# Effect of imidazolinium salts bearing hydroxy substituents on palladium-catalysed Suzuki–Miyaura and Heck coupling reactions

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**Abstract:** Palladium anionic complexes with imidazolinium cations containing hydroxyl substituents were used as catalyst precursors in the Suzuki–Miyaura and the Heck cross-coupling. High activity of anionic complexes was noted in the Suzuki–Miyaura reaction of 2-bromotoluene with phenylboronic acid at 40 °C in 2-propanol and a 2-propanol/water mixture using conventional heating or microwaves. Similarly, bromonaphtalene and iodonaphtalene reacted efficiently with naphtylboronic acid and 4-methylnaphtylboronic acid. A remarkably lower activity was noted when anionic palladium complexes were employed in the Heck coupling of 2,3-dihydrofuran with iodobenzene. An increase in conversion in the Heck reaction was achieved when $Pd(OAc)_2$ was used as a catalyst precursor together with imidazolinium salts as co-catalysts.

## Introduction

Ionic liquids have found many applications in C-C cross-coupling reactions as components of biphasic systems offering efficient separation of the catalyst from the reaction products. It has also been evidenced that ionic liquids are not inert solvents but they can react with transition metal catalysts forming new complexes with reactivities different from those of the starting compounds [1-6].

Considering the possible functions of ionic liquids as ligands in transition metal complexes, two main groups of metal complexes should be mentioned, namely anionic type complexes of the formula $[IL]_2[MX_4]$ (IL = imidazolium or pyridinium cation) [7-11] and carbene-type complexes containing NHC ligands (NHC = N-heterocyclic carbene) formed by the deprotonation of the IL cation [12-18]. Palladium complexes with NHC ligands are very well known in the literature as very efficient catalysts for C-C cross-coupling reactions. In particular, the application of palladium complexes bearing bulky NHC ligands is considered very advantageous [13]. However, quite good results have also been obtained in catalysis for palladium complexes with smaller NHC ligands [19, 20]. Carbene complexes containing chiral imidazolinium-type ligands have found application in the asymmetric arylation of 2-methyl-1-tetralone [21] and in the enantioselective addition of $Et_2Zn$ to aldehydes [22].

In contrast, anionic complexes of the type $[IL]_2[MX_4]$ have been used as catalyst precursors only scarcely. For example, they have exhibited very good catalytic activity in the Suzuki–Miyaura reaction [8, 23] at 40 °C. In this reaction, an effect of the imidazolium cation on the reaction course has been observed. The high catalytic activity of these complexes in the carbonylation of iodobenzene has been reported. Recently, very good results have also been obtained with anionic complexes in the oxidative Heck coupling [24].

The studies presented in this paper aimed at the synthesis of new anionic palladium complexes with imidazolinium cations and their application as catalysts for Suzuki–Miyaura and Heck reactions. The imidazolinium salts used in these studies were obtained from chiral amino alcohols in enantiopure form. Therefore, it was interesting to check not only their catalytic efficiency but also their possible asymmetric induction in the presence of chiral imidazolinium cations introduced to the reaction system.

## Results and discussion

### 1. Imidazolinium ionic liquids and palladium complexes

The imidazolinium salts used in the present studies were obtained from chiral amino alcohols according to the literature methods.

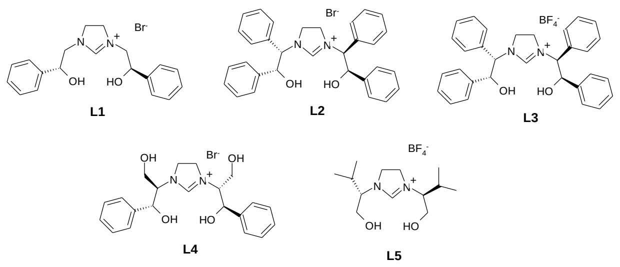

**Figure 1**. Imidazolinium ionic liquids.

Three of them, L1, L2, and L4, were used for the synthesis of new palladium anionic complexes in reaction with $PdCl_2(cod)$. The composition of the palladium complexes, $[IL]_2[PdCl_2Br_2]$ (IL = imidazolinium cation), was confirmed by spectroscopic methods. The presence of imidazolinium cations was evidenced by $^1H$ NMR spectra, in which a signal at ca. 8-9 ppm is characteristic of the proton bonded to the C2 atom of the imidazolinium ring located between two N atoms (Table 1). The data collected in Table 1 indicated the shift of some signals as a result of complex formation. For example, in the $^1H$ NMR spectrum of complex Pd-L1, the signal of the OCHPh proton is shifted downfield by 0.66 ppm. Similarly, the signals of $CH_2$ groups of the imidazoline ring are shifted by 0.22 and 0.5 ppm. Analogous effects were also observed in the $^1H$ NMR spectra of complexes Pd-L2 and Pd-L4. Thus, the coordination shifts in the spectrum of Pd-L2 are in the range of 0.14–0.17 ppm upfield. The biggest coordination shift in the spectrum of Pd-L4 was 0.26 ppm for the

