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Palladium-catalyzed asymmetric Heck arylation of 2,3-dihydrofuran – effect of prolinate salts†‡

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Chiral ionic liquids (CILs) containing L-prolinate and L-lactate anions and non-chiral quaternary ammonium cations were employed in the palladium catalyzed enantioselective Heck arylation of 2,3-dihydrofuran with aryl iodides (iodobenzene, 4-iodotoluene, 2-iodoanisole, 4-iodoanisole, 4-iodoacetophenone). In all the reactions 2-aryl-2,3-dihydrofuran (**3**) was obtained as the main product with the yield up to 52% at the total conversion reaching 83%. Product **3**, 2-phenyl-2,3-dihydrofuran, was obtained with excellent enantioselectivity (>99% ee) in a 6 h reaction with tetrabutylammonium L-prolinate. In the proposed homogeneous reaction Pd(0) nanoparticles are considered as a resting state of the catalyst and a source of soluble palladium species catalyzing the Heck reaction. The yield and stereoselectivity of the Heck reaction are strongly influenced by the kind of non-chiral cations present in CILs.

Introduction

The Heck cross-coupling is one of the most efficient new carbon–carbon bond formation methods leading to arylated olefins as the reaction products.[1] The broad applicability of the Heck reaction is due to the fact that it can be used for the arylation of olefins bearing electron-withdrawing substituents (EWG, *e.g.* –COOR, –CN), as well as for electron-rich olefins, such as olefins with the –OR group.[1]

In particular, the Heck coupling involving an olefin bearing a hydrogen atom in the allylic position may be accompanied by migration of the carbon–carbon double bond resulting in the formation of a product with a chiral carbon atom. Reactions of this type can be distinguished in respect to the kind of the substrate used: (i) arylation of allylic alcohols where double bond migration results in the formation of carbonyl products;[2] (ii) arylation of linear olefins;[3] (iii) arylation of cyclic olefins including ring-closing Heck coupling;[4] (iv) arylation of heterocyclic olefins.[5]

Arylation of cyclic olefins (*e.g.* cyclohexene, cyclopentene) was studied mainly in the presence of non-chiral catalysts, such as monomolecular palladium complexes or palladium nanoparticles.[4] Spectacular examples of highly stereoselective Heck coupling of cyclopentene were reported recently.[5] Successful enantioselective arylation of unactivated cyclic olefins was also carried out with an arenediazonium salt using chiral bisoxazolines as the ligands.[6]

The coupling reaction of 2,3-dihydrofuran (DHF) with aryl triflates is probably the most explored Heck reaction of a cyclic olefin containing a heteroatom.[4a,7] Arylation of DHF takes place exclusively at the C2 position (Fig. 1); however, due to carbon–carbon double bond migration, three products, namely **2**, **3** and **4**, might be formed. According to the mechanistic considerations 2-aryl-2,5-dihydrofuran (**2**) is the kinetic product whereas 2-aryl-2,3-dihydrofuran (**3**) is the thermodynamic one.[4a,7b,8] Consequently, it should be expected that **3** will be formed as the major product and such selectivity was in fact observed when palladium complexes with bidentate P–P ligands[9] were used. However, in reactions with monodentate phosphorous ligands[10] and bidentate ligands with P–N,[5] P–As,[11] P–S,[12] or P–O[13] donor atoms predominantly product **2** was formed. Several phosphane-free catalysts for the Heck reaction of DHF have also been reported.[14]

The stereoselective version of the Heck arylation of DHF was intensively tested with various phosphorous ligands.[4a,7,15] The high ee value for product **3** was achieved with BINAP phosphine as the chiral ligand added *in situ* to the palladium

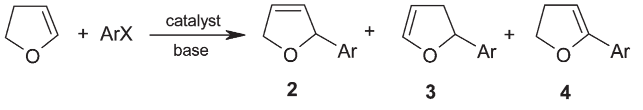

Fig. 1 Heck cross-coupling of 2,3-dihydrofuran with iodobenzene.

