Dalton Transactions

PAPER

View Article Online
View Journal | View Issue



Cite this: *Dalton Trans.*, 2014, **43**, 7533

# Catalyst life in imidazolium-based ionic liquids for palladium-catalysed asymmetric allylic alkylation†

I. Guerrero-Ríos and E. Martin*

Received 16th January 2014,
Accepted 17th February 2014

DOI: 10.1039/c4dt00169a

www.rsc.org/dalton

A Pd/(*S*)-BINAP system was successfully applied to the asymmetric allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (**I**) using imidazolium-based ionic liquids (ILs) attaining up to 225 $h^{-1}$ TOF and 88% ee of the (*R*)-product. Although the system was barely active in the recycling experiments, the catalyst life was confirmed after recharging the system with substrate/reactants resulting in an alkylated product. In the latter case, the conversion rates and enantiomeric excesses were similar or lower compared to those in the first cycle. In order to explain the observed catalyst performance in the recycling as well as in the recharging experiments, we investigated the reactivity between the catalyst precursors, substrate and reactants in ILs. We were able to identify the species involved in the catalytic reactions under various conditions by means of $^{31}P$ NMR analyses. Allylpalladium intermediates (**3**) were found to be the active and selective species at a high substrate concentration. When the substrate was consumed, competing reactions took place leading to different palladium complexes. [PdCl(NHC$^{Bu,Me}$)((*S*)-BINAP)]Cl (**4**), together with [Pd((*S*)-BINAP)$_2$] (**5**), were recognised as the species responsible for the loss of activity, meanwhile, the decrease in enantioselectivity was accounted for by the formation of mixed (NHC)(monophosphine)-palladium species.

## Introduction

The use of ionic liquids (ILs) in metal-catalysed reactions has become a viable alternative to organic solvents in many processes due to the feasibility of product separation and reuse of the IL-catalytic phase.[1] The field of asymmetric catalysis profits from IL technologies, as demonstrated by research groups in academia.[2] However, the use of imidazolium-based ILs in asymmetric allylic alkylation (AAA) reactions has failed to reproduce the activity and enantioselectivity after recycling of the IL-catalytic system.[3] The latter has been attributed to the possible formation of inactive species during the catalytic process. It is generally agreed that imidazolium-based ILs react with catalytic palladium species *via* oxidative addition to generate stable N-heterocyclic-carbene (NHC) palladium complexes, or by deprotonation of the C(2)–H bond of the imidazolium cation in the presence of a base.[4] Additionally, protons at the C(4) and C(5) positions could react to afford "abnormal" carbenic species.[5] Although NHC-palladium precursors have been successfully applied in diverse catalytic reactions (*i.e.* cross coupling, allylic alkylation, polymerization, carbonylation, C–H activation, oxidation, reduction, addition, telomerization reactions, *etc.*),[6] its application to allylic alkylation has been limited to the non-asymmetric version,[7] where the presence of phosphine ligands is required to achieve high conversions. In order to avoid the formation of NHC-palladium species in imidazolium-based ILs and therefore produce recyclable systems, pyrrolidonium-based ILs have been used to reproduce ees and yields in asymmetric allylic amination and phosphination reactions.[8] Recently, imidazolium-based ILs were successfully applied in palladium catalysed AAA under MW irradiation to increase the reaction rate, thus avoiding the formation of inactive and non-selective carbenic species, which are otherwise observed.[9]

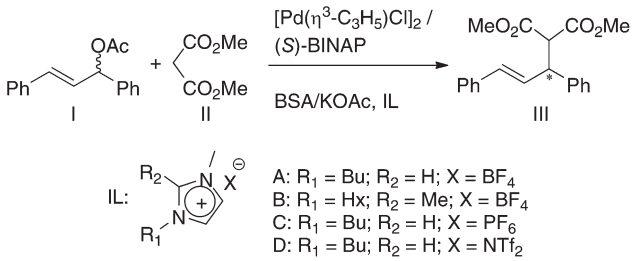
In order to gain insight into the role of palladium species involved in catalysed AAA in imidazolium-based ILs, we assessed the abilities of the catalytic system Pd/(*S*)-BINAP to perform AAA in a variety of imidazolium-based ILs (Scheme 1). Furthermore, we investigated the species responsible for the activity and selectivity observed.

## Results and discussion

We studied the palladium-catalysed alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (**I**) using dimethylmalonate (**II**) as the

*Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional Autónoma de México, Av. Universidad 3000, 04510 D.F., México.*
*E-mail: erikam@unam.mx; Fax: +525556223720*

†Electronic supplementary information (ESI) available: Description of procedures for recycling experiments (Table S1); $^{1}H$ and $^{31}P$ NMR spectra of AAA stoichiometric reaction studies (Fig. S1–S3, S9–S11) NMR, MS-FAB and HRMS (ESI-TOF) spectra of complex **4** (Fig. S4–S8). See DOI: 10.1039/c4dt00169a




