Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 246 (2006) 59–64

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Palladium catalysed hydroethoxycarbonylation in imidazolium-based ionic liquids

Gábor Rangits [a], László Kollár [a,b,*]

[a] *University of Pécs, Department of Inorganic Chemistry, H-7624 Pécs, Ifjúság u. 6, P.O. Box 266, Hungary*
[b] *Research Group for Chemical Sensors of the Hungarian Academy of Sciences, H-7624 Pécs, P.O. Box 266, Hungary*

Received 27 September 2005; received in revised form 17 October 2005; accepted 17 October 2005

Abstract

Imidazolium-based ionic liquids with $[PF_6]^-$, $[BF_4]^-$ and $[GaCl_4]^-$ counterions have been synthesised and used in hydroethoxycarbonylation of styrene. In addition to the formation of the expected ethyl 2-phenyl- and 3-phenyl-propionates, the oligomerization (polymerization) of the substrate depending on the counterion of the ionic liquid was also observed. Moderate to high regioselectivities towards branched esters have been obtained with the 'preformed' $PdCl_2(PPh_3)_2$ catalyst. The addition of 1,1′-bis(diphenylphosphino)ferrocene (dppf) favoured the formation of the linear isomer, however, complete linear regioselectivity has been obtained only in acetonyl-methyl-imidazolium hexafluorophosphate. It was found that the regioselectivity is strongly influenced by the structure of the ionic liquid: in $[BMIM][PF_6]$ the formation of the linear ester is slightly favoured, however, the substitution of the butyl substituent with benzyl or acetonyl group resulted in complete branched selectivity.

Keywords: Carbonylation; Ionic liquid; Imidazolium; Palladium; Hydroalkoxycarbonylation

---

1. Introduction

Among the recently used alternative solvents ionic liquids play an important role due to their environmentally benign properties like extremely low vapour pressure, chemical and thermal stability, high ionic conductivity and good solvent properties towards both ionic and covalent compounds [1–6]. A major drive of these efforts with ionic liquid in industry and fundamental research is the substitution of more environmentally friendly technologies for traditional ones in which damaging and volatile organic solvents are generally used. Ionic liquids are considered as promising substitutes for organic solvents, not only because of their properties above, but also because of their ability to act as catalysts. Several well-known organic reactions like Diels–Alder reaction, Friedel–Crafts reaction, esterification, alkylation, etc. have been carried out successfully in ionic liquids [1,2].

Among the several types of homogeneous catalytic reactions (hydrogenation, oxidation, hydrodimerization, various coupling reactions like Heck-reaction, Suzuki and Trost–Tsuji couplings) carried out in ionic liquids [2], less carbonylation reactions have been published under similar conditions [1,2,7]. Some examples for hydroformylation with various transition metal catalysts in ionic liquid are known [8–12], however, to the best of our knowledge, sporadic results can be found for palladium catalysed hydroalkoxycarbonylation of olefins in ionic liquid [13,14].

The transition metal catalysed hydroalkoxycarbonylation of various olefins under conventional conditions is one of the basic reactions in synthetic organic chemistry [15,16]. The use of carbon monoxide as a 'carboxyl-source' in rhodium or palladium catalysed hydroalkoxycarbonylation reaction is a widely known methodology for the synthesis of chiral esters [17]. Due to the pharmacological importance of the resulted branched esters (2-aryl-propionates) as intermediates for non-steroidal antiinflammatory agents (NSAI), vinylaromatics (styrene, 2-vinylnaphthalene, 2-phenyl-propene) were mainly used as substrates [18–21].

The influence of the reaction conditions (temperature, carbon monoxide pressure and solvent) has been discussed for a long time [22]. Similarly, detailed investigations have been carried out by the variation of the catalytic precursor as well as potential additives like acids [23]. It has to be added that most of

---

* Corresponding author. Tel.: +36 72 327622/4153; fax: +36 72 501527.
E-mail address: kollar@ttk.pte.hu (L. Kollár).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.10.019

the investigations have been carried out in conventional organic solvents like toluene and benzene.

