Utilisation of ionic liquid solvents for the synthesis of Lily-of-the-Valley fragrance {β-Lilial®; 3-(4-*t*-butylphenyl)-2-methylpropanal}

Stewart A. Forsyth[a,b], H.Q. Nimal Gunaratne[a,b], Christopher Hardacre[a,b,*],
Angela McKeown[a,b], David W. Rooney[b,c], Kenneth R. Seddon[a,b]

[a] *School of Chemistry, The Queen's University of Belfast, Belfast BT95AG, Northern Ireland, UK*
[b] *QUILL Research Centre, The Queen's University of Belfast, Belfast BT95AG, Northern Ireland, UK*
[c] *School of Chemical Engineering, The Queen's University of Belfast, Belfast BT95AG, Northern Ireland, UK*

Abstract

The Heck arylation of 2-methylprop-2-en-1-ol in ionic liquids and organic solvents is reported using a range of homogeneous and heterogeneous palladium catalysts. Higher activity is observed in the ionic liquid media compared with *N*-methylpyrrolidinone and under solventless conditions. The ionic liquid-catalyst system may be recycled easily with little loss in activity, although significant palladium leaching from the heterogeneous catalyst was observed. In the case of *trans*-bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)diiodopalladium(II) reported to be highly active for this transformation, significant induction periods were observed indicating that nanoparticles may be responsible for the catalysis. Using the ionic liquid Heck reaction, a recyclable synthesis for the fragrance β-Lilial® has been developed.
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Keywords: Ionic liquids; Recycling; Heck; Lilial; Fragrance; Palladium catalyst

1. Introduction

The formation of C–C bonds using the Heck reaction is of major importance in organic chemistry, and is widely used industrially. It has been studied extensively using a variety of catalysts and solvent systems, and has recently been extensively reviewed [1,2]. In the vast majority of reactions, palladium complexes and salts catalyse the reaction of aromatic halides with olefins [3]. Although a large range of electron-deficient and unreactive olefins have been studied, only limited usage of allylic alcohols as a Heck coupling reagent has been reported. Using this route, commercially important arylaldehydes have been synthesised using bromoarenes [4–8] iodoarenes, [9–11] diazonium salts, [12] and aryl triflates [13].

Despite the large number of studies of the Heck reaction, there are very few studies which examine the recyclability of the catalyst used. Commonly in the organic solvents used, typically *N,N*-dimethylmethanamide, *N,N*-dimethylethanamide, *N*-methylpyrrolidinone (NMP) or 1,4-dioxane, the catalyst is lost on the workup of the reaction thus preventing efficient recycle. In contrast, the use of ionic liquids has been reported to allow the Heck reaction to proceed efficiently [14–17] and to provide a medium in which the catalyst may be recycled.

As well as the use of homogeneous catalysts, there has been considerable interest in the use of heterogeneous catalysts or supported palladium complexes for the Heck reaction [2,18,19]. The solid catalysts allow the catalyst to be simply recovered by filtration and have been shown to be effective for a number of activated haloarenes in both organic media and, more recently, in ionic liquids [20,21]. It is not clear; however, whether the catalyst is truly heterogeneous or whether the palladium dissolves into the solvent and the reaction proceeds in
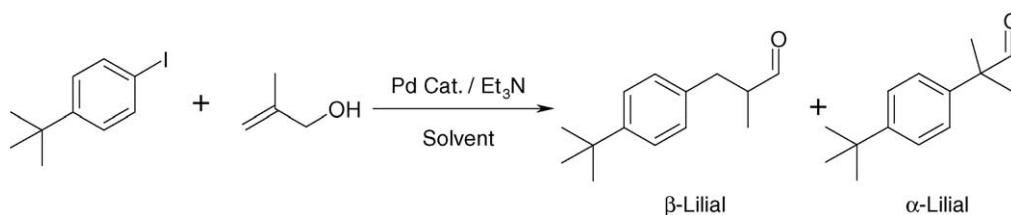
Fig. 1. Reaction showing the formation of β-Lilial® and α-Lilial® from 1-*t*-butyl-4-iodobenzene and 2-methylprop-2-en-1-ol.

solution [22]. Recently Djakovitch et al. have shown that the reaction of aryl bromides with cycloalkenes proceeded via a surface catalysed and homogeneous mechanism [19].

