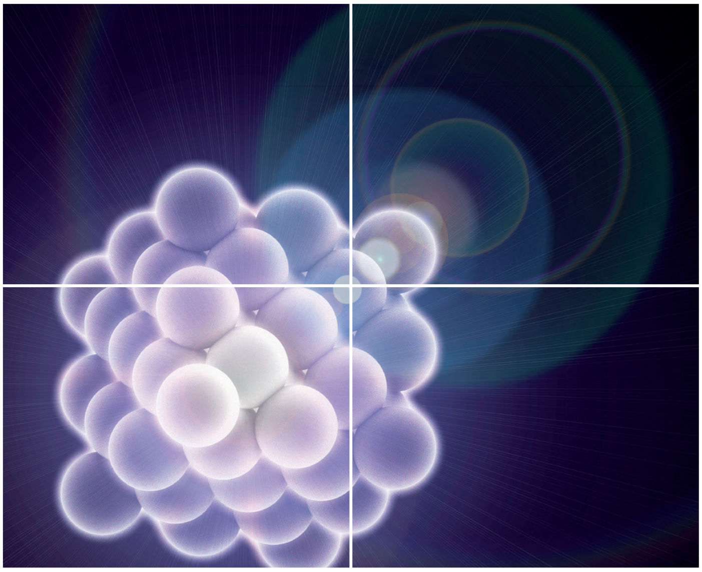
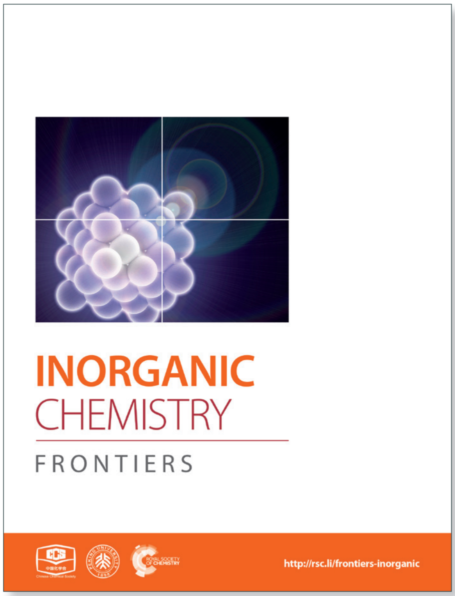
INORGANIC CHEMISTRY
FRONTIERS



Accepted Manuscript



中国化学会
Chinese Chemical Society
PEKING UNIVERSITY 1898
ROYAL SOCIETY OF CHEMISTRY
http://rsc.li/frontiers-inorganic

Bis(*N*-substituted oxamate)palladate(II) complexes as effective catalysts for sustainable Heck carbon-carbon coupling reactions in *n*-Bu_4NBr as solvent†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Francisco Ramón Fortea-Pérez,[a] Berit L. Rothenpieler,[a] Nadia Marino,[b] Donatella Armentano,[b] Giovanni De Munno,[b] Miguel Julve*[a] and Salah-Eddine Stiriba*[a,c]

Five bis(oxamato)palladate(II) complexes of formula (n-$Bu_4N)_2$[Pd(4-Fpma$)_2$] (**1**), (n-$Bu_4N)_2$[Pd(4-Clpma$)_2$] (**2**), (n-$Bu_4N)_2$[Pd(4-Brpma$)_2$] (**3**), (n-$Bu_4N)_2$[Pd(4-Brpma$)_2$] $\cdot$ H_2O (**3a**), n-$Bu_4N)_2$[Pd(4-MeOpma$)_2$] (**4**) and (n-$Bu_4N)_2$[Pd(4-Isopma$)_2$] (**5**) (n-Bu_4N^+ = tetra-*n*-butylammonium, 4-Fpma = *N*-4-fluorophenyloxamate, 4-Clpma = *N*-4-clorophenyloxamate, 4-Brpma = *N*-4-bromophenyloxamate, 4-MeOpma = *N*-4-methoxyphenyloxamate and 4-isopma = *N*-4-isopropylphenyloxamate) have been easily prepared and characterized by spectroscopic methods and the crystal structures of two of them (**3a** and **4**) have been determined by single crystal X-ray diffraction. Each palladium(II) ion in **3a** and **4** is four-coordinate with two oxygen and two nitrogen atoms from two fully deprotonated oxamate ligands building a centrosymmetric square planar PdN_2O_2 surrounding. The values of the Pd-N and Pd-O bond lengths vary in the ranges 2.034(3)-2.043(4) and 1.999(4)–2.013(3) Å, respectively. The reduced bite of the chelating oxamate ligands [81.3(2)-81.7(1) (**3a**) and 81.61(7)º (**4**)] is at the origin of the mean distortion of the ideal square environment. The catalytic role of compounds **1**-**5** as structurally well-defined precatalysts for the Heck-vinylation of a series of aryl iodide/bromide derivatives in n-Bu_4NBr as a benign nonaqueous ionic liquid (i.d. molten salt) has been examined and compared to some commercially available palladium(II/0) complexes. From this study, it appears that the oxamate-containing precatalysts **1**-**5** are not just ecologically benign, but also highly efficient, easily recoverable and reusable at least eight times without any relevant loss of catalytic activity or leaching from the ionic liquid medium.

Introduction

The synthetic method based on metal-catalyzed cross-coupling reactions where the substitution of an aryl, vinyl and alkyl halide/pseudohalide by a nucleophile takes place has been subject of thorough investigation since the early 1970's.[1,2] These impressive worldwide research efforts were rewarded with the Nobel Prize in chemistry to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki, in 2010.[3] One of the main reasons to pursue this type of chemistry is its great impact on the chemical industry and relevance for the design of new ligands, with consequences on other frontier research fields including supramolecular and polymer chemistry, molecular magnetism, bioinorganic chemistry, materials science, etc.[4,5]

A good number of palladium-based systems with excellent catalytic performances in carbon-carbon cross-coupling reactions has been developed during the last five decades, their efficiency being largely examined. Without being exhaustive, representative examples are those with phosphine ligands,[6] palladacycle catalysts,[7] *N*-heterocyclic carbene-containing catalysts (NHCs),[8] nanoparticles[9] and immobilized palladium catalysts[10] in both homogenous and heterogenous regimes. It deserves to be noted that, in most cases, the activity of homogeneous catalysts was found to be higher than that of their heterogenous analogues.[11]

Nowadays, the search for new, ecologically benign procedures of the carbon-carbon cross-coupling type is still a challenge. These are some of the main conditions to be fulfilled: (i) low catalyst amount (ii) high catalyst activity and selectivity, (iii) mild reaction conditions for energy costs saving and (iv) efficient catalyst recycling and reuse with regular yields over a large number of runs. Keeping this in mind, part of our current research endeavours have focused onto the design and use of simple, cheap, and recyclable palladium(II)-based active catalysts together with environment-friendly green solvents. In this context, we bet on ionic liquids as alternative green solvents,[12] in particular on the tetra-*n*-butylammonium bromide (n-Bu_4NBr), a widely used molten salt.[13] This appears as an appropriate medium for our anionic bis(*N*-substituted oxamate)palladate(II) systems (*vide infra*), especially for the presence of the same cation in our palladium(II) systems and for electrostatic/stability reasons.[14] By performing cross-coupling Heck reactions following an alternative green catalytic route with no ecologically harmful chemicals (phosphine ligands for instance) and avoiding difficult-to-handle carbene ligands, our idea to employ low-cost, versatile *N,O* ligands[15] to build new catalytic systems seems advantageous as both sustainable synthetic organic methodology and suitable strategy for catalyst recovery.[12i,16] Noteworthy, chelating ligands containing oxygen or nitrogen as donor atoms have been shown to stabilize palladium complexes.[17]

---

[a] *Instituto de Ciencia Molecular (ICMol), Universitat de València, C/ Catedrático José Beltrán 2, 46980 Paterna (València), Spain. E-mail: miguel.julve@uv.es, stiriba@uv.es*
[b] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036 Rende, Cosenza, Italy. E-mail: donatella.armentano@unical.it*
[c] *Equipe de Chimie Moléculaire, Matériaux et Modélisation – C3M, Faculté Polydisciplinaire de Safi, Université Cadi Ayyad, Safi, Morocco*

† Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format, detailed synthesis of the proligands, stability of the precatalyst in water (Fig. S1), data of palladium-catalyzed Heck C-C coupling reactions (Tables S1-S4) and ^{1}H-NMR, ^{13}C-NMR and Dept-135-NMR of the catalytic products (Figs. S2-S8). See DOI: 10.1039/x0xx00000x

