Turkish Journal of Chemistry
http://journals.tubitak.gov.tr/chem/
Research Article

Turk J Chem
(2015) 39: 281 – 289

doi:10.3906/kim-1408-33

The synthesis of 1,3-dialkyl-4-methylimidazolinium salts and their application in palladium catalyzed Heck coupling reactions

Murat YİĞİT[1,*], Gülin BAYAM[1], Beyhan YİĞİT[1], İsmail ÖZDEMİR[2]
[1]Department of Chemistry, Faculty of Science and Arts, Adıyaman University, Adıyaman, Turkey
[2]Department of Chemistry, Faculty of Science and Arts, İnönü University, Malatya, Turkey

Received: 13.08.2014 • **Accepted/Published Online:** 25.11.2014 • **Printed:** 30.04.2015

Abstract: Seven novel 1,3-dialkyl-4-methylimidazolinium chloride salts **3a**–**g** were prepared as precursors of N-heterocyclic carbenes by reacting N,N'-alkyl-1,2-diaminopropane, triethyl orthoformate, and ammonium chloride. The salts were characterized spectroscopically. The in situ prepared palladium complexes derived from the imidazolinium salts and palladium acetate were used as catalyst in Heck coupling reactions between aryl bromides and styrene. The corresponding Heck products were obtained in good yields.

Key words: Heck reaction, imidazolinium salt, palladium, N-heterocyclic carbene, catalyst

1. Introduction

The palladium-catalyzed coupling reaction of aryl or vinyl halides with various alkenes, the Mizoroki–Heck reaction, is an extremely valuable method for carbon–carbon bond formation.[1–4] This powerful reaction has been widely used in the synthesis of important functionalized compounds. Traditionally, Heck reactions of aryl halides with alkenes are carried out using various palladium phosphine catalysts.[5–11] In recent years, a great deal of attention has been paid to the design and synthesis of palladium complexes that can be used as an alternate to air-sensitive and toxic palladium phosphine catalysts. Thus, N-heterocyclic carbenes, Schiff bases, amines, oxazolines, pyridines, hydroxyquinolines, hydrazones, tetrazoles, and N-phenylurea have been used as ligands in Heck and Suzuki coupling reactions.[12–25] N-heterocyclic carbenes have received a great deal of attention as alternatives to phosphine-based ligands in palladium-catalyzed coupling reactions.[26–28] Both metal/NHC complexes and metal/imidazolium salts systems can be used in a number of coupling reactions.[29–36] The imidazolinium and benzimidazolium salts are an effective ligand precursor for palladium-catalyzed carbon–carbon bond forming reactions.[37–41] These salts are readily prepared by alkylation of dihydroimidazole and by cyclization reactions of a secondary bisamine with triethyl orthoformate in the presence of ammonium salt or N,N'-dialkyl-1,2-diaminoethane dihydro halides with triethyl orthoformate.[42–44]

The number, nature, and position of the substituents on the nitrogen atoms or NHC ring have tremendous influence on the rate of catalyzed reactions and stability of complexes of NHCs against heat, moisture, and air. Therefore, NHC ligands can be easily modified by changing the substituents on the nitrogen atoms or carbene ring. Thousands of free and metal-coordinated N-heterocyclic carbenes have been reported, but NHCs bearing different groups on the backbone of the carbenes are relatively rare.[45–56]

*Correspondence: myigit@adiyaman.edu.tr

Herein we report the synthesis and characterization of new imidazolinium chloride salts bearing benzyl substituents on nitrogen atoms and methyl-substituent on the 4-position as N-heterocyclic carbene precursors and the use of the in situ generated catalytic system composed of $Pd(OAc)_2$ and these salts for Heck cross-coupling of aryl bromides with styrene.

