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Synthesis of novel 1-alkylimidazoline and 1-alkylbenzimidazole palladium(II) complexes as efficient catalysts for Heck and Suzuki reactions involving arylchlorides

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Abstract

Six palladium(II) complexes of the type $[PdCl_2(PR_3)L]$, {$PR_3 = PPh_3$ or $PPhMe_2$; L = 1-alkyl-2-imidazoline (**1**) or 1-alkylbenzimidazole-(**2**)} have been prepared by reactions of $[PdCl_2(PR_3)]_2$. The complexes were characterized by conventional spectroscopic methods and elemental analyses. The incorporation of *N*-coordinated imidazoline and benzimidazole complexes of palladium(II) gave high catalytic activity in the Suzuki coupling and Heck reaction of aryl bromides and deactivated aryl chloride substrates.

Keywords: Palladium; Imidazolidine; Benzimidazole; Suzuki; Heck

1. Introduction

The olefination of aryl halides (via Heck reaction Scheme 1a), or the reaction of aryl halides with arylboronic acids (via Suzuki reaction, Scheme 1b) is one of the most general C–C coupling reactions in organic synthesis, is catalyzed by palladium complexes in homogeneous solution [1,2].

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 and especially, by use of bulky and electron-rich tertiary phosphines as catalyst modifiers systems [5,6]. 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, transition metal complexes with ligands containing nitrogen-donor atoms have been shown their potential to successfully promote the catalytic transformation of organic compounds [8,9]. These discoveries motivate the search for the new metal complexes with *N*-coordinated ligands and the evaluation of their catalytic properties.

Our contribution to this field has started with syntheses of 2-imidazoline and benzazole complexes of Pt(II), Rh(I) and Ru(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in good yields [10–14]. The imidazoline and benzimidazole complexes are cheap to prepare, insensitive to air and moisture and are thermally stable in both the solid state and in solution.

However, the development of new ligands or the application of existing ligands in Suzuki and Heck reactions, particularly those involving aryl chlorides as substrates, is still of considerable importance.

We report here the straightforward preparation of a series phosphinepalladium complexes of *N*-coordinated 1-alkyl-2-imidazoline and benzimidazole derivatives. These com-

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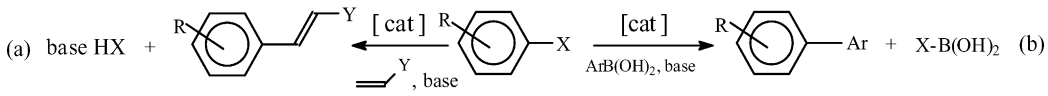


Scheme 1. Heck and Suzuki reactions.

plexes were shown to be effective catalysts for Heck and Suzuki reactions especially with arylchlorides.

2. Experimental

All reactions were performed using Schlenk-type flask under argon and standard high vacuum-line techniques. Solvents were analytical grade and distilled under argon from sodium benzophenone (Et_2O, dioxane, toluene, *n*-hexane). NMR spectra were recorded at 297 K on a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C). FT-IR spectra were recorded on a Mattson 1000 spectrophotometer. Samples were prepared as KBr discs. Elemental analyses were performed by TUBITAK Microlab (Ankara).

2.1. Preparation of 1-(2,4,6-trimethylbenzyl)-2-imidazoline dichloro(dimethylphenylphosphine)palladium(II), ***1a***

A solution of 1-(2,4,6-trimethylbenzyl)imidazoline (150 mg, 0.742 mmol) in toluene (15 ml) and $[PdCl_2(PPhMe_2)]_2$ (234 mg, 0.371 mmol) was heated for 2 h under reflux. *n*-Hexane (5 ml) was added to the warm solution. Upon cooling to room temperature orange crystals of complex **1a** were filtered off, washed with hexane (2 × 5 ml) and dried in vacuum, mp = 156–157 °C, and the yield was 311 mg, 81%, $\nu_{(CN)} = 1611\,cm^{-1}$.

