


Palladium Nanoparticles in Suzuki Cross-Couplings: Tapping into the Potential of Tris-Imidazolium Salts for Nanoparticle Stabilization

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Abstract: Inspired by the proclivity of various palladium sources to form nanoparticles in imidazolium-based ionic liquids, we now report that tris-imidazolium salts bearing hexadecyl chains and a bridging mesitylene moiety are potent stabilizers of palladium nanoparticles efficiently prepared *via* a Chaudret-type hydrogenation of the bis(dibenzylideneacetone)palladium(0). The palladium nanoparticles have been isolated in pure form and characterized by ¹H nuclear magnetic resonance, transmission electron microscopy, electron diffraction and dynamic light scattering. The new materials proved effective in Suzuki cross-coupling at a loading of 0.2% palladium.

Thus, using a tris-imidazolium iodide-palladium material, a series of biaryl products has been prepared starting from aryl bromides and some activated chlorides. The possibility that this catalytic activity might be due to the formation of palladium N-heterocyclic carbenes has been addressed through solid state ¹³C NMR and the synthesis of an imidazolium analogue in which the acidic 2-H was replaced with a methyl group.

Keywords: imidazolium salts; nanoparticles; palladium; Suzuki–Miyaura reaction

Introduction

Transition metal nanoparticles^[1] have attracted much attention in the last decade as efficient catalysts^[2] due to their unique properties based on quantum size effect and high surface-to-volume ratio. Generally, the thermodynamic propensity of nanoparticles to agglomerate to bulk metal can be prevented by the use of a protective agent.^[3] The stabilization of NPs in solution can be achieved by electrostatic and/or steric protection (electrosteric stabilization). Different types of capping agents have been developed such as polymers, dendrimers, β -cyclodextrins, ionic and non-ionic surfactants, in addition to nitrogen-, phosphorus- and sulfur-based ligands as well as several ionic compounds. The nature of the protecting shield determines, to a great extent, the solubility of the resulting metal colloid. Moreover, in the case of catalytic applications, the activity and selectivity of the nanocatalyst will depend not only on the relative abundance of different types of active sites but also on the concentration and type of stabilizers present in the medium.

Imidazolium-based ionic liquids (ILs) have been largely used in the past decade in a wide range of catalytic reactions as green alternatives to volatile organic solvents, as a consequence of some of their peculiar physical and chemical properties, such as negligible vapor pressure, non-flammability and high thermal stability.^[4] However, the non-innocent nature of imidazolium ILs as solvents has been pointed out.^[5] For instance, in the presence of an appropriate base, the deprotonation at the C-2 position of the imidazolium salt takes place, generating N-heterocyclic carbenes capable of acting as ligands. Even under neutral conditions, imidazolium halides can give rise to palladium-carbene complexes in the presence of Pd(OAc)₂. In what may (or may not) be a related phenomenon, *in situ* generation of palladium nanoparticles from palladium-carbene species has been observed in palladium-catalyzed Heck reactions performed in ionic liquids.^[5b,6]

Dispersions of transition metal NPs (Pd, Pt, Rh, Ru, Ir) in ILs have been prepared by reduction of metal salts or decomposition of organometallic compounds in the zero oxidation state dissolved in the

imidazolium-based ILs.^[7] These dispersions have been used directly in hydrogenation reactions of alkenes, arenes and ketones^[4e,8] and in carbon-carbon cross-coupling reactions in the case of Pd NPs,^[9] with the aim of recycling the catalytic system. It is likely that Pd NPs act as a reservoir for catalytically active molecular species leached into the medium. A drawback to using imidazolium-based ILs in certain palladium-catalyzed C–C bond forming reactions is the fact that salts formed stoichiometrically as by-products remain in the IL layer and accumulate in successive runs, having a deleterious effect on the effective recovery and reuse of the catalyst. Other detected problems are the leaching of palladium from the ionic phase into the organic phase and the aggregation of Pd NPs upon recycling (Ostwald ripening). The addition^[10] of another external capping agent (a polymer, a ligand or a support for the NPs immobilization) or, alternatively, the presence^[10b,11] of a coordinating group in the imidazolium salt (such as cyano, amino, hydroxy, mercapto and carboxyl) is most often needed to enhance the longevity of metal NPs in an IL medium.

Our interest in this topic stems from the recent work in our group on the preparation of mesitylene-containing bis- and tris-imidazolium salts (with I[−] and BF₄[−] counterions) and their use as ionic liquid crystals.^[12] These species bear long hexadecyl chains and, contrarily to imidazolium-based ionic liquids, are solids at room temperature. We reasoned that their particular structural features should render them efficient in the stabilization of metal nanoparticles (electrosteric and steric stabilization), and that they could be added in smaller amounts than the high-cost imidazolium-based ILs. We also envisioned that the resulting metal NPs could be isolated, characterized and then used in catalysis in a solvent of choice. We were

especially interested in applying such nanocatalysts to the coupling of aryl bromides and chlorides, given that these are less reactive, but more affordable than the aryl iodides.