**Scheme 1** Asymmetric allylic alkylation in imidazolium-based ILs.

**Table 1** Pd/(*S*)-BINAP catalysed asymmetric allylic alkylation of **I** in ILs

| | | | 1st cycle[a] | | 2nd cycle[b] | |
|---|---|---|---|---|---|---|
| Entry | IL | L*/Pd | Conv.[c] (%) | ee[c] (%) | Conv.[c] (%) | ee[c] (%) |
| 1 | A | 1.25 | 97 | 72 | 90 | 36 |
| 2 | B[d] | 1.25 | 97 | 80 | 53 | 38 |
| 3 | C | 1.25 | 100 | 84 | 54 | 56 |
| 4 | D | 1.25 | 100 | 88 | 69 | 76 |
| 5 | A | 1[e] | 98 | 77 | 98 | 68 |
| 6 | D | 1[e] | 90 | 86 | 93 | 56 |
| 7 | D | 2.5 | 100 | 87 | 26 | 75 |

[a] 20 °C; 120 min; 1% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$; **I** (0.5 mmol); **I**/**II**/BSA 1/3/3 (BSA = *N*,*O*-bis(trimethylsilyl)acetamide); KOAc (0.005 mmol); IL (1 mL). [b] 2nd cycle recharging the system with **I** (0.5 mmol); **I**/**II**/BSA 1/1/1. [c] Determined by HPLC; ee values for (*R*)-configuration. [d] Performed at 50 °C. [e] 2% $[Pd(\eta^3\text{-}C_3H_5)$-((*S*)-BINAP)]$BF_4$ (**1**).

nucleophile under basic Trost conditions (Scheme 1).[10] Catalytic species were formed either *in situ* by reacting $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with the appropriate amount of (*S*)-BINAP (Pd : L ratio of 1.25 or 2.5), or by addition of the preformed complex $[Pd(\eta^3\text{-}C_3H_5)$((*S*)-BINAP)]$BF_4$ (**1**).[11] Regarding ILs, we focused our attention on anion effects and cation C(2)-substitutions (**A**–**D** in Scheme 1).

Table 1 summarises the catalytic results we obtained. Complete conversions and good enantioselectivities (up to 88%) were reached within two hours at 20 °C in all the ionic liquids tested (Table 1, 1st cycle column). It is worth mentioning that the catalytic behaviour was independent of the catalyst generation method (Table 1, entries 1 *vs.* 5 and 4 *vs.* 6, 1st cycle column).

When the reactions were carried out in [BMIM][$BF_4$] (**A**) and [HDMIM][$BF_4$] (**B**), the enantioselectivities proved to be lower than those in the reactions performed in [BMIM][$PF_6$] (**C**) and [BMIM][$NTf_2$] (**D**) (Table 1, entries 1–2 *vs.* 3–4, 1st cycle column). Since ILs **A**[12] and **B**[13] are more viscous than **C**[12] and **D**,[12] the observed catalytic behaviour can be rationalised in terms of the reactants' diffusion, especially the nucleophile diffusion. The limited mobility of the reactants reduced the rate of nucleophilic attack and, consequently, the isomerisation reactions of the allylic entities gave rise to diverse allylpalladium isomers.[14] Furthermore, when the nucleophilic attack takes place at the terminal allylic carbons of the allylpalladium isomers, a drop in ee occurs as we observed for the more viscous media **A** and **B**.

Catalytic reactions using the preformed catalyst $[Pd(\eta^3\text{-}C_3H_5)$((*S*)-BINAP)]$BF_4$ (**1**)[11] in ILs **A** and **D** showed comparable activities and enantioselectivities to those exhibited by analogous systems (*in situ* formed catalyst "$[Pd(\eta^3\text{-}C_3H_5)$((*S*)-BINAP)]-Cl") (Table 1, entries 5 and 6 *vs.* 1 and 4, 1st cycle column). These results contrast with previous observations about the presence of coordinating anions as chlorides and their effect on reaction selectivity. Lloyd-Jones and coworkers found that chlorides have a detrimental effect on the reaction enantioselectivity,[15] furthermore, Norrby and coworkers proposed that chlorides can exert positive memory effects but also favour the isomerisation of allylpalladium intermediates affecting the reaction stereocontrol.[16]

Attempts to reuse the IL-catalytic system, after product extraction with hexane, resulted in poor conversion for all ILs used (<10%, Table S1 in ESI†), which is in agreement with the pioneering work of Toma and coworkers.[3] Since the catalyst activity drop in recycling systems is commonly attributed to catalyst loss or poisoning during product extraction, we assessed the catalyst life upon recharging the system with the substrate and reactants consumed during the first cycle (Table 1, 2nd cycle column). The systems were still active in the second cycle but failed to reproduce the enantioselectivities and conversions of the first cycle. Interestingly, when the preformed catalyst **1** was used, the activity was maintained although the enantioselectivity was reduced (Table 1, entries 5 and 6, 2nd cycle column). Similar behaviour was displayed by the *in situ* generated catalyst in **A**, which achieved 90% conversion and 36% ee of (*R*)-**III** in the second cycle (Table 1, entry 1, 2nd cycle column).