$OCH_2$ signal. In general, the changes observed in $^1H$ NMR spectra as a result of palladium complex formation were relatively small because imidazolinium cations were not directly bonded to palladium. However, the changes observed in $^1H$ NMR spectra could be explained by the formation of hydrogen bonds with halide ligands coordinated to palladium.

Besides conventional heating, microwaves (MW) were also used as an alternative energy source. The results presented in Table 2 confirm the very good catalytic activity of the studied complexes, which produced 80–90% of 2-methylbiphenyl after 1 h. The best result, 94% conversion, was noted for complex Pd-L2 in 2-propanol. Similar conversion, 93%, was obtained with complex Pd-L4 in a 2-propanol/water mixture under MW irradiation.

**Table 1.** $^1H$ NMR data of ligands and palladium complexes.

| | **L1**<br>δ ppm | **Pd-L1**<br>δ ppm | | **L2**<br>δ ppm | **Pd-L2**<br>δ ppm | | **L4**<br>δ ppm | **Pd-L4**<br>δ ppm |
|---|---|---|---|---|---|---|---|---|
| NC**H**N | 8.50 | 8.49 | NC**H**N | 8.59 | 8.33 | NC**H**N | 8.39 | 8.39 |
| Ar-**H** | 7.46 – 7.38 | 7.46 – 7.37 | Ar-**H** | 7.41 – 7.25 | 7.25 – 7.14 | Ar-**H** | 7.33 – 7.16 | 7.34 – 7.17 |
| $\mathrm{NC\mathbf{H}_2}$ | 5.97 | 5.95 | NC**HPh** | 6.02 | 5.88 | $\mathrm{HOC\mathbf{H}_2}$ | 4.99 | 5.25 |
| OC**H**Ph | 4.92 | 5.58 | OC**H**Ph | 5.36 | 5.19 | HOC**H**Ph | 4.86 | 4.88 |
| O**H** | 4.91 | 4.93 | O**H** | 4.92 | 4.77 | $\mathrm{C\mathbf{H}_2}$ | 4.05 | 4.08 |
| $\mathrm{C\mathbf{H}_2}$ | 3.83 | 4.05 | $\mathrm{C\mathbf{H}_2}$ | 3.83 | 3.69 | $\mathrm{C\mathbf{H}_2}$ | 3.90 | 3.91 |
| $\mathrm{C\mathbf{H}_2}$ | 3.45 | 3.95 | $\mathrm{C\mathbf{H}_2}$ | 3.46 | 3.32 | NC**H** | 3.81 | 3.85 |

## 2. Suzuki-Miyaura reaction

The Suzuki–Miyaura reaction was carried out at 40 °C in 2-propanol or a 2-propanol/water mixture.

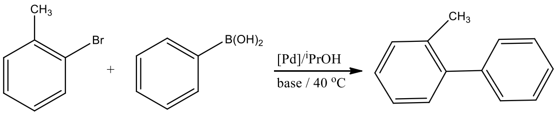

**Figure 2**. Scheme of Suzuki-Miyaura reaction.

**Table 2.** Results of Suzuki – Miyaura reaction of 2-bromotoluene with phenylboronic acid.

| complex | Pd-L2 | | | | Pd-L1 | | Pd-L4 | |
|---|---|---|---|---|---|---|---|---|
| solvent | 2-propanol | 2-propanol /water | 2-propanol MW | 2-propanol /water MW | 2-propanol | 2-propanol /water MW | 2-propanol | 2-propanol /water MW |
| conversion* (%) | 93.6 | 71.6 | 90.0 | 90.8 | 70.0 | 88.0 | 87.6 | 93.0 |

* conversion is equivalent to GC yield

Next, Suzuki–Miyaura reactions were carried out for naphthalene substrates according to the Figure 3.

