

Synthesis, characterization and catalytic activity in Heck-type reactions of orthometallated Pd^{II} and Pt^{II} complexes derived from (1*R*,2*R*)-1,2-diaminocyclohexane

Judith Bravo ^a, Carlos Cativiela ^a, Rafael Navarro ^{b,*}, Esteban P. Urriolabeitia ^{b,*}

^a Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain

^b Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain

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Abstract

The chiral bis-imine (1*R*,2*R*)-C₆H₁₀-[E-N=CH-C₆H₃-3,4-(OMe)₂]₂ **1** (LH) reacts with [Pd(OAc)₂] (1:1 molar ratio; OAc = acetate) giving the orthometallated [Pd(OAc)(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)] **2** (abbreviated as [Pd(OAc)(L-κ-C,N,N)]), through C–H bond activation on only one of the aryl rings and *N,N*-coordination of the two iminic N atoms. **2** reacts with an excess of LiCl to give [Pd(Cl)(L-κ-C,N,N)] **3**. The reaction of **3** with AgClO₄ and neutral or anionic ligands L' (1:1:1 molar ratio) affords [Pd(L-κ-C,N,N)(L')(ClO₄)] (L' = PPh₃ **4a**, NCMe **5**, pyridine **6**, *p*-nitroaniline **7**) or [Pd(I)(L-κ-C,N,N)] **8**. Complex **4a** reacts with wet CDCl₃ giving [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-NH₂-κ-C,N,N)(PPh₃)](ClO₄) **4b** as a result of the hydrolysis of the C=N bond not involved in the orthometallated ring. The molecular structure of **4b**·CH₂Cl₂ has been determined by X-ray diffraction methods. Cleavage of the Pd–N bond *trans* to the C_{aryl} atom can be accomplished by coordination of strongly chelating ligands, such as acetylacetonate (acac) or bis(diphenylphosphino)ethane (dppe), forming [Pd(acac-*O,O'*)(L-κ-C,N)] **9** and [Pd(L-κ-C,N)(dppe-P,P')](ClO₄) **12**, while classical *N,N'*-chelating ligands such as 1,10-phenantroline (phen) or 2,2'-bipyridyl (bipy) behave as monodentate N-donor ligands yielding [Pd(L-κ-C,N,N)(κ¹-N-phen)](ClO₄) **10** and [Pd(L-κ-C,N,N)(κ¹-N-bipy)](ClO₄) **11**. Treatment of **1** with PtCl₂(DMSO)₂ (1:1 molar ratio) in refluxing 2-methoxyethanol gives Cl₂Pt[(NH₂)₂C₆H₁₀-N,N'] **13a** and [Pt(Cl)(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-NH₂-κ-C,N,N)] **13b**, while [Pt(Cl)(L-κ-C,N,N)] **14** can be obtained by reaction of [Pt(μ-Cl)(η³-2-Me-C₃H₄)₂] with **1** in refluxing CHCl₃. Complexes **2** and **3** catalyzed the arylation of methyl acrylate giving good yields of the corresponding methyl cinnamates and TON up to 847 000. Complex **3** also catalyzes the hydroarylation of 2-norbornene, but with lower yields and without enantioselectivity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Platinum; Orthometallated; Chiral; Heck reactions; Catalysis

1. Introduction

The chiral synthon (1*R*,2*R*)-1,2-diaminocyclohexane (DACH), its enantiomer (1*S*,2*S*), and its derivatives, have been widely used as powerful stereodirecting reagents or ligands in asymmetric synthesis, and most of their chemistry has been reviewed recently [1]. Almost as a general rule, the enantiomers are derivatized and we can find very interesting examples of such

derivatizations in the synthesis of chiral macrocycles of C₂-symmetry [2], in the synthesis of new chiral ligands [3] and complexes [4] and in their applications in asymmetric catalysis [5]. Recently, C,N,N-orthometallated Pt^{II}-complexes based on *cis*- and *trans*-1,2-DACH have been reported by Puddephatt [6]. This type of complexes shows exciting properties, such as a high stereoselectivity in the coordination of olefins [6a, 6b], the structural modelization of electrophilic polynuclear complexes [6c], the stereoselective formation of Pt–C bonds [6d, 6e, 6g], the carbon atom being a stereogenic center, or the stereoselective oxidative addition to Pt^{II} centers [6f].

* Corresponding authors.

E-mail addresses: rafanava@posta.unizar.es (R. Navarro), esteban@posta.unizar.es (E.P. Urriolabeitia).

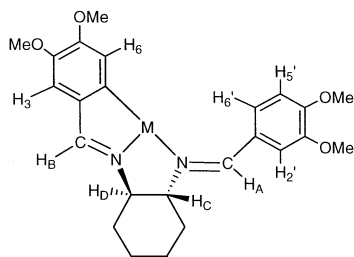


Fig. 1. Schematic representation and proton numbering for the cyclometallated unit in complexes **2–8** and **14**.

Given these precedents, and as part of our ongoing work on the synthesis of orthometallated complexes of Pd^{II} and Pt^{II} with additional functionalities [7,8], we have now focussed our attention on chiral entities derived from DACH. Our aim at the beginning of this work was the synthesis of chiral, orthometallated, complexes of Pd^{II} and Pt^{II}, in which three of the four possible coordination sites were blocked by the cyclometallated ligand (see Fig. 1), leaving only one available position with a very specific stereochemistry. Moreover, the chiral C,N,N-palladacycles could very likely behave as catalysts in specific C–C couplings, such as the Heck reaction, a field, which is in continuous growth [9–12].

In this paper, we report the synthesis of chiral palladium and platinum orthometallated complexes derived from the bis-imine (1*R*,2*R*)-C₆H₁₀–[*E*-N=CH–C₆H₃–3,4-(OMe)₂]₂ (**1**) and their behavior as catalysts in some

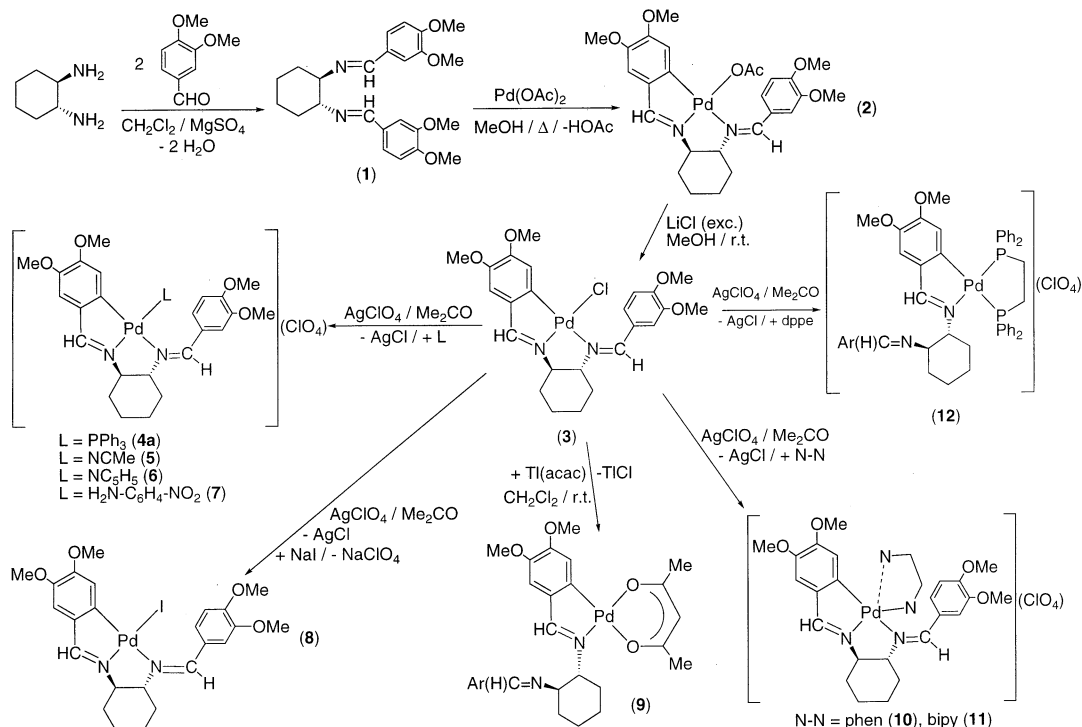
C–C bond forming reactions, such as the arylation of methyl acrylate and the hydroarylation of 2-norbornene.

2. Results and discussion

2.1. Synthesis of the orthometallated complexes

The bis-imine **1** (see Scheme 1) can be easily obtained by condensation of 3,4-dimethoxybenzaldehyde with (1*R*,2*R*)-1,2-DACH (1:1 molar ratio, CH₂Cl₂ room temperature), in the presence of anhydrous MgSO₄. The formation of the iminic N=C bond can be inferred from the IR spectrum of **1** due to the presence of a strong absorption at 1647 cm^{−1}. The NMR spectra of **1** show that the molecule retains the C₂-symmetry, since, only one set of resonances is observed in each spectrum. This fact also implies that the two C=N bonds display the same configuration (*E*). The iminic proton appears in the ¹H-NMR as a singlet at 8.04 ppm, the aromatic protons appear as a singlet (H₂) and an AB spin system (H₅ and H₆), and resonances attributed to the methoxy groups and to the protons of the C₆H₁₀ skeleton are also observed. The ¹³C{¹H}-NMR spectrum of **1** shows all the expected resonances.

The treatment of a methanolic suspension of Pd(OAc)₂ with **1** (1:1 molar ratio) at the reflux temperature produces its gradual dissolution and the change of its color from orange to bright yellow. The evapora-



Scheme 1.

tion of the solution and Et₂O addition gives complex [Pd(OAc)(L-κ-C,N,N)] (**2**) (see Scheme 1) as a yellow solid. Further reaction of **2** with LiCl (excess, MeOH, room temperature) affords [Pd(Cl)(L-κ-C,N,N)] (**3**) as a yellow solid.

The elemental analyses and the mass spectra of **2** and **3** are in keeping with the presence of one acetate (**2**) or one chloride (**3**) ligand and one anionic L[−] ligand per Pd atom. The mononuclear nature of **2** (and, by extrapolation, of **3**) can be inferred from the value obtained in the determination of the molecular weight of **2** in CHCl₃ solution (670 g mol^{−1}), which is closer to that calculated for a monomeric structure (574.96) than that calculated for a binuclear system (1149.92). The IR spectrum of **2** shows a very complicated pattern of six intense absorptions in the 1650–1520 cm^{−1} region, showing the presence of acetate, imine and aromatics, but precluding their complete assignment.

The IR spectrum of **3** is very similar to that of **2**, but shows in addition a medium intensity band at 282 cm^{−1}, due to the Pd–Cl stretch.