In addition to vinylaromatics, various unsaturated steroids and terpenes have been converted to the corresponding esters of practical importance by palladium catalysed hydroalkoxycarbonylation showing its synthetic potential [24–29]. Similarly, the intramolecular version of this reaction, i.e. the carbonylation of hydroxy-olefins resulted in lactones in high yields [30].

In this paper, the palladium catalysed hydroethoxycarbonylation of styrene in imidazolium type ionic liquids will be described.

2. Experimental

2.1. Reagents

Palladium(II) chloride, 1,1′-bis(diphenylphosphino)ferrocene (dppf), chloroacetone, 4-chlorobutyronitrile and 1,4-dichlorobutane were purchased from Aldrich and were used without further purification. [BMIM][PF_6] ionic liquid was purchased from Aldrich and also prepared according to a published procedure [31]. Similarly, [dodecyl-MIM][PF_6] was synthesised as described before [32]. The synthesis and characterization of tetrachlorogallate ionic liquid [EMIM][$GaCl_4$] possessing closely related structure to [BMIM][$GaCl_4$] has been published during the preparation of the present paper [33]. A similar ‘metallate method’ has been used for the synthesis of [BMIM][$GaCl_4$].

Solvents were dried according to standard procedures. Styrene was freshly distilled before use. $PdCl_2(PPh_3)_2$ was prepared on the bases of an early described method [34].

2.2. General procedures

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer at 400.13, 100.62 and 161.9 MHz, respectively. Chemical shifts δ are reported in ppm relative to $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively) or H_3PO_4 (85%). Elemental analyses were measured on a 1108 Carlo Erba apparatus.

Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

2.3. Synthesis of ionic liquids

2.3.1. Synthesis of [acetonyl-MIM][PF_6]

4.93 g (60 mmol) of 1-methylimidazole was stirred under argon atmosphere at room temperature and 5.55 g (60 mmol) of chloroacetone was added dropwise (five drops per minute). After an exoterm reaction the black highly viscous material was stirred at 70 °C (oil bath) for 24 h under argon atmosphere. The [acetonyl-MIM]Cl product was dissolved in 60 g of distilled water and 19 g of 60 w/w% HPF_6-solution (containing 78 mmol HPF_6) was dripped to it, then stirred at room temperature for 3 h. The organic phase was separated from the aqueous phase by a separating funnel and was washed with distilled water (to remove HPF_6-solution and any water-soluble impurities) until it was neutral. The final product was dried under high vacuum (<1 mmHg) at 70 °C for 3 h.

^{1}H NMR (DMSO-d_6/$CDCl_3$, 400 MHz): δ 8.88 (s, 1H); 7.54 (s, 1H); 7.44 (s, 1H); 5.22 (s, 2H); 3.86 (s, 3H); 2.18 (s, 3H); ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100.6 MHz): δ 199.0; 137.4; 123.5; 122.8; 57.1; 35.8; 26.6. Mp: 59–67 °C.

2.3.2. Synthesis of [cyanopropyl-MIM][PF_6]

4.93 g (60 mmol) of 1-methylimidazole and 7.46 g (72 mmol) of 4-chlorobutyronitrile were mixed under argon atmosphere and stirred at 70 °C (oil bath) for 4 days. The excess of 4-chlorobutyronitrile was removed under high vacuum at 70 °C (oil bath) for 2 h. The [cyanobutyl-MIM]Cl product was dissolved in 60 g distilled water and 19 g 60 w/w% HPF_6-solution (containing 78 mmol HPF_6) was added dropwise then stirred at room temperature for 3 h. The solid product was separated by a (Büchner-funnel), and was washed with distilled water (to remove HPF_6-solution and any water-soluble impurities) until it was neutral. The final product was dried under vacuum at 70 °C for 3 h.

