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The coupling of aryl halides in the ionic liquid [bmim]PF_6

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Abstract

Several aryl halides have been coupled using the zero valent nickel catalyst $[(PPh_3)_nNi(0)]$, to give the biaryl in moderate to good yield, employing the ionic liquid [bmim]PF_6. The ionic liquid and catalyst were recycled after extraction of the biaryl. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: ionic liquid; [bmim]PF_6; coupling; catalyst.

The ionic liquids [emim]PF_6 and [emim]BF_4, where $[emim]^+$ is the 1-ethyl-3-methylimidazolium cation, were first discovered in 1994 and 1992, respectively.[1] The analogous [bmim]PF_6 **1** and [bmim]BF_4 ionic liquids, where $[bmim]^+$ is the 1-butyl-3-methylimidazolium cation, followed shortly after.[2] These liquids have several very interesting properties; they can solvate a wide range of organic and inorganic materials, they are highly polar yet non-coordinating, they are immiscible with a wide range of organic solvents, and they have a nonvolatile nature. The search for clean technologies to minimise industrial waste requires the redesign and rethinking of many important industrial processes. One area of obvious interest is the replacement of environmentally damaging solvents used on a large scale, especially those that are volatile and difficult to contain. Moisture stable ionic liquids may provide an alternative, and unlike the moisture sensitive imidazolium based chloroaluminate ionic liquids, they do not require specialist facilities. As such a rapid growth in the investigation of the [bmim]PF_6 and [bmim]BF_4 type ionic liquids as substitutes for classical solvents is underway. Several important reactions have already been carried out and investigated in [bmim]PF_6 and [bmim]BF_4, such as a simple Diels–Alder reaction between cyclopentadiene and methyl methacrylate,[3] *N*-alkylation of indole and *O*-alkylation of 2-naphthol,[4] hydrogenations,[5] hydroformylation,[6] dimerisation of olefins,[7] oxidation of aromatic aldehydes,[8] and the Heck reaction.[9]

Herein we report, as far as we are aware, the results of the first low valent metal catalysed coupling of aryl halides **2a**–**g** using $[(PPh_3)_nNi(0)]$ as the catalyst **3**, to be carried out in the new and versatile solvent [bmim]PF_6, a further, and industrially important example of the general

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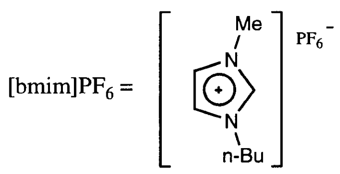

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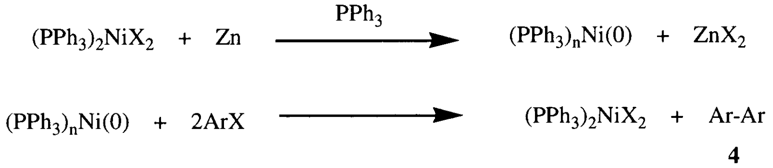
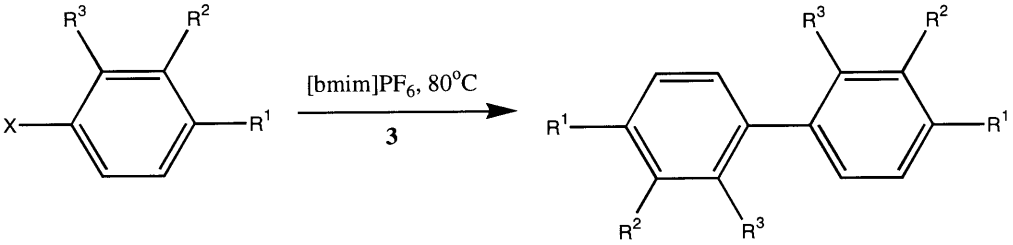


$$(PPh_3)_2NiX_2 + Zn \xrightarrow{PPh_3} (PPh_3)_nNi(0) + ZnX_2$$

$$(PPh_3)_nNi(0) + 2ArX \longrightarrow (PPh_3)_2NiX_2 + \underset{\mathbf{4}}{Ar\text{-}Ar}$$

