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C–N-palladacyclic-catalyzed Heck reaction in EGME/water: Rate and regioselectivity controlled by the solvents ratio

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ABSTRACT

Novel as well as known C,N-palladacyclic neutral complexes were tested as precatalyst in the Heck reaction between bromobenzene and styrene under aerobic conditions. The catalytic system Pd(II) complex/K_2CO_3/EGME–H_2O (EGME = ethylene glycol monomethyl ether) showed to be highly efficient. Best performances of the catalysts were achieved by controlling the amount of water: generally a H_2O content within the 25–50% v/v range resulted in the highest conversion of the substrates into *trans*-stilbene. As a matter of fact, bromobenzene and styrene can be converted quantitatively using only 0.01 mol% of precatalyst with very high regioselectivity for the *trans* product and with a TOF of 10000 h^{-1}. In the absence of water, all complexes were less efficient and differences in their activity were found, while such a differentiation disappeared when water was added.

1. Introduction

The Heck reaction is one of the most powerful metal-catalyzed processes for the synthesis of functionalised aryl-alkenes through C–C bond formation [1–16]. However, despite great efforts mainly focused on the use of palladium salts and complexes as catalyst, only a few significative industrial applications of this process have appeared [17–20]. Thus, Heck and related reactions, especially the Suzuki aryl–aryl coupling, continue to stimulate the researchers in both academia and industrial laboratories. Starting from the early 1990, the use of safe, low cost and (claimed) “environmentally friendly” [21] protocols has found growing interest, and such issues are nowadays of fundamental importance for the possible industrial-scale applications. In this context, the use of water as solvent is a challenging issue. Since the first studies on the Heck reaction run in water in the late 1980s, this solvent has found wide use in this type of catalyzed reaction, and several reports dealt with the exclusive use of water as solvent [22]. Also, widely explored is the Heck reaction run in water/organic solvent mixtures [22e,22h,22s,23]. Kinetic studies have outlined favourable [24] or slightly unfavourable [25] effect played by water on the rate of the reaction.

Since the first report by Herrmann and co-workers dealing with the use of tri(*o*-tolyl)phosphine [26], it has been clearly demonstrated that cyclopalladated complexes exhibit a superior catalytic efficiency in Heck and related reactions. However, the search for easily-handling, thermally robust and possibly low-cost catalysts has addressed the research toward the development of phosphane-free palladacyclic complexes, for example, those bearing C,N-, C,O- and C,S-coordinated ligands [27–30]. We herein report the results of a study focused on the catalytic application of a series of different C,N-cyclometalated Pd(II) complexes to the Heck reaction with the aim to develop an operationally simple protocol, starting from relatively cheap materials. Using different C,N-cyclopalladates as precatalysts, we have now found that the combination of H_2O–ethylene glycol monomethyl ether (EGME)–K_2CO_3 is effective in promoting the Heck reaction starting from non activated reagents such as bromobenzene and styrene. It is demonstrated that a controlled water content in the organic solvent can increase the reaction rate and improve the regioselectivity. Furthermore, the catalytic reaction can be conveniently accomplished in air using small amounts of the palladium precatalyst. Thus, a nearly quantitative formation of *trans*-stilbene was obtained using 0.01 mol% of catalyst with a very high TOF value (10000 h^{-1}).

2. Experimental

2.1. Materials and methods

All reagents were purchased from Aldrich and used without further purification. Commercial solvents were dried according to

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standard methods and freshly distilled under argon before use. The syntheses of the complexes were carried out in an atmosphere of oxygen-free argon by using standard Schlenk techniques. The ^{1}H and ^{13}C NMR spectra (at 200.13 and 50.32 MHz, respectively) have been recorded on a Bruker AC 200 F QNP spectrometer. For both nuclei the chemical shifts were referenced to $SiMe_4$. The GC–MS analyses, run to control the identity of the compounds obtained in the catalytic trials, were carried out with a Fisons TRIO 2000 gas-chromatograph–mass spectrometer working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 250 °C and the column (Supelco® SE-54, 30 m long, 0.25 mm i.d., coated with a 0.5 μm phenyl methyl silicone film) temperature was programmed from 50 °C to 290 °C with a gradient of 10 °C/min. The GC analyses were run on a Fisons GC 8000 Series gaschromatograph equipped with a Supelco® PTA-5 column (30 m long, 0.53 mm i.d., coated with a 3.0 μm poly(5% diphenyl–95% dimethylsiloxane) film) injector and column temperatures as indicated above. The elemental analyses (C, H, N) have been carried out in the microanalytical laboratory of our department.

2.2. Synthesis of (S)-(−)-N-benzylidene-α-methylbenzylamine (**6**)

Benzaldehyde (0.265 g, 2.5 mmol) and (*S*)-(−)-α-methylbenzylamine (0.303 g, 2.5 mmol) were stirred at room temperature for 4 h in methanol (25 mL) in the presence of an excess of anhydrous Na_2SO_4 (1.136 mg, 8.0 mmol). After elimination of the solid by filtration, the solvent was removed under reduced pressure giving a colorless oil, yield: 415 mg (79%); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.35$ (s, 1H, N=C*H*), 7.70–7.83 (m, 2H, Ar*H*), 7.16–7.47 (m, 8H, Ar*H*), 4.53 (q, $^{3}J_{H,H} = 6.6$ Hz, 1H, C*H*), 1.59 (d, $^{3}J_{H,H} = 6.6$ Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz): $\delta = 159.4$ (N=*C*H), 145.1 (C_i), 136.3 (C_i), 130.50 (C_p), 128.5 (C_{Ph}), 128.4 (C_{Ph}), 128.2 (C_{Ph}), 126.8 (C_p), 126.5 (C_{Ph}), 69.7 (*C*H), 24.8 (CH_3).

2.3. Improved synthesis of complexes **10** and **11**

These complexes have been prepared in acetic acid by the method described in detail for the synthesis of **12**. Complexes **10** and **11** have been isolated as a yellow powder in 82% yield and an off-white solid in 72% yield, respectively. The spectroscopic data of **10** were identical to that reported in the literature [23i], while **11** is an insoluble material [31].

