Ionic Liquids as Reaction Media for Palladium-Catalysed Cross-Coupling of Aryldiazonium Tetrafluoroborates with Potassium Organotrifluoroborates

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The system comprising a palladium complex in a 1-butyl-3-methylimidazolium tetrafluoroborate/methanol mixture efficiently catalyses the cross-coupling reaction between *p*-tolyldiazonium tetrafluoroborate and potassium phenyltrifluoroborate at room temperature. The presence of methanol (or water) in the reaction mixture is necessary in order to achieve quantitative conversions, due to its scavenging behaviour towards the BF_3 formed during the reaction. Yields higher than 90% were obtained using $Pd_2(dba)_3$ or the azapalladacycle **10** as the palladium source. With the latter complex a turnover frequency of about 6000 h^{-1} was attained in the coupling of aryldiazonium tetrafluoroborates with potassium vinyltrifluoroborate. Recycling of the catalytic solution could be performed provided that a slight excess of diazonium salt was used in the first run.

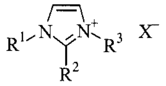
Introduction

Palladium-catalysed cross-coupling utilizing organoboron compounds (the Suzuki reaction) is a powerful tool for the formation of carbon−carbon bonds.[1,2] The practical advantages of this reaction are mainly related to the wide range of functionalized substrates that can be used under mild conditions. Typical reaction protocols exploit aryl iodides, bromides and triflates, which are not as cheap and readily available as aryl chlorides, although the latter are less reactive. It has been demonstrated[3−8] that aryldiazonium tetrafluoroborates derived from inexpensive and easily accessible anilines can be efficiently used in the cross-coupling with organoboronic acids or esters. Moreover, the cross-coupling has also been performed at room temperature and without added base using potassium organotrifluoroborates, which are more stable and reactive than the corresponding boronic acid derivatives.[9]

Ionic liquids (ILs) have emerged as potentially useful reaction media in catalysis because of their peculiar physical and chemical properties.[10] The latest efforts of the scientific community have been addressed towards finding new, possibly recyclable catalytic systems that exhibit higher activity than with classical solvents.

The palladium-catalyzed Suzuki reaction between boronic acids and aryl halides has been successfully carried out in ILs. Welton et al.[11−13] have demonstrated that, under suitable conditions, the use of imidazolium-based IL/H_2O mixtures leads to increased reactivity and selectivity compared to conventional reaction media and permits the recycling of the catalytic solutions. Other catalytic systems employed for the same reaction include $PdCl_2$ in alkylammonium tetrafluoroborate/H_2O mixtures,[14] $Pd_2(dba)_3$ in a ternary system made up of tetradecyltrihexylphosphonium chloride, water and toluene[15] and phosphane-free $Pd(OAc)_2$ or bisimidazolin-2-ylidene palladium complex in IL/MeOH mixtures under ultrasonic irradiation.[16]

In the framework of our studies on metal-catalysed carbon−carbon bond forming reactions in ILs[17−20] we decided to investigate the palladium-catalysed cross-coupling of aryldiazonium salts with organotrifluoroborates. Figure 1 shows the ILs used in this work.



$[bmim]^+$: R^1 = methyl, R^2 = H, R^3 = *n*-butyl
$[bmmim]^+$: R^1, R^2 = methyl, R^3 = *n*-butyl
$[bbim]^+$: R^1, R^3 = *n*-butyl, R^2 = H
X^-: BF_4^-, PF_6^-, $N(SO_2CF_3)_2^-$

Figure 1. Ionic liquids employed: $[bmim]BF_4$, $[bmim]PF_6$, $[bmim]N(SO_2CF_3)_2$, $[bmmim]BF_4$, $[bbim]BF_4$

Results and Discussion

Optimisation of the Solvent

The cross-coupling reaction between *p*-tolyldiazonium tetrafluoroborate (**1a**) and potassium phenyltrifluoroborate (**2**) was chosen as the model system (Reaction 1).

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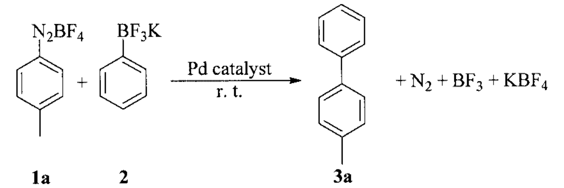


Reaction 1. Cross-coupling between *p*-tolyldiazonium tetrafluoroborate and potassium phenyltrifluoroborate

Table 1 summarises the results obtained when carrying out reaction 1 in several ILs with 2.0 mol % $Pd(OAc)_2$ as catalyst, which is a palladium loading less than half of that used in previous works.[9]

Table 1. Solvent screening; reaction conditions: IL: 10 mmol; $Pd(OAc)_2$: 0.02 mmol; **1a**: 1.0 mmol; **2**: 1.2 mmol

Entry	Solvent	Time [h]	Conv.[a] (%)	Isolated yield (%)
1-1	$[bmim]BF_4$	6	51	49
2-1	$[bmim]N(SO_2CF_3)_2$	6	60	38
3-1	$[bmim]PF_6$	14	50	41
4-1	$[bmmim]BF_4$	12	53	45
5-1	$[bbim]BF_4$	12	45	34

[a] Calculated at the time at which a plateau was reached in the consumption of the diazonium salt.

