

Pd(OAc)₂/1,1'-Methylene-3,3'-bis[*N*-(isopropyl)imidazol-2-ylidene]: An Efficient Catalyst for the Heck Arylation of Various Olefins

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The Mizoroki-Heck coupling reaction has been carried out using Pd(OAc)₂ and bisimidazolium (1,1'-methylene-3,3'-bis[*N*-(isopropyl)imidazol-2-ylidene]dibromide) for aryl bromides as well as less reactive chlorobenzene with mono- and di-substituted olefins. Only 0.025 mol% of Pd(II) shows a high activity toward the coupling reaction with turnover number (TON) ≈ 600-3960. Further, this catalyst system, Pd(OAc)₂/Bisimidazolium, exhibits the excellent selectivity for the *trans*-isomer coupling products and the terminal arylation coupling products for mono- and di-substituted olefins, respectively. The nature of olefins (*n*-butyl acrylate, styrene, and 1,1-disubstituted olefins) has a significant contribution on the yield of the coupling products.

Keywords: Bisimidazolium, Heck reaction, Homogeneous, Mono- and di-substituted olefins, Selectivity

INTRODUCTION

The N-heterocyclic carbene (NHC) ligands are cheap, nontoxic, and easily prepared from commercial azolium salts [1-3]. In recent years, numerous carbene ligands with different steric and electronic parameters have been synthesized [1,4-6]. Among them, especially chelating bis(NHC) ligands have attracted considerable attention in organometallic chemistry, due to the high stability of their complexes under acidic and oxidizing conditions [7,8]. Moreover, the NHC ligands derived from imidazolium and 4,5-dihydroimidazolium salts are widely used in homogeneous catalysis and organometallic chemistry (Fig. 1). The free NHC ligands compared to their transition metal complexes have significant thermodynamic stability in heat, air, and moisture. They are extensively used in many organic transformations such as alkene activation [9-11], alkyne hydration [12,13], hydroamination [14-16], hydrosilylation [17,18], enyne cycloisomerization [9,19], rearrangement of propargylic esters [9,20], cross-coupling reactions [21-23], and *etc.* Various unsaturated intermediates formed in

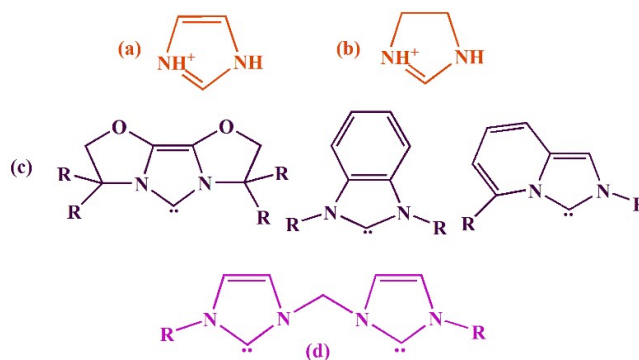


Fig. 1. (a) Imidazolium salt, (b) 4,5-dihydroimidazolium salt, (c) mono-dentate, and (d) bis-dentate NHC ligands.

catalytic cycles can be stabilized by NHC ligands with strong σ -donating and negligible π -accepting properties [1,23]. In organic reactions cycles, catalyst degradation is prevented by the presence of NHC ligands in the reaction medium.

Owing to the main benefits of the NHC ligands, they are used as an excellent alternative to phosphines in many Pd-catalyzed reactions. More recently, many palladium(II) complexes with NHC ligands have been synthesized and their catalytic activity has also been investigated at different

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conditions of the Mizoroki-Heck cross-coupling reactions [3,23-27].

We have recently employed various homogeneous [28-31] and heterogeneous [32,33] catalysts for Mizoroki-Heck coupling reactions. Therefore, according to the unique electronic and steric properties of the NHC ligands, we decided to study the Mizoroki-Heck coupling reaction of various aryl halides and mono- or di-substituted olefins using Pd(OAc)₂/Bisimidazolium (1,1'-methylene-3,3'-bis[*N*-(isopropyl)imidazol-2-ylidene] dibromide) catalyst.

EXPERIMENTAL

Materials and Methods

Pd(OAc)₂, aryl halides, *n*-butyl acrylate, styrene, 1,1-disubstituted olefins, K₂CO₃, sodium acetate (NaOAc), sodium *tert*-butoxide (NaOtBu), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), toluene, acetonitrile (ACN), ethyl acetate (EtOAc), *n*-heptane, MeOH, CH₂Cl₂, and MgSO₄ were purchased from Merck Company in analytical grades. The chemicals were used without further purification. Bisimidazolium was synthesized according to the previous report [1]. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance spectrometer at room temperature in CDCl₃ solvent. Thin layer chromatography (TLC) on the precoated silica gel fluorescent 254 nm (0.2 mm) was used to monitor the progress of the reactions.

