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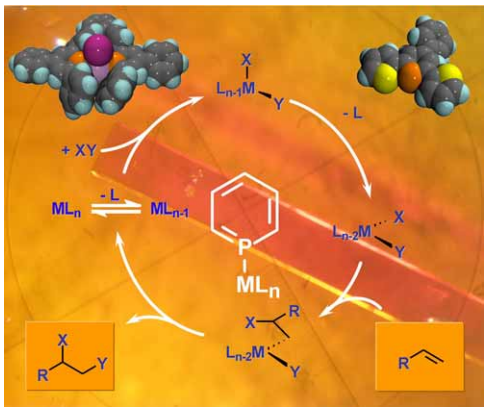

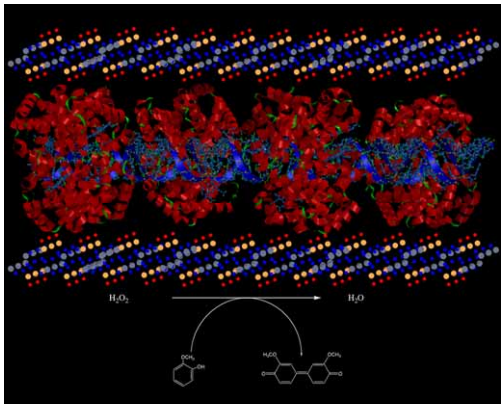

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Palladium catalyzed Suzuki C–C couplings in an ionic liquid: nanoparticles responsible for the catalytic activity

Fernando Fernández,[a,b] Beatriz Cordero,[a,b] Jérôme Durand,[a] Guillermo Muller,[b] François Malbosc,[c] Yolande Kihn,[d] Emmanuelle Teuma[a] and Montserrat Gómez*[a]

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A new family of functionalized ligands derived from norborn-5-ene-2,3-dicarboxylic anhydride has been used in Suzuki C–C cross-couplings between aryl boronic acids and aryl bromide derivatives in [BMI][PF_6] (BMI = 1-*n*-butyl-3-methyl-imidazolium), using palladium acetate as catalytic precursor. High conversions and yields are obtained when amine ligands containing hydroxy groups are involved. TEM analyses after catalysis show the formation of small nanoparticles, in contrast to the agglomerates observed when nanoparticles are intentionally preformed, with a consequent decrease in the catalytic activity in the latter case. Some tests, including the correlation effect between solvent and ligand, are carried out to try to identify the true nature of the catalyst. All the results obtained suggest that formation of nanoparticles is required to lead to a catalytically active system.

Introduction

Since the 1990's, Pd-catalyzed carbon–carbon couplings (Heck, Suzuki, Sonogashira and Stille reactions as the most common couplings) have developed into an important tool in organic synthesis, predominantly for pharmaceutical and agrochemical purposes.[1] Among them, Heck[2] and Suzuki[3] couplings have specially attracted the attention of many researchers, in essence due to the small loading of metal required to afford high turnover frequencies,[4] so low that the term "homeopathic palladium" is currently employed.[2d,5]

Ligand-free palladium catalysts such as palladium acetate have been largely studied, in particular in ionic liquids (ILs) containing imidazolium cations,[6,7] due to the stabilization of metal clusters avoiding the formation of catalytic inactive bulk metal.[8] The use of ILs as (co)solvents overcomes the main drawbacks of homogeneous catalysis, *i.e.* product separation and catalyst recovery, by immobilization of the catalyst in the ionic liquid phase.[9,10]

In ILs, the addition of Lewis bases as catalytic auxiliaries is not necessary to stabilize metallic nanoparticles (in fact, they are considered as ligand-free metallic systems if anions coming from the metallic salts are not considered), but their presence may enhance the stability of the nanoparticles, as observed when functionalized ionic liquids are employed,[11] besides their probable role in selective catalytic processes.

From a mechanistic point of view, the presence of metal nanoparticles in the catalytic reaction lead us to consider the nature of the catalytically active species. In these cases, an unambiguous distinction between colloidal and molecular catalysis is however often very difficult.[12] Concerning the nature of the active palladium species involved in Heck and Suzuki couplings, Jones and co-workers have recently published an extensive review.[13] In contrast to the widespread work carried out for Heck couplings,[14] less attention has been paid to identifying the nature of the catalyst for Suzuki cross-coupling reactions. Hu and Liu, based on catalyst recycling and TEM analysis, have recently proposed that for Suzuki couplings using Pd nanoparticles, leaching of discrete Pd(II) species occurs during the process, regenerating Pd(0) nanoparticles after the reductive elimination,[15] similarly to that suggested by Dupont *et al.*[14a] (in ionic liquid) and de Vries[14b] (in organic solvent) for Heck reactions, where nanoparticles are considered as catalyst reservoirs.

In the last years, we have been interested in the synthesis of metallic nanoparticles stabilized by ligands[16] and functionalized polymers[17] in organic solvents, in order to find pattern reactions[18] or specific catalytic inductions[19] helping us to discriminate between colloidal and homogeneous catalysts. In the studied systems, the presence of aryl groups became crucial in stabilizing the interaction between the metal and the ligand or substrate, probably due to π-coordination between the metallic surface and aromatic moieties.[19] More recently, we have prepared palladium nanoparticles in ILs from organometallic precursors to be applied in catalytic C–C couplings.[20]

With this analysis in mind, we looked for functionalized ligands with aromatic-free backbones in order to mainly favour the electrostatic stabilization of the palladium nanoparticles by the IL, to be subsequently used as catalysts in C–C couplings of aryl substrates; for this purpose, we chose norbornene derived ligands. *endo*-Norbornene monomers have largely been used as substrates for ring-opening metathesis polymerization, in particular using Grubbs ruthenium catalysts.[21] This kind of monomer, in particular the imide derivatives, can be readily prepared by Diels–Alder cycloadditions from maleimides[22] or norborn-5-ene-2,3-dicarboxylic anhydride.[23] To the best of our knowledge, these compounds have

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not been previously reported as ligands in metal-catalyzed organic processes.

Herein we report the synthesis and characterization of new ligands coming from *endo*-norborn-5-ene-2,3-dicarboxylic anhydride (**1–10**, Fig. 1) and their catalytic effect in palladium-catalyzed Suzuki C–C coupling reactions using arylbromides and arylboronic acid derivatives in ionic liquid [BMI][PF_6] (BMI = 1-*n*-butyl-3-methyl-imidazolium). Evaluation of the nature of the plausible catalyst is also described.

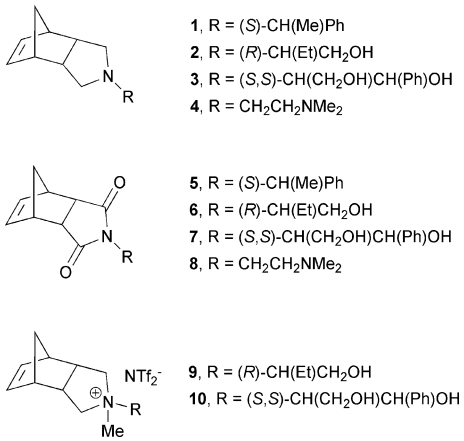
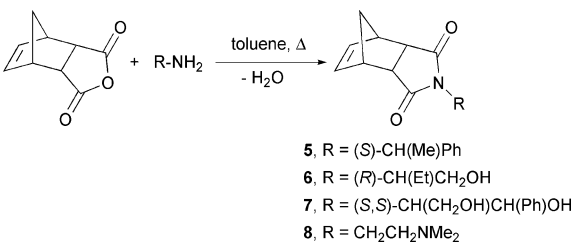


Fig. 1 Amines (**1–4**), imides (**5–8**) and ammonium (**9** and **10**) ligands derived from *endo*-carbic anhydride.

