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N-donor complexes of palladium as catalysts for Suzuki cross-coupling reactions in ionic liquids

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Abstract

Palladium imidazole complexes have been used as catalyst precursors for the Suzuki cross-coupling reaction in 1-butyl-3-methylimidazolium-based ambient temperature ionic liquids. The system provides a stable, recyclable method for iodo- and bromoarenes. The preferred reaction conditions are explored and the effect of changing the ionic liquid components is investigated.

Keywords: Cross-coupling reaction; Ionic liquids; Palladium imidazole complexes

1. Introduction

Palladium catalysed coupling and cross-coupling reactions remain a method of choice for the formation of C–C bonds. Recent developments have led to the activation of aryl chlorides [1] and room temperature catalysis [2]. Significant innovations have been made in the discoveries of novel phosphine systems and in the modification of traditional phosphines. The replacement of the commonly used triarylphosphine ligands with sterically-hindered and electron-rich trialkylphosphines [3] phosphites [4] and phospha-palladacycles (for a review see [5]) have all given rise to highly active systems in palladium catalysed coupling reactions.

Our interest has been in the use of ionic liquids as solvents for the Suzuki reaction [6]. The application of ionic liquids as solvents for transition metal catalysis is an area of intense interest [7] and a wide range of processes are under investigation. The first reported example of a palladium catalysed coupling reaction in an ionic liquid was the Heck reaction in phosphonium and ammonium based ionic liquids [8]. Since then, palladium catalysed coupling reactions have become one of the most active areas of catalyst research in ionic liquids (some examples [9]). To date, we have reported the use of various palladium sources, either with phosphine ligands or added phosphines. However, unexpected activity observed during control experiments led us to investigate the use of palladium complexes of *N*-donor ligands as catalysts in ionic liquids. It is this work that we report here.

The use of *N*-coordinated ligands in palladium catalysed coupling reactions has been an area of limited activity. Most examples involve cyclometallated palladium complexes incorporating either the imine [10,11], amine [12], oxime [13] or oxazoline [14] moieties. The remainder include either chelating bi- or terdentate *N*-coordinating ligands such as diazabutanes [15,16] bis(oxazolinyl)pyrrole [17] or dipyridyl [18] ligands, respectively. A series of methyl palladium(II) complexes have also been reported, incorporating *N*-coordinated bis- and tris-imidazole chelates that were found to be catalytically active in the Heck reaction of 4-bromoacetophenone with *n*-butyl acrylate [19]. Recently, an example of a mixed imidazolylidene-imidazole palladium complex and its application in Sonogashira coupling reactions has been reported [20]. We have reported the use of palladium(II) imidazole based complexes in molecular solvents as catalysts for the Suzuki reaction [21] (Scheme 1).

2. Results and discussion

While searching for soluble sources of palladium for the palladium/phosphine catalysed Suzuki reactions in ionic

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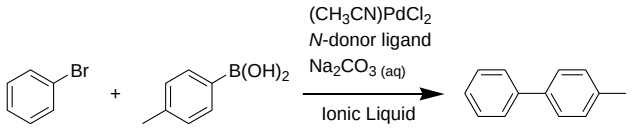

Scheme 1. The Suzuki coupling reaction of a bromobenzene with tolylboronic acid.

Table 1
The Suzuki reaction of bromobenzene and tolylboronic acid in $[C_4C_1im][BF_4]$ with a variety of palladium sources

Palladium source	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
$[C_4C_1im]_2[PdCl_4]$	45.3[d]	113	3.7
$[C_4C_1im]_2[PdCl_4]/4PPh_3$	65.8	165	2.9
$Pd(PPh_3)_4$[6]	68.2	171	2.1

Conditions: 1.2 mol% catalyst, temperature = 110 °C, time = 20 min.
[a] Isolated yields of 4-methylbiphenyl, based on bromobenzene.
[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.
[c] Homo-coupled 4,4′-dimethylbiphenyl yield.
[d] Extensive catalyst decomposition and leaching.

liquids the tetrachloropalladate salt, $[C_4C_1im]_2[PdCl_4]$[1] was investigated. Its use in combination with triphenylphosphine in $[C_4C_1im][BF_4]$, gave an active system for the reaction of bromobenzene and tolylboronic acid (Table 1), with a 65.8% yield of 4-methylbiphenyl in 20 min at 110 °C without any apparent catalytic decomposition. This was typical of several of the palladium sources that we used in this reaction. However, unlike the other palladium sources used, which were inactive in the absence of PPh_3, the use of $[C_4C_1im]_2[PdCl_4]$ alone gave rise to a 45.3% yield of 4-methylbiphenyl in 20 min (Table 1). Extensive catalyst decomposition was evident. $[C_4C_1im]_2[PdCl_4]$ has also been reported to act as a catalyst for the Heck reaction in $[C_4C_1im][PF_6]$ [22].

