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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

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Abstract

The chiral bis-imine (1*R*,2*R*)-C_6H_{10}-[*E*–N=CH–C_6H_3–3,4-$(OMe)_2$]$_2$ **1** (LH) reacts with [$Pd(OAc)_2$] (1:1 molar ratio; OAc = acetate) giving the orthometallated [Pd(OAc)(C_6H_2–4,5-$(OMe)_2$–2-CH=*N*-(1*R*,2*R*)-C_6H_{10}–*N*=CH–C_6H_3-3′,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 $AgClO_4$ and neutral or anionic ligands L′ (1:1:1 molar ratio) affords [Pd(L-κ-C,N,N)(L′)](ClO_4) (L′ = PPh_3 **4a**, NCMe **5**, pyridine **6**, *p*-nitroaniline **7**) or [Pd(I)(L-κ-C,N,N)] **8**. Complex **4a** reacts with wet $CDCl_3$ giving [Pd(C_6H_2–4,5-$(OMe)_2$–2-CH=*N*-(1*R*,2*R*)–C_6H_{10}–*N*H_2-κ-C,N,N)(PPh_3)](ClO_4) **4b** as a result of the hydrolysis of the C=N bond not involved in the orthometallated ring. The molecular structure of **4b**·CH_2Cl_2 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′)](ClO_4) **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)(κ^1-N-phen)](ClO_4) **10** and [Pd(L-κ-C,N,N)(κ^1-N-bipy)](ClO_4) **11**. Treatment of **1** with $PtCl_2(DMSO)_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol gives Cl_2Pt[(*N*H_2)$_2$$C_6H_{10}$–N,N′] **13a** and [Pt(Cl)(C_6H_2–4,5-$(OMe)_2$–2-CH=*N*-(1*R*,2*R*)–C_6H_{10}–*N*H_2-κ-C,N,N)] **13b**, while [Pt(Cl)(L-κ-C,N,N)] **14** can be obtained by reaction of [Pt(μ-Cl)(η^3-2-Me–C_3H_4)]$_2$ with **1** in refluxing $CHCl_3$. 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.

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 C_2-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].

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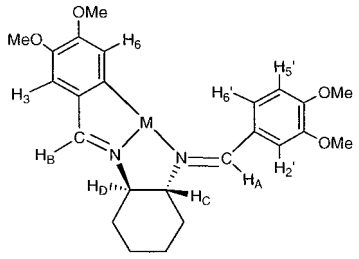


Fig. 1. Schematic representation and proton numbering for the cyclometallated unit in complexes **2**–**8** and **14**.

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].

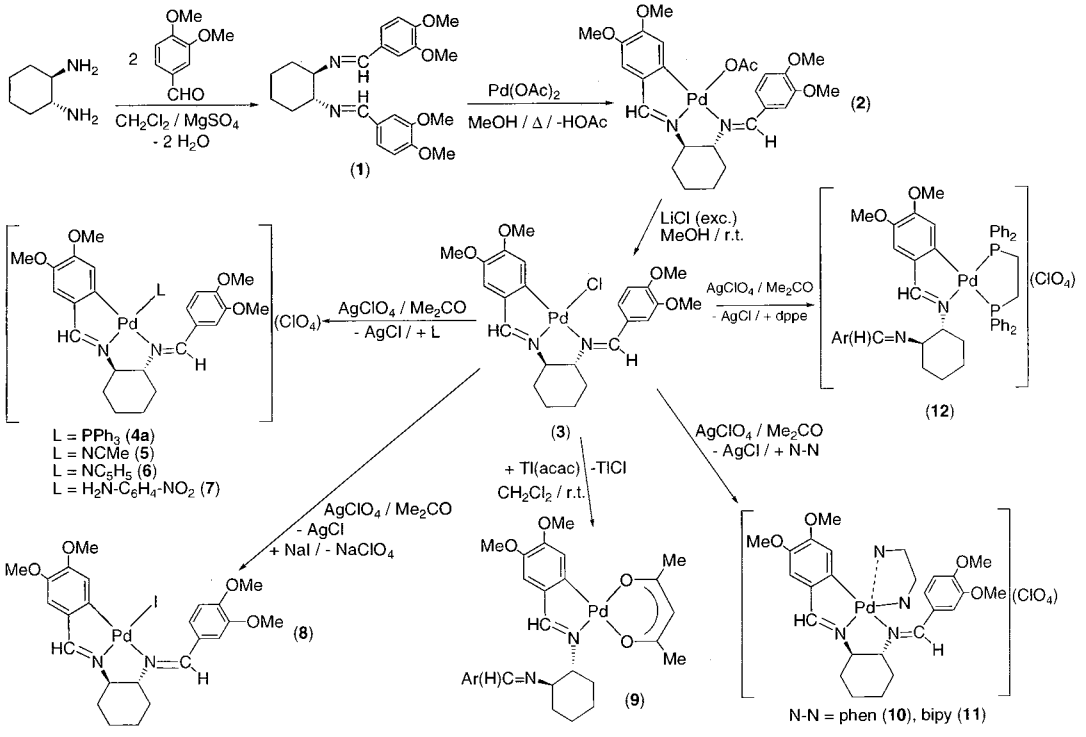
In this paper, we report the synthesis of chiral palladium and platinum orthometallated complexes derived form the bis-imine (1*R*,2*R*)–C_6H_{10}–[*E*-N=CH–C_6H_3–3, 4-$(OMe)_2$]$_2$ (**1**) and their behavior as catalysts in some C–C bond forming reactions, such as the arylation of methyl acrylate 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*)-l,2-DACH (1:1 molar ratio, CH_2Cl_2 room temperature), in the presence of anhydrous $MgSO_4$. 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 C_2-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 ^{1}H-NMR as a singlet at 8.04 ppm, the aromatic protons appear as a singlet (H_2) and an AB spin system (H_5 and H_6), and resonances attributed to the methoxy groups and to the protons of the C_6H_{10} skeleton are also observed. The $^{13}C\{^1H\}$-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 Et_2O 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 $CHCl_3$ 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.