Anal. Cal. for $C_{21}H_{29}N_2\,PPdCl_2$; C: 48.70, H: 5.60, N: 5.41; found C: 48.75, H: 4.58, N: 5.37.

^{1}H-NMR (δ, $CDCl_3$): 2.18 and 2.21 [s, 9H, 2,4,6-(CH_3)$_3$ $C_6H_2CH_2$]; 4.21 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.79 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 1.71 and 1.74 [s, 6H, $P(C_6H_5)(CH_3)_2$]; 7.37 and 7.73 [m, $P(C_6H_5)(CH_3)_2$]; 3.21 [t, J = 10.3 Hz, NCH_2CH_2NPd]; 3.85 [t, J = 10.3 Hz, NCH_2CH_2N-Pd]; 7.30 [s, 1H, NC*H*N]; ^{13}C{H}-NMR (δ, $CDCl_3$): 21.21 and 21.48 [2,4,6-(CH_3)$_3C_6H_2CH_2$]; 52.95 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 128.97, 129.73, 129.84, 138.58 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 14.25 and 14.64 $[P(C_6H_5)(CH_3)_2]$; 130.41, 131.82, 132.24 and 139.40 $[(C_6H_5)(CH_3)_2]$; 46.03 $[NCH_2CH_2NPd]$; 48.93 $[NCH_2CH_2NPd]$; 160.23 [NCHN].

2.2. Preparation of 1-methoxyethyl-2-imidazolinedichloro(dimethylphenylphosphine)-palladium(II), ***1b***

Compound **1b** was prepared in the same way as **1a** from 1-methoxyethylimidazoline (100 mg, 0.781 mmol) and $[PdCl_2(PPhMe_2)]_2$ (246 mg, 0.390 mmol) to give orange crystals of **1b** in 270 mg, 78% yield, mp = 168–169 °C, $\nu_{(CN)} = 1605\,cm^{-1}$.

Anal. Cal. for $C_{14}H_{23}N_2OPPdCl_2$; C: 37.89, H: 5.19, N: 6.31; found C: 37.94, H: 5.22, N: 6.29.

^{1}H-NMR (δ, $CDCl_3$): 3.53 (t, J 9.80, $CH_2CH_2OCH_3$); 4.1 (t, J 9.80, $CH_2CH_2OCH_3$), 3.19 (s, $CH_2CH_2OCH_3$); 3.23 [m, 4H, NCH_2CH_2NPd]; 1.67 and 1.70 [s, 6H, $P(C_6H_5)(CH_3)_2$]; 7.30 and 7.68 [m, $P(C_6H_5)(CH_3)_2$]; 7.25 [s, 1H, NC*H*N]; ^{13}C{H}-NMR (δ, $CDCl_3$): 57.26 ($CH_2CH_2OCH_3$); 70.35 ($CH_2CH_2OCH_3$); 58.81 (CH_2CH_2O CH_3)]; 47.10 $[NCH_2CH_2NPd]$; 49.04 $[NCH_2CH_2NPd]$; 14.05 and 14.44 $[P(C_6H_5)(CH_3)_2]$; 129.31, 130.63, 131.94 and 138.27 $[P(C_6H_5)(CH_3)_2]$; 161.22 [NCHN].

2.3. Preparation of 1-(2,4,6-trimethylbenzyl)benzimidazole dichloro(dimethylphenylphosphine)palladium(II), ***2a***

Compound **2a** was prepared in the same way as **1a** from 1-(2,4,6-trimethylbenzyl)benzimidazole (150 mg, 0.599 mmol) and $[PdCl_2(PPhMe_2)]_2$ (189 mg, 0.299 mmol) to give orange crystals of **2a** in 291 mg, 86% yield, mp = 205–206 °C, $\nu_{(CN)} = 1609\,cm^{-1}$.

Anal. Cal. for $C_{25}H_{29}N_2PPdCl_2$; C: 53.06, H: 5.13, N: 4.95; found C: 52.96, H: 5.08, N: 4.87.