With the aim of identifying species involved in the catalytic cycle that could explain the failure of the recycling experiments, as well as the complex catalytic behaviour observed under recharging conditions, we performed $^1H$ and $^{31}P$ NMR experiments on the Pd/(*S*)-BINAP catalytic system in the presence of a substrate, nucleophile and IL **D** (Fig. 1 and S1†). Initially, complex $[Pd(\eta^3\text{-}C_3H_5)$((*S*)-BINAP)]Cl (**2**) was formed

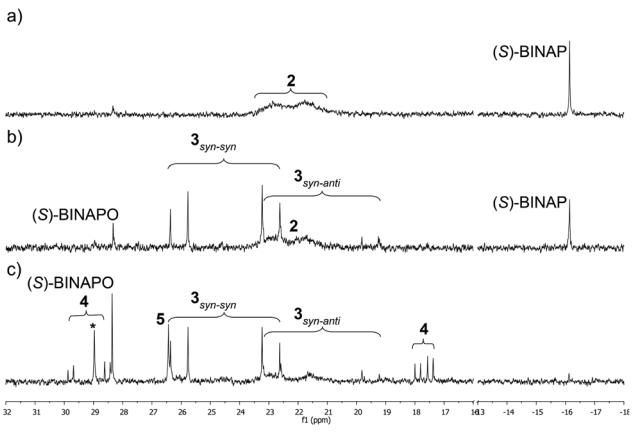
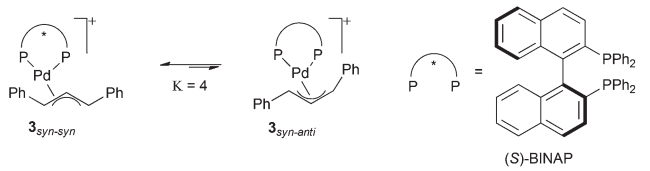



**Fig. 1** $^{31}P$ NMR (121 Hz) spectra of the stoichiometric AAA reaction using **2** ((*S*)-BINAP/Pd = 1.25) in $CD_2Cl_2$: (a) **2** in the presence of **D**; (b) addition of **I**, **II** and BSA in a 1 : 1 : 1 ratio with respect to Pd; (c) addition of **II** and BSA in a 1 : 1 ratio with respect to Pd. (*) Unknown species.




Scheme 2 Isomeric species of **3**.

from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and (*S*)-BINAP (the (*S*)-BINAP : Pd ratio was 1.25) in the presence of **D** and $CD_2Cl_2$. In the $^{31}P$ NMR spectrum (Fig. 1a), the signal centred at 22.5 ppm was assigned to **2**, and the broadening peak and chemical shift is a consequence of interactions between **2** and **D**. It is important to note that in the absence of **D**, a sharp signal at 19.1 ppm was observed for complex **2**. After the addition of equimolar amounts of **I**, **II** and BSA, species **2** turned, upon nucleophilic attack, into the species $[Pd(\eta^3\text{-}Ph_2C_3H_3)((S)\text{-BINAP})]Cl$ (**3**) together with oxidised diphosphine ligand (*S*)-BINAPO[17] (Fig. 1b). Species **3** was identified as a mixture of conformational isomers,[18] assigned as *syn–syn* and *syn–anti* isomers,[18b] in a 4 : 1 ratio (Scheme 2). Upon the addition of a second equivalent of **II** and BSA (Fig. 1c) a new species was formed, and we were able to assign it as the NHC-carbenic species $[PdCl(NHC^{Bu,Me})((S)\text{-BINAP})]Cl$ (**4**) since we carried out its independent synthesis (below). The formation of carbenic species **4** should be a consequence of the oxidative addition of an imidazolium cation to the Pd(0) species generated *in situ*,[4b,c] although C(2) deprotonation of the imidazolium ring by base and subsequent attack to the metal centre cannot be disregarded.[19] Additionally, $[Pd((S)\text{-BINAP})_2]$ (**5**)[20] was identified together with a smaller amount of an unknown species. Similar experiments performed in the absence of IL did not generate the NHC-carbenic species **4**; addition of an IL, just after the second nucleophilic attack, resulted in the generation of NHC species **4** (Fig. S2–S3 in ESI†).

To further investigate the viability of carbenic species **4**, we looked at its independent synthesis to assess its stability and catalytic activity in AAA. Species **4** was obtained by the reaction of $[PdCl_2((S)\text{-BINAP})]$ with $AgCl(NHC^{Bu,Me})$ in good yield (Fig. 2). The $^{31}P$ NMR spectrum of complex **4** corresponds to four set of doublets, two in the region of 17–18 ppm and two in the 28–30 ppm region. 2D $^{31}P$–$^{31}P$ experiments indicated a correlation between the doublets at 29.8 ppm and 18.0 ppm and between the doublets at 28.6 and 17.6 ppm. Therefore, complex **4** consists of a mixture of two diastereoisomeric species (**4a** and **4b**, Fig. 2). The formation of similar diastereoisomeric species has been observed in platinum complexes bearing a chiral ligand (*S*,*S*)-ChiraPhos and a dissymmetrical NHC-carbene.[21] The existence of both isomers, **4a** and **4b**, stems from the dissymmetry of the carbene ligand together with the axial chirality of (*S*)-BINAP, resulting in a palladium complex exhibiting $C_1$ symmetry caused by the hindered rotation of the carbene ligand. We were not able to separate the diastereoisomeric species by crystallisation, instead, we attained mixtures enriched in **4a** (**4a**/**4b** = 1.5), whereby each

