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Journal of Molecular Catalysis A: Chemical 209 (2004) 23–28
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Improved palladium-catalyzed coupling reactions of aryl halides using saturated *N*-heterocarbene ligands

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Received 12 May 2003; received in revised form 4 August 2003; accepted 5 August 2003

Abstract

The incorporation of saturated *N*-heterocyclic carbenes into palladium pre-catalysts gives high catalyst activity in the Suzuki coupling of aryl iodides, bromides and deactivated aryl chloride substrates, whereas the yield of the palladium catalyzed Heck reaction of deactivated aryl chlorides is negligible. The complexes were generated in the presence of $Pd(OAc)_2$ by in situ deprotonation of 1,3-dialkylimidazolinium salts LHX (**1**) which were characterized by conventional spectroscopic methods and elemental analyses.

Keywords: Palladium; Imidazolidin-2-ylidene; Aryl halides; Phenylboronic acid; Suzuki; Styrene; Heck

1. Introduction

The palladium-catalyzed reaction of aryl chlorides with arylboronic acid (the Suzuki reaction, Scheme 1a) or with alkenes (the Heck reaction, Scheme 1b) is one of the most common methods for C–C bond formation and has attracted much current interest [1,2]. The reactions are usually carried out homogeneously in the presence of a base under inert atmosphere.

The reactivity of the aryl halide component decreases drastically in the order X = I > Br > Cl and electron withdrawing substituents R are required for the chlorides to react [1–3]. The low reactivity of aryl chlorides in cross-coupling reactions is generally ascribed to their reluctance to oxidatively add to Pd(0) [3]. Current interest focuses on the use of aryl chlorides since they are cheaper and more readily accessible than bromides and iodides [4]. Significant advances have been recently achieved by use of palladacycles [5] and especially, by use of bulky and electron-rich tertiary phosphines [6] as catalyst modifiers systems. However, the major drawback of these is that the phosphine ligands are comparatively difficult to make or rather expensive. Furthermore, tertiary phosphines require air-free handling to prevent their oxidation and are susceptible to P–C bond cleavage at elevated temperatures [7]. On the other hand, palladium complexes of *N*-heterocyclic carbene ligands (NHCs), [8] in particular have proved to be excellent catalysts not only for the Suzuki and Heck reaction, but also for Stille and Sonagashira reactions [9]. The NHC complexes are cost efficient to prepare, insensitive to air and moisture and are thermally stable in both the solid state and in solution; the carbenes are non-dissociative ligands. However, the development of new ligands or the application of existing ligands in these reactions, particularly those involving aryl chlorides as substrates, is still of considerable importance.

Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of saturated NHC ligands in coupling reactions is a neglected area. In order to find more efficient palladium catalysts we have prepared a series of new 1,3-diorganylimidazolinium salts LHX, **1** (Scheme 2), containing a saturated imidazole ring. We reasoned that by making the backbone of the imidazole ring saturated, the structure would augment the electron density on the carbene carbon atom [10].

2. Results and discussion

1,3-Dialkylimidazolinium salts, LHX (**1**) are conventional NHC precursors. According to Scheme 2, the salts

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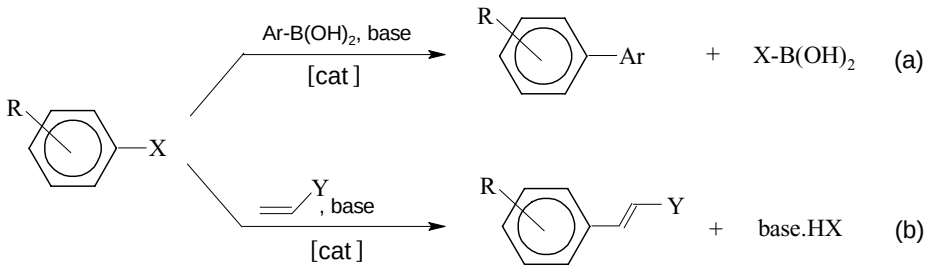
doi:10.1016/j.molcata.2003.08.002



Scheme 1. Cross-coupling of an aryl halide: (a) the Suzuki and (b) Heck reaction.