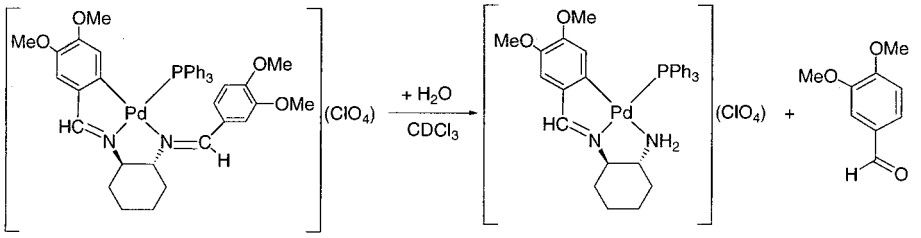
The ^{1}H-NMR spectra of **2** and **3** unambiguously reveal the presence of the orthopalladated L^- ligand, since the aromatic region shows seven well separated signals, two attributed to the iminic protons (H_A and H_B, see Fig. 1), three assigned to the aromatic protons of the non-metallated ring ($H_{2'}$, $H_{6'}$ and $H_{5'}$) and two attributed to the H_3 and H_6 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 ^{1}H-^{1}H COSY and NOESY experiments performed on complex **3**. The key feature for this attribution is the observation of the protons $H_{5'}$ and $H_{6'}$ as an AB spin system ($H_{6'}$, dd, 7.58 ppm; $H_{5'}$ d, 6.89 ppm). The COSY spectrum correlates $H_{6'}$ with $H_{2'}$ (d, 8.32 ppm) and the NOESY spectrum correlates $H_{6'}$ 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 H_6 and H_3 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 $AgClO_4$ (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′)]ClO_4 (L′ = PPh_3 **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 PPh_3 in **4a**, and a singlet at 2.01 ppm is attributed to the NC*Me* 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 pyligand around the Pd–N bond. Moreover, the resonance attributed to H_6 (see Fig. 1) appears at 5.85 ppm, strongly shifted to high-field due to the anisotropic shielding produced by the pyligand [13], reflecting their mutually *cis* disposition. For **7**, the *N*-coordination can be inferred from the observation of an AB spin system for the NH_2 protons. Finally, for **8**, the pattern of resonances is very similar to that described for **3**. The ^{13}C{^{1}H}-NMR spectra of **4a**–**8** show the expected signals, and the ^{31}P{^{1}H}-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 CD_2Cl_2 or $CDCl_3$, 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 NH_2, 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 cm^{-1}). The ^{1}H-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 $^{31}P\{^1H\}$-NMR spectrum of **4b** shows a single peak at 36.86 ppm and the $^{13}C\{^1H\}$-NMR spectrum shows the expected signals.



(1)

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 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 C=N bond and one amine type atom. The bond distances Pd–C, Pd–N(amine), Pd–N(imine) and Pd–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

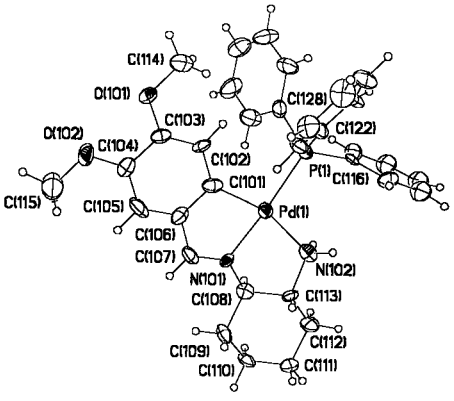


Fig. 2. Thermal ellipsoid plot of complex **4b**. Only one of the two independent molecules is shown. Non-hydrogen atoms are drawn at the 50% probability level.

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

Empirical formula	$C_{34}H_{36}Cl_3N_2O_6PPd$
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 ($R_{int} = 0.0635$)
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 (e Å^{-3})	0.759 and −0.594

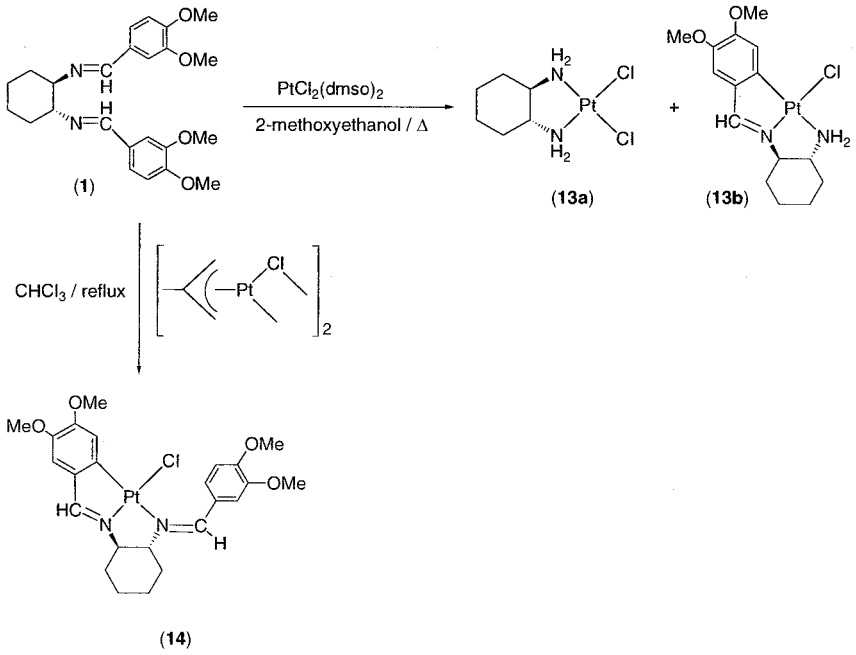
Table 2
Selected bond lengths (Å) and angles (°) for **4b**-CH_2Cl_2

Bond lengths			
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)
Bond angles			
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 PPh_3 ligand and the iminic fragment –N=C(H)C_6H_3-3′,4′-$(OMe)_2$ which, moreover, presents *E* configuration and is directed towards the PPh_3 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 PPh_3 (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 Tl(acac) (1:1 molar ratio, CH_2Cl_2, acac = acetylacetonate) produces the immediate precipitation of TlCl, 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 ^{1}H-NMR spectrum shows the C^3–*H* proton at 5.36 ppm, and the $^{13}C\{^1H\}$-NMR spectrum shows the C^3 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 $AgClO_4$ 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′)}ClO_4 **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 $^{31}P\{^1H\}$-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)]$ClCO_4$ reacts with the N–N ligands (N–N = phen, bipy) (**3**: $AgClO_4$: N–N = 1:1:1 molar ratio) giving complexes of stoichiometry [Pd(L)(N–N)]-ClO_4 (N–N = phen **10**, bipy **11**) according to their elemental analyses and mass spectra. The ^{1}H-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 (CD_2Cl_2, 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, $PtCl_2(DMSO)_2$ (DMSO = Me_2S=O) has been employed in a wide variety of C–H bond activation reactions [17]. The treatment of a white suspension of $PtCl_2(DMSO)_2$ 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 $Cl_2Pt[(NH_2)_2C_6H_{10}$–N,N′], while complex **13b**, soluble in 2-methoxyethanol and isolated after evaporation and precipitation with Et_2O, is the orthometallated derivative [Pt(Cl)(C_6H_2-4,5-$(OMe)_2$-2-CH=*N*-(1*R*,2*R*)-C_6H_{10}–NH_2-κ-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.