2.4. Synthesis of complex **12**

A mixture of $[Pd_3(OAc)_6]$ (337 mg, 0.50 mmol) and **6** (345 mg, 1.65 mmol) in 20 mL of acetic acid was stirred at 60 °C for 4 h. The solution was then evaporated under vacuum leaving a yellow gum which was dissolved in acetone (5 mL). Addition of *n*-hexane (30 mL) afforded a yellow solid which was filtered off, washed with *n*-hexane and little cold diethyl ether, and dried under vacuum. Yield 439 mg (78%); *Anal.* Calc. for $C_{34}H_{34}N_2O_4Pd_2$ (747.50): C, 54.63; H, 4.58; N, 3.75. Found: C, 53.94; H, 4.69; N, 3.87%. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.35$–7.01 (m, 7 H, Ar*H*), 6.96 (d, $^{4}J_{H,H} = 1.3$ Hz, 1H, N=C*H*), 6.27 (m, 2H, Ar*H*), 4.60 (dq, $^{2}J_{H,H} = 6.9$ Hz, $^{4}J_{H,H} = 1.3$ Hz, 1H, C*H*), 2.19 (s, 3H, CH_3); 1.75 (d, $^{2}J_{H,H} = 6.9$ Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz): $\delta = 180.9$ (*C*O), 170.4 (N=*C*H), 154.4 (C_i), 146.7 (C_i), 137.7 (C_i), 132.0 (C_{Ph}), 128.8 (C_o), 128.4 (C_m), 127.9 (C_{Ph}), 126.8 (C_{Ph}), 126.5 (C_{Ph}), 124.0 (C_{Ph}), 64.4 (*C*H), 24.5 (CH_3), 19.5 (CH_3).

2.5. Synthesis of complex **13**

A mixture of complex **10** (144 mg, 0.20 mmol) and 2,4-pentanedione (50 mg, 0.50 mmol) in dichloromethane (20 mL) was stirred for 2 h at room temperature. All volatiles were then removed and the residue was dissolved in acetone (5 mL). Addition of *n*-hexane (30 mL) afforded a yellow solid which was filtered off, washed with *n*-hexane, and dried under vacuum. Yield 147 mg (92%). *Anal.* Calc. for $C_{38}H_{38}N_2O_4Pd_2$ (799.57): C, 57.08; H, 4.79; N, 3.50. Found: C, 57.03; H, 4.86; N, 3.45%. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.87$ (br t, 1H, N=C*H*), 7.50 (dd, 1H, Ar*H*), 7.44–6.95 (m, 8H, Ar*H*), 5.34 (s, 1H, C*H*), 4.85 (br s, 2H, CH_2), 2.04 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz): $\delta = 188.0$ (*C*O), 186.3 (*C*O), 174.6 (N=*C*H), 157.3 (C_i), 146.1 (C_i), 136.5 (C_i), 130.8 (C_{Ph}), 129.7 (C_{Ph}), 129.0 (C_o), 128.6 (C_m), 127.0 (C_{Ph}), 126.7 (C_{Ph}), 124.2 (C_{Ph}), 100.4 (*C*H), 60.5 (*C*H), 52.1 (*C*H2), 27.8 (CH_3), 27.5 (CH_3).

2.6. Synthesis of complex **14**

A mixture of palladium propionate (252 mg, 1.0 mmol) and **4** (215 mg, 1.1 mmol) in THF (20 mL) was stirred for 4 h at reflux. The mixture was cooled to room temperature and passed through a column of Celite® to eliminate traces of palladium black. The solution was concentrated to ca. 5 mL and cold *n*-hexane (30 mL) was added affording a yellow solid, which was filtered off, washed with cold *n*-hexane, and dried under vacuum. Yield 272 mg (73%). *Anal.* Calc. for $C_{34}H_{34}N_2O_4Pd_2$ (747.50): C, 54.63; H, 4.58; N, 3.75. Found: C, 54.18; H, 4.76; N, 3.77%. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.29$–7.20 (m, 3H, Ar*H*), 7.17–6.98 (m, 4H, Ar*H*), 7.09 (t, $^{4}J_{H,H} = 1.6$ Hz, 1H, N=C*H*), 6.83–6.78 (m, 2H, Ar*H*), 4.58 (dd, $^{2}J_{H,H} = 15.9$ Hz, $^{4}J_{H,H} = 1.6$ Hz, 1H, HC*H*), 3.95 (dd, $^{2}J_{H,H} = 15.9$ Hz, $^{4}J_{H,H} = 1.6$ Hz, 1H, HC*H*), 2.42 (q, 2H, CH_2), 1.16 (t, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz): $\delta = 184.1$ (*C*O), 171.8 (N=*C*H), 155.3 (C_i), 146.2 (C_i), 134.7 (C_i), 131.9 (C_{Ph}), 129.7 (C_o), 129.5 (C_{Ph}), 128.7 (C_m), 128.0 (C_{Ph}), 126.6 (C_{Ph}), 123.9 (C_{Ph}), 61.4 (CH_2), 31.0 (CH_2), 10.9 (CH_3).

2.7. General procedure for the Heck reaction

A 10 mL Schlenk flask was charged with the appropriate amount of palladium complex (5 μmol), bromobenzene (0.5 mmol), styrene (0.6 mmol) and the base (0.6 mmol). After addition of the solvent (2 mL), the flask was capped with a silicon stopper and heated at 120 °C in an oil bath. When requested, all operations were run under an argon atmosphere. The reaction mixture was extracted from the flask by syringe and treated with a small amount of water. The organic compounds were extracted with dichloromethane, the solution was dried over Mg_2SO_4 and analyzed by GC. This procedure was adopted for all catalytic trials with 1 mol% palladium complex. Otherwise, suitable amounts of solutions of the palladium complex prepared by dilution of a standard solution were used in all other trials with a lower precatalyst charge (0.1–0.001%).

2.8. Catalyst reuse check

A 10 mL Schlenk flask containing a magnetic stir bar was charged with complex 10 (5 μmol), bromobenzene (0.5 mmol), styrene (0.6 mmol) and K_2CO_3 (0.6 mmol). After addition of EGME (1.5 mL) and H_2O (0.5 mL), the flask was capped with a silicon stopper and heated at 120 °C in an oil bath for 24 h. After cooling to room temperature, bromobenzene (0.5 mmol) and styrene (0.6 mmol) were added and the flask was heated at 120 °C. Further workup as indicated above.