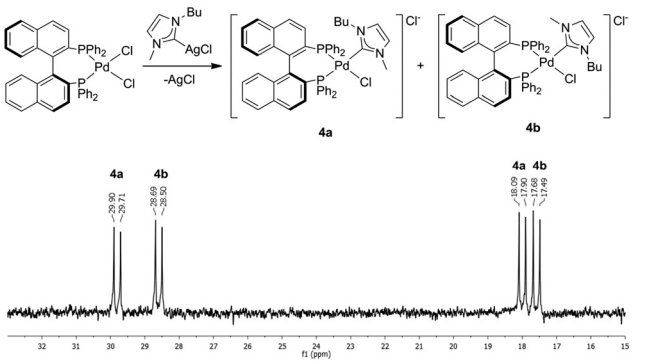


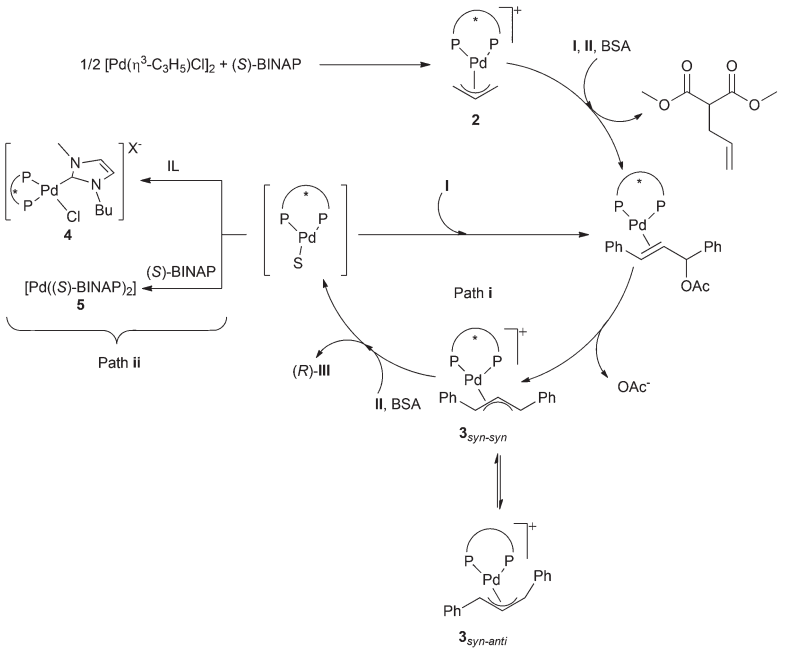

Fig. 2 Formation of NHC-species **4** and its corresponding $^{31}P$ NMR spectrum displaying a 1 : 1 diastereoisomeric mixture.

isomer was completely characterised by NMR spectroscopy (Fig. S4–S7 in ESI†). It is worth mentioning that complex **4** was not active in the asymmetric allylic alkylation, reaching less than 8% conversion in three days in dichloromethane with 66% ee of the (*R*)-product. In addition, saturated species **5** was not active in AAA until dissociation of a (*S*)-BINAP ligand occurred, thus forming intermediate **3**.

The different selectivity attained on recharging the IL-catalytic systems indicates that different palladium species were formed during the catalytic reactions affecting the activities and selectivities in all the ILs tested in subsequent cycles. According to the $^{31}P$ NMR monitoring experiments and the catalytic behaviour of **4** (above), it is possible to propose that the catalytic performance in IL **D**, in the first cycle, is due to species **3** (Path **i** in Scheme 3) and that the drop in activity in subsequent cycles is due to the formation of species **4–5** (Table 1, entry 4). In a similar way, it is possible to propose that inactive species **4–5** are responsible for the failure in recycling experiments, since their formation was favoured when the substrate was consumed and the Pd(0) species reacted with IL or (*S*)-BINAP (Path **ii**, Scheme 3).

When the system was recharged with substrate and reactants, moderate enantioselectivities were attained in the second cycle, suggesting that the observed behaviour is a consequence of the ratio of species **3** (Path **i** in Scheme 3) and possible mixed (NHC)(monophosphine)Pd(II) species. Analogous systems, containing triphenylphosphine and NHC-ligands, have been previously reported as very active catalysts in allylic alkylation reactions.[7] The differences in catalytic performance in the second cycle for all the ILs tested, could be accounted for in terms of the relative ratios of **3**, **4**, **5** and mixed (NHC)(monophosphine)Pd(II) species. The three latter species are formed when **I** is totally consumed (Scheme 3). Attempts to isolate the mixed Pd(II) complex containing (*S*)-BINAP were unsuccessful presumably because bulkier substituents on the imidazole ring are required.[22]

In an analogous stoichiometric experiment using preformed complex **1** and IL **A**, the initial palladium complex turned, upon a second nucleophilic attack, into species **3** and a new species, with a chemical shift at 25.3 ppm, which could




**Scheme 3** Palladium species involved in AAA in the presence of ILs.

be attributed to the mixed (NHC)(monophosphine)Pd(II) species (Fig. S8–S9 in ESI†).[7] Surprisingly, species **4** and **5** were not formed in this case. The presence of **3** and the mixed (NHC)(monophosphine)Pd(II) complex is accountable for the observed catalytic performance. During the first cycle, species **3** is responsible for the high activity and enantioselectivity obtained. The activity is maintained in the second cycle since both species, **3** and the (NHC)(monophosphine)Pd(II), are active, and furthermore, the enantioselectivity is reduced by the presence of the latter complex (Table 1, entries 5–6).[7]