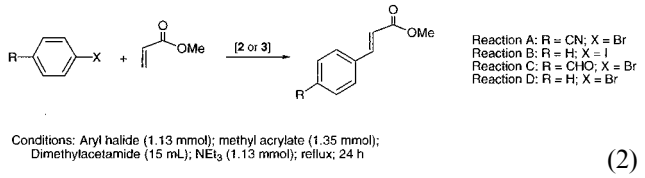
The synthesis of [Pt(Cl)(L-κ-C,N,N] **14** is easily accomplished by reacting **1** and the dimer [18] [Pt(μ-Cl)(η^3-2-Me–C_3H_4)]$_2$ (2:1 molar ratio) in refluxing $CHCl_3$ for 5 h (see Scheme 2). This is a very convenient method for the synthesis of cycloplatinated derivatives [19]. The spectral data of **14** are very similar to those of **3**, with the logical differences arising from the coordination to the Pt center instead to the Pd center. Thus, the ^{1}H-NMR spectrum of **14** reveals the resonances attributed to the iminic protons H_A, H_B and H_6 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 $^3J_{Pt–H}$ for the iminic protons (N=CH_A, 8.77 ppm, $^3J_{Pt–H} = 44$ Hz; N=CH_B, 8.21 ppm, $^3J_{Pt–H} = 147$ 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 Pt–N(=CH_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 [Pd(μ-OAc)($CH_2C_6H_4$-2-P(*o*-tolyl)$_2$)]$_2$ (*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.



(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-BrC_6H_4CN; reaction B: IC_6H_5; reaction C: 4-BrC_6H_4CHO; reaction D: BrC_6H_5; 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

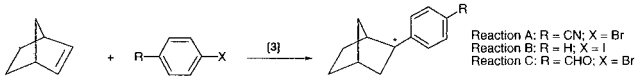
[a] Calculated with respect to aryl halide.
[b] Isolated product.

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_6H_4Me [c]	**3**	1	–	–	–
13	BrC_6H_4OMe [c]	**3**	1	–	–	–

[a] Calculated with respect to uryl 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-bromoanisol) 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); NEt_3 (15 mmol); 90 °C; 15 h

(3)

However, the optical purity of the arylnorbornanes 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 Pd^0 generated by decomposition of the catalyst. The presence of Pd^0 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 the catalyst at the end of the reaction; (iii) the absence of Pd^0 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 [(C_6H_2-4,5-$(OMe)_2$-2-CH=*N*-(1*R*,2*R*)-C_6H_{10}–*N*=CH–C_6H_3-3′,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 arylic 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 [(C_6H_2-4,5-$(OMe)_2$-2-CH=*N*-(1*R*,2*R*)-C_6H_{10}–*N*H_2-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. ^{1}H (300.13 MHz), $^{13}C\{H\}$ (75.47 MHz) and $^{31}P\{^{1}H\}$ (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; ^{1}H and $^{13}C\{^{1}H\}$ were referenced using the solvent signal as the internal standard and $^{31}P\{^{1}H\}$ was externally referenced to H_3PO_4 (85%). The two dimensional ^{1}H-^{1}H COSY and ^{1}H–^{1}H 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 *(1R,2R)-C_6H_{10}-[E-N=CH–C_6H_3-3,4-$(OMe)_2$]$_2$* (**1**)

To a solution of 3,4-$(OMe)_2$–C_6H_3–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 $C_{24}H_{30}N_2O_4$: 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 (*v*, cm^{-1}): 1647(N=CH), 1602, 1586, 1511 (C=C). ^{1}H-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, $^{3}J_{H-H} = 7.80$ Hz), 3.81 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 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}). $^{13}C\{^{1}H\}$-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 (OCH_3), 32.99, 24.55 (CH_2, C_6H_{10}).

4.3. Preparation of *[Pd(OAc)(C_6H_2-4,5-$(OMe)_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-$(OMe)_2$-κ-C,N,N)]* (**2**)

To a suspension of $[Pd(OOCCH_3)_2]$ (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 Et_2O (20 ml) was added, giving **2** as a yellow solid, which was filtered, washed with Et_2O (20 ml) and air dried. Obtained: 1.189 g (93% yield). Anal. Calc. for $C_{26}H_{32}N_2O_6Pd$: 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 (*v*, cm^{-1}): 1644, 1619, 1601, 1587, 1545, 1520 (N=CH + OAc + C=C). ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.36 (d, 1H, N=CH_A, $^{4}J_{H-H} = 1.8$ Hz), 7.85 (d, 1H, $H_{2'}$, $^{4}J_{H2'-H6'} = 1.8$ Hz), 7.82 (d, 1H, N=CH_B, $^{4}J_{H-H} = 2.1$ Hz), 7.57 (dd, 1H, $H_{6'}$, $^{3}J_{H6'-H5'} = 8.4$ Hz), 6.92 (d, 1H, $H_{5'}$), 6.84, 6,75 (2s, 2H, $H_3 + H_6$), 4.11 (m, 1H, N–C*H), 4.05 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 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}). $^{13}C\{^{1}H\}$-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 ($C_6H_2 + C_6H_3$), 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)(C_6H_2-4,5-$(OMe)_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-$(OMe)_2$-κ-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 Et_2O (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–C1)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.32 (d, 1H, $H_{2'}$, $^4J_{H2'-H6'} = 2.1$ Hz), 8.26 (s, broad, 1H, N=CH_A), 7.88 (d, 1H, N=CH_B, $^4J_{H-H} = 2.1$ Hz), 7.58 (dd, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 8.4$ Hz), 7.37 (s, 1H, H6), 6.89 (d, 1H, $H_{5'}$), 6.85 (s, 1H, H_3), 4.06 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.90 (s. 3H, OCH_3), 3.84 (m, 1H, N–C*H), 3.75 (s, 3H, OCH_3), 3.14 (m, 1H, N–C*H), 2.40 (m, 1H, C_6H_{10}), 2.15 (m, 1H, C_6H_{10}), 1.84 (m, 2H, C_6H_{10}), 1.55–1.05 (m, 4H, C_6H_{10}), ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3$), 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 (CH_2 of C_6H_{10}).