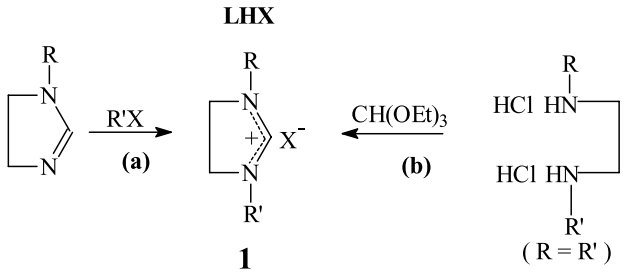
(**1a**–**f**) were obtained in almost quantitative yield by quarternazition of 1-alkyl-2-imidazoline in DMF with an excess of alkyl halide (route a). The rest of the salts (**1g**–**i**) were prepared by treatment of 1,2-dialkyl-1,2-diaminoethane dihydro halides with triethyl orthoformate (route b) [11]. The salts are air- and moisture stable both in the solid state and in solution. The structures of **1** were determined by their characteristic spectroscopic data and elemental analyses (Section 3).

2.1. Palladium/NHC catalyzed Suzuki coupling reactions

It has been found that the in situ formation of the ligand by deprotonation of the 1,3-diarylimidazolium salts, $[HC(Ar)NCH{=}CHN(Ar)]^+$, leads to significantly better results than use of the preformed carbene [12].

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions: a wide range of bases and solvents, as well as catalysts, have been employed with varying degrees of success according to the substrates [1]. To find optimum conditions a series of experiments has been performed with 4-iodoanisole and phenylboronic acid as model compounds. As a base, Cs_2CO_3 was the best choice and as a solvent dioxane was found to be better than other solvents. After having established the optimized coupling reaction conditions, the scope of the reaction and efficiencies of the salts were evaluated by investigating the coupling of $C_6H_5B(OH)_2$ with various *p*-substituted aryl halides. The results were summarized in Table 1. The salt **1a**, previously used with Ru(II) complexes, [13] serves as an efficient ligand for the palladium-catalyzed coupling of 4-iodoanisole with $C_6H_5B(OH)_2$ (Table 1, entry 1). The yields were good to excellent (83–97%). The unusual cross-coupling activity furnished by the saturated NHC precursors LHX may be attributable to their electron-richness [12]. From the results in Table 1, it is evident that the NHC precursors that contain electron donating methoxyethyl substituent (**1b**–**d**) are the most effective of the salts examined (runs 2, 11). The coordinating ability of the alkoxy group may be an important contributor to the increase in reactivity, as has been demonstrated by previous examples [14].

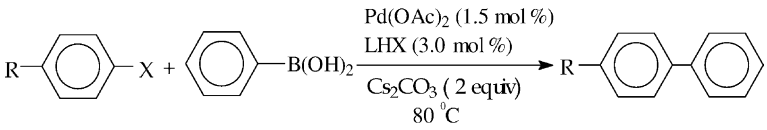
Previous researchers have reported induction periods for Suzuki reactions promoted by $Pd(OAc)_2$/imidazolium salts. It was proposed that during these induction periods Pd(II)/NHC complexes were formed and were then slowly



1a	R = R' = $CH_2C_6H_2(CH_3)_3$-2, 4, 6	X = Cl
1b	R = $(CH_2)_2OCH_3$, R' = $CH_2C_6H_2(CH_3)_3$-2, 4, 6	X = Cl
1c	R = $(CH_2)_2OCH_3$, R' = $CH_2C_6H_5$	X = Cl
1d	R = $(CH_2)_2OC_2H_5$, R' = $CH_2C_6H_2(CH_3)_3$-2, 4, 6	X = Cl
1e	R = $CH(CH_3)_2$, R' = $CH_2C_6H_2(CH_3)_3$-2, 4, 6	X = Br
1f	R = $CH_2CH{=}CH_2$, R' = $CH_2C_6H_2(CH_3)_3$-2, 4, 6	X = Br
1g	R = R' = $CH_2C_6H_2(OCH_3)_3$-2, 4, 6	X = Cl
1h	R = R' = $CH_2C_6H_2(OCH_3)$-3, 4, 5	X = Cl
1i	R = R' = C_6H_{11}	X = Cl

Scheme 2.