In this paper, we report the reaction of 2-methylprop-2-en-1-ol with a range of aryl halides using both homogeneous and heterogeneous catalysts in organic solvents and in ionic liquids. In particular, the formation of 3-(4-*t*-butylphenyl)-2-methylpropanal (β-Lilial®) is examined in detail (Fig. 1). β-Lilial® is used both as an intermediate for the production of fenpropimorph (Corbel®) (a biodegradable fungicide) and as a fragrance and fragrance intermediate. It is produced on the kiloton scale by a multistep synthesis using volatile organic solvents [23]. Here, the efficient and rapid synthesis of β-Lilial® using an ionic liquids one-step Heck coupling is described.

2. Experimental

Unless otherwise stated, all reagents, solvents and catalysts were obtained from Aldrich and used as supplied. 1-Butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}amide ([bmpyrr][NTf$_2$] was prepared according to MacFarlane et al. from the corresponding halide salt [24]. The complex *trans*-bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)diiodopalladium(II) ([Pd(btz)$_2$I$_2$]) (Fig. 2) was prepared as described by Calò et al. [25]. 1-Butyl-1-methylpyrrolidinium tetrachloropalladate(II) ([bmpyrr]$_2$[PdCl$_4$]) was prepared from 1-butyl-1-methylpyrrolidinium chloride and palladium(II) chloride heated in ethanenitrile for 3 h under reflux, before allowing the salt to crystallise from solution on cooling.

2.1. General synthetic procedure

To a thick-walled glass tube were added haloarene (10 mmol), 2-methylprop-2-en-1-ol (12 mmol), triethylamine (12 mmol), palladium catalyst (0.05 mmol equivalent
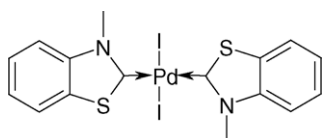

Fig. 2. Structure of *trans*-bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)diiodopalladium(II) ([Pd(btz)$_2$I$_2$]).

of palladium) and solvent (3 cm^3). The tube was then fitted with a septum, purged with N$_2$ and stirred at 600 rpm at 100 °C. Throughout the reaction, samples of the reaction mixture were taken and analysed by GC-FID. Following reactions using ionic liquids, the reaction mixture was extracted using cyclohexane (6 × 3 cm^3). The cyclohexane was then removed in vacuo, which afforded a mixture of 3-(4-*t*-butylphenyl)-2-methylpropanal and 2-(4-*t*-butylphenyl)-3-methylpropanal (α-Lilial®). In the case of reactions performed in NMP or under solventless conditions, the samples were analysed without extraction. The reaction products were verified using GC-MS and ^{1}H NMR spectroscopy. For the recycle experiments, after extraction with cyclohexane, the ionic liquid-catalyst solution was also washed with distilled deionised water (18.2 MΩ). The ionic liquid solution was then dried at 100 °C overnight and recharged with reagents and the reaction repeated.

^{1}H NMR spectra were recorded on a Bruker Advance DRX 500 MHz NMR spectrometer. GC-FID samples were analysed using a Hewlett Packard 6890 GC fitted with an RTX-5 column (30 m, 0.25 μm diameter). The retention time of the peaks were compared against authentic samples.

The conversions are quoted with respect to the removal of the haloarene whereas selectivities are calculated with respect to the β-product compared with the α-product, e.g. 100β-Lilial®/(α-Lilial® + β-Lilial®).

3. Results and discussion

Table 1 and Fig. 3 compare the results of the Heck coupling of 1-*t*-butyl-4-iodobenzene with 2-methylprop-2-en-1-ol in a range of solvents and palladium catalysts. It is clear that using either ionic liquid, tetrabutylammonium bromide ([NBu$_4$]Br) or [bmpyrr][NTf$_2$], higher rates of reaction and yields are found compared with performing the reaction in NMP or under solventless conditions. In all reactions, the solution became dark orange and, as the reaction progressed, a small amount of palladium black formation was observed. Significantly more palladium black was produced under solventless conditions and in NMP compared with the ionic liquids, and this may be the reason for the much lower rates of reaction.