2. Results and discussion

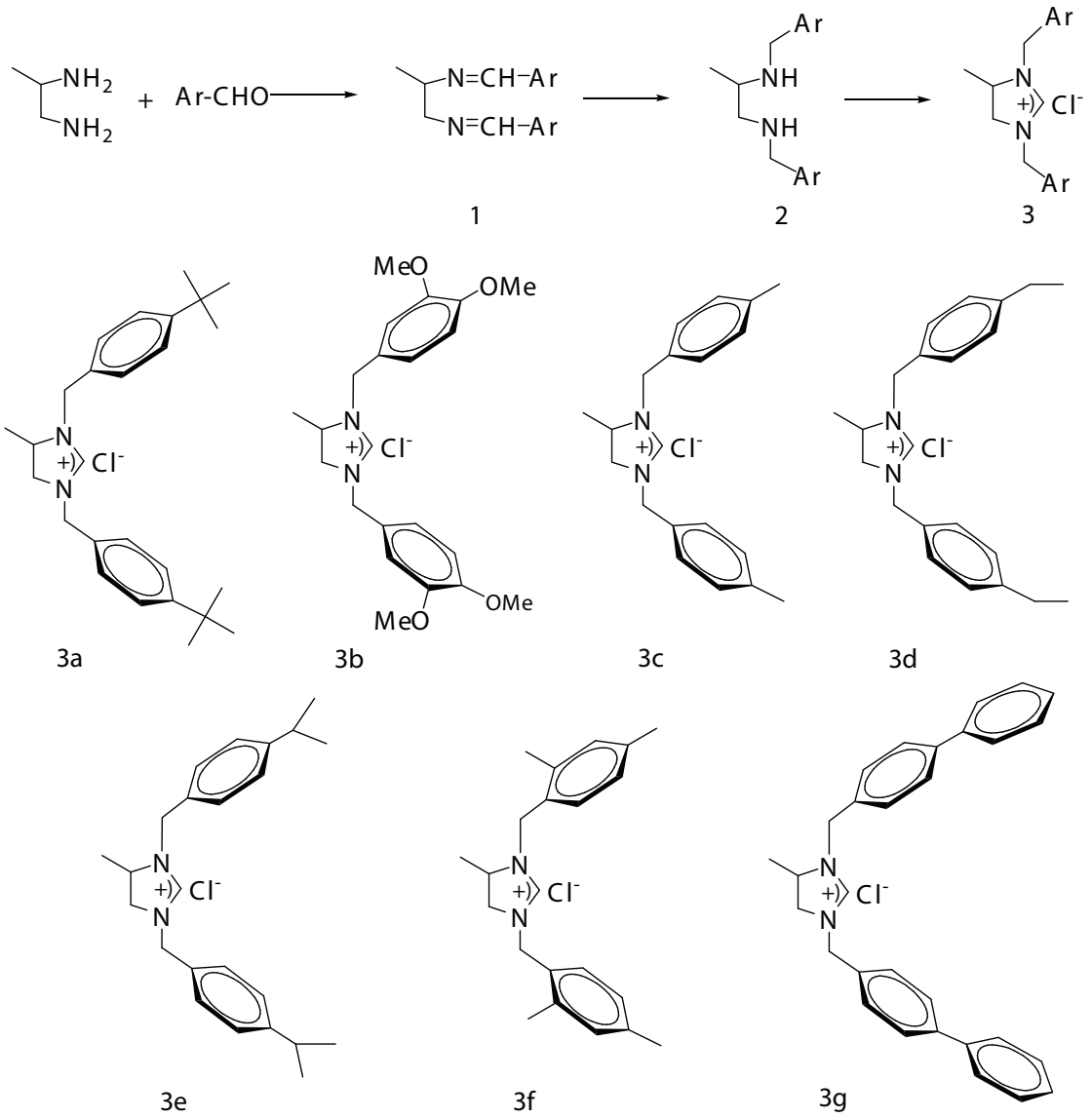
2.1. Synthesis and characterization of imidazolinium salts, 3a–g

As shown in the Scheme, the synthesis of the symmetrical 1,3-dialkyl-4-methylimidazolinium salts **3** was achieved in three steps. The condensation reaction of 1,2-diaminopropane with two molar equivalents of the aromatic aldehydes in ethanol gave the corresponding Schiff bases **1**, which were subsequently treated with sodium borohydride in methanol at room temperature to produce the corresponding benzylic diamines **2**. The cyclization of N,N'-dialkylpropane-1,2-diamines leading to the symmetrical 1,3-dialkyl-4-methylimidazolinium salts **3** was carried out with triethyl ortoformate and ammonium chloride. After purification, pure products were obtained as colorless solids in good yields (76%–89%). The salts are soluble in the common polar solvents and are air- and moisture-stable both in the solid state and in solution. The structures of the 1,3-dialkyl-4-methylimidazolinium salts have been fully identified by ^1H and ^{13}C NMR spectroscopy, FTIR, and elemental analysis. All results were in agreement with the proposed structure. They show a characteristic $\upsilon_{(NCN)}$ band at 1556–1638 cm^{-1}. NMR spectroscopic data confirm the formation of **3a**–**g**. The ^{13}C NMR resonances of the imine groups of **3a**–**g** appeared at the range 158.23–158.70 ppm as single signals, while the resonances of the benzylic groups were observed at the range 54.34–56.50 ppm as two signals. In the ^1H NMR spectrum, the resonances of the C(2)-H for the imidazolinium salts were observed as sharp singlets at δ = 10.55, 10.65, 10.57, 10.56, 10.63, 10.55, and 10.74 ppm for **3a**–**g**, respectively. These NMR and IR values were similar to those reported for 1,3-dialkylimidazolinium salts.[39,48]