The results show that there is an effect of the IL used on the course of the reaction. Using $[bmim]BF_4$ (bmim = 1-*n*-butyl-3-methylimidazolium) gave 51% conversion after 6 h with 96% selectivity towards **3a** (Entry 1-1). Catalysis in $[bmim]N(SO_2CF_3)_2$ was more efficient (60% conv. after 6 h) but significantly less selective (63%, Entry 2-1), whereas when $[bmim]PF_6$ was used as solvent a drop in both activity (50% conv. after 14 h) and selectivity (82%) was observed (Entry 3-1 vs. Entry 1-1). The effect of the cation of the IL is shown in Entries 1-1, 4-1 and 5-1, from which it is apparent that comparable yields of **3a** were obtained after significantly different times. Among all the ILs tested $[bmim]BF_4$ gave the best results in terms of both activity and selectivity and was chosen as solvent for further investigations.

A common point which emerges from Table 1 is that, after variable times, the reactions did not reach completion but stopped when the conversion was about 50–60%. Figure 2 shows the reaction course in the case of Entry 1-1.

Such a behavior could, in theory, be ascribed to two causes: a) catalyst deactivation, or b) formation of a product that inhibits the reaction.

The first hypothesis was ruled out by the observation that the conversion did not improve significantly when performing the reaction with a higher amount of palladium: carrying out the catalysis with 5 or 10 mol % Pd resulted in 65% or 70% conversion, respectively.

In search of the reaction product that could act as inhibitor for the reaction we focused our attention on BF_3. It is known[21,22] that BF_3 reacts with **2** in halogenated solvents to afford potassium tetrafluoroborate and phenyldifluoroborane (Reaction 2).

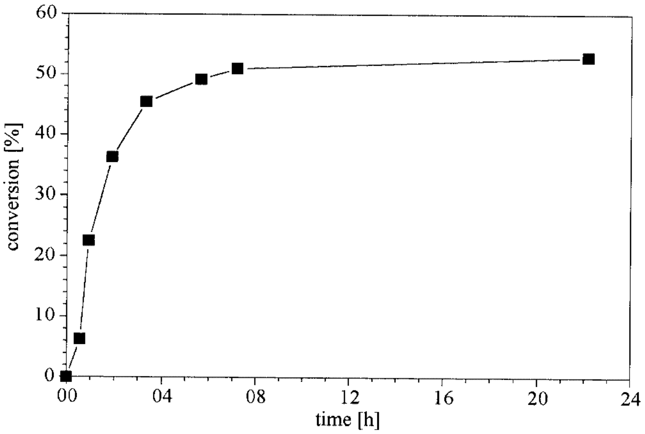


Figure 2. Reaction course of Entry 1-1

$BF_3 + KPhBF_3 \rightarrow PhBF_2 + KBF_4$

Reaction 2

This reaction could therefore be responsible for unsatisfactory conversions as the formed $PhBF_2$ is inactive in Suzuki cross-coupling.

The detrimental effect of BF_3 on the reaction course was circumvented by using MeOH as a BF_3 scavenger. In fact, reactions performed in $[bmim]BF_4$/MeOH mixtures gave quantitative conversions. Figure 3 shows the effect of the molar fraction (x_{MeOH}) of added methanol on the catalysis performed in $[bmim]BF_4$. Isolated yields of **3a** and reaction times are dependent on the molar fraction of MeOH. At $x_{MeOH} = 0.25$ the reaction reaches completion in 120 min with a 68% yield of **3a**. The discrepancy between yield and conversion is due to decomposition of the diazonium salt, since only traces of homo-coupling products (biphenyl and 4,4′-dimethylbiphenyl) were formed. At $x_{MeOH} = 0.75$ a 67% yield of **3a** was achieved along with the formation of biphenyl (25%) and 4,4′-dimethylbiphenyl (6%) by-products. The reaction carried out in pure MeOH was very fast and exothermic but poorly selective, giving only 47% yield of **3a**, 30% of biphenyl and 16% of 4,4′-dimethylbiphenyl. Hence, MeOH has the side effect of accelerating the decomposition of the diazonium salt over long reaction times when used at low molar fractions; at high x_{MeOH} the selectivity of the reaction is strongly reduced, mainly owing to formation of homocoupling by-products. Carrying out the reaction with a x_{MeOH} of 0.50 gave the best result (83% yield of **3a** after 30 min). In this case the formation of

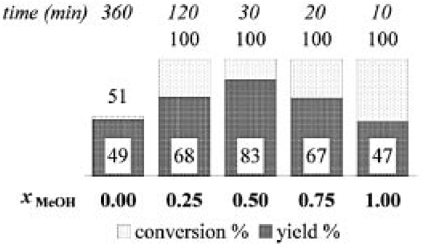


Figure 3. Effect of the MeOH molar fraction

homo-coupling products was negligible and the decomposition of diazonium salt minimised.

