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Sustainable carbon–carbon bond formation catalyzed by new oxamate-containing palladium(II) complexes in ionic liquids

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ABSTRACT

New and versatile bis(oxamato)palladate(II) complexes of formula $(n\text{-}Bu_4N)_2[Pd(2\text{-}Mepma)_2]\cdot 4H_2O$ (**1a**) and $(n\text{-}Bu_4N)_2[Pd(4\text{-}Mepma)_2]\cdot 2H_2O\cdot MeCN$ (**1b**) ($n\text{-}Bu_4N^+$ = tetra-*n*-buthylammonium, 2-Mepma = *N*-2-methylphenyloxamate and 4-Mepma = *N*-4-methylphenyloxamate) have been synthesized and characterized by spectroscopic methods and single crystal X-ray diffraction. Each palladium(II) ion in **1a** and **1b** is four-coordinate with two oxygen and two nitrogen atoms from two fully deprotonated oxamate ligands building a centrosymmetric square planar surrounding. Their catalytic role has been investigated for both Heck and Suzuki coupling reactions using a series of aryl iodide/bromide derivatives in tetra-*n*-butylammonium bromide ($n\text{-}Bu_4NBr$) as ionic liquid, i.e. molten salt. These pre-catalysts appear as highly efficient, easily recovered and reused at least eight times without any drastic loss of their exceptional reactivity or leaching from the ionic liquid medium.

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1. Introduction

Palladium-catalyzed cross-coupling coupling of aryl halides with olefins or aryl boronic acids, known as Heck and Suzuki reactions respectively, are among the most versatile and efficient methods for the formation of carbon–carbon (C–C) bonds in organic synthesis [1,2]. Their use in the synthesis of pharmaceuticals, fine chemicals, natural products and conducting polymers is motivated by their versatility and tolerance towards different functional groups [3]. Many palladium-based systems with excellent catalytic performances have been developed and largely employed, such as those with phosphine ligands [4], palladacycle catalysts [5], *N*-heterocyclic carbene-containing catalysts (NHCs) [6] and immobilized phosphine-free catalysts [7], in both homogenous and heterogenous phases, conducting largely the catalytic reactions in polar aprotic solvents, such as dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) and *N*-methylpyrrolidone (NMP). However, organic solvents not only enhance the reaction rate but also result in environmental pollution due to their toxicity.

The design and use of simple, cheap, and recyclable active catalysts together with environment-friendly green solvents are highly desirable to set up greener catalytic protocols [2c]. In this context, the performance of Heck and Suzuki coupling reactions in alternative green solvents such as ionic liquids by phosphine- and carbene-free palladium catalysts containing inexpensive *N*,*O* ligands [8], should be advantageous as environmentally friendly organic reaction methodology and also as a strategy for recycling catalysts [9]. Furthermore, it has been shown that chelating ligands containing *O* or *N* donor atoms result in more stable and efficient palladium catalysts, a feature which prevents their deactivation after the reductive elimination step [10].

Among the variety of potential ligands having *N* and *O* as donor atoms, the inexpensive and readily prepared chelating and bis-chelating oxamate type ligands have been extensively used for the synthesis of complexes with divalent (Cu^{II} and Ni^{II}) and trivalent (Co^{III}, Fe^{III} and Mn^{III}) transition metal ions having interesting magnetic properties or catalytic performance in oxidation and epoxidation processes [11,12]. However, to the best of our knowledge, only the synthesis and structural details of two anionic oxamate-containing mononuclear palladium(II) complexes and a neutral oxamate-bridged Pd(II)Co(II) chain are known [13]. The catalytic activity of anionic bis(oxamato)palladate(II) complexes in the C–C coupling reactions and their immobilization in ionic liquids, followed by their separation from reagents and products as well as

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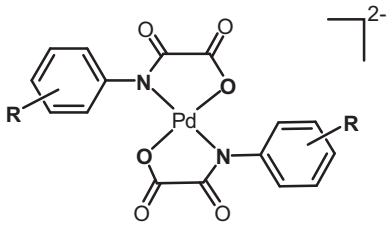
recycling and reuse in further catalytic cycles have never been addressed. Herein, we describe the synthesis and characterization of two structurally well-defined oxamate-containing palladium(II) complexes of formula $(n\text{-}Bu_4N)_2[Pd(2\text{-}Mepma)_2]\cdot 4H_2O$ (**1a**) and $(n\text{-}Bu_4N)_2[Pd(4\text{-}Mepma)_2]\cdot 2H_2O\cdot MeCN$ (**1b**) ($n\text{-}Bu_4N^+$ = tetra-*n*-buthylammonium, 2-Mepma = *N*-2-methylphenyloxamate and 4-Mepma = *N*-4-methylphenyloxamate). Their efficiency as catalysts in the cross-coupling reactions of aryl halides with olefins or aryl boronic acids in tetra-*n*-butylammonium bromide ($n\text{-}Bu_4NBr$) as the ionic liquid solvent (i.e. molten salt) and triethylamine (Et_3N) as the base without any other additive is also explored and reported herein Ref. [14].