Table 1
The Suzuki coupling reaction of aryl halides with phenylboronic acid



Entry	R	X	LHX	Time (h)	Yield[a,b,c,d] (%)
1	CH_3O	I	**1a**	0.5	92
2	CH_3O	I	**1b**	0.5	96
3	CH_3O	I	**1c**	0.5	83
4	CH_3O	I	**1d**	0.5	93
5	CH_3O	I	**1e**	1.0	88
6	CH_3O	I	**1f**	1.0	89
7	CH_3O	I	**1g**	0.5	94
8	CH_3O	I	**1h**	0.5	97
9	CH_3O	I	**1I**	0.5	91
10	$COCH_3$	Br	**1a**	1.0	91
11	$COCH_3$	Br	**1b**	1.0	92
12	$COCH_3$	Br	**1d**	1.0	88
13	$COCH_3$	Br	**1h**	1.0	91
14	H	I	**1a**	0.5	86
15	H	I	**1b**	0.5	88
16	H	I	**1d**	0.5	91
17	CH_2Br	Br	**1a**	1.0	97[d]
18	CH_2Br	Br	**1b**	1.0	94[d]
19	CH_2Br	Br	**1c**	1.0	82[d]
20	CH_2Br	Br	**1d**	1.0	93[d]
21	CH_2Br	Br	**1e**	1.0	91[d]
22	CH_2Br	Br	**1f**	1.0	89[d]
23	CH_2Br	Br	**1g**	1.0	92[d]
24	CH_2Br	Br	**1h**	1.0	94[d]
25	CH_2Br	Br	**1I**	1.0	88[d]
26	CH_3	Cl	**1a**	2.0	95[d]
27	CH_3	Cl	**1b**	2.0	93[d]
28	CH_3	Cl	**1d**	2.0	94[d]
29	CH_3	Cl	**1h**	2.0	90[d]
30	CHO	Cl	**1b**	2.0	88
31	CHO	Cl	**1g**	2.0	90
32	CHO	Cl	**1h**	2.0	86

[a] Reaction conditions: 1.0 mmol of R–C_6H_4X-*p*, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1.50 mol % $Pd(OAc)_2$, 3 mol % LHX, dioxane (3 ml).
[b] Isolated yield (purity and yield check by NMR).
[c] All reactions were monitored by TLC.
[d] Temperature 100 °C.

reduced to catalytically active Pd(0)/NHC complexes [15]. It is important to note that these induction periods could be avoided with the present catalyst system.

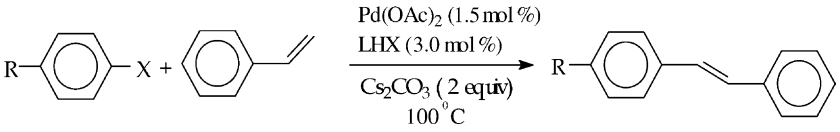
2.2. Palladium/NHC catalyzed Heck-type reactions

In initial catalytic experiments the coupling of 4-iodoanisole and styrene was attempted using the in situ formed carbene complexes as pre-catalysts (Table 2, runs 1–9). All complexes led to good conversions at low catalyst concentration (2.0 mol%). Following this, the olefination of styrene with the aryl bromides was tested and all produced near quantitative conversions (runs 10–21). In contrast, the Heck coupling reactions of unactivated (electron neutral) and deactivated (electron-rich) aryl chlorides, under the same catalytic conditions, did not give a dedectable amount of product.

2.2.1. Conclusion

From readily available starting materials, such as 1-alkyl-2-imidazoline or 1,2-dialkyl-1,2-diaminoethane, nine new 1,3-dialkylimidazolinium salts LHX (**1a**–**i**) have been prepared and characterized. Through the use of LHX and $Pd(OAc)_2$ as a pre-catalyst mixture, aryl halides undergo efficient coupling reactions with $C_6H_5B(OH)_2$ or styrene in the presence of Cs_2CO_3; only aryl chlorides are reluctant to give the Heck reaction in the presence of $Pd(OAc)_2$/LHX. The procedure is simple and efficient towards various aryl halides and does not require induction periods.

