMF	47.0	47
21	**11** (1%)	*p*-BrC_6H_4CHO	DMF	14.4	14
22	**13** (1%)	*p*-BrC_6H_4CHO	DMF	15	15
23	**1** (1%)	*p*-BrC_6H_4CN	DMF	5.0	5
24	**4** (1%)	*p*-BrC_6H_4CN	DMF	23.0	23
25	**11** (1%)	*p*-BrC_6H_4CN	DMF	4.1	4
26	**13** (1%)	*p*-BrC_6H_4CN	DMF	11.5	11

All selected complexes behave as moderate to good catalysts (see Experimental Section and Table 3) in the arylation of methyl acrylate to give methyl (*E*)-cinnamate in refluxing DMF (entries 1–14) when phenyl iodide is employed. The best yields are obtained when the amount of catalyst is 10^{-2} (mmol catalyst per mmol aryl halide; entries 1, 5, 9 and 12) but this amount can be as low as 10^{-6} (entries 4, 8, 11 and 14) and still give reasonable yields of isolated products and very high turnover numbers. However, as is evident from Table 3, the yield of isolated cinnamates drops when the concentration of catalyst decreases. The best reaction solvent for this type of process was found to be DMF. In spite of its similarity, very poor yields were obtained when *N*,*N*-dimethylacetamide (DMA) was used (entries 1–4 vs. entries 15–18), and the reaction was completely inhibited in NMP (*N*-methylpyrrolidinone). A comparison of the different catalysts shows that complexes **1** and **4** give better conversions than complexes **11** or **13**, and this fact could be related to the presence of the highly stable terdentate ligand [C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N] in **11** and **13** (see below). The presence of weakly bonded ligands in **4** or **13** seems also to improve the yields, with respect to **1** or **11**, at low concentrations of catalyst. On the other hand, a comparison of the different substrates shows that the reactivity of deactivated bromoarenes (*p*-BrC_6H_4CN or *p*-BrC_6H_4CHO) is substantially lower for all catalysts than that described for PhI (entries 19–26). Due to these low conversions, no reactions were attempted with activated bromoarenes or with chloroarenes.

As general trends, we have observed that all reactions start after an induction period of approx. 30 min. During this time, the initial yellow or pale-yellow solution becomes dark red but without evidence of formation of palladium black. After the reaction, we attempted the recovery of the catalyst during the workup, but all these attempts were unsuccessful. Moreover, the analysis of the crude of the catalytic reaction, after removal of solvent (DMF) by distillation, by $^{31}P\{^1H\}$ NMR spectroscopy shows only peaks due to O=PPh_3 and other unidentified species; signals due to the initial catalyst were not observed. That is, the orthometallated unit is lost during the catalytic cycle. Interestingly, the resulting dark red solutions obtained at the end of the catalysis are still catalytically active and, after the addition of a second batch of reagents, the catalysis can be reassumed without an induction period. However, the yields drop from the first to the second and following runs, showing the deactivation of the catalytically active species. For instance, in a series of test experiments of four consecutive runs under the conditions described in entry 1 (1% catalyst **1**, PhI, DMF, reflux 24 h for each run) the obtained yields of methyl (*E*)-cinnamate were 90% (1st run), 60% (2nd run), 20% (3rd run) and 0% in the last run.

The observation of an induction period in all catalytic experiments, the evidence of the decomposition of the catalyst by NMR spectroscopy, the obvious impossibility to recover the catalyst after the end of the first run, and the confirmation that the catalysis can be reassumed after the first run strongly suggest that the organometallic derivatives **1**, **4**, **11** or **13** are not the true catalysts, but only the precatalysts. What, therefore, is the nature of the true catalytic species? Recent studies in this area show that, in many cases, the orthopalladated derivatives behave only as palladium reservoirs which, depending on the nature of the metallated unit, produces either low-coordinate Pd^0 species (cyclometallated phosphanes) or palladium nanoparticles (for instance, *C*,*N*-cyclopalladated complexes),[39–41,50,69,78] which are the true catalysts. Since our orthometallated iminophosphoranes can be considered to be closely related to a *C*,*N*-cyclometallated complex, we investigated the plausible formation of nanoparticles of Pd^0 from our catalysts. With this

purpose, we checked the stability of the complexes under the reaction conditions (DMF, refluxing for 24 h). Thus, complexes **1**, **4**, **11** and **13** were refluxed in DMF for 24 h, and the resulting solutions were analysed by TEM, since this method is one of the best for detecting nanoparticles.[79–81] In all studied cases, the presence of nanoparticles (averaged diameter 10 nm) was evident. Figure 2 shows a TEM image obtained from a solution of complex **4** after thermal treatment. It is worthy of mention that the amount of nanoparticles detected is not the same in all cases. For complexes **1** and **4**, the amount of nanoparticles is substantially higher than that found in solutions of complexes **11** and **13**, after the same thermal treatment. Thus, the simple heating of the complexes in the reaction solvent produces their decomposition and the formation of the nanoparticles, and it is known that nanoparticles of Pd catalyze the MH reaction.[79–81]

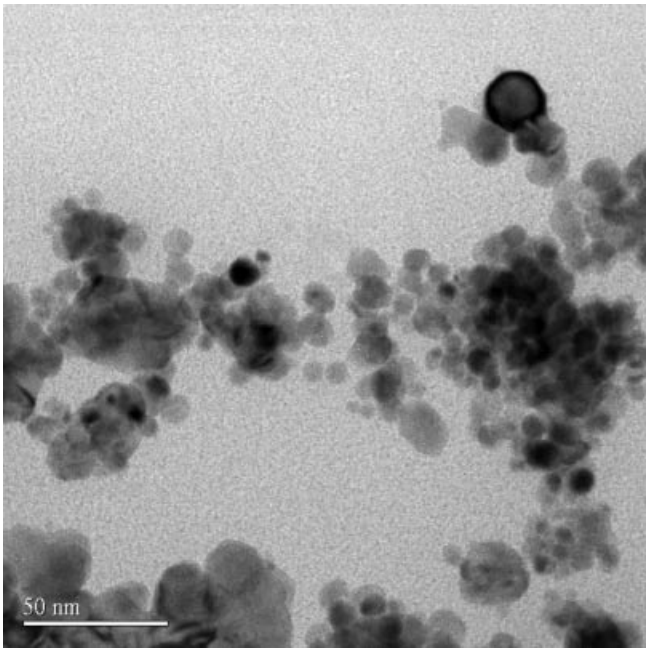


Figure 2. TEM image taken from a solution of complex **4** after 24 h in refluxing DMF.