Comparing palladium(II) chloride and palladium(II) ethanoate, the chloride showed the highest rates of reaction with an initial rate of 0.13 mol s^{-1} (mol of Pd)$^{-1}$ in [bmpyrr][NTf$_2$] compared with 0.05 mol s^{-1} (mol of Pd)$^{-1}$

Table 1
Conversion and selectivity with respect to β-Lilial® compared with α-Lilial® following the reaction of 1-*t*-butyl-4-iodobenzene with 2-methylprop-2-en-1-ol in a range of solvents and palladium catalysts after 2 and 24 h

Catalyst	Solvent	After 2 h		After 24 h	
		Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
$PdCl_2$	No solvent	44	95	98	94
	NMP	84	96	100	96
	[NBu$_4$]Br	92	97	100	96
	[bmpyrr][NTf$_2$]	98	93	100	87
[bmpyrr]$_2$[PdCl$_4$]	No solvent	23	96	82	95
	NMP	31	97	100	96
	[NBu$_4$]Br	93	96	100	95
	[bmpyrr][NTf$_2$]	89	91	100	90
Pd(OAc)$_2$	No solvent	30	97	100	97
	NMP	36	97	100	96
	[NBu$_4$]Br	83	96	100	95
	[bmpyrr][NTf$_2$]	92	96	100	96
10 wt.% Pd/C	No solvent	20	95	93	95
	NMP	23	100	98	95
	[NBu$_4$]Br	97	95	100	95
	[bmpyrr][NTf$_2$]	74	92	99	89
[Pd(btz)$_2$I$_2$]	No solvent	1	100	83	96
	NMP	1	100	42	95
	[NBu$_4$]Br	6	100	100	95
	[bmpyrr][NTf$_2$]	66	92	100	90

using the ethanoate. Similar activity to palladium(II) chloride was also observed when the salt [bmpyrr]$_2$[PdCl$_4$] was used. In addition, the use of [NBu$_4$]Br compared with [bmpyrr][NTf$_2$] showed little difference in activity when these catalysts were employed.

It is likely that palladium nanoparticles are a key species in these reactions, which may explain the similarity in rates. Recently, the formation of 1–2 nm palladium colloids has been observed in ionic liquids during the Heck reaction using EXAFS and TEM [17,26]. Tetraalkylammonium salts have been reported to stabilise palladium nanoparticles [27] and were shown to decrease the particle size in the ionic liquids [26]. Commonly stabilising phosphines are added to the reaction mixture when organic solvents are employed to prevent metal precipitation. In this study, no phosphine was used, demonstrating that ionic liquids can stabilise the nanoparticles. This view is consistent with the decrease in the formation of palladium black observed in the ionic liquid media compared with NMP and solventless reactions.

Table 1 also compares the Heck reaction using [Pd(btz)$_2$I$_2$] as the catalyst. It is clear that stabilisation of the palladium with carbene ligands, under these conditions, reduces the initial activity of the catalyst. An examination of the time dependence of the reaction for all the homogeneous catalysts studied shows that, with the exception of [Pd(btz)$_2$I$_2$], all show a significant reaction rate at the start of the reaction. For the [Pd(btz)$_2$I$_2$] catalyst, an induction period is observed which depends strongly on the solvent medium. In particular, significantly longer induction periods are observed in the organic solvents than in the ionic liquids.

Induction periods have been observed previously [26] in ionic liquids, and these were found to be a function of the pretreatment and the ionic liquid used. For example, much longer induction periods were observed using palladium ethanoate in [C$_6$mim]Cl than with [C$_4$mim][PF$_6$] or [N$_{2,2,2,6}$][NTf$_2$] (where [C$_4$mim]$^+$ = 1-butyl-3-methylimidazolium, and [N$_{2,2,2,6}$]$^+$ = triethylhexylammonium). These induction periods were related to the rate of formation of palladium nanoparticles. In the presence of 1,3-dialkylimidazolium halide ionic liquids, stable palladium carbene complexes were observed which then decomposed to palladium nanoparticles, whereas in [PF$_6$]$^-$ and [NTf$_2$]$^-$ ionic liquids, the nanoparticles formed rapidly. The long induction period observed for the [Pd(btz)$_2$I$_2$] catalyst may simply reflect the relative stability of the carbene species before transforming into nanoparticles. It is interesting to note that the halide ionic liquid had a significantly longer induction period compared with the [NTf$_2$]$^-$ ionic liquid. Fig. 4 shows a comparison of the yield of β-Lilial® versus time for [Pd(btz)$_2$I$_2$] in [bmpyrr][NTf$_2$] and in [NBu$_4$]Br. No induction period is observed for [bmpyrr][NTf$_2$] whereas little reaction is found for 2 h in [NBu$_4$]Br. Preheating the catalyst in [NBu$_4$]Br in the absence of the reactants removes the induction period. Similar pretreatment was also found to reduce the induction period found for Pd(OAc)$_2$ in [C$_4$mim][PF$_6$] for the Heck reaction at 50 °C [26]. The difference between Br$^-$ and [NTf$_2$]$^-$ ionic liquids may also be explained by the formation of stable [PdBr$_x$I$_{4-x}$]$^{2-}$ species. EXAFS studies in chloride ionic liquids have also shown that [PdCl$_4$]$^{2-}$ forms under