Table 2
The olefination of aryl halides with styrene



Entry	R	X	LHX	Time (h)	Yield[a,b,c] (%)
1	CH_3O	I	**1a**	1.0	93
2	CH_3O	I	**1b**	1.0	92
3	CH_3O	I	**1c**	1.5	75
4	CH_3O	I	**1d**	1.0	92
5	CH_3O	I	**1e**	2.0	80
6	CH_3O	I	**1f**	1.0	89
7	CH_3O	I	**1g**	1.0	95
8	CH_3O	I	**1h**	1.0	87
9	CH_3O	I	**1i**	1.0	89
10	CH_3O	I	**2a**	1.0	95
11	CH_3O	I	**2b**	2.0	78
12	CH_3O	I	**4**	1.0	92
13	$COCH_3$	Br	**1a**	1.5	92
14	$COCH_3$	Br	**1b**	1.5	90
15	$COCH_3$	Br	**1d**	1.0	91
16	$COCH_3$	Br	**1e**	1.5	82
17	$COCH_3$	Br	**1f**	1.0	89
18	$COCH_3$	Br	**1g**	1.0	90
19	$COCH_3$	Br	**1h**	1.5	94
20	$COCH_3$	Br	**1i**	1.0	97
21	CH_2Br	Br	**1a**	1.0	92
22	CH_2Br	Br	**1b**	1.0	90
23	CH_2Br	Br	**1h**	1.0	86
24	H	I	**1a**	0.5	94

[a] Reaction conditions: 1.0 mmol of R–C_6H_4X-*p*, 1.5 mmol of styrene, 2 mmol Cs_2CO_3, 1.50 mol % $Pd(OAc)_2$, 3.0 mol % LHX, dioxane (4 ml).
[b] Isolated yield (purity and yield check by NMR).
[c] All reactions were monitored by TLC.

3. Experimental

All reactions were performed using Schlenk-type flask under argon and standard high vacuum-line techniques. Solvents were analytical grade and distilled under Ar from sodium benzophenone (Et_2O, dioxane). ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C). FT-IR spectra were recorded on a Mattson 1000 spectrophotometer. Elemental analyses were performed by TUBITAK Microlab.

*3.1. Preparation of 1,3-bis(2,4,6-trimethylbenzyl)-imidazolinium chloride (**1a**)*

To a solution of 1-(2,4,6-trimethylbenzyl)imidazoline (2.02 g, 10 mmol) in DMF (10 ml) was added slowly 2,4,6-trimethylbenzyl chloride (1.68 g, 10.1 mmol) at 25 °C and the resulting mixture was stirred at rt for 6 h. Diethyl ether (15 ml) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3 × 15 ml), dried under vacuum, mp = 295–296 °C, and the yield was 3.56 g, 96%, $\nu_{(CN)} = 1660\,cm^{-1}$.

Anal. Cal. for $C_{23}H_{31}N_2Cl$; C: 74.49, H: 8.37, N: 7.56; found C: 73.97, H: 8.59, N: 7.49.

^1H NMR (δ, $CDCl_3$): 2.30 and 2.21 [s,18H, 2,4,6-(C*H*$_3$)$_3$-$C_6H_2CH_2$]; 3.68 [s, 4H, NC*H*$_2$C*H*$_2$N], 4.86 [s, 4H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.82 [s, 4H, 2,4,6-$(CH_3)_3C_6H_2$ CH_2]; 9.87 [s, 1H, NC*H*N]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 20.38 and 21.25 [2,4,6-(*C*H$_3$)$_3$C$_6$H$_2$CH$_2$]; 46.64 [N*C*H$_2$*C*H$_2$N]; 47.83 [2,4,6-(CH$_3$)$_3$C$_6$H$_2$*C*H$_2$]; 125.84, 130.14, 138.16 and 139.31 [2,4,6-(CH$_3$)$_3$*C*$_6$H$_2$CH$_2$]; 158.46 [N*C*HN].