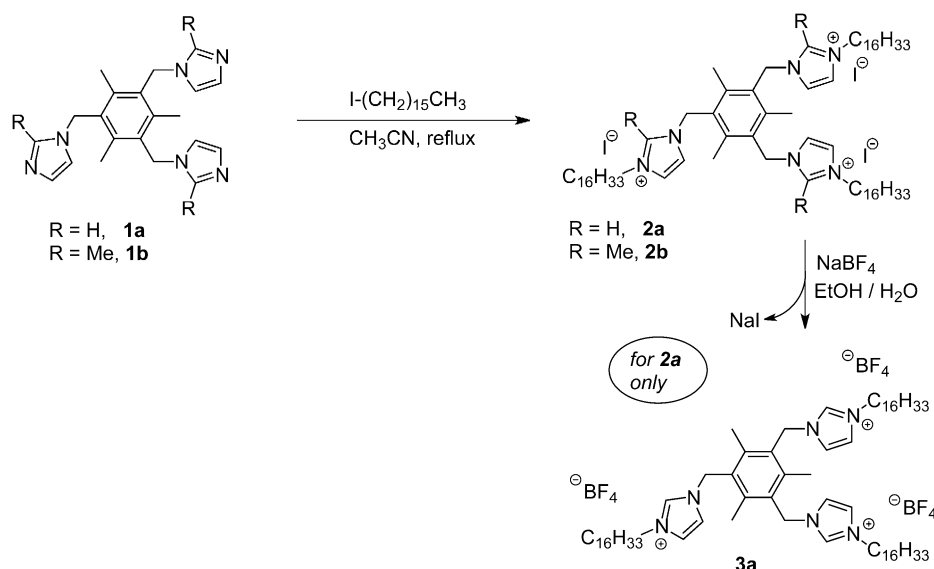
Following from studies on the preparation of a variety of Pd NP types^[13] for use in C–C bond forming reactions, we report herein the synthesis of palladium nanoparticles stabilized by tris-imidazolium iodides and tetrafluoroborates and their catalytic activity in the Suzuki–Miyaura cross-coupling^[14] reaction, in light of the importance of this transformation for the production of biaryls in the pharmaceutical, agrochemical and fine chemical industries.^[15]

Results and Discussion

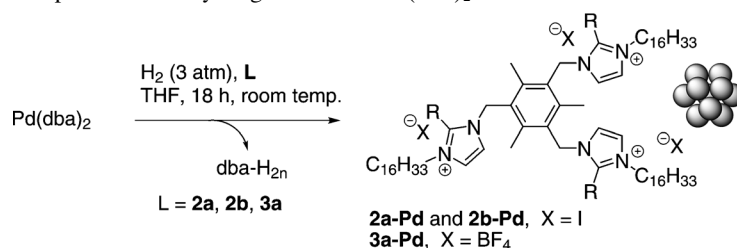
Tris-Imidazolium-Stabilized Pd Nanoparticles

We followed our earlier reported procedure^[12] to synthesize the tris-imidazolium salts **2a** and **3a** from the C₃-symmetric tris-imidazole **1a** (Scheme 1).

The alkylation of **1a**^[16] with 3 equivalents of 1-iodo-*n*-hexadecane in refluxing acetonitrile afforded the tris-iodide **2a** in 90% yield; subsequent anion metathesis with excess NaBF₄ in ethanol/water mixture afforded the corresponding tris-tetrafluoroborate **3a** in 77% yield. Although the anion exchange proved to be quite efficient, this treatment with NaBF₄ was repeated twice again to ensure complete removal of potential traces of iodide (see the Supporting Information). The synthesis of both the iodide and the tetrafluoroborate salts (**2a** and **3a**) was undertaken so as to gauge the counterion effect on nanoparticle synthesis and on their properties, including the catalytic activity. Additionally, the tris-iodide salt **2b** bearing 2-Me



Scheme 1. Synthesis of the stabilizers **2a**, **2b** and **3a**.

Table 1. Preparation of Pd nanoparticles *via* hydrogenation of Pd(dba)₂.^[a]

Entry	L (mmol)	mmol Pd ^[b]	% Pd ^[c]	Yield [%] ^[d]	Ø [nm] ^[e]
1	2a (0.423)	0.423	14.4	82	4.2 ± 0.5
2	3a (0.425)	0.425	8.1	75	2.9 ± 0.5
3	2b (0.051)	0.051	5.8	67	4.2 ± 0.9

^[a] [Pd] = 0.007 mol/L.

^[b] Based on % Pd in Pd(dba)₂ determined by ICP.

^[c] By ICP.

^[d] [(mmol Pd in nanoparticles)/(initial Pd)] × 100%.

^[e] Mean diameter determined by TEM.

imidazolium substituents was prepared from the methylated tris-imidazole **1b** (Scheme 1, Supporting Information).

With compounds **2a**, **2b** and **3a** in hand, we tested the ability of the tris-imidazolium salts to stabilize palladium nanoparticles. Although chemical reduction of Pd(II) salts remains the most widely used method for the synthesis of Pd(0) nanoparticles,^[1] a careful and laborious search for optimal reaction conditions is often necessary. In the present case, we were also interested in avoiding basic conditions and a Pd(II) precursor, which could give rise to the formation of carbene species. The organometallic approach, consisting in the reduction and subsequent displacement of a ligand from an M(0) organometallic precursor, developed by Chaudret and co-workers^[17] offers a more straightforward and reliable alternative for the controlled synthesis of metal nanoparticles with narrow size distribution. In fact, the generation of metal nanoparticle dispersions in ionic liquids using this approach has been reported.^[18] In collaboration with Chaudret and Philippot, we have previously succeeded in the preparation of ruthenium^[19] and platinum^[20] nanoparticles in the presence of heavily fluorinated protecting agents. We, therefore, opted for this methodology, which, in the case of palladium, consists in hydrogenating Pd(dba)₂^[21] in the presence of the appropriate stabilizer. This process was carried out in the presence of salts **2a**, **3a** and **2b** overnight in a stirred THF solution at 3 bar H₂. The results are shown in Table 1.

In all three cases, a Pd:L ratio of 1:1 and a [Pd] of about 0.007M were used to obtain palladium nanoparticles of a mean diameter of 2.9–4.2 nm (determined by TEM, see Figure 1) in good yields. Given that TEM in our case is only sensitive to the metal

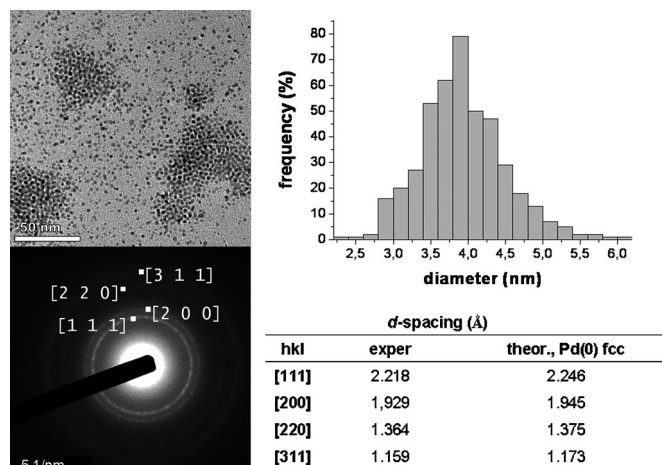


Figure 1. (Top) HR-TEM image and particle size distribution diagram for **2a-Pd**; (bottom) electron diffraction pattern for **2a-Pd**.