2.9. Catalyzed synthesis of trans-stilbene on a gram-scale

A 250 mL three necked flask containing a magnetic stir bar was charged in air with complex **10** (18 mg, 50 μmol) bromobenzene (7.85 g, 50 mmol), styrene (6.25 g, 60 mmol) and K_2CO_3 (8.29 g, 60 mmol). After addition of EGME (150 mL) and H_2O (50 mL), the mixture was heated under stirring at 120 °C in an oil bath for 30 h. The solvents were eliminated under reduced pressure overnight, at 60 °C, and the residual solid was purified on a silica gel column using dichloromethane as the eluent affording 8.40 g (yield 93%) of white crystalline *trans*-stilbene, whose purity (98%) was checked by GC and ^{1}H NMR.

2.10. Crystallographic structure determination

Diffraction data for the structure reported were collected at room temperature on a Nonius DIP-1030H system (Mo Kα radiation, λ = 0.71073 Å). Cell refinement, indexing and scaling of the data set were carried out using packages DENZO and SCALEPACK [32]. The structure was solved by direct methods and subsequent Fourier analyses [33] and refined by the full-matrix least-squares method based on F^2 with all observed reflections [33]. The contribution of H atoms at calculated position was introduced in the final cycles of refinement. All the calculations were performed using the WINGX system, Ver 1.70.01 [34].

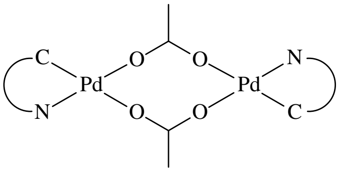
Crystal data for **12**: $C_{34}H_{34}N_2O_4Pd_2$, $M = 747.43$, monoclinic, space group $P2_1$, $a = 11.571(3)$, $b = 19.696(4)$, $c = 13.746(3)$ Å, $\beta = 90.20(2)°$, $V = 3132.7(12)$ Å^3, $Z = 4$, $D_{calc} = 1.585$ g/cm^3, μ(Mo Kα) = 1.188 mm^{-1}, $F(000) = 1504$, $\theta_{range} = 1.48–27.10°$. Final $R_1 = 0.0459$, $wR_2 = 0.1067$, $S = 0.934$ for 762 parameters and 38 636 reflections, 11 172 unique [$R_{int} = 0.0366$], of which 8614 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 1.860 and −0.465 e Å^{-3}.

3. Results and discussion

3.1. Synthesis and properties of the cyclometalated complexes

The ligands **1**–**6** used in this study (Fig. 1) have the common feature to form a cyclometalate 5-membered ring via deprotonation of a phenyl ring. The imine (*S*)-(−)-*N*-benzylidene-α-methylbenzylamine (**6**) was synthesized in high yield as an oily liquid by the reaction between benzaldehyde and (*S*)-(−)-α-methylbenzylamine in 1:1 molar ratio. The Pd(II) cyclometalated complexes **7**–**11** (Fig. 2) bearing the ligands **1**–**5** in the deprotonated form are known compounds [23i,35–37], while complex **12** was isolated in good yield by reacting $Pd_3(OAc)_6$ and **6** in 1:3 molar ratio, in pure acetic acid at 60 °C for 4 h. It was characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy, and its solid state structure was established by an X-ray diffraction analysis. The crystallographic investigation evidenced a *trans* stereochemistry (Fig. 2), as found for the closest analogue **10** [23i].

By using the acetic acid route, the synthesis of complexes **10** and **11** was improved. The former, previously obtained in 68% yield in refluxing THF [23i], was isolated in 82% yield. Analogously, complex **11** was obtained as a white insoluble material in 72% yield, while the same compound was obtained from benzene at room temperature in 52% yield [31]. Noticeably, it was reported that this complex was isolated as a dark yellow solid from acetone at reflux [37].



ligand	complex
1	7
2	8
3	9
4	10
5	11
6	12

Fig. 2. The dimeric structure of complexes **7**–**12**.

In addition to the acetato derivatives, the complexes [Pd(acetylacetonate)(**4′**)] (**13**) and [Pd_2(propionate)$_2$(**4′**)$_2$] (**14**) (**4′** represents the deprotonated ligand **4**) were also prepared (Fig. 3). Complex **13** was synthesized in good yield from precursor **10** by anion metathesis [38]. Attempts to prepare **13** directly from palladium(II) acetylacetonate in refluxing THF or 2,4-pentanedione failed, in both cases the unreacted starting Pd(II) complex was recovered from the reaction mixture. The NMR characterization of complex **13** confirmed the mononuclear nature of this species [38]. In particular, couples of resonances for the CH_3 groups in the ^{1}H spectrum and two resonances for the CO groups in the ^{13}C NMR spectrum are in agreement with *trans* C–Pd–O and N–Pd–O arrangements. Complex **14** was obtained in good yield as yellow microcrystals by reacting Pd(II) propionate and ligand **10** in 1:1.1 molar ratio in refluxing THF. The ^{1}H and ^{13}C NMR spectra confirmed the formation of a single pure stereoisomer, whose chemical shift and coupling constant values closely resemble that of complex **10** [23i].