Palladium(II) salts have previously been reported to catalyse coupling reactions without added ligands, although long reaction times are generally required [23]. However, $[C_4C_1im]_2[PdCl_4]$ has been previously reported as a palladium source for the hydrodimerisation of 1,3-butadiene in both $[C_4C_1im][BF_4]$ and $[C_4C_1im][PF_6]$ [24]. Here it was claimed that the active species was $(mim)_2PdCl_2$ generated in situ from a reaction of the $[C_4C_1im]_2[PdCl_4]$ with the ionic liquids. This led us to test the possibility that a similar chain of events was occurring in our Suzuki reactions, leading to palladium/imidazole complexes that act as catalysts, or their immediate precursors, in these ionic liquids.

ESI mass spectra of a solution of $[C_4C_1im]_2[PdCl_4]$ in dry $[C_4C_1im][BF_4]$ revealed peaks attributable only to the $[C_4C_1im]_2[PdCl_4]$ $\{[(C_4C_1im)_2PdCl_3]^+$, 491 Da; $[(C_4C_1im)_3PdCl_4]^+$, 667 Da; $[(C_4C_1im)_4PdCl_5]^+$, 842 Da$\}$ and the ionic liquid itself, even after 4 weeks stored under N_2. However, upon addition of water the ESI MS revealed a new peak at 307 Da, corresponding to $[(mim)_2PdCl]^+$. This confirmed the formation of $(mim)_2PdCl_2$ in the ionic liquid and that its formation is not due to 1-methylimidazole impurities in the ionic liquid. In our Suzuki reactions $NaCO_3$ is added as an aqueous solution, so giving conditions for the potential formation of $(mim)_2PdCl_2$. Hence, we chose to investigate the use of palladium/imidazole catalysts for the Suzuki reaction in ionic liquids.

Initial experiments, with 1-methylimidazole to determine the reaction conditions to be used found that the addition of $(CH_3CN)_2PdCl_2$ and 1-methylimidazole directly to the ionic liquid was the preferable method for the introduction of the catalyst. The solutions were then heated to 110 °C, during which time the yellow colour of the palladium faded. Performing the Suzuki reaction without this prior heating of the $(CH_3CN)_2PdCl_2$/4mim (where mim = 1-methylimidazole) in the $[C_4C_1im][BF_4]$ resulted in decomposition of the catalyst during the reaction and a decreased yield of 4-methylbiphenyl. Thus, as with the palladium/phosphine catalytic system that we have previously reported [6], the initiation of the catalyst was fundamental to the success of the ionic liquid mediated Suzuki reaction. The resulting solution was cooled to room temperature, the aqueous Na_2CO_3 solution and the starting materials added and the reaction carried out at 110 °C for 20 min. In contrast to the palladium/phosphine system, the catalyst preparation in the ionic liquid could be conducted under air, without any detrimental effect on the eventual Suzuki reaction.

It was found that, in order to prevent catalyst decomposition, at least 4 equivalents of 1-methylimidazole were required, relative to the palladium, whilst more than 4 equivalents inhibited the reaction. Using 4 equivalents of 1-methylimidazole the reaction had reached its maximum yield after 1 h at 110 °C, achieving a 83.3% yield, with only a marginal increase after 3 h (Table 2). The reaction could also be performed at room temperature, achieving a 78.7% yield in 24 h. Unreacted bromobenzene was detected at the end of all the reactions and less than a 4% yield of 4,4′-dimethylbiphenyl was generated from homo-coupling.

Table 2
Investigation of reaction conditions $(CH_3CN)_2PdCl_2$/4mim catalysed Suzuki reactions

Time	Reaction temperature (°C)	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
20 min	110	42.4	106	3.3
1 h	110	83.3	69	2.0
3 h	110	86.1	24	3.8
24 h	25	78.7	3	2.9

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1.
[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.
[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.
[c] Homo-coupled 4,4′-dimethylbiphenyl product.