2.2. Heck reaction

The catalytic activities of 1,3-dialky-4-methylimidazolinium salts in a Heck reaction involving the cross-coupling of aryl bromides with styrene were investigated. Reactions were performed in air and without any additive. Initially, the Heck reaction of bromobenzene with styrene was chosen as the model reaction. Various parameters including catalyst loading, bases, solvent, temperature, and time were screened to optimize the reaction conditions. After the preliminary test of various bases and solvents, we chose K_2CO_3 as a base and DMF-water as a solvent, which are most commonly used in the Heck reaction. The optimized conditions were applied to Heck reactions between styrene with various aryl bromides (*p*-bromoacetophenone, *p*-bromotoluene, *p*-bromobenzaldehyde, *p*-bromoanisol, and bromobenzene). Control experiments showed that palladium acetate in the absence of 1,3-dialky-4-methylimidazolinium salts was inactive under these conditions for the Heck reaction. However, the activated (electron-poor) and deactivated (electron-rich) aryl chlorides basically do not react under these reaction conditions, and yields are less than 5%.

Both the electron-rich, electron-deficient, and unsubstituted aryl bromides gave desirable Heck products in high yields using this catalytic system (Table). Of the five different aryl bromides, as expected, good yields were obtained in the reactions of the styrene and aryl bromide with electron-withdrawing substituent such as COMe and CHO (Table, entries 1–7 and 15–21). Use of aryl bromide bearing electron-donating groups such as Me and OMe slightly decreased the yields under the same conditions (Table, entries 8–14 and 22–28). Among the tested salts, the imidazolinium salt bearing methoxy groups on the aromatic ring (**3b**) was the most effective



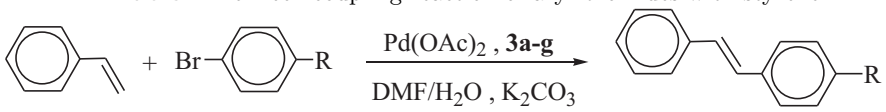
Scheme. Synthesis of 1,3-dialkyl-4-methylimidazolinium salts.

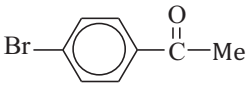
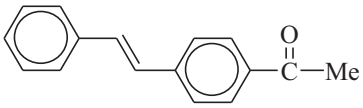
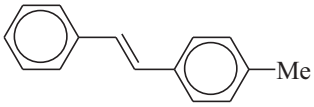
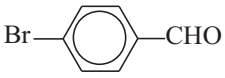
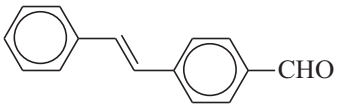
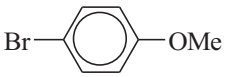
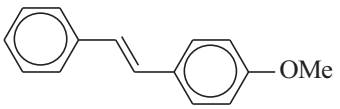
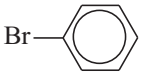
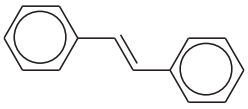
for catalytic activity in Heck coupling reactions. These catalysts give similar activities to those of other in situ prepared $Pd(OAc)_2$/NHC systems.[38,39]

3. Experimental

All reactions for the preparation of 1,3-dialkyl-4-methylimidazolinium salts **3a**–**g** were carried out under argon using standard Schlenk-type flasks. Heck coupling reactions were carried out in air. 1,2-Diaminopropane, aldehydes, and other reagents were purchased from Aldrich Chemical Co. (Turkey). All ^{1}H and ^{13}C NMR 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) are in hertz. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC was performed by GC-FID on an Agilent 6890N gas chromatograph equipped with

Table. The Heck coupling reaction of aryl bromides with styrene.



Entry	Aryl bromide	Product	Catalyst	Yield[a,b,c] (%)
1			**3a**	98
2			**3b**	99
3			**3c**	94
4			**3d**	97
5			**3e**	96
6			**3f**	95
7			**3g**	93
8			**3a**	86
9			**3b**	88
10			**3c**	82
11			**3d**	85
12			**3e**	86
13			**3f**	83
14			**3g**	81
15			**3a**	90
16			**3b**	91
17			**3c**	85
18			**3d**	87
19			**3e**	89
20			**3f**	88
21			**3g**	86
22			**3a**	82
23			**3b**	84
24			**3c**	79
25			**3d**	78
26			**3e**	80
27			**3f**	76
28			**3g**	75
29			**3a**	94
30			**3b**	95
31			**3c**	89
32			**3d**	92
33			**3e**	93
34			**3f**	93
35			**3g**	91

[a] Reaction conditions: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2.0 mmol of K_2CO_3, 1.0 mmol of $Pd(OAc)_2$, 2.0 mol% **3a**–**g**. [b] Purity of compounds is checked by NMR and isolated yields are based on aryl bromide. [c] All reactions were monitored by GC.

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 are uncorrected. Elemental analyses were performed at İnönü University research center.