General Procedure for the Mizoroki-Heck Coupling Reaction

In a typical reaction, aryl halide (4 mmol), NaOtBu (6 mmol), and olefin (6 mmol) were mixed in DMF in a reaction flask under a dry nitrogen atmosphere. A solution of Pd(OAc)₂ (0.025 mol% in 1 ml of DMF) was added through a rubber septum and followed by a solution of bisimidazolium (0.025 mol% in 3 ml of DMF). The obtained mixture was stirred and heated at 135 °C. TLC technique was used to evaluate the progress of the Mizoroki-Heck coupling. After completion of the reaction, the resulting mixture was cooled to room temperature and quenched with H₂O. After cooling, the organic phase was extracted using CH₂Cl₂ (3 × 20 ml), dried over MgSO₄, filtered, and then evaporated using a rotary evaporator to dryness. Purification of the crude

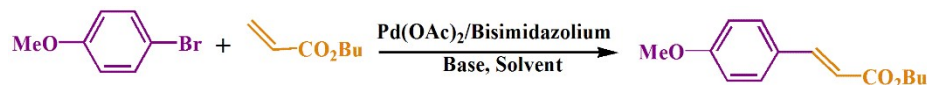
residue was performed using silica-gel chromatography. Elution with EtOAc/*n*-heptane gave the pure Mizoroki-Heck coupling product. The solvent was evaporated and the coupling product was characterized using ¹H NMR spectroscopy.

RESULTS AND DISCUSSIONS

Mizoroki-Heck coupling is highly dependent on the nature of the base. K₂CO₃ and NaOAc are the common bases in the Pd-catalyzed Mizoroki-Heck coupling reactions. However, in our catalytic system, the coupling product was not found using these bases (Table 1, entries 1,2). Only very strong bronsted bases such as NaOtBu and NaOAc/NaOtBu could act very effectively in the coupling reactions (Table 1, entries 3,4). These results are in agreement with the previous studies on the direct metal complexation of NHCs through the typical deprotonation of imidazolium salt with potassium *tert*-butoxide [34,35]. For the direct metalation of NHCs, one proton must be lost to effectively coordinate with the metal ions.

Moreover, the coupling product was not obtained after 24 h in the absence of Pd(OAc)₂ (Table 1, entry 5). The influence of the molar ratio of palladium to ligand was also studied using various amounts of bisimidazolium. Similarly, the coupling product was not observed after 24 h in the absence of bisimidazolium (Table 1, entry 6). The coupling product yield in the presence of Pd(OAc)₂/Bisimidazolium with the 1:1 molar ratio was greater compared to the 1:2 and 1:3 molar ratios (Table 1, entries 3,7,8). Therefore, the 1:1 molar ratio was used to optimize the other reaction parameters. Decreasing the amounts of both Pd(OAc)₂ and bisimidazolium while maintaining the 1:1 ratio resulted in a significant decrease in the coupling product yield (Table 1, entries 9,10). Further increasing the Pd(OAc)₂ and bisimidazolium loading (0.05 mol%) did not change the yield of coupling product (Table 1, entry 11). These results indicate that both Pd(OAc)₂ and bisimidazolium loading as well as their ratio have critical and inevitable roles in the catalytic system.

Finally, the coupling product was obtained with excellent and good yields in DMF and DMAc as solvent, respectively (Table 1, entries 3,12). While, the yield of coupling product was poor in the presence of ACN as solvent (Table 1, entry

Table 1. Optimization of Reaction Conditions for Mizoroki-Heck Coupling of 4-Bromoanisole and *n*-Butyl Acrylate^a

Entry	Pd(OAc) ₂ (mol%)	BI (mol%) ^b	Pd:BI ^b	Base/Solvent	Yield (%) ^c	TON ^d /TOF (h ⁻¹) ^e
1	0.025	0.025	1:1	K ₂ CO ₃ /DMF	0	-/-
2	0.025	0.025	1:1	NaOAc/DMF	0	-/-
3	0.025	0.025	1:1	NaOtBu/DMF	95	3800/158
4	0.025	0.025	1:1	NaOAc + NaOtBu/DMF	61	2400/100
5	-	0.025	0:1	NaOtBu/DMF	0	-/-
6	0.025	-	1:0	NaOtBu/DMF	0	-/-
7	0.025	0.05	1:2	NaOtBu/DMF	66	2600/108
8	0.025	0.075	1:3	NaOtBu/DMF	15	600/25
9	0.0125	0.0125	1:1	NaOtBu/DMF	71	2800/117
10	0.00625	0.00625	1:1	NaOtBu/DMF	54	2200/92
11	0.05	0.05	1:1	NaOtBu/DMF	96	3800/158
12	0.025	0.025	1:1	NaOtBu/DMAc	69	2800/117
13	0.025	0.025	1:1	NaOtBu/ACN	24	1000/42
14	0.025	0.025	1:1	NaOtBu/Toluene	0	-/-
15	0.025	0.025	1:1	NaOtBu/Water	0	-/-