3.2. Single crystal X-ray structure determination of complex 12

The crystal structure of **12** evidences the formation of a dimeric cyclometalated species and Fig. 4 reports an Ortep view of the two crystallographic independent molecules, while a selection of bond lengths and angles is reported in Table 1. The palladium centres adopt approximately square planar coordination geometry, achieved through two oxygens from each of the two bridging acetate anions, the imine nitrogen donor and the *ortho*-carbon atom of phenyl supporting the carbon atom of the imine group. The two independent complexes, having a pseudo (non-crystallographic) C_2 symmetry and thus a *trans* configuration, present a close comparable geometry, not only in bond lengths and angles but also in the overall conformation. The configuration is closely related to that of

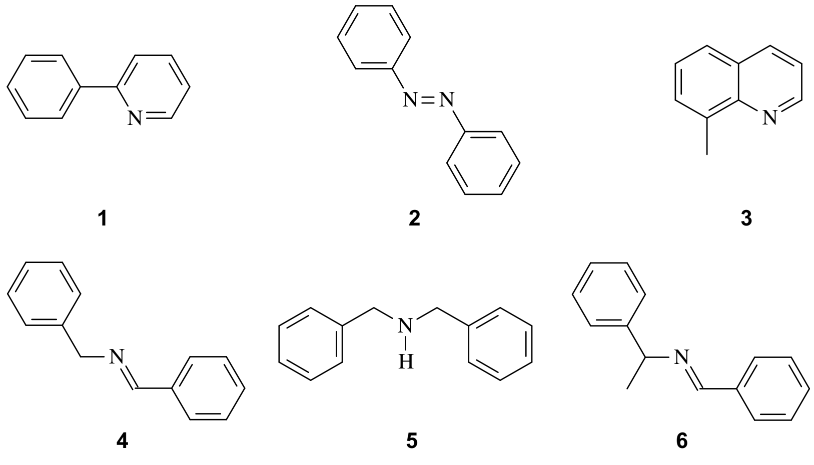
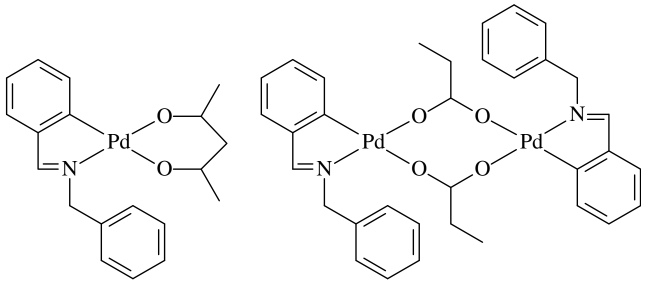


Fig. 1. The nitrogen ligands used in this work.



13 **14**

Fig. 3. Novel complexes bearing the deprotonated ligand **4**.

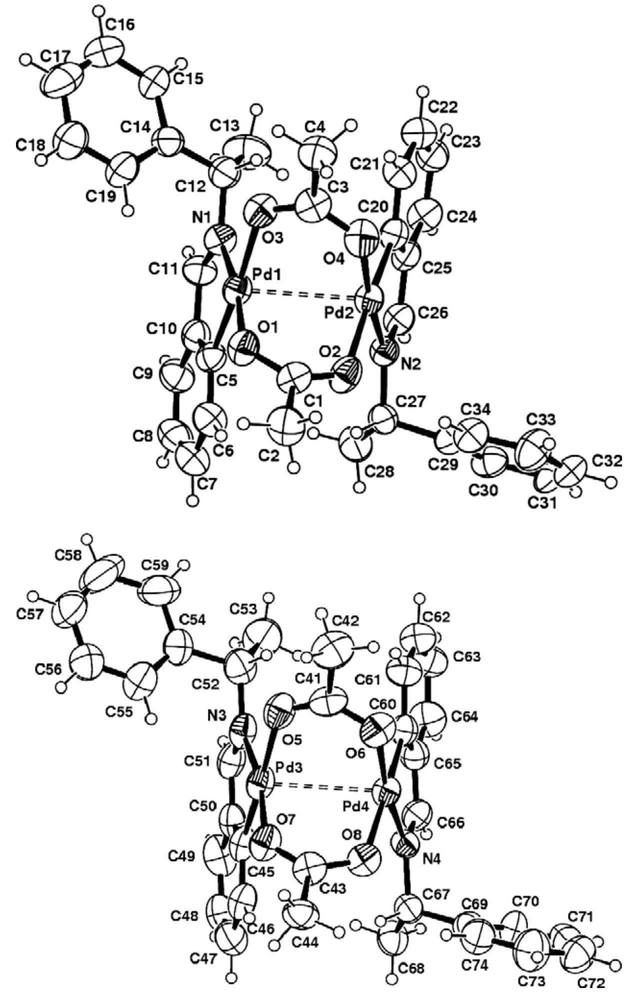


Fig. 4. ORTEP drawing (35% probability ellipsoids) of complexes **12**-A (top) and **12**-B (bottom) with atom labelling scheme.

Table 1
Selected coordination bond lengths (Å) and angles (°) for complex **12**

Molecule A		Molecule B	
Pd(1)–N(1)	2.009(7)	Pd(3)–N(3)	2.003(7)
Pd(1)–C(5)	1.976(9)	Pd(3)–C(45)	1.991(12)
Pd(1)–O(1)	2.051(6)	Pd(3)–O(7)	2.038(6)
Pd(1)–O(3)	2.139(7)	Pd(3)–O(5)	2.129(8)
Pd(2)–N(2)	2.021(6)	Pd(4)–N(4)	2.027(7)
Pd(2)–C(20)	1.962(9)	Pd(4)–C(60)	1.981(10)
Pd(2)–O(4)	2.044(6)	Pd(4)–O(6)	2.046(7)
Pd(2)–O(2)	2.159(7)	Pd(4)–O(8)	2.159(7)
Pd(1)–Pd(2)	2.857(1)	Pd(3)–Pd(4)	2.883(1)
N(1)–Pd(1)–C(5)	82.2(4)	N(3)–Pd(3)–C(45)	81.5(4)
N(1)–Pd(1)–O(1)	172.1(3)	N(3)–Pd(3)–O(7)	170.5(3)
N(1)–Pd(1)–O(3)	94.4(3)	N(3)–Pd(3)–O(5)	93.5(3)
C(5)–Pd(1)–O(1)	92.6(4)	C(45)–Pd(3)–O(7)	93.5(4)
C(5)–Pd(1)–O(3)	175.6(3)	C(45)–Pd(3)–O(5)	174.9(4)
O(1)–Pd(1)–O(3)	90.5(3)	O(7)–Pd(3)–O(5)	91.6(3)
N(2)–Pd(2)–C(20)	81.1(3)	N(4)–Pd(4)–C(60)	81.4(4)
N(2)–Pd(2)–O(4)	173.0(3)	N(4)–Pd(4)–O(6)	171.4(3)
N(2)–Pd(2)–O(2)	97.2(3)	N(4)–Pd(4)–O(8)	97.8(3)
C(20)–Pd(2)–O(4)	92.8(3)	C(60)–Pd(4)–O(6)	92.3(4)
C(20)–Pd(2)–O(2)	177.3(3)	C(60)–Pd(4)–O(8)	178.1(4)
O(2)–Pd(2)–O(4)	88.7(3)	O(6)–Pd(4)–O(8)	88.6(3)