Results and discussion

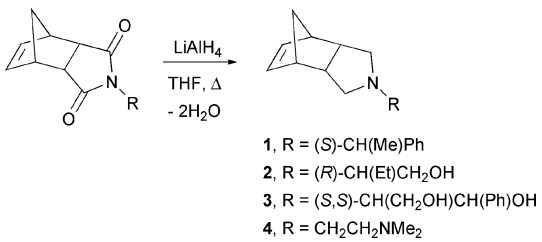
Synthesis of ligands

Imides **5–8** (Fig. 1) were prepared by condensation of *endo*-norborn-5-ene-2,3-dicarboxylic anhydride with the appropriated primary amine in toluene at reflux (Scheme 1), based on the methodology described in the literature.[23]



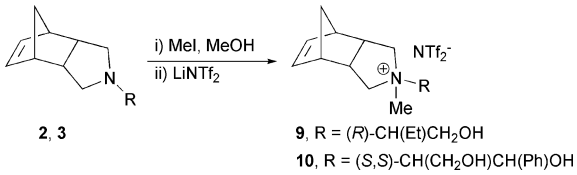
Scheme 1 Synthesis of imides **5–8**.

The corresponding amines, **1–4**, were obtained by standard reduction of carbonyl groups with $LiAlH_4$,[24] from the corresponding isolated imides (Scheme 2).



Scheme 2 Synthesis of amines **1–4**.

Ammonium derivatives, **9** and **10**, were prepared by classical amine quaternization from the appropriated amine, **2, 3**, with iodomethane,[25] followed by an anion exchange reaction using lithium bis(trifluoromethanesulfonyl)imide, $LiNTf_2$ (Scheme 3).[26]

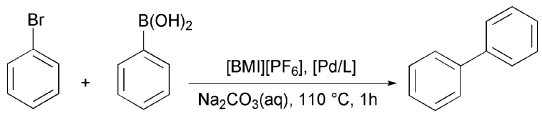


Scheme 3 Synthesis of ammonium derivatives **9** and **10**.

The three types of compounds (amines, imides and ammonium derivatives) were obtained in good yields (in the range 68–95%), and the overall yield for ammonium ligands was 50–55%.

Catalytic results

Suzuki cross-coupling between bromobenzene and phenylboronic acid under basic biphasic conditions, [BMI][PF_6]–H_2O (water was necessary to favour the solubility of phenyl boronic acid and sodium carbonate),[27] was carried out using palladium catalysts containing amines (**1–4**), imides (**5–8**) or ammonium (**9–10**) ligands (Scheme 4). Catalytic precursor was generated *in situ* from palladium acetate and the appropriate ligand. The catalytic results are summarized in Table 1.



Scheme 4 Pd-catalyzed C–C coupling between bromobenzene and phenylboronic acid (L = **1–10**).

The best results (up to 98% isolated yield in biphenyl) were obtained using amines functionalized by hydroxy groups, ligands **2** and **3** (entries 2 and 3, Table 1). The corresponding amide systems, **6** and **7**, and ammonium derivatives, **9** and **10**, were less efficient (entries 6, 7 and 9, 10 respectively, Table 1), with yields in the 27–48% range, due to the loss of electron-donor character

Table 1 Suzuki C–C coupling of bromobenzene with phenylboronic acid catalyzed by palladium acetate containing amines (**1–4**), imides (**5–8**) and ammonium (**9–10**) derivatives (Scheme 4)[a]

Entry	Ligand	Yield of isolated product (%)
1	**1**	28
2	**2**	83[b]
3	**3**	98
4	**4**	5
5	**5**	24
6	**6**	34
7	**7**	48
8	**8**	43
9	**9**	27
10	**10**	46
11	TMEDA	1

[a] Reaction conditions: Pd : L : bromobenzene : phenylboronic acid : sodium carbonate = 2.5 : 6.25 : 100 : 120 : 250 mmol in 1 cm^3 of [BMI][PF_6] and 2 cm^3 of water at 110 °C during 24 h; all reactions in duplicate. [b] Under the same conditions but not using deoxygenated water, the yield was 60%.

of the heterocyclic nitrogen atom. But for mono- or bis-amine systems, ligands **1** and **4** respectively, the yields were very low, in particular for **4** (entries 1 and 4, Table 1); for this latter system, the yellow colour of the ionic liquid phase remained after the reaction time, in contrast to the black colour observed for the other systems. In order to confirm this behaviour, the symmetrical bis(amine) *N*,*N*,*N*′*N*′-tetramethylethane-1,2-diamine (TMEDA) was also tested, leading to an inactive catalytic system (entry 11, Table 1), analogous to that observed for **4** (entry 4, Table 1). This lack of activity could be due to the formation of stable palladium(II) complexes containing bidentate coordinated ligands, which do not evolve towards Pd(0) active species.

From these preliminary results, we can prove the crucial role of hydroxy groups together with a heterocyclic amine moiety, to give active palladium catalysts in ionic liquid.[28]

It is also important to underline the inhibitor effect of oxygen. The product yield diminishes when water is not deoxygenated, as indicated for the Pd/**2** system (entry 2, Table 1).

With the best catalytic system, Pd/**3**, temperature, palladium content, palladium : ligand ratio and reaction time, were optimized for the model coupling reaction (Scheme 4). The results are shown in Table 2.

Although the system was even active at room temperature (entry 3, Table 2), the reaction rate decreased notably below 60 °C (entries 1–3, Table 2). The kinetics is probably due to the required time to form the catalytic active species. Palladium loading (entries 1, 4 and 5, Table 2) and Pd : ligand ratio (entries 4 and 6, Table 2) adjusments led to an excellent catalytic system working at 1 mol% of palladium with a 1 : 1.2 Pd : **3** ratio (entry 6, Table 2). Remarkably high rates were observed at short reaction times (entry 8 *vs*. 6 and 7, Table 2). The ligand-free system (if acetate is not considered) gave a low yield in biphenyl (entry 9, Table 2).

Under the optimized conditions (entry 6, Table 2) and after 1 h of reaction, 1 mmol of substrate was added to the catalytic mixture, obtaining in this second run 70% yield in biphenyl. This fact shows that the catalytic system is still active after the first run.

The palladium content in biphenyl was determined by ICP-MS for the isolated product obtained under optimized conditions at different reaction times (60, 30 and 10 minutes; see entries 6–8 in Table 2). The palladium content diminution with the conversion increase shows a notary metal leaching from the ionic liquid phase to the organic phase at low substrate conversions (63 ppm, entry 8 in Table 2), but less than 10 ppm for quantitative yields (entry 8, Table 4). A similar trend was observed for Heck reactions using both palladium heterogeneous catalyst precursors[29] and preformed nanoparticles;[14a] in the latter case, it was proposed that palladium nanoparticles act as a reservoir of catalytically active molecular species.

Table 2 Suzuki C–C coupling of bromobenzene with phenylboronic acid catalyzed by palladium acetate containing ligand **3**[a]

Entry	Pd/mol%	L/mol%	*T*/°C	*t*/min	Yield of isolated product (%)
1	2.5	6.25	60	60	98
2	2.5	6.25	50	60	29
3	2.5	6.25	rt	5760 (4 d)	87
4	1	2.5	60	60	88
5	0.25	0.625	60	60	24
6	1	1.2	60	60	93 (27.5)[b]
7	1	1.2	60	30	84 (40.0)[b]
8	1	1.2	60	10	56 (63.0)[b]
9	1	0	60	60	46

[a] Reaction conditions: bromobenzene : phenylboronic acid : sodium carbonate = 1 : 1.2 : 2.5 mmol in 1 cm^3 of [BMI][PF_6] and 2 cm^3 of water; all reactions in duplicate. [b] In brackets, palladium content determined by ICP-MS (in ppm).