^{1}H NMR (DMSO-d_6/$CDCl_3$, 400 MHz): δ 9.09 (s, 1H); 7.67 (s, 1H); 7.59 (s, 1H); 4.23 (t, 5.7 Hz, 2H); 3.82 (s, 3H); 2.48 (t, 5.8 Hz, 2H); 2.12 (qi, 11.5 Hz, 2H); ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100,6 MHz): δ 136.8; 123.7; 122.2; 118.8; 47.6; 35.7; 25.3; 13.5. Mp: 69–74 °C.

2.3.3. Synthesis of [acetonyl-MIM][BF_4]

The [acetonyl-MIM]Cl product was synthesised as described above (synthesis of [acetonyl-MIM][PF_6]). The same amount as above was dissolved in 60 g distilled water and 13.7 g of 50 w/w% HBF_4-solution (containing 78 mmol HBF_4) was added dropwise then stirred at room temperature for 3 h. The solution was carefully (because of foaming) distilled by a rotadest apparatus and washed with distilled water (to remove HPF_6-solution and any water-soluble impurities) until it was neutral. The final product was dried under vacuum at 70 °C for 3 h.

^{1}H NMR (DMSO-d_6/$CDCl_3$, 400 MHz): δ 8.72 (s, 1H); 7.48 (s, 1H); 7.38 (s, 1H); 5.18 (s, 2H); 3.85 (s, 3H); 2.17 (s, 3H); ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100.6 MHz): δ 199.1; 137.1; 123.4; 122.8; 57.0; 35.7; 26.3. Mp: 70–72 °C.

2.3.4. Synthesis of [butylene-MIM_2][BF_4]$_2$

6.57 g (80 mmol) of 1-methylimidazole and 5.08 g (40 mmol) of 1,4-dichlorobutane were mixed under argon atmosphere and stirred at 70 °C (oil bath) for 4 days. The [butylene-MIM_2]Cl product was dissolved in 60 g distilled water and 18.3 g of 50 w/w% HBF_4-solution (containing 104 mmol HBF_4) was added dropwise then stirred at room temperature for 3 h. The solution was carefully distilled (because of foaming) by a rotadest apparatus and washed with distilled water (to remove HPF_6-solution and any water-soluble impurities) until it was neutral. The final product was dried under vacuum at 70 °C for 3 h.

^{1}H NMR (DMSO-d_6/$CDCl_3$, 400 MHz): δ 8.84 (s, 1H); 7.52 (s, 1H); 7.48 (s, 1H); 4.14 (br s, 2H); 3.80 (s, 3H); 1.79 (br s, 2H); ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100,6 MHz): δ 136.2; 123.4; 122.0; 48.1; 35.5; 25.9. Mp: 52–55 °C.

2.3.5. Synthesis of [benzyl-MIM][BF_4]

4.93 g (60 mmol) of 1-methylimidazole and 7.60 g (60 mmol) of benzyl chloride were mixed under argon atmosphere and stirred at 70 °C (oil bath) for 24 h. The [benzyl-MIM]Cl product was dissolved in 60 g distilled water and 13.7 g 50 w/w% HBF_4-solution (containing 78 mmol HBF_4) was added dropwise then stirred at room temperature for 3 h. The product (organic phase) was separated from the aqueous phase by a separating funnel and was washed with distilled water (to remove HPF_6-solution and any water-soluble impurities) until it was neutral. The final product was dried under vacuum at 70 °C for 3 h.

^{1}H NMR (DMSO-d_6/$CDCl_3$, 400 MHz): δ 9.04 (s, 1H); 7.55 (s, 1H); 7.51 (s, 1H); 7.38-7.32 (m, 5H); 5.34 (s, 2H); 3.82 (s, 3H); ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100.6 MHz): δ 136.3; 133.9; 128.8; 128.7; 128.4; 128.3 128.1; 123.7; 122.1; 52.2; 35.7. Mp: 28–32 °C.