3.1. General procedure for the preparation of Schiff bases

A solution of the aldehydes (10 mmol) and 1,2-diaminopropane (5 mmol) in ethanol (30 mL) was heated under reflux for 3 h; then volatiles were removed under vacuum to dryness. The crude product was crystallized from toluene/hexane.

3.2. General procedure for the preparation of diamines

Sodium borohydride (15 mmol) was added portionwise over 30 min to a solution of diimine (10 mmol) in MeOH (30 mL) at room temperature and the reaction mixture was stirred for 12 h and then heated under reflux for 1 h. Upon cooling to room temperature, the mixture was treated with 1 N HCl and the organic phase was extracted with CH_2Cl_2 (3 $\times$ 30 mL). After drying over $MgSO_4$ and evaporation, the crude product was crystallized from toluene/hexane.

3.3. General procedure for the preparation of imidazolinium salts (3a–g)

A mixture of N,N'-alkyl-1,2-diaminopropane (6.2 mmol), NH_4Cl (6.2 mmol), and triethyl orthoformate (10 mL) was heated for 12 h at 110 °C. Upon cooling to room temperature, colorless crystals were obtained. The crystals were filtered, washed with diethyl ether (3 $\times$ 15 mL), and dried under vacuum. The crude product was recrystallized from $EtOH/Et_2O$.

3.3.1. 1,3-Bis(4-tert-butylbenzyl)-4-methylimidazolinium chloride, (3a)

Yield, 2.28 g, 89%; mp: 248–250 °C. IR: $\nu_{(N=CH)}$ = 1634.80 cm^{-1}. Anal. Calc. for $C_{26}H_{37}N_2Cl$: C, 75.63; H, 8.96; N, 6.78. Found: C, 75.84; H, 8.67; N, 6.57%. ^{1}H NMR (δ, $CDCl_3$): 1.27 (s, 18H, $CH_2C_6H_4C(CH_3)_3$-*p*), 1.32 (d, 3H, J= 6.3 Hz, $NCH(CH_3)CH_2N$), 3.24–3.31 (m, 1H, $NCH(CH_3)CH_2N$), 3.81–3.88 (m, 1H, $NCH(CH_3)CH_2N$), 4.02–4.06 (m, 1H, $NCH(CH_3)CH_2N$), 4.40 (d, 1H, J= 15.6 Hz, CH_2Ar), 4.83 (s, 2H, CH_2Ar), 5.22 (d, 1H, J= 15.6 Hz, CH_2Ar), 7.28 (d, 4H, J= 7.8 Hz, $CH_2C_6H_4C(CH_3)_3$-*p*), 7.36 (d, 4H, J= 7.8 Hz, $CH_2C_6H_4C(CH_3)_3$-*p*), 10.55 (s, 1H, 2-C*H*). ^{13}C NMR (δ , $CDCl_3$): 18.18 ($NCH(CH_3)CH_2N$), 31.22(×2) ($CH_2C_6H_4C(CH_3)_3$-*p*), 34.62(×2) ($CH_2C_6H_4C(CH_3)_3$-*p*), 49.17 ($NCH(CH_3)CH_2N$), 51.98 ($NCH(CH_3)CH_2N$), 54.45, 55.20 (CH_2Ar), 126.13, 126.17, 128.42, 128.55, 129.48, 129.54, 152.06(x2) ($CH_2C_6H_4C(CH_3)_3$-*p*), 158.33 (2-*C*H).

3.3.2. 1,3-Bis(3,4-dimethoxybenzyl)-4-methylimidazolinium chloride, (3b)

Yield, 2.14 g, 82%; mp: 181–183 °C. IR: $\nu_{(N=CH)}$ = 1638.70 cm^{-1}. Anal. Calc. for $C_{22}H_{29}N_2O_4Cl$: C, 62.78; H, 6.89; N, 6.65. Found: C, 62.57; H, 6.93; N 6.69%. ^{1}H NMR (δ,$CDCl_3$): 1.34 (d, 3H, J= 6.6 Hz, $NCH(CH_3)CH_2N$), 3.22–3.29 (m, 1H, $NCH(CH_3)CH_2N$), 3.82–3.86 (m, 1H, $NCH(CH_3)CH_2N$), 3.87 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-3,4), 3.95 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-3,4), 4.04–4.10 (m, 1H, $NCH(CH_3)CH_2N$), 4.38 (d, 1H, J= 14.6 Hz, CH_2Ar), 4.76 (d, 1H, J= 14.6 Hz, CH_2Ar), 4.82 (d, 1H, J= 14.6 Hz, CH_2Ar), 5.17 (d,

1H, J = 14.6 Hz, CH_2Ar), 6.80–6.90 (m, 4H, $CH_2C_6H_3(OCH_3)_2$-3,4), 7.13–7.17 (m, 2H, $CH_2C_6H_3(OCH_3)_2$-3,4), 10.65 (s, 1H, 2-CH). ^{13}C NMR (δ, $CDCl_3$): 18.27 (NCH(CH_3)CH_2N), 49.23 (NCH(CH_3)CH_2N), 52.08 (NCH(CH_3)CH_2N), 54.30(×2), 55.21, 55.87 ($CH_2C_6H_3(OCH_3)_2$-3,4), 56.40, 56.50 (CH_2Ar), 111.13(×2), 111.94, 112.03(×2), 121.21, 121.40(×2), 124.99, 125.00, 149.50, 149.67 ($CH_2C_6H_3(OCH_3)_2$-3,4), 158.23 (2-CH).