Palladium Source

Results obtained using several Pd sources in [bmim]BF_4/MeOH (x_{MeOH} = 0.50) as catalysts for reaction 1 are summarized in Table 2. A comparison of Entry 1-2 with Entry 2-2 clearly shows the strong influence exerted by the anion of the Pd^{II} salt on the catalysis: $PdCl_2$ gave only 40% conversion and 15% yield of **3a** after 28 h. The reactions involving Pd^0 complexes gave nearly quantitative conversions. In particular, $Pd_2(dba)_3$ gave a higher yield (90%) than that (63%) obtained with $Pd(PPh_3)_4$, but needed a longer reaction time (Entries 3-2 and 4-2).

Table 2. Screening of palladium source; reaction conditions: degassed solvent mixture IL/MeOH (x_{MeOH} = 0.50): 2.0 mL; Pd: 0.02 mmol; **1a**: 1.0 mmol; **2**: 1.2 mmol

Entry	Catalyst	Time [min]	Conv. (%)	Isolated yield (%)
1-2	$Pd(OAc)_2$	30	100	83
2-2	$PdCl_2$	1680	40	15
3-2	$Pd_2(dba)_3\cdot CHCl_3$	330	95	90
4-2	$Pd(PPh_3)_4$	150	100	63
5-2	**4**	1800	80	44
6-2	**5**	1260	23	traces
7-2	**6**	1320	64	54
8-2	**7**	900	98	86
9-2	**8**	30	100	65
10-2	**9**	10	100	84
11-2	**10**	30	100	93
12-2	**10**[a]	15	100	55
13-2	**10**[b]	120	96	87
14-2	**10**[c]	720	83	67

[a] Pure methanol (4 mL) as solvent. [b] Solvent mixture: 4 mL; Pd: 5.0×10^{-3} mmol; **1a**: 2.0 mmol; **2**: 2.4 mmol. [c] Pd: 1.0×10^{-3} mmol.

Several palladium(II) acetate derivatives (Figure 4) were tested. Mononuclear complexes bearing chelating ligands gave unsatisfactory results: 2,2′-bipyridyl complex **4** gave a 44% yield of **3a** while the 1,2-bis(diphenylphosphanyl)ethane complex **5** was almost inactive (Entries 5-2 and 6-2). Conversely, dinuclear phosphapalladacycles were found to be active catalysts for reaction 1: complex **6** gave 64% conversion together with 54% yield after 22 h (Entry 7-2), while **7** gave a quantitative conversion and 86% yield in a shorter reaction time (Entry 8-2). The dinuclear azapalladacycles **8**−**10** were found to be the most active catalysts. In all cases quantitative conversions were obtained in 30 min or less, with selectivities towards the desired product **3a** ranging from 65% obtained with the 8-methylquinoline derivative **8** (Entry 9-2) to 93% obtained with the azobenzene derivative **10** (Entry 11-2). A remarkably short reaction time was observed with the iminopalladacycle **9**, which afforded an 84% yield in less than 10 min (Entry 10-2). Complex **10** was also used for comparison in pure methanol, giving only 55% yield after 15 min (Entry 12-2).

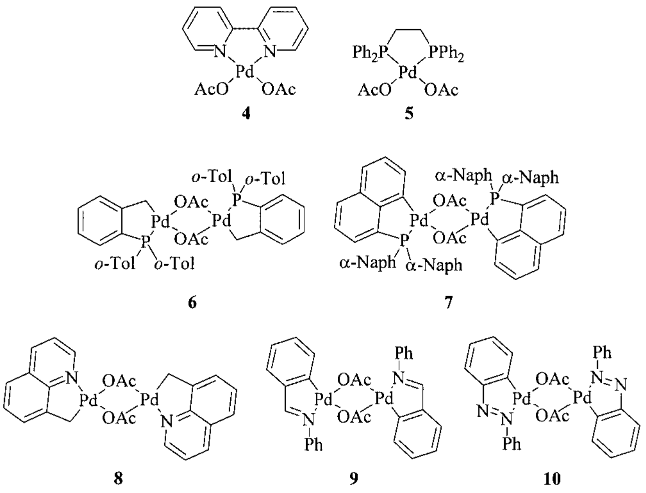


Figure 4. Palladium acetate derived catalysts; Naph = naphthyl

$Pd(OAc)_2$ and complexes **6**−**10** were also used in an equimolar mixture of [bmim]BF_4 and H_2O. In all cases quantitative conversions were achieved owing to the ability of water to act as a BF_3 scavenger. $Pd(OAc)_2$ gave 65% yield of **3a** after 2 h whereas the yields obtained with complexes **6** and **7** were 85% and 87%, respectively, after 20 h. Complexes **8**−**10** gave 64%, 60% and 70% isolated yields, respectively, in less than 30 min. Figure 5 shows a comparison of the results obtained with $Pd(OAc)_2$ and complexes **6**−**10** in IL/MeOH with those in IL/H_2O. All the catalysts shown in Figure 5, except phosphapalladacycles **6** and **7**, were more selective when the cosolvent was MeOH.

