Transition Met Chem (2012) 37:183–188
DOI 10.1007/s11243-011-9573-0

The synthesis and catalytic properties of imidazolinium salts and their palladium(II) complexes

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Received: 2 November 2011 / Accepted: 9 December 2011 / Published online: 21 December 2011

Abstract Three 1,3-dialkylimidazolinium chloride salts and their palladium(II) complexes have been synthesized and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The catalytic activities of the 1,3-dialkylimidazolinium chloride salts and their complexes in the Heck and Suzuki coupling reactions were investigated.

Introduction

The isolation of the first stable *N*-heterocyclic carbenes (NHCs) by Arduengo and their successful use as ancillary ligands for the preparation of various metal complexes initiated an intensive search for new *N*-heterocyclic carbene ligands and their metal complexes [1–6]. The strong electron donating ability of NHC ligands combined with their easily varied steric demands has made them attractive ligands in a variety of metal-catalyzed processes. NHC metal complexes of palladium, ruthenium, rhodium, platinum and nickel have been shown to act as effective pre-catalysts in many C–C and C–N arylation, olefin metathesis, hydrogenation and hydrosilylation reactions [7–15]. Among these systems, the palladium-catalyzed Heck and Suzuki reactions are perhaps the most widespread and successful applications of carbene complexes. These reactions have been used extensively for the synthesis of a range of useful stilbene and biaryl derivatives [16–23]. Palladium(II) carbene complexes can be easily prepared by the reaction of palladium(II) acetate with two equivalents of a suitable azolium salt [24] or the use of silver carbene complexes as carben transfer reagents [25–28]. Generally, silver NHC complexes are prepared by the treatment of silver oxide, silver carbonate or silver acetate with the corresponding azolium salts [29–31].

Palladium complexes with 1,3-di[(R)-1-phenylethyl] imidazolin-2-ylidene ligands were described by Herrmann, who showed that the NHC-palladium complexes were effective as catalysts for Heck, Suzuki and Stille reactions [32, 33]. *N*,*N*′-dibenzhydrybenzimidazolium-palladium systems have been reported to be suitable for the Suzuki coupling of aryl bromides with arylboronic acid [34]. Palladium complexes with benzimidazolylidene ligands bearing an (*S*)-α-methylbenzyl group on the N atom were reported by Page et al. [35]. Recently, Kündig et al. [36] showed that chiral NHC-palladium complexes are well suited as catalysts for the asymmetric synthesis of fused indolines.

We have previously reported the synthesis of *N*-heterocyclic carbene derivative ligands and their palladium(II) carbene complexes and investigated their catalytic activity in the Heck and Suzuki reactions [37–39]. Herein, we report the synthesis of new imidazoliniums *3a–c* (Scheme 1) and their palladium(II) complexes *4a–c* (Scheme 2), and their application in Heck and Suzuki cross-coupling using aryl halides.

Experimental

All reactions for the preparation of 1,3-dialkylimidazolinium salts *3a–c* and their palladium complexes were carried