*3.2. Preparation of 1-methoxyethyl-3-(2,4,6-trimethylbenzyl)imidazolinium chloride (**1b**)*

Compound **1b** was prepared in the same way as **1a** from 1-methoxyethylimidazoline (1.27 g, 10 mmol) and 2,4,6-trimethylbenzyl chloride (1.70 g, 10.1 mmol) to give white crystals of **1b** in 2.64 g, 89% yield, mp = 74–75 °C, $\nu_{(CN)} = 1651\,cm^{-1}$.

Anal. Cal. for $C_{16}H_{25}N_2OCl$; C: 64.76, H: 8.43, N: 9.44; found C: 64.44, H: 8.47, N: 9.34.

^1H NMR (δ, $CDCl_3$): 2.15 and 2.22 [s, 9H, 2,4,6-(C*H*$_3$)$_3$-$C_6H_2CH_2$]; 3.20 [s, 3H, $CH_2CH_2OCH_3$]; 3.43 and 3.57 [t, 4H, J = 5 Hz, NC*H*$_2$C*H*$_2$N]; 3.68 [t, 2H, J = 3.3 Hz,

$CH_2CH_2OCH_3$]; 3.82 [t, 2H, $J = 3.3$ Hz, $CH_2CH_2OCH_3$]; 4.61 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.84 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 8.72 [s, 1H, NC*H*N]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 19.86 and 21.05 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 45.64 [$CH_2CH_2OCH_3$]; 47.20 [$CH_2CH_2OCH_3$]; 58.46 [$CH_2CH_2OCH_3$]; 48.16 and 48.63 [NCH_2CH_2N]; 68.12 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 126.87, 129.74 and 138.33 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 158.07 [NCHN].

3.3. Preparation of 1-methoxyethyl-3-benzylimidazolinium chloride (1c)

Compound **1c** was prepared in the same way as **1a** from 1-methoxyethylimidazoline (1.27 g, 10.05 mmol) and benzyl chloride (1.98 g, 15.64 mmol) to give white crystals of **1c** in 2.27 g, 89% yield, mp = 78–79 °C, $\nu_{(CN)} = 1651\ cm^{-1}$.

Anal. Cal. for $C_{13}H_{19}N_2OCl$; C: 61.30, H: 7.47, N: 11.00; found C: 61.26, H: 7.39, N: 11.15.

^1H NMR (δ, $CDCl_3$): 2.78 [s, 3H, $CH_2CH_2OCH_3$]; 3.04 and 3.23 [t, 4H, $J = 5.5$ and 4.5 Hz, NCH_2CH_2N]; 3.30 [t, 2H, $J = 10$ Hz, $CH_2CH_2OCH_3$]; 3.51 [t, 2H, $J = 10$ Hz, $CH_2CH_2OCH_3$]; 4.32 [s, 2H, $C_6H_5CH_2$], 6.77 [m, 5H, $C_6H_5CH_2$]; 9.55 [s, 1H, NCHN]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 47.69 and 47.97 [NCH_2CH_2N]; 52.15 [$CH_2CH_2OCH_3$]; 58.80 [$CH_2CH_2OCH_3$]; 59.29 [$CH_2CH_2OCH_3$]; 68.78 [$C_6H_5CH_2$]; 128.44, 129.06, 129.36 and 132.76 [$C_6H_5CH_2$]; 158.68 [NCHN].

3.4. Preparation of 1-ethoxyethyl-3-(2,4,6-trimethylbenzyl)imidazolinium chloride (1d)

Compound **1d** was prepared in the same way as **1a** from 1-ethoxyethylimidazoline (1.42 g, 10 mmol) and 2,4,6-trimethylbenzyl chloride (1.70 g, 10.05 mmol) to give white crystals of **1d** in 2.89 g, 93% yield, mp = 135–136 °C, $\nu_{(CN)} = 1652\ cm^{-1}$.

Anal. Cal. for $C_{17}H_{27}N_2OCl$; C: 65.70, H: 8.69, N: 9.02; found C: 65.81, H: 7.49, N: 9.17.

