Dalton Transactions

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ARTICLE

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

Cite this: DOI: 10.1039/x0xx00000x

I. Guerrero-Ríos and E. Martin*

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

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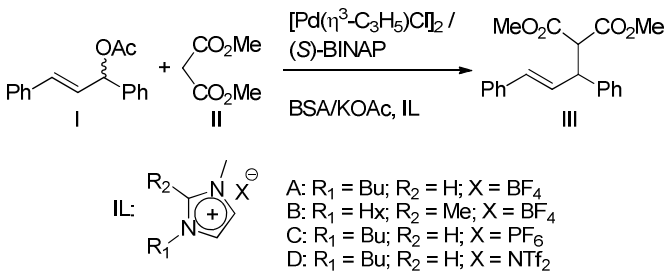
The system Pd/(*S*)-BINAP was successfully applied to asymmetric allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (**1**) using imidazolium-based ionic liquids (IL's) attaining up to 225 h^{-1} of TOF and 88% *ee* of (*R*)-product. Albeit the system was barely active in recycling experiments, catalyst life was confirmed upon recharging the system with substrate/reactants resulting in alkylated product. In the latter case, 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 recycling as well as in recharging experiments, we investigated the reactivity between catalyst precursors, substrate and reactants in IL's. 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 as the active and selective species at 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 responsible species 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 (IL's) in metal-catalysed reactions have become a viable alternative to organic solvents in many processes due to the feasibility of product separation and reuse of IL-catalytic phase.[1] The field of asymmetric catalysis profits from IL technologies, as has been demonstrated by research groups in academia.[2] However, the use of imidazolium-based IL's in asymmetric allylic alkylation (AAA) reactions have failed to reproduce activity and enantioselectivity on recycling the IL-catalytic system.[3] The latter has been attributed to possible formation of inactive species during the catalytic process. It is generally agreed that imidazolium-based IL's react with catalytic palladium species via oxidative addition to generate stable N-heterocyclic-carbene (NHC) palladium complexes or by deprotonation of C(2)-H bond of the imidazolium cation in the presence of a base.[4] Additionally, protons at C(4) and C(5) positions could react to afford "abnormal" carbenic species.[5] Although NHC-palladium precursors had 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 IL's and therefore produce recyclable systems, pyrrolidonium-based IL's has been used to reproduce *ee*'s and yields in asymmetric allylic amination and phosphination reactions.[8] Recently, imidazolium-based IL's were successfully applied in palladium catalysed AAA under MW irradiation to speed the reaction rate, thus avoiding formation of inactive and non-selective carbenic species otherwise observed.[9]

In order to get insights about the role of palladium species involved in the catalysed AAA in imidazolium-based IL's, we assessed the catalytic system Pd/(*S*)-BINAP to perform AAA in a variety of imidazolium-based IL's (Scheme 1). Furthermore, we investigated the species responsible for the activity and selectivity observed.



Scheme 1 Asymmetric allylic alkylation in imidazolium-based IL's.

Results and discussion

We studied the palladium-catalysed alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (**I**) using dimethylmalonate (**II**) as 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 $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-BINAP})]BF_4$ (**1**).[11] As regards IL's, we focused our attention on anion effects and cation C(2)-substitution as well (**A-D** in Scheme 1).

In Table 1 are summarised the catalytic results obtained. Complete conversions and enantioselectivities between 72-88% of (*R*)-product were reached within two hours at 20°C in all the ionic liquids tested (Table 1, 1st cycle column). It is worth mentioning that catalytic behaviour was independent of the catalyst generation method (Table, 1 *vs* 5 and 4 *vs* 6, 1st cycle column).

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

Entry	IL	L*/Pd	1st cycle[a]		2nd cycle[b]	
			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. [d] Performed at 50°C. [e] 2% $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-BINAP})]BF_4$ (**1**)

When the reactions were carried out in $[BMIM][BF_4]$ (**A**) and $[HDMIM][BF_4]$ (**B**), 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 IL's **A**[12] and **B**[13] are more viscous than to **C**[12] and **D**[12], the observed catalytic behaviour can be rationalised in terms of the reactants' diffusion, especially the nucleophile difussion. The limited mobility of reactants reduces the rate of nucleophilic attack and, consequently, isomerisation reactions of the allylic entities give rise to diverse allylpalladium isomers.[14] Furthermore, when 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 $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-BINAP})]BF_4$ (**1**)[11] in IL's **A** and **D** showed comparable activities and enantioselectivities to those exhibited by analogous systems (*in situ* formed catalyst "$[Pd(\eta^3\text{-}C_3H_5)((S)\text{-BINAP})]Cl$") (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] besides Norrby and coworkers propose that chlorides can exert a positive memory effects but also favoured the isomerisation of allylpalladium intermediates affecting reaction stereocontrol.[16]