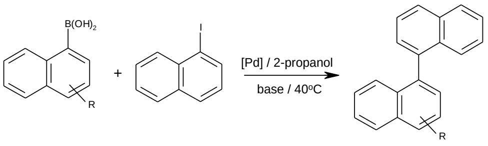

**Figure 3**. Scheme of Suzuki-Miyaura reaction.

In these experiments naphthaleneboronic acid and 4-methyl-1-naphtaleneboronic acid were coupled with bromonaphtalene and iodonaphtalene in the presence of complex Pd-L2 as catalyst.

The results were quite satisfactory considering the mild reaction conditions (40 $^oC$) and a relatively short time (2 h) (Table 3).

**Table 3**. Conversion[*] (%) obtained in Suzuki-Miyaura reaction (Fig. 3).

| naphtaleneboronic acid | | 4-methyl-1-naphtalenoboronic acid | |
|---|---|---|---|
| iodonaphtalene | bromonaphtalene | iodonaphtalene | bromonaphtalene |
| 88.7 | 87.8 | 98.5 | 87.5 |

[*] conversion is equivalent to GC yield

For further catalytic tests, the Heck coupling of iodobenzene with 2,3-dihydrofuran was selected. This reaction in most cases produced three products as a result of double bond isomerization in the arylated product.

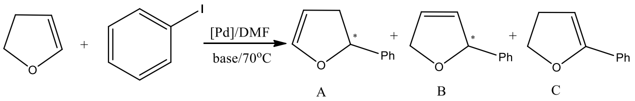

**Figure 4**. Heck reaction of 2,3-dihydrofuran

In our previous studies we obtained product A with high enantioselectivity in the presence of a palladium catalyst modified with prolinate salt, [$Bu_4N$][PRO] [25]. In this case, the chiral anion appeared very efficient in asymmetric induction. In the present studies, a positive effect of the chiral imidazolinium cation on the reaction course was expected.

Surprisingly, the studied complexes showed a very low catalytic efficiency under the conditions applied, illustrated by a conversion below 10%. Only complex Pd-L4 formed 11.5% of the coupling product. In fact, the observed reactivity was very similar to that presented by an unmodified $PdCl_2$(cod) complex.

**Table 4.** Results of the Heck reaction of iodobenzene and 2,3-dihydrofuran.

| Precursor | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | A | B | C |
| $PdCl_2$(cod) | 5.5 | 4.7 | - | 0.8 |
| Pd-L1 | 6.1 | 4.7 | - | 1.4 |
| Pd-L2 | 6.6 | 5.2 | - | 1.4 |
| Pd-L4 | 11.5 | 7.5 | - | 4.0 |

Better results were obtained when the catalytic system was changed and $Pd(OAc)_2$ was used as a catalyst together with a 2- or 4-fold excess of the imidazolinium ionic liquid.

**Table 5**. Results of Heck reaction of iodobenzene and 2,3-dihydrofuran – an effect of imidazolinium ionic liquids.

| $Pd(OAc)_2$ + | [IL]/[Pd] | conversion (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | A | B | C |
| - | - | 22.1 | 18.3 | 3 | 0.8 |
| L1 | 2 | 32.6 | 26.3 | 3.4 | 2.9 |
| | 4 | 37.0 | 29.9 | 3.7 | 3.4 |
| L2 | 2 | 26.2 | 21.8 | 2.4 | 2 |
| | 4 | 27 | 22.4 | 2.2 | 2.4 |
| L3 | 2 | 36.5 | 28.9 | 4.2 | 3.2 |
| | 4 | 34.5 | 27.3 | 3.5 | 2.7 |
| L4 | 2 | 31.5 | 25.6 | 3.3 | 2.6 |
| | 4 | 38.5 | 30.4 | 3.4 | 4.7 |
| L5 | 2 | 20.4 | 16.4 | 2.6 | 1.4 |
| | 4 | 23.8 | 19.1 | 3 | 1.7 |

In most cases, the addition of an ionic liquid resulted in the increase of iodobenzene conversion above the 22% obtained with $Pd(OAc)_2$ alone.

The best result, about 40% conversion, was obtained in the presence of L4. A similar effect was also noted for L1.

Interestingly, different conversions of ca. 10% were observed for L2 and L3, containing the same cation and bromide and tetrafluoroborate anions. The weakly coordinating anion $BF_4^-$ gave better results. Thus, an effect of the anion can be noted here.