4.5. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)-(PPh_3)](ClO_4) (**4a**)

Complex **3** (0.100 g, 0.181 mmol) was dissolved in acetone (10 ml) and treated with $AgClO_4$ (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 PPh_3 (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 Et_2O (40 ml), giving **4a** as a yellow solid. Obtained: 0.148 g (93.1% yield). Crystals of **4a** $0.25CH_2Cl_2$ were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **4a**. The presence of solvent of crystallization was checked by ^{1}H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for $C_{42}H_{44}ClN_2O_8PPd{\cdot}0.25\ CH_2Cl_2$: 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 (ClO_4). Mass Spect. (FAB +) [m/z, (%)]: 777 (100%) [(M–ClO_4)$^+$], 515 (90%) [(M–ClO_4–PPh_3)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.42 (dd, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 9.9$ Hz, $^4J_{H2'-H6'} = 2.1$ Hz), 8.28 (dd, 1H, N=CH_B, $^4J_{P-H} = 8.1$ Hz, $^4J_{H-H} = 1.8$ Hz), 8.27 (s, broad, 1H, N=CH_A), 7.45–7.24 (m, 16H, H_3 + PPh_3), 6.55 (d, 1H, $H_{2'}$), 6.50 (d, 1H, $H_{5'}$), 5,86 (d, 1H, H_6, $^4J_{P-H} = 4.2$ Hz), 4.12 (m, 1H, N–C*H), 3.81 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.41 (m, 1H, N–C*H), 2.80 (s. 3H, OCH_3), 2.69 (m, 1H, C_6H_{10}), 2.27 (m, 1H, C_6H_{10}), 1.93 (m, 2H, C_6H_{10}), 1.61 (m, 2H, C_6H_{10}), 1.31 (m, 2H, C_6H_{10}). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ (ppm) 35.87. ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_3 + C_6H_2$), 134.44 (d, $J_{P-C} = 12.1$ Hz), 131.37, 128.71 (d, $J_{P-C} = 10.6$ Hz) (PPh_3, 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 (CH_2 of C_6H_{10}).

4.6. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–NH_2-κ-C,N,N)(PPh_3)](ClO_4) (**4b**)

Complex **4a** was dissolved in wet $CDCl_3$ (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 $C_{33}H_{36}ClN_2O_6PPd$: 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 (NH_2). 1686, 1621, 1588, 1520 (N=CH + C=C), 1094, 623 (ClO_4). Mass Spect. (FAB +) [m/z, (%)]: 630 (100%) [(M–ClO_4)$^+$]. ^{1}H-NMR (CD_2Cl_2): δ (ppm), 8.05 (dd, 1H, N=CH, $^4J_{P-H} = 9.9$ Hz, $^4J_{H-H} = 2.1$ Hz), 7.69–7.62 (m, 6H, H_o, PPh_3), 7.59–7.44 (m, 9H, $H_m + H_p$, PPh_3), 6.98 (s, 1H, H_3), 5.87 (d, 1H, H_6, $^4J_{P-H} = 3.3$ Hz), 3.74 (s, 3H, OCH_3), 3.67 (m, 1H, N–C*H), 3.36 (t, 1H, NH_2, $^2J_{H-H} = {}^3J_{P-H} = 12$ Hz), 2.91 (s, 3H, OCH_3), 2.78 (m, 1H, N–C*H), 2.48 (m, 1H, NH_2), 1.94 (m, 1H, C_6H_{10}), 1.79 (m, 3H, C_6H_{10}), 1.51 (m, 1H, C_6H_{10}), 1.35 (m, 2H, C_6H_{10}), 1.27–1.12 (m, 1H, C_6H_{10}). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 36.86. ^{13}C{^{1}H}-NMR (CD_2Cl_2): 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 (C_6H_2), 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) (PPh_3), 67.37, 62.99 (N–C*H), 56.35, 55.43 (OMe), 35.29, 29.29, 24.97, 23.94 (CH_2 of C_6H_{10}).

4.7. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)-(NCMe)](ClO_4) (**5**)

Complex **3** (0.100 g, 0.181 mmol) was suspended in acetonitrile (10 ml) and treated with $AgClO_4$ (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 Et_2O (40 ml), giving **5** as a yellow solid. Obtained: 0.084 g (70.7% yield). Anal. Calc. for $C_{26}H_{32}ClN_3O_8Pd$: 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 (ClO_4). Mass Spect. (FAB +) [m/z, (%)]: 515 (100%) [(M–ClO_4–NCMe)$^+$]. ^{1}H-NMR (CD_2Cl_2): δ (ppm), 8.66 (d, 1H, N=CH_A, $^4J_{H-H} = 1.8$ Hz), 7.99 (d. 1H, $H_{2'}$, $^4J_{H2'-H6'} = 2.1$ Hz), 7.71 (dd, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 8.4$ Hz), 7.57 (d, 1H, N=CH_B, $^4J_{H-H} = 1.8$ Hz). 7.09 (d, 1H, $H_{5'}$), 7.06 (s, 1H, H_6), 6.58 (s, 1H, H_3), 3.97 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.90 (s, 4H, OCH_3 + N–C*H), 3.79 (s, 3H, OCH_3), 3.40 (m, 1H, N–C*H), 2.55 (m, 2H, C_6H_{10}), 2.01 (m, broad, 5H, NCMe + C_6H_{10}), 1.56–1.34 (m, 4H, C_6H_{10}). ^{13}C{^{1}H}-NMR

(CD_2Cl_2): 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 ($C_6H_2 + C_6H_3 + CN$), 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 (CH_2 of C_6H_{10}), 3.22 (NCMe).