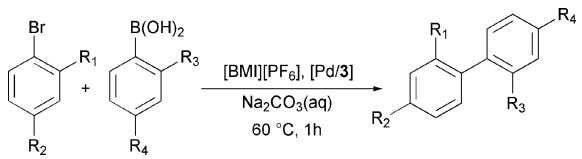
Table 3 Effect of the solvent in Suzuki C–C coupling of bromobenzene with phenylboronic acid catalyzed by palladium acetate containing ligands **3** and **4**[a]

Entry	Ligand	Solvent	*t*/h	*T*/°C	Yield of isolated product (%)
1	**3**	[BMI][PF_6]–H_2O	1	60	93
2	**3**	Toluene–H_2O	1	60	0
3	**3**	Toluene–H_2O	6	100	36
4	**4**	Toluene–H_2O	6	100	57
5	**4**	[BMI][PF_6]–H_2O	6	100	4
6[b]	**3**	Neat H_2O	24	60	50

[a] Reaction conditions: Pd : L : bromobenzene : phenylboronic acid : sodium carbonate = 1 : 1.2 : 100 : 120 : 250 mmol in 1 cm^3 of [BMI][PF_6] or toluene and 2 cm^3 of water; all reactions in duplicate. [b] Catalytic reaction in 3 cm^3 of water.

The requirement to employ well-adapted ligands to the medium could be demonstrated by the cross-coupling reactions in toluene and [BMI][PF_6], with $Pd(OAc)_2$/**3** and $Pd(OAc)_2$/**4** as catalytic systems (Table 3). While Pd/**3** behaved as an outstanding system in ionic liquid (entry 1, Table 3), no activity was observed under the same conditions in toluene (entry 2, Table 3); the expected product was only obtained at harsh conditions but in low yield (entry 3, Table 3). On the contrary, Pd/**4** was actually active in toluene (entries 4 *vs*. 5, Table 3). In addition, when neat water was used as solvent, the Pd/**3** catalytic system was less efficient (entry 1 *vs*. 6, Table 3) due to the less effective catalyst stabilization than that observed under biphasic conditions, [BMI][PF_6]–water. These results together with that observed for TMEDA (entry 11, Table 1) show that palladium(II) precursors containing a N,N-bidentate ligand are more robust towards reduction to Pd(0) in the ionic liquid than in toluene, avoiding the formation of active Pd(0) species in [BMI][PF_6].

Arylbromide and arylboronic acid derivatives bearing functional groups in *ortho* or *para* position to bromide and/or boronic acid moieties, were tested using our best catalytic system ($Pd(OAc)_2$/**3**) under the optimized conditions (Scheme 5), to give mono- or di-substituted biaryl products. The results are summarized in Table 4.



Scheme 5 Formation of substituted biaryl compounds from mono-substituted bromobenzene and arylboronic acid derivatives by Pd-catalyzed cross-coupling.

Mono-substituted biaryl compounds. When either methoxy or trifluoromethyl groups were introduced in the *para* position of the bromide substrate, the corresponding mono-substituted

Table 4 Suzuki C–C coupling of substituted-bromobenzene and substituted-phenylboronic acid derivatives catalyzed by palladium acetate containing ligand **3** (Scheme 5)[a]

Entry	R_1	R_2	R_3	R_4	Conversion[b] (%)	Yield of cross-coupling product (%)	Products ratio[c] (cc/by-products)
1	H	CF_3	H	H	100	>99	100/0
2	H	OCH_3	H	H	87	87	15/1 (cc/hcb)
3	H	H	H	CF_3	100	71	4/1 (cc/hcb)
4	H	H	H	OCH_3	100	66	7/1 (cc/hcb)
5	CH_3	H	H	H	41	41	4/1 (cc/hcb)
6	H	H	CH_3	H	74	71	100/0
7	H	H	OCH_3	H	69	13	1/3 (cc/db)
8	H	CF_3	H	OCH_3	100	99 (9.5)[d]	100/0
9	H	OCH_3	H	CF_3	71	53	15/5/1/2 (cc/hcb/hch/dh)
10	H	CF_3	CH_3	H	99	95	55/1/1.5 (cc/hcb/hch)
11	[e]	[e]	H	H	70	70	3/1 (cc/hcb)
12	H	H	—	—	97	—	—
13	—	—	H	H	100	—	—

[a] Reaction conditions: Pd : **3** : arylbromide : arylboronic acid derivative : sodium carbonate = 1 : 1.2 : 100 : 120 : 250 mmol in 1 cm^3 of [BMI][PF_6] and 2 cm^3 of water at 60 °C during 1 h; all reactions in duplicate. [b] Based on arylbromide consumption. [c] Determined by ^1H NMR. Products obtained are shown in brackets (**cc**: cross-coupling product; hcb: homocoupling product from arylboronic acid; hch: homocoupling product from arylbromide; db: deboronation product; dh: dehalogenation product). [d] In brackets, palladium content determined by ICP-MS (in ppm). [e] 1-Bromo-2-methylnaphthalene used as substrate; reaction time: 24 h.

biphenyl compound was obtained in high yield (entries 1 and 2, Table 4), especially for the trifluoromethyl derivative. Attempts to obtain the same products but starting from the appropriate boronic acid, led to lower yields in the cross-coupling product. Formation of the boronic acid homocoupling by-product (entries 3 and 4, Table 4), was particularly significant in the case of 4-trifluoromethylphenylboronic acid (entry 3, Table 4). In all these cases, no significant differences due to the electronic character of the substituents could be observed either in the substrate or in the boronic acid derivative (entries 1 *vs*. 2 and 3 *vs*. 4, Table 4).

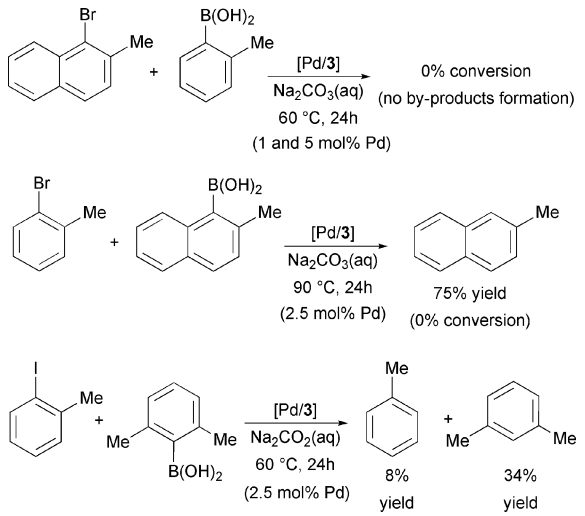
When the functionalization was introduced in the *ortho* position, from 2-methylbromobenzene or 2-methylphenylboronic acid (entries 5 and 6 respectively, Table 4), a significant steric influence for the substrate (41% yield) but less important for the boronic acid (71% yield) was observed. In addition, the introduction of a methoxy group in the *ortho* position of the boronic acid caused a dramatic decrease of the yield in cross-coupling product with important formation of deboronation product (entry 7, Table 4). Cross-coupling between 1-bromo-2-methylnaphthalene and phenylboronic acid gave the desired product in 70% yield, with 38% yield of boronic acid homocoupling after 24 h of reaction (entry 11, Table 4), an analogous trend to that observed for 2-methylbromobenzene (entry 5, Table 4).

Di-substituted biaryl compounds. Suzuki C–C cross-coupling reactions between both substituted-arylbromide and substituted-arylboronic acid derivatives were also studied. Quantitative yield was obtained from 4-trifluoromethylbromobenzene and 4-methoxyphenylboronic acid (entry 8, Table 4). With the same substrate, the *ortho*-methyl-substituted boronic acid led to 95% yield in the cross-coupling product (entry 10, Table 4). In contrast, the introduction of an electron donating group in the arylbromide and an electron withdrawing one in the boronic acid led to a moderate yield in the desired biaryl compound, together with several by-products (entry 9, Table 4).

These data clearly show that only the substrate containing the electron withdrawing trifluoromethyl group in the *para* position, 4-trifluoromethylbromobenzene (entries 1, 8 and 10, Table 4) allows an activity increase compared with the formation of biphenyl (entry 6, Table 2). However, the substituents in the *ortho* position lead to an activity decrease (entries 5, 6 and 7 Table 4 *vs*. entry 6 Table 2) due to steric hindrance, except when the activated 4-trifluoromethylbromobenzene was used as substrate (entry 10, Table 4); this effect is dramatic when 2-methoxyphenylboronic acid is used, giving the lowest yield in the cross-coupling product (entry 7, Table 4).