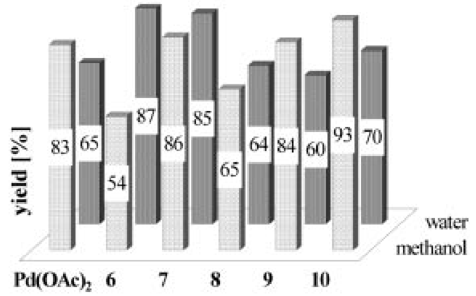


Figure 5. Performance of catalysts **4**−**10** in equimolar [bmim]BF_4/cosolvent mixtures

Palladium Loading and Recycling

The effect of palladium loading was investigated using complex **10** in an equimolar [bmim]BF_4/MeOH mixture. At 0.5% Pd loading (0.25 mol % of the dinuclear complex) the catalyst was still active and selective, reaching nearly quantitative conversion with an 87% yield after 2 h (Entry 13-2); at 0.1% loading the reaction afforded 67% of **3a** with an 83% conversion after 12 h (Entry 14-2).

Optimization tests aimed at recycling the catalytic solution, performed with complex **10** in IL, showed that an excess of the aryldiazonium **1a** was necessary in order to obtain a recyclable catalytic solution. When a 20% excess of phenyltrifluoroborate **2** was employed the second cycle did not reach completion (60% conv. after 3 d), giving only 37% of **3a**; the catalyst decomposed into Pd black (formation of Pd black during the reaction was observed in almost all the reactions described so far). On the other hand, when a 20% excess of **1a** was used no Pd black formed after the first run and the catalytic solution was recyclable (Figure 6). The excess of **1a** renders the catalytic system less efficient as, with an excess of **2**, a 93% yield was achieved after 30 min (Entry 11-2), whereas with **1a** in excess a 72% yield was achieved after 2 h.

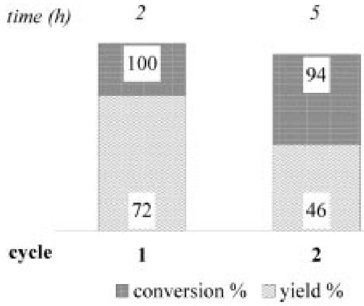


Figure 6. Recyclability of the catalytic solution (initial **1a/2** molar ratio = 1.2)

Possible Active Species: Preliminary Investigations

Mechanistic investigations on Suzuki coupling involving aryldiazonium salts have not been performed so far. However, different active species have been suggested for "classical" Suzuki reactions in ILs. Zou et al. have proposed that the catalytic activity observed in alkylammonium tetrafluoroborate/H_2O mixtures is due to palladium metal stabilised by the reaction medium.[14] On the other hand, Srinivasan's group has ruled out colloidal Pd nanoparticles as the active species in the Suzuki reaction performed in imidazolium-based IL/MeOH mixtures.[16] Welton et al.[12] have suggested the intermediacy of mixed (carbene)(phosphane)Pd^{II} complexes formed by reaction of $Pd(PPh_3)_4$ with [bmim]BF_4 in the presence of aryl halide and a halide salt under basic conditions.

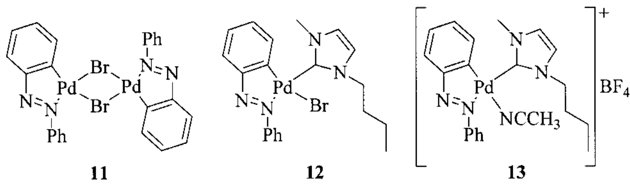
Although palladium nanocolloids are known to catalyze the strictly related Heck reaction in ILs,[23] in our case the progressive formation of palladium black observed nearly invariably during catalysis is more probably the consequence of catalyst decomposition, since no Pd black formed in the catalytic solutions that could be successfully recycled. That palladium metal is not involved in the catalytic act is further demonstrated by poisoning experiments with Hg metal.[24] When performing reaction 1 catalyzed by complex **10** in the presence of added Hg (Hg/Pd = 150 mol/mol) no inhibition was observed (Entry 1-3, Table 3). This result suggests that palladium nanocolloids are not involved in the catalytic cycle and that a homogeneous mechanism should be operating.

Table 3. Reaction conditions: degassed solvent mixture LI/MeOH (x_{MeOH} = 0.50): 2.0 mL; Pd: 0.02 mmol; **1a**: 1.0 mmol; **2**: 1.2 mmol

Entry	Catalyst	Time [min]	Isolated yield (%)[a]
1-3[b]	**10**	30	85
2-3	**11**	260	65
3-3	**12**	1600	45
4-3	**13**	480	55
5-3[c]	**10**	40	90

[a] Quantitative conversions. [b] Hg added; Hg/Pd = 150 mol/mol. [c] Reaction performed in [bmmim]BF_4/MeOH.