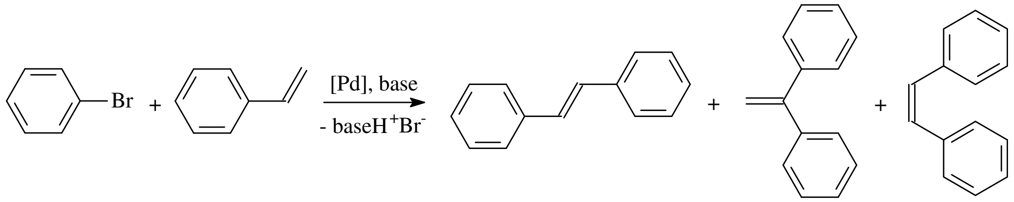
10 [23i] and other *cis*-bis(μ-carboxy1ato)-dipalladium complexes bearing a C,N-coordinated imine [39–42].

The Pd–N and Pd–C bond distances vary in a range from 2.003(7) to 2.027(7) Å and from 1.962(9) to 1.991(12) Å, respectively, while the Pd–O bond lengths having nitrogen donors in *trans* position (2.038(6)–2.051(6) Å range) are significantly shorter than those *trans* to aromatic carbons (2.129(8)–2.159(7) Å), for the *trans*-lengthening influence of the σ-bonded carbon. The Pd–N and Pd–C bonds form the basis for a five-membered chelate ring; the "bite" angles average to 81.5°. The metal coordination planes form a dihedral angle of ca. 29.3° (mean of the two complexes), and for interligand repulsion each plane is slightly tilted with respect to the other by an angle of ca. 17.2° in molecule A and 9.6° in B (average values of C–Pd–Pd–N torsion angles). All distances and angles within the acetate and the aromatic groups are normal, the two acetate bridges are separated by a dihedral angle of 84.7(4) and 89.7(4)° in the two complexes. The Pd–Pd distance in the two complexes is 2.857(1) and 2.883(1) Å, a value that does not exclude a possible metal–metal interaction, being shorter than the sum of palladium van der Waals radii. As a matter of fact, an indication of metal–metal interaction in 12 can be inferred from the observation that each metal is displaced by 0.06 Å from its mean coordination plane towards the other metal. It should be noted that a longer Pd–Pd distance (3.226 Å) was measured in the dimeric imine complex with metals bridged by trifluoroacetate anions [43]. The crystal packing does not evidence any significant π–π interaction between aromatic rings. The geometrical parameters are very similar to those found in complex **10** and in the correspondent *N*-phenyl analogue [23i], with the exception of the intramolecular metal–metal separation (2.999 and 2.940 Å) and of the interplanar coordination plane angle (33.0°, 37.1°), which differ significantly in the cited complexes [23i].

3.3. Catalysis

The initial catalytic study involved complexes **7**–**11**, whose catalytic activity was checked in the standard reaction between bromobenzene and styrene (Scheme 1). The catalytic potential of complexes **7** [44] and **10** [23i] in the Heck coupling has been previously investigated in *N*,*N*-dimethylacetamide (DMA). The reaction was initially performed in EGME, under argon at 120 °C and in the presence of Cs_2CO_3. The choice of the solvent was based on our previous studies which demonstrated the superior performance of a Pd(II) cationic complex in EGME with respect to *N*,*N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP) [45]. As almost identical results were obtained working in air, the catalytic trials were conveniently run under aerobic conditions. Selected data among those collected within the 2–20 h range using 1 mol% of complex are shown in Table 2 (entries 1–5).

Complexes **7**–**11** behaved as active precatalysts in EGME, generally showing a very good regioselectivity for *trans*-stilbene. Among all, complex **10** exhibited a superior efficiency, in fact *trans*-stilbene yield after 20 h was about 89%, and the selectivity was higher than 97% (the main byproduct was 1,2-diphenylethene). A commonly observed feature was the high *trans*-stilbene yield detected



Scheme 1.

Table 2
Comparison of the catalytic activity of complexes **7**–**14**[a]

Entry	Complex	*trans*-Stilbene yield[b] (%)		
		2 h	4 h	20 h
1	**7**	72.1 [74.3]	76.6 [78.8]	79.1 [81.7]
2	**8**	80.9 [83.1]	82.6 [84.9]	85.3 [87.7]
3	**9**	61.4 [64.0]	63.0 [66.3]	64.7 [68.5]
4	**10**	79.1 [81.0]	83.6 [85.5]	88.7 [91.0]
5	**11**	62.8 [65.2]	65.4 [66.9]	69.4 [71.5]
6	**12**	71.6 [72.9]	74.8 [76.3]	82.1 [84.2]
7	**13**	71.5 [74.1]	73.6 [76.5]	75.3 [78.7]
8	**14**	68.1 [70.0]	70.4 [72.4]	73.3 [75.5]
9	**10**[c]	61.7 [63.7]	62.4 [64.3]	67.8 [70.7]

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), Cs_2CO_3 (0.6 mmol), complex (5 μmol, 1 mol%), EGME (2 mL), *t* = 120 °C, on air.
[b] Bromobenzene conversion (%) in brackets.
[c] 0.5 μmol (0.1 mol%) complex.

after 2 h, which only poorly increased within 20 h owing to catalyst decomposition. On the basis of the very good catalytic behaviour of complex **10**, we decided to examine new related cyclopalladated species. Thus, complexes **12** (Fig. 2), **13** and **14** (Fig. 3) were prepared and explored as precatalyst to establish whether modifications in the structure of the cyclometalated ligand or the O,O-donor anion could affect the catalytic activity of the Pd(II) complex. Complexes **12**–**14** were shown to be slightly less efficient than **10**.