Concerning chemoselectivity, 4-trifluoromethylbromobenzene directs the reaction towards the formation of cross-coupling product (entries 1, 8 and 10, Table 4). However in the other cases, except for the reaction between bromobenzene and 2-methylphenylboronic acid (entry 6, Table 4), formation of by-products (homocoupling, deboronation and dehalogenation products) was observed. Among them, homocoupling from arylboronic acids was the most important side-reaction, being remarkable when electron-deactivated boronic acid and/or substrate (entries 2, 3 and 9, Table 4) were involved or sterically hindered substrates were used (entries 5 and 11, Table 4), most probably due to its activation towards oxidative addition, in competition with that of arylbromide substrate. It is important to mention the coupling between bromobenzene and 2-methoxyphenylboronic acid, giving as major product the corresponding deboronation product (entry 7, Table 4). Dehalogenation (entry 9, Table 4) and homocoupling from substrate were occasionally obtained in low yield (less than 7%, entries 9 and 10, Table 4).

Taking into account that 2-methylbromobenzene and 1-bromo-2-methylnaphthalene with phenylboronic acid (entries 5 and 11 respectively, Table 4), and also 2-methylphenylboronic acid with bromobenzene (entry 6, Table 4) gave mainly the *ortho*-substituted cross-coupling product in moderated yield, we planned to evaluate the asymmetric induction in Suzuki C–C coupling (Scheme 6). Unfortunately, no cross-coupling product was obtained in any case. Under harsh conditions, only dehalogenation and deboronation products were obtained in agreement with the reactivity involving heterogeneous catalysts (see below).



Scheme 6 Asymmetric Suzuki C–C coupling reactions using $Pd(OAc)_2$/**3** as catalyst in [BMI][PF_6] (Pd : **3** ratio = 1 : 1.2).

Catalyst nature

The remarkable effect observed in terms of catalytic activity depending on the ligand nature and the solvent involved (see above) led us to study more carefully the catalyst nature of the species generated from palladium acetate in [BMI][PF_6].

Poison tests. Mercury is a classical test to identify heterogeneous catalysts,[30] but also other metal(0) species, such as molecular complexes and colloids, can be identified.[31] On the other hand, Lewis bases represent a tool to identify homogeneous catalysts.[32]

In our case, addition of mercury (for a typical procedure, see Experimental section), after 10 min of reaction between bromobenzene and phenylboronic acid (at this time, conversion is *ca.* 60%), quenched the reaction; only 68% yield was obtained after 1 h in contrast to that obtained without mercury (93%, entry 6 in Table 2). This result reveals that Pd(0) species (molecular or heterogeneous) are involved in the catalytic process.

On the other hand, triphenylphosphine was added to the catalytic reaction in two different Pd : PPh_3 ratios, 1 : 0.3 and 1 : 4 (for a typical procedure, see Experimental section). In both cases, the reaction was inhibited (after 1 h, 75% and 55% yield were respectively obtained for 1 : 0.3 and 1 : 4 Pd : PPh_3 ratio), the reaction being completely stopped for Pd : PPh_3 = 1 : 4. It is important to mention that using $Pd(OAc)_2$: PPh_3 (1 : 2) as catalytic precursor gave 65% yield, under our optimized conditions. This behaviour is in agreement with that observed for molecular palladium/mono(phosphine) systems in organic solvents, the optimum Pd : P ratio being 1 : 1; higher phosphine contents lead to less active systems for the most cases.[33] But it also agrees with the reported induction period observed for Heck couplings using triphenylphosphine and palladium acetate as precursors of nanoparticles in ionic liquids.[34] Therefore, these results point to the presence of catalytically active molecular species.

It is also important to underline the inhibitor effect of oxygen. As described above, the product yield diminishes when solvents are not deoxygenated. This trend cannot be justified in terms of homogeneous palladium catalysts. Homocoupling of arylboronic acids (in our case, this would increase the yield in biphenyl) is more efficient in the presence of oxidants, in particular dioxygen,[35] due to the formation of peroxo-palladium complexes, key intermediates for this reaction.[36]

TEM analysis. TEM micrographs of the post-catalysis ionic liquid phase was carried out for the coupling of bromobenzene with phenylboronic acid (entry 8, Table 2). In fact, small nanoparticles were observed (*ca.* mean diameter 8 nm) showing a pile organization in the ionic liquid (Fig. 2a).

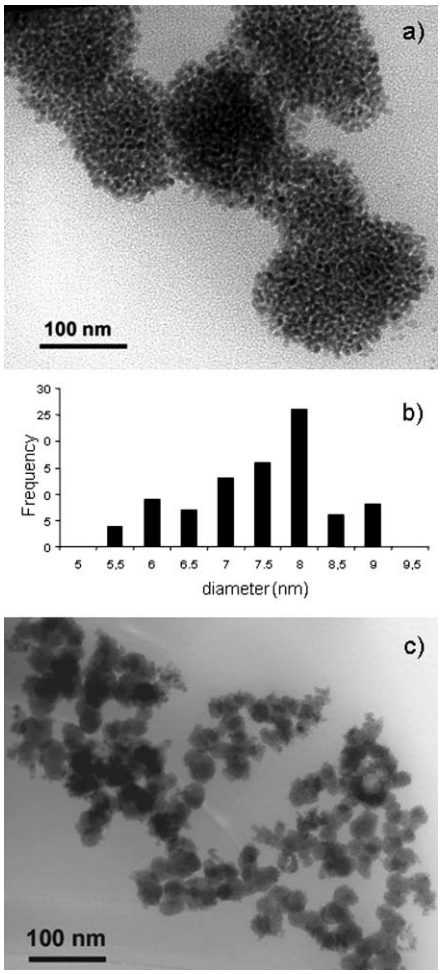
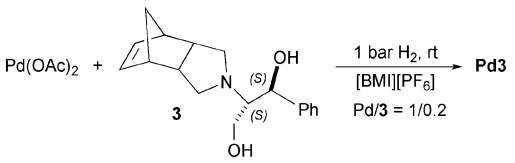


Fig. 2 TEM micrographs of: a) post-catalytic solution using $Pd(OAc)_2$/**3** as catalyst (see entry 7 in Table 2) and b) the corresponding size histogram (90 nanoparticles measured); c) preformed **Pd3** nanoparticles dispersed in [BMI][PF_6].

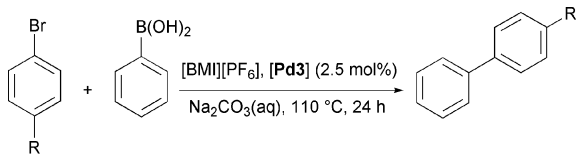
In order to compare the catalytic behaviour of the particles generated under catalytic conditions with that observed using preformed material, palladium nanoparticles were prepared following the methodology previously described.[20,37] **Pd3** nanoparticles were synthesised from palladium acetate in the presence of ligand **3** under a hydrogen atmosphere in [BMI][PF_6] (Scheme 7). TEM images essentially revealed the formation of agglomerates (Fig. 2c).

Pd3 was used as catalytic precursor in the cross-coupling catalytic reaction between bromobenzene and phenylboronic acid (110 °C, 24 h, 2.5 mol% Pd). The low yield obtained (52%) is in agreement with the agglomerated material used in comparison with that formed during the catalytic reaction (Fig. 2a), as found



Scheme 7 Synthesis of palladium nanoparticles containing ligand **3**.

by Narayanan and El-Sayed for Suzuki reactions using palladium nanoparticles stabilized by polyvinylpyrrolidone.[38] However the system was more active when 4-methoxybromobenzene was used as substrate, giving 70% yield of cross-coupling product (Scheme 8), the opposite trend to that found for the catalyst using palladium acetate as precursor (93%, entry 6 in Table 2, *vs*. 87%, entry 2 in Table 4), indicating, in the latter case, the presence of molecular species.