We then compared the catalytic process described in entry 1 with that performed under the same experimental conditions but using nanoparticles. Monitoring by ^{1}H NMR spectroscopy showed that in the reaction carried out with nanoparticles, generated from **1** as described above, the presence of the reaction product can be detected only 10 min after the start of the reaction (time required to reach reflux temperature), that is, without an induction period, while in the process performed with catalyst **1** (entry 1) the presence of the products of the reaction is not detected until 30 min of additional refluxing. This additional time matches very well with the induction period (change of colour of the solution) observed in all catalytic reactions performed with complexes **1**, **4**, **11** and **13**. The yields obtained in these two processes are very similar (92% with catalyst **1** vs. 98% with nanoparticles). A second test to check the role of the nanoparticles as the catalytically active species is the mercury drop test (poisoning experiments).[78,82–84] The addition of an excess of Hg (with respect to the catalyst) to the process described in entry 1 completely inhibits the reaction and no product, even at trace levels, was detected at the end of the reaction.

In summary, the complexes with orthopalladated iminophosphoranes are precatalysts for the MH arylation of methyl acrylate to give the corresponding (*E*)-cinnamates in moderate to good yields. The true catalytic species are nanoparticles of elemental palladium, whose presence was confirmed by TEM, generated by decomposition of the catalyst.

Conclusions

The orthopalladated complexes [Pd(μ-Cl)(C_6H_4-2-PPh_2=NPh-κ-C,N)]$_2$ (**1**) and [Pd(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)Cl] (**11**) have been obtained by reaction of Pd(OAc)$_2$ with the iminophosphoranes Ph_3P=NPh and Ph_3P=N-C(O)-2-NC_5H_4, respectively, in the presence of excess LiCl. The orthoplatinated derivative [Pt(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)Cl] (**12**) can be obtained by reaction of [$PtCl_2(NCPh)_2$] with Ph_3P=N-C(O)-2-NC_5H_4 in refluxing 2-methoxyethanol. The reactivity of **1** in cleavage reactions with neutral ligands (**2**–**4**) or substitution reactions of the halide-bridging system by anionic (**5**) or neutral ligands (**6**–**10**) shows that the five-membered orthometallated iminophosphorane is quite stable, and behaves similarly to other *C*,*N*-orthometallated complexes derived from different amines. The reactivity of **11** shows that the bonding of the terdentate ligand [C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N] to the Pd atom is remarkably stable. The decoordination of the pyridine fragment is not achieved with classical chelating ligands (dppm, phen, bipy) and even in the presence of strongly chelating groups (dppe) only a competitive dynamic process is observed. The complexes **1**, **4**, **11** and **13** are precatalysts for the MH arylation of methyl acrylate to give the corresponding (*E*)-cinnamates in moderate to good yields. The true catalytic species are nanoparticles of elemental palladium, whose presence is confirmed by TEM, generated by decomposition of the catalyst.

Experimental Section

CAUTION: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great care.*[85]

General Methods: Solvents were dried and distilled under argon using standard procedures. Elemental analyses were performed on a Perkin–Elmer 2400-B microanalyser. Infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer from nujol mulls between polyethylene sheets. Mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (other temperatures are specified) on Bruker

ARX-300 or Avance400 spectrometers operating, respectively, at 300.13 MHz (ARX300) and 400.13 MHz (Avance400). The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual solvent signal as internal standard and the $^{31}P\{^1H\}$ NMR spectra to external H_3PO_4 (85%). The starting material Ph_3P=NPh is commercially available (Aldrich) and Ph_3P=N-C(O)-2-NC_5H_4 was prepared following published methods.[46]

Complex 1: $Pd(OAc)_2$ (1.000 g, 4.45 mmol) was added to a solution of Ph_3P=NPh (1.572 g, 4.45 mmol) in dry CH_2Cl_2 (20 mL) under argon, and this mixture was refluxed for 1.5 h. The initial orange-brown solution evolved slowly during the reaction time to give a deep orange solution. After cooling, the solvent was removed to dryness, the residue was dissolved in MeOH (20 mL), treated with an excess of anhydrous LiCl (0.755 g, 17.8 mmol) and then stirred at room temperature. After a few seconds complex **1** precipitated as a deep-yellow solid, although stirring was continued for an additional 30 min. After this time **1** was filtered off, washed with MeOH (20 mL) and Et_2O (50 mL) and air dried. Yield: 2.108 g (95.9%). $C_{48}H_{38}Cl_2N_2P_2Pd_2$ (988.50): calcd. C 58.32, H 3.87, N 2.83; found C 58.58, H 3.93, N 2.91. IR: $\tilde{\nu}$ = 1292, 1263 (ν_{PN}) cm^{-1}. NMR spectroscopic data have been reported previously.[38]

Complex 2: PPh_3 (0.041 g, 0.158 mmol) was added to a suspension of **1** (0.078 g, 0.079 mmol) in 5 mL of CH_2Cl_2. The initial orange suspension gradually dissolved and, after 5 min stirring at room temperature, a pale-yellow solution was obtained. The evaporation of this solution and treatment of the oily residue with 20 mL of Et_2O gave **2** as a white solid, which was filtered off, washed with additional Et_2O (10 mL) and air dried. Yield: 0.092 g (77%). $C_{42}H_{34}ClNP_2Pd$ (756.54): calcd. C 66.68, H 4.53, N 1.85; found C 66.51, H 4.47, N 1.85. IR: $\tilde{\nu}$ = 1289 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 720 (25) $[M - Cl]^+$. ^1H NMR ($CDCl_3$): δ = 6.46 (tt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.2 Hz, 1 H, C_6H_4), 6.59–6.75 (m, 3 H, C_6H_4), 6.83–6.98 (br. m, 5 H, NPh), 7.18–7.24 (m, 6 H, H^m, PPh_3), 7.27–7.33 (m, 3 H, H^p, PPh_3), 7.48–7.62 [m, 12 H, PPh_3 (6 H^o) + PPh_2 (4 H^m + 2 H^p)], 7.89–7.96 (m, 4 H, H^o, PPh_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.46 (d, $^3J_{P,P}$ = 4.7 Hz, 1 P, Pd–PPh_3), 38.69 (d, $^3J_{P,P}$ = 4.7 Hz, 1 P, P=N) ppm.