Attempts to reuse the IL-catalytic system, after product extraction with hexane, resulted in poor conversion for all IL's used (<10%, Table S1 in ESI) in agreement with pioneering work of Toma and coworkers.[3] Since catalytic 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 on a second cycle but failed to reproduce enantioselectivities and conversions of the first cycle. Interestingly, when preformed catalyst **1** was used, the activity was maintained although the enantioselectivity was reduced (Table 1, entries 5-6, 2nd cycle column). A similar behaviour was displayed by the *in situ* generated catalyst in **A**, which attained 90% conversion and 36% *ee* of (*R*)-**III** in a second cycle (Table 1, entry 1, 2nd cycle column).

With the aim to identify species involved in the catalytic cycle that could explain the failure of recycling experiments as well as, the complex catalytic behaviour observed under recharging conditions, we performed ^1H and ^{31}P NMR experiments of the catalytic system Pd/(*S*)-BINAP in the presence of substrate, nucleophile and IL **D** (Fig. 1 and S1). Initially, complex $[Pd(\eta^3\text{-}C_3H_5)((S)\text{-BINAP})]Cl$ (**2**) was formed from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and (*S*)-BINAP ((*S*)-BINAP:Pd = 1.25 ratio) in the presence of **D** and CD_2Cl_2. In ^{31}P NMR spectrum (Fig. 1a), the signal centred in 22.5 ppm was assigned to **2**, which broadening 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 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, respectively (Scheme 2). Upon addition of a second equivalent of **II** and BSA (Fig. 1c) a new species 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 oxidative addition of

imidazolium cation to Pd(0) species generated *in situ*,[4b,4c] although C(2) deprotonation of imidazolium ring by base and subsequent attack to metal centre cannot be discarded.[19] Additionally, [Pd((*S*)-BINAP)$_2$] (**5**)[20] was identified together with an unknown species in smaller amount. Similar experiments performed in absence of IL did not generate the NHC-carbenic species **4**; addition of IL, just after the second nucleophilic attack, achieved the NHC species **4** (Fig. S2-S3 in ESI).

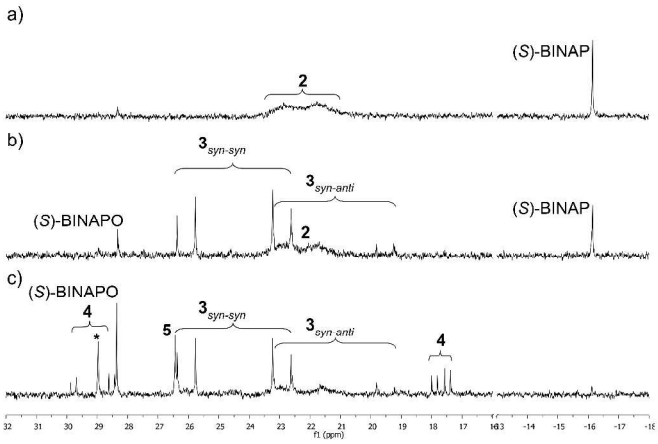
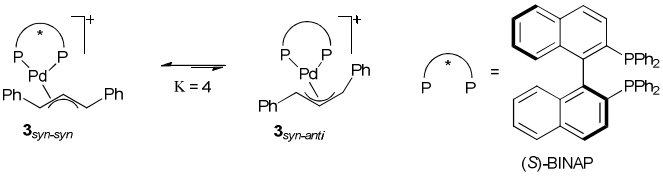


Fig. 1 ^{31}P NMR (121 Hz) spectra for stoichiometric AAA reaction using **2** ((*S*)-BINAP/Pd = 1.25) in CD_2Cl_2: a) **2** in the presence of **D**; b) Addition of **I**, **II**, BSA in 1:1:1 ratio with respect to Pd; c) Addition of **II**, BSA in 1:1 ratio respect to Pd. (*) Unknown species.



Scheme 2 Isomeric species of **3**.