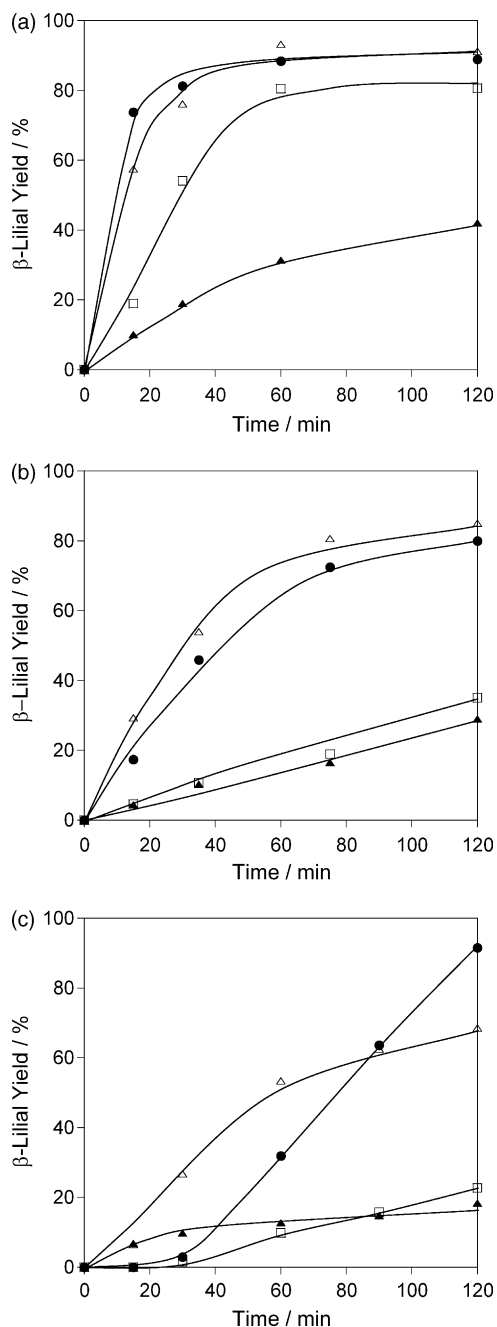Fig. 3. Yield of β-Lilial® from the Heck coupling of 1-t-butyl-4-iodobenzene and 2-methylprop-2-en-1-ol using (a) PdCl₂, (b) Pd(OAc)₂ and (c) 10 wt.% Pd/C in NMP (□), [NBu₄]Br (●), [bmpyrr][NTf₂] (△) and under solventless conditions (▲) at 100 °C as a function of time.

Fig. 4. Yield of β-Lilial® from the Heck coupling of 1-t-butyl-4-iodobenzene and 2-methylprop-2-en-1-ol using [Pd(btz)₂I₂] in [bmpyrr][NTf₂] (△), [NBu₄]Br (●) and in [NBu₄]Br preheated to 100 °C for 4 h before addition of the reactants (×) as a function of time.

these conditions prior to palladium nanoparticle formation [26].