When the influence of the cation is analysed, the lowest efficiency of L5 as an additive should be mentioned. In fact, the presence of L5 in the catalytic system had no influence on the reaction course, and the conversion remained at ca. 20%, practically the same as for unmodified $Pd(OAc)_2$.

Unfortunately, the *ee* values in these reactions were below 2%, indicating that these chiral cations were not efficient in the generation of asymmetric induction.

## Experimental

General procedure for the preparation of imidazolinium halides [21, 22]

An amino alcohol and dibromoethane in the molar ratio of 2:1 were placed in an autoclave under nitrogen atmosphere. The autoclave was closed and the reaction mixture was heated at 100 °C for 16 h. The resulting solid product was dissolved in water, washed with $CHCl_3$, and treated with 2 M NaOH water solution to pH = 13. The product, a bis-amino alcohol, was extracted with $CHCl_3$ (3 x 30 mL). The combined extracts were dried on $MgSO_4$ for 48 h. After that time, the bis-amino alcohol was placed in the autoclave under nitrogen atmosphere, and triethoxymethane and $NH_4X$ salt were added in the molar ratio of 1:1:1. The autoclave was closed and heated at 120 °C for 16 h. The resulting imidazolinium salt was washed with n-hexane (10 mL) and diethyl ether (10 mL) and dried.

L1: 1,3-bis((*R*)-2-hydroxy-2-phenylethyl)imidazolinium bromide

Yield: 73%
$[\alpha]^{26}_D = -42.9$ (DMSO c = 0.0177 M)
found (calc. for $C_{19}H_{23}N_2O_2Br$): %C 57.26 (58.32), %N 7.80 (7.16), %H 6.56 (5.92)
$^1H$ NMR (500 MHz, $[D_6]$DMSO): $\delta = 8.50$ (s, 1H, NCHN), 7.46 – 7.8 (m, 10H, Ar-H), 5.97 (d, 4H,$NCH_2$), 4.92 (m, 2H, OCHPh), 4.91 (d, 2H, OH), 3.83 (m 2H,$CH_2$), 3.45 (m 2H $CH_2$) ppm.

$^{13}$C NMR (125 MHz, [D$_6$]DMSO) δ = 158.2; 140.8; 128.1; 128.0; 127.9; 127.4; 127.0 125.6; 69.0; 54.6; 49.4 ppm.

L2: 1,3-bis-((*1S,2R*)-2-hydroxy-1,2-diphenylethyl) imidazolinium bromide

Yield: 84%.
$[\alpha]^{25}_{D}$ = - 32.2 (MeOH c = 0,01802 M)
Found (calc. for $C_{31}H_{31}N_2O_2Br$): %C = 69.63 (68.51), %N = 5.5 (5.15), %H = 5.9 (5.75)
$^{1}$H NMR (500 MHz, [D$_6$]DMSO): δ = 8.59 (s, 1H, NCHN), 7.41 – 7.25 (m, 20H, Ar-H), 6.02 (d, 2H,NCHPh), 5.36 (dd, 2H, OCHPh), 4.92 (d, 2H, OH), 3.83 (m 2H,CH$_2$), 3.46 (m 2H CH$_2$) ppm.
$^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 156.2; 141.5; 134.0; 129.1; 128.4; 128.2; 128.1; 127.7; 126.5; 71.4; 66.0; 46.7 ppm.

L3: 1,3-bis-((*1S,2R*)-2-hydroxy-1,2-diphenylethyl) imidazolinium tetrafluoroborate

Yield: 80%
$[\alpha]^{25}_{D}$ = - 23.7 (MeOH c = 0,01856 M)
Found (calc. for $C_{31}H_{31}N_2O_2BF_4$: %C = 67.01 (67.65), %N = 6.25 (5.09), %H = 6.09 (5.68)
$^{1}$H NMR (500 MHz, [D$_6$]DMSO): δ = 8.36 (s, 1H, NCHN), 7.40 – 7.20 (m, 20H, Ar-H), 5.96 (d, 2H,NCHPh), 5.25 (m, 2H, OCHPh), 4.85 (d, 2H, OH), 3.80 (m, 2H,CH$_2$), 3.40 (m, 2H,CH$_2$) ppm.

$^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 126.1; 141.6; 134.1; 129.0; 128.5; 128.1; 128.0; 127.6; 126.5; 71.4; 65.9; 46.6 ppm.