Apart from their interest in magnetic studies as diamagnetic spacers to build heterometallic compounds,[18] oxamate-containing palladium(II) complexes exhibit cytotoxic activity against leukemia[19] and they have also shown catalytic activity for the palladium-catalyzed Suzuki and Heck reactions.[14,20] Focusing on their interest in catalysis, the present work deals with the design and spectroscopic characterization of new five bis(oxamato)palladate(II) complexes of formula $(n\text{-}Bu_4N)_2[Pd(4\text{-}Fpma)_2]$ (**1**), $(n\text{-}Bu_4N)_2[Pd(4\text{-}Clpma)_2]$ (**2**), $(n\text{-}Bu_4N)_2[Pd(4\text{-}Brpma)_2]$ (**3**), $(n\text{-}Bu_4N)_2[Pd(4\text{-}Brpma)_2] \cdot H_2O$ (**3a**), $(n\text{-}Bu_4N)_2[Pd(4\text{-}MeOpma)_2]$ (**4**) and $(n\text{-}Bu_4N)_2[Pd(4\text{-}Isopma)_2]$ (**5**) ($n\text{-}Bu_4N^+$ = tetra-*n*-butylammonium, 4-Fpma = *N*-4-fluorophenyloxamate, 4-Clpma = *N*-4-clorophenyloxamate, 4-Brpma = *N*-4-bromophenyloxamate, 4-MeOpma = *N*-4-methoxyphenyloxamate and 4-isopma = *N*-4-isopropylphenyloxamate), the X-ray structure of **3a** and **4** and the catalytic activity/recycling of **1**-**5** in the Heck cross-coupling reaction of aryl iodine/bromide derivatives with olefins using $n\text{-}Bu_4NBr$ ionic liquid as solvent.

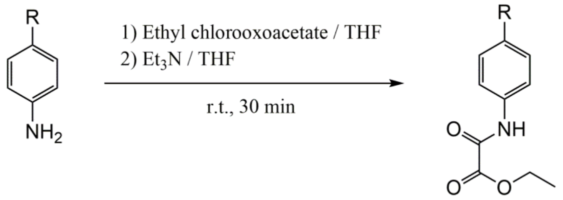
Experimental section

Material and general characterization

Aniline derivatives, $K_2[PdCl_4]$, $[Pd_3(OAc)_6]$, $[PdCl_2]$, $n\text{-}Bu_4NOH$, ethyl chlorooxalate and all the solvents for the syntheses were purchased from commercial sources and used without further purification. $[Pd(bda)_2]$ (bda = dibenzylideneacetone) was prepared as previously reported.[21] Infrared samples were prepared as KBr pellets, and spectra were performed in the 4000-450 cm^{-1} range using a Nicolet 5700 FT-IR instrument. ^1H- and ^{13}C-NMR spectra were recorded on an Avance DRX 300 Bruker instrument at room temperature and referenced to the residual proton in the solvent for ^1H NMR and the same solvent ^{13}C signal for ^{13}C NMR. The elemental analysis (C, H and N) was carried out on a EuroEA3000 analyzer by the Servei Central d'Instrumentació Científica at the University of Jaume I. The value of the Pd:Cl (**2**) and Pd:Br (**3**) molar ratio (1:2) was determined through electron probe X-ray microanalysis by using a Philips XL-30 scanning electron microscope (SEM) from the Central Service for Support to Experimental Research (SCSIE) at the University of Valencia. All GC-MS spectra were performed on an Agilent 6890N gas chromatograph equipped with capillary columns from the SCSIE at the University of Valencia, using perfluorotributylamine (PFTBA) as internal standard.

Synthesis of the proligands

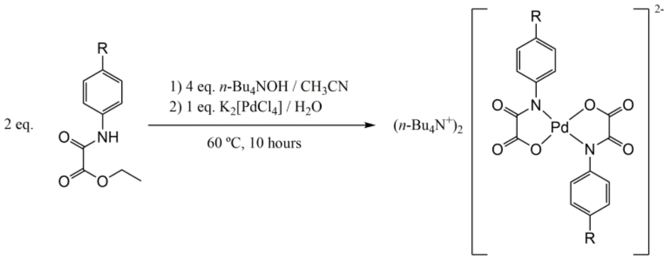
The preparation of the proligands as ethyl esters was carried out by following the procedure shown in Scheme 1. The corresponding derivative of aniline (83 mmol) was dissolved in THF (250 mL) under nitrogen atmosphere in a two neck round flask equipped with a dropping funnel and a stirring bar. The solution was treated with ethyl chloroacetate (9.3 mL, 83 mmol) in the presence of triethylamine (12 mL, 83 mmol) at room temperature under continuous stirring for 30 minutes. The white Et_3NCl precipitate was separated by filtration and the remaining pale yellow solution was removed under vacuum to afford an oily crude that rapidly became solid. The obtained white solid was suspended in water and filtered off, washed with a small amount of diethyl ether and dried under reduced pressure. Details of the yield and spectroscopic characterization are given in the ESI.



Scheme 1. Preparative route of the proligands: R = F, Cl, Br, MeO and Isopropyl for EtH-4-Fpma, EtH-4-Clpma, EtH-4-Brpma, EtH-4-MeOpma and EtH-4-Isopma, respectively.

Synthesis of the complexes 1-5

The general synthetic method for the *bis*(*N*-substituted oxamato)palladate(II) complexes-**1**-**5** is depicted in Scheme 2:



Scheme 2. Preparative route of the bis(*N*-substituted oxamato)palladate(II) complexes.

A methanolic solution of $n\text{-}Bu_4NOH$ (1.0 M, 1.5 mL, 1.2 mmol) was added directly to a two-neck round flask equipped with a condenser containing a suspension of the corresponding *N*-substituted oxamate proligand (0.6 mmol) in 10 mL of acetonitrile at 60 °C. Then, an aqueous solution of $K_2[PdCl_4]$ (100 mg, 0.3 mmol) was added dropwise to the resulting solution and the reaction mixture was heated at 60 °C for 10 hours. The obtained mixture was filtered and the acetonitrile was removed under reduced pressure. Dichloromethane (three times, 15 mL) was added to extract the complex from the aqueous solution. The recovered organic fractions were combined and concentrated under reduced pressure to afford a pale yellow solid. This solid was washed with *n*-hexane, collected by filtration and dried under vacuum. X-ray quality crystals as pale yellow prisms were grown for **3** (as **3a**) and **4** by two different methods: slow vapor diffusion of ether into an acetonitrile solution (**3a**) or slow evaporation at room temperature of a water/acetonitrile mixture (2:1 v/v) (**4**) where a fraction of the corresponding solid was dissolved. The crystals of **3a** appeared overnight whereas those of **4** were grown after two weeks.

$(n\text{-}Bu_4N)_2[Pd(4\text{-}Fpma)_2]$ (1): Yield: 54 %; IR (KBr/cm^{-1}): 3423 (O-H), 2961, 2933, 2875 (C–H), 1671, 1655, 1619, 1586 (C=O); ^1H NMR ($CDCl_3$) δ (ppm): 0.90 – 0.94 (t, J = 7.2 Hz, 24H, *n*-

Bu$_4$N$^+$), 1.24 – 1.46 (m, *J* = 7.0 Hz, *J*= 6.9 Hz, 32H, *n*-Bu$_4$N$^+$), 2.93 – 2.99 (t, *J* = 13.1 Hz, *J*= 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 6.63 – 6.66 (d, *J* = 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$), 7.27 – 7.30 (d, *J* = 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$). Anal. Calcd for $C_{48}H_{80}F_2N_4O_6Pd$ (954 g mol^{-1}): C 60.46, H 8.46, N 5.88. Found: C 60.23, H 8.27, N 5.79 %.

(*n*-Bu$_4$N)$_2$[Pd(4-Clpma)$_2$] (2): Yield: 51 %; IR (KBr/cm^{-1}): 3423 (O-H), 2961, 2930, 2874 (C–H), 1671, 1655, 1619, 1582 (C=O); ^{1}H NMR (CDCl$_3$) δ (ppm): 0.91–0.96 (t, *J* = 7.2 Hz, 24H, *n*-Bu$_4$N$^+$), 1.28 – 1.40 (m, *J* = 7.0 Hz, *J*= 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 1.46 – 1.56 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 3.08 – 3.14 (t, *J* = 13.1 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 7.02 – 7.05 (d, , 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$), 7.33 – 7.36 (d, , *J* = 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$). Anal. Calcd for $C_{48}H_{80}Cl_2N_4O_6Pd$ (987 g mol^{-1}): C 58.44, H 8.17, N 5.68. Found: C 58.32, H 8.05, N 5.61 %.