2.3.6. Synthesis of [BMIM][$GaCl_4$]

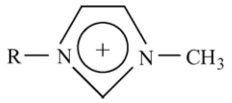
22.7 g (276 mmol) of 1-methylimidazole and 35 ml (331 mmol) of 1-chlorobutane were mixed under argon atmosphere and stirred at 75 °C (oil bath) for 4 days. The excess of 1-chlorobutane was removed under vacuum at 80 °C. The pale yellow [BMIM]Cl ionic liquid solidified at 60 °C forming a white solid.

5.13 g (28.4 mmol) of [BMIM]Cl and 5.00 g of gallium(III)-chloride were mixed under argon atmosphere and stirred at 70 °C (oil bath) for 24 h. The viscous material was used as obtained.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.07 (s, 1H); 7.69 (s, 1H); 7.63 (s, 1H); 4.12 (t, 5.8 Hz, 2H); 3.82 (s, 3H); 1.74 (qi, 11.8 Hz, 2H); 1.24 (sx, 15.1 Hz, 2H); 0.87 (t, 6.0 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100,6 MHz): δ 136.4; 123.6; 122.2; 48.6; 35.8; 31.3; 18.8; 13.2. Mp: liquid even at −78 °C.

2.3.7. Hydroalkoxycarbonylation reaction

In a typical reaction 7.0 mg (0.01 mmol) of $PdCl_2(PPh_3)_2$ (and in case of the in situ systems 0.01 mmol dppf) was dissolved in 0.5 ml of ionic liquid under argon. Fifty-seven microlitres (0.5 mmol) of styrene, 2 mmol of ethanol was added. The atmosphere was changed to carbon monoxide and the reaction mixture was kept at 100 °C for 24 h. The organic products were extracted with 1.0 ml of toluene. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1 by using *n*-dodecane as internal standard.



$[BMIM]^+$	R= $CH_3(CH_2)_3$–
$[acetonyl\text{-}MIM]^+$	R= CH_3COCH_2–
$[cyanobutyl\text{-}MIM]^+$	R= $CN(CH_2)_3$–
$[dodecyl\text{-}MIM]^+$	R= $CH_3(CH_2)_{11}$–
$[benzyl\text{-}MIM]^+$	R= $C_6H_5CH_2$–
$[butylene\text{-}MIM_2]^{2+}$	R= $MIM(CH_2)_4$–

Fig. 1. The ionic liquids used in hydroethoxycarbonylation in the present work.

3. Results

3.1. Synthesis of ionic liquids

Since the ionic liquid itself is one of the most important variables in synthesis, we decided to synthesise some imidazolium-based ionic liquids for systematic investigation of homogeneous catalytic reactions.

The synthesis of the $[BMIM]^+$ analogues ($[acetonyl\text{-}MIM]^+$, $[cyanopropyl\text{-}MIM]^+$, $[benzyl\text{-}MIM]^+$ and $[butylene\text{-}MIM_2{}^+]$) is based on the alkylation of 1-methyl-imidazol with chloroacetone, 4-chlorobutyronitrile, benzylchloride and 1,4-dichlorobutane, respectively (Fig. 1). In addition to these imidazolium-cations the parent $[BMIM]^+$ and $[dodecyl\text{-}MIM]^+$ analogues have been also used in carbonylation reactions. This way, the corresponding chlorides have been obtained which were transferred to the tetrafluoroborate, hexafluorophophate or tetrachlorogallate derivatives by metathesis or metallate methods [1], respectively (see Section 2). A tetrachlorogallate ionic liquid [EMIM][$GaCl_4$], a close analogue to the [BMIM][$GaCl_4$] [33] as well as a cyanomethyl-tetramethylammonium based ionic liquid have been published quite recently [35].

It has to be noted that only a few of the imidazolium salts can be considered as room temperature ionic liquid (RT-IL) but all of them possess melting point below 100 °C [2] and are suitable for hydroalkoxycarbonylation reactions.