3.3.3. 1,3-Bis(4-methylbenzyl)-4-methylimidazolinium chloride, (3c)

Yield, 1.58 g, 78%; mp: 112–115 °C. IR: $\nu_{(N=CH)}$ = 1556 cm^{-1}. Anal. Calc. for $C_{20}H_{25}N_2Cl$: C, 73.05; H, 7.61; N, 8.52. Found: C, 73.34; H, 7.82; N, 8.56%. ^{1}H NMR (δ,$CDCl_3$): 1.27 (d, 3H, J = 6.3 Hz, NCH(CH_3)CH_2N), 2.30 (s, 6H, $CH_2C_6H_4$(CH_3)-p), 3.20–3.26 (m, 1H, NCH(CH_3)CH_2N), 3.78–3.85 (m, 1H, NCH(CH_3)CH_2N), 3.96–4.05 (m, 1H, NCH(CH_3)CH_2N), 4.38 (d, 1H, J = 14.7 Hz, CH_2Ar), 4.76 (d, 1H, J = 14.7 Hz, CH_2Ar), 4.85 (d, 1H, J = 14.7 Hz, CH_2Ar), 5.18 (d, 1H, J = 14.7 Hz, CH_2Ar), 7.14 (d, 4H, J = 7.8 Hz, $CH_2C_6H_4CH_3$-p), 7.24 (d, 4H, J = 7.8 Hz, $CH_2C_6H_4CH_3$-p), 10.57 (s, 1H, 2-CH). ^{13}C NMR (δ, $CDCl_3$): 18.20 (NCH(CH_3)CH_2N), 21.15(×2) ($CH_2C_6H_4(CH_3)$-p), 49.31 (NCH(CH_3)CH_2N), 52.02 (NCH(CH_3)CH_2N), 54.34, 55.20 (CH_2Ar), 128.61, 128.78, 129.48, 129.51, 129.88, 129.91, 138.91, 138.93 ($CH_2C_6H_4CH_3$-p), 158.27 (2-CH).

3.3.4. 1,3-Bis(4-ethylbenzyl)-4-methylimidazolinium chloride, (3d)

Yield, 1.68 g, 76%; mp: 129–135 °C. IR: $\nu_{(N=CH)}$ = 1634.92 cm^{-1}. Anal. Calc. for $C_{22}H_{29}N_2Cl$: C, 74.22; H, 8.13; N, 7.85. Found: C, 74.45; H, 8.36; N, 7.96%. ^{1}H NMR (δ,$CDCl_3$): 1.18 (t, 6H, J = 7.3 Hz, $CH_2C_6H_4CH_2CH_3$-p), 1.28 (d, 3H, J = 6.3 Hz, NCH(CH_3)CH_2N), 2.58 (q, 4H, J = 7.5 Hz, $CH_2C_6H_4CH_2CH_3$-p), 3.15–3.28 (m, 1H, NCH(CH_3)CH_2N), 3.74–3.87 (m, 1H, NCH(CH_3)CH_2N), 3.97–4.06 (m, 1H, NCH(CH_3)CH_2N), 4.37 (d, 1H, J = 14.2 Hz, CH_2Ar), 4.76 (d, 1H, J = 14.2 Hz, CH_2Ar), 4.85 (d, 1H, J = 14.2 Hz, CH_2Ar), 5.18 (d, 1H, J = 14.2 Hz, CH_2Ar), 7.15 (d, 4H, J = 6.9 Hz, $CH_2C_6H_4CH_2CH_3$-p), 7.27 (d, 4H, J = 6.9 Hz, $CH_2C_6H_4CH_2CH_3$-p), 10.56 (s, 1H, 2-CH). ^{13}C NMR (δ, $CDCl_3$): 15.37(×2) ($CH_2C_6H_4CH_2CH_3$-p), 18.19 (NCH(CH_3)CH_2N), 21.05(×2) ($CH_2C_6H_4CH_2CH_3$-p), 49.33 (NCH(CH_3)CH_2N), 51.69 (NCH(CH_3)CH_2N), 54.40, 55.25 (CH_2Ar), 128.67, 128.70, 128.84, 129.80, 129.98, 145.14, 156.48, 158.31 ($CH_2C_6H_4CH_2CH_3$-p), 158.30 (2-CH).