^{1}H-NMR (δ, $CDCl_3$): 2.17 and 2.26 [s, 9H, 2,4,6-(CH_3)$_3$ $C_6H_2CH_2$]; 5.17 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.89 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 1.80 and 1.83 [s, 6H, $P(C_6H_5)(CH_3)_2$]; 7.40 and 7.82 [m, $P(C_6H_5)(CH_3)_2$]; 7.39 and 8.29 [m, 4H, NC_6H_4N]; 7.66 [s, 1H, NC*H*N]; ^{13}C{H}-NMR (δ, $CDCl_3$): 20.19 and 21.65 [2,4,6-(CH_3)$_3$ $C_6H_2CH_2$]; 44.47 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 129.84, 129.95, 131.09, 139.24 [2,4,6-$(CH_3)_3C_6H_2CH_2$]; 14.24 and 14.63 $[P(C_6H_5)(CH_3)_2]$; 132.04, 132.07, 132.26 and 132.36 $[P(C_6H_5)(CH_3)_2]$; 100.61, 111.06, 122.14, 124.65, 125.13 and 125.72 $[NC_6H_4N]$; 144.15 [NCHN].

2.4. Preparation of 1-(2,4,6-trimethylbenzyl)benzimidazole dichloro(triphenylphosphine)palladium(II), ***2b***

Compound **2b** was prepared in the same way as **1a** from 1-(2,4,6-trimethylbenzyl)benzimidazole (150 mg, 0.599 mmol) and $[PdCl_2(PPh_3)]_2$ (263 mg, 0.299 mmol) to give orange crystals of **2b** in 342 mg, 83% yield, mp = 267–268 °C, $\nu_{(CN)} = 1610\,cm^{-1}$.

Anal. Cal. for $C_{35}H_{33}N_2PPdCl_2$; C: 60.92, H: 4.78, N: 4.06; found C: 61.18, H: 4.73, N: 4.12.

^{1}H-NMR (δ, $CDCl_3$): 2.22 and 2.31 [s, 9H, 2,4,6-(CH_3)$_3$ $C_6H_2CH_2$]; 5.22 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 6.94 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$]; 7.44 [m, 15H, $P(C_6H_5)_3$]; 7.81 [m, 4H, NC_6H_4N]; 8.46 [s, 1H, NC*H*N]; ^{13}C{H}-NMR

(δ, $CDCl_3$): 20.09 and 21.52 [2,4,6-(CH_3)$_3$$C_6H_2CH_2$]; 44.29 [2,4,6-($CH_3$)$_3$$C_6H_2CH_2$]; 128.61, 131.32, 135.28, 135.51 [2,4,6-(CH_3)$_3$$C_6H_2CH_2$]; 129.22, 130.34, 131.67 and 139.69 [P(C_6H_5)$_3$]; 110.42, 121.59, 123.96, 124.40, 126.25 and 128.37 [NC_6H_4N]; 143.49 [NCHN].

2.5. Preparation of 1-methoxyethylbenzimidazoledichloro(dimethylphenylphosphine)-palladium(II), **2c**

Compound **2c** was prepared in the same way as **1a** from 1-methoxyethylbenzimidazole (120 mg, 0.681 mmol) and $[PdCl_2(PPhMe_2)]_2$ (214 mg, 0.340 mmol) to give orange crystals of **2c** in 291 mg, 87% yield, mp = 102–103 °C, $\nu_{(CN)} = 1613\,cm^{-1}$.

Anal. Cal. for $C_{18}H_{23}N_2OPPdCl_2$; C: 43.96, H: 4.68, N: 5.69; found C: 43.89, H: 4.61, N: 5.71.