To further investigate the viability of carbenic species **4**, we aimed at its independent synthesis to assess its stability and catalytic activity in AAA. Species **4** was obtained by reaction of [PdCl$_2$((*S*)-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 28-30 ppm. 2D ^{31}P-^{31}P experiments indicated a correlation between the doublets at 29.8 ppm and at 18.0 ppm and between the doublets at 28.6 and at 17.6 ppm. Therefore, complex **4** consists of a mixture of two diasteroisomeric species (**4a** and **4b**, Fig. 2). Formation of similar diasteroisomeric 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**, stem 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 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 (*R*)-product. In addition, saturated species **5** was not active in AAA until dissociation of a (*S*)-BINAP ligand occurred, thus forming the intermediate **3**.

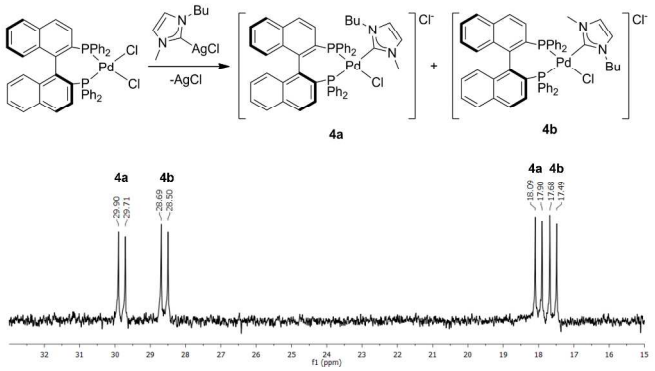
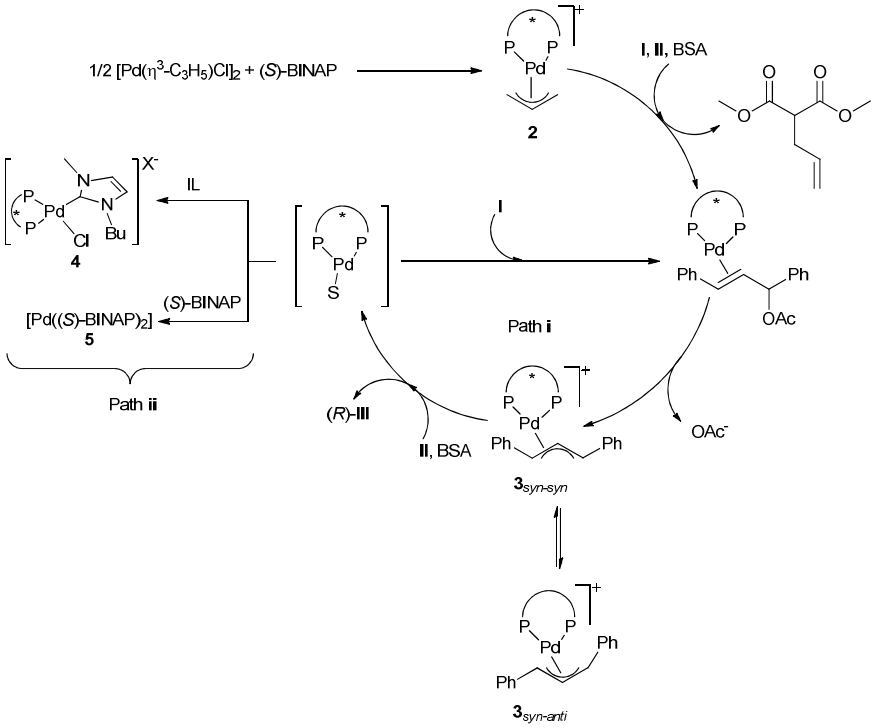


Fig. 2 Formation of NHC-species **4** and its corresponding ^{31}P NMR spectrum displaying a 1:1 diasteroisomeric mixture.

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

When the system was recharged with substrate and reactants, moderately enantioselectivities were attained in the second cycle, thus 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 reaction.[7] The differences in catalytic performance in the second cycle for all the IL's 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]



Scheme 3 Palladium species involved in AAA in presence of IL.