In order to prevent the formation of inactive NHC species **4** during the catalytic reaction in ILs, we envisaged that the addition of trapping ligands could stabilise the Pd(0) active species [Pd((*S*)-BINAP)(Solvent)] and a further trapping ligand de-coordination would regenerate the catalyst in subsequent cycles. Therefore, we explored (*S*)-BINAP as a stabilising ligand (in a (*S*)-BINAP/Pd = 2.5 ratio) in similar stoichiometric experiments as previously described (Fig. 3 and S10†). $^{31}$P NMR showed that initially formed species **2** in the presence of **D** (Fig. 3a) reacted with **I**, **II** and BSA resulting in the formation of species **3**, (*S*)-BINPO,[23] (*S*)-BINAPO[17] and a small amount of **4** (Fig. 3b). The subsequent addition of **II** and BSA led to the formation of [Pd((*S*)-BINAP)$_2$] (**5**),[20] a small amount of **3**, (*S*)-BINPO, and (*S*)-BINAPO (Fig. 3c). When a (*S*)-BINAP/Pd ratio of 2.5 was tested, under catalytic conditions in **D**, similar activities were reached in the first cycle compared to the system with a lower (*S*)-BINAP/Pd ratio (Table 1, entry 4 *vs.* 7, 1st cycle column), which is in agreement with the results of the monitoring experiments (Fig. 3b). The system failed to maintain the conversion rates in the second cycle due to the formation of species **4** and **5** (Fig. 3c), meanwhile the ee values fell by only *ca.* 10%. Attempts to recycle the catalytic system

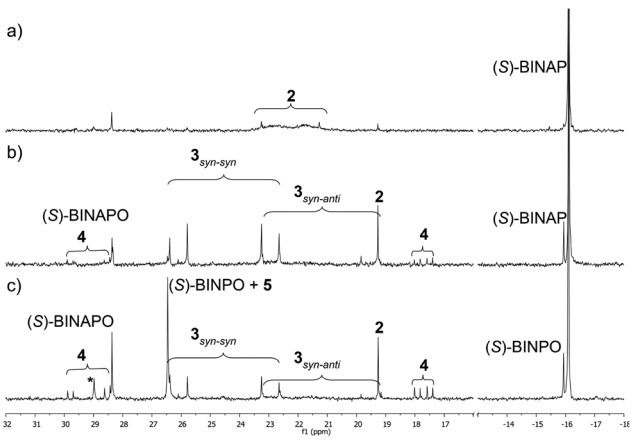



**Fig. 3** $^{31}$P NMR (121 Hz) spectra for the stoichiometric AAA reaction using **2** ((*S*)-BINAP/Pd = 2.5) in $CD_2Cl_2$: (a) **2** in the presence of **D**; (b) addition of **I**, **II** and BSA in a 1 : 1 : 1 ratio with respect to [Pd]; (c) addition of **II** and BSA in a 1 : 1 ratio with respect to [Pd]. (*) Unknown species.

with a higher (*S*)-BINAP/Pd ratio resulted in a loss of both activity and enantioselectivity after product extraction with hexane, which was related to the formation of the inactive species **4** and **5** (Table S1 in ESI†). Formation of the latter species also explains the previous results by Toma[3a] in AAA in IL **C**, since a fourfold excess of the chiral ligand was used, where the catalyst showed high activity and ee in the first cycle but the recycled system underwent a dramatic drop in both activity and enantioselectivity.

Additionally, we tested different trapping ligands such as cyclooctadiene and norbornadiene, or coordinating solvents such as acetonitrile in the AAA in IL **A**. After extraction of the

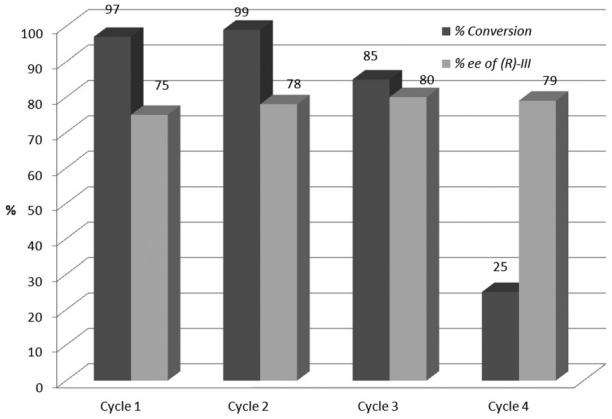



**Fig. 4** Pd/(*S*)-BINAP catalysed asymmetric allylic alkylation of **I** in [HDBU][OAc].

product with hexane, the IL-catalytic systems failed to maintain the catalytic performance upon recycling (Table S1 in ESI†). This suggests a possible replacement of the trapping ligands by (NHC) ligands derived from the IL, generating the inactive species **4** and non-enantioselective species such as (NHC)(monophosphine)-Pd(II).

Given that the use of imidazolium-based ILs did not allow recycling of the catalytic system when base or low-valent catalytic species were present (as discussed above), we explored a less reactive IL, [HDBU][OAc], in the AAA of **I**. The preliminary results demonstrated the feasibility of recycling in this IL using the same catalytic system. High conversions with good enantioselectivities are reached along three cycles and the activity only decreased in a forth cycle (Fig. 4). A profound catalytic study using this promising system is in progress.

## Conclusions

High activities and enantioselectivities in imidazolium-based ionic liquids were attained. Recycling of the IL-catalytic system failed due to the formation of (NHC)-palladium complexes, even in the case of the 2-methyl substituted IL **B**, suggesting abnormal (NHC)-palladium complex formation.