Giving these results, next catalytic experiments were performed using complex **10** only. The activity of this complex in EGME was dramatically lowered below 120 °C, thus only ca. 40% and 9% *trans*-stilbene was formed after 20 h at 100 and 80 °C, respectively, using 1 mol% of complex. The catalytic efficiency of complex **10** in other solvents such as DMF, 1,4-dioxane, NMP, 1,1,1-trifluorotoluene, and protic *n*-amyl alcohol and 2,2′-thiodiethanol was also examined. The data (Table 3) show that EGME is the solvent of choice for the Heck coupling of bromobenzene with styrene in the presence of Cs_2CO_3. It was reported that complex **10** can convert almost quantitatively bromobenzene and styrene into *trans*-stilbene, at 140 °C in DMA/NaOAc within 24 h, however with low regioselectivity (90%) [23i].

Table 3
Influence of the solvent on the Heck coupling of bromobenzene with styrene using complex **10**[a]

Solvent	*trans*-Stilbene yield (%)		
	2 h	4 h	20 h
EGME	79.1	83.6	88.7
DMF	39.3	64.5	74.6
1,4-Dioxane	38.0	50.8	53.7
NMP	0.9	1.1	1.4
$C_6H_5CF_3$	14.0	20.3	25.9
n-$C_5H_{11}OH$	22.0	24.3	28.9
$S(CH_2CH_2OH)_2$	0.7	1.2	1.7

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), Cs_2CO_3 (0.6 mmol), **10** (5 μmol, 1 mol%), solvent (2 mL).

The influence of the base on the catalytic efficiency of **10** in EGME was also investigated. The results are reported in Table 4. The activity decreased in the following order: Cs_2CO_3 > NaOAc > K_2CO_3 > K_3PO_4 ≈ dimethylcyclohexylamine. Thus, Cs_2CO_3 is the base of choice in combination with EGME, most probably for its ready complete solubilization in this solvent.

The following conclusions can be drawn for the first part of the investigation: (i) the imine palladacycle **10** seems to behave as the best precatalyst, (ii) the protic solvent EGME is superior to other solvents commonly used in the Heck reaction, (iii) best performances of the catalysts in EGME are obtained using Cs_2CO_3 as the base.

In several reports on the Heck reaction, the crucial kinetic role played by water added to a given organic solvent was pointed out [22c,22e,23a–d,23f,23g,23k,23l,23n,23o,24]. Furthermore, in a case of intramolecular Heck annulation it was found that also the regiochemistry of the reaction was influenced by the presence of small amounts of water [23e]. Starting from these observations, the effects of water addition to EGME were analyzed. Selected data among those collected in the 0.5–4 h range, using complex **10** as the precatalyst, are reported in Table 5. As a matter of fact, a small amount of H_2O added to EGME such as 5% v/v (entry 2) is sufficient to strongly accelerate the rate of the reaction, which was found to

Table 4
Influence of the base on the Heck coupling of bromobenzene with styrene in EGME using complex **10**[a]

Base	*trans*-Stilbene yield[b] (%)		
	2 h	4 h	20 h
Cs_2CO_3	79.1 [81.0]	83.6 [85.5]	88.7 [91.0]
K_2CO_3	25.0 [27.0]	28.4 [31.0]	29.4 [31.5]
NaOAc	64.3 [73.9]	66.0 [75.4]	68.3 [77.9]
K_3PO_4	13.4 [15.8]	13.7 [16.0]	15.1 [18.0]
DMCA[c]	13.0 [14.8]	17.3 [19.4]	19.5 [22.3]

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), base (0.6 mmol), **10** (5 μmol, 1 mol%), EGME (2 mL).
[b] Bromobenzene conversion (%) in brackets.
[c] DMCA = dimethylcyclohexylamine.

Table 5
Influence of the EGME/H_2O ratio on *trans*-stilbene yield and regioselectivity using complex **10**[a]

Entry	Solvent volume (mL)		*trans*-Stilbene yield[b] (%)		
	EGME	H_2O	0.5 h	1 h	4 h
1	2.0	–	52.4 [53.4]	68.7 [70.1]	83.6 [85.5]
2	1.9	0.1	71.2 [74.7]	88.2 [89.9]	95.5 [96.7]
3	1.5	0.5	88.4 [89.6]	95.2 [96.2]	98.4 [99.5]
4	1.0	1.0	88.3 [89.9]	94.1 [95.8]	97.8 [99.0]
5	0.8	1.2	81.6 [83.7]	87.8 [90.2]	92.1 [95.1]
6	0.5	1.5	48.4 [51.2]	64.2 [68.1]	80.3 [85.6]
7[c]	1.5	0.5	91.0 [91.9]	95.5 [96.4]	98.7 [99.8]

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), Cs_2CO_3 (0.6 mmol), **10** (5 μmol, 1 mol%), total solvent (2 mL).
[b] Bromobenzene conversion (%) in brackets.
[c] Using K_2CO_3 (0.6 mmol) instead of Cs_2CO_3.

increase when the water content progressively raised. The highest values of product yield were found using amounts of water in the 25–50% v/v range (entries 3 and 4). However, when the volume of H_2O exceeded that of EGME, the reaction rate diminished (entries 5 and 6). Noteworthy, a high water content such as 75% v/v gave an opposite effect on the reaction rate, in fact *trans*-stilbene yield was lower than that obtained using pure EGME (entry 6 versus entry 1). Furthermore, it should be noted that also regioselectivity slightly benefits by the presence of 5–50% v/v H_2O. As well shown in Fig. 5, the minimum difference between bromobenzene conversion and *trans*-stilbene yield is reached when the amount of water is in the 5–50% v/v range, (entries 2–4), i.e., higher the conversion higher the regioselectivity. Thus, selectivity, likewise yield, is markedly reduced using high water amounts (entries 5 and 6). Notably, for 3:1 EGME/H_2O solutions, the use of K_2CO_3 instead of Cs_2CO_3 did not affect the catalytic activity of **10** (entry 7 versus entry 3). This is indeed a clear economic advantage in the case of application of our catalytic system to a large-scale production of arylalkenes via Heck reaction.