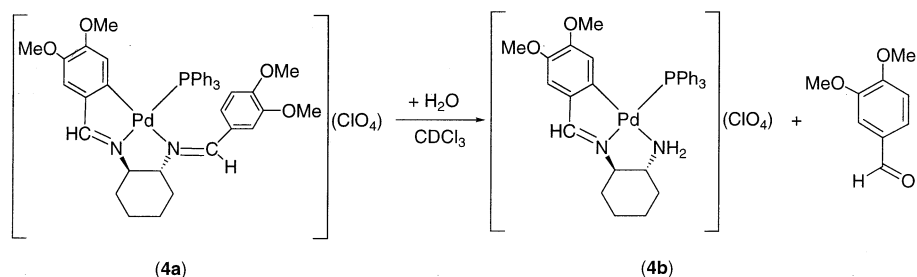
The ¹H-NMR spectra of **2** and **3** unambiguously reveal the presence of the orthopalladated L[−] ligand, since the aromatic region shows seven well separated signals, two attributed to the iminic protons (H_A and H_B, see Fig. 1), three assigned to the aromatic protons of the non-metallated ring (H₂, H₆ and H₅) and two attributed to the H₃ and H₆ protons of the metallated ring. In addition, the NMR spectra shows the presence of four sharp resonances in the 4.00–3.75 ppm region, due to the methoxy groups, flanked by two broad multiplets attributed to the protons attached to the chiral carbon atoms (NC*H). In the high-field region, the aliphatic protons of the cyclohexane unit appear as complex multiplets (2.50–1.29 ppm for **2**, 2.42–1.05 ppm for **3**). For complex **2**, the acetate ligand appears as a singlet resonance at 1.63 ppm. The complete attribution of these resonances has been carried out with the help of the two-dimensional ¹H-¹H COSY and NOESY experiments performed on complex **3**. The key feature for this attribution is the observation of the protons H₅ and H₆ as an AB spin system (H₆, dd, 7.58 ppm; H₅, d, 6.89 ppm). The COSY spectrum correlates H₆ with H₂ (d, 8.32 ppm) and the NOESY spectrum correlates H₆ with the resonance at 8.26 ppm which, according with Fig. 1, should be the iminic proton H_A. In addition, two singlet signals at 7.37 and 6.85 ppm are attributed to the H₆ and H₃ protons of the metallated ring, respectively, the latter showing a clear NOE effect with the resonance at 7.88 ppm, which is attributed to the iminic proton H_B. The *E*-configuration of the two iminic N=C bonds comes from the observation of a clear NOE effect between the resonances of H_A (8.26 ppm) and H_B (7.88 ppm) with aliphatic protons of the cyclohexane ring (2.15 and 2.40 ppm, respectively).

The chloride ligand in **3** can be replaced by a variety of neutral and anionic ligands. Treatment of **3** with AgClO₄ (acetone, 1:1 molar ratio) results in the precipitation of AgCl, which is removed by filtration. Further reaction of the freshly prepared solvato derivative with neutral L' ligands affords the cationic [Pd(L-κ-C,N,N)(L')]ClO₄ (L' = PPh₃ **4a**, NCMe **5**, pyridine **6** or *p*-nitroaniline **7**), while treatment of the solvato complex with NaI affords the neutral [Pd(I)(L-κ-C,N,N)] **8** (see Scheme 1).

All complexes **4a–8** show correct elemental analyses and mass spectra for the proposed stoichiometries (see Section 4). The IR spectra of **4a–8** show: (i) the disappearance of the absorption due to the Pd–Cl stretch (282 cm^{−1}); (ii) absorptions corresponding to the presence of the L-κ-C,N,N bonded ligand (1650–1500 cm^{−1}); and (iii) absorptions assigned to the coordinated L' ligands (see Section 4). For **6**, the typical bands of the pyridine could not be observed due to overlapping in the 1600 cm^{−1} region, and for **8** the Pd–I stretch drops to 200 cm^{−1}, the lowest limit of detection of the spectrophotometer. The NMR spectra of **4a–8** show the expected resonances for the C,N,N-metallated ligand, in addition to signals, which are characteristic of each ligand. Thus, three multiplets in the low field region account for the presence of PPh₃ in **4a**, and a singlet at 2.01 ppm is attributed to the NCMe ligand in **5**. For **6** three resonances in the low field zone are assigned to the pyridine ligand (8.49 ppm, H_{ortho}; 7.57 ppm, H_{para}; 7.18 ppm, H_{meta}) showing the free rotation of the pyridine around the Pd–N bond. Moreover, the resonance attributed to H₆ (see Fig. 1) appears at 5.85 ppm, strongly shifted to high-field due to the anisotropic shielding produced by the pyridine [13], reflecting their mutually *cis* disposition. For **7**, the *N*-coordination can be inferred from the observation of an AB spin system for the NH₂ protons. Finally, for **8**, the pattern of resonances is very similar to that described for **3**. The ¹³C{¹H}-NMR spectra of **4a–8** show the expected signals, and the ³¹P{¹H}-NMR spectrum of **4a** shows a singlet at 35.87 ppm.

All complexes hitherto described (**2–8**) are stable at room temperature to the oxygen and to the moisture for long periods of time, both in solid state and in solution, except **4a**. This complex evolves slowly in solution in wet solvents. When a solution of **4a** is allowed to stand for 24 h in wet CD₂Cl₂ or CDCl₃, a new complex **4b** crystallized as yellow plates in nearly quantitative yield. In the remaining solution it is possible to detect 3,4-dimethoxybenzaldehyde, showing that the hydrolysis of one iminic C=N bond has occurred, as portrayed in Equation 1. As a result of the hydrolysis of the C=N bond the amine unit NH₂, which remains coordinated to the Pd center, is regenerated together with the corresponding aldehyde, detected in solution. Hydrolysis is suppressed when **4a** is handled under Ar

in dry solvents. The elemental analysis and mass spectrum of **4b** are in keeping with the structure depicted in Equation 1 (see Section 4), and the IR spectrum of **4b** shows absorptions attributed to the presence of the NH_2 group ($3320, 3254 \text{ cm}^{-1}$). The ^1H -NMR spectrum of **4b** reveals, in the low field region, the signals attributed to the PPh_3 ligand and only three additional resonances, corresponding to the iminic proton (8.05 ppm , H_B) and to the H_3 (6.98 ppm) and H_6 (5.87 ppm) protons of the orthometallated ring. In the central region of the spectrum two singlet resonances can be observed due to the methoxy groups (3.74 and 2.91 ppm), and four complex multiplets assigned to the NC^*H (3.67 and 2.78 ppm) and NH_2 (3.36 and 2.48 ppm) protons. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **4b** shows a single peak at 36.86 ppm and the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum shows the expected signals.



The determination of the crystal structure of **4b**· CH_2Cl_2 provides more structural information. The complex crystallizes in the monoclinic, non-centrosymmetric space group $P2_1$, showing that there is only one diastereoisomer in the unit cell. There are two independent molecules in the asymmetric unit, whose structural parameters are almost identical, without significant deviations, as can be seen from Table 2. A drawing of one of the organometallic cations is presented in Fig. 2. Relevant crystallographic parameters of data collection and crystal structure solution and refinement are indicated in Table 1 and selected bond distances and angles

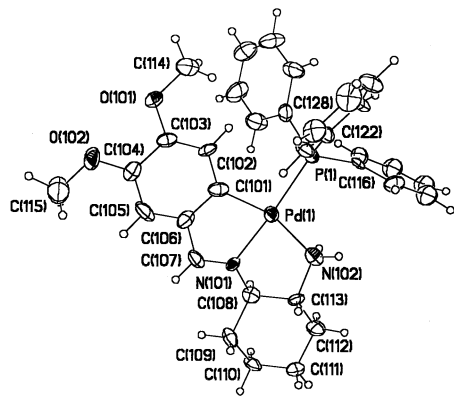


Fig. 2. Thermal ellipsoid plot of complex **4b**. Only one of the two independent molecules is shown. Non-hydrogen atoms are drawn at the 50% probability level.

are presented in Table 2. The palladium atom is located in a distorted square-planar environment, surrounded by the orthometallated carbon atom, the P atom of the PPh_3 ligand and by the two nitrogen atoms, one with an iminic $\text{C}=\text{N}$ bond and one amine type atom. The bond distances $\text{Pd}-\text{C}$, $\text{Pd}-\text{N}(\text{amine})$, $\text{Pd}-\text{N}(\text{imine})$ and $\text{Pd}-\text{P}$ and the intramolecular bond angles do not reveal any notable features and are similar, within experimental errors, to those found in related orthometallated complexes [7,8,14].

The easy generation of **4b** from **4a**, in contrast to the high stability of the other compounds obtained, is worthy of comment. For instance, the synthesis of **2** is accomplished in refluxing methanol, and that of **3** is also carried out in the same solvent (which always contains water), without noticeable signs of hydrolysis. The most important difference between **4a** and the

Table 1
Crystal data and structure refinement for **4b**· CH_2Cl_2

Empirical formula	$\text{C}_{34}\text{H}_{36}\text{Cl}_3\text{N}_2\text{O}_6\text{PPd}$
Formula weight	812.37
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	14.4343(11)
b (Å)	17.5308(13)
c (Å)	14.6634(11)
β (°)	107.238(2)°
V (Å ³)	3543.8(5)
Z	4
D_{calc} (mg m^{-3})	1.523
Absorption coefficient (mm^{-1})	0.841
$F(000)$	1656
Crystal size (mm)	$0.16 \times 0.15 \times 0.12$
θ Range for data collection (°)	1.45–28.77
Reflections collected/unique	23 745/15 370 ($R_{\text{int}} = 0.0635$)
Max/min transmission	0.9058, 0.8772
Data/restraints/parameters	15 370/13/875
Goodness-of-fit on F^2	0.730
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0510$, $wR_2 = 0.0736$
R indices (all data)	$R_1 = 0.1025$, $wR_2 = 0.0889$
Absolute structure parameter	−0.01(4)
Largest difference peak and hole ($\text{e} \text{ Å}^{-3}$)	0.759 and −0.594