Scheme 1.

application of this type of solvent. Zero valent nickel complexes are excellent catalysts for the coupling of aryl halides,[10] and it is easy to reduce nickel from its divalent to zero valent state using zinc. In our study of aryl halide coupling reactions in the ionic liquid [bmim]PF_6 we used zinc powder to reduce bis(triphenylphosphine)nickel(II) dichloride in the presence of triphenylphosphine to generate [$(PPh_3)_n$Ni(0)], to which the aryl halide was added, subsequently producing the biaryl **4** (Scheme 1). The results for seven aromatic halides are given in Scheme 2.



	X	R¹	R²	R³
2a	**Br**	**H**	**H**	**H**
2b	**Br**	**OMe**	**H**	**H**
2c	**Br**	**Me**	**H**	**H**
2d	**I**	**H**	**H**	**CO_2Me**
2e	**Br**	**H**	**CO_2Me**	**H**
2f	**Br**	**COMe**	**H**	**H**
2g	**Br**	**CHO**	**H**	**H**

	R¹	R²	R³	Yield%
4a	**H**	**H**	**H**	**87**
4b	**OMe**	**H**	**H**	**55**
4c	**Me**	**H**	**H**	**76**
4d	**H**	**H**	**CO_2Me**	**40**
4e	**H**	**CO_2Me**	**H**	**71**
4f	**COMe**	**H**	**H**	**60**
4g	**CHO**	**H**	**H**	**44**

Scheme 2.

General procedure for the [$(PPh_3)_n$Ni(0)] catalysed coupling of aryl halides **2a**–**g** in the ionic liquid [bmim]PF_6, using bromobenzene **2a** as an example: [$(PPh_3)_2$Ni(II)Cl_2] (3.63 g, 5 mmol), PPh_3 (2.62 g, 10 mmol) and Zn powder (0.66 g, 10 mmol) were added to a Schlenk tube containing dry (heat at 60°C under vacuum for 48 h), O_2-free [bmim]PF_6 (25 mL).[11] The flask was evacuated, filled with dry N_2, and heated to 80°C with rapid stirring for 24 h. During this time the colour changed from the initial dark blue to dark green and then to light green/yellow. After 24 h bromobenzene (1.57 g, 10 mmol) was added and the reaction was stirred for a further 48 h at 80°C under dry N_2. After cooling the [bmim]PF_6 was extracted with diethyl ether (3×20 mL) and after drying the combined extractions ($MgSO_4$) removal of solvent and recrystallisation gave the biphenyl[12] (1.34 g, 87% yield).

It is interesting to note that in general the aryl bromides substituted at the *ortho* or *para* position by an electron withdrawing substituent give lower yields of the biaryl than the simple bromobenzene **2a**, compound **2d** giving the lowest yield of all. In the case of **2d** it is unlikely that this low yield is because we have employed an aryl iodide instead of an aryl bromide, as aromatic iodides consistently give high yields for this reaction in DMF, except when there is acyl substitution at the *para* or *ortho* position. The low yield is therefore consistent with these earlier findings and is due to the influence of the ester group in the *ortho* position. It is also known that aryl bromides show dramatic variations in yields of the biaryl as a result of substitution in the aromatic ring.[13]

The yields obtained using the ionic liquid [bmim]PF_6 as the solvent for the reaction were comparable to those yields obtained in the usual solvent for this reaction, DMF.[10] However, we were able to recycle the ionic liquid and the nickel catalyst. The used [bmim]PF_6 containing the spent catalyst was dried under vacuum at 60°C for 48 h and then deoxygenated. The $[(PPh_3)_n Ni(0)]$ could be reformed and used once more in the above procedure without requiring the addition of further $[(PPh_3)_2 Ni(II)Cl_2]$. There was however a small decrease in the yield of biaryls, for example the second run for bromobenzene only produced an 81% yield of the biphenyl.

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