A careful AAA stoichiometric study demonstrated that the substrate and the IL compete for the palladium(0) species to form AAA active species and inactive (NHC)-palladium complexes, respectively. The observed catalytic performance is a result of the relationship between species **3**, **4**, **5** and mixed (NHC)(monophosphine)Pd(II). Additionally, it was observed that the use of complex **1** prevents the formation of inactive species (*i.e.* **4**). Active carbene species such as mixed (NHC)-(monophosphine)Pd(II) and **3** are responsible for the high activities however, the former causes a drop in enantioselectivity in subsequent cycles.

Our results prove that imidazolium-based ionic liquids, employed in AAA under basic conditions, generate inactive (NHC)-palladium complexes as well as active mixed (NHC)-(monophosphine)Pd(II) complexes, which reduce the catalytic activity and enantioselectivity, respectively. The use of trapping agents for palladium(0) species were inadequate to prevent the formation of undesired (NHC)-palladium compounds. When carbene species formation is suppressed by the use of alternative ionic liquids such as [HDBU][OAc], it is possible to successfully recycle the IL-catalytic system.

## Experimental

### General materials, methods and instruments

All manipulations of air- and moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. Reagents were purchased from commercial suppliers and used without further purification. Hexane and $CH_2Cl_2$ were dried over $CaH_2$ and distilled under nitrogen prior to use. [Pd($\eta^3$-$C_3H_5$)((*S*)-BINAP)]-[$BF_4$],[11] [$PdCl_2$((*S*)-BINAP)],[24] [BMIM][$NTf_2$],[25] [HDMIM][$BF_4$],[25] [BMIM][Cl][26] and [HDBU][OAc][27] were prepared following procedures reported in the literature. NMR spectra were recorded on Varian Inova 300 and 400 instruments. Chemical shifts are given in ppm referenced to the solvent ($^1$H and $^{13}$C) or the external reference of 85% aqueous solution of $H_3PO_4$ ($^{31}$P), and the coupling constants are given in hertz (Hz). $FAB^+$ mass spectra were acquired using a Jeol SX102A inverse geometry spectrometer using a 3-nitrobenzylalcohol matrix. High-resolution mass spectra were obtained using an Agilent G1969A electrospray-ionization time-of-flight mass spectrometer. HPLC analyses of the catalytic reaction mixtures were performed on an Alliance-Waters apparatus, equipped with a photodiode array detector, using Diacel OJH as the column and 10% 2-propanol–hexane, with a flow rate of 1 mL $min^{-1}$, as the eluent ($\lambda$ = 254 nm, guard cartridge 4 × 3 mm). The absolute configuration of the chiral products was assigned by comparing their retention time with that of optically pure compounds.

### Synthetic procedures

**[PdCl(NHC$^{Bu,Me}$)((*S*)-BINAP)]Cl (4).** A solution of [BMIM]Cl (12.2 mg, 0.07 mmol) in 2 mL of $CH_2Cl_2$ was treated with $Ag_2O$ (9 mg, 0.04 mmol) overnight in the dark. A solution of AgCl(NHC$^{Bu,Me}$) was formed, then filtered through celite and the filtrate was received on a Schlenk containing a solution of [$PdCl_2$((*S*)-BINAP)] (47.9 mg, 0.06 mmol) in $CH_2Cl_2$ (2 mL). The reaction mixture was stirred in the dark for 24 h. The solution was filtered through celite and the solvent was removed under reduced pressure. The product was recrystallised from a mixture of $CH_2Cl_2$ and cyclohexane to afford the desired product (42 mg, 77% yield). Spectral data for **4a** (from the mixture): $^{31}$P NMR ($CD_2Cl_2$, 121 MHz) $\delta$ 29.8 (d, $J_{P-P}$ = 23.3 Hz), 18.0 (d, $J_{P-P}$ = 23.3 Hz); $^1$H NMR ($CD_2Cl_2$, 400 MHz) $\delta$ 8.2–6.7 (32H, Ar) 7.15 (1H, NC*H*), 6.65 (d, $J$ = 8.5 Hz, 1H, NC*H*), 4.27 (m, 1H, NCH*H*), 4.15 (3H, N*Me*), 3.70 (m, 1H, NC*H*H), 1.95 (m, 1H, $NCH_2CHH$), 1.64 (m, 1H, $NCH_2CHH$), 1.53 (2H, $N(CH_2)_2CH_2$), 1.05 (3H, $N(CH_2)_3CH_3$); $^{13}$C NMR ($CD_2Cl_2$, 76.4 MHz) $\delta$ 136–120 (Ar), 127.8 (N*C*H), 127.3 (N*C*H), 51.2 ($NCH_2$), 38.9 (N*Me*), 32.3 ($NCH_2CH_2$), 20.5 ($N(CH_2)_2CH_2$), 13.9