L4: 1,3-bis((*1R,2R*)-1,3-dihydroxy-1-phenylprop-2-yl)imidazolinium bromide

Yield: 88 %.
$[\alpha]^{22}_{D}$ = - 116.2 (acetone c = 0.37 M)
Found (calc. for $C_{21}H_{27}N_2O_4Br$: %C = 51.01 (55.88), %N = 6.92 (6.21), %H = 6.80 (6.03)
$^{1}$H NMR (500 MHz, [D$_6$]-acetone) δ = 8.39 (s, 1H, NCHN), 7.33 – 7.16 (m, 10H, Ar-H), 4.99 (m, 2H, HOCH$_2$), 4.86 (d, 2H, HOCHPh), 4.05 (m, 2H,CH$_2$), 3.90 (m, 2H CH$_2$), 3.81 (m, 2H, NCH), 3.60 – 3.36 (m, 6H) ppm.
$^{13}$C NMR (125 MHz, [D$_6$]-acetone) δ = 160.1; 142.6; 129.4; 128.7; 127.5; 71.0; 68.0; 59.5; 48.1 ppm

L5: 1,3-bis((*S*)-1-hydroxy-3-methyl-butan-2-yl)imidazolinium tetrafluoroborate
Yield: 85%.
$[\alpha]^{25,5}_{D}$ = - 1.3 (acetone c = 0.04658 M)
Found (calc. for $C_{13}H_{27}N_2O_2BF_4$: %C = 46.23 (47.29), %N = 9.70 (8.48), %H = 9.06 (8.24)
$^{1}$H NMR (500 MHz, [D$_6$]-acetone) δ = 8.26 (s, 1H, NCHN), 4.03 – 3.93 (m, 4H, CH$_2$ – CH$_2$), 3.75 – 3.72 (dd, 4H, CH$_2$), 3.63 – 3.59 (m, 2H, OH), 3.41 – 3.37 (td, 2H, NCH$^{i}$Pr), 1.93 – 1.86 (m, 2H,CH(CH$_3$)$_2$), 1.1 – 0.8 (m, 12H CH$_3$) ppm.

$^{13}$C NMR (125 MHz, [D$_6$]-acetone) δ = 158.8; 65.8; 58.2; 45.0; 26.6; 19.5; 18.9 ppm.
MS (ESI$^+$): m/z = 243,2

General procedure for the preparation of palladium complexes [IL]$_2$[PdX$_4$] [8]
PdCl$_2$(cod) and ionic liquid ([IL]X) in the molar ratio 1:2 were placed in a Schlenk flask. CH$_3$CN (10 mL) was added and the mixture was stirred at 50°C for 1h. During that time reactants were dissolved and solution color changed from yellow to dark-red. Solvent was removed under vacuo, small amount of Et$_2$O was added and evacuation of liquids was repeated. The resulted oil was left for 18 h forming brown solid.

Pd-L1: bis(1,3-bis((*R*)-2-hydroxy-2-phenylethyl)-imidazolinium) dibromodichloropalladate
Yield: 77%
Found (calc. for: [C$_{19}$H$_{23}$N$_2$O$_2$]$_2$PdBr$_2$Cl$_2$: %C = 50.65 (47.55), %N = 5.31 (5.84), %H = 6.14 (4.83)
$^1$H NMR (500 MHz, [D$_6$]DMSO) δ = 8.49 (s, 1H, NCHN), 7.46 – 7.37 (m, 10H, Ar-H), 5.95 (d, 4H,NCH$_2$), 5.58 (d, 2H, OH), 4.93 (m, 2H,OCHPh), 4.05 (m 2H,CH$_2$), 3.95 (m 2H CH$_2$) ppm.
$^{13}$C NMR (125 MHz, [D$_6$]DMSO) δ = 158.3; 140.8; 128.6; 128.2; 127.9; 127.5; 125.7 125.6; 69.2; 54.5; 49.4 ppm.

Pd-L2: bis(1,3-bis-((*1S,2R*)-2-hydroxy-1,2-diphenylethyl)-imidazolinium dibromodichloropalladate
Yield: 81%
Found (calc. for [C$_{31}$H$_{31}$N$_2$O$_2$]$_2$PdBr$_2$Cl$_2$: %C = 59.24 (58.90), %N = 4.54 (4.43), %H = 5.30 (4.94)
$^1$H NMR (500 MHz, [D$_6$]DMSO) δ = 8.33 (s, 1H, NCHN), 7.25 – 7.14 (m, 20H, Ar-H), 5.88 (d, 2H,NCHPh), 5.19 (dd, 2H, OCHPh), 4.77 (d, 2H, OH), 3.69 (m 2H,CH$_2$), 3.32 (m 2H CH$_2$) ppm.
$^{13}$C NMR (125 MHz, [D$_6$]DMSO) δ = 156.2; 141.5; 134.0; 129.1; 128.4; 128.3; 128.2; 127.7; 126.5; 71.5; 66.0; 46.6 ppm.