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, that could be attributed to the mixed (NHC)(monophosphine)Pd(II) species (Fig. S8-S9 in ESI).[7] Surprisingly, species **4** or **5** were not formed in this case. The presence of **3** and the mixed (NHC)(monophosphine)Pd(II) complex are accountable for the observed catalytic performance. During the first cycle, species **3** are responsible for the high activity and enantioselectivity attained. The activity is maintained in the second cycle since both species, **3** and the (NHC)(monophosphine)Pd(II), are active, notwithstanding 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 catalytic reaction in IL's, we envisaged that addition of trapping ligands could stabilise 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 stabilising ligand (in a (*S*)-BINAP/Pd = 2.5 ratio) in similar stoichiometric experiments previously described (Fig. 3 and S10). ^{31}P NMR showed that initially formed species **2** in presence of **D** (Fig. 3a) reacted with **I**, **II** and BSA resulting in formation of species **3**, (*S*)-BINPO,[23] (*S*)-BINAPO[17] and a small amount of **4** (Fig. 3b). Subsequent addition of **II** and BSA led to 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 are in agreement with the results of the monitoring experiments (Fig. 3b). The system failed to maintain conversion rates in the second cycle as a consequence of the formation of species **4** and **5** (Fig. 3c), meanwhile the *ee* values fell down by only c.a. 10%. Attempts to recycle the catalytic system 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 inactive species **4** and **5** (Table S1 in ESI). Formation of the latter species also explain the previous results by Toma[3a] in AAA in IL **C**, since a fourfold excess of 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.

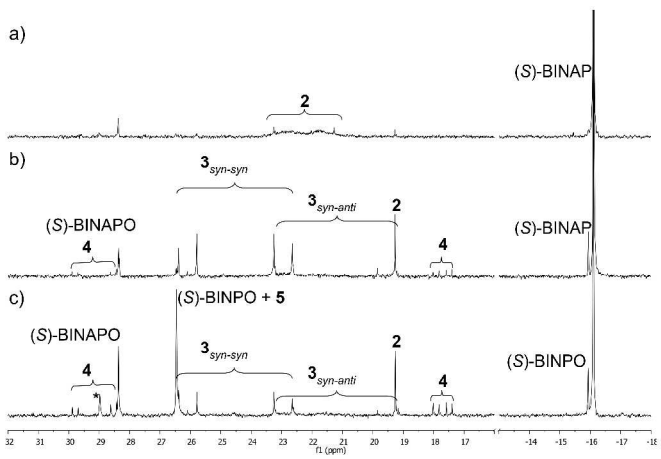


Fig. 3 ^{31}P NMR (121 Hz) spectra for stoichiometric AAA reaction using **2** ((*S*)-BINAP/Pd = 2.5) in CD_2Cl_2: a) **2** in presence of **D**; b) Addition of **I**, **II**, BSA in a 1:1:1 ratio with respect to [Pd]; c) Addition of **II**, BSA in a 1:1 ratio respect to [Pd]. (*) Unknown species.

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 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 IL's did not allow recycling of the catalytic system when base or low-valent catalytic species are present (as discussed above) we explored a less reacting IL, [HDBU][OAc] in AAA of **I**. 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 only the activity decreased in a forth cycle (Fig 4). A profound catalytic study using this promising system is in progress.

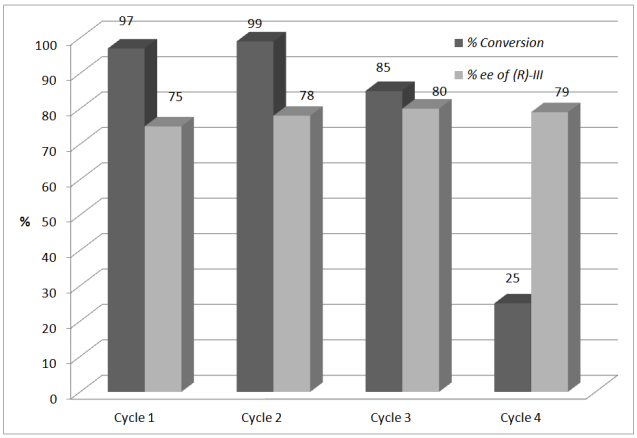


Fig. 4 Pd/(*S*)-BINAP catalysed asymmetric allylic alkylation of **I** in [HDBU][OAc].

Conclusions

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

A careful AAA stoichiometric study demonstrated that substrate and IL compete for 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). Additionaly, 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 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, reducing 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 as [HDBU][OAc] it is possible to recycle the IL-catalytic system with success.