The results presented here contrast with those reported by Calò et al. [4]. Although reasonable activity was found using [Pd(btz)₂I₂] in [NBu₄]Br, significantly higher activity was observed in [bmpyrr][NTf₂]. Calò et al. reported high activity for similar Heck coupling reactions using [Pd(btz)₂I₂], but only when [NBu₄]Br was used. Using tosylate and tetratfluoroborate ionic liquids, little reaction was observed [4]. It
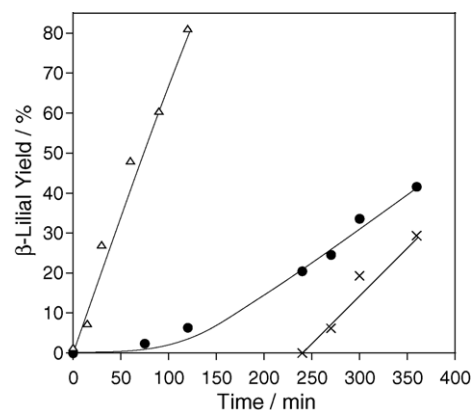
has been reported that ionic liquids containing co-ordinating halides are required in order to obtain high activity [15]. However, it is clear from the results presented here that at least equivalent activity, in the cases of palladium(II) chloride and palladium(II) ethanoate, is found in [bmpyrr][NTf₂], compared with [NBu₄]Br, and higher activity is seen in [bmpyrr][NTf₂] using [Pd(btz)₂I₂]. Therefore nucleophilic anions are not required to promote the Heck reaction or stabilise the palladium nanoparticles in the absence of phosphine.

Reactions catalysed by Pd/C catalyst (10 wt.%) showed a similar increase in rate in the ionic liquids compared with NMP and under solventless conditions. As found with the [Pd(btz)₂I₂] catalyst, with the exception of reactions in [bmpyrr][NTf₂], an induction period was also observed. In comparison with the homogeneous reactions, the rates using the heterogeneous catalysts, following any induction period, were similar. In general, porous solid catalyst reactions in ionic liquids appear to be significantly mass transfer limited and, therefore, the high rates of reaction are surprising if the reaction is surface catalysed [28]. ICP-AES performed on the reactions in the ionic liquid following reaction indicated that a significant amount of the palladium had been leached from the support. Analysis showed 120 ppm palladium following reaction in [bmpyrr][NTf₂], which equates to 9% of the total palladium leached from the carbon support. It is, therefore, likely that the induction periods observed for the supported palladium catalyst are due to the dissolution of the palladium, forming nanoparticles in solution which then catalyse the reaction. Previous studies using heterogeneous catalysts for the Heck reaction in ionic liquids have also shown similar levels of leaching from both silica and carbon supports [21].

In order to examine the cause of the leaching, the catalyst was stirred in [bmpyrr][NTf₂] under similar reaction conditions, in the absence of reagents, both with and without triethylamine present. ICP-AES analysis of the filtered solutions showed 12 and 4 ppm palladium in the presence and absence of amine, respectively. In addition, performing the

Table 2

Conversion and selectivity with respect to β-product compared with α-product following the Heck coupling of 2-methylprop-2-en-1-ol with 4-X-C_6H_4Y using Pd(OAc)$_2$ and triethylamine in [bmpyrr][NTf$_2$] at 100 °C

X, Y	Time (h)	Conversion (%)	Selectivity (%)
I, H	1	95	96
I, CF$_3$	1	99	88
I, I	1	99	74[a]
I, Br	1	99	94
I, CH$_3$CO	2	97	94
I, CH$_3$O	3	96	85
Br, (CH$_3$)$_3$C	24	<1	–

[a] Selectivity with respect to the formation of 3-(4-iodophenyl)-2-methylpropanal with respect to 1,4-di-(2-methylpropanal)benzene.

Heck reaction on the filtered solution in each case resulted in <5% conversion after 24 h. The much lower leaching found in the absence of reagents indicates that it is the reaction which causes the dissolution and not the presence of the ionic liquid or amine. This is understandable, given that the proposed mechanism of the Heck reaction involves the oxidative addition of the haloarene to the palladium(0) centre, forming an ionic species which can then dissolve in the ionic liquid.

The selectivity with respect to β-Lilial® compared with α-Lilial® had only a weak dependence on the selection of solvent and catalyst combination In general, a small decrease in selectivity was observed with increasing conversion, for example using palladium(II) ethanoate in [bmpyrr][NTf$_2$], 95% selectivity is found at 29% conversion whereas at 100% conversion, the selectivity drops to 92%.