core of the nanoparticles, dynamic light scattering (DLS) was used to estimate the total diameter in solution. This was found to be $\text{Ø} = 10.6 \pm 2.1$ nm for **2a-Pd**, 7.7 ± 1.9 nm for **2b-Pd** and 13.0 ± 3.6 nm for **3a-Pd** (see Figure 2). In all cases, the resulting homogeneous black suspension was filtered through a nylon membrane filter (Milli-Pore filter, 0.45 µm) to eliminate residual palladium black, the solvent was removed under vacuum and the black residue was washed with diethyl ether to eliminate the 1,5-diphenylpentan-3-one side-product. The insoluble residue was further purified by washings with methanol and additional portions of diethyl ether. After centrifugation and decantation, the resulting black solid was examined by high resolution transmission electron microscopy (HR-TEM) (Figure 1). In both cases, the presence of

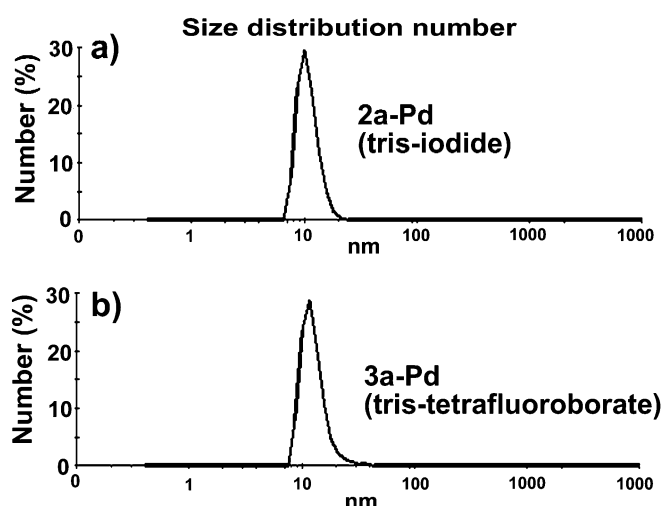


Figure 2. Dynamic light scattering size distribution (nm) for a) **2a-Pd** $\bar{\phi} = 10.6 \pm 2.1$; b) **3a-Pd** $\bar{\phi} = 13.0 \pm 3.6$. Logarithmic scale is used.

the corresponding stabilizer was confirmed *via* IR and ^1H NMR and the metal content in the samples was determined by inductively coupled plasma (ICP). Electron diffraction (ED) confirmed the presence of palladium(0) with a face-centered cubic (fcc) structure (Figure 1). The synthesis method was found to be reproducible in all cases. The newly obtained nanomaterials were soluble in toluene, THF, CH_2Cl_2 and CHCl_3 , and insoluble in hexane, diethyl ether, methanol and ethyl acetate. The tris-iodide **2a** was somewhat more efficient as a stabilizer, giving 82% yield of **2a-Pd**, as opposed to 75% for tris- BF_4 **3a-Pd**.^[22] It was also found that the methylated salt **2b** was less efficient than the 2-H derivative **2a**, giving a 67% yield of **2b-Pd**. The presence of three imidazolium rings was beneficial in nanoparticles stabilization, with lower yields of Pd nanoparticles obtained when using

analogous bis-imidazolium salts previously reported by our group.^[12]

The counterion effect was also evident in the appearance of the ^1H NMR spectra of the iodide salts **2a** and **2b** and the tetrafluoroborate **3a** (see the Supporting Information). While the ^1H NMR spectrum of the tris-tetrafluoroborate **3a-Pd** was very similar to that of the free stabilizer, the spectra of the tris-iodides **2a-Pd** and **2b-Pd** showed a complex spectral pattern with broad and ill-defined signals, most pronounced in the region corresponding to the imidazolium ring (7–10 ppm). In general, this significant alteration of the stabilizer NMR signals in metal nanoparticles (with respect to the free stabilizer) is in line with a stronger stabilizer-nanoparticles interaction.^[23] Thus, the broadened ^1H NMR signals in the tris-iodide salts might suggest a much greater interaction of the imidazolium cations with the metal surface than that found in the tetrafluoroborate **3a-Pd**. Initially, the possibility of a strong interaction between the BF_4^- anion and the nanoparticles surface was tested by NMR. However, we found that the ^{11}B NMR signals appear at the same chemical shift in both the **3a** and **3a-Pd**; similarly, the ^{19}F NMR spectra of both **3a** and **3a-Pd** show the same two isotopomeric signals (^{10}B , $I=3$, 19% natural abundance and ^{11}B , $I=3/2$, 81% natural abundance). A possible insight into the exceptional behavior of material **2a-Pd** was glimpsed from the solid state (CP-MAS) ^{13}C NMR spectra of the stabilizers **2a** and **3a** and the corresponding Pd nanoparticles **2a-Pd** and **3a-Pd** (Figure 3). While no important change in the carbon resonances was observed in going from **3a** to **3a-Pd**, a significant difference was indeed observed between **2a** and **2a-Pd**. The change in **2a-Pd** consisted in a considerable reduction of the C-2 carbon peak, accompanied by the appearance of a very broad resonance at ~ 167 ppm, consistent with the formation of an N-heterocyclic carbene (NHC)-