Scheme 8 Suzuki cross-coupling catalyzed by preformed palladium nanoparticles containing ligand **3**.

In order to check whether nanoparticles are formed from *N*-heterocyclic palladium complexes,[31a,39] $Pd(OAc)_2$ and $[BMI][PF_6]$ were mixed at room temperature and at 110 °C for 24 h. In any case, a *N*-heterocyclic carbene palladium complex was formed as ^1H and ^{13}C NMR monitoring revealed, in contrast to what was found by Xiao and co-workers using [BMI][Br],[40] probably due to the poor coordinating ability of the hexafluorophosphate anion. This experiment rules out the formation of palladium nanoparticles from carbene intermediates, but it does not exclude the formation of carbenes at the metallic surface when nanoparticles are present.[41]

Catalytic selectivity. Reactivity patterns, mainly concerning hydrogenation, have been used to distinguish between homogeneous and heterogeneous catalysts, although it is really difficult to find reactions that solely work with homogeneous and not heterogeneous catalysts, and vice versa.[32] But not only the (in)activity may suggest the identity of the catalyst. Recent reported cases point to a distinction taking into account the selectivity trend, in particular concerning the asymmetric induction.[19,42]

Chemoselectivity for Heck and Suzuki couplings could also be a useful tool in discussing the nature of the catalyst, taking into account the fact that homocoupling, dehalogenation and deboronation reactions of aryl derivatives are typically catalyzed by heterogeneous palladium species.[43,44] In our case, homocoupling side products were obtained in many cross-coupling reactions (see Table 4); in addition, bromobenzene in the absence of phenylboronic acid and phenylboronic acid in the absence of bromobenzene gave quantitative debromination and deboronation products respectively, without formation of homo-coupling product (entries 12 and 13, Table 4). These facts suggest that *in situ* generated PdNPs are responsible for this reactivity.

Conclusions

The most important conclusion of this work concerns the effect of the solvent together with the ligand nature in the catalytic activity for Suzuki C–C coupling. While in organic solvents, homogeneous catalytic species are stable enough in the presence of good donor ligands, as for bidentate nitrogen donor ligands (otherwise inactive agglomerates are formed), in ionic liquids, palladium systems are only active when nanoparticles are formed *in situ*. In this latter case, the presence of ligands containing hydroxy groups enhances the stability of the metallic nanoparticles. The formation of palladium(II) molecular precursors in $[BMI][PF_6]$ prevents the formation of Pd(0) species and consequently the catalytic system becomes inactive.

Concerning the nature of the catalyst in $[BMI][PF_6]$ from palladium acetate, poison tests reveal that Pd(0) species are involved in the catalytic process. Formation of PdNPs in $[BMI][PF_6]$ (exhibited by TEM analysis) is required to give an active catalytic system. These particles are catalytically active towards dehalogenation and deboronation of the corresponding aryl compounds and we cannot exclude their role in the C–C coupling processes, in view of the homocoupling observed in many cases.

Therefore, the mechanism proposed for Pd-catalyzed Heck C–C coupling where palladium nanoparticles act as a reservoir of active molecular species,[13] seems to be also reasonable for Suzuki coupling, although the catalytic activity of nanoparticles cannot be excluded at this time.

More detailed studies are currently in progress in order to shed light on the interactions between ligand and metallic surface.

Experimental

General

All compounds were prepared under a purified nitrogen or argon atmosphere using standard Schlenk and vacuum-line techniques. The organic solvents were purified by standard procedures and distilled under nitrogen. ILs were supplied by Solvionic (99.5+%; chloride contents certified to <1 ppm). ILs were treated under reduced pressure at 70 °C overnight prior to use. NMR spectra were recorded on Varian Bruker DRX 500 (^1H, standard $SiMe_4$), Varian Gemini (^{13}C, 50 MHz, standard $SiMe_4$) and Bruker DRX 250 (^{31}P, 101.2 MHz, standard H_3PO_4) spectrometers in $CDCl_3$ unless otherwise cited. Chemical shifts were reported downfield from standards. IR spectra were recorded on a FTIR Nicolet Impact 400 spectrometer. Mass chromatograms were carried out by the "Servei d'Espectrometria de Masses" of the Universitat de Barcelona (Chemical ionization on a ThermoFinnigan Trace DSQ instrument using methane or ammonia as reactant gas; electronic impact on a Hewlett Packard 5989A apparatus and electrospray on a ZQ (Micromass, UK) instrument). Optical rotations were measured in a Perkin Elmer 241MC polarimeter. Elemental analyses were carried out by the "Serveis Cientifico-Tècnics" of the Universitat Rovira i Virgili (Tarragona) on an Eager 1108 microanalyzer. The elemental analysis of palladium was determined by ICP-MS and carried out by Antellis. The images of particles dispersed in $[BMI][PF_6]$ were obtained from a transmission electron microscope running at 120 kV. A drop of solution was deposited on a holey carbon grid and the excess

of [BMI][PF_6] was removed in order to obtain a film as thin as possible. Images were recorded on the film of IL lying on the holes of the grid. The size of the nanoparticles was directly determined from TEM images recorded with a high magnification (>500 000). Due to the overlapping of nanoparticles, the diameter was individually measured on particles at the boundary of agglomerates.

Synthesis of ligands

General procedure for the synthesis of *endo*-bicyclo[2.2.1]hept-5-en-2,3-dicarboximides (5–8). *endo*-Norborn-5-ene-2,3-dicarboxylic anhydride (1.64 g, 10.0 mmol) was dissolved in distilled toluene (50 cm^3) and the resulting suspension was vigorously stirred until total dissolution. The appropriate primary amine (15.0 mmol) was added dropwise and a yellowish suspension was immediately formed. The mixture was heated at 80 °C and allowed to stir for 24 or 48 h. The cooled colourless solution was concentrated under vacuum, giving a white oil which was then dissolved in dichloromethane (20 cm^3) and consecutively washed with 1 M H_2SO_4 (3 × 20 cm^3) and water (3 × 20 cm^3). The aqueous phases were washed with 20 cm^3 of dichloromethane. The combined organic phases were dried with anhydrous Na_2SO_4, filtered and the solvent evaporated under reduced pressure, yielding the corresponding imide.

Imide ***5***. Obtained from (*S*)-1-phenylethylamine (1.82 g, 15.0 mmol). The crude product was recrystallized in a mixture of hexane–ethyl acetate (5 : 1), giving a white solid (2.43 g, 91%). $[\alpha]_D^{25}$ +72.4° (*c* 1.0 in $CHCl_3$); ν_{max}(KBr pellet)/cm^{-1} 3065 (=CH), 3000, 2943, 2874, 1761 (CO), 1696 (CO), 1387, 1365, 1217, 1196, 1109, 1022, 739, 726 and 700; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.47 (1 H, d, *J* 8.4, C*H*H′ bridge), 1.65 (1 H, d, *J* 8.0, CH*H*′ bridge), 1.68 (3 H, d, *J* 7.5, CHC*H*$_3$Ph), 3.12–3.19 (2 H, m, 2 × CH_{olefin}C*H*CH_2bridge), 3.33 (2 H, br d, *J* 9.3, 2 × C*H*CON), 5.24 (1 H, q, *J* 7.5, C*H*MePh), 5.85 (1 H, dd, *J* 2.9 and 5.6, C*H*=CH′), 6.00 (1 H, dd, *J* 2.9 and 5.6, CH=C*H*′) and 7.22–7.36 (5 H, m, CHMe*Ph*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 16.5 (CH_3), 45.2 (CH), 45.3 (CH), 45.35 (CH), 45.4 (CH), 49.8 (CH), 52.1 (CH_2), 127.2–128.2 (5 × CH), 134.4 (CH), 139.7 (C), 177.6 (CO) and 177.6 (CO); *m*/*z* (CI, CH_4) 268.3 (M + H^+. $C_{17}H_{18}NO_2^+$ requires 268.3).