Pd-L4: bis(1,3-bis((*1R,2R*)-1,3-dihydroxy-1-phenyloprop-2-yl)imidazolinium dibromodichloropalladate
Yield: 80%
Found (calc. for [C$_{21}$H$_{27}$N$_2$O$_4$]$_2$PdBr$_2$Cl$_2$: %C = 45.84 (46.71), %N = 5.64 (5.19), %H = 6.26 (5.34)
$^1$H NMR (500 MHz, [D$_6$]-acetone) δ = 8.39 (s, 1H, NCHN), 7.34 – 7.17 (m, 10H, Ar-H), 5.25 (m, 2H, HOCH$_2$), 4.88 (d, 2H, HOCHPh), 4.08 (m, 2H,CH$_2$), 3.91 (m, 2H CH$_2$), 3.85 (m, 2H, NCH), 3.62 – 3.45 (m, 6H) ppm.
$^{13}$C NMR (125 MHz, [D$_6$]-acetone) δ = 160.1; 142.6; 129.3; 128.7; 127.5; 71.2; 67.9; 59.8; 48.1 ppm

## Suzuki–Miyaura reactions

The Suzuki–Miyaura reaction was carried out in a 50 mL Schlenk flask. The solid substrates: base, KOH (0.067 g, 1.2 mmol), and phenylboronic acid (0.184 g, 1.5 mmol), were weighed and placed in the Schlenk flask. Next, 5 mL of the solvent (2-propanol or 2-propanol/water) and 2-bromotoluene (0.12 mL, 1 mmol) were added. The flask was closed and heated to 40 °C. The palladium complex (0.01 mmol) was added, and the reaction mixture was stirred at 40 °C for 2 h or for 1 h when MW heating was used. After the specified reaction time, the flask was cooled down, and the organic products were extracted with 10 mL of n-hexane, and 0.076 mL of dodecane was added as an internal standard. The organic products were analysed using the GC-MS method (instrument HP 5890 II with a capillary column).

The Suzuki–Miyaura reaction was performed as above using naphtaleneboronic acid (0.2579 g, 1.5 mmol) or 4-methyl-1-naphtaleneboronic acid (0.279 g, 1.5 mmol).

## Heck reaction

The Heck reaction was carried out in a 50 mL Schlenk tube under nitrogen atmosphere. The solid substrates: base, $K_2CO_3$ (0.6 g, 4.34 mmol), catalyst precursor $Pd(OAc)_2$ (0.008 g, 0.0356 mmol, 1 mol %), and the ionic liquid $[IL]^+X^-$, were weighed and placed in the Schlenk tube. Next, DMF (6 mL), and the liquid reactants: PhI (0.4 mL, 3.57 mmol), DHF (0.7 mL, 8.59 mmol) were added. The reactor was closed with a rubber plug, and the reaction mixture was stirred at 70 °C for 2 h. After that time, the tube was cooled down, $H_2O$ (5 mL) was added, and the organic products were extracted with diethyl ether (3 x 5 mL). Mesitylene (0.15 mL) was added to the extract as an internal standard, and a GC-MS analysis was performed.

Heck reactions with Pd-L1, Pd-L2 and Pd-L4 were performed as above without ionic liquid, using 1 mol% of palladium complexes.

## Conclusions

It was shown that palladium anionic complexes with bulky imidazolinium cations containing hydroxy substituents efficiently catalysed Suzuki–Miyaura reaction under mild conditions. Good yields were obtained in reactions with phenyl boronic acid and with naphtylboronic acid.

The same palladium complexes showed only a very low activity in the Heck coupling of 2,3-dihydrofuran with iodobenzene. However, a conversion increase was achieved in this reaction when $Pd(OAc)_2$ was applied together with imidazolinium ionic liquids. The most efficient were systems containing L1 and L4, whereas only a very small effect was noted for L5. Unfortunately, only racemic mixtures of arylated products were formed in all reactions.

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