(*n*-Bu$_4$N)$_2$[Pd(4-Brpma)$_2$] (3): Yield: 47 %; IR (KBr/cm^{-1}): 3422 (O-H), 2961, 2933, 2874 (C–H), 1671, 1648, 1606, 1577 (C=O); ^{1}H NMR (CDCl$_3$) δ (ppm): 0.90 – 0.95 (t, *J* = 7.2 Hz, 24H), 1.26 – 1.38 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 1.41 – 1.52 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 3.01 – 3.07 (t, , *J* = 13.1 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 6.75 – 6.81 (t, *J* = 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$), 7.31 – 7.36 (m, *J* = 8.9 Hz, *J* = 2.9 Hz, 4H, H$_{aryl}$). Anal. Calcd for $C_{48}H_{80}Br_2N_4O_6Pd$ (1075 g mol^{-1}): C 53.61, H 7.50, N 5.21. Found: C 53.48, H 7.41, N 5.15 %. X-ray quality crystals of (*n*-Bu$_4$N)$_2$[Pd(4-Brpma)$_2$] $\cdot$ H$_2$O **(3a)** as pale yellow prisms were grown overnight by slow vapor diffusion of ether into an acetonitrile solution of a solid sample of **3** and its stoichiometry was determined by X-ray diffraction on single crystals.

(*n*-Bu$_4$N)$_2$[Pd(4-MeOpma)$_2$] (4): Yield: 50 %; IR (KBr/cm^{-1}): 3422 (O-H), 2960, 2930, 2874 (C–H), 1667, 1647, 1610 (C=O); ^{1}H NMR (CDCl$_3$) δ (ppm): 0.97 – 1.02 (t, *J* = 7.2 Hz, 24H, *n*-Bu$_4$N$^+$), 1.35 – 1.47 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 1.50 – 1.60 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 3.11 – 3.17 (t, *J* = 13.1 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 3.73 (s, 6H, OCH$_3$), 6.71 – 6.74 (d, *J* = 8.8 Hz, *J* = 2.8 Hz, 4H, H$_{aryl}$), 7.37 – 7.40 (d, *J* = 8.8 Hz, *J* = 2.8 Hz, 4H, H$_{aryl}$). Anal. Calcd for (978 g mol^{-1}): C 61.43, H 8.87, N 5.73. Found: C 61.28, H 8.71, N 5.65 %. Single crystals of **4** as pale yellow prisms were grown by slow evaporation at room temperature of a water/acetonitrile (2:1 v/v) mixture where the obtained solid was dissolved. The crystals of **4** appeared within 2-4 weeks.

(*n*-Bu$_4$N)$_2$[Pd(4-Isopma)$_2$] (5): Yield: 52 %; IR (KBr/cm^{-1}): 3422 (O–H), 2959, 2933, 2873 (C–H), 1669, 1648, 1619, 1597 (C=O); ^{1}H NMR (CDCl$_3$) δ (ppm): 0.97 – 1.02 (t, *J* = 7.2 Hz, 24H, *n*-Bu$_4$N$^+$), 1.19 – 1.21 (d, *J* = 7.0 Hz, 12H, CH$_3$), 1.36 – 1.48 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 1.52 – 1.62 (m, *J* = 7.0 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 2.76 – 2.85 (m, 2H, CH), 3.15 – 3.21 (t, *J* = 13.1 Hz, *J* = 6.9 Hz, 16H, *n*-Bu$_4$N$^+$), 7.02 – 7.05 (d, *J* = 8.8 Hz, *J* = 2.8 Hz, 4H, H$_{aryl}$), 7.35 – 7.38 (d, 8.8 Hz, *J* = 2.8 Hz, 4H, H$_{aryl}$). Anal. Calcd for $C_{54}H_{94}N_4O_8Pd$ (1002 g mol^{-1}): C 64.74, H 9.46, N 5.59. Found: C 64.55, H 9.31, N 5.42 %.

General procedure for the Heck reaction and recycling of catalysts

A test-tube with screw cap and valve was charged with a magnetic stir bar and loaded with the precatalyst 0.25-0.5 mol%, the aryl halide (0.50 mmol), Et$_3$N (1.00 mmol) the olefin (0.75 mmol), and 3–4 g of *n*-Bu$_4$NBr. The mixture was heated under continuous stirring for a given time at 120 °C. The reaction was monitored by thin layer chromatography on silica gel. The reaction mixture was cooled and extracted with 5 mL of *n*-pentane. After the first extraction, the test-tube containing the palladium(II) catalyst in the ionic solvent was charged again with a fresh portion of aryl halide (0.50 mmol), Et$_3$N (1.00 mmol) and the olefin (0.75 mmol) to start another run (a minimum of 3 runs and a maximum of 8 runs were performed). Each extract was characterized by gas chromatography-mass spectrometry (GC-MS). The catalytic products were purified by column chromatography and characterized by ^{1}H, ^{13}C and Dept-135 NMR spectroscopy. Yields were determined by GC-MS analysis using perfluorotributylamine as internal standard. The isolated products of the first and final catalytic run of each protocol were analyzed by ^{1}H NMR and FT-IR spectroscopy to check the presence of typical signals and bands of the palladium(II) precatalysts. The lack of palladium traces in the isolated dried products was verified by SEM-Edax microscopy.

X-ray crystallography

X-ray diffraction data on single crystals of **3a** and **4** were collected with a Bruker-Nonius X8-APEXII CCD area detector system by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were processed through the SAINT[22] reduction and SADABS[23] absorption software. A summary of the crystallographic data and structure refinement for the two compounds is given in Table 1. The structures of **3a** and **4** were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL-2013 software package,[24] then refined by the full-matrix least-squares refinements based on F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the tetra-*n*-butylammonium cation and those of the *N*-substituted oxamate ligands were included at geometrically calculated positions and refined using a riding model. In **3a**, one of the *n*-Bu$_4$N$^+$ cations was found disordered; two sets of atoms where defined for it, whose relative occupancy reached values of about 0.7 and 0.3 at convergence. The disorder was refined with the aid of similarity restraints on 1,2- and 1,3 distances as well as rigid-bond restraints, by using established methods.[25] Disordered water molecules of crystallization were also found in **3a**; five partially occupied sites were defined, for a total of one water molecule per Pd atom. These sites [O(1w), O(2w), O(2wA), O(3w) and O(3wA),] were only refined isotropically. The final geometrical calculations were performed using the XP utility within SHELXTL[24] whereas the graphical manipulations were performed with the CrystalMaker software.[26] Selected bond lengths and angles are listed in Tables 2 (**3a**) and 3 (**4**).

CCDC reference numbers are 1402358 (**3a**) and 1402359 (**4**). Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for $(n\text{-}Bu_4N)_2[Pd(4\text{-}Brpma)_2] \cdot H_2O$ (**3a**) and $(n\text{-}Bu_4N)_2[Pd(4\text{-}MeOpma)_2]$ (**4**)

Compound	**3a**	**4**
Formula	$C_{144}H_{246}Br_6N_{12}O_{21}Pd_3$	$C_{50}H_{86}N_4O_8Pd$
fw	3280.17	977.62
Crystal system	Triclinic	Monoclinic
Space group	*P(–1)*	$P2_1/c$
a/Å	13.524(2)	9.7928(5)
b/Å	16.287(3)	16.3297(8)
c/Å	20.967(3)	16.0978(8)
α/ deg	100.901(8)	90
β/deg	103.304(8)	95.392(2)
γ/ deg	99.809(8)	90
V/Å^3	4301.1(13)	2562.9(2)
Z	1	2
D_c/g cm^{-3}	1.266	1.267
T/K	296(2) K	100(2)
μ/mm^{-1}	1.763	0.416
F(000)	1710	1048
Refl. collected	88674	60847
Refl. indep. [R_{int}]	18125 (0.0508)	5228 (0.0661)
Refl. obs. [$I > 2\sigma(I)$]	9794	5228 (0.0661)
Data/restraints/param.	18125/808/1006	5228 / 0 / 286
Goodness-of-fit on F^2	1.005	1.200
R_1[a] [$I > 2\sigma(I)$] (all)	0.0587 (0.1231)	0.0329 (0.0453)
wR_2[b] [$I > 2\sigma(I)$] (all)	0.865/-0.487	0.0830 (0.0957)
$\Delta\rho_{max,\,min}$/e Å^{-3}	0.841/-0.499	0.461/-0.895

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2\}^{1/2}$ and $w = 1/[\sigma^2(F_o)^2 + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$, m = 0.1225 (**3a**) and 0.0475 (**4**), and n = 0.0000 (**3a**) and 1.5167 (**4**).

Results and discussion

Synthesis and IR spectroscopy

The *N*-substituted oxamate proligands were easily prepared as the respective ethyl ester derivatives by the straightforward condensation of the ethyl chlorooxoacetate with the corresponding 4-halo- or 4-methoxoaniline in THF, in presence of Et_3N as a base at room temperature. They were isolated in very satisfactory yields (ca. 80–96 %). Their IR spectra exhibit a typical absorption peak at ca. 3000 – 3300 cm^{-1} for the N-H stretching vibration and two intense bands at ca. 1727 and 1677 cm^{-1} which are attributed to the stretching frequencies from the ester and amide groups, respectively^{1}H and ^{13}C NMR spectra support the presence of the N-H amide function as well as those corresponding to the ethyl ester group ($-CH_2CH_3$). The lack of the signals of the N-H amide and ethyl groups in the infrared spectra of the isolated complexes **1**-**5** together with the occurrence of two strong peaks at ca. 1638 and 1600 cm^{-1} support the deprotonation and hydrolysis of the proligands, resulting in the formation of *N*-substituted which is subsequently coordinated to the Pd(II) ions. The X-ray structures of **3a** and **4** (see below) fully support these spectroscopic evidences.