($N(CH_2)_3CH_3$) ppm. Spectral data for **4b** (from the mixture): $^{31}P$ NMR ($CD_2Cl_2$, 121 MHz) $\delta$ = 28.6 (d, $J_{P-P}$ = 23.2 Hz), 17.6 (d, $J_{P-P}$ = 23.2 Hz); $^1H$ NMR ($CD_2Cl_2$, 400 MHz) $\delta$ 8.2–6.7 (32H, Ar), 7.11 (1H, NC*H*), 6.58 (d, $J$ = 8.5 Hz, 1H, NC*H*), 4.39 (m, 1H, NCH*H*), 4.22 (m, 1H, NC*H*H), 3.84 (3H, N*Me*), 2.05 (m, 1H, $NCH_2CHH$), 1.97 (m, 1H, $NCH_2CHH$), 1.53 (2H, $N(CH_2)_2CH_2$), 1.03 (3H, $N(CH_2)_3CH_3$); $^{13}C$ NMR ($CD_2Cl_2$, 76.4 MHz) $\delta$ 136–120 (Ar), 127.6 (N*C*H), 127.2 (N*C*H), 51.8 ($NCH_2$), 38.3 (N*Me*), 32.7 ($NCH_2CH_2$), 20.6 ($N(CH_2)_2CH_2$), 14.0 ($N(CH_2)_3CH_3$) ppm. MS (FAB): $m/z$ = 903 for $[C_{52}H_{46}ClN_2P_2Pd]^+$. HRMS (ESI-TOF$^+$): $m/z$ calcd for $[C_{52}H_{46}ClN_2P_2Pd]^+$: 901.1854 $[M + H]^+$; found: 901.1855. E.A. calcd for $C_{52}H_{46}Cl_2N_2P_2Pd$ C, 65.79; H, 5.11; N, 3.08%; found: C, 66.57; H, 4.94; N, 2.99.

### Catalysed allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (I)

**General procedure using imidazolium-based IL's.** A solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and (*S*)-BINAP in the corresponding ratio (L/Pd = 1.25 and 2.5) in $CH_2Cl_2$ (1 mL) was stirred for 0.5 h. Subsequently, the IL was added (1 mL) and $CH_2Cl_2$ was removed under reduced pressure. Using a micropipette, **I** (126 mg, 0.5 mmol, 117 μL), dimethyl malonate (**II**) (198 mg, 1.5 mmol, 126 μL), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (305 mg, 1.5 mmol, 366 μL) and solid KOAc (2 mg) were added to start the catalytic reaction. Aliquots were taken from the reaction mixture at certain time intervals, diluted with diethyl ether, washed with saturated aqueous ammonium chloride solution, filtered over silica using diethyl ether as the eluent and analysed by HPLC. When catalyst **1** was employed, it was dissolved in the IL (1 mL) overnight at 20 °C, and the catalytic reaction started with the addition of **I**, **II**, BSA and KOAc in the appropriate amounts (see above).

**General procedure for recycling experiments.** At the end of the reaction, the product (**III**) was extracted with dry hexane (8 × 3 mL) and the ionic liquid was dried for 3 h at 60 °C and stirred in order to remove any trace solvent. The IL-catalytic system was reused for another catalytic reaction by simply adding **I**, **II**, BSA and KOAc in the appropriate amounts (see above).

**General procedure for recharging experiments.** At the end of the reaction, the IL-catalytic system was recharged for another catalytic reaction by simply adding **I** (0.5 mmol), **II** and BSA in a **I**/**II**/BSA 1 : 1 : 1 ratio.

**General procedure using [HDBU][OAc].** A solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and (*S*)-BINAP in the corresponding ratio (L/Pd = 1.25) in $CH_2Cl_2$ (1 mL) was stirred for 0.5 h. Subsequently, [HDBU][OAc] was added (1 mL) and $CH_2Cl_2$ was removed under reduced pressure. Using a micropipette, **I** (126 mg, 0.5 mmol, 117 μL), **II** (99 mg, 0.75 mmol, 86 μL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (76 mg, 0.5 mmol, 75 μL) were added to start the catalytic reaction. The reaction was stirred at 50 °C for 2 h. At the end of the reaction, product **III** was extracted with hexanes (8 × 3 mL), the IL was dried under reduced pressure at 60 °C for 3 h with stirring. The system was charged with **I**, **II** and DBU in the quantities described above. The recycling was repeated for 4 cycles.

### Stoichiometric experiments of catalysed allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (I) in the presence of an IL

An NMR tube was charged with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (4.5 mg, 0.012 mmol) and (*S*)-BINAP in the corresponding ratio (L/Pd = 1.25 and 2.5) or with preformed catalyst **1** (10.2 mg, 0.012 mmol) and $CD_2Cl_2$ (0.5 mL). After the addition of the IL (0.123 mmol), the solution was stirred for 0.5 h. Subsequently, **I** (6.2 mg, 0.024 mmol), dimethyl malonate (**II**) (3.2 mg, 0.024 mmol, 2.8 μL), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (24.8 mg, 0.024 mmol, 6.0 μL) and solid KOAc (1 mg) were added and stirred manually for 10 min, and then analysed by $^1H$ and $^{31}P$ NMR. The same operation was repeated after addition of **II** (3.2 mg, 0.024 mmol, 2.8 μL) and BSA (24.8 mg, 0.024 mmol, 6.0 μL).

## Acknowledgements

Authors thank the DGAPA PAPIIT-IN231211 project and Postdoctoral Fellowship Program of UNAM.

## Notes and references

1 (*a*) *Ionic liquids in synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Wienheim, 2nd edn, 2008, vol. 2; (*b*) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459; (*c*) H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal., A*, 2010, **373**, 1.

2 (*a*) L. Xu and J. Xiao, in *Recoverable and Recyclable Catalysts*, ed. M. Benaglia, John Wiley & Sons, Ltd, Chichester, 2009, p. 259; (*b*) A. F. Trindade, P. M. P. Gois and C. A. M. Afonso, *Chem. Rev.*, 2009, **109**, 418.

3 (*a*) I. Kmentová, B. Gotov, E. Solcániováb and S. Toma, *Green Chem.*, 2002, **4**, 103; (*b*) S. Toma, B. Gotov, I. Kmentová and E. Solcániová, *Green Chem.*, 2000, **2**, 149.