Table 2
Selected bond lengths (Å) and angles (°) for **4b**-CH₂Cl₂

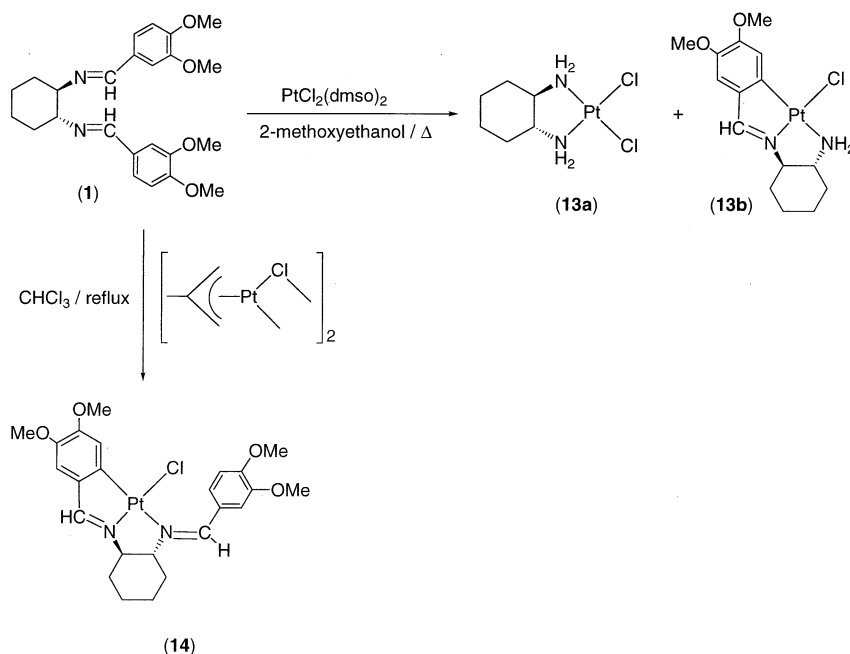
<i>Bond lengths</i>			
Pd(1)–C(101)	1.988(12)	Pd(2)–C(201)	2.003(10)
Pd(1)–N(101)	2.035(8)	Pd(2)–N(201)	1.992(8)
Pd(1)–N(102)	2.122(9)	Pd(2)–N(202)	2.144(8)
Pd(1)–P(1)	2.257(3)	Pd(2)–P(2)	2.236(3)
C(101)–C(102)	1.378(12)	C(201)–C(202)	1.423(13)
C(101)–C(106)	1.394(15)	C(201)–C(206)	1.353(13)
C(102)–C(103)	1.378(15)	C(202)–C(203)	1.427(14)
C(103)–O(101)	1.356(10)	O(201)–C(204)	1.388(13)
C(103)–C(104)	1.432(15)	C(203)–C(204)	1.332(13)
O(101)–C(114)	1.410(12)	O(201)–C(214)	1.402(12)
C(104)–O(102)	1.344(12)	O(202)–C(205)	1.400(11)
C(104)–C(105)	1.412(14)	C(204)–C(205)	1.378(15)
O(102)–C(115)	1.393(12)	O(202)–C(215)	1.452(11)
C(105)–C(106)	1.371(16)	C(205)–C(206)	1.385(16)
C(106)–C(107)	1.444(14)	C(202)–C(207)	1.485(13)
C(107)–N(101)	1.249(12)	C(207)–N(201)	1.294(12)
N(101)–C(108)	1.457(10)	N(201)–C(208)	1.427(10)
C(108)–C(113)	1.531(10)	C(208)–C(213)	1.491(10)
C(108)–C(109)	1.563(12)	C(208)–C(209)	1.460(12)
C(109)–C(110)	1.520(13)	C(209)–C(210)	1.533(13)
C(110)–C(111)	1.478(12)	C(210)–C(211)	1.506(12)
C(111)–C(112)	1.514(12)	C(211)–C(212)	1.533(13)
C(112)–C(113)	1.462(12)	C(212)–C(213)	1.536(12)
C(113)–N(102)	1.511(10)	C(213)–N(202)	1.511(11)
<i>Bond angles</i>			
C(101)–Pd(1)–N(101)	81.1(4)	N(201)–Pd(2)–C(201)	82.7(3)
C(101)–Pd(1)–N(102)	161.9(4)	C(201)–Pd(2)–N(202)	162.6(4)
N(101)–Pd(1)–N(102)	81.0(3)	N(201)–Pd(2)–N(202)	80.3(3)
C(101)–Pd(1)–P(1)	97.4(3)	C(201)–Pd(2)–P(2)	96.1(3)
N(101)–Pd(1)–P(1)	174.9(2)	N(201)–Pd(2)–P(2)	178.7(2)
N(102)–Pd(1)–P(1)	100.7(2)	N(202)–Pd(2)–P(2)	100.8(2)

other complexes lies probably in the steric requirements of the L' ligand, and this could be a reasonable argument to explain the moderate stability of **4a**. Thus, the *cis* arrangement of the bulky PPh₃ ligand and the iminic fragment –N=C(H)C₆H₃-3',4'-(OMe)₂ which, moreover, presents *E* configuration and is directed towards the PPh₃ group, could contribute to the destabilization of the resulting molecule **4a** by steric hindrance. This is not observed in the other complexes, probably because, the ligands coordinated in this position are smaller than PPh₃ (Cl **3**, I **8**), or linear (NCMe **5**), or they can accommodate through free rotation in a given position to minimize steric repulsions (OAc **2**, pyridine **6**, *p*-nitroaniline **7**). We have not performed any other reactions with bulky ligands and different donor atoms in order to establish whether or not this reaction is a general process.

In complexes **2–8** the ligand L acts as a C,N,N-terdentate group. The Pd–N bond *trans* to the orthometallated carbon atom can be easily cleaved by reaction of **3** (or its solvato derivative) with strong chelating ligands. Treatment of **3** with Ti(acac) (1:1 molar ratio, CH₂Cl₂, acac = acetylacetonate) produces the immediate precipitation of TiCl₃, which is removed by filtration. From the resulting solution, the complex

[Pd(acac-*O,O'*)(L-κ-C,N)] **9** can be obtained as a yellow solid. The *O,O'*-chelate coordination of the acac ligand can be inferred from the position of the carbonyl stretch in the IR spectrum (1588 and 1515 cm^{–1}), characteristic of this bonding mode [15], and from the analysis of its NMR spectra: the ¹H-NMR spectrum shows the C³–H proton at 5.36 ppm, and the ¹³C{¹H}-NMR spectrum shows the C³ carbon atom at 99.96 ppm and the C(O) atoms at 187.71 and 186.06 ppm, all of them being typical values for O-coordination [15]. The structure depicted in Scheme 1 for **9** resumes all these facts. On the other hand, the reaction of **3** with AgClO₄ in acetone, followed by removal of the AgCl and treatment of the resulting solution with dppe [bis(diphenylphosphino)ethane] (1:1:1 molar ratio, room temperature) results in the synthesis of [Pd(L-κ-C,N)(dppe-P,P')]ClO₄ **12**, according to its elemental analyses and mass spectrum (see Scheme 1). In this case, the P,P'-bonding mode of the dppe ligand can be inferred from the position of the resonances in the ³¹P{¹H}-NMR spectrum (60.85 and 40.61 ppm), which are very similar to those found in related P,P'-complexes [8].

However, the behavior of other classic strong chelating ligands, such as 1,10-phenantroline (phen) and 2,2'-bipyridyl (bipy) differs notably from that described for **9** and **12**. The solution of the solvato complex [Pd(L-κ-C,N,N)(acetone)]ClO₄ reacts with the N–N ligands (N–N = phen, bipy) (**3**: AgClO₄: N–N = 1:1:1 molar ratio) giving complexes of stoichiometry [Pd(L)(N–N)]ClO₄ (N–N = phen **10**, bipy **11**) according to their elemental analyses and mass spectra. The ¹H-NMR spectra of these complexes are particularly informative. At room temperature, they show seven sharp signals, assigned to the orthometallated unit, and four broad resonances. On cooling (CD₂Cl₂, 213 K) these four broad signals split into eight sharp resonances, attributed to the eight inequivalent protons of the N–N ligands. These facts suggest that the L-κ-C,N,N group behaves statically in the NMR time scale, in the range of temperatures measured, and that the terdentate coordination is preserved. These facts also suggest that the two rings of the N–N ligands behave equivalently (on the NMR time scale) at room temperature and inequivalently at low temperatures. Moreover, the equivalence of the two halves of the N–N ligands at room temperature means that the molecular plane behaves as a symmetry plane, in spite of the presence of chiral centers. A reasonable explanation could be the assumption that the N–N ligands are coordinated only through one nitrogen atom and that there is a rapid exchange of the N-bonded atoms at room temperature, which almost ceases at low temperatures. This fast exchange of the N atoms can be easily rationalized through either a dissociative mechanism of the Pd–N bond or through a fluxional process, which could be 'a single oscillatory



Scheme 2.

motion of the potentially didentate ligand via a trigonal–bipyramidal transition state'. Similar proposals have been reported for related systems [8].

We have also attempted to prepare orthometallated Pt^{II} complexes, starting from Pt^{II} substrates and **1** through C–H activation. Pt^{II} complexes have been used frequently to promote C–H bond activation [16]. For instance, $\text{PtCl}_2(\text{DMSO})_2$ ($\text{DMSO} = \text{Me}_2\text{S}=\text{O}$) has been employed in a wide variety of C–H bond activation reactions [17]. The treatment of a white suspension of $\text{PtCl}_2(\text{DMSO})_2$ with **1** (1:1 molar ratio) in refluxing 2-methoxyethanol for 22 h results in the formation of a mixture of two products (**13a** and **13b**, see Scheme 2), which are easily separable due to their different solubility. Complex **13a**, insoluble in the alcoholic medium, is the coordination compound $\text{Cl}_2\text{Pt}[(\text{NH}_2)_2\text{C}_6\text{H}_{10}\text{-N,N}']$, while complex **13b**, soluble in 2-methoxyethanol and isolated after evaporation and precipitation with Et_2O , is the orthometallated derivative $[\text{Pt}(\text{Cl})(\text{C}_6\text{H}_2\text{-4,5-(OMe)}_2\text{-2-CH=N-(1R,2R)-C}_6\text{H}_{10}\text{-NH}_2\text{-}\kappa\text{-C,N,N})]$. The analytical and spectroscopic parameters of **13a** and **13b** unambiguously establish their stoichiometry and stereochemistry (see Scheme 2, Section 4). Probably, the strong reaction conditions and the protic nature of the solvent are responsible for the behavior observed.

The synthesis of $[\text{Pt}(\text{Cl})(\text{L-}\kappa\text{-C,N,N})]$ **14** is easily accomplished by reacting **1** and the dimer [18] $[\text{Pt}(\mu\text{-Cl})(\eta^3\text{-2-Me-C}_6\text{H}_4)]_2$ (2:1 molar ratio) in refluxing CHCl_3 for 5 h (see Scheme 2). This is a very convenient method for the synthesis of cycloplatinated derivatives [19]. The spectral data of **14** are very similar to those of **3**, with the logical differences arising from the coordina-

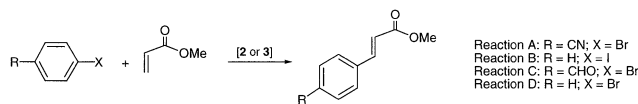
tion to the Pt center instead to the Pd center. Thus, the $^1\text{H-NMR}$ spectrum of **14** reveals the resonances attributed to the iminic protons H_A , H_B and H_C with ^{195}Pt satellites, showing values of the coupling constants, which are similar to others reported in the literature [6]. The different values of the $^3J_{\text{Pt-H}}$ for the iminic protons ($\text{N}=\text{CH}_\text{A}$, 8.77 ppm, $^3J_{\text{Pt-H}} = 44$ Hz; $\text{N}=\text{CH}_\text{B}$, 8.21 ppm, $^3J_{\text{Pt-H}} = 147$ Hz) could be due to the different *trans* influences of their respective *trans* ligands, even if both iminic C=N bonds show the same geometry. Thus, the iminic proton H_A is located *trans* to the orthometallated carbon atom, while the iminic proton H_B is located *trans* to the chlorine atom; the higher *trans* influence of the carbon atom with respect to the Cl atom results in a higher labilization of the $\text{Pt-N}(\text{=CH}_\text{A})$ bond, and then in a lower value of the coupling constant.