2. Results and discussion

The bis(oxamate)palladate(II) complexes **1a** and **1b** were prepared in a straightforward one step reaction of K_2PdCl_4 with two equivalents of the corresponding proligand in an acetonitrile/water mixture and an excess of NBu_4OH dissolved in methanol under aerobic conditions at 60 °C. **1a** and **1b** were obtained as pale yellow solids which are soluble in polar solvents such as dichloromethane, chloroform, methanol and water. Both complexes were fully characterized by elemental analysis, IR, ^1H NMR and single crystal X-ray diffraction.



Complex	R
1a	*o*-CH_3
1b	*p*-Ca_3

X-ray diffraction on single crystals of **1a** and **1b** shows the occurrence of centrosymmetric mononuclear $[PdL_2]^{2-}$ units (L = bidentate oxamate ligand) (Fig. 1) and $n\text{-}Bu_4N^+$ as counter cations. Each palladium(II) ion is four-coordinate with two amidate-nitrogen and two carboxylate-oxygen atoms from the two oxamate ligands in a *trans* arrangement building a distorted square-planar surrounding. The reduced bite of the bidentate oxamate [82.14(5) (**1a**) and 81.89(6)° (**1b**)] accounts for the deviations of the ideal value of 90° for the square planar surrounding. The average Pd–N and Pd–O bond lengths for **1a**/**1b** are 2.0209(11)/2.0207(13) Å and 2.0384(13)/2.0214(14) Å, respectively (see Table 1). These values agree with those found in the mononuclear species $Na[Pd(Hpba)]\cdot 2H_2O$ [H_4pba = 1,3-propylenebis(oxamic acid)] [Pd–N = 1.97 Å and Pd–O = 2.04 Å] and $(PPh_4)_2[Pd(opba)]\cdot 2H_2O$ [H_4opba = 1,2-phenylenebis(oxamic acid) and PPh_4^+ = tetraphenylphosphonium cation] [Pd–N = 1.93 Å and Pd–O = 2.05 Å] [13]. The values of the dihedral angle between the basal plane at the palladium(II) ion and the mean plane of the oxamate groups for **1a**/**1b** are 7.4(1)/3.9(1)°, whereas those between the square plane and the phenyl ring are 51.1(1)/52.2(1)°. The values of the peripheral C(1)–O(2) and C(2)–O(3) bond distances [1.2413(18) and 1.2543(19) Å (**1a**) and 1.217(2) and 1.241(2) Å (**1b**)] are somewhat shorter than the inner C(1)–O(1) bond [1.309(2) (**1a**) and 1.300(2) Å (**1b**)] in agreement with the greater double bond character of the former carbonyl groups.

The distances and angles of each tetrahedral $[(n\text{-}C_4H_9)_4N]^+$ cation in **1a** and **1b** are quite as expected. The little discrepancy in the N–C and C–C distances and in the N–C–C and C–C–C angles arises from crystallographic disorder, which is a quite common feature observed in most of the crystals containing this organic cation.

The complex anions of **1a** and **1b** are well separated from each other by the bulky Bu_4N^+ cations in the resulting three-dimensional ionic lattices (Fig. 2) and no π–π stacking interactions are present. The values of the shortest Pd···Pd distances are 10.829(1) (**1a**) and 11.855(1) Å (**1b**) [Pd(1)···Pd(1b); (b) = −1 + *x*, *y*, *z*]. Very weak but non-negligible C–H···O type interactions [C···O = 3.5–3.6 Å] involving the methyl groups from the acetonitrile molecules and NBu_4^+ cations with the peripheral oxygen atoms of the oxamate groups contribute to the stabilization of the structure. Furthermore very weak C–H···N interactions [C···N = 3.6–3.8 Å] take place between the acetonitrile molecules and the methyl groups from the Bu_4N^+ cations.

The applicability of the synthesized anionic complexes **1a** and **1b** in palladium-catalyzed Heck and Suzuki coupling reactions was next investigated by using a variety of aryl iodide and less-reactive aryl bromide derivatives in ionic liquids as solvents. These type of solvents, i.e. molten salts with a melting point below ambient, seemed to be promising over conventional reaction conditions, making easier the separation of the product by simple extraction or distillation from the ionic "solvent", a feature which allows