Description of the structures 3a and 4

Compounds **3a** and **4** crystallize in the triclinic space group *P*-1 and monoclinic space group $P2_1/c$ respectively, and their crystal structures consist of centrosymmetric $[Pd(4\text{-}Brpma)_2]^{2-}$ (**3a**) and $[Pd(4\text{-}MeOpma)_2]^{2-}$ (**4**) complex anions [Figs. 1 (**3a**) and 2 (**4**)], organic $n\text{-}Bu_4N^+$ cations (**3a** and **4**) and free water and methanol molecules (**3a**) , held together by electrostatic forces. Three crystallographic independent complex anions are present in the asymmetric unit of **3a** whereas only one occurs in **4**.

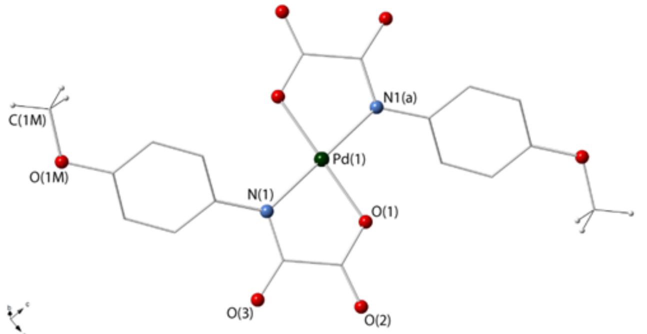


Fig. 1. A perspective view of the three crystallographically independent $[Pd(4\text{-}Brpma)_2]^{2-}$ units in **3a** showing the atom numbering [symmetry codes: (a) -*x*+1, -*y*+1, -*z*+1; (b) -*x*, -*y*, -*z*, (c) -*x*+2, -*y*+2, -*z*+1].

The palladium(II) ions in **3a** [Pd(1), Pd(2) and Pd(3)] and **4** [Pd(1)] are four-coordinate with two amidate-nitrogen and two carboxylate-oxygen atoms from two bidentate oxamate ligands at each metal centre building a centrosymmetric square-planar surrounding. The reduced bite of the bidentate oxamate [81.5(1), 81.7(1) and 81.3(2)° at Pd(1), Pd(2) and Pd(3) in **3a** and 81.61(7)° at Pd(1) in **4**] mainly accounts for the deviations from the ideal geometry. Each Pd(II) ion is located exactly in the plane of the four donor atoms for symmetry reasons. The Pd-N/Pd-O bond lengths [see Tables 2 (**3a**) and 3 (**4**)] compare well with those found in the oxamato-containing palladium(II) complexes $\{[Na(H_2O)]_2$*trans*-$[Pd(2,6\text{-}Me_2pma)_2]\}_n$ ($2,6\text{-}Me_2pma$ = *N*-2,6-dimethylphenyloxamate), $(n\text{-}Bu_4N)_2[Pd(2\text{-}Mepma)_2]\cdot 2H_2O$ (2-Mepma = *N*-2-methylphenyloxamate), $(n\text{-}Bu_4N)_2[Pd(4\text{-}Mepma)_2]\cdot 2H_2O\cdot MeCN$ (4-Mepma = *N*-4-methylphenyloxamate), $[Pd(H_2O)_4][Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$, $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2CHCl_3$, $Na[Pd(Hpba)]\cdot 2H_2O$ [H_4pba = 1,3-propylenebis(oxamic acid)], $K_2[Pd(opba)]\cdot 2H_2O$ [H_4opba = *N,N'*-1,2-phenylenebis(oxamic acid), $[Pd(NH_3)_4][Pd(opba)$ and $\{[K_4(H_2O)(dmso)][Pd_2mpba)_2]\}$ [H_4mpba = 1,3-phenylenebis(oxamic acid)] [average Pd-N/Pd-O distances of 2.020(1)/2.009(1), 2.0209(11)/2.0384(13), 2.0207(13)/2.0214(14), 2.023(3)/2.020(3), 2.03(2)/1.97(2), 1.970/2.040, 1.928/2.055, 1.942(10)/2.045(8) and 2.000(3)/2.026(2) Å, respectively].[14,18,19,20,27]

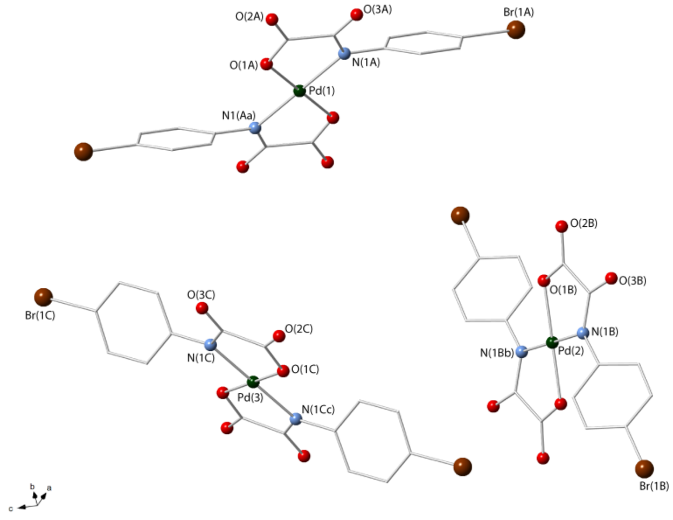


Fig. 2 Perspective view of the anionic $[Pd(4\text{-}MeOpma)_2]^{2-}$ entity in **4** showing the atom numbering [symmetry code: (a) = -*x*+2, -*y*, -*z*+2].

The values of the dihedral angle between the square plane at the palladium(II) ion and the mean plane of the oxamate groups (ϕ) are 6.53(8) [Pd(1)], 7.00(1) [Pd(2)] and 1.79(4)° [Pd(3)] in **3a** and 7.9(1)° in **4**, whereas those between each oxamate mean plane and the corresponding phenyl ring (Φ) are 53.8(2), 49.8(2) and 43.8(2)° [ligands A, B and C in Fig. 1] for **3a** and 31.67(6)° for **4**. The bond lengths of the peripheral C(1)-O(2) and C(2)-O(3) bond distances [values in the range 1.220(5)-1.255(4) Å (**3a**) and 1.225(3)-1.240(3) Å (**4**)] are somewhat shorter than the inner C(1)-O(1) bond [1.288(5)-1.294(5) Å (**3a**) and 1.302(3)Å (**4**)] in agreement with the greater double bond character of the free carbonyl groups.

Table 2. Selected bond distances (Å) and angles (deg) for **3a***

Pd(1)-N(1A)	2.034(3)	C(1A)-O(1A)	1.288(5)
Pd(1)-O(1A)	2.011(3)	C(1A)-O(2A)	1.228(5)
		C(2A)-O(3A)	1.255(5)
Pd(2)-N(1B)	2.038(3)	C(1B)-O(1B)	1.288(5)
Pd(2)-O(1B)	2.020(3)	C(1B)-O(2B)	1.228(5)
		C(2B)-O(3B)	1.238(4)
Pd(3)-N(1C)	2.046(4)	C(1C)-O(1C)	1.292(8)
Pd(3)-O(1C)	2.006(5)	C(1C)-O(2C)	1.221(8)
		C(2C)-O(3C)	1.255(7)
O(1A)-Pd(1)-N(1A)	81.5(1)	Pd(1)···Pd(2)	11.759(2)
O(1Aa)-Pd(1)-N(1A)	98.5(1)	Pd(1)···Pd(3)	9.658(1)
O(1B)-Pd(2)-N(1B)	81.7(1)	Pd(2)···Pd(3)	18.793(3)
O(1Bb)-Pd(2)-N(1B)	98.3(1)	Pd(3)···Pd(2d)	10.483(2)
O(1C)-Pd(3)-N(1C)	81.3(2)		
O(1Cc)-Pd(3)-N(1C)	98.7(2)		

*Symmetry codes used to generate equivalent atoms: (a) = -*x*+1, -*y*+1, -*z*+1; (b) = -*x*, -*y*, -*z*, (c) = -*x*+2, -*y*+2, -*z*+1.