Complex 3: Complex **3** was prepared following a synthetic procedure similar to that reported for **2**. Thus, **1** (0.200 g, 0.202 mmol) in CH_2Cl_2 (5 mL) was treated with $PPhMe_2$ (57.6 μL, 0.404 mmol) to give **3** as a cream solid. Yield: 0.232 g (90.7%). $C_{32}H_{30}ClNP_2Pd$ (632.4): calcd. C 60.78, H 4.78, N 2.21; found C 60.61, H 4.74, N 1.91. IR: $\tilde{\nu}$ = 1291, 1260 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 631 (20) $[M]^+$, 596 (100) $[M - Cl]^+$. ^1H NMR ($CDCl_3$): δ = 1.68 (d, $^2J_{P,H}$ = 10.5 Hz, 6 H, PMe_2), 6.69–6.74 (m, 1 H, C_6H_4), 6.78–6.95 [m, 8 H, C_6H_4 (3 H) + NPh], 7.30–7.38 (m, 3 H, H^m + H^p, PPh), 7.45–7.51 (m, 4 H, H^m, PPh_2), 7.54–7.60 (m, 2 H, H^p, PPh_2), 7.69–7.76 (m, 2 H, H^o, PPh), 7.83–7.89 (m, 4 H, H^o, PPh_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.75 (s, 1 P, Pd-$PPhMe_2$), 34.12 (s, 1 P, P=N) ppm.

Complex 4: Complex **4** was prepared following a synthetic procedure similar to that reported for **2**. Thus, **1** (0.200 g, 0.202 mmol) in CH_2Cl_2 (10 mL) was treated with pyridine (65.1 μL, 0.808 mmol) to give **4** as a yellow solid. Yield: 0.198 g (85.3%). Complex **4** was characterised spectroscopically (NMR) as a mixture of the isomers **4a/4b** in a molar ratio of 4.1:1. $C_{29}H_{24}ClN_2PPd$ (573.35): calcd. C 60.75, H 4.22, N 4.89; found C 60.80, H 4.10, N 5.06. IR: $\tilde{\nu}$ = 1589 (py), 1285 (ν_{PN}) cm^{-1}. ^1H NMR ($CDCl_3$) (not all signals for the minor isomer **4b** could be detected due to overlap): δ = 6.30 (dd, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 1.6 Hz, H^6, **4b**), 6.56 (tm, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, H^p, NPh, **4a**), 6.65 (t, $^3J_{H,H}$ = 7.2 Hz, H^m, NPh, **4a**), 6.79 (dm, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, H^o, NPh, **4a**), 6.86 (ddd, $^3J_{P,H}$ = 10.4, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, H^3, C_6H_4, **4a**), 6.94–6.99 (m, H^m, py, **4a**), 7.00–7.04 (m, H^4, C_6H_4, **4a**), 7.13 (dm, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.2 Hz, H^o, NPh, **4b**), 7.22 (tt, $^3J_{H,H}$ = 7.2, $^4J_{H,H} \approx {}^5J_{P,H}$ = 1.6 Hz, H^5, C_6H_4, **4a**), 7.31–7.35 (m, H^m, py, **4b**), 7.43 (tt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, H^p, py, **4a**), 7.48–7.55 (m, H^m, PPh_2, **4a** + **4b**), 7.59–7.63 (m, H^p, PPh_2, **4a** + **4b**), 7.74–7.79 (m, H^o, PPh_2, **4a**), 7.88–7.93 (m, H^o, PPh_2, **4b**), 8.30 (ddd, $^3J_{H,H}$ = 7.2, $^4J_{P,H}$ = 1.6, $^4J_{H,H}$ = 1.2 Hz, H^6, C_6H_4, **4a**), 8.52 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.6 Hz, H^o, py, **4a**), 8.90 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.6 Hz, H^o, py, **4b**) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) (not all signals for the minor isomer **4b** could be detected due to overlap): δ = 121.74 (d, $^5J_{P,C}$ = 2.0 Hz, C^p, NPh, **4a**), 123.83 (s, C^m, py, **4a**), 124.04 (d, $^3J_{P,C}$ = 14.1 Hz, C^4, C_6H_4, **4a**), 125.02 (s, C^m, py, **4b**), 127.43 (d, $^3J_{P,C}$ = 9.1 Hz, C^o, NPh, **4a**), 127.72 (s, C^m, NPh, **4a**), 128.24 (d, $^2J_{P,C}$ = 21.1 Hz, C^3, C_6H_4, **4a**), 128.61 (d, $^1J_{P,C}$ = 86.5 Hz, C^{ipso}, PPh_2, **4a**), 128.86 (d, $^3J_{P,C}$ = 11.1 Hz, C^m, PPh_2, **4a**), 128.90 (d, $^3J_{P,C}$ = 11.1 Hz, C^m, PPh_2, **4b**), 130.29 (d, $^4J_{P,C}$ = 3.0 Hz, C^5, C_6H_4, **4b**), 130.38 (d, $^4J_{P,C}$ = 3.1 Hz, C^5, C_6H_4, **4a**), 132.75 (d, $^4J_{P,C}$ = 2.0 Hz, C^p, PPh_2, **4a**), 133.23 (d, $^2J_{P,C}$ = 9.1 Hz, C^o, PPh_2, **4a**), 133.50 (d, $^2J_{P,C}$ = 10.1 Hz, C^o, PPh_2, **4b**), 134.43 (d, $^3J_{P,C}$ = 15.1 Hz, C^6, C_6H_4, **4b**), 136.48 (s, C^p, py, **4a**), 137.35 (s, C^p, py, **4b**), 138.53 (d, $^3J_{P,C}$ = 15.1 Hz, C^6, C_6H_4, **4a**), 140.55 (d, $^1J_{P,C}$ = 139 Hz, C^2, C_6H_4, **4a**), 147.12 (d, $^2J_{P,C}$ = 3.0 Hz, C^{ipso}, NPh, **4a**), 147.19 (d, $^2J_{P,C}$ = 3.0 Hz, C^{ipso}, NPh, **4b**), 151.04 (s, C^o, py, **4a**), 152.27 (d, $^2J_{P,C}$ = 20.1 Hz, C^1, C_6H_4, **4a**), 153.73 (s, C^o, py, **4b**), 156.39 (d, $^2J_{P,C}$ = 20.1 Hz, C^1, C_6H_4, **4b**) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 44.31 (**4b**), 48.21 (**4a**) ppm.