3.2. Hydroethoxycarbonylation of styrene in imidazolium-based ionic liquids in the presence of $PdCl_2(PPh_3)_2$ catalytic precursor or that of the $PdCl_2(PPh_3)_2$ + dppf in situ catalyst

Styrene (**1**) as a model substrate was reacted with carbon monoxide and ethanol in the presence of either a ‘preformed’ palladium catalyst ($Pd(PPh_3)_2Cl_2$) or the in situ palladium catalyst obtained from $Pd(PPh_3)_2Cl_2$ and dppf. Imidazolium-based

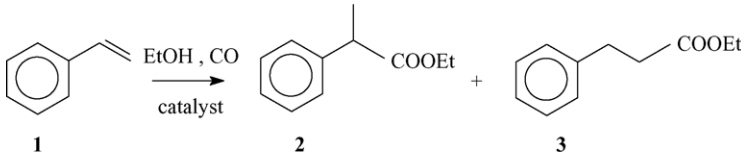


Fig. 2. Palladium catalysed hydroethoxycarbonylation of styrene.

Table 1
Ethoxycarbonylation of styrene in various imidazolium-based ionic liquids in the presence of $PdCl_2(PPh_3)_2$ catalyst[a]

Run	Ionic liquid	Composition of the reaction mixture (%)			R_{br}[c] (%)
		Olig./polym.[b]	**2**	**3**	
1	[BMIM][PF_6]	32[d]	13	19	41
2	[Acetonyl-MIM][PF_6]	30[d]	70	0	100
3	[Cyanobutyl-MIM][PF_6]	33[d]	35	8	81
4	[Dodecyl-MIM][PF_6]	28[d]	54	18	75
5	[BMIM][BF_4]	19[d]	48	11	81
6	[Acetonyl-MIM][BF_4]	14[e]	86	0	100
7	[Butylene-MIM_2][BF_4]$_2$	15[e]	39	6	87
8	[Benzyl-MIM][BF_4]	35[d]	65	0	100
9	[BMIM][$GaCl_4$]	13[e]	67	20	77

[a] Reaction conditions: Pd/styrene = 1/50; reaction temperature: 100 °C; p(CO) = 100 bar; reaction time: 24 h.

[b] Dimers, oligomers, polymers [determined by GC (dodecane internal standard)], the amount of the non-converted substrate **1** is not indicated in the columns.

[c] Regioselectivity towards branched ester regioisomer [mole of **2**/(mole of **2** + mole of **3**) × 100].

[d] Mainly styrene polymer was formed (dimers < 1%).

[e] ca. 10% styrene polymer was formed.

ionic liquids of systematically varied structure (Fig. 1) have been used as solvents at 100 °C under 100 bar carbon monoxide pressure.

The hydroalkoxycarbonylation of styrene (**1**) resulted in the formation of the branched (ethyl 2-phenylpropionate, **2**) and the linear (ethyl 3-phenylpropionate, **3**) ester regioisomers (Fig. 2). As a general observation it has to be noted that in all cases the oligomerization (polymerization) of styrene took also place to some extent resulting in the 'loss' of part of the substrate.

Table 2
Ethoxycarbonylation of styrene in various imidazolium-based ionic liquids in the presence of $PdCl_2(PPh_3)_2$ + dppf in situ catalyst[a]

Run	Ionic liquid	Composition of the reaction mixture (%)			R_{br}[c] (%)
		Olig./polym.[b]	**2**	**3**	
1	[BMIM][PF_6]	20[d]	11	49	18
2	[Acetonyl-MIM][PF_6]	17[d]	0	83	0
3	[Cyanobutyl-MIM][PF_6]	18[d]	18	54	25
4	[Dodecyl-MIM][PF_6]	22[d]	17	61	22
5	[BMIM][BF_4]	14[d]	23	41	36
6	[Acetonyl-MIM][BF_4]	27[e]	13	60	18
7	[Butylene-MIM_2][BF_4]$_2$	24[e]	22	54	29
8	[Benzyl-MIM][BF_4]	30[e]	33	37	47
9	[BMIM][$GaCl_4$]	31[e]	26	43	38

[a] Reaction conditions: Pd/styrene = 1/50; reaction temperature: 100 °C; p(CO) = 100 bar; reaction time: 24 h.