[1] Note on nomenclature. The substituted imidazolium cations used in this paper are abbreviated to $[C_nC'_nim]^+$, where n and n′ are the chain lengths of the respective alkyl chains. For example, $[C_4C_1im]^+$ is the 1-butyl-3-methylimidazolium cation.

Table 3
The reaction of bromobenzene and tolylboronic acid in a variety of solvents

Solvent	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
$[C_4C_1im][BF_4]$ run 1	42.4	106	3.3
$[C_4C_1im][BF_4]$ run 2	45.4	114	3.8
$[C_4C_1im][BF_4]$ run 3	43.2	108	2.5
$[C_4C_1im][BF_4]$ run 4	40.7	102	3.2
$[C_4C_1im][BF_4]$ run 5	42.9	107	2.7
Dioxane [21]	95.7[d]	239	0
Toluene [21]	89.8[d]	225	0
THF (60 °C) [21]	36.8[d]	92	0
Water (100 °C) [21]	92.8[d]	232	0

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1, temperature = 110 °C, time = 20 min.

[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.

[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.

[c] Homo-coupled tolylboronic acid yield.

[d] Yellow–orange solution afforded from the initiation process. Extensive catalyst decomposition and leaching.

2.1. Comparison with molecular solvents

We have reported the reaction of bromobenzene and tolylboronic acid in molecular solvents previously (Table 3) [21]. It can be seen immediately that the reaction yields and turnover numbers are greater in most of the molecular solvents used. The only exception to this is THF, which due to its boiling point operates at a significantly lower temperature with an associated reduction in rate. It is also noticeable that the reaction in molecular solvents leads to no homo-coupled product being formed. However, in all of these solvents the catalyst was seen to decompose and after extraction it was not possible to repeat the reaction.

Only in the ionic liquid was it possible to recycle and reuse the reaction system. The reaction in $[C_4C_1im][BF_4]$ was, therefore, repeated. After washing with hexane to remove the products the solution was further washed with aliquots of water until a single phase was formed on addition of the aliquot. The ionic liquid was then dried and fresh base and starting materials added. It can be seen (Table 3) that the ionic liquid provided a stable reaction system for the reaction, with no significant loss in activity.

Clearly there are two regimes, the first is highly active, but unstable, the second is less active, but very stable. We have previously invoked the formation of palladium/imidazolylidene complexes in $[C_4C_1im]^+$ ionic liquids to explain the reactivity of palladium/phosphine mixtures in ionic liquids [6]. It is possible that analogous mixed imidazolylidene/imidazole catalysts are being formed in this reaction.

2.2. The ESI-MS catalytic investigation in $[C_4C_1im][BF_4]$

In order to confirm the reason for the stability of the catalyst system in the ionic liquids, we investigated the species formed in solution with ESI-MS. When $(CH_3CN)_2PdCl_2$ and 1-methylimidazole were added to the $[C_4C_1im][BF_4]$ and heated at 110 °C for 1 h under N_2 the ESI-MS revealed signals at 387 $\{[(mim)_3PdCl]^+\}$, 371 {unidentified Pd complex}, 346 {unidentified Pd complex}, 270 $\{[(mim)_2Pd]^+\}$ and 83 $\{[Hmim]^+\}$ *m/z*. Upon addition of aqueous sodium carbonate and reheating of the solution a new signal at 443 $\{[(mim)_2Pd(C_4C_1imy)Cl]^+\}$ (where C_4C_1imy = 1-butyl-3-methylimidazolylidene) appeared. This provides evidence that mixed imidazolylidene/1-methylimidazole palladium complexes could be generated in situ under conditions similar to those used in catalytic reactions. However, it should be stressed that, unlike the phosphine system, other palladium containing signals are present, some of which are unidentified, that may result from other species that could be catalysing the reaction. Attempts to independently prepare the $[(mim)_2Pd(C_4C_1imy)Cl]^+$ complex were unsuccessful.

2.3. Variation of ionic liquid-cation effect

If the formation of palladium/imidazolylidene complexes is important in the catalysis, it would be expected that there would be a significant effect of changing the cation of the ionic liquid on the reaction. Hence, a study of the effect of different ionic liquids on the Suzuki reaction of bromobenzene with tolylboronic acid was performed with the $(CH_3CN)_2PdCl_2$/4mim system (Table 4).