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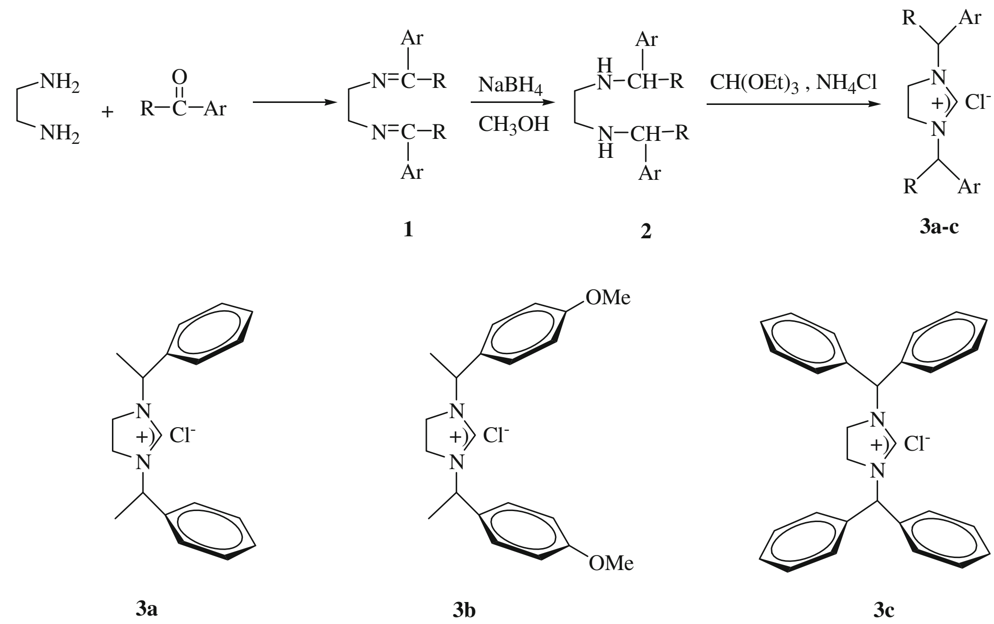
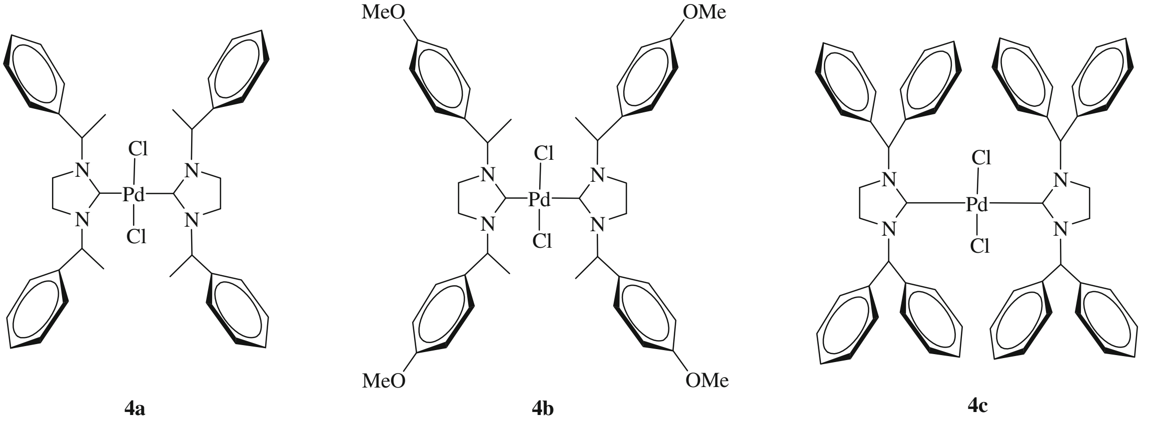


Scheme 1 Synthesis of 1,3-dialkylimidazolinium salts



Scheme 2 Palladium–carbene complexes reported in this work

out under argon using standard Schlenk-type flasks. Heck and Suzuki coupling reactions were carried out in air. All reagents were purchased from Aldrich (Turkey). All ^{1}H and ^{13}C n.m.r. spectra were recorded in $CDCl_3$ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hertz. FTIR spectra were recorded as KBr pellets in the range 400–4,000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC spectra were recorded on an Agilent 6890 N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at Inönü University Research Center.

1,3-Di(1-phenylethyl)imidazolinium chloride, (*3a*)

To a solution of 1,2-bis(1-phenylethylamino)ethane (2.00 g, 7.46 mmol), $CH(OEt)_3$ (3 mL, 18.06 mmol) and NH_4Cl (0.40 g, 7.46 mmol) were added, and reaction mixture was heated for 12 h at 110 °C. The white precipitate was filtered off and recrystallized from ethanol.