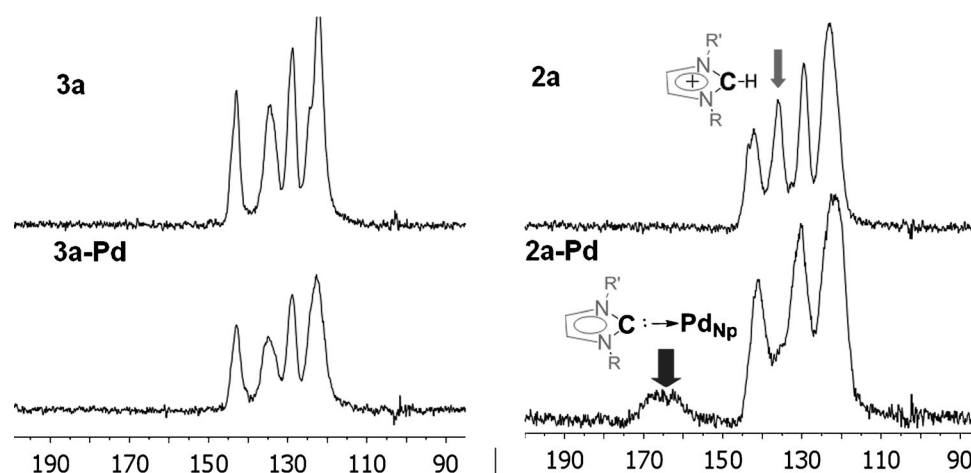


Figure 3. Comparison of the ^{13}C CP-MAS solid state NMR spectra of the stabilizers **2a** and **3a** with their corresponding palladium nanoparticle materials.

Pd interaction.^[24] We, therefore, conclude that due to the enhanced basicity of I^- , as compared to that of BF_4^- , the formation of a surface carbene is more favored in the **2a** than in **3a**.

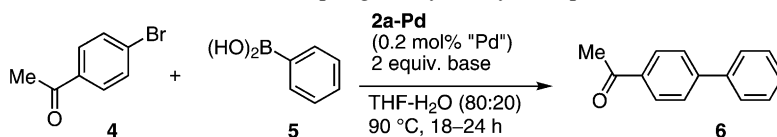
Use of 2-Pd in Suzuki–Miyaura Cross-Coupling

Material **2a-Pd** was chosen for development of the coupling method, with the catalytic activity of these nanoparticles first being tested in a model Suzuki cross-coupling between *p*-bromoacetophenone, **4**, and phenylboronic acid, **5**, to give *p*-acetylbiphenyl, **6**. The tests were conducted using a 0.2 mol% loading of palladium, 2 equivalents of base and an excess of the boronic acid (1.5 equivalents). First, we sought to determine the optimal base to use in the reaction. Based on some previous results, our initial base screen was performed in an 80:20 THF:H₂O solvent mixture at 90 °C for 15–24 h (Table 2). The test of a series of or-

ganic and inorganic bases showed that potassium hydroxide, the acetate salts and triethylamine were inefficient (entries 1–4) and that the process could be improved somewhat by employing potassium phosphate, cesium fluoride and even sodium bicarbonate (entries 5–7). Finally, excellent yields of **6** were achieved using the carbonate bases (entries 8–10).

Given that highest yields were achieved using anhydrous K₂CO₃, we went on to examine the performance of this carbonate base in several additional solvent systems (Table 3 and the Supporting Information). It was found that replacing THF with toluene in the solvent mixture allowed for the reaction time to be reduced from 24 h to just 30 min (Table 3, entries 1 and 2). Toluene alone led to a slower reaction, although in this case raising the temperature to 130 °C once again allowed the coupling to be complete in 30 min (Table 3, entries 3 and 4). A TEM analysis of the Pd NP material isolated after the reaction (from Table 3, entry 2, see Supporting Information) revealed

Table 2. Initial base screen in a model Suzuki cross-coupling catalyzed by nanoparticles **2a-Pd**.^[a]

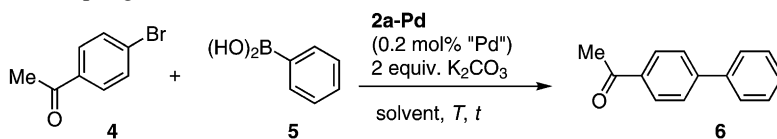


Entry	Base	Yield [%] of 6 ^[b]	Entry	Base	Yield [%] of 6 ^[b]
1	KOH	< 3	6	CsF	55
2	NaOAc	35	7	NaHCO ₃	62
3	CsOAc	42	8	Na ₂ CO ₃	93
4	NBu ₃	8	9	K₂CO₃	98
5	K ₃ PO ₄	54	10	Cs ₂ CO ₃	96

^[a] In closed vessels (40 mL) in a multireactor using 2.5 mmol of **4**, 3.75 mmol of **5** (1.5 equiv.), 5 mmol base (2 equiv.), in 2.5 mL of solvent; reaction times not optimized.

^[b] GC yields corrected to internal *n*-C₁₁H₂₄.

Table 3. Solvent effect in the coupling of **4** and **5**.^[a]



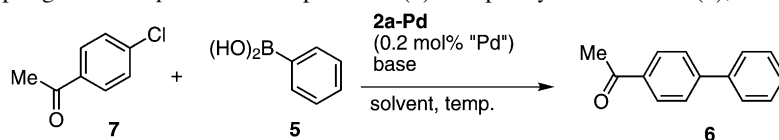
Entry	Solvent	Temperature <i>T</i> [°C]	Time <i>t</i> [h]	Yield [%] of 6
1	THF-H ₂ O (80:20)	90	24	98
2	toluene-H ₂ O (80:20)	90	0.5	95 (85) ^[b,c]
3	toluene	90	22	80
4	toluene	130	0.5	95
5 ^[d]	toluene-H ₂ O (80:20)	90	0.5	46
6 ^[d]	toluene-H ₂ O (80:20)	90	24	94

^[a] As in Table 2 (see Experimental Section and Supporting Information).

^[b] Isolated yield.

^[c] A second cycle performed with this material required 7 h for complete conversion.

^[d] Using **3a-Pd**.