3.3.5. 1,3-Bis(4-isopropylbenzyl)-4-methylimidazolinium chloride, (3e)

Yield, 1.92 g, 81%; mp: 167–169 °C. IR: $\nu_{(N=CH)}$ = 1577.31 cm^{-1}. Anal. Calc. for $C_{24}H_{33}N_2Cl$: C, 74.90; H, 8.58; N, 7.28. Found: C, 74.52; H, 8.87; N, 7.41%. ^{1}H NMR (δ,$CDCl_3$): 1.18 (d, 12H, J = 8.7 Hz, $CH_2C_6H_4CH(CH_3)_2$-p), 1.28 (d, 3H, J = 6.3 Hz, NCH(CH_3)CH_2N), 2.79–2.89 (m, 2H, $CH_2C_6H_4CH(CH_3)_2$-p), 3.22–3.29 (m, 1H, NCH(CH_3)CH_2N), 3.81–3.89 (m, 1H, NCH(CH_3)CH_2N), 3.97–4.06 (m, 1H, NCH(CH_3)CH_2N), 4.36 (d, 1H, J = 14.6 Hz, CH_2Ar), 4.76 (d, 1H, J = 14.6 Hz, CH_2Ar), 4.82 (d, 1H, J = 14.6 Hz, CH_2Ar), 5.18 (d, 1H, J = 14.6 Hz, CH_2Ar), 7.16 (d, 4H, J = 8.1 Hz, $CH_2C_6H_4CH(CH_3)_2$-p), 7.26 (d, 4H, J = 8.1 Hz, $CH_2C_6H_4CH(CH_3)_2$-p), 10.63 (s, 1H, 2-CH). ^{13}C NMR (δ, $CDCl_3$): 18.20 (NCH(CH_3)CH_2N), 23.82(×2) ($CH_2C_6H_4CH(CH_3)_2$-p), 33.79(×2) ($CH_2C_6H_4CH(CH_3)_2$-p), 49.24 (NCH(CH_3)CH_2N), 52.00 (NCH(CH_3)CH_2N), 54.42, 55.21 (CH_2Ar), 127.26, 127.30, 128.66, 128.83, 129.81, 129.85, 149.78(×2) ($CH_2C_6H_4CH(CH_3)_2$-p), 158.28 (2-CH).

3.3.6. 1,3-Bis(2,4-dimethylbenzyl)-4-methylimidazolinium chloride, (3f)

Yield, 1.83 g, 83%; mp: 210–215 °C. IR: $\nu_{(N=CH)}$ = 1575.13 cm^{-1}. Anal. Calc. for $C_{22}H_{29}N_2Cl$: C, 74.05; H, 8.13; N, 7.85. Found: C, 74.32; H, 8.47; N, 7.61%. ^{1}H NMR (δ,$CDCl_3$): 1.29 (d, 3H, J= 6.3 Hz, NCH(CH_3)CH$_2$N), 2.27 (s, 6H, CH$_2$C$_6$H$_4$(CH_3)$_2$-2,4), 2.31 (s, 6H, CH$_2$C$_6$H$_4$(CH_3)$_2$-2,4), 3.19–3.25 (m, 1H, NCH(CH$_3$)CH_2N), 3.74–3.82 (m, 1H, NCH(CH$_3$)CH_2N), 3.93–3.99 (m, 1H, NCH(CH$_3$)CH$_2$N), 4.47 (d, 1H, J= 14.9 Hz, CH_2Ar), 4.80 (d, 1H, J= 14.9 Hz, CH_2Ar), 4.92 (d, 1H, J= 14.9 Hz, CH_2Ar), 5.20 (d, 1H, J= 14.9 Hz, CH_2Ar), 6.97–7.14 (m, 6H, CH$_2$C$_6H_3$(CH$_3$)$_2$-2,4), 10.55 (s, 1H, 2-CH). ^{13}C NMR (δ, $CDCl_3$): 18.62 (NCH(*C*H$_3$)CH$_2$N), 19.27, 19.39, 21.02, 21.04 (CH$_2$C$_6$H$_3$(*C*H$_3$)$_2$-2,4), 47.65 (NCH(CH$_3$)*C*H$_2$N), 50.09 (N*C*H(CH$_3$)CH$_2$N), 54.5, 55.23 (*C*H$_2$Ar), 127.31, 127.36, 127.42(×2), 129.59, 129.80, 131.93, 132.09, 136.84, 136.87, 139.10, 139.15 (CH$_2$*C*$_6$H$_3$(CH$_3$)$_2$-2,4), 158.44 (2-*C*H).