Yield: 1.90 g, 81%, m.p. 143–145 °C. I.r., $\nu_{(NCN)}$: 1,644 cm^{-1}. (Found: C, 72.4; H, 7.4; N, 8.9. $C_{19}H_{23}N_2Cl$ calcd.: C, 72.5; H, 7.3; N, 8.9%). ^{1}H-n.m.r. ($CDCl_3$): δ 1.77 (d, 6H, $J = 6.6$ Hz, $CH(CH_3)C_6H_5$); 5.30 (quart., 2H, $J = 6.6$ Hz, $CH(CH_3)C_6H_5$); 3.53 and 3,71 (m, 4H, NCH_2CH_2N); 7.28 and 7.42 (m, 10H, Ar–*H*); 10.65 (s, 1H, NC*H*N). ^{13}C-n.m.r. ($CDCl_3$): δ 19.1 ($CH(CH_3)C_6H_5$); 45.5 (NCH_2CH_2N); 57.6 ($CH(CH_3)C_6H_5$); 127.1; 128.8; 128.9; 129.2; 137.3 and 137.4 (Ar–*C*); 156.8 (N*C*HN).

1,3-Di[1-(4-methoxyphenyl)ethyl]imidazolinium chloride, (*3b*)

This compound was prepared in the same way as *3a* from 1,2-bis[1-(4-methoxyphenyl)ethylamino]ethane (1.91 g, 5.82 mmol), $CH(OEt)_3$ (3 mL, 18.06 mmol) and NH_4Cl (0.31 g, 5.80 mmol) to give white crystals of *3b*.

Yield: 1.61 g, 74%, m.p. 147–150 °C. I.r., $\nu_{(NCN)}$: 1,639 cm^{-1}. (Found: C, 67.4; H, 7.2; N, 7.4. $C_{21}H_{27}N_2O_2Cl$ calcd.: C, 67.3; H, 7.2; N, 7.5%). ^{1}H-n.m.r. ($CDCl_3$): 1.70 (d, 6H, $J = 6.9$ Hz, $CH(CH_3)C_6H_4(OMe)$-4); 3.49 and 3,69 (m, 4H, NCH_2CH_2N); 3.77 (s, 6H, $CH(CH_3)C_6H_4(OMe)$-4); 5.26 (quart., 2H, $J = 6.9$ Hz, $CH(CH_3)C_6H_4(OMe)$-4); 6.86 and 7.36 (d, 8H, $J = 8.1$ Hz and $J = 7.5$ Hz, $CH(CH_3)C_6H_4(OMe)$-4); δ 10.60 (s, 1H, NCHN). ^{13}C-n.m.r. ($CDCl_3$): δ 19.0 ($CH(CH_3)C_6H_4(OMe)$-4); 45.2 (NCH_2CH_2N); 55.3 $CH(CH_3)C_6H_4(OMe)$-4); 57.1 ($CH(CH_3)C_6H_4(OMe)$-4); 114.0; 114.5; 128.1; 128,5; 129.3; 129.4 and 156.7 (Ar–C); 159.8 (NCHN).

1,3-Dibenzhydrylimidazolinium chloride, (*3c*)

This compound was prepared in the same way as *3a* from 1,2-bis(dibenzhydrylamino)ethane (2.00 g, 5.09 mmol), $CH(OEt)_3$ (3 mL, 18.06 mmol) and NH_4Cl (0.27 g, 5.05 mmol) to give white crystals of *3c*.

Yield: 1.92 g, 86%, m.p. 197–198 °C. I.r., $\nu_{(NCN)}$: 1,631 cm^{-1}. (Found: C, 79.4; H, 6.2; N, 6.4. $C_{29}H_{27}N_2Cl$ calcd.: C, 79.4; H, 6.1; N, 6.4%). ^{1}H-n.m.r. ($CDCl_3$): δ 4,07 (s, 4H, NCH_2CH_2N); 6.42 (s, 2H, $CH(C_6H_5)_2$); 7.10 and 7.41 (m, 20H, Ar–H); 8.24 (s, 1H, NCHN). ^{13}C-n.m.r. ($CDCl_3$): δ 48.7 (NCH_2CH_2N); 66.3 ($CH(C_6H_5)_2$); 128.4; 128,9; 129.3 and 135.6 (Ar–C); 158.6 (NCHN).