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† This paper is dedicated to Professor David Cole-Hamilton, good friend and great chemist, on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

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precursor.[4a] The excellent asymmetric induction was also noted when the isolated palladium complex with coordinated BINAP was applied. Comparably good results were reported for the systems containing $[Pd_2(dba)_3]\cdot dba$ (dba = dibenzylideneacetone) and different biaryl phosphite-oxazoline ligands. Interestingly, when BINAP(O) (monooxidized BINAP) was applied, product **2** was formed as the major one with a high yield and ee up to 94%.[16] The phosphine-free system based on chiral oxazoline derivatives used in the Heck arylation of DHF enabled us to obtain up to 29% ee for compound **2** and up to 60% for product **3**.[17]

Alternatively to the chiral ligands, ionic liquids containing stereogenic centers (CILs) can be used to introduce asymmetric induction in the Heck reaction.[18] There are many reports about successful application of CILs in metal-catalyzed organic reactions, however only a few of them refer to the Heck coupling. Gayet *et al.*[19] reported the arylation of DHF with iodobenzene catalyzed by a pyridinium CIL with $[PdCl_4]^{2-}$ as a counterion in $[BMIM]PF_6$ medium, nevertheless no enantiomeric excess was observed. Two other examples of the Heck-type arylation involving CILs are the oxyarylation of 7-benzyloxy-2*H*-chromene,[20] which gave a desirable product with 5% ee, and the arylation of aza-endocyclic acrylate[21] in various imidazolium and pyridinium CILs, which produced only racemic mixtures.

Recently, we have shown that CILs with stereogenic centers present in the anions are promising co-catalysts in the Heck coupling of DHF with iodobenzene.[22] The best result, yet still rather moderate (ee up to 9.9%), has been obtained for quinate and mandelate morpholinium salts. It should be also pointed out that **2** was formed with ee 17.3% in the presence of dimethyldidodecylammonium (*S*)-lactate.

Considering the promoting effect of the chiral anion present in CIL on the asymmetric induction, one may expect that the ammonium salts bearing chiral anions can also be attractive co-catalysts in the asymmetric Heck reaction leading to the stereoselective formation of the coupling products. The expected advantage of that type of CIL is a reasonable cost and simplicity of the synthesis, especially when salts of amino acids are used as the substrates. The amino acids represent a very attractive class of the substrates for preparation of CILs, being often available in both enantiomeric forms which might be used as the chiral anions. CILs of that type have been recently employed in the asymmetric Michael addition.[23] Moreover, their anti-bacterial and anti-fungal activities were confirmed.[23] Herein, we present studies of the model asymmetric Heck reaction with a palladium catalyst modified by four CILs containing (L)-lactate and (L)-prolinate anions and non-chiral quaternary cations.

Results and discussion

Arylation of DHF

The arylation of DHF with iodobenzene was carried out using $Pd(OAc)_2$ as the catalyst precursor in DMF, under the conditions optimized in our previous studies (temperature 70 °C, K_2CO_3 as a base).[22] Four CILs were applied as the co-catalysts in the catalytic systems: [DDA][L-PRO] (DDA = didodecyldimethylammonium cation, L-PRO = (L)-prolinate), [BA][L-PRO] (BA = cation with $C_{12}H_{25}$ and $C_{14}H_{29}$ alkyl groups in proportions equal to 60 and 40%, respectively), $[Bu_4N]$[L-PRO] and $[Bu_4N]$[L-Lact] (L-Lact = L-lactate anion).

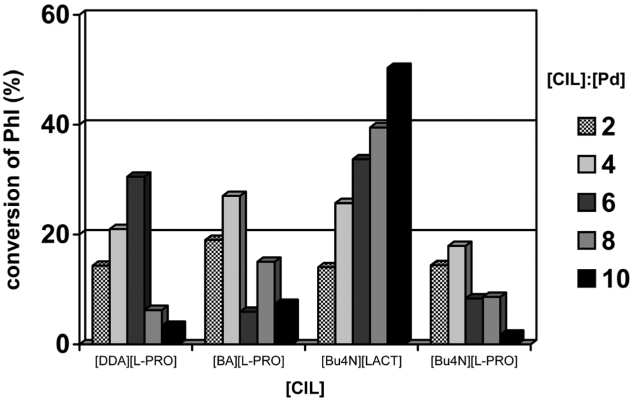

Fig. 2 Effect of the [CIL] : [Pd] ratio on conversion in Heck cross-coupling of DHF with PhI.