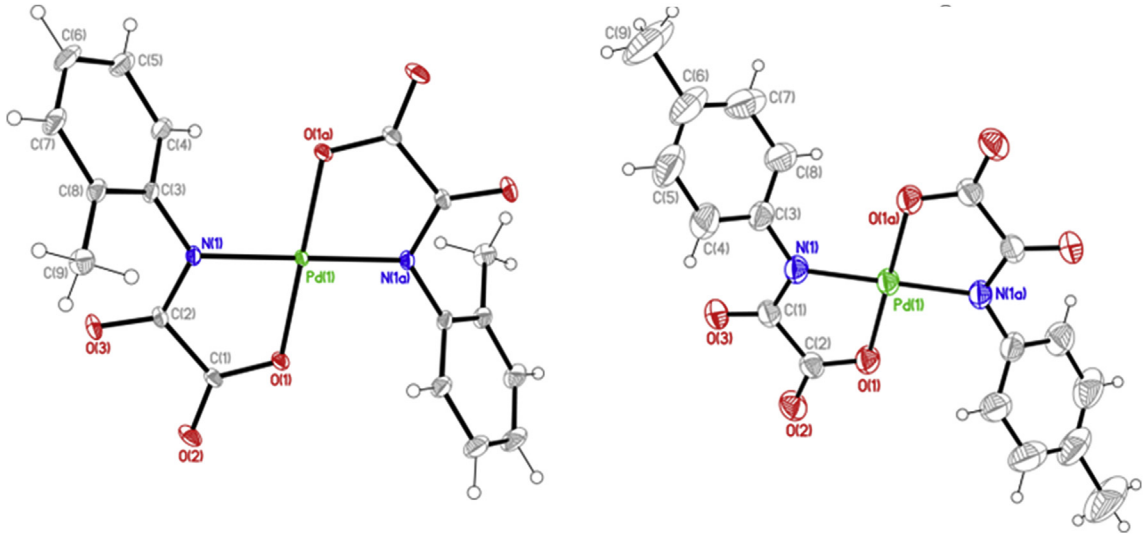


Fig. 1. Ortep diagrams of the anionic entity of **1a** (left) and **1b** (right). Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond lengths (Å) and angles (deg) for **1a**[a] and **1b**.[b]

	1a	1b
Pd(1)–O(1)	2.021(1)	2.021(1)
Pd(1)–N(1)	2.038(1)	2.021(1)
C(1)–O(1)	1.309(2)	1.300(2)
C(1)–O(2)	1.240(2)	1.217(2)
C(1)–C(2)	1.566(2)	1.557(3)
C(2)–O(3)	1.253(29)	1.241(2)
C(2)–N(1)	1.350(2)	1.341(2)
N(1)–C(3)	1.435(2)	1.433(2)
O(1)–Pd(1)–N(1)	82.13(5)	81.89(6)
O(1)–Pd(1)–N(1a)	97.87(5)	98.11(6)
O(1)–Pd(1)–O(1a)	180.00(1)	180.00(6)
N(1)–Pd(1)–N(1a)	180.00(5)	180.00(1)
Pd(1)–O(1)–C(1)	114.45(10)	114.75(12)
Pd(1)–N(1)–C(2)	113.92(10)	114.42(12)
Pd(1)–N(1)–C(3)	125.83(10)	126.24(12)
C(2)–N(1)–C(3)	119.71(13)	119.17(14)

[a] Symmetry code for **1a**: (a) = $-x+2, -y+2, -z+2$.
[b] Symmetry code for **1b**: (a) = $-x+2, -y, -z+2$.

recycling the whole catalyst-solvent system. Bearing this concept in mind, we first screened several ionic liquids with **1a** as catalyst for the coupling of iodobenzene with either phenylboronic acid or ethyl acrylate by using 5 mol% or 1 mol% of catalyst, respectively.

In terms of productivity, stability and recyclability of the catalysts, *n*-Bu_4NBr provided the best results as compared to other tested salts such as tetra-*n*-butylammonium chloride (*n*-Bu_4NCl) and other imidazolium salts (Table 2). Contrary to the tetrahedral shape of the tetraalkylammonium cation, the imidazolium one has a planar structure, a feature that makes easier its aggregation with the planar complex anions. This would decrease the anion availability for the stabilization of the catalytically active Pd(0) species, which may be formed in the reaction mixture either by thermal reduction of Pd(II) precatalyst or by an excess of the olefin itself as well as triethylamine employed as base, during the catalytic process [15]. *n*-Bu_4NBr was described as an excellent reaction medium for the stabilization of catalytically active palladium and copper species for C–C coupling reactions via electrostatic interactions [16]. Catalyst loading of 5 mol% (**1a**) and 1 mol% (**1b**) for Suzuki and Heck reactions respectively, which was carried out with iodobenzene and Et_3N as base, afforded the highest yields in short time reaction (ca. half an hour). However, lower catalyst loadings of 1 mol % (**1a**) gave lower yields for the Suzuki reactions. Interestingly, while catalyst **1a** showed a higher catalytic performance in Suzuki coupling of aryl iodide with phenylboronic acid compared to **1b**, the Heck coupling of aryl iodide with olefins was efficiently promoted by using **1b** compared to **1a** (Entry 1–4, Table 2). In the Heck process, the rate of reaction and regioselectivity are sensitive to the steric hindrance about C=C bond of the vinylic partner. In fact, steric effects play a major role in directing the attack by the metal i.e. palladium in the insertion step. Catalyst **1a** features pronounced steric effects around the palladium catalytic centre due to the presence of a methyl group in the *ortho*-position to the oxamate ligand, which would cause a lowering of its reactivity in the Heck reactions.