2.2. Catalytic reactions

After the discovery of the exceptional activity in the Heck reaction [20] of the orthometallated complex $[\text{Pd}(\mu\text{-OAc})(\text{CH}_2\text{C}_6\text{H}_4\text{-2-P}(o\text{-tolyl}))_2]$ (*o*-tolyl = *ortho*- MeC_6H_4) [21], the investigation of the catalytic properties of different C,X-cyclopalladated complexes in Heck-type reactions is, at present, one of the most active fields of research in Pd-catalyzed processes [9–12]. We have studied the catalytic activity of complexes **2** and **3** in Heck or Heck-type reactions.

Complexes **2** and **3** effectively catalyze the arylation of methyl acrylate (see Equation 2; Section 4; Table 3) in refluxing *N,N*-dimethylacetamide [21a] for 24 h,

giving the corresponding methyl *E*-cinnamates, as white solids or yellow oils, in moderate to good yields. We have observed some general features: (i) all reactions start after an induction period of, ca. 30 min, in which the initial yellow solution becomes an orange or red suspension, but with no evidence of black palladium in this suspension; (ii) it has not been possible to recover the catalyst at the end of the reaction; (iii) however, these solutions can reassume the catalytic reaction after the addition of a second batch of reagents, although, with a lower activity than that shown in the first run. For instance, **3** (1%) catalyzes the phenylation of methyl acrylate to give the methyl cinnamate in 82.6% yield (entry 12). If, instead of the workup, a second batch of reagents is added at the end of this first run and heating is maintained a further 24 h, the methyl cinnamate is obtained with a global yield of 61.4%, which means that the yield of the second run is 40.2%, assuming the same yield for the first run.



Conditions: Aryl halide (1.13 mmol); methyl acrylate (1.35 mmol); Dimethylacetamide (15 mL); NEt₃ (1.13 mmol); reflux; 24 h

(2)

As can be seen in Table 3, both complexes **2** and **3** are effective catalysts in the Heck reaction of methyl acrylate with iodobenzene, bromobenzene or activated aryl bromides. In some cases, the concentration of the

catalyst can be as low as 10^{-6} (mmol catalyst per mmol aryl halide) (entries 4, 8, 11 and 15) giving the corresponding methyl cinnamates in moderate to good yields. The comparison of the different haloarenes (reaction A: 4-BrC₆H₄CN; reaction B: IC₆H₅; reaction C: 4-BrC₆H₄CHO; reaction D: BrC₆H₅; see Equation 2) shows that in general, the yields of the isolated products using iodobenzene or 4-bromobenzonitrile are more or less similar (for instance, entries 2 and 9, 3 and 10, 4 and 11), that slightly lower yields are obtained with 4-bromobenzaldehyde (entries 2, 9, 16 or 5, 12, 18) and that the lowest yields are obtained with bromobenzene (entries 21, 22). No reaction was observed using chlorobenzene (catalyst **3**, 1%). With respect to the compared activity of **2** and **3**: complex **3**, in general, gives better yields (entries 1 and 5, 2 and 6, 3 and 7, for instance) although, the differences are not spectacular and can be the opposite in some cases (entries 4 and 8, 9 and 13).

Prompted by the results obtained in the arylation of methyl acrylate and taking advantage of the chiral character of our catalysts, we decided to explore the catalytic behavior of **3** in asymmetric Heck reactions [22], namely in the hydroarylation of 2-norbornene. This reaction, catalyzed enantioselectively by Pd complexes, has been known since 1991 [23] but it is being exhaustively studied at the present time [24] given that this methodology could be successfully employed in the synthesis of natural products analogous to the epibatidine alkaloid [25]. The reaction scheme is presented in

Table 3
Catalytic Heck arylation of methyl acrylate

Run	Reaction	Catalyst	Catalyst (%mmol) ^a	Yield (%) ^b	TON
1	A	2	1	78.4	78.4
2	A	2	0.1	84.6	846
3	A	2	0.01	62.0	6200
4	A	2	0.0001	74.0	740 000
5	A	3	1	86.7	86.7
6	A	3	0.1	89.9	899
7	A	3	0.01	100	10 000
8	A	3	0.0001	64.1	641 000
9	B	2	0.1	79.0	790
10	B	2	0.01	66.8	6680
11	B	2	0.0001	84.7	847 000
12	B	3	1	82.6	82.6
13	B	3	0.1	74.7	747
14	B	3	0.01	95.7	9570
15	B	3	0.0001	42.6	426 000
16	C	2	0.1	74.7	747
17	C	2	0.01	38.5	3850
18	C	3	1	74.5	74.5
19	C	3	0.1	71.5	715
20	C	3	0.01	66.0	6600
21	D	3	1	68.1	68.1
22	D	3	0.1	0.0	0.0

^a Calculated with respect to aryl halide.

^b Isolated product.

Table 4
Catalytic Heck hydroarylation of 2-norbornene

Run	Reaction	Catalyst	Catalyst (% mmol) ^a	Yield (%) ^b	TON	Optical yield ^d
1	A	3	1	53	53	
2	A	3	0.1	57.2	572	
3	A	3	0.01	—	—	—
4	B	3	1	81	81	
5	B	3	0.1	89.2	892	
6	B	3	0.01	100	10 000	
7	B	3	0.0001	—	—	—
8	C	3	1	84	84	
9	C	3	0.1	66.4	664	
10	C	3	0.01	—	—	—
11	ClPh ^c	3	1	—	—	—
12	BrC ₆ H ₄ Me ^c	3	1	—	—	—
13	BrC ₆ H ₄ OMe ^c	3	1	—	—	—

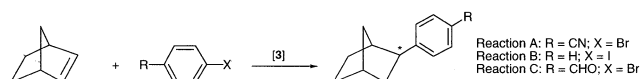
^a Calculated with respect to aryl halide.

^b Isolated product.

^c Same reaction conditions.

^d See text.

Equation 3 (also see Section 4) and the results obtained are presented in Table 4. As can be seen from Table 4, **3** catalyzes the arylation of 2-norbornene giving the corresponding aryl norbornanes in moderate to excellent yields. However, the amount of catalyst required is higher than in the arylation of methyl acrylate, and concentrations of catalyst lower than 10^{-4} (mmol **3** per mmol aryl halide) did not give detectable conversions (entry 7). The best results were obtained with phenyl iodide, and activated aryl bromides gave lower conversions (entries 1, 4, 8 and 2, 5, 9). The amount of catalyst in the case of aryl bromides must be at least 10^{-3} (mmol **3** per mmol aryl halide) to achieve good conversions, since lower concentrations did not give detectable conversions (entries 3 and 10). Electron-rich aryl bromides (4-bromotoluene or 4-bromoanisole) were unreactive (entries 12 and 13), as well as chlorobenzene (entry 11), even with 1% of catalyst **3**.



Conditions: Aryl halide (5 mmol); 2-norbornene (15 mmol); HCOOH (10 mmol)
Dimethylsulfoxide (10 mL); NEt₃ (15 mmol); 90 °C; 15 h

(3)

However, the optical purity of the aryl norbornanes obtained, based on the $[\alpha]_D$ values, is close to zero in all cases, showing the absence of enantiomeric discrimination. Thus, although these complexes are more or less effective catalysts in Heck-type processes, they are not suitable for producing asymmetric induction in the reported conditions, which are similar to others described in the literature [24]. A reasonable explanation for this lack of enantioselectivity can be given on the basis of recent work in this area [9, 12a, 12b], which suggests that the C,N-orthopalladated complexes are

actually pre-catalysts, and that the true catalytic species are nanoparticles [26] of Pd⁰ generated by decomposition of the catalyst. The presence of Pd⁰ nanoparticles has been proved in some cases [26] and is suspected in other cases [12a, 12b]. This hypothesis could explain our observations on: (i) the presence of an activation period; (ii) the non-recovery of the catalyst at the end of the reaction; (iii) the absence of Pd⁰ black, as the nanoparticles generated are stabilized in the presence of ammonium salts, formed during the reaction [26] and (iv) the lack of enantioselectivity, as the chiral environment of the Pd center is destroyed during the activation period.

Other studies are currently in progress in order to obtain new ligands, based on the chiral entity (1*R*,2*R*)-diaminocyclohexane, which could act as efficient catalysts in enantio- and diastereoselective asymmetric Heck reactions.

3. Conclusions

We have reported several new palladium and platinum neutral and cationic complexes, based on the orthometallated chiral diimine ligand [(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)]]. This ligand acts mainly as a C,N,N-terdentate ligand [M(L-κ-C,N,N)], even in presence of classic chelating ligands such as phen or bipy, showing the stability of the C,N,N-coordination. The Pd–N bond *trans* to the aryl carbon atom can be cleaved by strong chelating ligands such as acac or dppe. The iminic C=N bonds can be hydrolyzed once, generating the new C,N,N-ligand [(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-NH₂-κ-C,N,N)] (**4b** and **13b**) or twice,

regenerating the starting DACH, which remains *N,N*-coordinated (**13a**). Complexes [Pd(OAc)(L- κ -CN,N)] (**2**) and [Pd(Cl)(L- κ -C,N,N)] (**3**) are adequate pre-catalysts for Heck or Heck-type reactions. However, they are not suitable precursors in asymmetric Heck reactions in the conditions studied.

4. Experimental

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See J. Chem. Ed. 50 (1973) A335.

4.1. General methods

Solvents were dried and distilled under argon before use. Elemental analyses were carried out in a Perkin–Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}\text{C}\{^1\text{H}\}$ (75.47 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (121.49 MHz)-NMR spectra were recorded in CDCl_3 or CD_2Cl_2 solutions at room temperature (r.t.) (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}\text{C}\{^1\text{H}\}$ were referenced using the solvent signal as the internal standard and $^{31}\text{P}\{^1\text{H}\}$ was externally referenced to H_3PO_4 (85%). The two dimensional ^1H - ^1H COSY and ^1H - ^{13}C NOESY experiments for complexes **3** and **8** were performed at a measuring frequency of 300.13 MHz. The data were acquired using a phase-sensitive method into a 512×1024 matrix, and then transformed into 1024×1024 points using a sine window in each dimension. The mixing time was 400 ms for the NOESY experiments. Mass spectra (positive ion F.A.B.) were recorded on a V.G. Autospec spectrometer from CH_2Cl_2 solutions.