Table 4. Suzuki cross-coupling between *p*-chloroacetophenone (**7**) and phenylboronic acid (**5**), catalyzed by **2a-Pd**.^[a]

Entry	Base	Solvent	Temperature <i>T</i> [°C]	Time <i>t</i> [h]	Yield [%] of 6 ^[b]
1	K ₂ CO ₃	toluene	90	46	6
2	K ₂ CO ₃	toluene	130	26	14
3	KOH	toluene	130	26	1
4	K ₂ CO ₃	toluene-H ₂ O (90:10)	130	26	51
5	K ₂ CO ₃	toluene-H ₂ O (80:20)	130	16	70
6	K ₂ CO ₃	toluene-H ₂ O (80:20)	130	40	92 (81) ^[c]
7	K ₂ CO ₃	toluene-H ₂ O (70:30)	130	16	63
8	K ₂ CO ₃	THF-H ₂ O (80:20)	130	26	5
9	K ₂ CO ₃	[BDMIM][BF ₄]	130	26	< 5

^[a] In closed vessels (40 mL) in a multireactor using 2.5 mmol of **7**, 3.75 mmol of **5** (1.5 equiv.), 5 mmol of base (2 equiv.) in 2.5 mL of solvent.

^[b] GC yields corrected to internal *n*-C₁₁H₂₄.

^[c] Isolated yield in parenthesis.

nanoparticles that were smaller and more closely aggregated than the original **2a-Pd**. Consequently, the use of this recycled material in the model Suzuki cross-coupling resulted in a somewhat longer time to reach completion (7 h).

Interestingly, under the conditions optimized for the tris-iodide **2a-Pd** (80:20 toluene:H₂O, Table 3, entry 2), the corresponding tris-tetrafluoroborate material **3a-Pd** only gave a 46% yield of the desired product (Table 3, entry 5). In this latter case, a longer reaction time (24 h) did lead to the complete conversion of the starting material (Table 3, entry 6).

Next, we turned our attention to the coupling between the more challenging *p*-chloroacetophenone, **7**, and phenylboronic acid, **5** (Table 4). Attempts to carry out the reaction in toluene using K₂CO₃ only gave small amounts of the coupling products (entries 1 and 2), and no improvement was observed by employing a stronger base like KOH (entry 3). As was the case for the reactions with the aryl bromide **4**, significant improvement was achieved by using toluene-water as solvent mixtures (entries 4–7). Thus, the best results were achieved, once again, using a 80:20 toluene:water system, with a 70% yield being reached after 16 h, and a 92% yield after 40 h at 130 °C (entries 5 and 6). The coupling proved extremely sluggish in THF:H₂O (entry 8). Finally, we were curious to see whether ionic liquids could serve as suitable solvents for our imidazolium-based catalyst. Disappointingly, the use of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BDMIM][BF₄] failed to lead to an active catalyst system (entry 9). This lack of activity was likely the result of the observed complete immiscibility of the catalyst with this ionic liquid.

In most cases, the formation of **6** from both the bromide **4** and chloride **7** was accompanied by small amounts of biphenyl (1–5% by GC) as a result of the homocoupling of the boronic acid **5**. Only trace amounts of acetophenone, a dehydrohalogenation product could be detected in concentrated samples.

The protocol optimized for **2a-Pd** NPs was then extended to the Suzuki coupling of a range of aryl bromides and chlorides with several aryl- and heteroaryl-boronic acids. The results are compiled in Table 5. Unless otherwise stated, all reactions were carried out using 0.2 mol% of Pd and the reagent molar ratio ArX/Ar'B(OH)₂/K₂CO₃ of 1:1.5:2 using toluene-H₂O (80:20) as the solvent at 90 °C.

In testing the substrate scope, the catalyst **2a-Pd** proved to be tolerant of a range of functional groups. Using phenylboronic acid **5**, good yields were obtained in the coupling of aryl bromides bearing aldehyde (entry 1), ketone (entries 2 and 3) as well as alcohol groups (entries 4 and 5), including the *ortho*-substituted bromoindanol **11**. The catalyst was also tolerant of aromatic OH and NH₂ substituents (entries 6 and 7). As expected, an excellent yield was reached using the electron-rich boronic acid **18** (entry 8). Coupling was more difficult in the case of heterocyclic boronic acids (entries 9–11) due to rampant protodeboronation. Still, in some cases potassium trifluoroborate salt could be used as an alternative to the boronic acid to obtain the coupling products (**31** and **32**, entries 10 and 11). Next, the coupling of aryl chlorides was investigated. While in this case the reaction was much more sluggish, activated ArCl did indeed afford the desired biaryls albeit in modest yields (entries 12 and 13). Still, in the case of the substrate **17** bearing two nitro groups an 85% yield of

Table 5. Suzuki cross-coupling between aryl bromides and chlorides and aryl (heteroaryl) boronic acids catalyzed by **2a-Pd**.^[a]

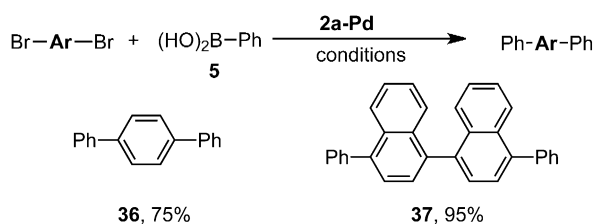
$ \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_4\text{X} + (\text{HO})_2\text{B}-\text{C}_6\text{H}_4\text{R}' \\ \downarrow \text{2a-Pd (0.2 mol\% "Pd"), 2 equiv. K}_2\text{CO}_3 \\ \text{toluene-H}_2\text{O (80:20), 90 }^\circ\text{C} \\ \text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4\text{R}' \end{array} $				
Entry	ArX	Ar'B(OH) ₂	Ar-Ar'	Yield [%] ^[b]
1				80
2				79
3				76
4				85
5				65
6				62
7				89
8				90
9				68
10				39 ^[c]
11 ^[d]				24 ^[c]
12 ^[d]				47
13 ^[d]				24
14				85

^[a] In closed vessels (10 mL) using 2.5 mmol of ArX, 1.5 equiv. of Ar'B(OH)₂, 2 equiv. K₂CO₃ in 2.5 mL of a 4:1 toluene-H₂O at 90 °C.

^[b] Isolated yield.

^[c] Using 1.2 equiv. HetBF₃K.