Suzuki coupling of aryl halide (0.5 mmol) and boronic acid (0.75 mmol), and Et_3N (1 mmol) with **1a** (5 mol%) in 2–3 g of *n*-Bu_4NBr at 120 °C led to the dissolution of the anionic palladium complex and the formation of diphenyl with a yield of 78% after 120 min (Entry 1, Table 3). The only side product observed was from deboronation. Interestingly, the catalytic reaction did not lead to visible palladium black formation, neither during the catalytic process nor after completion of the catalytic reaction, implying that the reaction does not occur at the surface of inactive palladium black. This feature would suggest that *n*-Bu_4NBr stabilizes the catalytic active species from precipitation into the insoluble and inactive black palladium(0) [17]. Under the same conditions, the coupling of a wide variety of acceptor and donor-substituted aryl iodide with phenylboronic acid mediated by **1a** in *n*-Bu_4NBr as solvent, efficiently yielded the corresponding asymmetrically substituted biaryl derivatives, demonstrating the greater activity/performance of these new catalyst (Entry 2–6, Table 3). Interestingly, the coupling of the less reactive bromobenzene with phenylboronic acid was also achieved in good yield (Entry 7–8, Table 3). Well known catalysts such as $Pd(OAc)_2$ and $Pd(dba)_2$ employed for Suzuki reaction resulted in similar catalytic activity and identical lower turnover numbers (TONs) like **1a** with the formation of palladium black, which could hamper recycling of these catalysts (Fig. 3S, Supporting information).

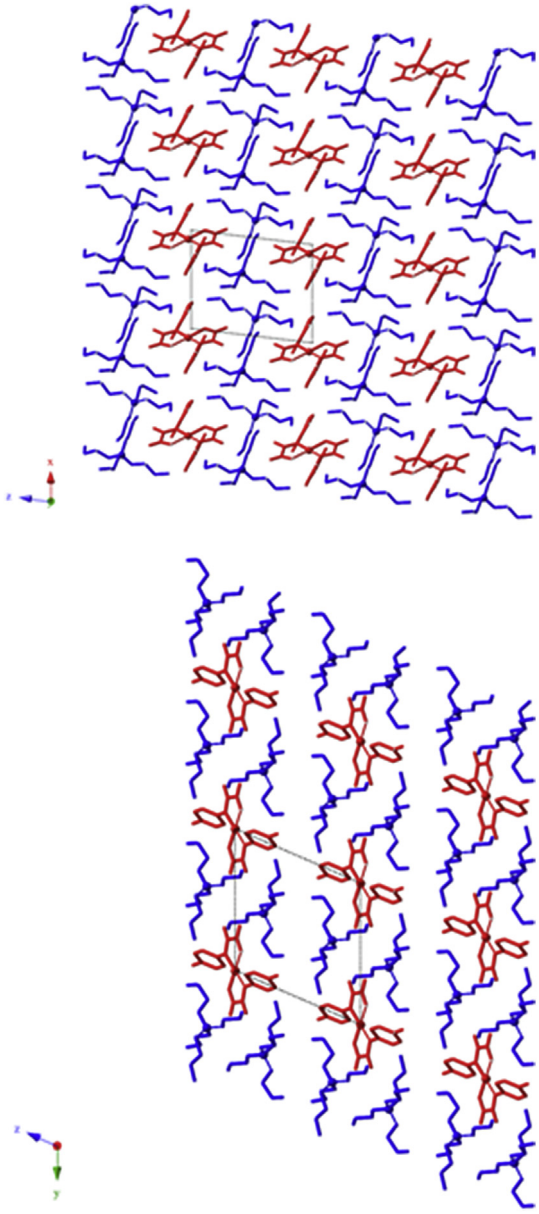


Fig. 2. Crystal packing of **1a** (top) and **1b** (bottom) showing the relative positions of the anionic complexes (red) and tetra-*n*-butylammonium cations (blue). The solvent molecules have been omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Screening of Suzuki (**1a**) and Heck (**1b**) reactions in different ionic liquids.