Fig. 2 presents the dependence of iodobenzene conversions on the amount of CILs at their different concentrations *versus* palladium. In all the cases **3** was the major reaction product, whereas the amounts of **2** and **4** were at the level of 15 and 8%, respectively. The most productive was $[Bu_4N]$[L-lact], which provided up to 50% of the arylated products after 2 h. Interestingly, only in the reactions with this co-catalyst the conversion increased with the increase of the CIL amount. For the remaining three CILs the best results were obtained at [CIL] : [Pd] ratios equal to 4 or 6, whereas the application of higher amounts of CILs resulted in a decrease of conversion. A possible reason for the observed trend might be a stronger bonding to palladium of the prolinate ligand than the lactate ligand. Consequently, these ligands efficiently compete with substrates for the place in the coordination sphere of the catalyst.

The analysis of the reaction enantioselectivity enabled us to discover a remarkable effect of the non-chiral cations on the products composition (Table 1). Apparently, while the ee values for the main product **3** were equal to 4–12 in the reaction with [DDA][L-PRO], they increased to 15–23 when [BA]-[L-PRO] was applied as the CIL. In both systems lower enantioselectivity was noted for product **2**, namely 1–5 in the presence of [DDA][L-PRO] and 4–10 in the reactions with [BA][L-PRO]. In the case of $[Bu_4N]$[L-PRO] the ee values ranged from 1.5 to 7.5%.

It should be pointed out that the stereoselectivity obtained with L-prolinate salts, especially with [BA][L-PRO], is remarkably higher than that observed by us earlier in the presence of morpholinium salts bearing different chiral anions.[22] These promising results encouraged us to continue the investigations and to check whether the studied systems are stable enough to

Table 1 Heck arylation of DHF with $Pd(OAc)_2$ and various CILs

	$[NBu_4]$[L-LACT]		[BA][L-PRO]		[DDA][L-PRO]		$[NBu_4]$[L-PRO]	
	Yield of **2** and **3**[a] (%) [ee%]							
[CIL]/[Pd]	**3**	**2**	**3**	**2**	**3**	**2**	**3**	**2**
2	11.1	1.7 [2.1]	11.4 [15.3]	5.8 [4.0]	8.6 [4.5]	4.4 [0.7]	9.4 [7.5]	5 [5.7]
4	19.5 [0.4]	3.8 [3.3]	15 [22.6]	9.7 [6.5]	12.7 [6.5]	6.3 [2.1]	7.4 [3.0]	10.5 [3.2]
6	24.5 [0.4]	4.9 [3.6]	12.6 [20]	10.5 [4.8]	19.2 [7.2]	9.4 [2.6]	4.8 [4.7]	3.5 [7.2]
8	28.3 [0.4]	6.3 [4.0]	8.5 [21.3]	6.5 [8.3]	3.3 [12.0]	2.9 [3.4]	5.6 [7.1]	3 [6.7]
10	35.4 [0.4]	7.5 [4.0]	3.4 [18.8]	3.9 [10.0]	1.8 [11.5]	1.5 [4.7]	1.3 [1.5]	0.5

[a] Conditions: $Pd(OAc)_2$ (1 mol%), 70 °C, 2 h, solvent DMF (6 mL), DHF (8.6 mmol), PhI (3.57 mmol), K_2CO_3 (4.34 mmol).

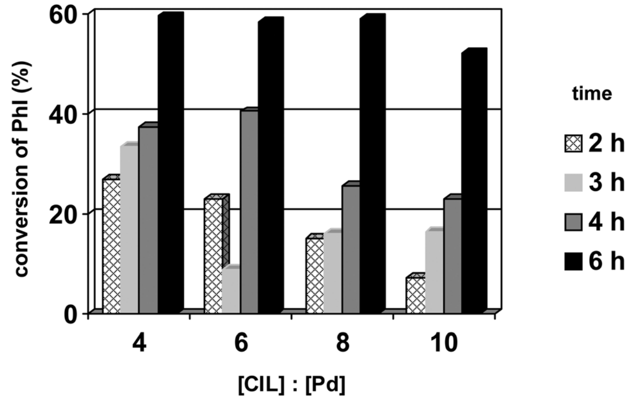

Fig. 3 Conversion in the Heck reaction over time at different [CIL] : [Pd] ratios (CIL = [BA][L-PRO]).

be used for a longer time. In fact, the experiments performed with [BA][L-PRO] gave very positive results illustrated by the increase of the iodobenzene conversion up to 60% after 6 h in the reactions carried out at the [CIL] : [Pd] ratio 4–10 (Fig. 3).