The first thing to notice is that the two ionic liquids for which imidazolylidene formation is not possible {$[C_4C_1C_1im][BF_4]$ (where bmmim = 1-butyl-2,3-dimethylimidazolium) and $[C_4C_1py][N(SO_2CF_3)_2]$ (where bmpy = 1-butyl-1-methylpyrolidimum)} give the highest yielding reactions and extensive catalyst decomposition. These ionic liquids generated a yellow–orange solution after the initiation of the catalyst, rather than the colourless solution formed by the lower yielding, but stable catalyst solutions.

Table 4
Scope of the Suzuki reaction with different ionic liquid-cation effects

Solvent	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
$[C_2C_1im][BF_4]$	18.8	47	1.7
$[C_4C_1im][BF_4]$	42.4	100	2.7
$[C_6C_1im][BF_4]$	32.4	81	2.0
$[C_4C_4im][BF_4]$	55.5	139	3.2
$[C_4C_1C_1im][BF_4]$	85.3[d]	213	1.4
$[C_4C_1py][N(SO_2CF_3)_2]$	83.4[d]	209	4.1

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1, temperature = 110 °C, time = 20 min.

[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.

[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.

[c] Homo-coupled tolylboronic acid yield.

[d] Yellow–orange solution afforded from the initiation process. Extensive catalyst decomposition and leaching.

Analogy with the previously reported palladium/phosphine systems [6] in ionic liquids suggests that the catalyst stability in the ionic liquids is generated by the ability of the imidazolium ions to form imidazolylidene ligands with the palladium. However, unlike the phosphine systems, the ionic liquids in which palladium/imidazolylidene complexes cannot be formed give more reactive catalysts, with reactivities similar to that found in molecular solvents. There is no obvious trend in the reactivities in the ionic liquids that can form imidazolylidene ligands.

2.4. Variation of ionic liquid-anion effect

The effect of the anion in 1-butyl-3-methyl imidazolium ionic liquids is less clear than that of the cation. Stable catalyst systems were formed in all of these ionic liquids. The highest yields were achieved in the $[C_4C_1im][OSO_2CF_3]$ and $[C_4C_1im][PF_6]$, (Table 5). $[C_4C_1im][N(SO_2CF_3)_2]$ and $[C_4C_1im][BF_4]$ gave lesser yields with $[C_4C_1im][OSO_2CH_3]$ and $[C_4C_1im]Cl$ giving no yield at all.

It has been shown that the basicity of the anions of the ionic liquid can affect the electrophilicity of transition metal centres [25]. The greater the basicity the stronger is the interaction with the metal centre and the slower the reaction. However, although this may be contributing to the observed reactivities here it cannot be the complete explanation. While it offers an explanation for the other ionic liquids, under this argument the reactivities of the $[N(SO_2CF_3)_2]^-$ and the $[OSO_2CF_3]^-$ liquids would be expected to be reversed. We are continuing to investigate this phenomenon.

2.5. Variation of imidazoles and other N-donor ligands

The Suzuki reaction of bromobenzene with tolylboronic acid, in a 1:1 ratio, was investigated with $(CH_3CN)_2PdCl_2$ and a small number of other potential *N*-donor ligands at 110 °C for 20 min (Tables 6 and 7). Under these conditions a 42.4% 4-methylbiphenyl yield was obtained, when 1-methylimidazole was used as a ligand, which was approximately in the middle of the affordable yield range (0–80%). Assuming other imidazoles exhibited similar activities, these conditions allowed the widest window to observe any improvements or deteriorations. Furthermore, it suggested some information about the reaction rates, as estimated by TOF (h^{-1}), for the different catalysts due to the presence of unreacted bromobenzene and absence of catalyst decomposition at the end of the reaction period.

Imidazoles incorporating an N–H bond gave no Suzuki cross-coupled product and unreacted bromobenzene was detected (Table 6). The 'ligandless' $\{(CH_3CN)_2PdCl_2\}$ catalytic system gave a 25.4% 4-methlybiphenyl yield and, therefore, these imidazoles must be actively inhibiting the Suzuki reaction.

Table 5
Scope of the Suzuki reaction with different ionic liquid-anion effect

Solvent	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
$[C_4C_1im][BF_4]$	42.4	100	2.7
$[C_4C_1im][PF_6]$	59.5	150	2.3
$[C_4C_1im][N(SO_2CF_3)_2]$	36.4	90	3.3
$[C_4C_1im][OSO_2CF_3]$	62.4	156	1.8
$[C_4C_1im]Cl$	0	0	0
$[C_4C_1im]Br$	24.9	63	1.3
$[C_4C_1im][OSO_2CH_3]$	0	0	0

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1, temperature = 110 °C, time = 20 min.
[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.
[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.
[c] Homo-coupled tolylboronic acid yield.