Among the possible candidates for the active species in the present reaction we focused our attention on (carbene)Pd^{II} species. According to Wasserscheid,[10] three simple experiments should be carried out to verify the intermediacy of carbene complexes as catalytically active species in ILs, namely variation of the ligands, tests with independently prepared, well-defined (carbene)Pd^{II} complexes, and reactions in ILs that are not capable of carbene formation. Replacing the bridging acetates with bridging bromides (Figure 7) in complex **10** resulted in a drop of activity (Entry 11-2 vs 2-3); this might be rationalised by invoking the inability of bromide to generate carbene species by abstraction of the acidic proton in the 2-position of the imidazolium ring. However, reactions performed with the preformed carbene complexes **12** and **13** (Entries 3-3 and 4-3) were much slower than that performed with complex **10** (Entry 11-2). This seems to indicate that, even if they form in the reaction mixture, carbene species are not mainly responsible for the catalytic activity observed with azapalladacycles. Accordingly, replacing [bmim]BF_4 with [bmmim]BF_4, an imidazolium-based IL that is not capable of carbene formation due to the presence of the methyl group in the 2-position, gave essentially equal activity and selectivity (see Entries 11-2 and 5-3).



11 **12** **13**

Figure 7. (Azobenzene)Pd^{II} complexes

The above-mentioned detrimental effect of bromides on catalysis could, therefore, be due to the strong coordinating ability of halide species towards palladium. This strong tendency to bind palladium could also be held responsible for the difference in activity between bromo complex **12** and acetonitrile complex **13**, and can also rationalize the sluggishness of the reaction catalyzed by $PdCl_2$ (Entry 2-2).

At this stage, the following points seem to emerge: (i) catalysis is molecular and influenced by the ligands on the palladium atom; (ii) the presence of easily dissociable ligands in palladium(II) precatalysts has a beneficial effect on catalysis (compare activities of acetate complex **10** vs. bromide complex **11** or of acetonitrile complex **13** vs. bromide complex **12**). Although no definitive conclusion can be drawn about the active species that triggers the catalysis starting from azapalladacycle **10**, these observations lead us to suggest, on the basis of the commonly accepted Pd^0/Pd^{II} cycle, the anionic Pd^0 complex depicted in Figure 8 as the possible active species. Such a species, which could be generated by reduction of **10** by **2**, might start the catalytic cycle by forming an arylpalladium complex by reaction with the diazonium salt.

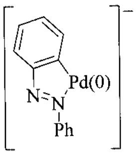


Figure 8. Possible active species in reactions catalysed by complex **10**

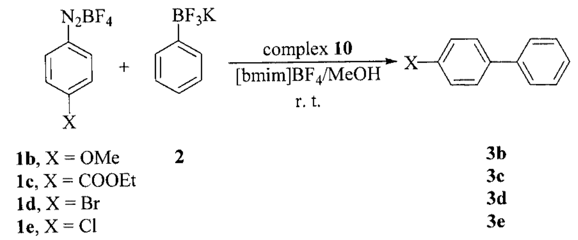
Anionic Pd^0 complexes have been suggested as active species in related cross-coupling reactions. Amatore et al.,[25] for example, have demonstrated that $[Pd(PPh_3)_2(OAc)]^-$, formed from $Pd(OAc)_2$ and PPh_3, is an active species for the catalytic cycle of Heck reactions between aryl halides and olefins, and Hermann et al.[26] have proposed the palladacycle [(di-*o*-tolylphosphanyl)benzyl]palladate(0) as the active species in Heck couplings catalyzed by complex **6**.

Screening of Substrates

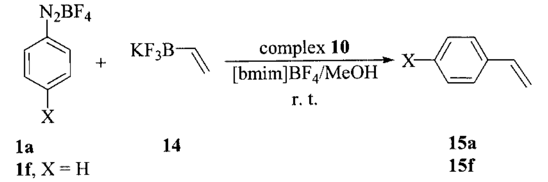
The reactivity of several substrates was explored (Table 4). Substituted aryldiazonium salts (Reaction 3) gave fair to good yields: 4-methoxybiphenyl was obtained with a 78% yield after 3 h (Entry 1-4) while aryldiazonium salt **1c**, containing an electron-withdrawing group (Entry 2-4), reacted faster to give the relevant biphenyl in 82% yield. Halogen-substituted substrates **1d** and **1e** were less reactive and required 4% palladium to give quantitative conversions and 79% and 95% yields, respectively (Entries 3-4 and 4-4). Vinyltrifluoroborates were far more reactive than the aromatic ones (Reaction 4): quantitative conversions and yields of up to 83% were obtained after 10 min using as little as 0.1% palladium (turnover frequency ≈ 6000 h^{-1}; Entries 5-4 and 6-4).