Complex 5: Tl(acac) (0.123 g, 0.404 mmol) was added to a suspension of **1** (0.200 g, 0.202 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 1 h, then filtered through Celite. The clear yellow solution was evaporated to dryness and the oily residue treated with cold *n*-hexane (10 mL) to give **5** as a yellow solid. This solid was filtered off and dried in vacuo. Yield: 0.184 g (81.5%). $C_{29}H_{26}NO_2PPd$ (557.91): calcd. C 62.43, H 4.69, N 2.51; found C 62.49, H 4.60, N 2.35. IR: $\tilde{\nu}$ = 1582, 1515 (ν_{CO}), 1287, 1262 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 557 (30) $[M]^+$. ^1H NMR (CD_2Cl_2): δ = 1.74 (s, 3 H, Me, acac), 2.06 (s, 3 H, Me, acac), 5.35 (s, 1 H, CH, acac), 6.83 (td, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^p, NPh), 6.95 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^3, C_6H_4), 6.99 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, H^m, NPh), 7.05–7.10 [m, 3 H, NPh (H^o) + C_6H_4 (H^4)], 7.27 (tt, $^3J_{H,H}$ = 7.6, $^4J_{H,H} \approx {}^5J_{P,H}$ = 1.6 Hz, 1 H, H^5, C_6H_4), 7.53–7.57 (m, 4 H, H^m, PPh_2), 7.64–7.68 (m, 2 H, H^p, PPh_2), 7.71 (dm, $^3J_{H,H}$ = 8.0 Hz, 1 H, H^6, C_6H_4), 7.82–7.87 (m, 4 H, H^o, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 27.14 (s, Me, acac), 27.31 (s, Me, acac), 99.75 (s, CH, acac), 121.39 (s, C^p, NPh), 124.17 (d, $^3J_{P,C}$ = 14 Hz, C^4, C_6H_4), 126.99 (d, $^3J_{P,C}$ = 10 Hz, C^o, NPh), 127.47 (s, C^m, NPh), 127.73 (d, $^2J_{P,C}$ = 22 Hz, C^3, C_6H_4), 128.21 (d, $^1J_{P,C}$ = 85 Hz, C^{ipso}, PPh_2), 128.91 (d, $^3J_{P,C}$ = 11 Hz, C^m, PPh_2), 129.64 (d, $^4J_{P,C}$ = 3 Hz, C^5, C_6H_4), 132.40 (d, $^3J_{P,C}$ = 14 Hz, C^6, C_6H_4), 132.79 (d, $^4J_{P,C}$ = 2 Hz, C^p, PPh_2), 133.22 (d, $^2J_{P,C}$ = 10 Hz, C^o, PPh_2), 140.75 (d, $^1J_{P,C}$ = 139 Hz, C^2, C_6H_4), 146.49 (d, $^2J_{P,C}$ = 3 Hz, C^{ipso}, NPh), 152.99 (d, $^2J_{P,C}$ = 20 Hz, C^1, C_6H_4), 185.42 (s, CO, acac), 187.92 (s, CO, acac) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 46.04 ppm.

Complex 6: $AgClO_4$ (0.084 g, 0.405 mmol) was added to a suspension of **1** (0.200 g, 0.202 mmol) in NCMe (15 mL) and the resulting mixture was stirred at room temperature for 30 min with exclusion of light. After this time the grey suspension was filtered through Celite and the resulting pale-yellow solution was evaporated to small volume (approx. 1 mL). Addition of *n*-pentane (10 mL) and continuous stirring gave **6** as a pale-yellow solid, which was filtered off and dried in vacuo. Yield: 0.226 g (87.5%). $C_{28}H_{25}ClN_3O_4PPd$ (640.35): calcd. C 52.52, H 3.93, N 6.56; found C 52.60, H 3.93, N

6.78. IR: $\tilde{\nu}$ = 2321, 2291 (ν_{CN}), 1287, 1260 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 499 (10) [M – ClO_4 – NCMe]$^+$, 458 (25) [M – ClO_4 – 2NCMe]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.26 (br. s, 3 H, NCMe), 2.50 (s, 3 H, NCMe), 6.85–6.99 [m, 6 H, NPh + C_6H_4 (H^3)], 7.09 (ddt, $^3J_{H,H}$ = 7.2, $^4J_{P,H}$ = 4.8, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^4, C_6H_4), 7.16–7.26 (m, 2 H, H^5 + H^6, C_6H_4), 7.48–7.54 (m, 4 H, H^m, PPh_2), 7.60–7.66 (m, 2 H, H^p, PPh_2), 7.67–7.74 (m, 4 H, H^o, PPh_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 54.29 ppm.

Complex 7: $AgClO_4$ (0.084 g, 0.405 mmol) was added to a suspension of **1** (0.200 g, 0.202 mmol) in acetone (20 mL) and the resulting mixture was stirred at room temperature for 30 min with exclusion of light. The grey suspension was then filtered through a Celite pad and dppm (0.155 g, 0.404 mmol) was added to the freshly prepared solution of the solvate to give a pale-orange solution. After stirring at room temperature for 4 h, the solvent was evaporated to dryness and the residue treated with Et_2O (10 mL) to give **7** as a pale-orange solid, which was filtered and air dried. Yield: 0.357 g (93.7%). $C_{49}H_{41}ClNO_4P_3Pd$ (942.65): calcd. C 62.43, H 4.38, N 1.48; found C 62.35, H 4.40, N 1.35. IR: $\tilde{\nu}$ = 1263 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 842 (100) [M – ClO_4]$^+$. ^{1}H NMR ($CDCl_3$): δ = 4.06 (dd, $^2J_{P,H}$ = 11.1, $^2J_{P,H}$ = 7.8 Hz, 2 H, CH_2), 6.52–6.59 (m, 3 H, NPh), 6.71–6.74 (m, 2 H, NPh), 6.91–6.98 (m, 2 H, C_6H_4), 7.03–7.12 [m, 6 H, C_6H_4 (2 H) + PPh_2], 7.20–7.26 (m, 4 H, PPh_2), 7.35–7.58 (m, 12 H, PPh_2), 7.61–7.76 (m, 10 H, PPh_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 40.97 (dd, $^1J_{P,C}$ = 28.4, $^1J_{P,C}$ = 21.5 Hz, CH_2), 122.76 (s, C^p, NPh), 125.70 (d, $^3J_{P,C}$ = 13.8 Hz, C^4, C_6H_4), 126.33 (d, $^1J_{P,C}$ = 30.7 Hz, C^{ipso}, PPh_2), 126.49 (d, $^3J_{P,C}$ = 9.5 Hz, C^o, NPh), 127.96 (d, $^1J_{P,C}$ = 30.7 Hz, C^{ipso}, PPh_2), 128.01 (d, $^1J_{P,C}$ = 30.6 Hz, C^{ipso}, PPh_2), 128.40 (s, C^5, C_6H_4), 129.12 (s, C^m, NPh), 129.19 (d, $^3J_{P,C}$ = 10.2 Hz, C^m, PPh_2), 129.20 (d, $^3J_{P,C}$ = 12.1 Hz, C^m, PPh_2), 129.62 (d, $^3J_{P,C}$ = 11.7 Hz, C^m, PPh_2), 131.37 (d, $^4J_{P,C}$ = 1.7 Hz, C^p, PPh_2), 132.60 (s, C^p, PPh_2), 132.69 (d, $^2J_{P,C}$ = 13.2 Hz, C^o, PPh_2), 133.05 (d, $^2J_{P,C}$ = 9.9 Hz, C^o, PPh_2), 133.39 (d, $^4J_{P,C}$ = 2.0 Hz, C^p, PPh_2), 133.75 (d, $^2J_{P,C}$ = 12.8 Hz, C^o, PPh_2), 138.86 (td, $^3J_{P,C}$ = 15.7, $^3J_{P,C}$ = 2.8 Hz, C^6, C_6H_4), 141.92 (d, $^1J_{P,C}$ = 97 Hz, C^2, C_6H_4), 148.85 (s, C^{ipso}, NPh), 160.97 (ddd, $^2J_{P,Ctrans}$ = 135.6, $^2J_{(N)P,C}$ = 23.5, $^2J_{P,Ccis}$ = 10.7 Hz, C^1, C_6H_4) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –34.16 (dd, $^2J_{P,P}$ = 68, $^3J_{P,P}$ = 14.5 Hz, 1 P, P *trans* to N), –10.60 (d, $^2J_{P,P}$ = 68 Hz, 1 P, P *trans* to C), 48.38 (d, $^3J_{P,P}$ = 14.5 Hz, 1 P, P=N) ppm.