Bis[1,3-di(1-phenylethyl)imidazolin-2-ylidene]dichloropalladium(II), (*4a*)

A stirred DMSO solution (10 mL) of 1,3-di(1-phenylethyl)imidazolinium chloride (0.34 g, 1.08 mmol) and $Pd(OAc)_2$ (0.12 g, 0.54 mmol) was heated at 60 °C for 3 h and then at 110 °C for a further 2 h. The volatile compounds were removed under vacuum and the precipitate was filtered off, then washed twice with THF. Recrystallization from CH_2Cl_2–Et_2O was carried out. The crystals were washed with diethyl ether (3 × 15 mL) and dried under vacuum.

Yield: 0.32 g, 80%, m.p. 282 °C. I.r., $\nu_{(NCN)}$: 1,510 cm^{-1}. (Found: C, 62.2; H, 5.9; N, 7.7. $C_{38}H_{44}N_4PdCl_2$ calcd.: C, 62.2; H, 6.0; N, 7.6%). ^{1}H-n.m.r. ($CDCl_3$): δ 1.77 and 1.85 (m, 12H, $CH(CH_3)C_6H_5$); 2.84 and 3,43 (m, 8H, NCH_2CH_2N); 6.70 (quart., 4H, $J = 6.6$ Hz, $CH(CH_3)C_6H_5$); 7.24 and 7.70 (m, 20H, Ar–H). ^{13}C-n.m.r. ($CDCl_3$): δ 16.52 ($CH(CH_3)C_6H_5$); 41.8 (NCH_2CH_2N); 56.9 ($CH(CH_3)C_6H_5$); 127.5; 128.0; 128,5; 139.4; 139.5; 139.6; 139.7 and 139.8 (Ar–C); 197.7 ($C_{carbene}$).

Bis[1,3-di(1-(4-methoxyphenyl)ethyl)imidazolin-2-ylidene]dichloropalladium(II), (*4b*)

Compound *4b* was prepared in a similar way to *4a*, from 1,3-di[1-(4-methoxyphenyl)ethyl]imidazolinium chloride (0.40 g, 1.08 mmol) and $Pd(OAc)_2$ (0.12 g, 0.54 mmol).

Yield: 0.32 g, 71%, m.p. 218 °C. I.r., $\nu_{(NCN)}$: 1,515 cm^{-1}. (Found: C, 59.1; H, 6.0; N, 6.6. $C_{42}H_{52}N_4O_4PdCl_2$ calcd.: C, 59.0; H, 6.1; N, 6.5%). ^{1}H-n.m.r. ($CDCl_3$): δ1.73 and 1.81 (m, 12H, $CH(CH_3)C_6H_4(OMe)$-4); 2.84 and 3,39 (m, 8H, NCH_2CH_2N); 3.78 and 3.82 (m, 12H, $CH(CH_3)C_6H_4(OMe)$-4); 6.63 and 6.67 (m, 4H, $CH(CH_3)C_6H_4(OMe)$-4); 6.85 and 7.59 (m, 16H, $CH(CH_3)C_6H_4(OMe)$-4). ^{13}C-n.m.r. ($CDCl_3$): δ 16.8 ($CH(CH_3)C_6H_4(OMe)$-4); 42.6 (NCH_2CH_2N); 55.2 $CH(CH_3)C_6H_4(OMe)$-4); 56.3 ($CH(CH_3)C_6H_4(OMe)$-4); 113.7; 129.1; 131,7; 131.8; 131.9 and 158.9 (Ar–C); 197.2 ($C_{carbene}$).

Bis(1,3-dibenzhydrylimidazolin-2-ylidene)dichloropalladium(II), (*4c*)

Compound *4c* was prepared in a similar way to *4a*, from 1,3-dibenzhydrylimidazolinium chloride (0.47 g, 1.08 mmol) and $Pd(OAc)_2$ (0.12 g, 0.54 mmol).