Entry	Ionic liquid	T (°C)	Yield (%) Suzuki[a]/**1a**	Time (min)	Yield (%) Heck[b]/**1b**	Time (min)
1	n-Bu_4NBr	120	78	120	99	30
2	n-Bu_4NCl	120	46	120	88	30
3	BMIMBr[c]	120	23	120	85	30
4	$BIMIMPF_6$[d]	120	33	120	66	30

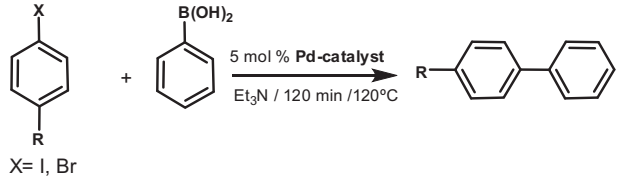
[a] Reaction conditions: 0.5 mmol of aryl iodide, 0.75 mmol of phenylboronic acid, 2 equiv of Et_3N, 5 mol % **1a**. Determined by GC–MS using diethyleneglycol-di-n-butyl ether as internal standard.
[b] Reaction conditions: 0.5 mmol of aryl iodide 0.75 mmol of ethyl acrylate, 2 equiv of Et_3N, 1 mol % **1b**. Determined by GC–MS using diethyleneglycol-di-n-butyl ether as internal standard.
[c] 1-n-Butyl-3-methylimidazole bromide.
[d] 1-n-Butyl-3-methylimidazole hexafluorophosphate.

Heck coupling of a variety of *para*-susbtituted aryl halide with donor- and acceptor substituents and different olefins was carried out under the same conditions like Suzuki reaction, by using lower loading of **1b** as catalyst (1 mol%). The coupling took place in a short time (ca. 30 min), in a quantitative yield (99%) without observation of the insoluble palladium black (Entry 1, Table 3). The extension of this method towards a wide variety of activated and deactivated aryl iodide derivatives and different olefins led to good and quantitative yields (60–99%) for both donor- and acceptor-substituted aryls (Entry 2–9, Table 4). The efficiency of the catalysts used here is also supported by the very good yields obtained by coupling the less reactive bromobenzene with two different olefins (99%, Table 4). The Precatalyst **1b** was found to be better than $PdCl_2$, $Pd(OAc)_2$ and $Pd(dba)_2$ in coupling bromobenzene with ethyl acrylate in terms of yield of product and TONs. One again, formation of palladium black was observed when using $Pd(OAc)_2$ and $Pd(dba)_2$. This new approach demonstrates the versatility of the oxamate-containing palladium(II) complexes toward the coupling reactions of different aryl halides with olefinic substrates in ionic liquids as reaction media.

The immobilization of the **1a** and **1b** precatalysts in molten n-Bu_4NBr, driven by their ionic interaction with this ionic liquid suggested the possibility of their reusability. Recycling of **1a** and **1b** dissolved in n-Bu_4NBr was achieved by the extraction of the reagents and products with n-pentane. The catalytic activity/recyclability of **1a** and **1b** was tested by reaction of iodobenzene with phenylboronic acid mediated by **1a** (5 mol%) and iodobenzene with ethyl acrylate mediated by **1b** (1 mol%). The catalytic protocol of recovery/reuse was performed until six (**1a**)/eight (**1b**) runs with good yields, as shown in Fig. 3.

No leaching of the palladium(II) compound employed was observed, as evidenced by the analysis of the final organic products using both ^1H NMR spectroscopy and SEM-Edax microscopy. In fact, the analysis of the isolated product by ^1H NMR and FT-IR spectroscopic techniques showed no signal of the palladium(II) precatalyst. This was also confirmed by the microscopic analysis that points out the absence of palladium(II) traces. In addition, during both recycling protocols, no palladium black was visually detected. The fact that the catalytic yields decreased during the protocol of recycling and reuse may be caused by the decomposition of the catalyst. Further investigations are in progress to elucidate the structure of the palladium species which remains in the ionic liquid medium.

Table 3
Suzuki coupling reactions of aryl halides and phenylboronic acid mediated by **1a** in n-Bu_4NBr.



Entry[a]	R	X	Pd-catalyst	Yield[b] (%)	TON (mol product mol^{-1} Pd)
1	H	I	1a	78	16
2	CN	I	1a	99	20
3	CH_3	I	1a	99	20
4	$COCH_3$	I	1a	47	10
5	OCH_3	I	1a	78	16
6	$COOCH_3$	I	1a	99	20
7	H	Br	1a	65	14
8	CH_3	Br	1a	60	12
9	H	Br	$PdCl_2$	5	1
10	H	Br	$Pd(OAc)_2$	60	14
11	H	Br	$Pd(dba)_2$	65	15

[a] Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol of phenylboronic acid, 2 equiv of Et_3N, 5 mol % **1a**, 2 g of n-Bu_4NBr.
[b] Determined by GC–MS using diethyleneglycol-di-n-butyl ether as internal standard.