Slightly lower conversion, *ca.* 50%, was noted when a higher excess of [BA][L-PROL] was used. Clearly, for gaining of the optimal conversions the amount of CIL should not exceed 8, whereas the optimal reaction time is *ca.* 6 h. As far as the enantioselectivity is concerned a decrease of the ee values in time should be mentioned (Table 2). In almost all the reactions carried out at the [CIL] : [Pd] in the range of 4–10, the ee values of *ca.* 22% were obtained after 3–4 h for the product **3**, while after a longer time (6 h) they decreased to 12–17%. For the minor product **2** up to 10% ee were obtained.

Similar experiments carried out for prolonged time with $[Bu_4N]$[L-PRO] as the CIL enabled us to find the best result for the studied Heck reaction, namely an excellent enantioselectivity at the reasonable yield of **3**. At the 2-fold excess of $[Bu_4N]$[L-PRO] to $Pd(OAc)_2$ after 3 and 6 h reactions practically one pure enantiomer of **3** was obtained with the yields of 57 and 83%, respectively. The application of higher amounts of $[Bu_4N]$[L-PRO] resulted in the remarkable decrease of both, the yield and enantioselectivity (Table 3).

The excellent enantioselectivity found in the studied reactions might be explained by the influence of the chiral L-prolinate anion on the step involving insertion of alkene into the Pd–Ar bond (Fig. 5). This step, followed by β-hydrogen elimination, may be decisive in the formation of the particular enantiomer. However, as it was already mentioned, the effect of the non-chiral cation on the reaction course should be also considered. For better confirmation of that statement, the Heck reactions were performed under the same conditions using L-proline and D-proline instead of quaternary ammonium L-prolinates. From the data collected in Table 4 it can be concluded that prolines have practically no influence on the conversion of iodobenzene which is close to 20%, similarly as for $Pd(OAc)_2$ used without any additives. Also the ee values were very low. Thus, the effect of the cations on the reaction course was confirmed.

In a further step of our studies the catalytic system with $[Bu_4N]$[L-PRO] salt was tested in the Heck cross-coupling of DHF with differently substituted iodobenzenes (Table 5). In all the cases good conversions (49–87%) were obtained after 6 h. With an increase of the reaction time the ee values also increased and the best result, 19.9%, was obtained for 4-iodotoluene. Merely slightly worse enantioselectivity was noted for other substrates with the only exception of 4-iodoacetophenone, which formed the respective 2,3-dihydrofuran derivative with the ee as low as 3.1%. Interestingly, the attempts to use phenyl triflate as the substrate instead of iodobenzene failed and only 3% of the coupling product was formed in the best case. However, since iodobenzene is a cheaper and more commonly available substrate than aryl triflate, the applicability of our catalytic system to aryl iodides shows its big advantage.

Mechanistic considerations

According to the literature, the nature of the catalyst active in the phosphane-free palladium system might be in part homogeneous and in part heterogeneous at the same time.[24] In particular, the formation of Pd(0) nanoparticles under the reaction conditions is very plausible.[24,25] Such nanoparticles can act as heterogeneous catalysts, however recently, it has often been postulated in the literature that these nanoparticles do not directly participate in the catalytic process but rather act as a reservoir of soluble catalytically-active palladium species. In such a case, a reaction mechanism might be based on the homogeneous catalysis pathway.