Table 4. Screening of substrates; reaction conditions: degassed solvent mixture LI/MeOH (x_{MeOH} = 0.50): 2 mL; ArN_2BF_4: 1.0 mmol; $KRBF_3$: 1.2 mmol; quantitative yields were obtained

Entry	ArN_2BF_4	$K(RBF_3)$	Pd loading [mmol]	Time [min]	Product	Isolated yield (%)
1-4	**1b**	**2**	0.02	180	**3b**	78
2-4	**1c**	**2**	0.02	5	**3c**	82
3-4	**1d**	**2**	0.04	180	**3d**	79
4-4	**1e**	**2**	0.04	3	**3e**	95
5-4	**1a**	**14**	0.001	10	**15a**	83
6-4	**1f**	**14**	0.001	10	**15f**	80



Reaction 3



Reaction 4

Conclusion

This study demonstrates that ILs are suitable solvents for the title reaction. Used neat, ILs give high selectivities for the cross-coupling product. High activity and selectivity were shown by catalytic systems comprised of azapalladacycles in [bmim]BF$_4$/MeOH mixtures. Using a slight excess of diazonium salt with respect to aryltrifluoroborate allowed the recycling of the catalytic solution. Preliminary mechanistic studies carried out with the precatalyst **10** indicate that a homogeneous process takes place and that carbene species are not the main active species. Further studies on this subject are in progress.

Experimental Section

General: Unless otherwise specified all the manipulations were conducted under an inert gas (nitrogen) using standard Schlenk techniques. Flash-chromatography was performed on SiO$_2$ Kieselgel 230−400 mesh. The NMR spectra were recorded with a Bruker AX400 spectrometer (400 MHz for ^{1}H) at 295.0 K; chemical shifts are reported in ppm referenced to SiMe$_4$ for ^{1}H and ^{13}C, and CFCl$_3$ for ^{19}F. LC-MS analyses of complexes **11**, **12** and **13** were performed with an Agilent HPLC system equipped with DAD, autosampler and MS systems (Agilent 1100 LC-MS SL series). All samples were dissolved in the same HPLC-grade solvent that was used as eluent. The used interfaces were APCI for neutral complexes **11** and **12**, and ESI for cationic complex **13**. APCI conditions: positive-ion mode, flow rate 0.5 mL/min, nitrogen as nebulizing and drying gas, nebulizer pressure 4 atm, vaporizer temperature 350 °C, corona current 4.0 μA, drying-gas flow 5 L/min, drying-gas temperature 350 °C, capillary voltage 4000 V. ESI conditions: positive-ion mode, flow rate 0.3 mL/min, nitrogen as nebulizing and drying gas, nebulizer pressure 2 atm, capillary voltage 4000 V. Mass spectrometry data were acquired in the scan mode (mass range *m/z* = 50−3000). C, H, N elemental analyses were carried out with a Eurovector CHNS-O Elemental Analyser. Pd analyses were performed with a Perkin−Elmer SIMAA6000 Atomic Absorption spectrometer. The IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. GC analyses were performed with an HP5890 instrument equipped with a Supelco SPB-1 capillary column (30 m × 320 µm × 0.25 µm). GC-MS analyses were performed with an HP6890-HP5973MSD instrument equipped with an HP-5MS capillary column (30 m × 250 µm × 0.25 µm). The halide content of the ionic liquids was determined in aqueous solution by a potentiometric automatic titration using a Metrohm 716 DMS Titrino (300 mg sample, ca. 30 mL deionized water, three runs) while the water content was determined by the Karl−Fischer method using a Metrohm 716 DMS Titrino equipped with a 703 titration stand using sodium tartrate-2-hydrate as standard and dry methanol as solvent (1 g sample, ca. 30 mL MeOH, three runs). All commercial reagents were used as received without further purification. Solvents were dried and distilled under nitrogen according to standard procedures; water (resistivity $> 17.5 \cdot \mathrm{M\Omega\ cm^{-1}}$) was deionized with a Millipore Simplicity unit. [bmim]Cl,[27] [bmmim]Cl,[27] [bbim]Br[28] and [bmim]Br[29] were synthesised from 1-chlorobutane or 1-bromobutane and the relevant imidazole salt according to literature procedures. [bmim]Cl, [bmmim]Cl and [bmim]Br were purified by crystallisation from acetonitrile/ethyl acetate (1:4) until a colourless mother liquor was obtained, and then filtered and dried under vacuum; all compounds were obtained as white solids. [bbim]Br was obtained as a viscous brown liquid, washed with CH_2Cl_2/diethyl ether (1:4) and dried under vacuum. All compounds were stored under nitrogen. [bmim]BF_4, [bmim]PF_6, [bmim]$N(SO_2CF_3)_2$, [bmmim]BF_4, [bbim]BF_4 were synthesised by metathesis from the corresponding alkali metal salts in dichloromethane; the resulting suspension was filtered through Celite and washed with the minimal amount of water until the $AgNO_3$ test on the aqueous layer was negative. The solvent was then evaporated and the resulting IL was dried at 40−50 °C under vacuum for 48 h and stored under nitrogen. The ionic liquids were obtained as pale-yellow or colourless liquids and fully characterised by multinuclear NMR spectroscopy. Their water content was less than 460 ppm whereas their halide content was below the detection limit of 0.38 mg/L. Complexes **4**,[30] **5**,[31] **6**,[26] **7**,[32] **8**,[33] **9**[34] and **10**[35] were synthesised according to literature procedures.