The organic tetra-*n*-butylammonium cations in **3a** and **4** exhibit the usual tetrahedral geometry and their bond lengths and angles are as expected. The complex anions in **3a** are well-separated from each other by bulky $n\text{-}Bu_4N^+$ cations and they weakly interact through hydrogen bonds involving terminal oxygen atoms of the oxamate ligands and disordered water molecules of crystallizations (O···O separations varying in the range 2.70-3.17 Å) giving rise to a supramolecular 1-D motif developing along the crystallographic *a*-axis (Fig. 3a).

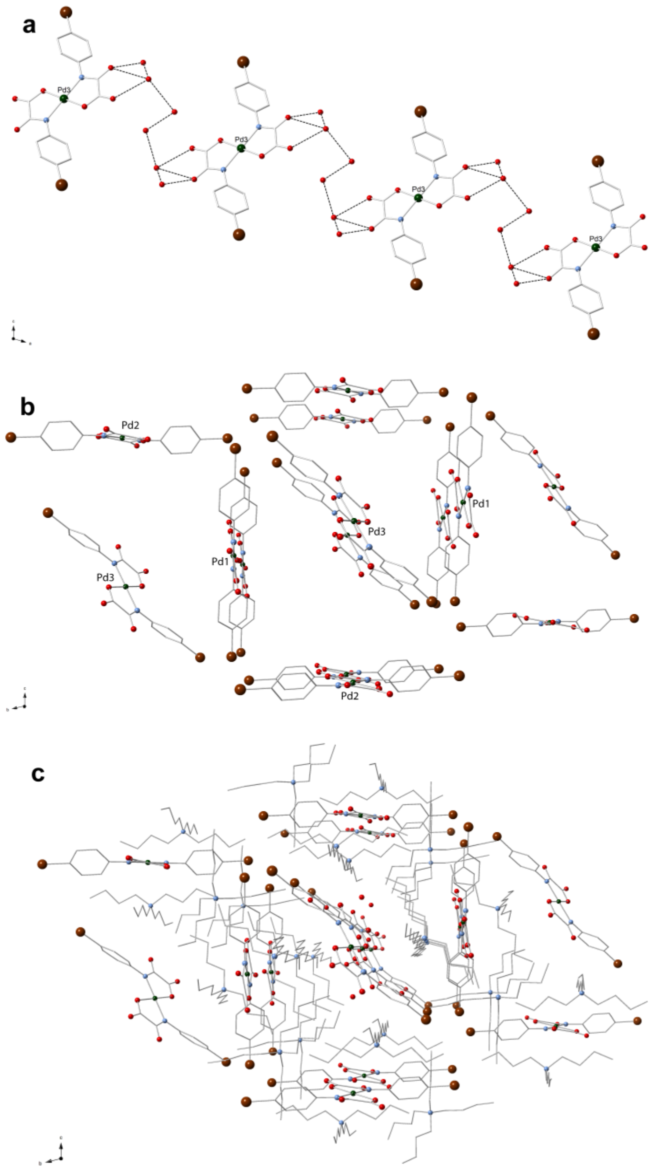


Fig. 3 (a) View along *b*-axis of the 1D supramolecular motif in **3a**. Projections of the crystal packing of **3a** along the crystallographic *a*-axis excluding **(b)** and including **(c)** the tetra-*n*-butylammonium cations.

The shortest values of the intermolecular palladium···palladium separation are 9.658(1) [Pd(1)···Pd(3)], 10.483(2) [Pd(3)···Pd(2d); symmetry code: (d) = *x*+1, *y*+1, *z*], 11.795(2) [Pd(1)···Pd(2)] and 18.793 Å [Pd(2)···Pd(3)]. In **4**, instead, the $[Pd(4\text{-}MeOpma)_2]^{2-}$ entities are pillared along the crystallographic *a* axis by means of weak C-H···O interactions and the cations are placed between the resulting anionic supramolecular columns.

Table 3. Selected bond distances (Å) and angles (deg) for **4***

Pd(1)-N(1)	2.044(2)	C(1)-O(1)	1.302(3)
Pd(1)-O(1)	2.003(2)	C(1)-O(2)	1.225(3)
		C(2)-O(3)	1.240(3)
O(1)-Pd(1)-N(1)	81.61(7)		
O(1a)-Pd(1)-N(1)	98.39(7)		

*Symmetry code used to generate equivalent atoms: (a) = -*x*+2, -*y*, -*z*+2.

The values of the shortest metal-metal separations in **4** are 9.7928(5) [Pd(1)···Pd(1b); (b) = *x*+1, *y*, *z*] and 11.4651(4) Å [Pd(1)···Pd(1c); (c) = -*x*+2, *y*-0.5, -*z*+1.5]. Views of fragments of the crystal packing of **3a** and **4** are given in Figs. 3 and 4, respectively.

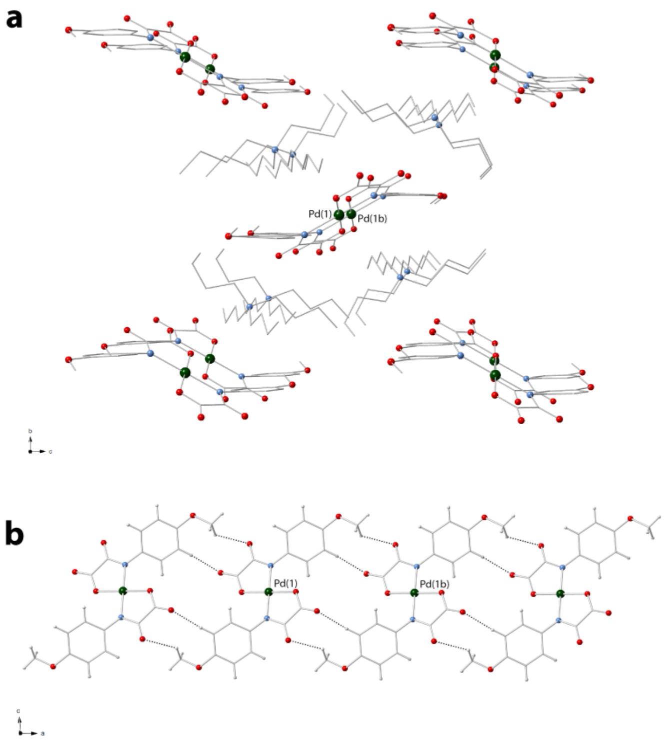


Fig. 4 (a) A projection of the crystal packing of 4 along the crystallographic a axis. **(b)** A view of a supramolecular column of the [Pd(4-MeOpma)$_2$]$^{2-}$ complex anions developing along the same direction.

Catalytic study

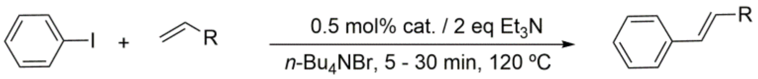
The bis(*N*-substituted oxamate)palladate(II) precatalysts **1**-**5** which exhibit different electron and steric properties have been checked for the Heck-vinylation of a series of aryl halides with various olefins using the ionic liquid *n*-Bu$_4$NBr as reaction medium. In this respect, it deserves to be noted that this ionic liquid has been previously used as an additive for this type of reactions, its role being qualified as essential.[28] In our case, the catalyst and solvent recovery and recycling is achieved by working with anionic bis(*N*-substituted oxamate)palladate(II) complexes in tetra-*n*-butylammonium bromide as a green solvent instead, not just an additive. We carried out the Heck reactions with 0.5 and 0.25 mol% of catalyst with Et$_3$N as base at the minimum temperature required for the *n*-Bu$_4$NBr to melt (120 °C). Very short reaction times were required to achieve high yields (see Tables 4 and S1). The catalytic activity of **1**-**5** was investigated by using a variety of aryl halides derivatives together with a selection of olefins and the obtained results improve previous findings of bis(*N*-substituted oxamate)palladate(II) in such carbon-carbon cross coupling reactions.[14]

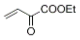
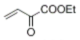
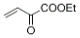
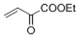
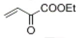
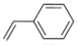
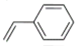
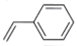
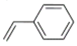
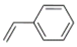
As shown in Table 4, high efficiency in recovery and recycling (at last 8 catalytic runs) are observed by using complexes **1**-**5** (0.5 mol%) for a Heck coupling of the active aryl iodides (0.5 mmol) and ethyl acrylate (0.75 mmol, entries 1-5) or styrene (0.75 mmol, entries 6-10) and Et$_3$N (1 mmol). A consistent yield value of 99% is achieved in each run for **1**-**5** with very short reaction times and satisfactory TOF values (5 minutes, entries 1-5 in Table 4; TOF ca. 2376 h^{-1}, see Table S1). Yields about 99% are also obtained by using a less activated olefin as styrene although only if the reaction time is increased (30 minutes, entries 6-10 in Table 4; TOF ca. 396 h^{-1}, see Table S1). These short reaction times and the green solvent used allow not only to work in mild reaction conditions but also to save energy costs.