Table 2 Heck arylation of DHF with $Pd(OAc)_2$ and different amounts of [BA][L-PRO] (CIL)[a]

	[CIL] : [Pd] = 4			[CIL] : [Pd] = 6			[CIL] : [Pd] = 8			[CIL] : [Pd] = 10		
Time (h)	Conversion[b] (%)	3 yield (%) [ee%]	2 yield (%) [ee%]	Conversion[b] (%)	3 yield (%) [ee%]	2 yield (%) [ee%]	Conversion[b] (%)	3 yield (%) [ee%]	2 yield (%) [ee%]	Conversion[b] (%)	3 yield (%) [ee%]	2 yield (%) [ee%]
2	27.0	15.0 [22.6]	9.7 [6.5]	23.1	11.4 [15.3]	5.8 [4.0]	15.0	8.5 [21.3]	6.5 [8.3]	7.3	3.4 [18.8]	3.9 [10.0]
3	33.5	18.9 [22.8]	12.6 [5.0]	8.8	5.1 [20.5]	3.7 [2.0]	16.0	8.5 [18.8]	7.5 [8.8]	16.3	8.8 [22.0]	7.5 [8.8]
4	37.5	19.8 [22.4]	14.4 [4.5]	40.5	24.4 [21.3]	15.7 [7.6]	25.5	14.6 [18.0]	10.9 [9.0]	23.0	13.1 [22.0]	10.9 [9.0]
6	59.5	33.5 [17.0]	19.4 [4.0]	58.2	37.0 [12.0]	19.7 [3.2]	59.0	37.3 [16.3]	21.3 [6.0]	52.0	33.4 [15.0]	21.3 [6.0]

[a] Conditions: $Pd(OAc)_2$ (1 mol%), 70 °C, solvent DMF (6 mL), DHF (8.6 mmol), PhI (3.57 mmol), K_2CO_3 (4.34 mmol). [b] Conversion of PhI.

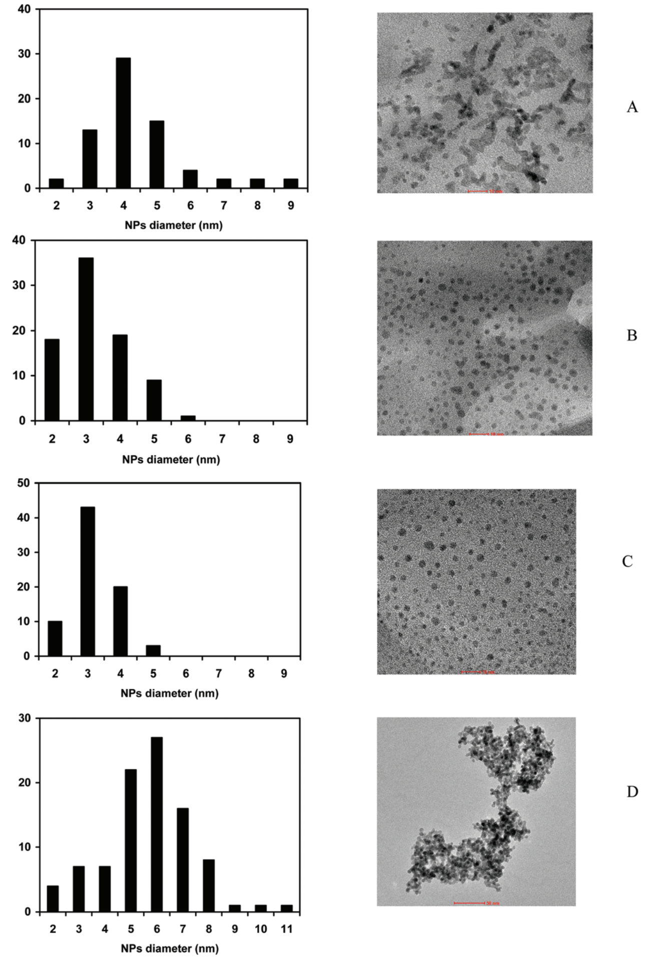

Fig. 4 TEM pictures and Pd(0) nanoparticles size distribution of: (A) $Pd(OAc)_2$ + K_2CO_3; (B) $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO]; (C) $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO] + PhI; (D) $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO] + PhI + DHF heated 30 min at 70 °C in DMF.

To get a closer insight into the mechanism of the catalytic process in our system the Hg(0) test was performed using 500-fold excess of mercury to palladium. An analogous reaction without Hg(0) addition was also performed for comparison. The analysis of the products composition after 2 h showed a decrease of the conversion from 62.3 in the reaction without Hg(0) to 26.8% in the presence of Hg(0). Thus, the inhibiting effect was clearly seen, however the reaction did not stop completely, as it would be expected for the heterogeneous process catalyzed by Pd(0) nanoparticles or ligand-free Pd(0) species.