[b] Dimers, oligomers, polymers [determined by GC (dodecane internal standard)], the amount of the non-converted substrate **1** is not indicated in the columns.

[c] Regioselectivity towards branched ester regioisomer [mole of **2**/(mole of **2** + mole of **3**) × 100].

[d] Mainly styrene polymer was formed (dimers < 1%).

[e] Mainly dimers were formed (ca. 5% styrene polymer was formed).

Moderate to high regioselectivities towards branched ester have been observed in the presence of the 'preformed' $Pd(PPh_3)_2Cl_2$ catalyst (Table 1). The regioselectivity of hydroethoxycarbonylation was varied by the structure of the ionic liquid in the range of 41–100%. It is worth noting that the lowest branched selectivity has been obtained with the most widely used [BMIM][PF_6] (run 1). Total conversion and complete branched selectivity have been observed with [acetonyl-MIM][PF_6], [acetonyl-MIM][BF_4] and [benzyl-MIM][BF_4] (runs 2, 6 and 8). The application of tetrafluoroborate or terachlorogallate counterions seems to enhance branched selectivity compared to hexafluorophosphate.

The formation of the linear ester (**3**) was favoured by using all of the ionic liquids when dppf has been used as bidentate ligand in the in situ system (Table 2). The regioselectivity towards branched ester was varied in the range of 0–47%. The reaction in [benzyl-MIM][BF_4] ionic liquid shows the nearly equimolar formation of **2** and **3** (run 8). The application of [acetonyl-MIM][PF_6] resulted in the exclusive formation of the linear ester (run 2).

4. Discussion

The hydroethoxycarbonylation of styrene in ionic liquids of systematically varied structure resulted in the following major observations:

(i) Some oligomerization (polymerization) reactions have been observed in all cases being most striking in case of hexafluorophosphate ionic liquids. (It has to be noted that hydroalkoxycarbonylation reactions in conventional solvents are also accompanied by these 'undesired' side-reactions but their extent is much lower. However, as a contrast to ionic liquid catalysis, it has to be noted that in case of aromatic solvents the addition of a few drops of cc.HCl is also necessary in order to avoid metallic palladium formation [36].) While the side-reactions are of less importance in case of tetrafluoroborate and tetrachlorogallate type ionic liquids, extended polymerization up to 35% can be detected with hexafluorophosphates. ^{31}P NMR investigations showed that $[PF_6]^-$ cannot be considered as innocent ion in ionic liquids and can be responsible for the acidification of the solvent [11,37].

(ii) The linear ester **3** has been observed as major regioisomer in all cases in the presence of dppf. The prevalent formation of the linear ester in the presence of palladium-diphosphine systems in conventional solvents is known for a long time [38,39,22]. $Pd(dppf)Cl_2$ is formed in situ via ligand substitution depending on the ionic liquid and are responsible for the decrease of the branched selectivity, i.e. the preferential formation of **3**. The formation of $Pd(dppf)Cl_2$ can be followed by ^{31}P NMR, e.g. in [BMIM][BF_4] the signal at 28.2 ppm (assigned to the catalytic precursor $PdCl_2(PPh_3)_2$) disappears upon substitution with dppf while a signal at 37.2 ppm (assigned to $PdCl_2(dppf)$) builds up together with the signal at −4.6 ppm (assigned to PPh_3). Similar chemical shifts these species (within the range of deviation of 0.5–0.7 ppm) have been observed also for other ionic liquids.