^[d] At 110 °C.



Scheme 2. Double arylation of dibromoarene substrates using **2a-Pd**. Reaction conditions: as in Table 5.

the desired biaryl (**35**) was obtained after 3 h at 90 °C (entry 14). Double arylation of dibromoarenes was also possible under the same reaction conditions to give products **36** and **37** in good yields (Scheme 2).

Additionally, a successful one-pot preparation of the asymmetrically substituted terphenyl **40** was achieved (Scheme 3) in an overall 60% isolated yield by selective monoarylation of 4-bromiodobenzene, **38**, with one equivalent of benzenboronic acid at 40 °C (intermediate **39**), followed by the addition of one equivalent of 4-methoxybenzenboronic acid. We found that the order of addition of areneboronic acids was quite important, since when this order was reversed, the corresponding intermediate 4-bromo-4'-methoxy-1,1'-biphenyl reacted sluggishly in the Suzuki coupling with benzenboronic acid under the same conditions.

At this point, we wondered whether the active catalyst might involve Pd-carbene species derived from the imidazolium moieties. The question was addressed by testing the catalytic performance of palladium nanoparticles stabilized by compound **2b** bearing an Me group at the heterocyclic C-2 and in which the formation of a carbenoid would be disfavored (Table 1, Figure 4).^[25]

Thus, the catalytic performance of **2b-Pd** was compared to that of **2a-Pd** in the coupling between 4-bromo- and 4-chloroacetophenones **4** and **7** and phenylboronic acid **5** (Scheme 4). While the performance of both catalysts was similar in the case of the aryl bromide, the coupling of more challenging aryl chloride was only possible with the non-methylated stabilizer **2a**. Thus, it can be concluded that although the presence of Pd-NHC species is not necessary for the

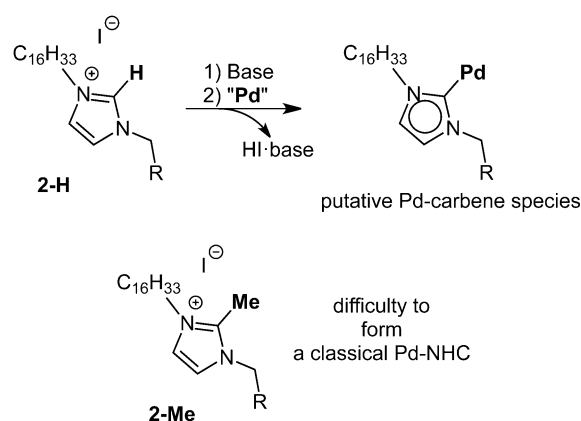
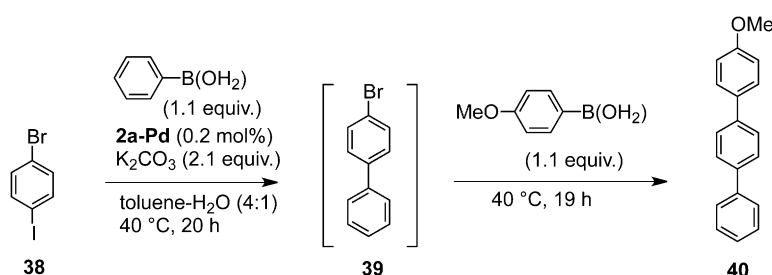


Figure 4. Potential formation of Pd-NHC system from **2a**.

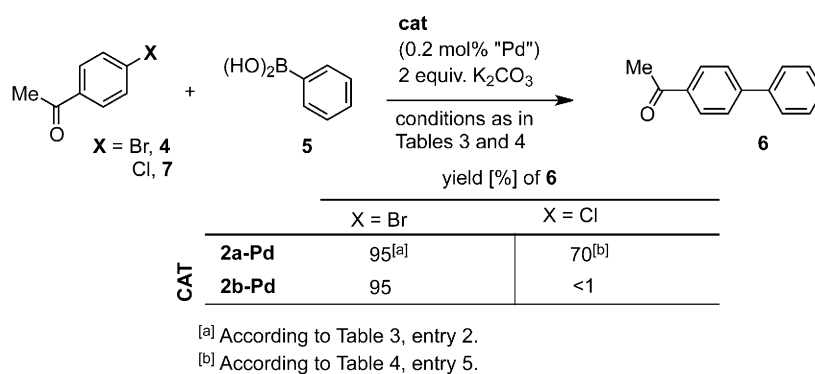
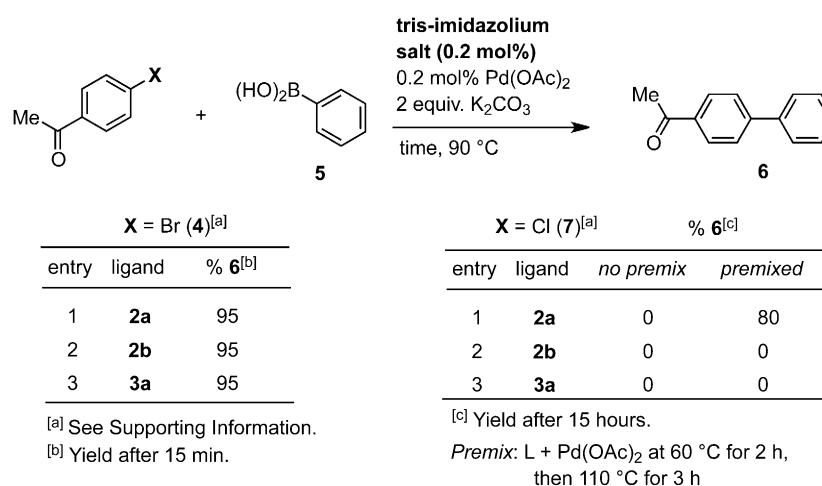
catalytic activity of imidazolium-stabilized nanoparticles, their involvement in the case of the more challenging substrates cannot be ruled out.