4.8. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)-(NC_5H_5)][ClO_4] (6)

Complex **6** was obtained as described for **4**. Complex **3** (0.100 g, 0.181 mmol) was reacted in acetone with $AgClO_4$ (0.037 g, 0.181 mmol) and pyridine (14.6 μl, 0.181 mmol) to give **6** as a yellow solid. Obtained: 0.114 g (90.5% yield). Anal. Calc. for $C_{29}H_{34}ClN_3O_8Pd$: 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 (ClO_4). Mass Spect. (FAB +) [m/z, (%)]: 594 (27%) [(M–ClO_4)$^+$], 515 (100%) [(M–ClO_4–NC_5H_5)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.68 (d, 1H, N=CH_A, $^4J_{H-H} = 1.8$ Hz), 8.49 (dd, 2H, H_o, py, $^3J_{H_o-H_m} = 6.3$ Hz, $^4J_{H_o-H_p} = 1.5$ 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, $H_{6'}$, $^3J_{H6'-H5'} = 8.4$ Hz, $^4J_{H6'-H2'} = 1.8$ Hz), 7.18 (dd, 2H, H_m, py), 7.15 (s, 1H. H_3), 7.08 (d, 1H, $H_{2'}$), 6.57 (d, 1H, $H_{5'}$, 5.85 (s, 1H, H_6), 4.04 (m, 1H, N–C*H), 3.80 (s. 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 3.30 (m, 1H, N–C*H), 2.63 (m, 1H, C_6H_{10}), 2.52 (m, 1H, C_6H_{10}), 1.73 (m, 1H, C_6H_{10}), 1.46–1.20 (m, 4H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3 + NC_5H_2$), 72.43, 68.49 (NC*H), 56.26 (2OMe), 56.08, 55.79 (OMe), 29.59, 29.44, 23.96, 23.81 (CH_2 of C_6H_{10}).

4.9. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)-(p-$NH_2C_6NO_2$)][ClO_4] (7)

Complex **7** was obtained as described for **4**. Complex **3** (0.150 g, 0.273 mmol) was reacted in acetone with $AgClO_4$ (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**·0.6CH_2Cl_2 were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **7**. The presence of solvent of crystallization was checked by ^{1}H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for $C_{30}H_{35}ClN_4O_{10}Pd$·0.6$CH_2Cl_2$: 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 (NH_2), 1639, 1598, 1548, 1515 (N=C + C=C), 1342, 1308 (NO_2), 1086, 624 (ClO_4). Mass Spect. (FAB +) [m/z, (%)]: 515 (100%) [(M–ClO_4–$C_6H_6N_2O_2$)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.35 (s, broad, 1H, N=CH_A), 8.25 (d, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 8.4$ Hz). 8.03 (m, 2H, C_6H_4), 7.83 (d, 1H, N=CH_B, $^4J_{H-H} = 2.1$ Hz), 7.79 (s, broad, 1H, $H_{2'}$, 7.30 (d, 1H, $H_{5'}$), 6.92 (m, 2H, C_6H_4), 6.87: 6.68 (2s, 2H, $H_3 + H_6$), 5.77 (d, 1H, NH_2, $^2J_{H-H} = 10.8$ Hz), 5.23 (d, 1H, NH_2), 3.97 (s, 4H, OCH_3 + N–C*H), 3.93 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.22 (m, 1H, N–C*H), 2.48 (m, 1H, C_6H_{10}), 2.35 (m, 1H, C_6H_{10}), 1.88 (m, 2H, C_6H_{10}), 1.49–1.27 (m, 4H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3 + C_6H_4$), 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 (CH_2 of C_6H_{10}).

4.10. Preparation of [Pd(I)(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H3-3′,4′-(OMe)$_2$-κ-C,N,N)] (8)

To a solution of **3** (0.193 g, 0.351 mmol) in acetone (15 ml) $AgClO_4$ (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 Et_2O (20 ml). Obtained: 0.187 g (83% yield). Anal. Calc. for $C_{24}H_{29}IN_2O_4Pd$: 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)$^+$]. ^{1}H-NMR (CD_2Cl_2): δ (ppm), 8.42 (d, 1H, N=CH_A, $^4J_{H-H} = 1.8$ Hz), 8.30 (d, 1H, $H_{2'}$, $^4J_{H2'-H6'} = 1.8$ Hz), 8.04 (d, 1H, N=CH_B, $^4J_{H-H} = 2.1$ Hz), 7.88 (s. 1H, H_6), 7.57 (dd, 1H, $H_{6'}$), $^3J_{H6'-H5'} = 8.4$ Hz), 6.94 (s, 1H, H_3), 6.93 (d, 1H, $H_{5'}$, 4.07 (m, 1H, N–C*H), 4.06 (s. 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3). 3.78 (s, 3H, OCH_3), 3.41 (m, 1H, N–C*H), 2.56 (m, 1H, C_6H_{10}), 2.35 (m, 1H, C_6H_{10}), 1.98(m, 2H, C_6H_{10}), 1.60–1.27 (m, 4H, C_6H_{10}). ^{13}C{^{1}H}-NMR (CD_2Cl_2): 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 ($C_6H_2 + C_6H_3$), 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 (CH_2 of C_6H_{10}).

4.11. Preparation of [Pd(acac-O,O′)(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N)] (9)

To a solution of **3** (0.200 g, 0.362 mmol) in CH_2Cl_2 (15 ml) Tl(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 Et_2O (10 ml) and continuous stirring **9** was obtained as a yellow solid, which was filtered and washed with Et_2O (10 ml). Obtained: 0.160 g (72% yield). Crystals of **9**·0.25CH_2Cl_2 were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **9**. The presence of solvent of crystallization was checked by ^{1}H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for $C_{29}H_{36}N_2O_6Pd$·0.25CH_2Cl_2: 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)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 8.42 (s, 1H, N=CH_A), 7.67 (s, 1H, N=CH_B), 7.24 (d, 1H, $H_{2'}$, $^4J_{H2'-H6'} = 1.8$ Hz), 7.10 (dd, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 8.4$ Hz), 6.98 (s, 1H, H_6), 6.76 (d, 1H, $H_{5'}$, 6.66 (s, 1H, H_3), 5.36 (s, 1H, CH, acac), 4.06 (m, 1H, N–C*H), 3.88 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.35 (m, 1H, N–C*H), 2.48 (m, 1H, C_6H_{10}), 2.04 (s, 3H, CH_3, acac), 2.01 (s, 3H, CH_3, acac), 1.93–1.71 (m, 7H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3$), 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 (CH_2 of C_6H_{10}), 28.10, 27.69 (CH_3, acac).