3. Conclusions

In summary, oxamate-containing palladium(II) complexes are very stable and efficient catalysts in palladium-catalyzed Suzuki and Heck reactions, by using both active and less reactive aryl halides. The anionic character of the catalytic units permits their facile immobilization in the ionic liquid, which has been found to influence positively their reactivity, stabilization and recycling [18]. Such stabilization may be due to the formation of individual catalytically active palladium(0) species, surrounded by a bulky n-Bu_4NBr salt [19]. This would impose a Coulomb barrier for collision which would prevent the precipitation of inactive palladium black and consequently extend the catalyst life for further catalytic runs. Research work about the influence of the steric and electronic nature of the substituents of the oxamate ligand on the Suzuki and Heck reaction mechanisms as well as the scope of oxamate-containing palladium(II) complexes in coupling other bromo- and chloro-aryl derivatives with different electronic demands are underway.

4. Experimental

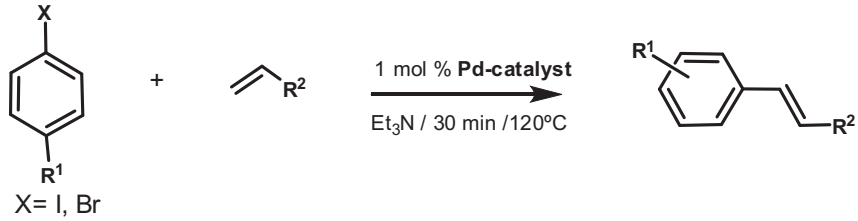
4.1. Materials and methods

Palladium(II) acetate and palladium chloride were purchased from Aldrich. Palladium dibenzylacetone $Pd(bda)_2$ (dba = dibenzylideneacetone) was prepared as reported [20] NMR spectra (^1H and ^{13}C) were recorded on an Avance DRX 300 Bruker instrument at room temperature and referenced to residual protons in the solvent (^1H) or the solvent ^{13}C signal (^{13}C). The elemental analysis (C, H and N) were carried out on a EuroEA3000 analyzer by the Servei Central d'Instrumentació Científica at the University of Jaume I. FT-IR spectra (4000–450 cm^{-1}) were recorded with a Nicolet 5700 FT-IR instrument. GC–MS spectra were recorded on an Agilent 5973N mass spectrometer equipped with capillary columns (split/splitless, pulsed split and pulsed splitless) at the SCSIE (Servicio Central de Soporte a la Investigación Experimental) of the University of Valencia. The SEM-Edax microscopy analysis was performed on a Philips mod. XL 30 ESEM with microanalysis EDAX mod. PV 9760 and HOT STAGE until 1000 °C.

4.2. General procedure for the preparation of the N-phenyloxamate proligands

The proligands as ethyl esters were prepared through the following synthetic procedure: the corresponding aniline derivative

Table 4
Heck coupling reactions of aryl halides and olefins mediated by **1b** in n-Bu_4NBr.



Entry[a]	R^1	X	Olefin	Pd-catalyst	Yield[b] (%)	TON (mol product mol^{-1} Pd)
1	H	I		1b	99	100
2	H	I		1b	64	64
3	H	I	CN	1b	61	60
4	H	I		1b	69	70
5	CN	I		1b	99	100
6	CH_3	I		1b	99	100
7	$COCH_3$	I		1b	99	100
8	OCH_3	I		1b	99	100
9	$COOCH_3$	I		1b	99	98
10	H	Br		1b	99	100
11	H	Br		1b	99	100
12	CH_3	Br		1b	99	100
13	CH_3	Br		1b	99	100
14	H	Br		$PdCl_2$	0	0
15	H	Br		$Pd(OAc)_2$	15	18
16	H	Br		$Pd(dba)_2$	74	75

[a] Reaction conditions: 0.5 mmol of aryl halide 0.75 mmol of olefin, 2 equiv of Et_3N, 1 mol% **1b**, 2 g of n-Bu_4NBr, 30 min.
[b] Determined by GC–MS using diethyleneglycol-di-n-butyl ether as internal standard.

(83 mmol) was dissolved in THF (250 mL) under a dinitrogen atmosphere in a two round flask equipped with a condenser and subsequently treated with ethyl chlorooxoacetate (9.3 mL, 83 mmol) in the presence of triethylamine (12 mL, 83 mmol) at room temperature under continuous stirring for 30 min. The resulting solution was filtered and the solvent was removed under vacuum to afford an oily colourless crude, which quickly becomes solid. The white solid was suspended into water and filtered off, then washed with a small amount of diethyl ether and dried under vacuum.

4.2.1. N-2-Methylphenyloxamate proligand

Yield: 95%; IR (KBr/cm^{-1}): $\bar{\nu}$ = 3216 (N–H), 3033, 2983, 2920 (C–H), 1735, 1699 (C=O); ^1H NMR ($CDCl_3$) δ(ppm): 1.35–1.42 (t, 3H, CH_3), 2.31 (s, 6H, CH_3), 4.39–4.48 (q, 2H, CH_2), 7.11–7.19 (m, 1H, $H_{aromatics}$), 7.21–7.30 (m, 2H, $H_{aromatics}$), 7.9–8.0 (d, 1H, $H_{aromatics}$), 8.83 (s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ(ppm): 14.41, 17.74, 64.13, 122.31, 127.31, 128.82, 130.79, 134.78, 154.31, 161.57; elemental analysis calculated (%) for $C_{11}H_{13}NO_3$ (207 g/mol): C 63.76, H 6.32, N 6.76; found: C 62.48, H 7.64, N 6.71.