In fact, the potential of the tris-imidazolium salts to act as both NP stabilizers and as ligands for soluble palladium carbene complexes may be relevant for the mode of catalyst action. Specifically, this raises the possibility that the nanoparticles act as reservoirs for soluble palladium species such as NHC-Pd.^[26] We, therefore, tested the catalytic activity of a mixture of each of the stabilizers with Pd(OAc)₂ (Scheme 5). We found that for a coupling of *p*-bromoacetophenone **4** with the phenylboronic acid **5**, simply heating the reagent mixture in toluene:H₂O (4:1, 90 °C) gives quantitative yields of **6** after only 15 min. In contrast, this procedure failed for all three ligands when *p*-chloroacetophenone **7** was used. In an attempt to favor the catalyst activation, the coupling of **7** was then carried out by first premixing the ligands with Pd(OAc)₂ in DMSO (60 °C to 110 °C).^[27] In this case, while this procedure did afford an active catalyst using **2a** (80% of **6** after 15 h), the method failed for **2b** and **3a**.

The results described here likely suggest multiple ways in which imidazolium-based palladium species may function as catalyst for Suzuki cross-coupling. We speculate that in the case of aryl bromides, the coupling may take place both at the nanoparticle surface or at the leached palladium species with or with-



Scheme 3. Preparation of 4-methoxy-1,1':4',1''-terphenyl.

Scheme 4. Comparison of **2a-Pd** and **2b-Pd** as catalyst.Scheme 5. Testing the *in-situ* formed imidazolium-derived catalysts in Suzuki cross-coupling.

out the intervention of the imidazolium stabilizer/ligand. TEM analysis of the catalytic nanomaterial after the first run (see Table 3, entry 2 and the Supporting Information) points towards a dissolution process. This conclusion is supported by the ability of **2b**-based palladium systems, where carbene formation is unlikely,^[25] to promote the coupling of **4**. On the other hand, in the case of the more challenging ArCl **7**, the fact that only **2a** gives an active catalyst indicates that the coupling in this case takes place at the Pd-NHC centers, and that the nanoparticles may then serve as a reservoir for active catalytic species. In this context, the decreased competence of the tetrafluoroborate **3a** in both NP stabilization and catalysis will be the subject of future work.

Conclusions

The previously reported tris-imidazolium salts **2a** (iodide) and **3a** (tetrafluoroborate) were used as stabilizers for palladium nanoparticles **2a-Pd** and **3a-Pd**. Both materials were prepared in an efficient manner *via* the hydrogenation of Pd(dba)₂ at 3 atm H₂ at

room temperature and were fully characterized. The tris-iodide **2a-Pd** proved to be an efficient catalyst for the Suzuki cross-coupling reaction of aryl bromides and activated aryl chlorides at a 0.2 mol% Pd loading. The catalyst proved tolerant of a range of functional groups, both for the aryl halides and the boronic acid coupling partners. Catalytic tests with a new 2-Me derivative **2b-Pd** and with premixed combinations of Pd(OAc)₂ with imidazolium salts suggest the formation of Pd-NHC species in the 2-H imidazolium salt **2a-Pd**. The solid state ¹³C CP MAS NMR spectrum of **2a-Pd** is also consistent with the presence of surface-bound NHC carbenes.

Experimental Section

General Remarks

Water Milli-Q was used in the preparation and purification of compounds. THF was purchased from Scharlau and dried over sodium/benzophenone and distilled prior to use. Catalytic runs with magnetic stirring were carried out in a Radleys Discovery System equipped with 12 sealed 40 mL glass vessels. All NMR measurements were carried out at the

Servei de Ressonància Magnètica Nuclear of the *Universitat Autònoma de Barcelona*. NMR spectra were recorded on Bruker AC250 (250 MHz for ^1H) or Avance360 (360 MHz for ^1H) spectrometers. Infrared spectra were recorded using a Bruker Tensor 27 instrument equipped with an ATR Golden Gate cell and a diamond window. ICP measurements of palladium contents were carried out at the *Servei d'Anàlisi* of the *Universitat Autònoma de Barcelona* using a Perkin–Elmer model Optima 4300 ICP-OES spectrometer. Transmission electron microscopy (TEM) analyses were performed at the *Servei de Microscòpia* of the *Universitat Autònoma de Barcelona*, using a JEOL JEM-2010 model at 200 kV. The TEM measurements were made by sonication of the nanoparticulate material in THF for few minutes; then a specially produced structureless carbon support film, which has a thickness of 4–6 nm, was placed in the solution for a few seconds and dried before observation. The size distributions were determined through a manual analysis of enlarged micrographs by measuring a high number of particles on a given grid to obtain a statistical size distribution and a mean diameter (Gatan Digital Micrograph Program). Dynamic light scattering (DLS) measurements were carried out at the ICN/CIN2 center (Bellaterra, Spain) in toluene solution using a quartz cuvette on a Malvern ZetaSizer Nano ZS instrument operating with a light source wavelength of 532 nm and a fixed scattering angle of 173° for DLS measurements. A volume of 0.8 mL of the colloidal solution of NPs was placed into a specific cuvette and the software was arranged with the specific parameters of refractive index and absorption coefficient of the material and the viscosity of the solvent. Gas chromatographic analysis was accomplished using an Agilent Technologies 7890 A GC system equipped with an Agilent HP-5 column (30 m \times 0.320 mm \times 0.25 μm). The integrated areas and peak positions in the chromatograms were referenced internally to undecane (Table 2, Table 3 and Table 4). Mass spectral analyses of the Suzuki products were carried out using an Agilent 6850 GC system equipped with a 5975C Triple Axis EI Mass Detector. Melting points were determined using a Reichert brand melting point apparatus and are uncorrected. Alugram® SIL G/UV₂₅₄ sheets (Macherey–Nagel) were used for thin-layer chromatography. Column chromatography was carried out using SDS brand silica gel with a grain size of 35–70 μm and a pore size of 60 Å. Compounds **1a**,^[16] **2a**^[12] and **3a**^[12] were prepared by adapting the previously described procedures (see the Supporting Information). Due to the potential continuum in the composition, the amounts of Pd(dba)₂^[21] used were calculated based on 17.5% Pd as determined by ICP for the batch used.