3.3.7. 1,3-Bis(4-phenylbenzyl)-4-methylimidazolinium chloride, (3g)

Yield, 2.19 g, 77%; mp: 250–251 °C. IR: $\nu_{(N=CH)}$ = 1566.00 cm^{-1}. Anal. Calc. for $C_{30}H_{29}N_2Cl$: C, 79.55; H, 6.41; N, 6.18. Found: C, 79.36; H, 6.21; N, 6.32%. ^{1}H NMR (δ, $CDCl_3$): 1.34 (d, 3H, J= 6.3 Hz, NCH(CH_3)CH$_2$N), 3.30–3.37 (m, 1H, NCH(CH$_3$)CH_2N), 3.90–3.98 (m, 1H, NCH(CH$_3$)CH_2N), 4.08–4.17 (m, 1H, NCH(CH$_3$)CH$_2$N), 4.53 (d, 1H, J= 14.8 Hz, CH_2Ar), 4.92 (d, 1H, J= 14.8 Hz, CH_2Ar), 5.00 (d, 1H, J= 14.8 Hz, CH_2Ar), 5.32 (d, 1H, J= 14.8 Hz, CH_2Ar), 7.28–7.58 (m, 18H, CH$_2$C$_6H_4$C$_6H_5$-*p*), 10.74 (s, 1H, 2-CH). ^{13}C NMR (δ,$CDCl_3$): 18.28 (NCH(*C*H$_3$)CH$_2$N), 49.31 (NCH(CH$_3$)*C*H$_2$N), 52.01(N*C*H(CH$_3$)CH$_2$N), 54.54, 55.49 (*C*H$_2$Ar), 127.05(×2), 127.69, 127.90, 127.92, 128.87(×2), 129.17, 129.37(×2), 131.56(×2), 140.08, 140.09, 141.86, 141.89 (CH$_2$*C*$_6$H$_4$*C*$_6$H$_5$-*p*), 158.70 (2-*C*H).

3.4. General procedure for the Heck coupling reactions

Pd(OAc)$_2$ (1.0 mmol%), the appropriate 1,3-dialky-4-methylimidazolinium salt **3a**–**g** (2 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), water (3 mL), and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated at 80 °C for 2 h. At the conclusion of the reaction, the mixture was cooled, extracted with EtOAc–hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified by flash chromatography on silica gel. All reactions were monitored by GC. The purity of the compounds was checked by NMR and the yields are based on aryl bromide.

4. Conclusions

Seven 1,3-dialkyl-4-methylimidazolinium chloride salts were synthesized by cyclization reactions of N,N'-dialkylpropane-1,2-diamines with triethyl orthoformate in the presence of ammonium chloride and the use of palladium complexes generated in situ from palladium acetate, and these salts were investigated as catalysts for the Heck coupling reactions of styrene with aryl bromides in water/DMF. The corresponding coupling products were obtained in good to excellent yields. All in situ prepared palladium complexes demonstrated good catalytic activity in Heck coupling reactions. This catalytic system provides good conditions for the coupling of aryl bromides without additives such as tetrabutylammonium bromide in air.

Acknowledgment

We thank the Adıyaman University Research Fund (FEFYL 2010-0001) for its financial support of this work.