Yield: 0.44 g, 84%, m.p. 306 °C. I.r., $\nu_{(NCN)}$: 1,504 cm^{-1}. (Found: C, 71.0; H, 5.4; N, 5.8. $C_{58}H_{52}N_4PdCl_2$ calcd.: C, 70.9; H, 5.3; N, 5.7%). ^{1}H-n.m.r. ($CDCl_3$): δ 3,29 (s, 8H, NCH_2CH_2N); 7.21 and 7.30 (m, 40H, Ar–H); 7.60 (s, 4H, $CH(C_6H_5)_2$). ^{13}C-n.m.r. ($CDCl_3$): δ 45.1 (NCH_2CH_2N); 65.6 ($CH(C_6H_5)_2$); 127.3; 128,1; 128.4; 129.0; 129.4 and 138.5 (Ar–C); 201.6 ($C_{carbene}$).

General procedure for the Heck-type coupling reactions

$Pd(OAc)_2$ (1.0 mmol %), salts *3a–c* (2.0 mmol %) or *4a–c* (1.5 mmol %), aryl bromide (1.0 mmol), styrene (1.5 mmol), Cs_2CO_3 (2.0 mmol) and dioxane (3 mL) were placed in a Schlenk tube under argon, and mixture was heated at 80 °C for 8 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, filtered through a pad of silica gel with copious washings, concentrated and purified by flash chromatography on silica gel. Purity of compounds was checked by NMR and GC. The yields are based on aryl bromide.

General procedure for the Suzuki-type coupling reactions

$Pd(OAc)_2$ (1.0 mmol %), salts *3a–c* (2.0 mmol %) or *4a–c* (1.5 mmol %), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol) and water (3 mL)-DMF (3 mL) were placed in a Schlenk tube under argon, and the mixture was heated at 80 °C for 5 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, filtered through a pad of silica gel with copious washings, concentrated and purified by flash chromatography on silica gel. Purity of the compounds was checked by NMR and GC. The yields are based on aryl chloride.

Results and discussion

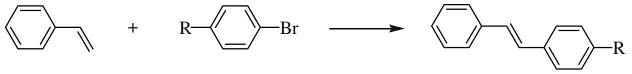
Saturated imidazolinium salts can be obtained by alkylation of dihydroimidazole and by cyclization reactions of *N,N′*-dialkyl-1,2-diaminoethane dihydro halides with triethyl orthoformate [40, 41]. The general route for the preparation of 1,3-dialkylimidazolinium salts is shown in Scheme 1. The condensation of 1,2-diaminoethane with ketones gave the corresponding imines *1* in high yields. Reduction of these imines with $NaBH_4$ in methanol leads to *N,N′*-dialkylethane-1,2-diamines *2*. The symmetrical 1,3-dialkylimidazolinium salts *3* were easily synthesized in high yields by reaction of 2 with triethyl orthoformate and ammonium chloride. After purification, the 1,3-dialkylimidazolinium salts *3a–c* were obtained in good yields (74–86%). The salts are soluble in the common polar solvents such as ethanol and dichloromethane and are stable under air and in the presence of moisture. The structures of *3* were deduced from their spectroscopic data and elemental analyses (see Experimental section). The ^{13}C n.m.r. spectra of *3a–c* show sharp high-field signals at 156.8 ppm (*3a*), 159.8 ppm (*3b*) and 158.6 ppm (*3c*) for the imino carbon. The ^{1}H n.m.r. spectra of the imidazolinium salts further supported the assigned structures. The C(2)-H resonances were observed as sharp singlets at δ 10.65, 10.60 and 8.24 ppm for *3a–c*, respectively. The IR data for *3a–c* clearly indicate the presence of the –C=N- group with a $\nu_{(C=N)}$ vibration at 1,644, 1,639 and 1,631 cm^{-1} for *3a–c*, respectively. These NMR and IR values are similar to those reported for other 1,3-dialkylimidazolinium salts [42].