^1H NMR (δ, $CDCl_3$): 1.07 [t, 3H, $J = 6.55$ Hz, $CH_2CH_2OCH_2CH_3$]; 2.14 and 2.23 [s, 9H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 3.35 [q, 2H, $J = 6.55$ Hz, $CH_2CH_2OCH_2CH_3$]; 3.41 and 3.54 [t, 4H, $J = 5.3$ Hz, NCH_2CH_2N]; 3.71 [t, 2H, $J = 9.53$ Hz, $CH_2CH_2OCH_2CH_3$]; 3.94 [t, 2H, $J = 9.53$ Hz, $CH_2CH_2OCH_2CH_3$]; 4.56 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.77 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 8.77 [s, 1H, NCHN]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 15.63 [$CH_2CH_2OCH_2CH_3$]; 19.27 and 21.64 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 45.78 [$CH_2CH_2OCH_2CH_3$]; 46.37 [$CH_2CH_2OCH_2CH_3$]; 47.53 [$CH_2CH_2OCH_2CH_3$]; 48.23 and 48.71 [NCH_2CH_2N]; 69.03 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 125.71, 129.97, 138.13 and 139.23 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 157.64 [NCHN].

3.5. Preparation of 1-isopyropyl-3-(2,4,6-trimethylbenzyl)imidazolinium bromide (1e)

Compound **1e** was prepared in the same way as **1a** from 1-(2,4,6-trimethylbenzyl)imidazoline (2.02 g, 10 mmol) and isopyropyl bromide (1.24 g, 10.05 mmol) to give pale yellow crystals of **1e** in 2.99 g, 92% yield, mp = 147–148 °C, $\nu_{(CN)} = 1643\ cm^{-1}$.

Anal. Cal. for $C_{16}H_{25}N_2Br$; C: 59.08, H: 7.69, N: 8.61; found C: 59.27, H: 7.63, N: 8.76.

^1H NMR (δ, $CDCl_3$): 3.66 and 3.95 [t, 4H, $J = 3.56$ Hz, NCH_2CH_2N]; 4.86 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.79 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 2.18 and 2.27 [s, 9H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 4.02 [sept, 1H, $J = 6.62$ Hz, $CH(CH_3)_2$]; 1.31 [d, 6H, $J = 6.66$ Hz, $CH(CH_3)_2$]; 9.61 [s, 1H, NCHN]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 45.90 and 46.14 [NCH_2CH_2N]; 47.35 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 125.42, 129.74, 137.77 and 138.83 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 19.85 and 21.01 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 50.55 [$CH(CH_3)_2$]; 20.80 [$CH(CH_3)_2$]; 156.37 [NCHN].

3.6. Preparation of 1-allyl-3-(2,4,6-trimethylbenzyl)-imidazolinium bromide (1f)

Compound **1f** was prepared in the same way as **1a** from 1-(2,4,6-trimethylbenzyl)imidazoline (2.02 g, 10 mmol) and allyl bromide (1.22 g, 10.05 mmol) to give white crystals of **1f** in 3,07 g, 95% yield, mp = 174–175 °C, $\nu_{(CN)} = 1660\ cm^{-1}$.

Anal. Cal. for $C_{16}H_{23}N_2Br$; C: 59.44, H: 7.12, N: 8.67; found C: 59.62, H: 7.19, N: 8.73.

^1H NMR (δ, $CDCl_3$): 2.34 and 2.82 [s, 9H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 3.86 [m, 4H, NCH_2CH_2N]; 4.17 [d, 2H, $J = 5.7$ Hz, $CH_2CH{=}CH_2$]; 4.69 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 5.36 [q, 2H, $J = 10.24$ Hz, $CH_2CH{=}CH_2$]; 5.92 [m, 1H, $CH_2CH{=}CH_2$]; 6.97 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 8.63 [s, 1H, NCHN]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 19.41 and 20.51 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 45.27 [$CH_2CH{=}CH_2$] 47.83 and 48.11 [NCH_2CH_2N]; 49.37 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 119.77 [$CH_2CH{=}CH_2$]; 126.24, 129.16 and 137.78 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 131.77 [$CH_2CH{=}CH_2$]; 156.78 [NCHN].