When the amount of the catalyst is decreased from 0.5 to 0.25 mol%, the consistency of the measured yields in the vinylation of iodobenzene with ethyl acrylate is lost. However, in this case yields appear to be improved with the successive runs attaining values in the range 83-99% at the eighth run (see Tables S2). This demonstrates that the recovery and recycling of **1**-**5** happens without leaching phenomena. It deserves to be noted that reaction times of 5 min are kept with high TOF values (ca. 4800 h^{-1}).

The behaviour of complexes **1**-**5** when working with a less reactive aryl halide such as bromobenzene is shown in Tables 5 and S3. One can see therein the increase in the reactions times from 5 min (entries 1-5 in Table 4) to 3 hours (entries 1-5 in Table 5) using ethyl acrylate or from 30 minutes (entries 6-10 in Table 4) to 4 hours (entries 1-5 in Table 5) using the less active styrene. Moreover, in our reaction conditions, complexes **1**-**5** are more efficient than the commercial catalysts [PdCl$_2$] and [Pd$_3$(OAC)$_6$] and even [Pd(dba)$_2$][29] (entries 6-8 in Table 5). The fact that catalytic activity using bromobenzene (Table 5) is somewhat lower and more variable than that observed when using iodobenzene (Table 4) is due to the different dissociation energies of the C-Br and C-I bonds (81 and 65 kcal/mol, respectively).[30] An increase in the yield when using bromobenzene could be achieved by working at higher temperatures; however, we are limited by the decomposition temperature of the *n*-Bu$_4$NBr molten salt,[31] i. e. ca. 130 °C. Having reached this point, one may consider if thinking at energy costs and pursue green catalytic routes it is worth the effort to carry out the reaction with cheaper chemicals for 4 hours (bromobenzene and styrene; entries 6-10 in Table 5) *vs.* using more expensive materials during 30 minutes (iodobenzene and styrene; entries 9-13 in Table 4).

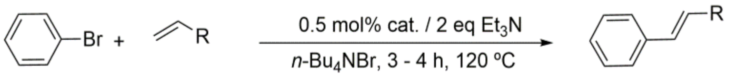
Table 4. Heck-vinylation of iodobenzene with olefins after different catalytic runs

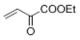
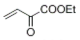
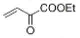
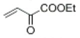
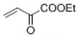
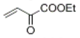
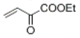
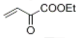
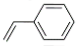
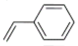
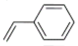
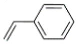
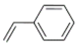


Entry[a]	Olefin	Cat.	Time (min)	Runs – Yield[b] (%)							
				1	2	3	4	5	6	7	8
1		**1**	5	99	99	99	99	99	99	99	99
2		**2**	5	99	99	99	99	99	99	99	99
3		**3**	5	99	99	99	99	99	99	99	-
4		**4**	5	98	99	99	99	99	99	98	92
5		**5**	5	92	99	99	99	99	98	98	96
6		**1**	30	99	97	99	99	99	99	99	99
7		**2**	30	70	95	96	99	99	98	98	98
8		**3**	30	99	99	99	98	90	90	97	95
9		**4**	30	86	99	99	99	98	98	99	99
10		**5**	30	88	77	99	99	99	99	99	96

[a] Reaction conditions: 0.5 mmol iodobenzene, 0.75 mmol olefin, 0.5 mol% cat., 1 mmol of Et_3N, 5-30 min, 120 °C in n-Bu_4NBr. [b] Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard.

Table 5. Heck reaction of bromobenzene and olefins after different runs

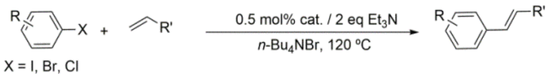


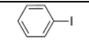
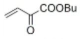
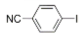
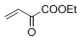
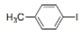
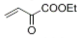
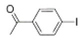
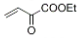
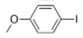
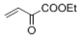
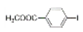
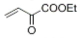
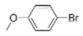
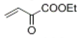
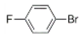
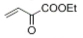
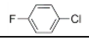
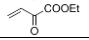
Entry[a]	Olefin	Catalyst	Time (h)	Runs – Yield[b] (%)							
				1	2	3	4	5	6	7	8
1		**1**	3	99	99	92	86	84	79	78	61
2		**2**	3	72	87	90	84	87	80	78	70
3		**3**	3	84	91	91	87	88	83	80	72
4		**4**	3	18	64	80	77	82	77	76	71
5		**5**	3	75	89	85	84	82	82	76	69
6		[$PdCl_2$]	3	0	0	0	0	0	0	-[c]	-[c]
7		[$Pd_3(OAc)_6$]	3	0	0	0	0	0	0	-[c]	-[c]
8		[$Pd(dba)_2$]	3	62	68	74	73	70	60	-[c]	-[c]
9		**1**	4	92	86	66	56	62	83	73	67
10		**2**	4	66	76	75	72	70	74	67	68
11		**3**	4	0	58	65	75	68	73	69	77
12		**4**	4	36	92	72	61	70	70	70	68
13		**5**	4	80	90	82	77	74	72	72	65

[a] Reaction conditions: 0.5 mmol bromobenzene, 0.75 mmol olefin, 0.5 mol% cat., 1 mmol of Et_3N, 3-4 h, 120 °C in n-Bu_4NBr. [b] Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard. [c] Not tested .

Similar results have been obtained with the use of different 4-monosubstituted aryl halides and olefins as shown in Tables 6 and S4. Once again, very short reaction times (5 minutes) and high yields (ca. 90%) are observed when working with aryl iodide derivatives (entries 1-5 in Table 6). An increase of the reaction times to achieve the same good yields is required for the bromo derivatives (entries 5 and 7 in Table 6), as mentioned above. Finally, it deserves to be noted that this type of palladium(II) complexes are unable to activate less active aryl halides such as chlorobenzenes (entry 9 in Table 6) which need higher temperatures to react (T > 120 °C),[32] a feature that precludes the use of n-Bu_4NBr as solvent.

Table 6. Scope of the Heck reaction of aryl halides and olefins in n-Bu_4NBr.



Entry	Aryl halide	Olefin	Time	Catalyst 1	2	3	4	5
1			5 min	75	88	97	90	92
2			5 min	89	99	99	89	88
3			5 min	90	85	96	99	99
4			5 min	93	93	98	99	99
5			5 min	93	92	99	99	99
6			15 min	99	99	95	99	99
7			1.5 h	99	99	99	99	99
8			4 h	92	94	93	91	94
9			72 h	*[c]	13	*[c]	*[c]	*[c]

[a]Reaction conditions: 0.5 mmol aryl halide, 0.75 mmol olefin, 0.5 mol% cat.,1 mmol Et_3N, 120 °C in (n-Bu_4N)Br. [b]Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard. [c]Not tested.

The characteristic event that stops a Pd(II)-catalyzed carbon-carbon coupling reaction is the formation of inactive metallic palladium.[33] In our catalytic conditions, this occurs when working with commercial palladium catalysts such as $[PdCl_2]$ and $[Pd_3(OAc)_6]$ (first two pictures in Fig. 5). However, the formation of the inactive palladium black does not occur if the reaction is performed with the oxamate-containing palladium(II) complexes of this work (last two pictures in Fig. 5).

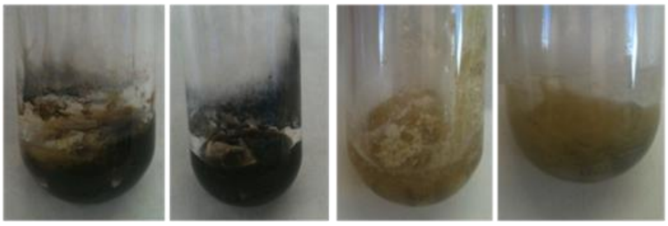
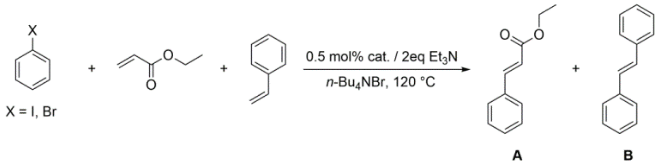
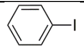
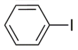
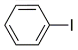
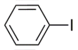
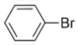
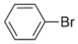
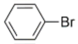
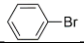


Fig. 5 From left to right: $[PdCl_2]$, $[Pd_3(OAc)_6]$, **3** and **4**, after the Heck reaction of bromobenzene with ethyl acrylate in n-Bu_4NBr at 120 °C during 3h.

Finally, the competing reaction between aryl halides and two different olefins (ethyl acrylate and styrene) was investigated. These reactions were carried out at two different times because of the reaction with ethyl acrylate runs faster than that with styrene (Table 7). The obtained results clearly show a higher activity for ethyl acrylate compared to styrene in the Heck reaction by using oxamate-containing palladium(II) complexes in n-Bu_4NBr, just the opposite trend with respect to that reported by Böhm and Herrmann in 2001 by using a phosphapalladacycle as catalyst.[34]

Table 7. Scope of olefin competition within the Heck reaction of ethyl acrylate (A) and styrene (B).