Imide ***6***. Obtained from (*R*)-2-aminobutanol (1.34 g, 15.0 mmol). Product obtained as a colourless oil (2.24 g, 95%). $[\alpha]_D^{25}$ +12.2° (*c* 1.0 in $CHCl_3$); ν_{max}(NaCl film)/cm^{-1} 3435 (OH), 2967 (=CH), 2937, 2874, 1765, 1692 (CO), 1456, 1396, 1373, 1297, 1190, 1131, 1068, 842 and 719; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.83 (3 H, t, *J* 7.5, NCHCH_2C*H*$_3$), 1.52 (1 H, d, *J* 8.7, C*H*H′ bridge), 1.60–1.72 (2 H, m, NCHC*H*$_2$CH$_3$), 1.70 (1 H, d, *J* 8.7, CH*H*′ bridge), 2.77 (1 H, br s, OH), 3.22–3.24 (2 H, m, 2 × CH_{olefin}C*H*CH_2bridge), 3.34 (2 H, br s, 2 × C*H*CON), 3.60 (1 H, dd, *J* 3.0 and 11.7, CHC*H*H′OH), 3.79 (1 H, dd, *J* 7.1 and 11.6, CHCH*H*′OH), 3.84–3.91 (1 H, m, *J* 1.2, 3.0 and 7.1, C*H*CHH′OH) and 6.11 (2 H, br s, C*H*=C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 10.5 (CH_3), 21.0 (CH_2), 45.05 (CH), 45.1 (CH), 45.45 (CH), 45.6 (CH), 52.1 (CH_2), 55.8 (CH), 62.4 (CH_2), 134.5 (CH), 134.6 (CH), 177.6 (CO) and 178.6 (CO); *m*/*z* (CI, CH_4) 236.3 (M + H^+. $C_{13}H_{18}NO_3^+$ requires 236.3).

Imide ***7***. Obtained from (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol (2.51 g, 15.0 mmol). Product obtained as a white crystalline solid (2.76 g, 88%). $[\alpha]_D^{25}$ +10.0° (*c* 1.0 in $CHCl_3$); ν_{max}(KBr pellet)/cm^{-1} 3447 (OH), 2994, 2975, 1676 (CO), 1394, 1368, 1294, 1262, 1184, 1085, 1057, 1019, 1007, 803, 764, 698, 663 and 620; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.45 (1 H, d, *J* 8.8, C*H*H′ bridge), 1.63 (1 H, d, *J* 8.8, CH*H*′ bridge), 3.16–3.20 (2 H, m, 2 × CH_{olefin}C*H*CH_2 bridge), 3.25–3.27 (2 H, m, 2 × C*H*CON), 3.80 (1 H, dd, *J* 6.8 and 12.0, C*H*H′CHCHPh), 3.87 (1 H, dd, *J* 5.2 and 12.0, CH*H*′CHCHPh), 4.59 (1 H, q, *J* 6.0, CHH′C*H*CHPh), 5.20 (1 H, d, *J* 6.0, CHH′CHC*H*Ph), 5.58 (1 H, br s, C*H*=CH′), 5.67 (1 H, br s, CH=C*H*′) and 7.23–7.36 (5 H, m, Ph); δ_C(100 MHz; $CDCl_3$; Me_4Si) 43.1 (CH), 43.2 (CH), 43.9 (CH), 44.2 (CH), 50.5 (CH_2), 56.8 (CH_2), 59.5 (CH), 69.8 (CH) 123.7 (2 × CH), 125.9 (CH), 126.7 (2 × CH), 132.4 (CH), 132.5 (CH), 138.9 (C), 179.0 (CO) and 179.4 (CO); *m*/*z* (EI) 314 (M^+. $C_{18}H_{19}NO_4^+$ requires 313.4).

Imide ***8***. Obtained from *N*,*N*-dimethylethylenediamine (1.32 g, 15.0 mmol). Product obtained as a white solid (2.01 g, 86%) (Found: C, 66.6; H, 7.9; N, 11.7. Calc. for $C_{13}H_{18}N_2O_2$: C, 66.6; H, 7.7; N, 12.0%); ν_{max}(KBr pellet)/cm^{-1} 2989, 2946, 2791, 1699 (CO), 1395, 1340, 1227, 1152, 1045, 1000, 914, 842 and 722; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.52 (1 H, d, *J* 8.4, C*H*H′ bridge), 1.71 (1 H, d, *J* 8.4, CH*H*′ bridge), 2.22 (6 H, s, 2 × CH_3), 2.33 (2 H, t, *J* 6.9, $CH_2CH_2NMe_2$), 3.24–3.26 (2 H, m, 2 × CH_{olefin}C*H*CH_2 bridge), 3.36–3.38 (2 H, m, 2 × C*H*CON), 3.44 (2 H, t, *J* 6.9, $CH_2CH_2NMe_2$) and 6.07 (2 H, br t, *J* 1.8, C*H*=C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 36.2 (CH_2), 44.95 (2 × CH), 45.4 (2 × CH_3), 45.9 (2 × CH), 52.2 (CH_2), 56.3 (CH_2), 134.5 (2 × CH) and 177.8 (2 × CO); *m*/*z* (EI) 234 (M^+. $C_{13}H_{18}N_2O_2^+$ requires 234.3).

General procedure for the synthesis of *endo*-4-aza-tricyclo-[5.2.1.$0^{2,6}$]dec-8-enes (1–4). The corresponding imide (6.0 mmol) was dissolved in freshly distilled THF (100 cm^3) and stirred until total dissolution. The solution was cooled at 0 °C and $LiAlH_4$ (2.28 g, 60.0 mmol) was slowly added, giving a white suspension. The mixture was heated at reflux for 48 h, then cooled at 0 °C. 20 cm^3 of diethyl ether and a saturated aqueous solution of Na_2SO_4 were added. The addition of the aqueous solution was slowly performed and was stopped when effervescence was no longer observed in the reaction mixture. The white gel was then filtered over Celite and the solution obtained was washed several times with a mixture of CH_2Cl_2–MeOH (9 : 1). The organic phase was washed with water (3 × 20 cm^3), dried with anhydrous Na_2SO_4, filtered and concentrated at reduced pressure, yielding the corresponding amine.

Amine ***1***. Obtained from **5** (1.60 g, 6.0 mmol). Product obtained as a yellow oil (1.26 g, 88%). $[\alpha]_D^{25}$ +68.5° (*c* 1.0 in $CHCl_3$); ν_{max}(NaCl film)/cm^{-1} 3060, 2967, 2864, 2798, 1489, 1453, 1370, 1307, 1137, 958, 762, 735 and 699; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.28 (3 H, d, *J* 6.8, CHC*H*$_3$Ph), 1.50 (1 H, d, *J* 8.0, C*H*H′ bridge), 1.63 (1 H, dt, *J* 1.8 and 8.4, CH*H*′ bridge), 1.80 (1 H, dd, *J* 7.4 and 9.4, CHC*H*H′N), 1.88 (1 H, dd, *J* 7.0 and 8.6, CHC*H*H′N), 2.51 (1 H, t, *J* 8.6, CHCH*H*′N), 2.70 (1 H, br s, CH_{olefin}C*H*CH_2 bridge), 2.76–2.84 (1 H, m, C*H*CHH′N), 2.79 (1 H, br s, CH_{olefin}C*H*CH_2 bridge), 2.88–2.95 (1 H, m, C*H*CHH′N), 2.98 (1 H, t, *J* 8.2, CHCH*H*′N), 3.12 (1 H, q, *J* 6.7, C*H*MePh), 6.09–6.14 (2 H, m, C*H*=C*H*), 7.17–7.23 (1 H, m, Ph) and 7.25–7.27 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$; Me_4Si) 23.0 (CH_3), 44.9 (CH), 45.0 (CH), 46.3 (CH), 46.4 (CH), 53.7 (CH_2), 55.7 (CH_2), 56.0 (CH_2), 66.0 (CH), 126.9 (CH), 127.3 (2 × CH), 128.3 (2 × CH), 137.1 (CH),

137.5 (CH) and 145.7 (C); *m/z* (ESI(+)) 240 ($M + H^+$. $C_{17}H_{22}N^+$ requires 240.2).