4.12. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)(N-phen)][ClO_4] (10)

To a solution of **3** (0.200 g, 0.362 mmol) in acetone (15 ml) $AgClO_4$ (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 Et_2O, giving **10** as a yellow solid. This solid was filtered, washed with Et_2O (20 ml) and air dried. Obtained: 0.262 g (91% yield). Crystals of **10**·0.5CH_2Cl_2 were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **10**. The presence of solvent of crystallization was checked by ^{1}H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for $C_{36}H_{37}ClN_4O_8Pd$·0.5CH_2Cl_2: 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)$^+$]. ^{1}H-NMR (CD_2Cl_2, 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, $2H_\delta$ phen, $^3J_{H-H} = 9.0$ Hz), 7.82 (dd, 1H, H_β phen), 7.04 (s, 1H, H_3), 6.73 (dd, 1H, $H_{6'}$ $^3J_{H6'-H5'} = 8.1$ Hz, $^4J_{H6'-H2'} = 2.1$ Hz), 6.50 (d, 1H, $H_{2'}$), 6.41 (d, 1H, $H_{5'}$) 6.26 (s, 1H, H_6), 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, C_6H_{10}), 1.97 (m, 1H, C_6H_{10}), 1.83(m, 4H, C_6H_{10}), 1.51 (m, 2H, C_6H_{10}). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 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, $C_6H_2 + C_6H_3$ + 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, $C_6H_2 + C_6H_3$ + 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 (CH_2 of C_6H_{10}).

4.13. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)(N-bipy)][ClO_4] (11)

Complex **11** was obtained as described for **10**. Complex **3** (0.176 g, 0.32 mmol) was reacted in acetone with $AgClO_4$ (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 $C_{34}H_{37}ClN_4O_8Pd$: 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)$^+$]. ^{1}H-NMR (CD_2Cl_2, 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, $2H_\gamma + H_\delta$ 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, H_3), 7.02 (dd, 1H, $H_{6'}$, $^3J_{H6'-H5'} = 8.1$ Hz, $^4J_{H6'-H2'} = 2.1$ Hz), 6.80 (d, 1H, $H_{2'}$, 6.55 (d, 1H, $H_{5'}$), 6.24 (s, 1H, H_6), 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, C_6H_{10}), 1.86 (m, 3H, C_6H_{10}), 1.69–1.52 (m, 2H, C_6H_{10}), 1.39 (m, 2H, C_6H_{10}). ^{13}C{^{1}H}-NMR (CD_2Cl_2): 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 ($C_6H_2 + C_6H_3$), 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 (CH_2 of C_6H_{10}).

4.14. Preparation of [Pd(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}-N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N)(dppe-P,P′)][ClO_4] (12)

Complex **12** was obtained as described for **10**. Complex **3** (0.200 g, 0.362 mmol) was reacted in acetone with $AgClO_4$ (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**·0.3CH_2Cl_2 were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **12**. The amount of solvent of crystallization was checked by ^{1}H-NMR. These crystals were used for analytical and spectroscopic purposes. Anal. Calc. for $C_{50}H_{53}ClN_2O_8P_2Pd$·0.3$CH_2Cl_2$: 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)$^+$]. ^{1}H-NMR ($CDCl_3$): 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, $H_{2'} + H_3$), 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, H_6, $^4J_{P-H} = 8.7$ 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, CH_2, dppe), 1.85 (m, 2H, CH_2, dppe), 1.56 (m, 1H, C_6H_{10}), 1.39(m, 1H, C_6H_{10}), 1.29–1.14 (m, 5H, C_6H_{10}), 0.04 (m, 1H, C_6H_{10}). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ (ppm), 60.85 (d, dppe, $^3J_{P-P} = 26.7$ Hz), 40.61 (d, dppe). ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3$), 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}, PPh_2), 132.51, 132.35 (2C), 131.73 (C_{para}, PPh_2), 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}, PPh_2), 125.77 ($J_{P-C} = 49$ Hz), 125.43 ($J_{P-C} = 36$ Hz) (C_{ipso}, PPh_2, 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 (CH_2 of C_6H_{10}), 30.71 (dd, $J_{P-C} = 35.6$ Hz, $J_{P-C} = 18.3$ Hz, CH_2, dppe), 27.56 (dd, $J_{P-C} = 29.6$ Hz, $J_{P-C} = 9.5$ Hz, CH_2, dppe).

*4.15. Preparation of $Cl_2Pt[(NH_2)_2C_6H_{10}$–N,N′] (**13a**) and [Pt(Cl)(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,R)-C_6H_{10}–NH_2-κ-C,N,N)] (**13b**)*

$PtCl_2(DMSO)_2$ (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 Et_2O (15 ml), giving **13b** as a red solid. Obtained: 0.044 g (18.3% yield based on Pt). Compound **13a**. Anal. Calc. for $C_6H_{14}Cl_2N_2Pt$: 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). ^{1}H-NMR (DMSO-d_6): δ (ppm), 5.55 (d, 1H, NH_{axial}, $^2J_{H-H} = 9.0$ Hz), 5.03 (t, 1H, NH_{eq}, $^2J_{H-H} \cong {}^3J_{H-H} = 9.0$ Hz), 2.11 (m, 1H, N–C*H), 1.84 (m, 1H, C_6H_{10}), 1.43 (m, 1H, C_6H_{10}), 1.22 (m, 1H, C_6H_{10}), 0.95 (m, 1H, C_6H_{10}). Compound **13b**. Anal. Calc. for $C_{15}H_{21}ClO_2N_2Pt$: 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 (NH_2), 1610, 1590, 1580, 1537 (N=C + C=C), 319 (Pt–Cl). Mass Spect. (FAB+) [m/z, (%)]: 492 (97%) [M^+], 455(100%) [(M–Cl)$^+$]. ^{1}H-NMR ($CDCl_3$): δ (ppm), 7.10 (s, 1H, H_6, C_6H_2, $^3J_{Pt-H} = 44$ Hz), 6.99 (d, 1H, N=CH, $^4J_{H-H} = 2.10$ Hz, $^3J_{Pt-H} = 152$ Hz), 6.53 (s, 1H, H3, C_6H_2), 4.45 (t, 1H, NH_2, $^2J_{H-H} \cong {}^3J_{H-H} = 10.8$ Hz), 4.10 (m, 1H, N–C*H), 3.88 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.58 (d, 1H, NH_2), 2.93 (m, 1H, N–C*H), 1.95 (m, 1H, C_6H_{10}), 1.87 (m, 1H, C_6H_{10}), 1.64 (m, 3H, C_6H_{10}), 1.22 (m, 1H, C_6H_{10}), 0.95 (m, 2H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) 166.08 (N=CH), 151.02, 144.90, 141.10, 140.21, 113.78, 111.00 (C_6H_2), 67.33, 63.31 (C*N, C_6H_{10}), 56.34, 55.89 (OCH_3), 34.73, 30.92, 24.56, 24.00 (C_6H_{10}).