^{1}H-NMR (δ, $CDCl_3$): 3.65 [t, 2H, J = 4.96 Hz, C$H_2$$CH_2OCH_3$]; 4.25 [t, 2H, J = 4.96 Hz, CH_2C$H_2$$OCH_3$]; 3.28 [s, 3H, $CH_2CH_2OCH_3$]; 1.89 and 1.94 [s, 6H, P(C_6H_5)(CH_3)$_2$]; 7.36 and 7.48 [m, P(C_6H_5)(CH_3)$_2$]; 7.29 and 8.31 [m, 4H, NC_6H_4N]; 8.32 [s, 1H, NCHN]; ^{13}C{H}-NMR (δ, $CDCl_3$): 45.65 [$CH_2CH_2OCH_3$]; 70.30 [$CH_2CH_2OCH_3$]; 59.04 [$CH_2CH_2OCH_3$]; 13.73 and 14.25 [P(C_6H_5)(CH_3)$_2$]; 130.84, 131.06, 131.85 and 133.01 [P(C_6H_5)(CH_3)$_2$]; 110.10, 120.84, 123.17, 123.89, 128.63 and 128.77 [NC_6H_4N]; 144.39 [NCHN].

2.6. Preparation of 1-isopropylbenzimidazoledichloro(dimethylphenylphosphine)-palladium(II), **2d**

Compound **2d** was prepared in the same way as **1a** from 1-isopropylbenzimidazole (118 mg, 0.737 mmol) and $[PdCl_2(PPhMe_2)]_2$ (232 mg, 0.368 mmol) to give orange crystals of **2d** in 311 mg, 89% yield, mp = 110–111 °C, $\nu_{(CN)} = 1597\,cm^{-1}$.

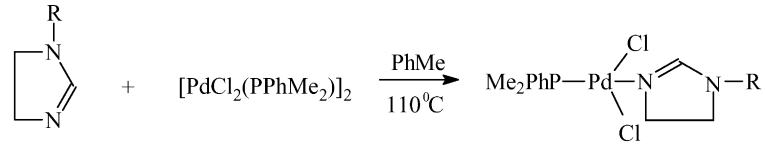
$C_{18}H_{23}N_2PPdCl_2$; C: 45.43, H: 4.84, N: 5.89; found C: 45.39, H: 4.76, N: 5.83.

^{1}H-NMR (δ, $CDCl_3$): 4.61 [sept, 1H, J = 6.72 Hz, CH(CH_3)$_2$]; 1.59 [d, 6H, J = 6.72 Hz, CH(CH_3)$_2$]; 1.89 and 1.94 [s, 6H, P(C_6H_5)(CH_3)$_2$]; 7.48 and 7.94 [m, P(C_6H_5)(CH_3)$_2$]; 7.30 [m, 4H, NC_6H_4N]; 8.32 [s, 1H, NCHN]; ^{13}C{H}-NMR (δ, $CDCl_3$): 48.68 [CH(CH_3)$_2$]; 22.44 [CH(CH_3)$_2$]; 13.70 and 14.22 [P(C_6H_5)(CH_3)$_2$]; 130.84, 130.87, 131.03 and 131.16 [P(C_6H_5)(CH_3)$_2$]; 110.44, 121.00, 123.19, 123.69, 128.61 and 128.74 [NC_6H_4N]; 141.22 [NCHN].

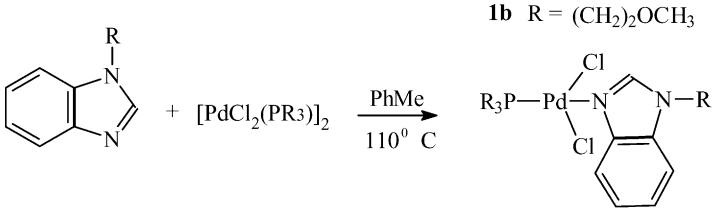
3. Results and discussion

The *N*-coordinated palladium complexes were synthesized according to the steps illustrated in Scheme 2. The reaction of the 1-alkyl-2-imidazoline or 1-alkylbenzimidazole with binuclear $[PdCl_2(PPhMe_2)]_2$ and $[PdCl_2(PPh_3)]_2$ proceeds smoothly, in refluxing toluene, to give the orange complexes **1b** (81%), **1b** (78%), **2a** (86%), **2b** (83%) and **2c** (89%) and **2d** (87%). The complexes **1** and **2** which are very stable in the solid state, have been characterized by analytical and spectroscopic data. The spectroscopic properties indicating that they all are *N*(3)-bonded.