Entry[a]	Aryl halide	Catalyst	Time (min)	A[b] (%)	B[b] (%)	$K_o = B/A$
1		**2**	6	95	5	0.05
2		**4**	6	99	0	0
3		**2**	30	91	9	0.10
4		**4**	30	88	12	0.14
5		**2**	3	99	0	0
6		**4**	3	80	0	0
7		**2**	4	60	0	0
8		**4**	4	60	0	0

[a]Reaction conditions: 1 mmol iodobenzene, 5 mmol ethyl acrylate, 5 mmol styrene, 0.5 mol% cat., 2 mmol Et_3N, 120 °C in n-Bu_4NBr. [b]Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard.

Conclusions

In summary, five novel functional palladium(II)-oxamate complexexes (**1-5**) with well-defined structures were synthesized, exhibiting several advantages over commercial available palladium(0) or palladium(II) catalysts. They are environment-friendly chemicals (in contrast to harmful phosphines) and their easy and cheap preparation (compared mainly to the harder and time-consuming carbene systems) makes them very suitable green systems for catalytic cross-coupling purposes. They appear robust, even under air (controlled atmosphere – N_2 or Ar – is commonly used with other palladium catalysts in carbon-carbon cross coupling reactions),[16a] without significant appearance of the non-catalytic palladium black species. They are also soluble and highly stable in water and remain unchanged under ambient conditions (Fig. S1).

The present study on the catalytic properties of **1-5** shows that they are suitable catalyst to work with iodo- and bromo-aryl derivatives with yields around ca. 80-99 %.

Moreover, in comparison with previous works,[14] the change of the R substituent group in the *para-* position of the aryl portion of the oxamate ligand allows a decrease in the amount of catalyst needed to carried out the reaction with high yields (0.5-0.25 mol% cat.) and in very short reaction times (a minimum of 5 min of catalytic reaction and maximum of TON/TOF ca. 400 / ca. 4800 h^{-1}).

Thinking at addressing upcoming environmental concerns, the n-Bu_4NBr solvent as a superior ionic liquid serves not only as an alternative, greener medium to perform Heck reactions, but also provides an easy work-up procedure in which various consecutive runs preclude the loss of catalyst in the unloading and recharges of products and reactives. Thus, the combination of oxamate-containing palladium(II) complexes as structurally-well defined precatalysts with ionic liquids open a new way to perform Heck reactions under greener conditions without abdication of the catalytic activity.

Acknowledgements

Financial support from the Spanish Ministerio de Ciencia e Innovación (MCIIN) through Project CTQ2013-448449, the Generalitat Valenciana (PROMETEOII/2014/070 and ISIC/2012/002), the Italian Ministero dell'Istruzione dell'Università e della Ricerca Scientifica (MiUR) and the European Community's Seventh Framework Program (FP7 2007-2013) through the MATERIA Project (PONa3_00370) is acknowledged. F. R. F-P. thanks the MCIIN for a predoctoral FPU grant and N. M. also thanks the European Commission, FSE (Fondo Sociale Europeo) and Calabria Region for a post-doctoral fellowship.

Notes and references

1 a) K. Tamao, K. Sumitani and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 4374; (b) R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 1972, 144a; (c) R. F. Heck and J. P. Nolley, *J. Org. Chem.*, 1972, **37**, 2320; (d) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev. 2011*, **111**, 1417.

2 Some selected examples: (a) R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146; (b) N. Miyaura, T. Yanagi, and A. Suzuki, *Synth. Commun*., 1981, **11**, 513–519; (c) M. Shibasaki, C. D. J. Boden, and A. Kojima, *Tetrahedron*, 1997, **53**, 7371; (d) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147; (e) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009; (f) W. A. Herrmann, V. P. W. Böhm, and C.-P. Reisinger, *J. Chem. Educ.*, 2000, **77**, 92; (g) F. Bellina, A. Carpita and R. Rossi, *Synthesis*, 2004, 2419; (h) J.-P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651; (i) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461; (j) J. F. Hartwig, *Nature*, 2008, **41**, 314.

3 (a) E. Negishi*, Angew. Chem.* 2011, **123***,* 6870; (b) E. Negishi, *Angew. Chem. Int. Ed.,* 2011, **50**, 6738; (c) A. Suzuki, *Angew. Chem*. 2011, **123**, 6854; (d) A. Suzuki, *Angew. Chem. Int. Ed* 2011, **50**, 6722; (e) D. Astruc, *Anal. Bioanal. Chem.*, 2011, **399**, 1811;

4 (a) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.,* 2005, **44**, 4442; (b) J.-P. Corbet and G. R. Migani, *Chem. Rev.,* 2006, **106**, 2651; (c) V. L. Budarin, P. S. Shuttleworth, J. H. Clark and R. Luque, *Industrial Applications of C-C Coupling Reactions*, Bentham Science Publishers, 2010.

5 (a) P. J. Steel, *Acc. Chem. Res.*, 2005; (b)J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem. Int. Ed.*, 2007, **46**, 8574; (c) T. Gadzikwa, B-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 3672; (d) Q. Meng, J. Gao, R. Li, L. Jiang, C. Wang, H. Zhao, C. Liu, H. Li, and W. Hu, *J. Mater. Chem.*, 2009, **19**, 1477; (e)J. A. Lipton-Duffin, O. Ivasenko, D. F. Perepichka and F. Rosei, *small*, 2009, **5**, 592; (f) M. Alyapyshev, V. Babain, N. Borisova, I. Eliseev, D. Kirsanov, A. Kostin, A. Legin, M. Reshetova and Z. Smirnova, *Polyhedron*, 2010, **29**, 1998; (g) P. Rattanatraicharoen, K. Yamabuki, T. Oishi, and K. Onimura, *Polym. J.*, 2011, **44**, 224; (h)M. Jurícek, J. C. Barnes, E. J. Dale, W.-G. Liu, N. L. Strutt, C. J. Bruns, N. A. Vermeulen, K. C. Ghooray, A. A. Sarjeant, C. L. Stern, Y. Y. Botros, W. A. Goddard and J. F. Stoddart, *J. Am. Chem. Soc.*, 2013, **135**, 12736; (i) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. R. Fortea-Pérez, S.-E. Stiriba, M. Julve and F. Lloret, *Acc.Chem.Res.*, 2015, **48**, 510.

6 (a) S. Sankaranarayanapillai, L. Wang and W. R. Thiel, *Adv. Synth. Catal.*, 2010, **352**, 425; (b) C. A. Fleckenstein and H. Plenio, *Chem. Soc. Rev*., 2010, **39**, 694; (c) R. J. Lundgren and M. Stradiotto, *Chem. Eur. J.,* 2012, **18**, 9758; (c) N. C. Bruno, M. T. Tudge and S. L. Buchwald, *Chem. Sci.*, 2013, **4**, 916.

7 (a) G.-C. Ge, D.-L. Mo, C.-H. Ding, L.X. Dai and X.-L. Hou, *Org. Lett.,* 2012, **14**, 5156; (b) G. R. Rosa and D. S. Rosa, *RSC Advances*, 2012, **2**, 5080; (c) K. Karami, N. Rahimi and M. B. Shehni, *Tetrahedron Lett.*, 2012, **53**, 2428; (d) S. J. Sabounchei and M. Ahmadi, *Inorg. Chim. Acta*, 2013, **405**, 15.

8 8 (a) G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151; (b) F. Godoy, C. Segarra, M. Poyatos and E. Peris, *Organometallics*, 2011, **30**, 684; (c) J. J. Dunsford and K. J. Cavel, *Dalton Trans*., 2011, **40**, 9131; (d) C. Valente, S. Çalimsiz, K. H. Hou, D. Mallik, M. Sayah and M. G. Organ, *Angew. Chem. Int. Ed.,* 2012, **51**, 3314; (e) Y.-M. Liu, Y.-C. Lin, W.-C. Chen, J.-H. Cheng, Y.-L. Chen, G. P. A. Yap, S.-S. Sun and T.-G- Ong, *Dalton Trans*., 2012, **41**, 7382.