Di-µ-bromo-bis[*o*-(phenylazo)phenyl]dipalladium(II) (11): Complex **10** (0.173 g, 0.25 mmol) and tetrabutylammonium bromide (0.167 g, 0.52 mmol) were dissolved in dry dichloromethane (10 mL). After stirring for 3 h, the volume was reduced in vacuo to a half and dry methanol (50 mL) was added. The resulting red solid was filtered off, washed with methanol (3 × 5 mL) and hexane (15 mL) and dried in vacuo to afford **11** as a red powder (0.151 g, 82%); m.p. > 250 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1575 (m), 1553 (w), 1482 (w), 1458 (w), 1444 (w), 1393 (m), 1318 (w), 1306 (w), 1263 (w), 1242 (w), 762 (m), 753 (m), 706 (w), 691 (m), 595 (w), 550 (w), 525 (w) cm^{-1}. ^1H NMR ([D]$_6$DMSO): δ = 7.07 (t, J = 7.31 Hz, 1 H), 7.17 (t, J = 7.31 Hz, 1 H), 7.44 (m, 3 H), 7.65 (m, 2 H), 7.86 (d, J = 7.31 Hz, 1 H), 7.89 (d, J = 7.92 Hz, 1 H) ppm. ^{13}C NMR ([D]$_6$DMSO): δ = 124.36, 126.06, 128.84, 130.24, 131.38, 132.22, 139.12, 150.88, 153.88, 164.13 ppm. LC-MS (CH_3CN/CH_2Cl_2, 9:1): exact mass calcd. for $C_{24}H_{18}Br_2N_4Pd_2$: 731.80; found 732 $[M]^+$, 773 $[M + CH_3CN]^+$. $C_{24}H_{18}Br_2N_4Pd_2$: calcd. C 39.21, H 2.47, N 7.62, Pd 28.95; found C 39.65, H 2.70, N 7.41, Pd 28.79.

Bromo(1-butyl-3-methylimidazolin-2-ylidene)[*o*-(phenylazo)phenyl]palladium(II) (12): Complex **10** (0.39 g, 0.56 mmol) and [bmim]Br (0.25 g, 1.13 mmol) were dissolved in dry THF (50 mL) in a round-bottomed flask. After refluxing under nitrogen for 3 h and cooling to ambient temperature, the solvent was evaporated in vacuo to give an orange solid. Crystallization from acetone/hexane afforded **12** as a dark-orange, microcrystalline solid (0.470 g, 82%); m.p. 202−205°. IR (KBr): $\tilde{\nu}_{max}$ = 3156 (w), 3124 (m), 3042 (w), 2954 (m), 2929 (m), 2870 (m), 1574 (m), 1551 (m), 1460 (m), 1445 (m), 1388 (m), 1254 (m), 1233 (m), 1204 (w), 1107 (w), 774 (s), 731 (m), 716 (m), 691 (s), 584 (w), 547 (w), 522 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.80 (t, J = 7.31 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.25 (m, 2 H, $CH_2C\mathit{H}_2CH_3$), 1.77 (m, 2 H, $CH_2C\mathit{H}_2CH_2$), 3.78 (s, 3 H, $NC\mathit{H}_3$), 4.18 (m, 2 H, $NC\mathit{H}_2$), 6.12 (d, J = 7.92 Hz, 1 H), 7.00 (m, 3 H), 7.16 (t, J = 7.31 Hz, 1 H), 7.41 (m, 3 H), 7.94 (d, J = 6.7 Hz, 1 H), 7.99 (m, 2 H, $NC\mathit{H}$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 13.40 ($\mathit{C}H_3$), 19.78 ($CH_2\mathit{C}H_2CH_3$), 32.20 ($CH_2\mathit{C}H_2CH_2$), 38.40 ($N\mathit{C}H_2CH_2$), 51.12 ($N\mathit{C}H_3$), 121.44, 122.54, 124.66, 125.14, 127.86, 130.35 ($N\mathit{C}H$), 130.48 ($N\mathit{C}H$), 132.57, 135.45, 151.93, 155.82, 164.54, 169.35 ($N\mathit{C}N$) ppm. LC-MS (CH_3CN/CH_3OH 99:1): exact mass calcd. for $C_{20}H_{23}BrN_4Pd$: 504.00; found 505 $[M + H]^+$, 465 $[M - Br + CH_3CN]^+$, 424 $[M - Br]$. $C_{20}H_{23}BrN_4Pd$: calcd. C 47.50, H 4.58, N 11.08, Pd 21.04; found C 47.78, H 4.75, N 10.86, Pd 20.96.