Like **10**, all other complexes were tested as precatalysts in 3:1 EGME/H_2O solutions. The results (Table 6) show that a dramatic increase of product yield is obtained for all complexes when water is present (see data reported in Table 2). In this case the activity of the catalyst is scarcely affected by the nature (ligand, coordinated anion, nuclearity) of the cyclopalladate precursor. The very high conversions and yields obtained are in line with the experimental finding that no visible palladium black was formed in all catalytic experiments run in EGME/H_2O. Interestingly, when methanol was used instead of water (entry 9) no marked differences were observed with respect to the reaction run in pure EGME (Table 2, entry 4), thus confirming the peculiar kinetic role played by water. When ligand-free $Pd_3(OAc)_6$ was used as the precatalyst, a very low reaction rate was observed and, notably, it decreased further upon addition of water (entries 10 and 11). The activity of palladium acetate became comparable with that of complexes **7**–**14** only when an excess of *n*Bu_4Br was added to the EGME/H_2O solution (Jeffery's protocol) [22d,22g] (entry 12). A comparison between the catalytic activity of **10** and $Pd_3(OAc)_6$ has been done also by adding the catalyst (1 mol%) to the hot reaction mixture (bromobenzene (0.5 mmol), styrene (0.6 mmol), Cs_2CO_3 (0.6 mmol), EGME (1.5 mL), water (0.5 mL), $t = 120\,°C$). A higher conversion of bromobenzene (94.7%) to products (92.8% *trans*-stilbene) within 10 min was observed using **10**, while in the case of $Pd_3(OAc)_6$ the reaction proceeded slower (79.4% *trans*-stilbene after 10 min). In the former case a clear green solution formed, on the contrary some palladium black was observed using $Pd_3(OAc)_6$.

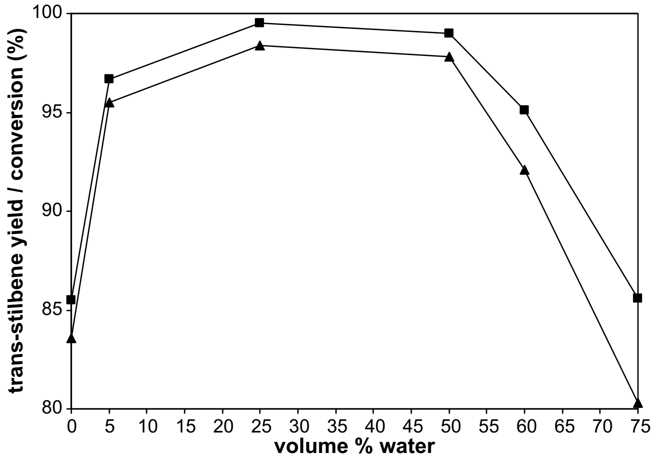


Fig. 5. Effect of water addition on *trans*-stilbene yield (▲) and bromobenzene conversion (■). Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), Cs_2CO_3 (0.6 mmol), **10** (5 μmol, 1 mol%), solvent (EGME + H_2O) 2 mL. The reported values have been measured after 4 h.

Table 6
Catalytic activity of complexes **7**–**14** and $Pd_3(OAc)_6$ in 3:1 EGME/water[a]

Entry	Complex	*trans*-Stilbene yield[b] (%)		
		0.5 h	2 h	20 h
1	**7**	88.4 [89.4]	93.4 [94.5]	98.1 [99.2]
2	**8**	87.8 [91.1]	95.9 [97.8]	98.0 [99.1]
3	**9**	80.5 [83.1]	93.6 [95.0]	95.7 [97.3]
4	**10**	91.0 [91.9]	98.1 [99.1]	99.0 [99.9]
5	**11**	81.8 [84.2]	92.4 [93.8]	95.8 [97.4]
6	**12**	85.3 [88.0]	94.9 [96.8]	98.2 [99.2]
7	**13**	91.3 [93.7]	96.4 [97.8]	98.7 [99.9]
8	**14**	86.1 [89.2]	94.4 [96.0]	97.8 [99.5]
9	**10**[c]	63.0 [65.4]	72.4 [74.5]	93.6 [94.9]
10	$Pd_3(OAc)_6$[d]	19.1 [20.0]	32.9 [34.7]	39.5 [41.4]
11	$Pd_3(OAc)_6$[e]	35.3 [36.5]	38.9 [40.2]	44.6 [46.5]
12	$Pd_3(OAc)_6$[f]	72.4 [75.2]	92.9 [94.4]	98.1 [99.4]

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), catalyst (5 μmol, 1 mol%), K_2CO_3 (0.6 mmol), EGME (1.5 mL), water (0.5 mL), $t = 120\,°C$.

[b] Bromobenzene conversion (%) in brackets.

[c] EGME (1.5 mL), CH_3OH (0.5 mL).

[d] In 3:1 EGME/water mixture.

[e] In pure EGME and using Cs_2CO_3 instead of K_2CO_3.

[f] In 3:1 EGME/water mixture, in the presence of *n*Bu_4Br (*n*Bu_4Br/Pd molar ratio = 10:1).

Having established that addition of water to EGME in the 5–50% v/v range resulted in a neat increase of activity of the catalyst, further measurements were run in order to establish the concentration limit at which complex **10** still gives acceptable activity in 3:1 EGME/H_2O. The data are shown in Table 7. After 20 h, both *trans*-stilbene yield and regioselectivity did not appreciably fade on lowering the precatalyst amount from 1 to 0.01 mol%. On the contrary, the reaction proceeded slowly when complex **10** load was further diminished to 0.001 mol%, as ca. 20% *trans*-stilbene only was formed after 20 h. As already reported [9,24,46,47], the TOFs (Table 7, TOF = moles of substrate per mole of complex per hour, at 50% conversion) clearly show that catalyst efficiency increases in diluted solutions. This feature can be ascribed to the less probable aggregation of metallic palladium particles in diluted solutions. The TOF value of 10 000 h^{-1} obtained using 0.01 mol% of **10** is a very high value indeed for a non activated starting material such as bromobenzene. In this regard, in Table 8 is shown a comparison between the activity of **10** and that, to the best of our knowledge, of the closely related species reported in the literature.