9 (a) N. J. S. Costa, P. K. Kiyohara, A. L. Monteiro, Y. Coppel, K. Philippot and L. M. Rossi, *J. Catal.*, 2010, **276**, 382; (b) S. S. Zalesskiy and V. P. Ananikov, *Organometallics,* 2012, **31**, 2302; (c) H. Firouzabadi, N. Iranpoor, F. Kazemi and M. Cholinejad, *J. Mol. Catal. A: Chem.*, 2012, **357**, 154; (d) M. Pérez-Lorenzo, *J. Phys. Chem. Lett.*, 2012, **3**, 167

10 (a) B. Karimi, D. Elhamifar, J. H. Clark and A. J. Hunt, *Chem. Eur. J.*, 2010, **16**, 8047; (b) M. H. G. Prechtl, J. D. Scholten and J. Dupont, *Molecules*, 2010, **15**, 3441; (c) B. Tamami, F. Farjadian, S. Ghasemi and H. Allahyari, *New. J. Chem*., 2013, **37**, 2011; (d) H. Li, M. Yang and Q. Pu, *Microporous Mesoporous Mater.*, 2012, **148**, 166; (e) A. S. Singh, U. B. Patil and J. M. Nagarkar, *Catalysis Comm*., 2013, **35**, 11.

11 (a) H.-U. Blaser, A. Indolese, A. Schnyder, H. Steiner and M. Studer, *J. Mol. Catal. A: Chem.*, 2001, **173**, 3; (b) T. Rosner, A. Pfaltz and D. G. Blackmond, *J. Am. Chem. Soc.*, 2001, **123**, 4621; (c) C. Rocaboy and J. A. Gladysz, *Org. Lett.*, 2002, **4**, 1993; (d) C. Rocaboy and J. A. Gladysz, *New J. Chem.*, 2003, **27**, 39; (e) S. Paul and J. H. Clark, *J. Mol. Catal. A: Chem.*, 2004, **215**, 107; (f) K. Yu and W. Sommer, J. M. Richardson, M. Weck and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161; (g) N. T. S. Phan, M. Van der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.

12 (a) R. Sheldon, *Chem. Commun.*, 2001, 2399; (b) C. M. Gordon, *Appl. Catal. A Gen.*, 2001, **222**, 101; (c) D. Zhao, M. Wu, Y. Kou, and E. Min, *Catal. Today*, 2002, **74**, 157; (d) R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792; (e) Holbrey John D., Turner Megan B., and Rogers Robin D., *Ionic Liquids as Green Solvents*, American Chemical Society, Washington, DC, 2003, vol. 856; (f) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459; (g) V. I. Pârvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; (h) G. Imperato, B. König, and C. Chiappe, *European J. Org. Chem.*, 2007, 1049; (i) H. Olivier-Bourbigou, L. Magna, and D. Morvan, *Appl. Catal. A Gen.*, 2010, **373**, 1; (j) P. Mastrorilli, A. Monopoli, M. M. Dell'Anna, M. Latronico, P. Cotugno, and A. Nacci, in *Topics in Organometallic Chemistry*, 2013.

13 Some selected examples: (a) V. P. W. Bohm and W. A. Herrmann, *Chem. Eur. J.* 2000, **6**, 1017; (b) F. Bellina and C. Chiappe, *Molecules*, 2010, **15**, 2211; (c) A. R. Hajipour and F. Rafiee, *Appl. Organomet. Chem.*, 2011, **25**, 542; (d) V. Hornillos, A. W. van Zijl and B. L. Feringa, *Chem. Commun.*, 2012, **48**, 3712; (d) A. Ataei, S. Nadri, E. Rafiee, S. Jamali and M. Joshaghani, *J. Mol. Catal. A: Chem.*, 2013, **366**, 30.

14 F. R. Fortea-Pérez, I. Schlegel, M. Julve, D. Armentano, G. De Munno and S.-E. Stiriba, *J. Organomet. Chem.,* 2013, **743**, 102.

15 (a) C. Zhou, J. Wang, L. Li, R. Wang and M. Hong, *Green Chem*., 2011, **13**, 2100; (b) M. Bagherzadeh, M. Amini, A. Ellern and L. K. Woo, *Inorg. Chim. Acta*, 2012, **383**, 46.

16 (a) A. Molnár, *Chem. Rev.*, 2011, **111**, 2251; (b) H.-P. Steinrück and P. Wasserscheid, *Catal. Lett.*, 2015, **145**, 380.

17 (a) M. Guerrero, J. García-Antón, M. Tristany, J. Pons, J. Ros, K. Philippot, P. Lecante and B. Chaudret, *Langmuir*, 2010, **26(19)**, 155532; (b) G. Sánchez, J. García, M. Martínez, A. R. Kapdi, J. Pérez, L. García and J. L. Serrano, *Dalton Trans.,* 2011, **40**, 12676; (c) D. Penno, F. Estevan, E. Fernández, P. Hirva, P. Lahuerta, M. Sanaú and M. A. Úbeda, *Organometallics*, 2011, **30**, 2083.

18 (a) W. X. C. Oliveira, M. A. Ribeiro, C. B. Pinheiro, W. C. Nunes, M. Julve, Y. Journaux, H. O. Stumpf and C. L. M. Pereira, *Eur. J. Inorg. Chem*., 2012, **34**, 5685; (b) W. X. C. Oliveira, M. A. Ribeiro, C. B. Pinheiro, M. M. da Costa, A. P. S. Fontes, W. C. Nunes, D. Cangussu, M. Julve, H. O. Stumpf and C. L. M. Pereira, *Cryst. Growth Des.*, 2015, **15**, 1325.

19 W. X. C. Oliveira, M. M. da Costa, A. P. S. Fontes, C. B. Pinheiro, F. C. S. de Paula, E. H. L. Jaimes, E. F. Pedroso, P. P. de Souza, E. C. Pereira-Maia and C. L. M. Pereira, *Polyhedron*, 2014, **76**, 16–21.

20 (a) F. R. Fortea-Pérez, N. Marino, D. Armentano, G. De Munno, M. Julve and S.-E. Stiriba, *CrystEngComm*., 2014, **16**, 6971; (b) F. R. Fortea-Pérez, D. Armentano, M. Julve, G. de Munno and S.-E. Stiriba, *J. Coord. Chem.*, 2014, **67**, 4003.

21 M. F. Rettig and P. M. Maitlis, *Inorg. Synth.*, 2007, **17**, 134.

22 SAINT, Version 6.45, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.

23 SADABS, Version 2.03, Bruker AXS Inc., Madison, WI, USA, 2000.

24 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2008, **64**, 112.

25 (a) P. Müller, *Cryst. Rev.*, 2009, **15**, 57. (b) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya, *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*; P. Müller Ed.; IUCr Texts on Crystallography; Oxford University Press: Oxford, U.K., 2006.

26 *CrystalMaker*, CrystalMaker Software, Bicester, England, 2015.

27 R. Kivekas, A. Pajunen, A. Navarrete and E. Colacio, *Inorganica Chim. Acta*, 1999, **284**, 292.

28 (a) R. B. Bedford, M. E. Blake, C. P. Butts and D. Holder, *Chem. Commun.*, 2003, 466; (b) C. Nájera, J. Gil-Moltó, S. Karlström and L. R. Falvello, *Org. Lett.*, 2003, **5**, 1451; (c) Q. Yao, E. P. Kinney and C. Zheng, *Org. Lett.*, 2004, **6**, 2997; (d) C. Wolf and R. Lerebours, *Org. Biomol. Chem.*, 2004, **2**, 2161; (e) F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron*, 2005, **61**, 11771; (f) F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron*, 2008, **64**, 3047; (g) S. M. Islam, P. Mondal, A. S. Roy, S. Mondal and D. Hossain, *Tetrahedron Lett.*, 2010, **51**, 2067; (h) W. Susanto, C.-Y. Chu, W. J. Ang, T.-C. Chou, L.-C. Lo and Y. Lam, *Green Chemistry*, 2012, **14**, 77; (i) A. Ataei, S. Nadri, E. Rafiee, S. Jamali and M. Joshaghani, *J. Mol. Catal.: A Chem.*, 2013, **366**, 30.

29 S. S. Zalesskiy, and V. P. Ananikov, *Organometallics*, 2012, **31**, 2302

30 V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047.

31 F. Bellina and C. Chiappe, *Molecules*, 2010, **15**, 2211.

32 (a) S. S. Pröckl, W. Kleist and K. Köhler, *Tetrahedron*, 2005, **61**, 9855. (b) P. Srinivas, P. R. Likhar, H. Maheswaran, B. Sridhar, K. Ravikumar and M. L. Kantam, *Chem. Eur. J.*, 2009, **15**, 1578. (c) W. Kleist and S. S. Pröckl, *Catal. Lett.*, 2008, **125**, 197. (d) L.C. Campeau, M. Parisien, A. Jean and K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 581.

33 (a) C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling, and J. Dupont, *Org. Lett.*, 2003, **5**, 983; (b) A. H. M. de Vries, J. M. C. a Mulders, J. H. M. Mommers, H. J. W. Henderickx, and J. G. de Vries, *Org. Lett.*, 2003, **5**, 3285; (c) G. Brasche, J. García-Fortanet, and S. L. Buchwald, *Org. Lett.*, 2008, **10**, 2207.

34 V. P. Böhm and W. A. Herrmann, *Chem. Eur. J.,* 2001, ***7***, 4191.