References

1. Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320–2322.
2. Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581.
3. Heck, R. F. *Palladium Reagents in Organic Synthesis,* Academic Press: London, UK, 1985.
4. Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945–2963.
5. Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10–11.
6. Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000.
7. Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923–5925.
8. Moore, L. R.; Shaughnessy, K. H. *Org. Lett.* **2004**, *6*, 225–228.
9. Ehrentraut, A.; Zapf, A.; Beller, M. *Synlett* **2000**, 1589–1592.
10. Lee, D. H.; Taher, A.; Hossain, S.; Jin, M. J. *Org. Lett.* **2011**, *13*, 5540–5543.
11. Sabounchei, S. J.; Ahmedi, M.; Panahimehr, M.; Bagherjeri, F. A.; Nasri, Z. *J. Mol. Catal. A: Chem.* **2014**, *383–384*, 249–259.
12. Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93–98.
13. Han, Y.; Huynh, H. W.; Koh, L. L. *J. Organomet. Chem.* **2007**, *692*, 3606–3613.
14. Özdemir, İ.; Yiğit, M.; Çetinkaya, E., Çetinkaya, B. *Appl. Organometal. Chem.* **2006**, *20*, 187–192.
15. Yang, W. H.; Lee, C. S.; Pal, S.; Chen, Y. N.; Hwang, W. S.; Lin, I. J. B.; Wang, J. C. *J. Organomet. Chem.* **2008**, *693*, 3729–3740.
16. Lee, C. S.; Lai, Y. B.; Lin, W. J.; Zhuang, R. R.; Hwang, W. S. *J. Organomet. Chem.* **2013**, *724*, 235–243.
17. Rao, G. K.; Kumar, A.; Singh, M. P.; Kumar, A.; Biradar, A. M.; Singh, A. K. *J. Organomet. Chem.* **2014**, *753*, 42–47.
18. Wu, K. M.; Huang, C. A.; Peng, K. F.; Chen, C. T. *Tetrahedron* **2005**, *61*, 9679–9687.
19. Lai, Y. C.; Chen, H. Y.; Hung, W. C.; Lin, C. C.; Hong, F. E. *Tetrahedron* **2005**, *61*, 9484–9489.
20. Tao, B.; Boykin, D. W. *Tetrahedron Lett.* **2003**, *44*, 7993–7996.
21. Gossage, P. A.; Jenkins, H. A.; Yadav, P. N. *Tetrahedron Lett.* **2004**, *45*, 7689–7691.
22. Buncmeiser, M. R.; Wurst, K. *J. Am. Chem. Soc.* **1999**, *121*, 11101–11107.
23. Iyer, S.; Kulkarni, G. M.; Ramesh, C. *Tetrahedron* **2004**, *60*, 2163–2172.
24. Mino, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191–2194.
25. Cui, X.; Zhou, Y.; Wang, N., Liu, L.; Guo, Q. X. *Tetrahedron Lett.* **2007**, *48*, 163–167.
26. Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181–222.
27. Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.
28. Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246.
29. Viciu, M, S.; Kelly, R. A.; Stevens, E. D.; Naud, F.; Studer, M.; Nolan, S. P. *Org. Lett.* **2003**, *5*, 1479–1482.
30. Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K. *J. Org. Chem.* **2007**, *72*, 5069–5076.
31. Trindade, A. F.; Gois, P. M. P.; Veiros, L. F.; Andre, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *J. Org. Chem.* **2008**, *73*, 4076–4086.
32. Schaub, T.; Fischer, P.; Steffen, A.; Braun, T.; Radius, U.; Mix, A. *J. Am. Chem. Soc.* **2008**, *130*, 9304–9317.
33. He, M.; Bode, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 418–419.
34. Matsumoto, Y.; Yamada, K.; Tomioka, A. *J. Org. Chem.* **2008**, *73*, 4578–4581.
35. Stauffer, S. R.; Lee, S.; Stambuli, J. F.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423–1426.

36. Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119–122.
37. Yigit, B.; Yiğit, M.; Özdemir, İ.; Çetinkaya, E. *Turk. J. Chem.* **2010**, *34*, 327–334.
38. Yiğit, B. *Transition Metal Chem.* **2012**, *37*, 183–188.
39. Özdemir, İ.; Gök, Y.; Gürbüz, N.; Çetinkaya, B. *Turk. J. Chem.* **2007**, *31*, 397–402.
40. Yigit, B.; Yiğit, M.; Özdemir, İ.; Çetinkaya, E. *Heterocycles* **2010**, *81*, 943–953.
41. Yigit, B.; Yiğit, M.; Özdemir, İ.; Çetinkaya, E. *Heterocycles* **2011**, *83*, 299–309.
42. Çetinkaya, E.; Hitchcock, P. P.; Jasim, H. A.; Lappert, M. F.; Spyropoulos, K. J. *Perkin Trans. 1.* **1992**, 561–567.
43. Saba, S.; Brescia, A.; Kaloustian, M. K. *Tetrahedron Lett.* **1991**, *32*, 5031–5034.
44. Arduengo, III, A. J.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523–14534.
45. Marshall, C.; Ward, M. F.; Harrison, W. T. A. *J. Organomet. Chem.* **2005**, *690*, 3970–3975.
46. Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596–609.
47. Corberan, R.; Sanau, M.; Peris, E. *Organometallic* **2007**, *26*, 3492–3498.
48. Yiğit, M.; Özdemir, İ.; Çetinkaya, E.; Çetinkaya, B. *Heteroatom Chem.* **2005**, *16*, 461–465.
49. Özdemir, İ.; Yiğit, M.; Çetinkaya, E.; Çetinkaya, B. *Heterocycles* **2006**, *68*, 1371–1379.
50. Yiğit, M., Özdemir, İ.; Çetinkaya, B.; Çetinkaya, E. *J. Mol. Catal. A: Chem.* **2005**, *241*, 88–92.
51. Ogle, J. W.; Zhang, J.; Reibenspies, J. H.; Abboud, K. A.; Miller, S. A. *Org. Lett.* **2008**, *10*, 3677–3680.
52. Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991–1994.
53. Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P. *J. Organomet. Chem.* **2005**, *690*, 5570–5575.
54. Türkmen, H.; Çetinkaya, B. *J. Organomet. Chem.* **2006**, *691*, 3749–3759.
55. Gülcemal, S.; Kahraman, S.; Daran, J. C.; Çetinkaya, E.; Çetinkaya, B. *J. Organomet. Chem.* **2009**, *694*, 3580–3589.
56. Rajabi, F.; Trampert, J.; Sun, Y.; Busch, M.; Brase, S.; Thiel, W. R. *J. Organomet. Chem.* **2013**, *744*, 101–107.