Complex 8: Complex **8** was prepared following a synthetic procedure similar to that reported for **7**. A solution of **1** (0.200 g, 0.202 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.084 g, 0.405 mmol) and dppe (0.161 g, 0.404 mmol) to give **8** as a pale-orange solid. Yield: 0.347 g (90%). $C_{50}H_{43}ClNO_4P_3Pd$ (956.67): calcd. C 62.77, H 4.53, N 1.46; found C 62.31, H 4.57, N 1.28. IR: $\tilde{\nu}$ = 1289, 1261 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 856 (100) [M – ClO_4]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.09, 2.16, 2.37, 2.46 (4m, 4 H, CH_2, dppe), 6.42–6.55 (m, 5 H, NPh), 6.79–6.98 (m, 4 H, C_6H_4), 7.14–7.66 (m, 30 H, PPh_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 43.81 (dd, $^3J_{P,P}$ = 26.2, $^3J_{P,P}$ = 16.0 Hz, 1 P, P *trans* to N), 45.31 (d, $^3J_{P,P}$ = 16.0 Hz, 1 P, P=N), 58.85 (d, $^3J_{P,P}$ = 26.2 Hz, 1 P, P *trans* to C).

Complex 9: Complex **9** was prepared following a synthetic procedure similar to that reported for **7**. A solution of **1** (0.200 g, 0.202 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.084 g, 0.405 mmol) and 1,10-phenanthroline (0.073 g, 0.404 mmol) to give **9** as a deep-yellow solid. Yield: 0.263 g (88%). $C_{36}H_{27}ClN_3O_4PPd$ (738.46): calcd. C 58.55, H 3.68, N 5.69; found C 58.32, H 3.56, N 5.72. IR: $\tilde{\nu}$ = 1290 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 638 (100) [M – ClO_4]$^+$. ^{1}H NMR (CD_2Cl_2): δ = 6.97 (td, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^p, NPh), 7.08 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H^m, NPh), 7.18 (br. d, 2 H, H^o, NPh), 7.22 (ddd, $^3J_{P,H}$ = 9.2, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^3, C_6H_4), 7.33 (tdd, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 5.2, $^4J_{H,H}$ = 0.8 Hz, 1 H, H^4, C_6H_4), 7.60–7.62 [m, 5 H, PPh_2 (4 H^m) + C_6H_4 (H^5)], 7.65 (dd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 4.8 Hz, 1 H, $H^{\beta'}$, phen), 7.69–7.74 (m, 2 H, H^p, PPh_2), 7.75 (br. d, $^3J_{H,H}$ = 8.0 Hz, 1 H, H^6, C_6H_4), 7.76–7.82 (m, 4 H, H^o, PPh_2), 8.00–8.03 (m, 2 H, H^β + $H^{\alpha'}$, phen), 8.12 (s, 2 H, H^δ + $H^{\delta'}$, phen), 8.62 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.2 Hz, 1 H, $H^{\gamma'}$, phen), 8.75 (dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.6 Hz, 1 H, H^γ, phen), 9.22 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, H^α, phen) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 122.77 (s, C^p, NPh), 125.26 (s, $C^{\beta'}$, phen), 125.33 (d, $^3J_{P,C}$ = 14.1 Hz, C^4, C_6H_4), 125.69 (s, C^β, phen), 126.64 (d, $^3J_{P,C}$ = 9.1 Hz, C^o, NPh), 126.68 (d, $^1J_{P,C}$ = 91 Hz, C^{ipso}, PPh_2), 127.40, 127.82 (2s, C^δ + $C^{\delta'}$, phen), 128.95 (s, C^m, NPh), 129.34 (d, $^2J_{P,C}$ = 17.1 Hz, C^3, C_6H_4), 129.37 (d, $^3J_{P,C}$ = 12.0 Hz, C^m, PPh_2), 130.11, 130.56 (2C^q, phen), 131.64 (d, $^4J_{P,C}$ = 3.0 Hz, C^5, C_6H_4), 133.36 (d, $^2J_{P,C}$ = 10.6 Hz, C^o, PPh_2), 133.73 (d, $^4J_{P,C}$ = 2.0 Hz, C^p, PPh_2), 135.17 (d, $^3J_{P,C}$ = 14.1 Hz, C^6, C_6H_4), 139.17 (s, C^γ, phen), 139.63 (s, $C^{\gamma'}$, phen), 144.21 (d, $^1J_{P,C}$ = 131 Hz, C^2, C_6H_4), 145.18, 147.14 (2 C^q, phen), 146.45 (d, $^2J_{P,C}$ = 3.0 Hz, C^{ipso}, NPh), 150.06 (s, C^α, phen), 152.15 (s, $C^{\alpha'}$, phen), 160.46 (d, $^2J_{P,C}$ = 18.1 Hz, C^1, C_6H_4) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 45.84 ppm.