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(η^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 literature procedures. NMR spectra were recorded on Varian Inova 300 and 400 instruments. Chemical shifts are given in ppm referenced to solvent (^1H and ^{13}C) or external reference of 85% aqueous solution of H_3PO_4 (^{31}P) and couplings constants in hertz (Hz). FAB^+ mass spectra were acquired in a Jeol SX102A inverse geometry spectrometer using 3-nitrobenzylalcohol matrix. High-resolution mass spectra were obtained on 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 column and 10% 2-propanol/hexane with a flow = 1 mL/min as eluent (λ = 254 nm, guard cartridge 4 x 3 mm). 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}) thus formed, was 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 under absence of light 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) δ 29.8 (d, $J_{P\text{-}P}$ = 23.3 Hz), 18.0 (d, $J_{P\text{-}P}$ = 23.3 Hz); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 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) δ 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) δ = 28.6 (d, $J_{P\text{-}P}$ = 23.2 Hz), 17.6 (d, $J_{P\text{-}P}$ = 23.2 Hz); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 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) δ 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.

Catalised 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, IL was added (1mL) 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) was 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 eluent and analysed by HPLC. When catalyst **1** was employed, it was dissolved in IL (1 mL) overnight at 20°C, and the catalytic reaction started with the addition of **I**, **II**, BSA and KOAc in the appropriate amount (see above).

General procedure for recycling experiments. At the end of the reaction the product (III) was extracted with dry hexane (8x3mL) and the ionic liquid was dried for 3 h at 60 °C and stirred in order to remove solvent traces. The IL-catalytic system was reused for another catalytic reaction by simply adding I, II, BSA and KOAc in the appropriate amount (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**, 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 (1mL) 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 (8x3mL), the IL was dried under reduced pressure at 60 °C for 3 h 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 presence of 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 preformed catalyst 1 (10.2 mg, 0.012mmol) and CD2Cl2 (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 analysed by 1H and 31P 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 to DGAPA PAPIIT-IN231211 project and Posdoctoral Fellowship Program of UNAM.

Notes and references

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

Electronic Supplementary Information (ESI) available: Description of procedures for recycling experiments (Table S1); ^{1}H and ^{31}P NMR spectra of AAA stoichiometric reaction study (Fig. S1-S3, S9-S11) NMR, MS-FAB and HRMS (ESI-TOF) spectra of complex **4** (Fig. S4-S8). See DOI: 10.1039/b000000x/

1 a) *Ionic liquids in synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Wienheim, 2nd edition, 2008, vol. 2; b) T. Welton, *Coord. Chem. Rev.* 2004, **248**, 2459; b) 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, 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 IL's 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, 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 M. Yamaguchi, M. Yakubi, T. Yamagishi, K. Sakai and T. Tsubomura, *Chem. Letters*, 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. T. Normand, A. Stasch, L.-L. Ooi, and K. J. Cavell, *Organometallics* 2008, **27**, 6507; b) S. Fantasia, S. P. Nolan, *Chem. Eur. J.*, 2008, **14**, 6987; c) S. Zheng, Y. Wang, C. Zhang, J. Liu and C. Xia, *App. Organomet. Chem.*, 2014, **28**, 48.

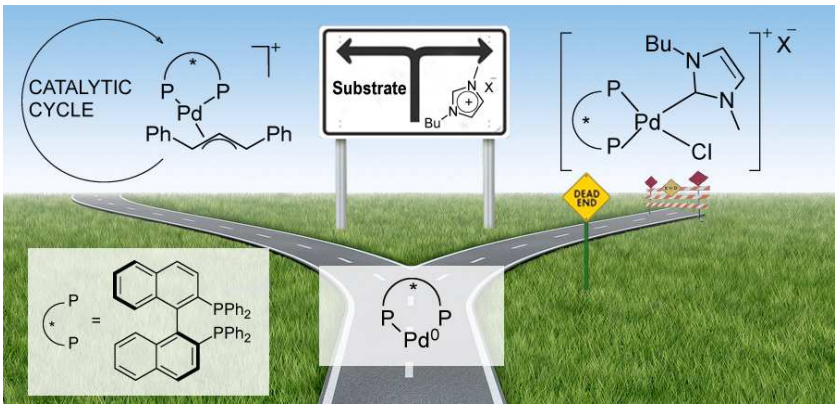
23 S. Gladiali, R. Taras, R. M. Ceder, M. Rocamora, G. Muller, X. Solans and M. Fort-Bardia, *Tetrahedron: Asymmetry*, 2004, **15**, 1477.

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. Cat. A: Chemical*, 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.



Highlights of the reactivity of palladium species in catalytic asymmetric allylic alkylation using imidazolium-based ionic liquids.