4.2.2. N-4-Methylphenyloxamate proligand

Yield: 95%; IR (KBr/cm^{-1}): $\bar{\nu}$ = 3338 (N–H), 3120, 2978, 2908 (C–H), 1732, 1705 (C=O); ^1H NMR (DMSO-d_6) δ(ppm): 1.28–1.33 (t, 3H, CH_3), 2.27 (s, 3H, CH_3), 4.28–4.31 (q, 2H, CH_2), 7.14–7.14 (d, 2H, $H_{aromatics}$), 7.61–7.64 (d, 2H, $H_{aromatics}$), 10.68 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ(ppm): 14.19, 20.85, 62.67, 120.76, 129.50, 134.20, 135.32, 155.74, 161.14; elemental analysis calculated (%) for $C_{11}H_{13}NO_3$ (207 g/mol): C 63.76, H 6.32, N 6.76; found: C 63.36, H 6.04, N 6.77.

4.3. General procedure for the preparation of the bis(oxamato) palladate(II) complexes

A general synthetic method for the preparation of the bis(oxamato)palladate(II) complexes is described as follows: a 1.0 M

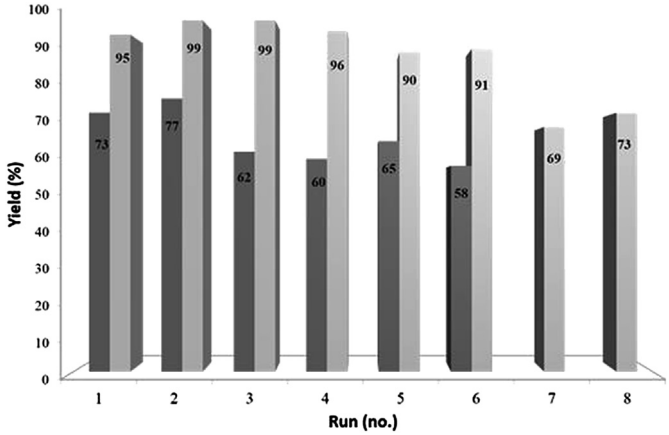


Fig. 3. Histogram of the recycling experiments of the Suzuki reaction (black) of iodobenzene with phenylboronic acid (black) and of the Heck reaction of iodobenzene and ethyl acrylate (grey) by using **1a** and **1b**, respectively.

methanolic solution of n-Bu_4NOH (1.5 mL, 1.2 mmol) was added directly to a suspension of the corresponding oxamate-aniline proligand (0.6 mmol in 10 mL of acetonitrile) in a two-neck round flask under continuous stirring. Then, an aqueous solution of K_2PdCl_4 (100 mg, 0.30 mmol) was added dropwise to the resulting solution and the reaction mixture was heated at 60 °C under N_2 for 10 h. The resulting mixture was filtered and the volume reduced under vacuum. The remaining concentrated solution was washed with diethyl ether to remove the unreacted ligand and subsequently treated three times with dichloromethane to extract the complex from the aqueous solution. The addition of n-hexane to the dichloromethane solution affords the complex as a pale yellow powder which was collected by filtration and dried in the open air.

4.3.1. (n-$Bu_4N)_2$[Pd(N-2-methylphenyloxamate)$_2$]·$4H_2O$ (**1a**)

Yield: 86%; IR (KBr/cm^{-1}): $\bar{\nu}$ = 3423 (O–H), 2961, 2930, 2874 (C–H), 1669, 1647, 1618, 1590 (C=O); ^{1}H NMR ($CDCl_3$) δ(ppm): 1.00–1.02 (t, 24H), 1.40–1.42 (m, 16H, n-Bu_4N^+), 1.51–1.59 (m, 16H, n-Bu_4N^+), 2.17 (s, 6H, CH_3), 3.18–3.24 (m, 16H, n-Bu_4N^+), 7.16–7.19 (m, 8H, $H_{aromatics}$); elemental analysis calculated (%) for $C_{50}H_{94}N_4O_{10}Pd$ (**1a**) (1018 g/mol): C 59.01, H 9.31, N 5.51; found: C 61.18, H 9.96, N 5.44. X-ray quality crystals of **1a** of formula (n-$Bu_4N)_2$[Pd(N-2-methylphenyloxamate)$_2$]·4MeCN were grown by slow vapour diffusion of ether into an acetonitrile solution of the palladium(II) complex.