Complex 10: Complex **10** was prepared following a synthetic procedure similar to that reported for **7**. A solution of **1** (0.200 g, 0.202 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.084 g, 0.405 mmol) and 2,2′-bipyridine (0.063 g, 0.404 mmol) to give **10** as a yellow solid. Yield: 0.289 g (100%). $C_{34}H_{27}ClN_3O_4PPd$ (714.43): calcd. C 57.16, H 3.81, N 5.88; found C 57.23, H 3.88, N 5.94. IR: $\tilde{\nu}$ = 1289, 1263 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 614 (100) [M – ClO_4]$^+$. ^{1}H NMR ($CDCl_3$): δ = 6.84 (td, NPh, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^p), 6.93 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, H^m, NPh), 6.95 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H^o, NPh), 7.05 (ddd, $^3J_{P,H}$ = 9, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, C_6H_4, H^3), 7.19 (tdd, $^3J_{H,H}$ = 7.0, $^4J_{P,H}$ = 5.1, $^4J_{H,H}$ = 1.5 Hz, 1 H, C_6H_4, H^4), 7.44 (tt, $^3J_{H,H}$ = 7.2, $^5J_{P,H}$ ≈ $^4J_{H,H}$ = 1.5 Hz, 1 H, C_6H_4, H^5), 7.46–7.66 [m, 15 H, PPh_2 + bipy (4 H, H^β + H^δ) + C_6H_4 (H^6)], 8.07 (br. t, $^3J_{H,H}$ = 6.9 Hz, 1 H, H^γ, bipy), 8.22 (br. t,, $^3J_{H,H}$ = 6.6 Hz 1 H, H^γ, bipy), 8.51 (br. s, 1 H, H^α, bipy), 8.68 (br. d, $^3J_{H,H}$ = 3.9 Hz, 1 H, H^α, bipy) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 45.96 ppm.

Complex 11: Ph_3P=NC(O)-2-NC_5H_4 (0.500 g, 1.307 mmol), was added to a solution of $Pd(OAc)_2$ (0.293 g, 1.307 mmol) in 20 mL of dry CH_2Cl_2 and the resulting solution was refluxed for 1 h. At this point, some decomposition was evident. After cooling, the black suspension was treated with charcoal for 30 min and then filtered through a Celite pad. The resulting orange solution was evaporated to dryness and the residue redissolved in MeOH (20 mL). An excess of LiCl (0.222 g, 5.23 mmol) was added to the methanolic solution, which was stirred vigorously at room temperature for 16 h. The yellow precipitate of **11** formed was collected by filtration, washed with MeOH (20 mL) and Et_2O (40 mL) and air dried. Yield: 0.604 g (88.3%). $C_{24}H_{18}ClN_2OPPd$ (523.25): calcd. C 55.09, H 3.47, N 5.35; found C 55.15, H 3.60, N 5.28. IR: $\tilde{\nu}$ = 1644 (ν_{CO}), 1332 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 523 (20) [M]$^+$, 487 (100) [M – Cl]$^+$. ^{1}H NMR (CD_2Cl_2): δ = 7.00 (ddd, $^3J_{P,H}$ = 11.1, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^3, C_6H_4), 7.13 (tdd, $^3J_{H,H}$ = 7.8, $^4J_{P,H}$ = 5.1, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^4, C_6H_4), 7.28 (tt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ ≈ $^5J_{P,H}$ = 1.5 Hz, 1 H, H^5, C_6H_4), 7.55–7.64 [m, 5 H, PPh_2 (4 H^m) + py (H^β)], 7.69–7.75 (m, 2 H, H^p, PPh_2), 7.87–7.94 [m, 5 H, PPh_2 (4 H^o) + py (H^δ)], 7.98 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^γ, py), 8.10 (ddd, $^3J_{H,H}$ = 8.1, $^4J_{P,H}$ = 2.7, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^6, C_6H_4), 8.97 (ddd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.5, $^5J_{H,H}$ = 0.6 Hz, 1 H, H^α, py) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 124.77 (d, $^1J_{P,C}$ = 90 Hz, C^{ipso}, PPh_2), 125.48 (s, C^3, py), 125.68 (s, C^5, py), 128.84 (s, C^5, C_6H_4), 129.69 (d, $^3J_{P,C}$ = 12.7 Hz, C^m, PPh_2), 130.60 (d, $^2J_{P,C}$ = 22.6 Hz, C^3, C_6H_4), 132.09 (d, $^3J_{P,C}$ = 3.0 Hz, C^4, C_6H_4),

133.79 (d, $^2J_{P,C}$ = 11.2 Hz, C^o, PPh_2), 134.52 (d, $^4J_{P,C}$ = 2.5 Hz, C^p, PPh_2), 138.48 (d, $^1J_{P,C}$ = 130 Hz, C^2, C_6H_4), 139.11 (d, $^3J_{P,C}$ = 14.5 Hz, C^6, C_6H_4), 139.51 (s, C^4, py), 149.18 (s, C^6, py), 152.98 (s, C^2, py), 153.19 (d, $^2J_{P,C}$ = 8.6 Hz, C^1, C_6H_4), 172.25 (d, $^2J_{P,C}$ = 4.6 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.88 ppm.

Complex 12: A suspension of $[PtCl_2(NCPh)_2]$ (0.200 g, 0.424 mmol) and Ph_3P=NC(O)-2-NC_5H_4 (0.162 g, 0.424 mmol) in 15 mL of 2-methoxyethanol was refluxed for 8 h. During this time the initial suspension dissolved, and a greenish solution (presence of Pt^0) was obtained. After cooling, complex **12** precipitated from the alcoholic medium as a green solid. This solid was filtered and washed with Et_2O (20 mL). The crude solid of **12** was further dissolved in CH_2Cl_2 (40 mL), treated with charcoal and filtered through Celite to give a yellow solution. The evaporation of the solvent to dryness and treatment of the residue with Et_2O (30 mL) gave **12** as a yellow solid. Yield: 0.118 g (45.7%). Complex **12** was recrystallised from CH_2Cl_2/OEt_2 to give yellow needles of **12**·CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{24}H_{18}ClN_2OPPt{\cdot}CH_2Cl_2$ (696.87): calcd. C 43.09, H 2.89, N 4.02; found C 42.98, H 2.84, N 4.24. IR: $\tilde{\nu}$ = 1646 (ν_{CO}), 1330 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 612 (95) $[M]^+$, 576 (100) $[M - Cl]^+$. ^1H NMR (CD_2Cl_2): δ = 6.95 (ddd, $^3J_{P,H}$ = 11.6, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^3, C_6H_4), 7.05 (tdd, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 5.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^4, C_6H_4), 7.23 (tt, $^3J_{H,H}$ = 7.6, $^4J_{H,H} \approx {}^5J_{P,H}$ = 1.6 Hz, 1 H, H^5, C_6H_4), 7.48–7.53 (m, 4 H, H^m, PPh_2), 7.60 (ddd, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, H$^\beta$, py), 7.62–7.67 (m, 2 H, H^p, PPh_2), 7.78 (dm, $^3J_{H,H}$ = 7.6 Hz, 1 H, H$^\delta$, py), 7.80–7.86 (m, 4 H, H^o, PPh_2), 7.98 (td, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, 1 H, H$^\gamma$, py), 8.02 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 3.2, $^4J_{H,H}$ = 1.2, $^3J_{Pt,H}$ = 30.4 Hz, 1 H, H^6, C_6H_4), 9.17 (ddd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 0.4, $^3J_{Pt,H} \approx$ 20 Hz, 1 H, H$^\alpha$, py) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.88 ($^2J_{Pt,P}$ = 452 Hz) ppm.