The nature of the bonding in the imidazoline and benzimidazole complexes **1** and **2** was readily shown by NMR spectroscopy (experimental part). ^{13}C NMR spectroscopy was the most useful tool for structure elucidation. Thus, from our previous experience [15] we expected that C-coordination would result in a shift of the carbene carbon nucleus signal toward low field i.e. 190–212 ppm, while *N*-coordination



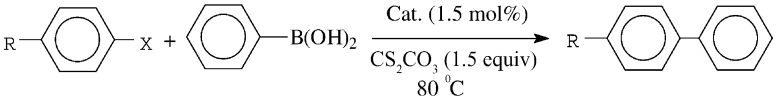
1a R = $CH_2C_6H_2(CH_3)_3$-2,4,6
1b R = $(CH_2)_2OCH_3$



2a R = $CH_2C_6H_2(CH_3)_3$-2,4,6 $PR_3 = PPhMe_2$
2b R = $CH_2C_6H_2(CH_3)_3$-2,4,6 $PR_3 = PPh_3$
2c R = $(CH_2)_2OCH_3$ $PR_3 = PPhMe_2$
2d R = $CH(CH_3)_2$ $PR_3 = PPhMe_2$

Scheme 2. Synthesis of Pd(II)-imidazoline and benzimidazole complexes.

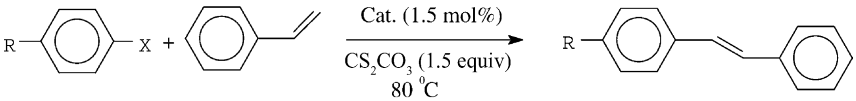
Table 1
The Suzuki coupling reaction of aryl halides with phenylboronic acid



Entry	R	X	Catalysts	Time (h)	Yield (%)[a,b,c]
1	$COCH_3$	Br	**1a**	2.0	95
2	$COCH_3$	Br	**1b**	2.0	94
3	$COCH_3$	Br	**2a**	2.0	95
4	$COCH_3$	Br	**2b**	2.0	87
5	$COCH_3$	Br	**2d**	2.0	94
6	OCH_3	Cl	**1a**	3.0	89
7	OCH_3	Cl	**1b**	3.0	87
8	OCH_3	Cl	**2a**	3.0	97
9	OCH_3	Cl	**2b**	3.0	92
10	OCH_3	Cl	**2c**	3.0	88
11	OCH_3	Cl	**2d**	3.0	90
12	CH_3	Cl	**1a**	3.0	84
13	CH_3	Cl	**1b**	3.0	83
14	CH_3	Cl	**2a**	3.0	90
15	CH_3	Cl	**2b**	3.0	91
16	CH_3	Cl	**2c**	3.0	93
17	CH_3	Cl	**2d**	3.0	92
18	CHO	Cl	**1a**	3.0	90
19	CHO	Cl	**1b**	3.0	90
20	CHO	Cl	**2a**	3.0	92
21	CHO	Cl	**2b**	3.0	88
22	CHO	Cl	**2c**	3.0	93
23	CHO	Cl	**2d**	3.0	95

[a] Reaction conditions: 1.0 mmol of *p*-R-C_6H_4X, 1.5 mmol of phenylboronic acid, 1.5 mmol Cs_2CO_3, 1.5 mol% Pd catalyst, dioxane (3 ml).
[b] Isolated yield (purity of yield checked by NMR).
[c] All reactions were monitored by TLC.