3.7. Preparation of 1,3-bis(2,4,6-trimethoxybenzyl)-imidazolinium chloride (1g)

A mixture of *N,N′*-bis(2,4,6-trimethoxybenzyl)ethane dihydrochloride (4.93 g, 10.0 mmol) in triethyl orthoformate (50 ml) was heated in a distillation apparatus until the ethanol distillation ceased. The temperature of the reaction mixture reached 110 °C. Upon cooling to rt a colorless solid precipitated which was collected by filtration, and dried in vacuum. The crude product was recrystallized from absolute ethanol to give colorless needles, and the solid was washed with diethyl ether (3 × 15 ml), dried under vacuum, and the yield was 4.57 g, 98% mp = 213–214 °C, $\nu_{(CN)} = 1637\ cm^{-1}$.

Anal. Cal. for $C_{23}H_{31}N_2O_6Cl$; C: 59.16, H: 6.64, N: 6.00; found C: 59.10, H: 6.51, N: 6.13.

^1H NMR (δ, $CDCl_3$): 3.69 [s, 4H, NCH_2CH_2N]; 3.75 and 3.86 [s,18H, 2,4,6-$(OCH_3)_3C_6H_2CH_2$]; 4.58 [s, 4H, 2,4,6-$(OCH_3)_3C_6H_2CH_2$]; 6.04 [s, 4H, 2,4,6-$(OCH_3)_3C_6H_2CH_2$];

8.65 [s, 1H, NC*H*N]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 40.78 and 48.35 [2,4,6-$(OCH_3)_3C_6H_2CH_2$]; 56.28 [NCH_2CH_2N], 56.31 [2,4,6-$(OCH_3)_3C_6H_2CH_2$]; 90.82, 101.95, 157.9 and 160.04 [2,4,6-$(OCH_3)_3C_6H_2CH_2$]; 162.67 [NCHN].

*3.8. Preparation of 1,3-bis(3,4,5-trimethoxybenzyl)-imidazolinium chloride (**1h**)*

Compound **1h** was prepared in the same way as **1g** from *N*,*N*′-bis(3,4,5-trimethoxybenzyl)ethane dihydrochloride (4.93 g, 10 mmol) in triethyl orthoformate (50 ml) to give white crystals of **1h** in 4.48 g, 96% yield, mp = 282–283 °C, $\nu_{(CN)} = 1666\,cm^{-1}$.

Anal. Cal. for $C_{23}H_{31}N_2O_6Cl$; C: 59.16, H: 6.64, N: 6.00; found C: 59.13, H: 6.52, N: 6.10.

^1H NMR (δ, $CDCl_3$): 3.29 and 3.84 [s,18H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 3.55 [s, 4H, NCH_2CH_2N]; 4.51 [s, 4H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 6.68 [s, 4H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 8.79 [s, 1H, NC*H*N]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 48.64 and 51.95 [3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 56.88 [NCH_2CH_2N]; 60.85 [3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 107.04, 130.20 and 138.35 [3,4,5-$(OCH_3)_3C_6H_2CH_2$]; 154.02 [NCHN].

*3.9. Preparation of 1,3-bis(cyclohexyl)imidazolinium chloride (**1i**)*

Compound **1i** was prepared in the same way as **1g** from *N*,*N*′-biscyclohexylethane dihydrochloride (2.96 g, 10 mmol) in triethyl orthoformate (50 ml) to give white crystals of **1i** in 2.44 g, 90% yield, mp = 265–266 °C, $\nu_{(CN)} = 1656\,cm^{-1}$.

Anal. Cal. for $C_{15}H_{27}N_2Cl$; C: 66.54, H: 9.98, N: 10.35; found C: 66.59, H: 10.03, N: 10.34.

^1H NMR (δ, $CDCl_3$): 1.09–1.93 [m, 22H, C_6H_{11}]; 3.93 [s, 4H, NCH_2CH_2N]; 9.82 [s, 1H, NC*H*N]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 24.82, 25.04, 31.41 and 57.67 [C_6H_{11}]; 45.72 [NCH_2CH_2N]; 156.74 [NCHN].

Acknowledgements

We thank to Technological and Scientific Research Council of Türkiye TÜBITAK (TÜBITAK COST D17) and Inönü University Research Fund (BAP 2002/23) for financial support of this work.

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