4.2. Preparation of (1*R*,2*R*)- C_6H_{10} -[*E*- $\text{N}=\text{CH}-\text{C}_6\text{H}_3-3,4-(\text{OMe})_2$]₂ (**1**)

To a solution of 3,4-(OMe)₂- $\text{C}_6\text{H}_3-\text{CHO}$ (2.920 g, 17.5 mmol) in CH_2Cl_2 (15 ml) at r.t., (1*R*,2*R*)-1,2-diaminocyclohexane (1.003 g, 8.79 mmol) and anhydrous MgSO_4 were added. The reaction mixture was stirred for 30 min and then filtered. The resulting solution was evaporated to dryness and the oily residue was treated with *n*-hexane (40 ml) and continuous stirring, giving **1** as a white solid. This solid was filtered, washed with additional *n*-hexane (20 ml) and air dried. Obtained: 3.086 g (85.5% yield). Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$: C, 70.22; H, 7.36; N, 6.82. Found: C, 69.79; H, 7.37; N, 7.32%. Mass Spect. (FAB +) [m/z , (%): 411 (100%) [(M + H)⁺]. IR (ν , cm^{-1}): 1647(N=CH), 1602, 1586,

1511 (C=C). ^1H -NMR (CDCl_3): δ (ppm), 8.04 (s, 1H, N=CH), 7.21 (s, 1H, H_2 , C_6H_3), 6.96 (d, 1H, H_5 , C_6H_3), 6.71 (d, 1H, H_6 , C_6H_3 , $^3J_{\text{H-H}} = 7.80$ Hz), 3.81 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 3.31 (br s, 1H, NC*H, C_6H_{10}), 1.81 (br s, 3H, C_6H_{10}), 1.43 (br s, 1H, C_6H_{10}). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ (ppm) 160.64 (N=CH), 150.96, 149.03, 129.60, 122.64, 110.31, 108.92 (C_6H_3), 73.58 (N-C*H), 55.90, 55.85 (OCH₃), 32.99, 24.55 (CH_2 , C_6H_{10}).

4.3. Preparation of [Pd(OAc)($\text{C}_6\text{H}_2-4,5-(\text{OMe})_2-2-\text{CH}=\text{N}-(1*R*,2*R*)-\text{C}_6\text{H}_{10}-\text{N}=\text{CH}-\text{C}_6\text{H}_3-3',4'-(\text{OMe})_2-\kappa\text{-C,N,N}$)] (**2**)

To a suspension of [Pd(OOCCH₃)₂] (0.500 g, 2.22 mmol) in MeOH (20 ml), **1** (0.9146 g, 2.23 mmol) was added. The resulting mixture was refluxed for 1 h. During the reaction time, some decomposition was evident. Once cooled, the resulting black suspension was treated with activated charcoal and filtered over Celite, giving a bright yellow solution. This solution was evaporated to small volume (2 ml) and Et₂O (20 ml) was added, giving **2** as a yellow solid, which was filtered, washed with Et₂O (20 ml) and air dried. Obtained: 1.189 g (93% yield). Anal. Calc. for $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_6\text{Pd}$: C, 54.31; H, 5.61; N, 4.87. Found: C, 54.41; H, 5.69; N, 4.70%. Mol. wt. (CHCl_3): Found: 670 (Calc. 574.95). Mass Spect. (FAB +) [m/z , (%): 515 (100%) [(M-OAc)⁺]. IR (ν , cm^{-1}): 1644, 1619, 1601, 1587, 1545, 1520 (N=CH + OAc + C=C). ^1H -NMR (CDCl_3): δ (ppm), 8.36 (d, 1H, N=CH_A, $^4J_{\text{H-H}} = 1.8$ Hz), 7.85 (d, 1H, H_2 , $^4J_{\text{H}_2'-\text{H}_6'} = 1.8$ Hz), 7.82 (d, 1H, N=CH_B, $^4J_{\text{H-H}} = 2.1$ Hz), 7.57 (dd, 1H, H_6 , $^3J_{\text{H}_6'-\text{H}_5'} = 8.4$ Hz), 6.92 (d, 1H, H_5), 6.84, 6.75 (2s, 2H, $\text{H}_3 + \text{H}_6$), 4.11 (m, 1H, N-C*H), 4.05 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.31 (m, 1H, N-C*H), 2.48 (m, 1H, C_6H_{10}), 2.41 (m, 1H, C_6H_{10}), 1.94 (m, 2H, C_6H_{10}), 1.63 (s, 3H, CO_2CH_3), 1.49–1.29 (m, 4H, C_6H_{10}). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ (ppm), 177.32 (CO_2), 167.66 (N=CH), 162.91 (N=CH), 152.46, 151.43, 150.33, 148.46, 146.39, 139.87, 125.91, 125.16, 115.76, 111.96, 110.57, 110.28 ($\text{C}_6\text{H}_2 + \text{C}_6\text{H}_3$), 70.98 (NC*H), 67.94 (NC*H), 56.25, 56.11, 56.04, 55.90 (4 OMe), 29.66, 29.49, 24.21, 23.99 (CH_2 of C_6H_{10}), 23.61 (CO_2CH_3).

4.4. Preparation of [Pd(Cl)($\text{C}_6\text{H}_2-4,5-(\text{OMe})_2-2-\text{CH}=\text{N}-(1*R*,2*R*)-\text{C}_6\text{H}_{10}-\text{N}=\text{CH}-\text{C}_6\text{H}_3-3',4'-(\text{OMe})_2-\kappa\text{-C,N,N}$)] (**3**)

To an orange solution of **2** (0.500 g, 0.87 mmol) in MeOH (20 ml), an excess of LiCl (0.147 g, 3.46 mmol) was added. A yellow solid precipitated almost instantaneously. After 5 min stirring, this solid was filtered, washed with MeOH (10 ml) and Et₂O (10 ml) and air dried. Obtained: 0.380 g (79.3% yield). Anal. Calc. for

$C_{24}H_{29}ClN_2O_4Pd$: C, 52.28; H, 5.30; N, 5.08. Found: C, 52.06; H, 5.38; N, 4.79%. IR (ν , cm^{-1}): 1644, 1618, 1602, 1588, 1545, 1520 (N=CH + C=C), 282 (Pd–Cl). Mass Spect. (FAB +) [m/z , (%): 515 (100%) [(M–Cl)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.32 (d, 1H, H₂, ⁴*J*_{H2'-H6'} = 2.1 Hz), 8.26 (s, broad, 1H, N=CH_A), 7.88 (d, 1H, N=CH_B, ⁴*J*_{H-H} = 2.1 Hz), 7.58 (dd, 1H, H₆, ³*J*_{H6'-H5'} = 8.4 Hz), 7.37 (s, 1H, H₆), 6.89 (d, 1H, H₅), 6.85 (s, 1H, H₃), 4.06 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 3.90 (s, 3H, OCH₃), 3.84 (m, 1H, N–C*H), 3.75 (s, 3H, OCH₃), 3.14 (m, 1H, N–C*H), 2.40 (m, 1H, C₆H₁₀), 2.15 (m, 1H, C₆H₁₀), 1.84 (m, 2H, C₆H₁₀), 1.55–1.05 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 168.53 (N=CH), 163.25 (N=CH), 152.96, 151.39, 149.58, 148.59, 146.14, 140.63, 126.72, 125.43, 117.87, 113.09, 110.95, 110.06 (C₆H₂ + C₆H₃), 71.58 (NC*H), 68.05 (NC*H), 56.84, 56.21, 56.11, 55.98 (4 OMe), 30.12, 29.42, 24.22, 23.93 (CH₂ of C₆H₁₀).

4.5. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N,N)-(PPh₃)](ClO₄) (**4a**)

Complex **3** (0.100 g, 0.181 mmol) was dissolved in acetone (10 ml) and treated with AgClO₄ (0.037 g, 0.181 mmol) in the absence of light. After 30 min stirring at r.t., the suspension was filtered and to the freshly obtained solution PPh₃ (0.0472, 0.181 mmol) was added. The resulting solution was stirred at r.t. for 30 min, the solvent evaporated to dryness and the oily residue treated with Et₂O (40 ml), giving **4a** as a yellow solid. Obtained: 0.148 g (93.1% yield). Crystals of **4a** 0.25CH₂Cl₂ were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution of **4a**. The presence of solvent of crystallization was checked by ¹H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for C₄₂H₄₄ClN₂O₈PPd·0.25 CH₂Cl₂: C, 56.45; H, 4.99; N, 3.11. Found: C, 56.01; H, 5.17; N, 3.04%. IR (ν , cm^{-1}): 1635, (605, 1595, 1555, 1525 (N=CH + C=C), 1094, 623 (ClO₄). Mass Spect. (FAB +) [m/z , (%): 777 (100%) [(M–ClO₄)⁺], 515 (90%) [(M–ClO₄–PPh₃)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.42 (dd, 1H, H₆, ³*J*_{H6'-H5'} = 9.9 Hz, ⁴*J*_{H2'-H6'} = 2.1 Hz), 8.28 (dd, 1H, N=CH_B, ⁴*J*_{P-H} = 8.1 Hz, ⁴*J*_{H-H} = 1.8 Hz), 8.27 (s, broad, 1H, N=CH_A), 7.45–7.24 (m, 16H, H₃ + PPh₃), 6.55 (d, 1H, H₂), 6.50 (d, 1H, H₅), 5.86 (d, 1H, H₆, ⁴*J*_{P-H} = 4.2 Hz), 4.12 (m, 1H, N–C*H), 3.81 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 3.69 (s, 3H, OCH₃), 3.41 (m, 1H, N–C*H), 2.80 (s, 3H, OCH₃), 2.69 (m, 1H, C₆H₁₀), 2.27 (m, 1H, C₆H₁₀), 1.93 (m, 2H, C₆H₁₀), 1.61 (m, 2H, C₆H₁₀), 1.31 (m, 2H, C₆H₁₀). ³¹P{¹H}-NMR (CDCl₃): δ (ppm) 35.87. ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 172.36, 165.30 (N=CH), 152.60, 148.62, 146.17, 143.17, 126.88, 121.20, 120.12, 114.23, 113.35, 110.71, 110.50, 109.01 (C₆H₃ + C₆H₂), 134.44 (d, *J*_{P-C} = 12.1 Hz), 131.37, 128.71 (d, *J*_{P-C} = 10.6 Hz) (PPh₃, the *C*_{ipso}

was not observed), 73.71, 70.07 (N–C*H), 56.19 (2OMe), 56.07 (OMe), 56.00 (OMe), 30.24, 28.93, 24.23, 23.94 (CH₂ of C₆H₁₀).