Table 2 summarises the time taken for 95% conversion for the Heck coupling of 2-methylprop-2-en-1-ol as a function of aryl substituent using palladium(II) ethanoate in [bmpyrr][NTf$_2$]. Clearly, under these conditions, only iodoarenes reacted. Similar conversions were observed for iodobenzene, 1-iodo-4-trifluoromethylbenzene, 1,4-diiodobenzene and 1-bromo-4-iodobenzene. In the case of 1,4-diiodobenzene, the selectivity of the 3-(4-iodophenyl)-2-methylpropanal with respect to 1,4-di(2-methylpropanal)benzene was 74%. 1-Bromo-4-iodobenzene afforded 3-(4-bromophenyl)-2-methylpropanal with only a small amount (<6%) of the regio-isomer 2-(4-bromophenyl)-2-methylpropanal; no reaction was observed with the bromine position. As expected, with decreasing electron donating substituents, the conversion decreases, i.e. 4-iodo-acetophenone > 1-iodo-4-methoxybenzene. It should be noted that substituting the halogen substituent with triflate, e.g. phenyl triflate, showed no conversion with 2-methylprop-2-en-1-ol using Pd(OAc)$_2$ in [bmpyrr][NTf$_2$] at 100 °C.

For ionic liquid systems, recycling of the ionic liquid-catalyst system is imperative. Table 3 shows the results of recycling the palladium(II) ethanoate and Pd/C catalyst (10 wt.%) in [bmpyrr][NTf$_2$] for the reaction of 1-*t*-butyl-4-iodobenzene and 2-methylprop-2-en-1-ol. For the heterogeneous catalyst, the solution was extracted with cyclohexane and water, and the reaction repeated five times. Little change in the yield or selectivity was observed over the recycles.

Table 3

Conversion and selectivity with respect to β-Lilial® as a function of recycling Pd(OAc)$_2$ and 10 wt.% Pd/C in [bmpyrr][NTf$_2$] for Heck coupling of 1-*t*-butyl-4-iodobenzene with 2-methylprop-2-en-1-ol

Catalyst	Conversion (Selectivity) /%				
	Run 1	Run 2	Run 3	Run 4	Run 5
Pd(OAc)$_2$	88 (94)	99 (95)	61 (93)[a]	85 (93)	81 (95)
10 wt.% Pd/C	96 (96)	94 (95)	95 (93)	91 (93)	93 (92)

[a] The reaction mixture was not dried prior to recycle.

However, the recycle does not necessarily indicate heterogeneous activity. If the carbon is filtered from the reaction mixture, similar activity of the ionic liquid was observed, in agreement with the palladium leaching found by ICP-AES analysis of the ionic liquid.

In the case of palladium(II) ethanoate, the first recycle (run 2) was performed as described in the experimental section. After run 2 was performed, the solution was not dried prior to performing the second recycle. At this point, a significant drop in yield was observed; however, this is not due to irreversible catalyst deactivation but due to the presence of water. The reactivity of the system was recovered following pre-treatment of the media at 100 °C overnight. Similar yields and selectivity were obtained, for the third and fourth recycles, as found in the initial reaction.

From the data presented, it is clear that the ionic liquid reactions have significant advantages over the organic solvents for the production of β-Lilial®. However, the choice of ionic liquid-catalyst system is important. For example, although high activity is found using [NBu$_4$]Br and Pd/C, there are important problems associated with each. Calò et al. reported that, whilst it was possible to recycle the [NBu$_4$]Br/[Pd(btz)$_2$I$_2$] system by extracting the reaction mixture with diethyl ether, a significant decrease in activity was observed [4,25]. This was attributed to a build up of NaBr by-product causing the reaction mixture to become highly viscous and preventing good mixing. In [bmpyrr][NTf$_2$], the salt by-product is removed by an aqueous wash; however, this is not possible using [NBu$_4$]Br. As [NBu$_4$]Br is a solid a room temperature, the efficient recycle of this ionic liquid difficult to achieve. In the case of the heterogeneous catalyst, much of the motivation is the ability to filter the catalyst or use a fixed bed for continuous operation. The high level of leaching from the heterogeneous catalyst into the ionic liquid negates these advantages.

4. Conclusions

Ionic liquids have been shown to be a versatile medium for carrying out Heck coupling reactions using allylic alcohols. Depending on the ionic liquid chosen, efficient recycling of the ionic liquid-homogeneous catalyst system is possible. Although recycling of the heterogeneous Pd/C catalyst was also possible, significant palladium leaching was observed. Induction periods were observed prior to reaction

for both Pd/C and [Pd(btz)$_2$I$_2$] catalysts, and these may be associated with the formation of palladium nanoparticles in solution.

Acknowledgements

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