4.3.2. (n-$Bu_4N)_2$[Pd(N-4-methylphenyloxamate)$_2$]·$2H_2O$·MeCN (**1b**)

Yield: 95%; IR (KBr/cm^{-1}): $\bar{\nu}$ = 3422 (O–H), 2961, 2930, 2874 (C–H), 1658, 1617, 1588, 1540 (C=O); ^{1}H NMR ($CDCl_3$) δ(ppm): 0.92–0.95 (t, 24H), 1.33–1.36 (m, 16H, n-Bu_4N^+), 1.48–1.52 (m, 16H, n-Bu_4N^+), 1.89 (s, 6H, CH_3), 3.07–3.13 (m, 16H, n-Bu_4N^+), 6.32–6.35 (d, 2H, $H_{aromatics}$), 6.43–6.46 (d, 2H, $H_{aromatics}$), 6.87–6.90 (d, 2H, $H_{aromatics}$), 7.00–7.02 (d, 2H, $H_{aromatics}$); elemental analysis calculated (%) for $C_{52}H_{93}N_5O_{10}Pd$ (**1b**) (1023 g/mol): C 61.07, H 9.17, N 6.85; found: C 61.55, H 10.31, N 6.35. X-ray quality crystals of **1b** of formula (n-$Bu_4N)_2$[Pd(N-4-methylphenyloxamate)$_2$]·4MeCN were grown by slow vapour diffusion of ether into an acetonitrile solution of the palladium(II) complex.

4.4. General catalytic procedures and recycling of catalysts

4.4.1. General procedure for the Suzuki reaction

A test-tube with screw cap and valve was charged with a magnetic stir bar, the pre-catalyst 5 mol% Pd, the aryl halide (0.50 mmol), NEt_3 (1.00 mmol), the aryl boronic acid (0.75 mmol) and 2–3 g of the ionic liquid. The mixture was heated under continuous stirring during 120 min at 120 °C for n-Bu_4NBr and in the range of temperature 80–120 °C for the other ionic liquids, namely n-Bu_4NCl, BMIMBr and $BIMIMPF_6$. The reaction was monitored by using thin liquid chromatography on silica gel. The reaction mixture was cooled and extracted with 5 mL of n-pentane. The products were examined by GC–MS, purified by column chromatography and finally characterized by ^{1}H NMR, ^{13}C NMR and ^{13}C NMR-Dept.

4.4.2. General procedure for the Heck reaction

A test-tube with screw cap and valve was charged with a magnetic stir bar, the pre-catalyst 1 mol % Pd, the aryl halide (0.50 mmol), NEt_3 (1.00 mmol), the olefin (0.75 mmol) and 2–3 g of the ionic liquid. The reaction was heated under continuous stirring during 30 min at 120 °C for n-Bu_4NBr and in the temperature range 80–120 °C for the other ionic liquids, namely n-Bu_4NCl, BMIMBr and $BIMIMPF_6$. The reaction was monitored using thin liquid chromatography on silica gel. Workup was identical to that described above for the Suzuki reaction.

4.4.3. Procedure for catalyst recycling

The catalysis was performed as described above. After completion of the reaction, the mixture was cooled and extracted with 5 mL of n-pentane. The products had to be prevented from early solidification by using a heat gun. The remaining ionic solvent containing the palladium(II) catalyst was charged once again with fresh aryl halide and the corresponding aryl boronic acid or olefin for further catalytic runs. The products were examined by GC–MS. Further purification of the products was performed by flash column chromatography.

4.5. Procedure for the analysis of the catalyst leaching

The isolated products of the first and final catalytic run of each protocol were analysed by ^{1}H NMR and FT-IR spectroscopy to check the presence of typical signals and bands of the palladium(II) pre-catalysts. The isolated dried products were also analyzed by SEM-Edax microscopy to verify the absence of palladium traces.

4.6. Crystal data collection and refinement

X-ray diffraction data on single crystals of **1a** and **1b** as acetonitrile solvates were collected with a Bruker–Nonius X8APEXII CCD area detector diffractometer. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. The data were processed through the SAINT [21] reduction and SADABS [22] absorption software. A summary of the crystallographic data and structure refinement for the two compounds is given in Tables S1 and S2.

The structures were solved by Patterson and subsequently completed by Fourier recycling using the SHELXTL software package [23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the counter ions as well as those of the solvent molecules were set in calculated positions and refined as riding. The final full-matrix least-squares refinements on F^2, minimizing the function $\sum w(|F_o| - |F_c|)^2$, reached convergence with the values of the discrepancy indices given in Tables S1 and S2. In particular, there is a high electronic residual density for **1a** which is located near the carbon atoms of the $[(n\text{-}C_4H_9)_4N]^+$ cations as a consequence of a static disorder that affect them.

The final geometrical calculations were carried out with the PARST [24] program whereas the graphical manipulations were performed with the XP utility of the SHELXTL system. Interatomic bond lengths and angles are listed in Tables S3 and S4.

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Appendix A. Supplementary material

CCDC 902499, 902500 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.06.041.

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