Table 2
The olefination of aryl halides with styrene



Entry	R	X	Catalysts	Time (h)	Yield (%)[a,b,c]
1	$COCH_3$	Br	**1a**	2.5	93
2	$COCH_3$	Br	**1b**	2.5	91
3	$COCH_3$	Br	**2a**	2.5	91
4	$COCH_3$	Br	**2b**	2.5	96
5	$COCH_3$	Br	**2c**	2.5	92
6	$COCH_3$	Br	**2d**	2.5	90
7	CHO	Br	**1a**	2.5	86
8	CHO	Br	**1b**	2.5	82
9	CHO	Br	**2a**	2.5	91
10	CHO	Br	**2b**	2.5	90
11	CHO	Br	**2c**	2.5	93
12	CHO	Br	**2d**	2.5	95
13	OCH_3	Cl	**1a**	4.0	90
14	OCH_3	Cl	**2a**	4.0	92
15	OCH_3	Cl	**2b**	4.0	95
16	OCH_3	Cl	**2c**	4.0	90
17	OCH_3	Cl	**2d**	4.0	94
18	CH_3	Cl	**1a**	4.0	65
19	CH_3	Cl	**2a**	4.0	60
20	CH_3	Cl	**2d**	4.0	63

[a] Reaction conditions: 1.0 mmol of *p*-R-C_6H_4X, 1.5 mmol of styrene, 1.5 mmol Cs_2CO_3, 1.5 mol% Pd catalyst, dioxane (3 ml).
[b] Isolated yield (purity of yield checked by NMR).
[c] All reactions were monitored by TLC.

would result in a higher field shift towards 160 ppm. ^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 160.23, 160.75, 144.15, 143.49, 144.39 and 141.22 ppm, respectively for complexes **1a** and **b** and **2a**–**d**. The ^{1}H NMR spectra of the complexes further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets in the 7.30, 7.15, 7.66, 8.46, 8.32, and 8.32 ppm, respectively for complexes **1a** and **b** and **2a**–**d**. The IR data for complexes **1** and **2** clearly indicate the presence of the –C=N– group with a ν(C=N) vibration at 1611, 1605, 1609, 1610, 1613 and 1597 cm^{-1}, respectively for complexes **1a** and **b** and **2a**–**d**. The NMR and IR values are similar to those found for *N*-coordinated metal complexes [10–14].

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]. In a first test of the activity of complexes **1** and **2** in the Suzuki type coupling of para-substituted aryl halides with phenyl boronic acid, classical conditions for solvent and base were chosen (dioxane as solvent, Cs_2CO_3 as base, and reaction temperature of 80 °C). The coupling of activated and deactivated aryl halogenides and phenylboronic acid proceeds in high yields and quite rapidly even with a low catalyst loading. The results were summarized in Table 1. Under those conditions, 4-bromoacetophenone, *p*-chloroanisole, *p*-chlorotoluene and *p*-chlorobenzaldehyde react very cleanly with phenylboronic acid in goods yields (Table 1, entries 3, 8, 16 and 23).

Palladium complexes **1** and **2** were found to be active catalysts for the Heck reaction and proved to be thermally robust for high temperature Heck olefination of aryl chlorides, bromides. Under our optimized reaction conditions (1.5% Pd-imidazoline **1**, or benzimidazole **2**, complexes, 1.5 equivalents of Cs_2CO_3, dioxane, 80 °C), excellent yields of coupled products could be obtained for a wide array of aryl bromides and chlorides with styrene (Table 2). For example, *p*-chloroanisole and *p*-chlorotoluene, lead to 95 and 65% yields, respectively could be reached in 2 h (Table 2, entries 15 and 18). The electron deficient 4-bromoacetophenone was completely converted to the coupled product in ca. 1.5 h (Table 2, entry 4). It should be noted that in all cases only the *trans* products were selectively obtained as confirmed by ^{1}NMR.

4. Conclusion

From readily available starting materials, such as 1-alkyl-2-imidazoline or 1-alkylbenzimidazole six new *N*-coordinated palladium complexes (**1** and **2**) have been prepared and characterized. Also we have found that the very easily synthesized, comparatively non-expensive complexes **1** and **2** show by far the highest activity yet reported in the Heck and Suzuki coupling of aryl halides, regardless of whether the substrates are electron rich or poor. The procedure is simple and efficient towards various aryl halides and does not require induction periods.

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