4 (*a*) J. Dupont and J. Spencer, *Angew. Chem., Int. Ed.*, 2004, **43**, 5296; (*b*) N. D. Clement, K. J. Cavell, C. Jones and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 2004, **43**, 1277; (*c*) J. D. Scholten, G. Ebeling and J. Dupont, *Dalton Trans.*, 2007, 5554.

5 (*a*) H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046; (*b*) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 2461.

6 (*a*) E. A. B. Kantchev, C. J. O'Brien and M. J. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768; (*b*) S. Diez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.

7 (*a*) A. Flahaut, S. Roland and P. Mangeney, *J. Organomet. Chem.*, 2007, **692**, 5754; (*b*) S. Roland, W. Cotet and P. Mangeney, *Eur. J. Inorg. Chem.*, 2009, 1796; (*c*) N. Toselli, D. Martin and G. Buono, *Org. Lett.*, 2008, **10**, 1453.

8 I. Favier, A. Balanta-Castillo, C. Godard, S. Castillón, C. Claver, M. Gómez and E. Teuma, *Chem. Commun.*, 2011, **47**, 7869.

9 V. De la Fuente, N. Fleury-Brégeot, S. Castillón and C. Claver, *Green Chem.*, 2012, **14**, 2715.
10 B. M. Trost and D. J. Murry, *Organometallics*, 1985, **4**, 1143.
11 A. M. Johns, M. Utsunomiya, C. D. Incarvito and J. F. Hartwig, *J. Am. Chem. Soc.*, 2006, **128**, 1828.
12 G. Yu, D. Zhao, L. Wen, S. Yang and X. Chen, *AIChE J.*, 2012, **58**, 2885.
13 Even when there is no reported viscosity data for [HDMIM]-[$BF_4$] (**B**), it was evidently more viscous than the rest of the ILs used, therefore catalytic reactions were performed at 50 °C.
14 (*a*) B. M. Trost and D. L. van Vranken, *Chem. Rev.*, 1996, **96**, 395; (*b*) G. Helmchen, U. Kazmaier and S. Förster, in *Catalytic asymmetric synthesis*, ed. I. Ojima, Wiley-VCH, New York, 2010, p. 497.
15 L. A. Evans, N. Fey, J. N. Harvey, D. Hose, G. C. Lloyd-Jones, P. Murray, G. Orpen, R. Osborne, G. J. J. Owen-Smith and M. Purdie, *J. Am. Chem. Soc.*, 2008, **130**, 14471.
16 P. Fristrup, T. Jensen, J. Hoppe and P.-O. Norrby, *Chem.–Eur. J.*, 2006, **12**, 5352.
17 (*a*) H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa and R. Noyori, *J. Org. Chem.*, 1986, **151**, 629; (*b*) C. Petit, A. Favre-Reguillon, B. Albela, L. Bonneviot, G. Mignani and M. Lemaire, *Organometallics*, 2009, **28**, 6379.
18 (*a*) M. Yamaguchi, M. Yakubi, T. Yamagishi, K. Sakai and T. Tsubomura, *Chem. Lett.*, 1996, 241; (*b*) A. Rosas, MSc, UNAM, 2012.
19 (*a*) L. J. Xu, W. P. Chen and J. L. Xiao, *Organometallics*, 2000, **19**, 1123; (*b*) C. J. Mathews, P. J. Smith, T. Welton, A. J. P. White and D. J. Williams, *Organometallics*, 2001, **20**, 3848.
20 Complete characterization of [Pd((*S*)-BINAP)$_2$], reported in: F. Ozawa, A. Kubo, Y. Matsumoto and T. Hayashi, *Organometallics*, 1993, **12**, 4188.
21 D. Brissy, M. Skander, P. Retailleau, G. Frison and A. Marinetti, *Organometallics*, 2009, **28**, 140.
22 (*a*) A. T. Normand, A. Stasch, L.-L. Ooi and K. J. Cavell, *Organometallics*, 2008, **27**, 6507; (*b*) S. Fantasia and S. P. Nolan, *Chem.–Eur. J.*, 2008, **14**, 6987; (*c*) S. Zheng, Y. Wang, C. Zhang, J. Liu and C. Xia, *Appl. Organomet. Chem.*, 2014, **28**, 48.
23 S. Gladiali, R. Taras, R. M. Ceder, M. Rocamora, G. Muller, X. Solans and M. Fort-Bardia, *Tetrahedron: Asymmetry*, 2004, **15**, 1477.
24 Similar synthesis followed for [$PdCl_2$((*R*)-BINAP)] reported in: G. Celentano, T. Benincori, S. Radaelli, M. Sada and F. Sannicolò, *J. Organomet. Chem.*, 2002, **643–644**, 424.
25 C. Cassol, G. Ebeling, B. Ferrera and J. Dupont, *Adv. Synth. Catal.*, 2006, **348**, 243. A similar procedure as described in this reference was followed for the synthesis of [HDMIM]-[$BF_4$] (see ESI†).
26 I. Hemeon and R. D. Singer, *J. Mol. Catal. A: Chem.*, 2004, **214**, 33.
27 A.-G. Ying, L. Liu, G.-F. Wua, G. Chen, X.-Z. Chen and W.-D. Ye, *Tetrahedron Lett.*, 2009, **50**, 1653.