In order to confirm the effectiveness of our catalytic method applied to the bromobenzene/styrene system, *trans*-stilbene was prepared on a gram-scale (8.40 g) in 93% isolated yield, using 18 mg (0.1 mol%) of complex **10**. Furthermore, a reuse of the catalyst (see Section 2 for details) was possible with still good yield and

Table 7
trans-Stilbene yield at different loadings of complex **10**[a]

Mol% **10**	*trans*-Stilbene yield (%)[b]			TOF (h^{-1})[c]
	0.5 h	2 h	20 h	
1	91.0 [91.9]	97.8 [99.1]	98.8 [99.9]	950
0.1	79.5 [82.7]	87.1 [89.5]	97.6 [99.3]	2 800
0.01	50.1 [51.5]	77.6 [79.4]	98.2 [99.9]	10 000
0.001	2.7 [3.6]	8.4 [9.6]	19.8 [20.4]	–

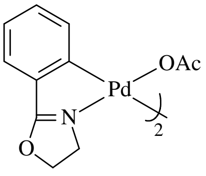
[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), K_2CO_3 (0.6 mmol), complex **10**, EGME (1.5 mL), water (0.5 mL).

[b] Bromobenzene conversion (%) in brackets.

[c] Turnover frequency (moles of substrate per mole of complex per hour) at 50% conversion.

Table 8
Comparison of the activity of C,N-cyclopalladated complexes in the reaction between bromobenzene and styrene

Complex (amount)	Solvent	Temperature (°C)	Yield (%)	TOF[a] (h^{-1})	Reference
10 (0.01 mol%)	EGME/H_2O[b]	120	98.2	10 000	This work
A (0.0014 mol%)[c]	NMP	140	93	511	[43]
B (0.1 mol%)[d]	DMA	140	38	5.3	[44]
C (0.001 mol%)	NMP	150	86.6	2 988	[48]
D (0.5 mol%)[e]	DMF	135	>99	66	[49]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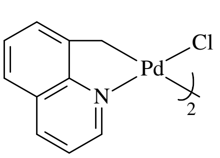
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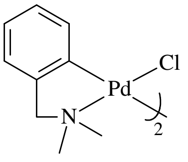
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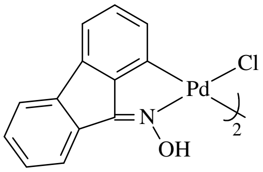
D

[a] Calculated at 50% conversion only in this work.
[b] In 3:1 v/v ratio.
[c] Using methyl acrylate.
[d] In the presence of nBu_4NBr.
[e] Using 4-bromoacetophenone.

selectivity. Thus, in the second use of the catalytic system *trans*-stilbene was formed in 87% yield after 20 h, while regioselectivity remained unchanged.

Although a mechanistic study was not undertaken, we tentatively suggest that a mechanism similar to that proposed for the high-temperature Heck reaction starting from bromoaryls should be effective. In accord with such a mechanism, Pd(0) nanoparticles (in the form of colloids) are formed [9,12,15,47,50–53], which are in equilibrium with the supposed effective catalyst. This hypothesis is well supported by the TOF/precatalyst concentration trend (Table 7). By contrast, a monitoring of the early stages of the reaction (Fig. 6) did not evidence an induction period, which is typical of the formation of Pd colloids [50], though their formation within an extremely short time cannot be ruled out. This fact is not unprecedented, as it was found that the induction period observed using dry DMA disappeared in DMA/water solution [24]. For our systems, the presence of water in the 25–50% v/v range can probably help in the stabilization of palladium nanoparticles of suitable size [51,54], not too large to induce palladium black formation. On the other hand, it has been claimed that water, which certainly favours the solubilization of the inorganic base, can also contribute, owing to its strong ligating ability, to the displacement of the organic ligand giving the requested low-ligated palladium catalyst [6].

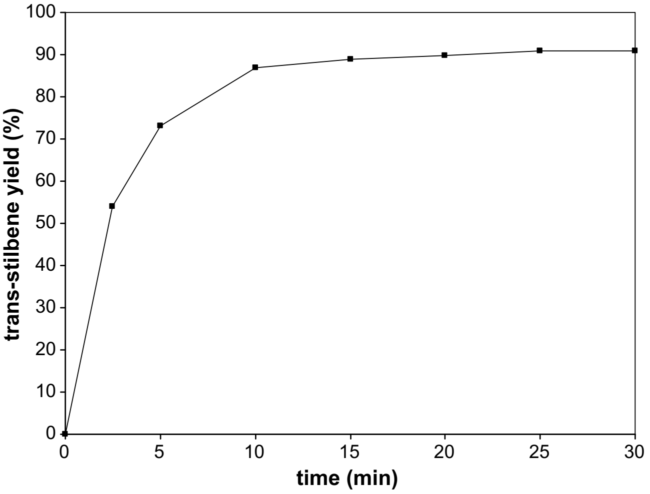

Fig. 6. *trans*-Stilbene yield in the early stages of the reaction. Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst **10** (1 mol%), solvent: EGME (1.5 mL) + H_2O (0.5 mL), $t = 120$ °C.

4. Conclusions

The catalyst system here described, based on the combination C,N-cyclopalladate complex/EGME/H_2O/M_2CO_3 (M = K or Cs), has shown to be highly efficient for promoting the Heck reaction starting from bromobenzene. The key-tool to maximize the performance of the catalyst is the use of a controlled amount of water, generally in the 25–50% v/v range. Under optimized conditions, bromobenzene and styrene can be converted quantitatively to *trans*-stilbene (yield > 98%) using 0.01 mol% of precatalyst **10** only. It has been recognized that water improves both rate of conversion and regioselectivity. Furthermore, the difference of catalytic activity shown by complexes **7–14** in pure EGME disappears when water is added. In other words, water seems to possess the property of enhancing the activity of the C,N-cyclopalladated precatalysts to a unique superior level. The activity of precatalyst **10** is higher than that exhibited by palladium acetate in the same experimental conditions, and only adopting the so-called Jeffery's protocol does the efficiency of palladium acetate parallel that of a C,N-cyclopalladated precatalyst. Thus, as already reported, the presence of ions in solution is essential for obtaining high performances of the catalyst system, most probably they can stabilize the palladium(0) colloidal nanoclusters, which are commonly supposed to act as the source of the true catalyst. It is likely that water could give an important contribution to the stability of the colloids, reducing thereby the formation of inactive palladium black.

Supplementary material

CCDC 664411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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