The palladium complexes *4a–c* were prepared by reaction of the 1,3-dialkylimidazolinium chlorides with $Pd(OAc)_2$ in DMSO (Scheme 2). The complexes were characterized by ^{1}H and ^{13}C n.m.r. spectroscopy, FTIR and elemental analysis. They show a characteristic $\upsilon_{(NCN)}$ band at 1,510, 1,515 and 1,504 cm^{-1} for *4a*, *4b* and *4c*, respectively. In the ^{1}H n.m.r. and ^{13}C n.m.r. spectra, the absence of signals for the acidic proton (2-C*H*) at 10.65, 10.60, 8.24 ppm and imidazolinium carbon (2-*C*H) at 156.8, 159.8, 158.6 ppm showed the formation of the expected palladium complexes. The ^{13}C n.m.r. chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that $C_{carbene}$ is substantially deshielded. The values of δ ($^{13}C_{carbene}$) are 197.7, 197.2 and 201.6 ppm for *4a*, *4b* and *4c,* respectively, and are similar to those found in other carbene complexes. These new complexes show typical spectroscopic signatures, which are in line with those recently reported for *trans*-$[PdCl_2(NHC)_2]$ complexes [43–46].

The Pd-catalyzed Heck reaction between aryl halides and alkenes is a very useful method to prepare styrene derivatives. The Heck coupling reactions of styrene with aryl bromides to form alkenes were undertaken with $Pd(OAc)_2$/*3a–c* or the complexes *4a–c* as catalysts in the presence of a base in air. The performance of such metal catalyzed cross-coupling reactions depends on a number of factors such as base, solvent, time, temperature, ligands and nature of the catalyst. The choices of base and solvent are usually important in achieving an efficient cross-coupling reaction. For optimization of the reaction conditions, the $Pd(OAc)_2$-catalyzed cross-coupling of bromobenzene with styrene was employed as a model reaction using ligand *3a* at 80 °C, and the commonly used bases Cs_2CO_3, K_2CO_3, K_3PO_4 and *t*-BuOK were tested. The coupling of aryl bromides and styrene was carried out in dioxane (3 mL) with 1 mol % $Pd(OAc)_2$, 2 mol % *3a–c* or 1.5 mol % *4a–c* and 2 equivalents of Cs_2CO_3 for 8 h at 80 °C. Reaction of *p*-bromoacetophenone, *p*-bromotoluene, *p*-bromobenzaldehyde, *p*-bromoanisol and bromobenzene with styrene gave high yields (77–99%) using this catalytic system, and the coupling reaction did not occur in the absence of salt or palladium complex. The results are summarized in table 1.

Of the five different aryl bromides, those bearing electron-withdrawing groups react with styrene to give the coupled products in excellent yields (Table 1, entries 2, 8, 13, 21 and 26). The imidazolinium salt bearing a methoxy group on the aromatic ring (*3b*) was the most effective in catalyzing these reactions. Similarly, the palladium carbene complex (*4b*) derived from (*3b*) showed better catalytic activity than the other complexes. Hence, the electron donating *p*-methoxy substituent increased the catalytic activity. As expected, in situ reaction of the azolium salts with palladium led to significantly better results than the use of the preformed palladium complexes. Recently, the Suzuki reactions of aryl chlorides catalyzed by palladium–NHC complexes have been extensively studied and these catalysts are very effective for Suzuki coupling of aryl chlorides in dioxane at 80 °C, with Cs_2CO_3 as base [45–47]. The Suzuki coupling of phenylboronic acid with aryl chlorides to form biaryls was therefore studied with $Pd(OAc)_2$/*3a–c* or *4a–c* as catalysts. Similar reaction conditions were employed as for the Suzuki reactions, with Cs_2CO_3 as the base. The coupling reactions of aryl chlorides and phenylboronic acid were carried out in DMF/H_2O

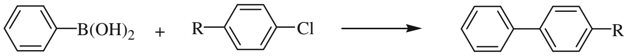
Table 1 The Heck coupling reaction of aryl bromides with styrene