Complex 13: $AgClO_4$ (0.040 g, 0.191 mmol) was added to a suspension of **11** (0.100 g, 0.191 mmol) in NCMe (20 mL). The resulting white suspension was stirred at room temperature with exclusion of light for 30 min, then filtered through Celite. The resulting pale-yellow solution was evaporated to small volume (approx. 1 mL). Addition of Et_2O (20 mL) and continuous stirring gave **13** as an off-white solid, which was filtered, washed with additional Et_2O (10 mL) and air dried. Yield: 0.081 g (67.5%). Complex **13** was recrystallised from CH_2Cl_2/OEt_2 to give colourless microcrystals of **13**·2CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{26}H_{21}ClN_3O_5PPd{\cdot}2CH_2Cl_2$ (798.17): calcd. C 42.14, H 3.16, N 5.26; found C 41.56, H 3.27, N 5.10. IR: $\tilde{\nu}$ = 2328 (ν_{CN}), 1669 (ν_{CO}), 1323, 1296 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 487 (100) $[M - NCMe - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ = 2.79 (s, 3 H, NCMe), 7.04 (ddd, $^3J_{P,H}$ = 10.6, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.1 Hz, 1 H, H^3, C_6H_4), 7.23 (tdd, $^3J_{H,H}$ = 7.5, $^4J_{P,H}$ = 5.1, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^4, C_6H_4), 7.37 (tt, $^3J_{H,H}$ = 7.3, $^4J_{H,H} \approx {}^5J_{P,H}$ = 1.7 Hz, 1 H, H^5, C_6H_4), 7.45 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 2.2, $^4J_{H,H}$ = 0.8 Hz, 1 H, H^6, C_6H_4), 7.56–7.63 (m, 4 H, H^m, PPh_2), 7.70–7.75 (m, 2 H, H^p, PPh_2), 7.84–7.91 [m, 5 H, PPh_2 (4 H^o) + py (H$^\beta$)], 7.95 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H$^\delta$, py), 8.09 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.8 Hz, 1 H, H$^\gamma$, py), 8.97 (dd, $^3J_{H,H}$ = 5.4, $^4J_{H,H}$ = 2.2 Hz, 1 H, H$^\alpha$, py) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.71 ppm.

Complex 14: $AgClO_4$ (0.103 g, 0.497 mmol) was added to a suspension of **11** (0.260 g, 0.497 mmol) in acetone (20 mL). The resulting suspension was stirred at room temperature with exclusion of light for 20 min, then filtered through Celite. PPh_3 (0.130 g, 0.497 mmol) was added to this freshly prepared solution and stirring was continued for an additional 30 min. The pale-yellow solution was evaporated to dryness and the oily residue was treated with Et_2O (20 mL). Continuous stirring gave **14** as a white solid, which was filtered, washed with Et_2O (10 mL) and air dried. Yield: 0.321 g (76.0%). Complex **14** was recrystallised from CH_2Cl_2/*n*-hexane to give pale-yellow crystals of **14**·2.5CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{42}H_{33}ClN_2O_5P_2Pd{\cdot}2.5CH_2Cl_2$ (1061.9): calcd. C 50.33, H 3.61, N 2.64; found C 49.76, H 3.42, N 2.48. IR: $\tilde{\nu}$ = 1651 (ν_{CO}), 1339 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 749 (55%) $[M - ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 6.78 (dd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 0.4 Hz, 1 H, py), 6.85–6.87 (m, 2 H, C_6H_4), 7.13–7.17 [m, 3 H, C_6H_4 (2 H) + py (1 H)], 7.52–7.57 (m, 6 H, H^m, PPh_3), 7.63–7.68 (m, 3 H, H^p, PPh_3), 7.71–7.76 (m, 4 H, H^m, PPh_2), 7.84–7.91 [m, 8 H, PPh_3 (6 H^o) + PPh_2 (2 H^p)], 7.96–8.04 [m, 5 H, PPh_2 (4 H^o) + py (1 H)], 8.07 (dm, $^3J_{H,H}$ = 8.0 Hz, 1 H, py) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.34 (s, 1 P, Pd–PPh_3), 49.18 (s, 1 P, P=N) ppm.

Complex 15: Complex **15** was prepared following a procedure similar to that reported for **14**. A solution of **11** (0.100 g, 0.191 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.040 g, 0.191 mmol) and dppm (0.073 g, 0.191 mmol) to give **15** as an orange solid. Yield: 0.163 g (87.8%). Complex **15** was crystallised from CH_2Cl_2/OEt_2 to give orange crystals of **15**·CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{49}H_{40}ClN_2O_5P_3Pd{\cdot}CH_2Cl_2$ (1056.6): calcd. C 56.84, H 4.00, N 2.65; found C 56.93, H 3.75, N 2.79. IR: $\tilde{\nu}$ = 1650 (ν_{CO}), 1338 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 871 (100) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ = 3.47 (d, $^2J_{P,H}$ = 11.1 Hz, 2 H, CH_2, dppm), 6.84–7.97 (m, 38 H, Ph; extensive overlap of the signals) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –24.75 (d, $^2J_{P,P}$ = 100 Hz, 1 P, free PPh_2), 27.05 (d, $^2J_{P,P}$ = 100Hz, 1 P, Pd–PPh_2), 49.14 (s, 1 P, P=N) ppm.

Complex 16: Complex **16** was prepared following a procedure similar to that reported for **14**. A solution of **11** (0.100 g, 0.191 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.040 g, 0.191 mmol) and dppe (0.076 g, 0.191 mmol) to give **16** as a cream solid. Yield: 0.157 g (83.3%). Complex **16** was recrystallised from CH_2Cl_2/*n*-hexane to give pale yellow crystals of **16**·CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{50}H_{42}ClN_2O_5P_3Pd{\cdot}CH_2Cl_2$ (1070.6): calcd. C 57.22, H 4.14, N 2.62; found C 57.53, H 4.02, N 2.64. IR: $\tilde{\nu}$ = 1622 (ν_{CO}), 1329 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 885 (70) $[M - ClO_4]^+$. Room temperature NMR spectroscopic data: ^1H NMR ($CDCl_3$): δ = 2.22–2.29 (br. s, 4 H, CH_2, dppe), 6.83–7.92 (m, 38 H, aromatics) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 47.28 (s, P=N) ppm. Low temperature NMR spectroscopic data (233 K): ^1H NMR ($CDCl_3$): δ = 2.31, 2.42, 2.88, 3.01 (4m, 4 H, CH_2, dppe), 6.60 (m, 1 H, C_6H_4), 6.92–7.11 (3m, 3 H, C_6H_4), 7.17–8.12 (m, 33 H, aromatics), 8.72 (dd, $^3J_{H,H}$ = 5.6, $^4J_{H,H}$ = 1.8 Hz, 1 H, H$^\alpha$, py) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 41.38 (dd, $^3J_{P,P}$ = 27.5, $^3J_{P,P}$ = 13.0 Hz, 1 P, P *trans* to N), 47.84 (dd, $^3J_{P,P}$ = 13.0, $^3J_{P,P}$ = 3.2 Hz, 1 P, P=N), 58.21 (d, $^3J_{P,P}$ = 27.5 Hz, 1 P, P *trans* to C) ppm.