Acetonitrile(1-butyl-3-methylimidazolin-2-ylidene)[*o*-(phenylazo)phenyl]palladium(II) Tetrafluoroborate (13): $AgBF_4$ (0.110 g, 0.57 mmol) dissolved in dry acetonitrile (5 mL) was added to a THF (30 mL) solution of complex **12** (0.286 g, 0.57 mmol). After stirring for 45 min, the solvent was evaporated in vacuo. The pale-orange residue was extracted with dry dichloromethane (30 mL) and the resulting suspension filtered through Celite. Crystallization from THF/hexane gave **13** as a pale-orange powder (0.276 g, 88%) m.p. 168° (dec.). IR (nujol mull): $\tilde{\nu}_{max}$ = 3167 (w), 3136 (w), 2318 (w) [ν(C≡N)], 2290 (w) [ν(C≡N)], 1575 (w), 1555 (w), 1463 (s), 1401 (w), 1377 (m), 1257 (w), 1236 (m), 1056 (vs) [ν(B−F)], 773 (m), 713 (m), 696 (m), 588 (w), 548 (w), 523 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.81 (br. t, J = 7.31 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.25 (br. sext, J = 7.31, 2 H, $CH_2C\mathit{H}_2CH_3$), 1.76 (br. quint, J = 7.31 Hz, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.13 (s, 3 H, $NCC\mathit{H}_3$), 3.83 (s, 3 H, $NC\mathit{H}_3$), 4.15 (br. t, J = 7.31 Hz, 2 H, $NC\mathit{H}_2$), 6.03 (d, J = 7.31 Hz, 1 H), 7.00 (t, J = 7.31 Hz, 1 H), 7.14 (s, 1 H, $NC\mathit{H}$), 7.18 (s, 1 H, $NC\mathit{H}$), 7.22 (t, J = 7.31 Hz, 1 H), 7.51 (br. s, 3 H), 7.72 (m, 2 H), 7.97 (d, J = 7.31 Hz, 1 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 2.78 ($NC\mathit{C}H_3$), 13.35 ($CH_2\mathit{C}H_3$), 19.62 ($CH_2\mathit{C}H_2CH_3$), 32.64 ($CH_2\mathit{C}H_2CH_2$), 38.45 ($N\mathit{C}H_2CH_2$), 51.18 ($N\mathit{C}H_3$), 122.48, 122.75, 123.98, 129.03, 131.51 ($N\mathit{C}H$), 131.62 ($N\mathit{C}H$), 133.25, 136.17, 151.22, 151.56, 164.92, 165.04 ppm. LC-MS (CH_3CN): exact mass calcd. for the cation $C_{22}H_{26}N_5Pd$: 466.12; found 466 $[M]^+$, 425 $[M - CH_3CN]^+$. $C_{22}H_{26}BF_4N_5Pd$: calcd. C 47.72, H 4.73, N 12.65, Pd 19.22; found C 47.61, H 4.85, N 12.74, Pd 19.12.

Substrates: The aryldiazonium tetrafluoroborates **1a**−**1f** were synthesised as reported in the literature[36] and characterised by ^1H and ^{13}C NMR (CD_3CN) and IR (nujol mull) spectroscopy. Potassium aryltrifluoroborate **2** and vinyltrifluoroborate **14** were also synthesised according to a literature procedure.[9]

General Procedure for the Catalytic Reactions: All catalytic runs were repeated at least three times and yields and conversions were reproducible within ±3%. The course of the reactions was monitored by measuring the evolution of N_2 vs. time by means of a mercury gas-burette. Reactions were stopped when no further gas evolution was observed. In neat ILs, the decomposition of diazonium salt was negligible (4−5% per day) as demonstrated by blank tests.

Typical Reaction in Neat IL: Compounds **2** (221 mg, 1.2 mmol) and **1a** (206 mg, 1.0 mmol) were added, with vigorous stirring, to a suspension of $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) in [bmim]BF_4 (2.260 g, 10 mmol) in a 10-mL Schlenk tube. At the end of reaction, the mixture was diluted with water (100 mL) and the products were extracted with diethyl ether (3 × 25 mL); the organic phases were collected and dried with Na_2SO_4. The products were purified by flash chromatography and characterised by GC-MS and the selectivity assessed by GC using naphthalene as internal standard.

Reactions in [bmim]BF_4/Cosolvent: 2 mL of the degassed solvent mixture was poured into a 10-mL Schlenk tube containing Pd catalyst (0.02 mmol of Pd), $KRBF_3$ (1.2 mmol) and ArN_2BF_4 (1.0 mmol) and stirred vigorously.

Recycle: Compounds **2** (184 mg, 1.0 mmol) and **1a** (247 mg, 1.2 mmol) were added, with vigorous stirring, to a suspension of **10** (6.93 mg, 0.01 mmol) in [bmim]BF_4 (2.260 g, 10 mmol) and MeOH (405 µL 10 mmol) in a 10-mL Schlenk tube. At the end of reaction, the MeOH was evaporated off in vacuo and the products were extracted with dry *n*-hexane (6 × 3 mL); after evaporation of the solvent, fresh MeOH (405 µL, 10 mmol), **2** (184 mg, 1.0 mmol) and **1a** (206 mg, 1.0 mmol) were added to the resulting catalytic solution.

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