(iii) The regioselectivity shows strong dependence also on the structure of the ionic liquid. Moderate branched selectivities have been obtained with $Pd(PPh_3)Cl_2$ catalyst when the butyl substituent is substituted for dodecyl, 4-cyanopropyl or butylene group of similar character. The introduction of acetonyl or benzyl substituent resulted in the exclusive formation of branched esters (Table 1, runs 2, 6 and 8). On the basis of our previous investigations these differences can be explained by the different structure of the ionic liquid. Even in the case of 1,3-dialkyl-imidazolium-based ionic liquids ($[C_{14}MIM][PF_6]$) the coordination of PF_6^- anion has been proved [40]. In case of the acetonyl and benzyl substituents the coordination of the PF_6^- or BF_4^- anions to the methylene hydrogens in a-position has to be much stronger. (The quantum mechanical calculations as well as spectrometric studies are under progress.) The use of palladium–monodentate phosphine ligand systems in conventional organic solvents results in the preferential formation of the branched ester [22].

(iv) Similarly, ionic liquids with electron releasing substituents on the imidazolium ring are less sensitive towards regioselectivity changes even in the presence of dppf. Nearly equal (low) branched selectivities have been obtained in these ionic liquids by using dppf containing in situ systems (Table 2, runs 1, 3 and 4).

(v) As for the counter-anions, the application of $[BF_4]^-$ anion instead of $[PF_6]^-$ results in a shift towards the formation of the branched ester (compare runs 1 and 5 (Table 1) as well as runs 1 and 5, runs 2 and 6 (Table 2)). Furthermore, the application of tetrafluoroborate type ionic liquids yielded much ‘cleaner’ reactions than that of hexafluorophosphates and tetrachlorogallates. This fact can be explained by the much higher stability of $[BF_4]^-$ than $[PF_6]^-$ towards hydrolysis, which might result in the acidification of the ionic liquid media. This undesired solvent degradation (hydrolysis of $[PF_6]^-$) has been also proved by ^{31}P NMR (see (i)) [11,37]).

(vi) Some attempts have been made in order to recycle the ionic liquid containing the catalytically active species. Although the ester regioisomers, the substrate and the oligomeric by-products can be extracted with toluene from the ionic liquid phase, the leaching of the catalyst could also be observed. The activity of the ‘recycled’ catalyst decreased by 10–25% in the first three runs even if some additional phosphine (two equivalents to palladium in each run) was added. Without adding phosphine to the recycled ionic liquid the decrease of the activity is even more drastic. This fact, as well as GC analyses showing the presence of PPh_3 (and $PPh_3(O)$ in the organic extract suggest that the leaching of the free phosphine occurs to much higher extent than that of the palladium complex.

5. Conclusions

As a summary, it can be stated that palladium catalysed hydroethoxycarbonylation of styrene in imidazolium-type ionic liquids can be carried out. Ethyl 2-phenyl-propionate and 3-phenyl-propionate with moderate to high regioselectivities can be obtained by tuning the structure of the ionic liquid. The regioselectivity of hydroalkoxycarbonylation is strongly influenced by the phosphine ligands. The application of a chelating diphosphine is favourable to the formation of the linear ester, which is the exclusive product in imidazolium-based ionic liquids possessing electron-withdrawing groups.