Amine ***2***. Obtained from **6** (1.41 g, 6.0 mmol). Product obtained as a yellow oil (1.02 g, 82%). $[\alpha]_D^{25}$ −28.8° (*c* 0.93 in $CHCl_3$); ν_{max}(NaCl film)/cm^{-1} 3396 (OH), 3060, 2957, 2874, 2818, 1463, 1346, 1111, 1054 and 729; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.86 (3 H, t, *J* 7.6, NCHCHH′C*H*$_3$), 1.18–1.26 (1 H, m, NCHC*H*H′CH$_3$), 1.42 (1 H, d, *J* 8.0, C*H*H′ bridge), 1.49–1.56 (1 H, m, NCHCH*H*′CH$_3$), 1.53 (1 H, d, *J* 8.4, CH*H*′ bridge), 2.29–2.32 (2 H, m, 2 × CHC*H*H′N), 2.36–2.42 (1 H, m, C*H*CHH′OH), 2.63 (1 H, t, *J* 8.2, CHCH*H*′N), 2.74–2.81 (3 H, m, CHCH*H*′N and 2 × CH_{olefin}C*H*CH$_2$bridge), 2.83 (2 H, br s, 2 × C*H*CHH′N), 3.18 (1 H, dd, *J* 8.0 and 10.4, CHC*H*H′OH), 3.52 (1 H, dd, *J* 4.8 and 10.4, CHCH*H*′OH) and 6.20 (2 H, br s, C*H*=C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 11.3 (CH_3), 19.3 (CH_2), 45.2 (CH), 45.3 (CH), 45.8 (CH), 45.9 (CH), 50.3 (CH_2), 52.3 (CH_2), 52.9 (CH_2), 60.8 (CH_2), 63.3 (CH), 136.3 (CH) and 136.5 (CH); *m/z* (ESI(+)) 208 ($M + H^+$. $C_{13}H_{22}NO^+$ requires 208.2).

Amine ***3***. Obtained from **7** (1.88 g, 6.0 mmol). Product obtained as a yellowish solid (1.66 g, 97%). $[\alpha]_D^{25}$ +58.1° (*c* 1.0 in $CHCl_3$) (Found: C, 75.0; H, 8.3; N, 5.0. Calc. for $C_{18}H_{23}NO_2$: C, 75.7; H, 8.1; N, 4.9%); ν_{max}(NaCl film)/cm^{-1} 3379 (OH), 2957, 1453, 1350, 1130, 1054 and 699; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.42 (1 H, d, *J* 8.0, C*H*H′ bridge), 1.52 (1 H, d, *J* 8.0, CH*H*′ bridge), 2.53–2.59 (2 H, m, 2 × CHC*H*H′N), 2.71–2.91 (6 H, m, CHCH*H*′N, CHH′C*H*CHPh, 2 × C*H*CHH′N and 2 × CH_{olefin}C*H*CH$_2$ bridge), 2.99 (1 H, t, *J* 8.0, CHCH*H*′N), 3.42 (1 H, dd, *J* 4.4 and 11.4, C*H*H′CHCHPh), 3.52 (1 H, dd, *J* 7.2 and 11.4, CH*H*′CHCHPh), 4.36 (1 H, d, *J* 9.2, CHH′CHC*H*Ph), 6.29 (2 H, s, C*H*=C*H*) and 7.25–7.35 (5 H, m, Ph); δ_C(100 MHz; $CDCl_3$; Me_4Si) 45.0 (CH), 45.3 (CH), 46.5 (CH), 46.5 (CH), 49.9 (CH_2), 52.5 (CH_2), 52.7 (CH_2), 59.5 (CH_2), 66.8 (CH), 72.2 (CH), 127.1 (2 × CH), 128.1 (CH), 128.7 (2 × CH), 136.3 (CH), 136.5 (CH) and 142.5 (C); *m/z* (CI, NH_3) 286.6 ($M + H^+$. $C_{18}H_{24}NO_2^+$ requires 286.4).

Amine ***4***. Obtained from **8** (1.41 g, 6.0 mmol). Product obtained as a pale brown oil (1.03 g, 83%). ν_{max}(NaCl film)/cm^{-1} 3402, 2964, 2868, 2818, 1649, 1453, 1340, 1254, 1137, 1041 and 729; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.57 (1 H, br d, *J* 8.0, C*H*H′ bridge), 1.69 (1 H, br dt, *J* 1.6 and 8.0, CH*H*′ bridge), 1.83 (2 H, br s, 2 × CHC*H*H′N), 2.21 (6 H, s, N(C*H*$_3$)$_2$), 2.36 (2 H, br t, *J* 7.0, CH$_2$C*H*$_2$NMe$_2$), 2.49 (2 H, br td, *J* 1.2 and 7.1, C*H*$_2$CH$_2$NMe$_2$), 2.78 (2 H, br s, 2 × CH_{olefin}C*H*CH$_2$ bridge), 2.93 (4 H, br s, 2 × C*H*CHH′N and 2 × CHCH*H*′N) and 6.12 (2 H, t, *J* 1.6, C*H*=C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 44.6 (2 × CH), 46.0 (2 × CH_3), 46.7 (2 × CH), 53.9 (CH_2), 54.4 (CH_2), 57.3 (2 × CH_2), 58.5 (CH_2) and 137.4 (2 × CH); *m/z* (EI) 206.0 (M. $C_{13}H_{22}N_2^+$ requires 206.2).

Synthesis of *endo*-*N*-methyl-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-enyl) bis(trifluoromethanesulfonyl)imides (9, 10).

Ionic ligand ***9***. Amine **2** (1.00 g, 4.8 mmol) was dissolved in 50 cm^3 of methanol and methyl iodide (3.42 g, 24.1 mmol) was added to the solution. The mixture was stirred at room temperature for 48 h and the solvent was then removed under reduced pressure. The white foam obtained was recrystallyzed from a MeOH–Et_2O (1 : 5) mixture at 4 °C, giving the iodide ionic derivative as a white solid (1.39 g, 82%).

The iodide ionic derivative (1.00 g, 2.9 mmol) was dissolved in 50 cm^3 of dichloromethane and lithium bis(trifluoromethanesulfonyl)imide (2.47 g, 8.6 mmol) was added to the solution. The mixture was stirred for 48 h at room temperature and a white suspension was formed. Salts were removed upon filtration, and the solution was washed with water (3 × 20 cm^3). The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give the product as a colourless oil (1.27 g, 88%). $[\alpha]_D^{25}$ +0.5° (*c* 0.95 in $CHCl_3$); ν_{max}(NaCl film)/cm^{-1} 3532, 2977, 2944, 2884, 1473, 1350, 1194, 1134, 1054, 789 and 739; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.04 (3 H, t, *J* 7.4, NCHCHH′C*H*$_3$), 1.68–1.73 (1 H, m, NCHC*H*H′CH$_3$), 1.72 (1 H, d, *J* 8.8, C*H*H′ bridge), 1.81–1.87 (1 H, m, NCHCH*H*′CH$_3$), 1.89 (1 H, dt, *J* 1.6 and 8.8, CH*H*′ bridge), 2.53 (1 H, t, *J* 10.4, CHC*H*H′N), 2.70 (1 H, t, *J* 10.6, CHC*H*H′N), 3.01 (2 H, br s, 2 × CH_{olefin}C*H*CH$_2$bridge), 3.01–3.06 (1 H, m, C*H*CHH′OH), 3.04 (3 H, s, NC*H*$_3$), 3.14–3.27 (2 H, m, 2 × C*H*CHH′N), 3.68 (1 H, dd, *J* 7.6 and 11.6, CHCH*H*′N), 3.85 (1 H, dd, *J* 7.6 and 13.2, CHCH*H*′N), 3.89 (1 H, d, *J* 14.0, CHC*H*H′OH), 4.04 (1 H, d, *J* 14.0, CHCH*H*′OH) and 6.33–6.38 (2 H, m, C*H*=C*H*); δ_C(100 MHz; $CDCl_3$; Me_4Si) 11.0 (CH_3), 19.3 (CH_2), 44.0 (CH), 44.6 (CH), 44.7 (CH), 46.3 (CH_3), 54.2 (CH_2), 58.5 (CH_2), 67.4 (CH_2), 67.6 (CH_2), 77.8 (CH), 119.9 (2 × CF_3, q, *J* 319.2), 137.3 (CH) and 137.8 (CH); *m/z* (ESI(+)) 222.3 (M^+. $C_{14}H_{24}NO^+$ requires 222.2); *m/z* (ESI(−)) 280.1 (M^-. $C_2F_6NO_4S_2^-$ requires 279.9).