Complex 17: Complex **17** was prepared following a procedure similar to that reported for **14**. A solution of **11** (0.100 g, 0.191 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.040 g, 0.191 mmol) and 2,2′-bipyridine (0.030 g, 0.191 mmol) to give **17** as a yellow solid. Yield: 0.110 g (77.5%). Complex **17** was crystallised from CH_2Cl_2/*n*-hexane to give yellow crystals of **17**·CH_2Cl_2, which were used for analytical and spectroscopic measurements. $C_{34}H_{26}ClN_4O_5PPd{\cdot}CH_2Cl_2$ (807.13): calcd. C 51.71, H 3.43, N 6.94; found C 51.79, H 2.87, N 7.18. IR: $\tilde{\nu}$ = 1652 (ν_{CO}), 1332 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 643 (25) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ = 6.33 (ddd, $^3J_{H,H}$ = 7.1, $^4J_{P,H}$ = 4.7, $^4J_{H,H}$ = 2.6 Hz, 1 H, H^6, C_6H_4), 6.92–6.99 (m, 1 H, C_6H_4), 7.08–7.12 (m, 2 H, C_6H_4), 7.55 (ddd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.2 Hz, 2 H, H$^\beta$, bipy),

7.58–7.67 [m, 5 H, PPh_2 (4 H^m) + py (H^β)], 7.71–7.74 (m, 2 H, H^p, PPh_2), 7.76–7.85 (m, 4 H, H^o, PPh_2), 7.87–7.92 (m, 2 H, H^δ + H^γ, py), 7.95 (dd, $^3J_{H,H}$ = 4.0, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^α, py), 8.02 (td, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.6 Hz, 2 H, H^γ, bipy), 8.30 (dt, $^3J_{H,H}$ = 7.7, $^4J_{H,H} \approx {}^5J_{H,H}$ = 1 Hz, 2 H, H^δ, bipy), 8.91 (ddd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.6 Hz, 2 H, H^α, bipy) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 53.96 ppm.

Complex 18: Complex **18** was prepared following a synthetic procedure similar to that reported for **14**. A solution of **11** (0.100 g, 0.191 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.040 g, 0.191 mmol) and 1,10-phenanthroline (0.034 g, 0.191 mmol) to give **18** as a yellow solid. Yield: 0.100 g (68.2%). $C_{36}H_{26}ClN_4O_5PPd$ (767.45): calcd. C 56.34, H 3.41, N 7.30; found C 56.15, H 3.08, N 7.09. IR: $\tilde{\nu}$ = 1645 (ν_{CO}), 1338 (ν_{PN}) cm^{-1}. MS (FAB+): *m*/*z* (%) = 667 (30) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ = 5.85 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, H^6, C_6H_4), 6.83–6.88 (m, 1 H, C_6H_4), 6.97–7.02 (m, 2 H, C_6H_4), 7.29 (dm, $^3J_{H,H}$ = 4.2, $^4J_{H,H}$ = 0.6 Hz, 1 H, H^α, py), 7.36 (ddd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.5 Hz, 1 H, H^β, py), 7.53–7.58 (m, 1 H, py), 7.63–7.69 (m, 4 H, H^m, PPh_2), 7.75–7.80 (m, 2 H, H^p, PPh_2), 7.88 (dd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 4.8 Hz, 2 H, H^β, phen), 7.94–8.01 [m, 5 H, PPh_2 (4 H^o) + py (1 H)], 8.10 (s, 2 H, H^δ, phen), 8.61 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.5 Hz, 2 H, H^γ, phen), 9.36 (dd, $^3J_{H,H}$ = 4.8, $^4J_{H,H}$ = 1.8 Hz, 2 H, H^α, phen) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 53.96 ppm.

Catalytic Mizoroki–Heck Arylations of Methyl Acrylate. General Procedure: Methyl acrylate (1.35 mmol), NEt_3 (1.13 mmol) and the corresponding catalyst (complexes **1**, **4**, **11** or **13**, see amounts in Table 3) were added to a solution of the corresponding aryl halide (1.13 mmol) in dimethylformamide or dimethylacetamide (15 mL). This mixture was refluxed under argon for 24 h. After cooling, water (10 mL) was added. The organic phase was extracted several times with CH_2Cl_2 (3 × 10 mL) and the combined extracts were dried with anhydrous $MgSO_4$. The solvents were distilled off and the residue was extracted with *n*-pentane. Evaporation of the pentane solution to dryness gave the arylation products as white waxy solids or colourless oils (yields are collected in Table 3).

Transmission Electron Microscopy: For the TEM experiments a few drops of a solution of the samples in dichloromethane was deposited onto carbon-coated copper grids. In this way the organic ligands were dissolved whereas the metallic particles remained undissolved and dispersed, thus allowing their observation in the TEM. The observations were carried out with a Jeol 2000FXII microscope (point to point resolution: 2.8 Å) equipped with an Oxford Instruments INCA 200 Energy Dispersive Spectroscopy analyzer and a Gatan MSC-794 CCD camera for recording the images.

Crystallography. Data Collection: Crystals of complex [Pd(C_6H_4-2-PPh_2=N-C(O)-2-NC_5H_4-κ-C,N,N)Cl] (**11**) were grown by slow vapour diffusion of Et_2O into a CH_2Cl_2 solution of the crude complex at room temperature. A crystal of dimensions 0.20 × 0.10 × 0.043 mm was mounted on a quartz fibre in a random orientation and covered with epoxy. Data collection was performed at 100 K on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A hemisphere of data was collected based on three ω-scan runs. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the program SAINT[86] and the integrated intensities were corrected for systematic errors with SADABS.[87]

Structure Solution and Refinement: The structure was solved by Patterson and Fourier methods.[88] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealised positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2-times the equivalent isotropic displacement parameter of its parent atom. The structure was refined to F_o^2, and all reflections were used in the least-squares calculations.[89]

CCDC-253369 (for **11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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