*4.16. Preparation of [Pt(Cl)(C_6H_2-4,5-(OMe)$_2$-2-CH=N-(1R,2R)-C_6H_{10}–N=CH–C_6H_3-3′,4′-(OMe)$_2$-κ-C,N,N)] (**14**)*

To a deoxigenated $CHCl_3$ solution (15 ml) of [Pt(μ-Cl)(η^3-2-Me–C_3H_4)]$_2$ (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 Et_2O (20 ml) giving **14** as an orange–red solid. Obtained: 0.191 g (42.6% yield). Anal. Calc. for $C_{24}H_{29}ClN_2O_4Pt$: 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)$^+$]. ^{1}H-NMR ($CDCl_3$): 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, H_6, $^3J_{Pt-H} = 48$ Hz), 6.94 (s, 1H, H_3), 6.91 (d, 1H, $H_{5'}$), 4.06 (m, 1H, N–C*H), 3.96 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.52 (m, 1H, N–C*H), 2.54 (m, 1H, C_6H_{10}), 2.35 (m, 1H, C_6H_{10}), 1.93 (m, 2H, C_6H_{10}), 1.59–1.26 (m, 4H, C_6H_{10}). ^{13}C{^{1}H}-NMR ($CDCl_3$): 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 ($C_6H_2 + C_6H_3$), 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 (CH_2 of C_6H_{10}).

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). An hemisphere of data was collected based on three ω-can runs (starting $\omega = -30°$) at values $\phi = 0$, 90, and 180° with the detector at $2\theta = 30°$. For each of these runs, frames (606, 435 and 23, respectively) were collected at 0.3° ontervals 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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References

[1] Y.L. Bennani, S. Hanessian, Chem. Rev. 97 (1997) 3161.
[2] (a) C. Jablonski, Z. Li, Inorg. Chem. 39 (2000) 2456;
(b) J. Balsells, J.M. Betancourt, P.J. Walsh, Angew. Chem. Int. Ed. Engl. 39 (2000) 3428;
(c) S. Fox, R.T. Stibrany, J.A. Potenza, S. Knapp, H.J. Schugar, Inorg. Chem. 39 (2000) 4950;
(d) I. Alfonso, F. Rebolledo, V. Gotor, Chem. Eur. J. 6 (2000) 3331;
(e) U. Gran, O. Wennerström, G. Westman, Tetrahedron Asymmetry 11 (2000) 3027.
[3] (a) J. Balsells, P.J. Walsh, J. Am. Chem. Soc. 122 (2000) 3250;
(b) M. Shi, W.S. Sui, Tetrahedron Asymmetry 11 (2000) 773;
(c) M. Shi, W.S. Sui, Tetrahedron Asymmetry 11 (2000) 835.
[4] (a) D.P. Steinhuebel, S.J. Lippard, Organometallics 18 (1999) 3959;
(b) R.A. Stinziano-Eveland, S.T. Nguyen, L.M. Liable-Sands, A.L. Rheingold, Inorg. Chem. 39 (2000) 2452;
(c) J.D.G. Correia, A. Domingos, I. Santos, Eur. J. Inorg. Chem. (2000) 1523;
(d) K, Polborn, K. Severin, Eur. J. Inorg. Chem. (2000) 1687.

[5] (a) A. Saitoh, K. Achiwa, K. Tanaka, T. Morimoto, J. Org. Chem. 65 (2000) 4227;
(b) B.M. Trost, R. Madsen, S.D. Guile, B. Brown, J. Am. Chem. Soc. 122 (2000) 5947;
(c) B.M. Trost, J.P. Surivet, J. Am. Chem. Soc. 122 (2000) 6291;
(d) B.M. Trost, G.M. Schroeder, J. Am. Chem. Soc. 122 (2000) 3785;
(e) B.M. Trost, J.P. Surivet, Angew. Chem. Int. Ed. Engl. 39 (2000) 3122;
(f) S.-E. You, X.-L. Hou, L.-X. Dai, B.-X. Cao, J. Sun, Chem. Commun. (2000) 1933;
(g) J.P. Duxbury, J.N.D. Warne, R. Mushtaq, C. Ward, M. Thornton-Pett, M. Jiang, R. Greatrex, T.P. Kee, Organometallics 19 (2000) 4445.

[6] (a) C.R. Baar, H.A. Jenkins, G.P.A. Yap, R.J. Puddephatt, Organometallics 17 (1998) 4329;
(b) C.R. Baar, H.A. Jenkins, M.C. Jennings, G.P.A. Yap, R.J. Puddephatt, Organometallics 19 (2000) 4870;
(c) C.R. Baar, M.C. Jennings, R.J. Puddephatt, Organometallics 18 (1999) 4373;
(d) C.R. Baar, L.P. Carbray, M.C. Jennings, R.J. Puddephatt, J. Am. Chem. Soc. 122 (2000) 176;
(e) C.R. Baar, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Organometallics 19 (2000) 4150;
(f) C.R. Baar, L.P. Carbray, M.C. Jennings, R.J. Puddephatt, Organometallics 19 (2000) 2482;
(g) C.R. Baar, L.P. Carbray, M.C. Jennings, R.J. Puddephatt, J.J. Vittal, Organometallics 20 (2001) 408.

[7] (a) L.R. Falvello, S. Fernández, R. Navarro, A. Rueda, E.P. Urriolabeitia, Organometallics 17 (1998) 5887;
(b) L.R. Falvello, S. Fernández, R. Navarro, E.P. Urriolabeitia, Inorg. Chem. 38 (1999) 2455;
(c) S. Fernández, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 602 (2000) 151;
(d) C. Larraz, R. Navarro, E.P. Urriolabeitia, New J. Chem. 24 (2000) 623;
(e) L.R. Falvello, S. Fernández, C. Larraz, R. Llusar, R. Navarro, E.P. Urriolabeitia, Organometallics 20 (2001) 1424.

[8] C. Cativiela, L.R. Falvello, J.C. Ginés, R. Navarro, E.P. Urriolabeitia, New J. Chem. 25 (2001) 344.

[9] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.

[10] (a) M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357;
(b) H. Weissman, D. Milstein, Chem. Commun. (1999) 1901;
(c) P.H. Leung, K.H. Ng, Y. Li, A.P.J. White, D.J. Williams, Chem. Commun. (1999) 2435;
(d) D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, Chem. Commun. (1998) 2095.