Ionic ligand ***10***. Amine **3** (700 mg, 2.45 mmol) was dissolved in 10 cm^3 of methanol and methyl iodide (1.74 g, 12.3 mmol) was added to the solution. The mixture was allowed to stir at room temperature overnight and the solvent was then removed under reduced pressure. The yellowish solid obtained was recrystallyzed from a MeOH–Et_2O (1 : 2) mixture at 4 °C, yielding the iodide ionic derivative as a white solid (720 mg, 69%).

The iodide ionic derivative (714 mg, 1.3 mmol) was dissolved in 1 cm^3 of methanol and then 20 cm^3 of dichloromethane and lithium bis(trifluoromethanesulfonyl)imide (1.5 g, 5.15 mmol) were added to the solution. The mixture was allowed to stir at room temperature for 24 h and the solvent was evaporated, obtaining a yellow oil. Salts were precipitated from a MeOH–Et_2O (1 : 2) mixture and then removed by filtration. The solvent was evaporated under reduced pressure to give the product as a yellow oil (909 mg, 93%). $[\alpha]_D^{25}$ +14.7° (*c* 1.0 in MeOH); ν_{max}(NaCl film)/cm^{-1} 3571 (OH), 1652, 1635, 1349, 1203, 1132, 1058, 798 and 745; δ_H(400 MHz; CD_3OD; Me_4Si) 1.80 (1 H, d, *J* 8.4, C*H*H′ bridge), 1.90 (1 H, dt, *J* 2.0 and 8.4, CH*H*′ bridge), 2.80 (1 H, t, *J* 11.0, CHC*H*H′N), 2.95–3.03 (3 H, m, CHC*H*H′N and 2 × CHCH*H*′N), 3.24–3.41 (4 H, m, 2 × C*H*CHH′N and 2 × CH_{olefin}C*H*CH$_2$bridge), 3.45 (3 H, s, NC*H*$_3$), 3.53 (1 H, dd, *J* 7.2 and 12.0, C*H*H′CHCHPh), 3.89 (1 H, dd, *J* 2.0 and 12.0, CH*H*′CHCHPh), 4.44 (1 H, dd, *J* 7.4 and 10.4, CHH′C*H*CHPh), 5.27 (1 H, d, *J* 10.4, CHH′CHC*H*Ph), 6.38 (1 H, dd, *J* 3.0 and 6.0, C*H*=CH′), 6.41 (1 H, dd, *J* 3.0 and 6.0, CH=C*H*′) and 7.25–7.40 (5 H, m, Ph); δ_C(100 MHz; CD_3OD; Me_4Si) 43.0 (CH), 44.5 (2 × CH), 45.1 (CH), 46.6 (CH_3), 53.6 (CH_2), 58.6 (CH_2), 66.7 (CH_2), 70.9 (CH), 71.3 (CH_2), 79.0 (CH), 120.0 (2 × CF_3, q, *J* 317.5), 127.4 (2 × CH), 128.65 (3 × CH), 137.1 (CH), 137.3 (CH) and 141.6 (C); *m/z* (ESI(+)) 300.3 (M^+. $C_{19}H_{26}NO_2^+$ requires 300.2); *m/z* (ESI(−)) 280.1 (M^-. $C_2F_6NO_4S_2^-$ requires 279.9).

Synthesis of palladium nanoparticles, Pd3

Palladium acetate (22.4 mg, 0.1 mmol) and ligand **3** (5.7 mg, 0.02 mmol) were placed in a Fisher–Porter bottle and dissolved

in 4 cm^3 of [BMI][PF_6]. The brown mixture was stirred under vacuum at room temperature for 1 h and the bottle was then filled with 1 bar pressure of hydrogen. After 20 min of reaction, the solution blackened and it was stirred for one additional hour before removing the hydrogen under reduced pressure. The black suspension was stored under an inert argon atmosphere.

General procedure for catalytic Suzuki C–C coupling in [BMI][PF_6]

Coupling using palladium acetate as catalytic precursor. Note: for simplicity reasons, only the experimental procedure of the catalytic Suzuki C–C coupling under the optimized conditions is described.

Palladium acetate (2.2 mg, 0.01 mmol) and the corresponding ligand (0.012 mmol) were dissolved in 1 cm^3 of [BMI][PF_6] previously deoxygenated and stirred for 1 h under vacuum at room temperature, giving a brown or yellow solution. After this time, the substrate (1.0 mmol), the boronic acid (1.2 mmol) and Na_2CO_3 (265.0 mg, 2.5 mmol) dissolved in 2 cm^3 of deoxygenated water were consecutively added, forming a biphasic system. The mixture was then heated at 60 °C during 1 h and then cooled to room temperature. The catalytic mixture was extracted with hexane (5 × 10 cm^3) and the combined organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding the product either as a white solid or as a yellow oil.

Coupling using preformed nanoparticles as catalytic precursor. 1 cm^3 of a 0.025 M solution of palladium nanoparticles in [BMI][PF_6] was placed under vacuum for 30 min and the substrate (1.0 mmol), the boronic acid (1.2 mmol) and Na_2CO_3 (265.0 mg, 2.5 mmol) dissolved in 2 cm^3 of deoxygenated water were consecutively added. The resulting biphasic system was heated at 110 °C during 24 h and then cooled to room temperature. The catalytic mixture was extracted with hexane (5 × 10 cm^3) and the combined organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding the product as a white solid.

General procedure for catalytic Suzuki C–C coupling in organic solvent

Palladium acetate (2.2 mg, 0.01 mmol) and the corresponding ligand (0.012 mmol) were dissolved in 1 cm^3 of freshly distilled toluene and allowed to stir for 30 min, forming a yellowish solution. After this time, bromobenzene (157.0 mg, 1.0 mmol), phenylboronic acid (146.3 mg, 1.2 mmol) and Na_2CO_3 (265.0 mg, 2.5 mmol) dissolved in 2 cm^3 of deoxygenated water were consecutively added. The resulting biphasic system was heated at 100 °C for 6 h and then cooled to room temperature. 20 cm^3 of diethyl ether were added and the mixture was filtered over Celite to remove the Pd(0) formed during the reaction. The reaction mixture was washed with an aqueous 1 M solution of Na_2CO_3 (3 × 20 cm^3) and with water until neutral pH. The organic phases were dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding the product as a yellowish solid or a yellow oil.

General procedure for poison tests in [BMI][PF_6]

The experimental procedure used for the poison tests was analogous to that described for the standard molecular conditions, adding the poison (Hg: 200.6 mg, 1 mmol; PPh_3: 0.8 mg, 3 × 10^{-3} mmol or 10.5 mg, 0.04 mmol depending on the molecular or colloidal conditions) after 10 min of catalytic reaction at 60 °C and heating at this temperature for 50 additional min after poison addition.

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