To verify the formation of palladium nanoparticles in the system under studies four TEM analyses have been done for the samples containing components of the Heck reaction in DMF:

A. $Pd(OAc)_2$ + K_2CO_3
B. $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO]
C. $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO] + PhI
D. $Pd(OAc)_2$ + K_2CO_3 + 2 $[Bu_4N]$[L-PRO] + PhI + DHF

Sample A, used as the reference, contained palladium nanoparticles of the average diameter 4 nm. In the presence of

Table 3 Heck arylation of DHF with $Pd(OAc)_2$ and different amounts of $[Bu_4N]$[L-PRO] (CIL)[a]

	[CIL] : [Pd] = 2			[CIL] : [Pd] = 4		
Time (h)	Conversion[b] (%)	**3** yield (%) [ee%]	**2** yield (%) [ee%]	Conversion[b] (%)	**3** yield (%) [ee%]	**2** yield (%) [ee%]
2	14.4	9.4 [7.5]	5.0 [5.7]	17.9	7.4 [3.0]	10.5 [3.2]
3	56.7	39.5 [>99]	12.7 [1.4]	39.3	27.7 [13.3]	11.2 [2.6]
6	83.0	51.8 [>99]	26.4 [2.2]	41.0	25.6 [9.3]	14.9 [1.1]

[a] Conditions: $Pd(OAc)_2$ (1 mol%), 70 °C, solvent DMF (6 mL), DHF (8.6 mmol), PhI (3.57 mmol), K_2CO_3 (4.34 mmol). [b] Conversion of PhI.