Table 6
Suzuki reactions with different imidazoles in $[C_4C_1im][BF_4]$

Ligand	Yield[a](%)	TOF (h^{-1})[b]	Homo[c] (%)
Imidazole	0	0	0
2-Methylimidazole	0	0	0
2-Phenylimidazole	0	0	0
Benzimididazole	0	0	0
2-Methylbenzimidazole	0	0	0
1-Methylimidazole	42.4	100	2.7
1-Butylimidazole	40.2	101	3.6
1-Phenylimidazole	76.0	190	2.5
1-Methylbenzimidazole	88.2	221	3.7
1,2-Dimethylimidazole	31.2	78	1.5
1-Butyl-2-methylimidazole	33.9	85	3.0
1,2,4,5-Tetramethylimidazole	29.2	73	2.2
1-Methyl-2-phenylimidazole	32.4	81	3.2
1-Butyl-2-phenylimidazole	28.9	72	2.2

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1, temperature = 110 °C, time = 20 min.
[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.
[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.
[c] Homo-coupled tolylboronic acid yield.

Table 7
Scope of Suzuki reactions with other potential *N*-coordinated ligand

Ligand	Yield[a] (%)	TOF (h^{-1})[b]	Homo[c] (%)
Pyrazole	0	0	0
Tetrazole	0	0	0
DBU	15.2	38	1.1
4-Methylthiazole	81.2[d]	203	2.0
Pyridine	75.4[d]	189	3.4
Et_3N	79.0[d]	200	2.6
1,4-Bis-(diisopropylphenyl)-1,3-diazabutadiene	92.3[d]	231	3.1
2,2′-Bipyridyl	68.2[d]	171	1.9

Conditions: 1.2 mol% catalyst, L:catalyst = 4:1, temperature = 110 °C, time = 20 min.
[a] Isolated yields of 4-methylbiphenyl product, based on bromobenzene.
[b] TOF (h^{-1}) = number of moles of desired product per mole of catalyst used per hour.
[c] Homo-coupled tolylboronic acid yield.
[d] Yellow–orange solution afforded from the initiation process. Extensive catalyst decomposition observed during reaction.

Different *N*-alkyl substituents had no effect on the yield, for example, 1-butylimidazole gave a comparable yield to 1-methylimidazole (Table 6). However, 1-phenylimidazole gave a yield of 76.0% under these conditions and 1-methylbenzimidazole was found to be the most active imidazole based systems tested (88.2% yield).

C-2 substitution of the imidazoles led to a reduction in the yield in comparison to the parent imidazole, irrespective of the nature of the C-2 substituent. For example, 1-butyl-2-phenylimidazole afforded a comparable yield to 1,2-dimethylimidazole.

Other *N*-donor ligands were also investigated (Table 7). The inhibiting nature of N–H bonds were also observed for pyrazole and tetrazole ligands (Table 7). Other *N*-coordinating ligands tested were shown to be highly active, albeit with extensive decomposition. This would suggest that the nature of the *N*-donor ligand is important in determining whether a palladium/imidazolylidene complex can form. Diazabicycloundecene (DBU) was found to produce a 15.2% yield of 4-methylbiphenyl with no decomposition.

The *N*-bidentate ligands, 1,4-bis-(diisopropylphenyl)-1,3-diazabutadiene and 2,2′-bipyridyl, investigated by Nolan [15] were also examined in $[C_4C_1im][BF_4]$ (Table 7). These catalytic systems performed significantly better in the ionic liquid than in dioxane, in which 80 and 13% yields were reported for the diazabutadiene and bipyridyl ligands, respectively. However, catalyst decomposition was clearly observed.

3. Conclusions

A number of substituted imidazoles, when used with palladium(II) sources in ionic liquids, provide a robust air-stable system for Suzuki reactions. A successful Suzuki reaction required the initiation of the catalytic system in the ionic liquid prior to the reaction. This was achieved by heating the palladium source with the imidazole in the ionic liquid to generate a completely colourless catalytic solution. Without the initiation low yields were obtained with catalytic decomposition. The catalytic activity and stability in the ionic liquids was strongly dependent on the nature of the imidazole ligands and on the natures of the anion and cation of the ionic liquid. The $(CH_3CN)_2PdCl_2$/4mim catalytic system was found to be highly active in $[C_4C_1py][N(SO_2CF_3)_2]$, $[C_4C_1C_1im][BF_4]$ and molecular solvents, although extensive catalyst decomposition occurred.