Acknowledgement

L.K. thanks the Hungarian Scientific Research Fund (OTKA T044800) for financial support.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071.
[2] H. Zhao, S.V. Malhotra, Aldrichim. Acta 35 (3) (2002) 75–83.
[3] C.M. Gordon, Appl. Catal. A: Gen. 222 (2001) 101.
[4] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A 182–183 (2002) 419.
[5] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157.
[6] W. Keim, Green Chem. 5 (2003) 105.
[7] E. Mizushima, T. Hayashi, M. Tanaka, Green Chem. 3 (2) (2001) 76–79, and references cited therein.
[8] Y. Chauvin, L. Mussmann, H. Olivier, European Patent, EP 776880 (1997).
[9] C.C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Organometallics 19 (2000) 3818.
[10] P. Wasserscheid, H. Waffenschmidt, J. Mol. Catal. A: Chem. 164 (2000) 61.
[11] G. Rangits, Z. Berente, T. Kégl, L. Kollár, J. Coord. Chem. 58 (10) (2005) 869.
[12] P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K.W. Kottsieper, O. Stelzer, Chem. Commun. (2001) 451.
[13] M.A. Klingshirn, S.J. P’Pool, K.H. Shaughnessy, R.D. Rogers, Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28–April 1, 2004.
[14] G. Rangits, L. Kollár, J. Mol. Catal. A: Chem. 242 (2005) 156.
[15] B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 1996.
[16] M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis vols. I–II, Wiley-VCH, Weinheim, 1998.
[17] R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994.
[18] G. Cometti, G.P. Chiusoli, J. Organomet. Chem. 236 (1982) C31.
[19] G. Consiglio, J. Organomet. Chem. 132 (1977) C26.
[20] T. Hayashi, M. Tanaka, I. Ogata, Tetrahedron Lett. (1978) 3925.
[21] H. Alper, N. Hamel, J. Am. Chem. Soc. 112 (1990) 2803.
[22] G. Consiglio, P. Pino, Adv. Chem. Ser. 196 (1982) 371.
[23] B. El Ali, M. Fettouchi, J. Mol. Catal. A: Chem. 182 (1) (2002) 195.
[24] S. Tőrös, B. Heil, G. Gálik, Z. Tuba, Tetrahedron Lett. 33 (1992) 3667.
[25] E. Nagy, B. Heil, S. Tőrös, J. Mol. Catal. A: Chem. 143 (1999) 229.
[26] C. Benedek, L. Prókai, S. Tőrös, B. Heil, J. Mol. Catal. A: Chem. 165 (2001) 15.
[27] L.L. da Rocha, A.O. Dias, E.N. dos Santos, R. Augusti, E. Gusevskaya, J. Mol. Catal. 132 (1998) 213.
[28] R. Naigre, T. Chenal, I. Cipres, Ph. Kalck, J.C. Duran, J. Vaissermann, J. Organomet. Chem. 480 (1994) 91.
[29] G. Lenoble, M. Urrutigoity, Ph. Kalck, J. Organomet. Chem. 643 (2002) 12.
[30] D.H. Nguyen, F. Hebrard, J. Duran, A. Polo, M. Urrutigoity, Ph. Kalck, Appl. Organomet. Chem. 19 (2005) 30–34.
[31] J.G. Huddleston, H.D. Willauer, R.P. Swatlowski, A.E. Visser, R.D. Rogers, Chem. Commun. (1998) 1765.

[32] E. Guillet, D. Imbert, R. Scopelliti, J.C.G. Bunzli, Chem. Mater. 16 (2004) 4063.
[33] J.-Z. Yang, Y. Jin, W.-G. Xu, Q.-G. Zhang, S.-L. Zang, Fluid Phase Equilib. 227 (2005) 41.
[34] F.R. Hartley, Organomet. Chem. Rev. A 6 (1970) 119.
[35] M. Egashira, S. Okada, J.-I. Yamaki, D.A. Dri, F. Bonadies, B. Scorsati, J. Power Sources 138 (2004) 240.
[36] L. Kollár, P. Sándor, G. Szalontai, J. Mol. Catal. 67 (1991) 191.
[37] G. Rangits, G. Petőcz, Z. Berente, L. Kollár, Inorg. Chim. Acta 353 (2003) 301.
[38] G. Cavinato, L. Toniolo, C. Botteghi, S. Gladiali, J. Organomet. Chem. 229 (1982) 93.
[39] S. Oi, M. Nomura, T. Aiko, Y. Inoue, J. Mol. Catal. A: Chem. 115 (1997) 289.
[40] S. Kunsági-Máté, B. Lemli, G. Nagy, L. Kollár, J. Phys. Chem. B 108 (26) (2004) 9246.