[11] W.A. Herrmann, V.P.W. Böhm, C.P. Reisinger, J. Organomet. Chem. 576 (1999) 23.

[12] (a) X. Gai, R. Grigg, M.I. Ramzan, V. Sridharan, S. Collard, J.E. Muir, Chem. Commun. (2000) 2053.
(b) M. Nowotny, U. Hanefeld, H. van Koningsveld, T. Maschmeyer, Chem. Commun. (2000) 1877 and references therein.
(c) A.A.D. Tulloch, A.A. Danopoulos, R.P. Tooze, S.M. Cafferkey, S. Kleinhenz, M.B. Hursthouse, Chem. Commun. (2000) 1247.
(d) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619.
(e) J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. 6 (2000) 1773.
(f) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R.E. Cramer, C.M. Jensen, Inorg. Chim. Acta 300-302 (2000) 958.
(g) A. Biffis, M. Zecca, M. Basato, Eur. J. Inorg. Chem. (2001) 1131.
(h) E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, Chem. Commun. (2001) 201.
(i) S. Gibson, D.F. Foster, G.R. Eastham, R.P. Tooze, D.J. Cole-Hamilton, Chem. Commun. (2001) 779.
(j) T. Rosner, J. Le Bars, A. Pfaltz, D.G. Blackmond, J. Am. Chem. Soc. 123 (2001) 1848.
(k) T. Rosner, A. Pfaltz, D.G. Blackmond, J. Am. Chem. Soc. 123 (2001) 4621.

[13] A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, New J. Chem. Soc. Dalton Trans. (1978) 1490.

[14] (a) L.R. Falvello, S. Fernández, R. Navarro, E.P. Urriolabeitia, Inorg. Chem. 35 (1996) 3064;
(b) L.R. Falvello, S. Fernández, R. Navarro, I. Pascual, E.P. Urriolabeitia, J. Chem. Soc. Dalton Trans. (1997) 763;
(c) L.R. Falvello, S. Fernández, R. Navarro, E.P. Urriolabeitia, Inorg. Chem. 36 (1997) 1136.

[15] J. Forniés, R. Navarro, M. Tomas, E.P. Urriolabeitia, Organometallics 12 (1993) 940.

[16] G.K. Anderson, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 9, Pergamon Press, Oxford, 1995, pp. 507–518 and references therein.

[17] L. Alexandrova, O.G. D'yachenko, G.M. Kazankov, V.A. Polyakov, P.V. Samuleev, E. Sansores, A.D. Ryabov, J. Am. Chem. Soc. 122 (2000) 5189.

[18] D.J. Mabbott, B.E. Mann, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 294.

[19] (a) M. Ghedini, D. Pucci, A. Crispini, G. Barberio, Organometallics 18 (1999) 2116 and references therein.
(b) K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, J. Organomet. Chem. 592 (1999) 155 and references therein.

[20] J. Tsuji, Palladium Reagents and Catalysts, Innovations in Organic Synthesis, Wiley, Chichester, UK, 1996.

[21] (a) W.A. Herrmann, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1844;
(b) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1848;
(c) W.A. Herrmann, C. Brossmer, C.P. Reisinger, T. Riermeier, K. Öfele, M. Beller, Chem. Eur. J. 3 (1997) 1357.

[22] (a) M. Shibasaki, C.D.J. Boden, A. Kojima, Tetrahedron 53 (1997) 7371;
(b) M. Shibasaki, E.M. Vogl, J. Organomet. Chem. 576 (1999) 1;
(c) A. Tenaglia, A. Heumann, Angew. Chem. Int. Ed. Engl. 38 (1999) 2180.

[23] (a) H. Brunner, K. Kramler, Synthesis (1991) 1121;
(b) S. Sakuraba, K. Awano, K. Achiwa, Synlett (1994) 291;
(c) F. Ozawa, Y. Kobatake, T. Hayashi, J. Chem. Soc. Chem. Commun. (1994) 1323;
(d) C. Moinet, J.C. Fiaud, Tetrahedron Lett. 36 (1995) 2051.

[24] (a) S. Cacchi, G. Fabrizi, F. Gasparrini, C. Villani, Synlett (1999) 345;
(b) M. Catellani, E. Motti, S. Ghelli, Chem. Commun. (2000) 2003;
(c) X.Y. Wu, H.D. Xu, Q.L. Zhou, A.S. Chan, Tetrahedron Asymmetry 11 (2000) 1255;
(d) J.M. Brunel, A. Heumnann, G. Buono, Angew. Chem. Int. Ed. Engl. 39 (2000) 1946;
(e) J.M. Brunel, M.H. Hirlemann, A. Heumann, G. Buono, Chem. Commun. (2000) 1869;
(f) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, Science 287 (2000) 1992;
(g) C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, Y. Fujiwara, J. Am. Chem. Soc. 122 (2000) 7252 (alkynes);
(h) S. Cacchi, G. Fabrizi, F. Gasparrini, P. Pace, C. Villani, Synlett (2000) 650 (α,β-unsaturated ketones);

(i) T. Ohe, T. Wakita, S. Motofusa, C.S. Cho, K. Ohe, S. Uemura, Bull. Chem. Soc. Jpn. 73 (2000) 2149 (α,β-unsaturated ketones).

[25] (a) A. Kasyan, C. Wagner, M.E. Maier, Tetrahedron 54 (1998) 8047;
(b) J.C. Namyslo, D.E. Kaufmann, Synlett (1999) 114.

[26] (a) M.T. Reetz, E. Westermann, Angew. Chem. Int. Ed. Engl. 39 (2000) 165;
(b) J. Le Bars, U. Specht, J.S. Bradley, D.G. Blackmond, Langmuir 15 (1999) 7621.

[27] SAINT version 5.0: Bruker analytical X-ray systems, Madison, WI.

[28] G.M. Sheldrick, SADABS: empirical absorption correction program, Göttingen University, 1996.

[29] G.M. Sheldrick, SHELXS-86, Acta Crystallogr. Sect. A 46 (1990) 467.

[30] G.M. Sheldrick, SHELXL-97: FORTRAN program for the refinement of crystal structures from diffraction data. Göttingen University, 1997. Molecular graphics were done using the commercial package SHELXTL-PLUS, Release 5.05/V: © 1996, Siemens Analytical X-ray Instruments, Inc., Madison, WI.