Entry	R	Catalyst	Yield (%)
1	$COCH_3$	3a	98
2	$COCH_3$	3b	99
3	$COCH_3$	3c	99
4	$COCH_3$	4a	92
5	$COCH_3$	4b	95
6	$COCH_3$	4c	94
7	CH_3	3a	85
8	CH_3	3b	87
9	CH_3	3c	84
10	CH_3	4a	79
11	CH_3	4b	81
12	CH_3	4c	77
13	CHO	3a	98
14	CHO	3b	97
15	CHO	3c	95
16	CHO	4a	90
17	CHO	4b	93
18	CHO	4c	90
19	OCH_3	3a	83
20	OCH_3	3b	85
21	OCH_3	3c	86
22	OCH_3	4a	80
23	OCH_3	4b	84
24	OCH_3	4c	83
25	H	3a	93
26	H	3b	97
27	H	3c	96
28	H	4a	89
29	H	4b	93
30	H	4c	90

1.0 mmol of *p*-R-C_6H_4Br, 1.5 mmol of styrene, 2 mmol Cs_2CO_3, 1 mmol % $Pd(OAc)_2$, 2 mmol % *3a–c* or 1.5 mmol % *4a–c*, dioxane (3 mL), 80 °C, 8 h; purity of compounds checked by n.m.r., and yields are based on aryl halide; All reactions were monitored by TLC

Table 2 The Suzuki coupling reaction of aryl chlorides with phenylboronic acid



Entry	R	Catalyst	Yield (%)
1	$COCH_3$	3a	98
2	$COCH_3$	3b	97
3	$COCH_3$	3c	95
4	$COCH_3$	4a	96
5	$COCH_3$	4b	95
6	$COCH_3$	4c	91
7	CH_3	3a	81
8	CH_3	3b	84
9	CH_3	3c	80
10	CH_3	4a	75
11	CH_3	4b	79
12	CH_3	4c	77
13	CHO	3a	94
14	CHO	3b	96
15	CHO	3c	94
16	CHO	4a	90
17	CHO	4b	93
18	CHO	4c	91
19	OCH_3	3a	83
20	OCH_3	3b	85
21	OCH_3	3c	80
22	OCH_3	4a	74
23	OCH_3	4b	79
24	OCH_3	4c	76
25	H	3a	87
26	H	3b	91
27	H	3c	90
28	H	4a	83
29	H	4b	86
30	H	4c	82

1.0 mmol of *p*-R-C_6H_4Cl, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1 mmol % $Pd(OAc)_2$, 2 mmol % *3a–c*, or 1.5 mmol % *4a–c*, DMF/H_2O (3/3 mL), 80 °C, 5 h; purity of compounds checked by n.m.r. and yields are based on aryl chloride; all reactions were monitored by TLC

(3:3 mL) with 1.0 mol % $Pd(OAc)_2$, 2.0 mol % *3a–c* or 1,5 mol % *4a–c* and 2 equivalents of Cs_2CO_3 for 5 h at 80 °C. We chose the coupling of 4-chloroacetophenone with phenylboronic acid for these experiments. The results are summarized in Table 2.

These salts proved to be effective catalyst precursors for the coupling of inactivated, activated and deactivated chlorides. These catalysts give similar activities to those of other Pd-NHC complexes [34, 47] or in situ prepared $Pd(OAc)_2$/NHC systems [42, 48, 49] and are in agreement with other reports [33, 50].

Conclusion

In summary, three 1,3-dialkylimidazolinium chloride salts *3a–c* and their palladium complexes *4a–c* were prepared and their catalytic activities in the Heck and Suzuki coupling reactions were investigated. The in situ catalytic system proved to be more effective than the preformed palladium complex in both the Heck reactions of aryl bromides with styrene and the Suzuki reactions of aryl chlorides with phenylboronic acid. More detailed investigations focusing on imidazolidin-2-ylidene and benzimidazolin-2-ylidene substituent effects, functional group tolerance and catalytic activities in other coupling reactions are ongoing.

Acknowledgment This research was supported by the Adiyaman University Research Fund (FEFBAP 2009-7).

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