4.6. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-NH₂- κ -C,N,N)-(PPh₃)](ClO₄) (**4b**)

Complex **4a** was dissolved in wet CDCl₃ (1 ml) and this solution was left to stand for 24 h. After this time, complex **4b** crystallized as small yellow plates. The yield was quantitative. Anal. Calc. for C₃₃H₃₆ClN₂O₆PPd: C, 54.33; H, 4.97; N, 3.84. Found: C, 54.52; H, 5.30; N, 3.79%. IR (ν , cm^{-1}): 3320, 3254 (NH₂). 1686, 1621, 1588, 1520 (N=CH + C=C), 1094, 623 (ClO₄). Mass Spect. (FAB +) [m/z , (%): 630 (100%) [(M–ClO₄)⁺]. ¹H-NMR (CD₂Cl₂): δ (ppm), 8.05 (dd, 1H, N=CH, ⁴*J*_{P-H} = 9.9 Hz, ⁴*J*_{H-H} = 2.1 Hz), 7.69–7.62 (m, 6H, H_o, PPh₃), 7.59–7.44 (m, 9H, H_m + H_p, PPh₃), 6.98 (s, 1H, H₃), 5.87 (d, 1H, H₆, ⁴*J*_{P-H} = 3.3 Hz), 3.74 (s, 3H, OCH₃), 3.67 (m, 1H, N–C*H), 3.36 (t, 1H, NH₂, ²*J*_{H-H} = ³*J*_{P-H} = 12 Hz), 2.91 (s, 3H, OCH₃), 2.78 (m, 1H, N–C*H), 2.48 (m, 1H, NH₂), 1.94 (m, 1H, C₆H₁₀), 1.79 (m, 3H, C₆H₁₀), 1.51 (m, 1H, C₆H₁₀), 1.35 (m, 2H, C₆H₁₀), 1.27–1.12 (m, 1H, C₆H₁₀). ³¹P{¹H}-NMR (CD₂Cl₂): δ (ppm) 36.86. ¹³C{¹H}-NMR (CD₂Cl₂): δ (ppm), 169.81 (N=CH), 154.74, 150.43, 146.82, 143.55, 121.82 (d, *J*_{P-C} = 9.8 Hz), 112.95 (C₆H₂), 134.91 (d, *J*_{P-C} = 12.8 Hz), 132.10, 129.76 (d, *J*_{P-C} = 41 Hz), 129.62 (d, *J*_{P-C} = 10.6 Hz) (PPh₃), 67.37, 62.99 (N–C*H), 56.35, 55.43 (OMe), 35.29, 29.29, 24.97, 23.94 (CH₂ of C₆H₁₀).

4.7. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N,N)-(NCMe)](ClO₄) (**5**)

Complex **3** (0.100 g, 0.181 mmol) was suspended in acetonitrile (10 ml) and treated with AgClO₄ (0.037 g, 0.181 mmol) in the absence of light. After 30 min stirring at r.t. the suspension was filtered, the resulting solution was evaporated to dryness and the oily residue was treated with Et₂O (40 ml), giving **5** as a yellow solid. Obtained: 0.084 g (70.7% yield). Anal. Calc. for C₂₆H₃₂ClN₃O₈Pd: C, 47.57; H, 4.91; N, 6.40. Found: C, 47.62; H, 4.84; N, 6.52%. IR (ν , cm^{-1}): 2324, 2320 (CN), 1640, 1602, 1548, 1520 (N=C + C=C), 1086, 623 (ClO₄). Mass Spect. (FAB +) [m/z , (%): 515 (100%) [(M–ClO₄–NCMe)⁺]. ¹H-NMR (CD₂Cl₂): δ (ppm), 8.66 (d, 1H, N=CH_A, ⁴*J*_{H-H} = 1.8 Hz), 7.99 (d, 1H, H₂, ⁴*J*_{H2'-H6'} = 2.1 Hz), 7.71 (dd, 1H, H₆, ³*J*_{H6'-H5'} = 8.4 Hz), 7.57 (d, 1H, N=CH_B, ⁴*J*_{H-H} = 1.8 Hz), 7.09 (d, 1H, H₅), 7.06 (s, 1H, H₆), 6.58 (s, 1H, H₃), 3.97 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 3.90 (s, 4H, OCH₃ + N–C*H), 3.79 (s, 3H, OCH₃), 3.40 (m, 1H, N–C*H), 2.55 (m, 2H, C₆H₁₀), 2.01 (m, broad, 5H, NCMe + C₆H₁₀), 1.56–1.34 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR

(CD₂Cl₂): δ (ppm), 172.52 (N=CH), 165.65 (N=CH), 153.39, 151.27, 151.17, 149.13, 147.78, 140.87, 127.10, 124.31, 122.31, 116.87, 112.99, 112.89, 111.20 (C₆H₂ + C₆H₃ + CN), 72.43 (NC*H), 69.19 (NC*H), 56.67, 56.62, 56.56, 56.52 (4OMe), 29.85, 29.72, 24.38, 24.20 (CH₂ of C₆H₁₀), 3.22 (NCMe).

4.8. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1R,2R)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N,N)-(NC₅H₅)](ClO₄) (6**)**

Complex **6** was obtained as described for **4**. Complex **3** (0.100 g, 0.181 mmol) was reacted in acetone with AgClO₄ (0.037 g, 0.181 mmol) and pyridine (14.6 μ l, 0.181 mmol) to give **6** as a yellow solid. Obtained: 0.114 g (90.5% yield). Anal. Calc. for C₂₉H₃₄ClN₃O₈Pd: C, 50.16; H, 4.93; N, 6.05. Found: C, 49.83; H, 5.06; N, 6.09%. IR (ν , cm⁻¹): 1635, 1610, 1585, 1555, 1545, 1520 (N=CH + C=C + py), 1100, 624 (ClO₄). Mass Spect. (FAB +) [m/z , (%): 594 (27%) [(M-ClO₄)⁺], 515 (100%) [(M-ClO₄-NC₅H₅)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.68 (d, 1H, N=CH_A, ⁴J_{H-H} = 1.8 Hz), 8.49 (dd, 2H, H₆, py, ³J_{H₆-H_m} = 6.3 Hz, ⁴J_{H₆-H_p} = 1.5 Hz), 8.08 (d, 1H, N=CH_B, ⁴J_{H-H} = 2.1 Hz), 7.57 (tt, 1H, H_p, py, ³J_{H_p-H_m} = 7.5 Hz), 7.36 (dd, 1H, H_{6'}, ³J_{H_{6'}-H_{5'}} = 8.4 Hz, ⁴J_{H_{6'}-H_{2'}} = 1.8 Hz), 7.18 (dd, 2H, H_m, py), 7.15 (s, 1H, H₃), 7.08 (d, 1H, H₂), 6.57 (d, 1H, H₅, 5.85 (s, 1H, H₆), 4.04 (m, 1H, N-C*H), 3.80 (s, 3H, OCH₃), 3.77 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 3.58 (s, 3H, OCH₃), 3.30 (m, 1H, N-C*H), 2.63 (m, 1H, C₆H₁₀), 2.52 (m, 1H, C₆H₁₀), 1.73 (m, 1H, C₆H₁₀), 1.46–1.20 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 171.45 (N=CH), 166.16 (N=CH), 152.69, 151.64, 151.40, 150.18, 148.08, 146.99, 141.50, 138.13, 126.76, 125.60, 122.03, 115.09, 112.97, 112.31, 110.66 (C₆H₂ + C₆H₃ + NC₅H₅), 72.43, 68.49 (NC*H), 56.26 (2OMe), 56.08, 55.79 (OMe), 29.59, 29.44, 23.96, 23.81 (CH₂ of C₆H₁₀).

4.9. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1R,2R)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N,N)-(p-NH₂C₆NO₂)](ClO₄) (7**)**

Complex **7** was obtained as described for **4**. Complex **3** (0.150 g, 0.273 mmol) was reacted in acetone with AgClO₄ (0.057 g, 0.273 mmol) and 4-nitroaniline (0.084 g, 0.608 mmol) to give **7** as an orange solid. Obtained: 0.206 g (100% yield). Crystals of 7·0.6CH₂Cl₂ were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution of **7**. The presence of solvent of crystallization was checked by ¹H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for C₃₀H₃₅ClN₄O₁₀Pd·0.6CH₂Cl₂: C, 45.69; H, 4.54; N, 6.96. Found: C, 45.53; H, 4.69; N, 7.17%. IR (ν , cm⁻¹): 3372, 3250 (NH₂), 1639, 1598, 1548, 1515 (N=C + C=C), 1342, 1308 (NO₂), 1086, 624 (ClO₄). Mass Spect. (FAB +) [m/z , (%): 515 (100%) [(M-ClO₄-C₆H₆-

N₂O₂)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.35 (s, broad, 1H, N=CH_A), 8.25 (d, 1H, H₆, ³J_{H_{6'}-H_{5'}} = 8.4 Hz), 8.03 (m, 2H, C₆H₄), 7.83 (d, 1H, N=CH_B, ⁴J_{H-H} = 2.1 Hz), 7.79 (s, broad, 1H, H₂), 7.30 (d, 1H, H₅), 6.92 (m, 2H, C₆H₄), 6.87: 6.68 (2s, 2H, H₃ + H₆), 5.77 (d, 1H, NH₂, ²J_{H-H} = 10.8 Hz), 5.23 (d, 1H, NH₂), 3.97 (s, 4H, OCH₃ + N-C*H), 3.93 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 3.22 (m, 1H, N-C*H), 2.48 (m, 1H, C₆H₁₀), 2.35 (m, 1H, C₆H₁₀), 1.88 (m, 2H, C₆H₁₀), 1.49–1.27 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 170.85 (N=CH), 164.26 (N=CH), 153.25, 150.67, 149.38, 147.38, 147.16, 144.83, 140.91, 126.27, 125.75, 124.38, 122.71, 120.36, 115.35, 113.43, 112.79, 112.36 (C₆H₂ + C₆H₃ + C₆H₄), 72.12 (NC*H), 68.87 (NC*H), 56.66, 56.39, 56.16, 56.09 (4OMe), 29.56, 29.19, 23.96, 23.68 (CH₂ of C₆H₁₀).

4.10. Preparation of [Pd(I)(C₆H₂-4,5-(OMe)₂-2-CH=N-(1R,2R)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N,N)] (8**)**

To a solution of **3** (0.193 g, 0.351 mmol) in acetone (15 ml) AgClO₄ (0.073 g, 0.351 mmol) was added in the absence of light. After 30 min stirring, the suspension was filtered and NaI (0.052 g, 0.346 mmol) was added to the freshly obtained solution. The resulting suspension was stirred (r.t.) for 1 h, filtered and the yellow solid (**8**) washed with acetone (10 ml) and Et₂O (20 ml). Obtained: 0.187 g (83% yield). Anal. Calc. for C₂₄H₂₉IN₂O₄Pd: C, 44.84; H, 4.55; N, 4.36. Found: C, 44.37; H, 4.75; N, 4.46%. IR (ν , cm⁻¹): 1642, 1588, 1543, 1520. Mass Spect. (FAB +) [m/z , (%): 641 (100%) [(M-H)⁺], 515 (100%) [(M-I)⁺]. ¹H-NMR (CD₂Cl₂): δ (ppm), 8.42 (d, 1H, N=CH_A, ⁴J_{H-H} = 1.8 Hz), 8.30 (d, 1H, H₂, ⁴J_{H_{2'}-H_{6'}} = 1.8 Hz), 8.04 (d, 1H, N=CH_B, ⁴J_{H-H} = 2.1 Hz), 7.88 (s, 1H, H₆), 7.57 (dd, 1H, H_{6'}, ³J_{H_{6'}-H_{5'}} = 8.4 Hz), 6.94 (s, 1H, H₃), 6.93 (d, 1H, H₅, 4.07 (m, 1H, N-C*H), 4.06 (s, 3H, OCH₃), 3.92 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.41 (m, 1H, N-C*H), 2.56 (m, 1H, C₆H₁₀), 2.35 (m, 1H, C₆H₁₀), 1.98 (m, 2H, C₆H₁₀), 1.60–1.27 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR (CD₂Cl₂): δ (ppm), 168.86 (N=CH), 164.07 (N=CH), 153.42, 151.69, 150.77, 148.41, 146.37, 141.63, 126.82, 126.77, 125.52, 114.98, 111.82, 110.44 (C₆H₂ + C₆H₃), 72.25 (NC*H), 69.18 (NC*H), 56.85, 56.44, 56.26, 56.21 (4OMe), 30.39, 29.79, 24.75, 24.43 (CH₂ of C₆H₁₀).