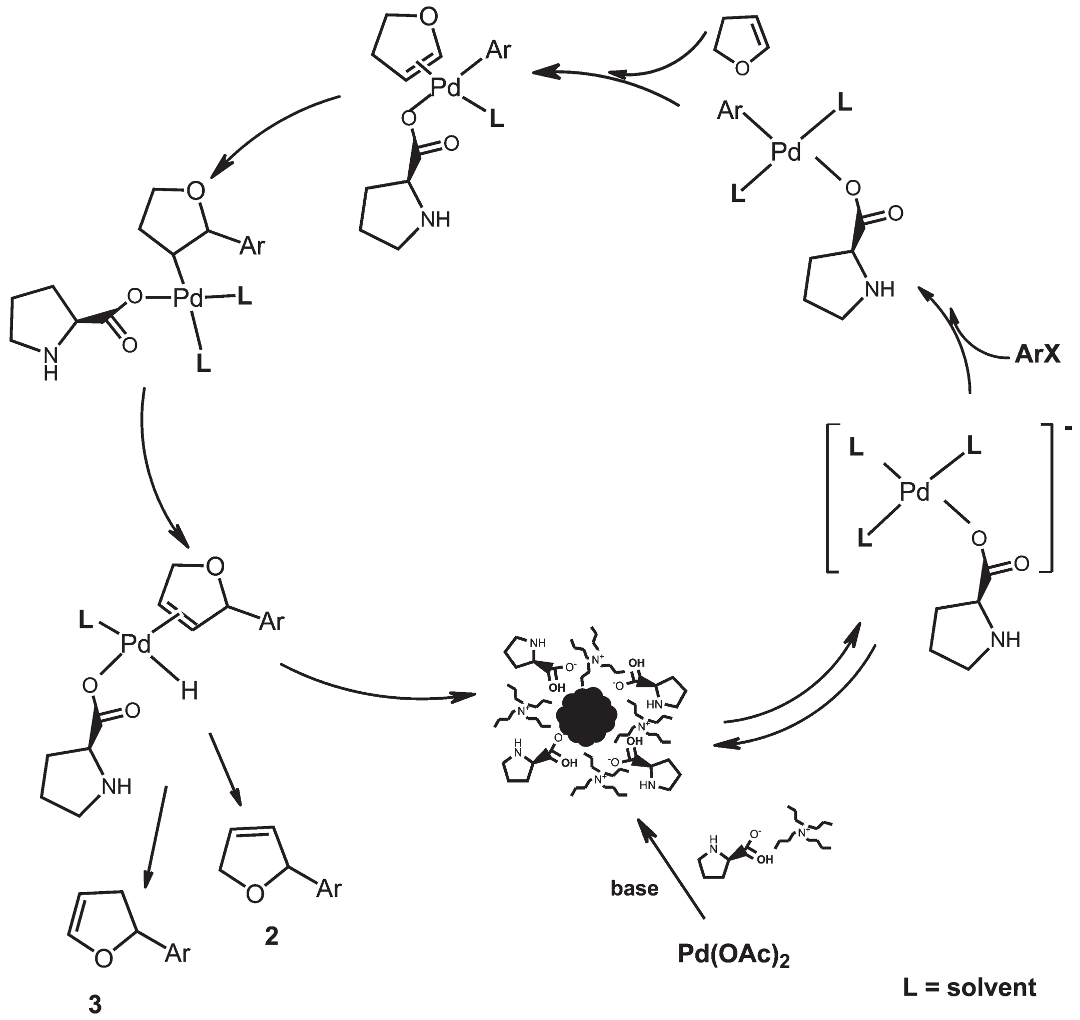

Fig. 5 The proposed mechanism of the Heck reaction in the presence of $[Bu_4N]$[L-PRO].

$[Bu_4N]$[L-PRO] slightly smaller nanoparticles were formed with a narrower size distribution. In the presence of iodobenzene these nanoparticles undergo dissolution forming the soluble active palladium catalyst. A partial dissolution of nanoparticles is in agreement with their redispersion observed in TEM. As is seen in Fig. 4 the nanoparticles are uniformly distributed, whereas in sample D, containing all components of the Heck-reaction, some agglomeration was observed and the average diameter of the nanoparticles increased to *ca.* 6 nm. It can be concluded from these results that Pd(0) nanoparticles, most probably stabilized by CILs, represent the resting state of the catalyst.

The proposed mechanism of the Heck reaction, based on the literature[26] and our observations, is presented in Fig. 5. Similarly as previously observed,[22] we propose the homogeneous halide-free pathway as a dominant one in the selective formation of arylated dihydrofurans. The chiral carboxylate anion, *e.g.* L-prolinate, competes efficiently with I^- for a place in the coordination sphere of palladium and is responsible for the asymmetric induction. The key palladium intermediate,

Table 4 Heck arylation of DHF with $Pd(OAc)_2$ and prolines[a]

	Conversion[b] (%)	**3** yield (%) [ee%]	**2** yield (%) [ee%]
[L-Proline] : [Pd]			
2	23.2	17.6 [1.3]	5.6 [2.2]
4	18.6	13.0 [1.8]	5.6 [4.9]
[D-Proline] : [Pd]			
2	19.4	14.9 [4.2]	4.5 [1.2]
4	21.8	16.3 [6.5]	5.5 [1.3]
$Pd(OAc)_2$	22.1	18.3	3.0

[a] Conditions: 1 mol% $Pd(OAc)_2$, 70 °C, 2 h, solvent DMF (6 mL), DHF (8.6 mmol), PhI (3.57 mmol), K_2CO_3 (4.34 mmol). [b] Conversion of PhI.

containing aryl and carboxylate ligands $ArPdL_2(RCO_2)$ (L = solvent), is analogous to that identified by Amatore and Jutand in the phosphane containing system for the Heck coupling.[26c]

The proposed reaction mechanism also illustrates the role of Pd(0) nanoparticles as the catalyst resting state and the source of soluble palladium species. The nanoparticles are stabilized by CILs due to electrostatic interactions.[27] Such interactions may also influence the rate of nanoparticles dissolution and at the same time the rate of the catalytic process. Consequently, the cationic part of the CIL plays an important role in the process and a strong influence of the cation on the reaction course was observed. In addition, the cations present in CILs may also determine a nucleophilicity of the chiral anion and its reactivity in the catalytic process. For example, Hayashi stated that a stronger base may generate the highly reactive acetate anion that induces the dissociation of (*S*)-**2** from the palladium center and formation of almost enantiomerically pure (*R*)-**3**.[4a]

From mechanistic point of view, the remarkable influence of the chiral anions on the enantioselectivity should be pointed out. An important effect of the anions on the reactivity of anionic Pd(0) complexes in the Heck reaction was also demonstrated by Amatore and Jutand.[25b,c] According to our results, L-prolinate is an anion of choice in the Heck arylation of DHF with aryl iodides. However, the proper selection of the non-chiral cation turned out to be also very important and particularly higher ee values were achieved with more bulky BA than with smaller DDA L-prolinate. The effect of the cation may be discussed in terms of its electrostatic interactions with the negatively charged surface of Pd(0) nanoparticles. The formation of nanoparticles, unequivocally confirmed by TEM, enables us to consider them as a reservoir of catalytically active soluble palladium species.