Synthesis of 1,1',1''-[(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene)]tris(2-methyl-1H-imidazole)

2-Methyl-1H-imidazole (1.32 g, 16.04 mmol) and potassium hydroxide (3.67 g, 65.17 mmol) were dissolved in dimethyl sulfoxide (40 mL) and the solution was stirred for 2 h at room temperature, then 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (2.00 g, 5.01 mmol) was added. After stirring for another 3 h at room temperature, an equivalent volume of water was added to the mixture and it was extracted with chloroform (4 \times 40 mL). The combined organic phases were washed with water (4 \times 30 mL), dried over anhydrous

sodium sulfate and filtered. Solvent was partially removed under vacuum and excess diethyl ether was added to the residue. A white powder precipitated, which was filtered and washed with diethyl ether. It was recrystallized in CH₂Cl₂–diethyl ether, affording the desired compound; yield: 1.48 g (73%). ^1H NMR (250 MHz, CDCl₃): δ = 2.22 (s, 3H, imid-CH₃), 2.49 (s, 3H, Ar-CH₃), 5.04 (s, 2H, -CH₂-), 6.20 (d, J = 1 Hz, 1H, H_{imid}), 6.82 (d, J = 1 Hz, 1H, H_{imid}); ^{13}C NMR (62.5 MHz, CDCl₃): δ = 13.5, 16.2, 44.9, 117.2, 127.5, 131.6, 138.9, 144.6; HR-MS (ESI): m/z = 403.2605, calcd. for C₂₄H₃₀N₆ [M]⁺: 403.2605.

Synthesis of 1,1',1''-[(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene)]tris(3-hexadecyl-2-methyl-1H-imidazol-3-ium) Iodide (**2b**)

A stirred solution of 1,1',1''-[(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)]tris(2-methyl-1H-imidazole) (500 mg, 1.24 mmol) and 1-iodohexadecane 95% (1.4 g, 4.09 mmol) in CH₃CN (20 mL) was heated to reflux for 72 h. The solvent was partially removed under vacuum and excess diethyl ether was added to the residue. A white powder precipitated, which was filtered and washed with diethyl ether to afford **2b**; yield: 1.36 g (75%). ^1H NMR (250 MHz, CD₂Cl₂): δ = 0.88 [t, J = 6.5 Hz, 9H, -(CH₂)₁₅-CH₃], 1.26 [m, 78H, -(CH₂)₁₃-], 1.85 (m, 6H, -CH₂CH₂-imid), 2.40 (s, 9H, Ar-CH₃), 2.96 (s, 9H, imid-CH₃), 4.08 (t, J = 7.75 Hz, 6H, -CH₂CH₂-imid), 5.56 (s, 6H, imid-CH₂-Ar), 7.27 (d, J = 2 Hz, 3H, H_{imid}), 7.30 (d, J = 2 Hz, 3H, H_{imid}); ^{13}C NMR (100.6 MHz, CDCl₃): δ = 13.2, 14.3, 19.0, 22.9, 26.72, 29.2, 29.5, 29.6, 29.7, 29.8, 29.84, 29.9, 30.1, 49.3, 121.7, 121.8, 129.1, 142.4, 143.6; HR-MS (ESI): calcd. for C₇₂H₁₂₉N₆I (loss of two I⁻): 1204.932, m/z = 602.4656, calcd. for z = 2: 1204.932/2 = 602.4656; anal. calcd. (%) for C₇₂H₁₂₉N₆I₃: C 59.25, H 8.91, N 5.76, I 26.08; found: C 58.32, H 8.94, N 5.68, I 25.56.

Synthesis of Palladium(0) Nanoparticles Stabilized by **2a** (2a-Pd) (entry 1 of Table 1)

A Fischer–Porter apparatus equipped with a magnetic stirrer was charged with **2a** (598 mg, 0.423 mmol) and Pd(dba)₂ (290.6 mg, 0.423 mmol Pd). The apparatus was closed and the contents were subjected to three evacuate-refill cycles with argon. THF (anhydrous, 60 mL) was added, the system was purged with H₂ three times, bringing the pressure of H₂ to 3 atm. and then the mixture was allowed to stir at room temperature for 18 h. The hydrogen was evacuated and the solution was filtered through a nylon membrane Milli-Pore filter. The solvent from the filtrate was evaporated and the black solid residue was washed successively with diethyl ether and methanol, in each washing the solid being recovered by centrifugation and decantation of the supernatant phase. The resulting black solid was dried under vacuum to afford **2a-Pd**; yield: 257 mg (82% with respect to initial palladium); Pd: 14.4% (ICP); size of the nanoparticles: 4.2 \pm 0.5 nm (TEM).

Nanoparticulate materials **2b-Pd** and **3a-Pd** were prepared by analogous procedures (see Table 1, Scheme 4 and the Supporting Information).

General Procedure for the Suzuki Cross-Coupling Catalyzed by 2a-Pd Nanoparticles (Table 5)

A screw-top sealable tube (10 mL) was charged with a magnetic stirbar, aryl halide (2.5 mmol), areneboronic acid (3.75 mmol, 1.5 equiv.), K_2CO_3 (2 equiv.) and **2a-Pd** NP (0.2 mol% Pd). A mixture of toluene-water (4:1, 2.5 mL) was added, the tube was sealed and heated to 90 °C for the period of time indicated in the Supporting Information (the consumption of aryl halide was monitored by GC). The tube was then allowed to cool to room temperature and the solvent was removed under vacuum. Diethyl ether was added and stripped under vacuum to facilitate removal of trace solvents. The residue was purified by column chromatography (SiO_2 , hexane-ethyl acetate mixtures). See Supporting Information for details and characterization of compounds.

Supporting Information

This contains details of the synthesis and characterization of stabilizers **2a**, **2b** and **3a** and of the corresponding nanoparticles **2a-Pd**, **2b-Pd**, **3a-Pd**; HR-TEM images and particle size distribution histograms for the Pd nanoparticles. Details of catalytic runs and characterization data of the corresponding cross-coupling products are also given therein.

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