4.11. Preparation of [Pd(acac-O,O')(C₆H₂-4,5-(OMe)₂-2-CH=N-(1R,2R)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂- κ -C,N)] (9**)**

To a solution of **3** (0.200 g, 0.362 mmol) in CH₂Cl₂ (15 ml) Ti(acac) (0.148 g, 0.487 mmol) was added. After 30 min stirring, the suspension was filtered and the resulting solution was evaporated to dryness, giving an

oily residue. By addition of Et₂O (10 ml) and continuous stirring **9** was obtained as a yellow solid, which was filtered and washed with Et₂O (10 ml). Obtained: 0.160 g (72% yield). Crystals of **9**·0.25CH₂Cl₂ were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution of **9**. The presence of solvent of crystallization was checked by ¹H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for C₂₉H₃₆N₂O₆Pd·0.25CH₂Cl₂: C, 55.21; H, 5.78; N, 4.40. Found: C, 55.11; H, 6.02; N, 4.36%. IR (ν, cm⁻¹): 1640 (N=CH), 1588, 1515 (acac). Mass Spect. (FAB +) [*m/z*, (%): 515 (100%) [(M-acac)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.42 (s, 1H, N=CH_A), 7.67 (s, 1H, N=CH_B), 7.24 (d, 1H, H₂, ⁴J_{H2-H6'} = 1.8 Hz), 7.10 (dd, 1H, H_{6'}, ³J_{H6'-H5'} = 8.4 Hz), 6.98 (s, 1H, H₆), 6.76 (d, 1H, H_{5'}, 6.66 (s, 1H, H₃), 5.36 (s, 1H, CH, acac), 4.06 (m, 1H, N-C*H), 3.88 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 3.35 (m, 1H, N-C*H), 2.48 (m, 1H, C₆H₁₀), 2.04 (s, 3H, CH₃, acac), 2.01 (s, 3H, CH₃, acac), 1.93–1.71 (m, 7H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 187.71 (CO, acac), 186.02 (CO, acac), 173.08 (N=CH), 161.42 (N=CH), 150.97, 150.13, 149.41, 148.93, 146.29, 136.84, 129.63, 122.69, 112.14, 110.36, 109.59, 109.41 (C₆H₂ + C₆H₃), 99.96 (CH, acac), 74.55 (NC*H), 69.37 (NC*H), 56.06, 55.92, 55.88, 55.69 (4OMe), 33.46, 30.25, 24.80, 24.08 (CH₂ of C₆H₁₀), 28.10, 27.69 (CH₃, acac).

4.12. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)(N-phen)](ClO₄) (**10**)

To a solution of **3** (0.200 g, 0.362 mmol) in acetone (15 ml) AgClO₄ (0.075 g, 0.362 mmol) was added in the absence of light. After 30 min stirring, the suspension was filtered and 1,10-phenanthroline (0.065 g, 0.362 mmol) was added to the freshly obtained solution. The resulting yellow solution was stirred (r.t.) for 1 h, then the solvent was evaporated to dryness and the oily residue was treated with Et₂O, giving **10** as a yellow solid. This solid was filtered, washed with Et₂O (20 ml) and air dried. Obtained: 0.262 g (91% yield). Crystals of **10**·0.5CH₂Cl₂ were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution of **10**. The presence of solvent of crystallization was checked by ¹H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for C₃₆H₃₇ClN₄O₈Pd·0.5CH₂Cl₂: C, 52.31; H, 4.57; N, 6.68. Found: C, 52.39; H, 4.84; N, 6.48%. IR (ν, cm⁻¹): 1636, 1586, 1546, 1516. Mass Spect. (FAB +) [*m/z*, (%): 695 (70%) [M⁺], 515 (100%) [(M-phen)⁺]. ¹H-NMR (CD₂Cl₂, 213 K): δ (ppm), 9.66 (d, 1H, H_α phen, ³J_{H-H} = 4.8 Hz), 8.85 (d, 1H, H_α phen, ³J_{H-H} = 4.8 Hz), 8.71 (d, 1H, H_γ phen, ³J_{H-H} = 8.1 Hz), 8.64 (d, 1H, H_γ phen, ³J_{H-H} = 8.1 Hz), 8.23 (s, 1H, N=CH), 8.21 (s, 1H, N=CH), 8.18 (dd, 1H, H_β phen), 8.11, 8.05 (AB spin system, 2H, 2H_δ phen, ³J_{H-H} = 9.0

Hz), 7.82 (dd, 1H, H_β phen), 7.04 (s, 1H, H₃), 6.73 (dd, 1H, H_{6'}, ³J_{H6'-H5'} = 8.1 Hz, ⁴J_{H6'-H2} = 2.1 Hz), 6.50 (d, 1H, H₂), 6.41 (d, 1H, H_{5'}), 6.26 (s, 1H, H₆), 4.04 (m, 1H, NC*H), 3.79, 3.71, 3.67 (3s, 9H, 3OMe), 3.43 (m, 1H, NC*H), 2.92 (s, 3H, OMe), 2.26 (m, 1H, C₆H₁₀), 1.97 (m, 1H, C₆H₁₀), 1.83 (m, 4H, C₆H₁₀), 1.51 (m, 2H, C₆H₁₀). ¹³C{¹H}-NMR (CD₂Cl₂, 213 K): δ (ppm), 175.67 (N=CH), 161.95 (N=CH), 151.32, 150.86, 149.93, 148.16, 146.98, 146.10, 144.97, 139.08, 130.39, 130.29, 128.84 (quaternary C atoms, C₆H₂ + C₆H₃ + phen), 152.26, 151.75, 139.93, 139.59, 128.54, 127.99, 126.69, 123.56, 115.06, 111.04, 111.00, 109.98, 107.22 (CH atoms, C₆H₂ + C₆H₃ + phen), 77.72 (NC*H), 68.54 (NC*H), 56.44, 56.35, 56.28, 56.20 (4OMe), 34.35, 31.45, 25.81, 24.66 (CH₂ of C₆H₁₀).

4.13. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)(N-bipy)](ClO₄) (**11**)

Complex **11** was obtained as described for **10**. Complex **3** (0.176 g, 0.32 mmol) was reacted in acetone with AgClO₄ (0.067 g, 0.32 mmol) and 2,2'-bipyridyl (0.050 g, 0.32 mmol) to give **11** as a yellow solid. Obtained: 0.238 g (97% yield). Anal. Calc. for C₃₄H₃₇ClN₄O₈Pd: C, 52.93; H, 4.83; N, 7.26. Found: C, 52.57; H, 4.81; N, 7.17%. IR (ν, cm⁻¹): 1639, 1603, 1586, 1547, 1513. Mass Spect. (FAB +) [*m/z*, (%): 671 (37%) [M⁺], 515 (100%) [(M-bipy)⁺]. ¹H-NMR (CD₂Cl₂, 213 K): δ (ppm), 9.21 (d, 1H, H_α bipy, ³J_{H-H} = 4.8 Hz), 8.61 (d, 1H, H_α bipy, ³J_{H-H} = 4.8 Hz), 8.12 (s, 1H, N=CH), 8.10 (s, 1H, N=CH), 8.07–8.01 (m, 3H, 2H_γ + H_δ bipy), 7.96 (d, 1H, H_δ bipy, ³J_{H-H} = 7.8 Hz), 7.75 (t, 1H, H_β bipy), 7.49 (t, 1H, H_β bipy), 7.06 (s, 1H, H₃), 7.02 (dd, 1H, H_{6'}, ³J_{H6'-H5'} = 8.1 Hz, ⁴J_{H6'-H2} = 2.1 Hz), 6.80 (d, 1H, H₂, 6.55 (d, 1H, H_{5'}), 6.24 (s, 1H, H₆), 3.78 (s, 3H, OMe), 3.72 (s, br, 4H, OMe + NC*H), 3.68, 3.48 (2s, 6H, 2OMe), 3.34 (m, 1H, NC*H), 2.33 (m, 1H, C₆H₁₀), 1.86 (m, 3H, C₆H₁₀), 1.69–1.52 (m, 2H, C₆H₁₀), 1.39 (m, 2H, C₆H₁₀). ¹³C{¹H}-NMR (CD₂Cl₂): δ (ppm), 173.68 (N=CH), 163.16 (N=CH), 156.34, 151.98, 150.88, 148.92, 147.64, 140.13, 128.16, 122.99, 115.82, 112.33, 110.84, 110.66 (C₆H₂ + C₆H₃), 151.83, 139.62, 126.65, 124.24 (CH atoms, bipy; the quaternary C atoms were not observed), 75.33 (NC*H), 68.75 (NC*H), 56.54, 56.30, 56.23, 56.15 (4OMe), 32.62, 30.92, 25.18, 24.99 (CH₂ of C₆H₁₀).

4.14. Preparation of [Pd(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,2*R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)(dppe-P,P')](ClO₄) (**12**)

Complex **12** was obtained as described for **10**. Complex **3** (0.200 g, 0.362 mmol) was reacted in acetone with AgClO₄ (0.075 g, 0.362 mmol) and 1,2-bis-(diphenylphosphino)ethane (dppe) (0.144 g, 0.362 mmol)