The reactivities of the different solutions that were stable depend on both the cation and the anion of the ionic liquid, the most active of those tested being $[C_4C_1im][PF_6]$ and $[C_4C_1im][OSO_2CF_3]$. It has also been shown that it is possible to use the imidazole ligand to improve reactivities, with 1-phenylimidazole and 1-methylbenzimidazole giving the most active catalysts in $[C_4C_1im][BF_4]$. Hence there is a great deal if synthetic flexibility that can be explored in to improve upon and develop this new catalyst system.

4. Experimental

4.1. General

Unless otherwise stated, all materials were used as-obtained without further purification. Acetonitrile, CH_2Cl_2, dioxane and ethyl acetate were distilled from CaH_2, The ionic liquids were prepared using methods that we have previously described [26]. The imidazoles were freshly distilled from KOH under reduced pressure, as were 3-methylthiazole, DBU, pyridine and triethylamine. Pyrazole and tetrazole were recrystallised from $CHCl_3$ and hexane. NMR spectra were recorded on a JEOL GSX-270 FT spectrometer. ESI-MS were performed on a Waters HPLC 600 with a micromass ZMD (capillary 3.64 kV; cone = 31 V; extractor = 8 V; source temperature 100 °C and desolvation temperature = 120 °C). GC analysis were performed with a Hitachi 163 gas chromatograph using a 2 m × 3 mm carbowax column.

4.2. Preparation of bis-(acetonitrile)dichloropalladium(II), $(CH_3CN)_2PdCl_2$

A suspension of $PdCl_2$ (2.00 g, 11.3 mmol) was heated at reflux in CH_3CN (100 cm^3) with vigorous stirring for 18 h under N_2. Hot filtration of the resultant wine-red coloured solution through a celite pad into stirred petroleum spirit (40–60 °C; 100 cm^3) at ambient temperature gave a yellow–orange solid. Recrystallisation from a CH_3CN (200 cm^3), CH_2Cl_2 (300 cm^3) and hexane (100 cm^3) mixture gave $(CH_3CN)_2PdCl_2$ (1.78 g, 65.3%) as a bright yellow powdery solid; m.p. 129–131 °C (decomp); Found: C, 18.63; H, 2.27; N, 10.77; $C_4H_6N_2Cl_2Pd$ requires C, 18.55; H, 2.33; N, 10.82%; ν_{max}(KBr)/cm^{-1} 3285, 2979, 2918, 2338, 1412, 1329, 1022, 959, 438 and 407; δ_H(270 MHz, d^6-DMSO)/ppm 2.06 (6H, s, $2CH_3$); δ_C(68 MHz, d^6-DMSO)/ppm 118.0 (s, CH_3CN) and 1.09 (s, CH_3CN).

4.3. A typical Suzuki reaction in ionic liquid

To a flask charged with $[C_4C_1im][BF_4]$ (1.6 cm^3) was injected $(CH_3CN)_2PdCl_2$ (2.36 mg, 9.12 μmol, 1.2 mol%) and 1-methylimidazole (3.00 mg, 36.5 μmol, 4.8 mol%) The yellow solution was stirred at 110 °C for 1 h under N_2, during which time the colour disappeared. The flask was then removed from the heat and allowed to cool to ambient temperature. To the colourless solution Na_2CO_3 (161 mg, 1.52 mmol, 2 equivalents) in deoxygenated water (0.80 ml), bromobenzene (119.3 mg (80.00 μl), 0.7597 mmol, 1 equivalent) and the tolylboronic acid (114 mg, 0.837 mmol, 1.1 equivalent) was added. The solution was then heated to 110 °C for 20 min. At that point the flask was rapidly cooled in a dry-ice/acetone bath (−78 °C), the reaction mixture was diluted with water (2 ml) and extracted with hexane (4 × 15 cm^3). The extracts were washed with brine (3 × 40 ml) and water (3 × 40 ml), filtered through a pad of silica and

evaporated to dryness to afford 4-methylbiphenyl (51.0 mg, 42.4%) as a colourless crystalline solid.

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