Conclusions

We have shown that the asymmetric Heck coupling of DHF with aryl iodides can be efficiently performed under phosphane-free conditions using $Pd(OAc)_2$ as a palladium source and CILs as chiral agents. The excellent enantioselectivity (>99% ee) obtained with the application of $[Bu_4N]$[L-PRO] should be highlighted. The CILs tested in this work are easily available, inexpensive and enable us to obtain very good results when used in small amounts.

Experimental

Materials

DHF, PhI, L-proline, D-proline, $[Bu_4N]OH$ and $[Bu_4N]$[L-LACT] were obtained from Aldrich and used without further purification. [BA][L-PRO] and [DDA][L-PRO] were obtained according to the literature.[23] $[Bu_4N]$[L-PRO] was obtained in the reaction of $[Bu_4N]OH$ with L-proline.

Heck reaction

The Heck arylation of DHF with PhI was carried out under a N_2 atmosphere using a standard Schlenk technique. The reagents were introduced into the Schlenk tube in the following order: $Pd(OAc)_2$ (8.0 mg, 0.0356 mmol, 1 mol%), solvent DMF (6 mL), IL (appropriate amount), K_2CO_3 (0.6 g, 4.34 mmol), PhI (0.4 mL, 3.57 mmol) mesitylene (internal standard, 0.15 mL) and DHF (0.7 mL, 8.59 mmol). The reaction was carried out at 70 °C for 2 h. Afterwards, the reaction mixture was quenched with H_2O (3 mL) and the organic products were separated by extraction with diethyl ether (3 times: 10 mL, 7 mL and 7 mL). The products were analyzed by GC-FID (Hewlett Packard 8454A). Products **2**, **3**, **4** were identified by comparison of the MS spectra and the retention times with the literature data.

The enantiomeric excess (ee) values were determined by GC-FID (Hewlett Packard 8454A) with a chiral β-cyclodextrin column.

Table 5 Heck arylation of DHF with different iodobenzenes, using $Pd(OAc)_2$ and $[Bu_4N]$[L-PRO][a]

	4-Iodotoluene		2-Iodoanisole		4-Iodoanisole		4-Iodoacetophenone	
	Conversion[b] (%) [ee%]							
Time (h)	$\mathbf{3}_1$	$\mathbf{2}_1$	$\mathbf{3}_2$	$\mathbf{2}_2$	$\mathbf{3}_3$	$\mathbf{2}_3$	$\mathbf{3}_4$	$\mathbf{2}_4$
3	46 [18.3]	15 [7.5]	3.2 [1.5]	2.4 [7.2]	27 [17.0]	13 [10.0]	22 [0.1]	8.6 [0.3]
6	52 [19.9]	24 [11.0]	30 [18.0]	17[10.0]	46 [18.1]	21 [10.6]	38 [3.1]	14.5 [5.9]

[a] Conditions: $Pd(OAc)_2$ (1 mol%), [CIL]:[Pd] = 2, 70 °C, solvent DMF (6 mL), DHF (8.6 mmol), ArX (3.57 mmol), K_2CO_3 (4.34 mmol). [b] Conversion of ArI $\mathbf{3}_1$, $\mathbf{3}_2$, $\mathbf{3}_3$, $\mathbf{3}_4$ = 2-aryl-2,3-dihydrofuran $\mathbf{2}_1$, $\mathbf{2}_2$, $\mathbf{2}_3$, $\mathbf{2}_4$ = 2-aryl-2,5-dihydrofuran.

TEM measurements

Samples for TEM analyses were prepared at 70 °C using the same amounts of reactants as in catalytic reactions. After 30 min, a droplet of the reaction mixture was placed on a carbon coated microscope grid and dried for 40 min. TEM measurements were carried out using an FEI Tecnai G^2 20 X-TWIN electron microscope (TEM) operating at 200 kV.

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