to give **12** as an orange solid. Obtained: 0.352 g (96% yield), Crystals of **12**·0.3CH₂Cl₂ were grown by vapor diffusion of Et₂O into a CH₂Cl₂ solution of **12**. The amount of solvent of crystallization was checked by ¹H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for C₅₀H₅₃ClN₂O₈P₂Pd·0.3CH₂Cl₂: C, 58.13; H, 5.20; N, 2.69. Found: C, 57.84; H, 5.38; N, 2.73%. IR (ν, cm⁻¹): 1640, 1605, 1585, 1549, 1511. Mass Spect. (FAB +) [*m/z*, (%): 913 (37%) [M⁺], 515 (100%) [(M-dppe)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.41 (d, 1H, N=CH, ⁴J_{P-H} = 8.7 Hz), 8.23 (s, 1H, N=CH), 8.14 (m, 2H, H_o, dppe), 7.86 (m, 2H, H_o, dppe), 7.63–7.43 [m, 15H, H_{6'} + (2H_o + 8H_m + 4H_p, dppe)], 7.31, 7.30 (2s, 2H, H_{2'} + H₃), 7.26–7.18 (m, 2H, H_o, dppe), 6.83 (d, 1H, H_{5'}, ³J_{H6'-H5'} = 8.4 Hz), 5.95 (dd, 1H, H₆, ⁴J_{P-H} = 8.7 Hz, ⁴J_{P-H} = 5.7 Hz), 3.89 (s, 3H, OMe), 3.79 (s, br, 4H, OMe + NC*H), 3.62 (s, 3H, OMe), 3.55 (m, 1H, NC*H), 2.83 (s, 3H, OMe), 2.10 (m, 2H, CH₂, dppe), 1.85 (m, 2H, CH₂, dppe), 1.56 (m, 1H, C₆H₁₀), 1.39 (m, 1H, C₆H₁₀), 1.29–1.14 (m, 5H, C₆H₁₀), 0.04 (m, 1H, C₆H₁₀). ³¹P{¹H}-NMR (CDCl₃): δ (ppm), 60.85 (d, dppe, ³J_{P-P} = 26.7 Hz), 40.61 (d, dppe). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 179.50 (N=CH): 161.76 (N=CH), 158.85 (d, J_{P-C} = 120 Hz), 151.12, 149.84 {dd, J_{P-C} = 10.3 Hz, J_{P-C} = 6 Hz}, 149.00, 146.79, 142.08, 127.68, 122.74, 120.73 (dd, J_{P-C} = 11 Hz, J_{P-C} = 3.6 Hz), 112.90 (d, J_{P-C} = 120 Hz), 110.71, 109.78 (C₆H₂ + C₆H₃), 135.15 (d, J_{P-C} = 13 Hz), 134.59 (d, J_{P-C} = 12.4 Hz), 133.47 (d, J_{P-C} = 12.4 Hz), 132.85 (d, J_{P-C} = 8.6 Hz) (C_{meta}, PPh₂), 132.51, 132.35 (2C), 131.73 (C_{para}, PPh₂), 129.98 (d, J_{P-C} = 14 Hz), 129.84 (d, J_{P-C} = 14.8 Hz), 129.64 (d, J_{P-C} = 14.8 Hz), 129.49 (d, J_{P-C} = 15 Hz) (C_{ortho}, PPh₂), 125.77 (J_{P-C} = 49 Hz), 125.43 (J_{P-C} = 36 Hz) (C_{ipso}, PPh₂, 2C_{ipso} were not detected), 74.66, 72.36 (J_{P-C} = 4.5 Hz) (2NC*H), 56.14, 56.04, 55.87, 55.18 (4OMe), 33.96, 32.96, 24.87, 23.80 (CH₂ of C₆H₁₀), 30.71 (dd, J_{P-C} = 35.6 Hz, J_{P-C} = 18.3 Hz, CH₂, dppe), 27.56 (dd, J_{P-C} = 29.6 Hz, J_{P-C} = 9.5 Hz, CH₂, dppe).

4.15. Preparation of Cl₂Pt[(NH₂)₂C₆H₁₀-N,N'] (13a**) and [Pt(Cl)(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,*R*)-C₆H₁₀-NH₂-κ-C,N,N)] (**13b**)**

PtCl₂(DMSO)₂ (0.2060 g, 0.488 mmol) was suspended in 2-methoxyethanol (10 ml), and the bis-imine **1** (0.2004 g, 0.488 mmol) was added. This mixture was heated at the reflux temperature for 22 h. After the initial dissolution of the reactants a yellow solid begins to precipitate. After the reaction time, the mixture was allowed to reach r.t. and the yellow solid was filtered. This solid was characterized as **13a**. Obtained: 0.069 g (37.1% yield based on Pt). The red alcoholic solution was evaporated to dryness and the residue treated with Et₂O (15 ml), giving **13b** as a red solid. Obtained: 0.044 g (18.3% yield based on Pt). Compound **13a**. Anal.

Calc. for C₆H₁₄Cl₂N₂Pt: C, 18.95; H, 3.71; N, 7.36. Found: C, 19.15; H, 3.53; N, 7.79%. IR (ν, cm⁻¹): 3278, 3188 (NH), 320, 313 (Pt-Cl). ¹H-NMR (DMSO-*d*₆): δ (ppm), 5.55 (d, 1H, NH_{axial}, ²J_{H-H} = 9.0 Hz), 5.03 (t, 1H, NH_{eq}, ²J_{H-H} ≅ ³J_{H-H} = 9.0 Hz), 2.11 (m, 1H, N-C*H), 1.84 (m, 1H, C₆H₁₀), 1.43 (m, 1H, C₆H₁₀), 1.22 (m, 1H, C₆H₁₀), 0.95 (m, 1H, C₆H₁₀). Compound **13b**. Anal. Calc. for C₁₅H₂₁ClO₂N₂Pt: C, 36.63; H, 4.30; N, 5.69. Found: C, 36.35; H, 4.19; N, 5.73. IR (ν, cm⁻¹): 3304, 3223 (NH₂), 1610, 1590, 1580, 1537 (N=C + C=C), 319 (Pt-Cl). Mass Spect. (FAB +) [*m/z*, (%): 492 (97%) [M⁺], 455(100%) [(M-Cl)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 7.10 (s, 1H, H₆, C₆H₂, ³J_{Pt-H} = 44 Hz), 6.99 (d, 1H, N=CH, ⁴J_{H-H} = 2.10 Hz, ³J_{Pt-H} = 152 Hz), 6.53 (s, 1H, H₃, C₆H₂), 4.45 (t, 1H, NH₂, ²J_{H-H} ≅ ³J_{H-H} = 10.8 Hz), 4.10 (m, 1H, N-C*H), 3.88 (s, 3H, OCH₃), 3.77 (s, 3H, OCH₃), 3.58 (d, 1H, NH₂), 2.93 (m, 1H, N-C*H), 1.95 (m, 1H, C₆H₁₀), 1.87 (m, 1H, C₆H₁₀), 1.64 (m, 3H, C₆H₁₀), 1.22 (m, 1H, C₆H₁₀), 0.95 (m, 2H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm) 166.08 (N=CH), 151.02, 144.90, 141.10, 140.21, 113.78, 111.00 (C₆H₂), 67.33, 63.31 (C*N, C₆H₁₀), 56.34, 55.89 (OCH₃), 34.73, 30.92, 24.56, 24.00 (C₆H₁₀).

4.16. Preparation of [Pt(Cl)(C₆H₂-4,5-(OMe)₂-2-CH=N-(1*R*,*2R*)-C₆H₁₀-N=CH-C₆H₃-3',4'-(OMe)₂-κ-C,N,N)] (14**)**

To a deoxygenated CHCl₃ solution (15 ml) of [Pt(μ-Cl)(η³-2-Me-C₃H₄)₂] (0.200 g, 0.35 mmol), **1** was added (0.287 g, 0.70 mmol). This solution was refluxed under an Ar atmosphere for 5 h, then evaporated to dryness. The oily residue was treated with Et₂O (20 ml) giving **14** as an orange-red solid. Obtained: 0.191 g (42.6% yield). Anal. Calc. for C₂₄H₂₉ClN₂O₄Pt: C, 45.04; H, 4.57; N, 4.38. Found: C, 44.63; H, 4.55; N, 4.40%. IR (ν, cm⁻¹): 1681, 1631, 1598, 1537, 1520 (N=CH + C=C), 290 (Pt-Cl). Mass Spect. (FAB +) [*m/z*, (%): 640 (55%) [M⁺], 604 (100%) [(M-Cl)⁺]. ¹H-NMR (CDCl₃): δ (ppm), 8.77 (s, broad, 1H, N=CH_A, ³J_{Pt-H} = 44 Hz), 8.38 (d, 1H, H_{2'}, ⁴J_{H2'-H6'} = 2.1 Hz), 8.21 (d, 1H, N=CH_B, ⁴J_{H-H} = 2.1 Hz, ³J_{Pt-H} = 147 Hz), 7.64 (dd, 1H, H_{6'}, ³J_{H6'-H5'} = 8.4 Hz), 7.22 (s, 1H, H₆, ³J_{Pt-H} = 48 Hz), 6.94 (s, 1H, H₃), 6.91 (d, 1H, H_{5'}), 4.06 (m, 1H, N-C*H), 3.96 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 3.52 (m, 1H, N-C*H), 2.54 (m, 1H, C₆H₁₀), 2.35 (m, 1H, C₆H₁₀), 1.93 (m, 2H, C₆H₁₀), 1.59–1.26 (m, 4H, C₆H₁₀). ¹³C{¹H}-NMR (CDCl₃): δ (ppm), 168.41 (N=CH, ²J_{Pt-C} = 113.2 Hz), 163.15 (N=CH), 153.56, 151.81, 148.62, 146.25, 140.58 (J_{Pt-C} = 96.6 Hz), 138.59, 126.58, 126.01, 116.02 (J_{Pt-C} = 68 Hz), 113.87, 112.05 (J_{Pt-C} = 44 Hz), 110.50 (C₆H₂ + C₆H₃), 74.65 (NC*H, ²J_{Pt-C} = 48 Hz), 69.82 (NC*H, ²J_{Pt-C} = 44 Hz), 56.52, 56.49, 56.25, 56.10 (4OMe), 30.27, 29.95, 24.87, 24.42 (CH₂ of C₆H₁₀).

4.17. Catalytic Heck arylations of methylacrylate.

General procedure

To a solution of the corresponding aryl halide (1.13 mmol) in dimethylacetamide (15 ml), methyl acrylate (1.35 mmol), NEt_3 (1.13 mmol) and the corresponding catalyst (**2** or **3**, see amounts in Table 1) were added. This mixture was refluxed under an Ar atmosphere for 24 h. Once cooled, 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 pentane. Evaporation of the pentane solution gives the arylation products as white solids or colorless oils (see Table 1 for yields).

4.18. Catalytic Heck hydroarylations of 2-norborene.

General procedures

To a solution of the appropriate aryl halide (5 mol) in dimethylsulfoxide (10 ml), 2-norbornylene (15 mmol), NEt_3 (15 mmol), HCO_2H (10 mmol) and the catalyst **3** (see amounts in Table 2) were added. This mixture was heated at 90 °C under an Ar atmosphere for 15 h. Once cooled, water (10 ml) was added. The organic phase was extracted several times with pentane (3×10 ml) and the combined extracts were dried with anhydrous MgSO_4 . The solvents were distilled giving the arylation products and colorless oils (see Table 2 for yields).

4.19. Crystal structure determination

Crystals of complex **4b** CH_2Cl_2 of adequate quality for X-ray measurements were obtained by slow evaporation of CH_2Cl_2 solution of the crude complex **4b**.

4.19.1. Data collection

A single crystal of dimension $0.16 \times 0.15 \times 0.12$ mm was mounted in a random orientation. Data collection was performed at $T = -100$ °C on a Bruker Smart CCD diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected based on three ω -can runs (starting $\omega = -30^\circ$) at values $\phi = 0, 90$, and 180° with the detector at $2\theta = 30^\circ$. For each of these runs, frames (606, 435 and 23, respectively) were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the program SAINT [27] and the integrated intensities were corrected for absorption with SADABS [28].

4.19.2. Structure solution and refinement

The structure was solved and developed by Patterson and Fourier methods [29]. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The hydrogen atoms were placed in idealized positions and treated as riding atoms, except for those of the methyl group which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the O–C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The chlorine atoms Cl4 and Cl6 of the interstitial dichloromethane are disordered over three equally populated positions. The structure was refined to F_o^2 , and 17 reflections were omitted in the least-squares calculations [30]. Crystallographic calculations were done on an ALPHASTATION (OPEN/VMS V6.2).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the CCDC number 167181 for compound **4b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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