^aReaction conditions: 4-bromoanisole (4 mmol), *n*-butyl acrylate (6 mmol), base (6 mmol), Pd(OAc)₂/Bisimidazolium, solvent (4 ml), 24 h, and N₂ atmosphere, ^bBI = Bisimidazolium, ^cIsolated yield, ^dTON = mmol of product/mmol of Pd catalyst, ^eTOF = TON/time (24 h).

13) and no coupling product was observed using toluene or water solvent (Table 1, entries 14,15). Therefore, DMF was chosen as the best solvent for the investigation of Mizoroki-Heck coupling reaction of *n*-butyl acrylate and styrene with various aryl halides in the next steps, which is comparable to those reported previously [28,32,33].

To evaluate the scope and generality of this new protocol, the Mizoroki-Heck coupling of various aryl halides with *n*-butyl acrylate (Tables 2,3) was investigated at optimized reaction conditions (Table 1, entry 3). Bromobenzene was converted into the corresponding *trans*-configured coupling product in about 99% yield with 100% selectivity after 1 h (Table 2, entry 1). There was a higher conversion of *para*-methylbromobenzene (4-bromotoluene) than its *meta*-isomer counterpart (3-bromotoluene) (Table 2, entries 2,3).

Most likely, this is due to the more confident electronic and steric effects of the methyl group at the *para* position. Other *para*-substituted aryl bromides could also react with good to excellent conversion for the corresponding coupling products (Table 2, entries 4-8). The selectivity was excellent in all cases except for 4-bromoaniline and 1-bromo-4-nitrobenzene. The *cis*-configured coupling products were also obtained for these two substrates (Table 2, entries 5,8). Furthermore, the yield of coupling products for the sterically hindered aryl bromides such as 4-bromobiphenyl and α -bromonaphthalene was low even after 24 h (Table 2, entries 9,10). The conversion of chlorobenzene was 99% with high selectivity for *trans*-configured product after 9 h (Table 2, entry 11). It is worth mentioning that the conversions did not change after 24 h for all aryl halides included in Table 2.

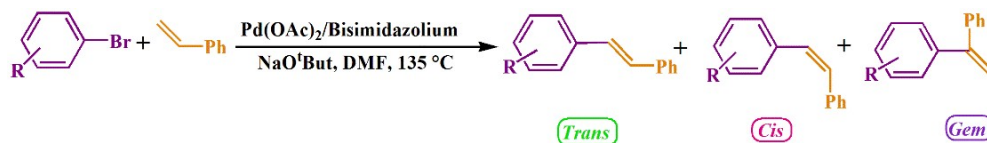
Table 2. The Mizoroki-Heck Coupling Reaction of *n*-Butyl Acrylate with Various Aryl Halides^a

Entry	Aryl bromide	<i>trans/cis/gem</i> (%) ^b	Time (h)	Conversion (%)	K_{SI}^c, K_{RI}^d	TON ^e /TOF (h ⁻¹) ^f
1		99/0/0	1	99	>99/1, >99/1	3960/165
2		99/0/0	1	99	>99/1, >99/1	3960/165
3		81/0/0	5	81	>99/1, >99/1	3200/133
4		95/0/0	5	95	>99/1, >99/1	3800/158
5		62/0/12	5	74	>99/1, 6	2800/117
6		90/2.5/2.5	5	95	36, 37	3800/158
7		83/0/0	5	83	>99/1, >99/1	3400/142
8		75/0/15	5	90	>99/1, >99/1	3600/150
9		15/0/0	5	15	>99/1, >99/1	600/25
10		22/0/0	5	22	>99/1, >99/1	800/33
11		99/0/0	9	99	>99/1, >99/1	3960/165

^aReaction conditions: aryl halide (4 mmol), *n*-butyl acrylate (6 mmol), NaOtBu (6 mmol), Pd(OAc)₂ (0.025 mol%), Bisimidazolium (0.025 mol%), DMF (4 ml), 135 °C, and N₂ atmosphere, ^bIsolated yield; All products are known and identified by comparing of their spectral data with those of the authentic samples [28,33,36], ^c*Stereo*-isomer ratio, $K_{SI} = \text{trans-isomer}/\text{cis-isomer}$, ^d*Regio*-isomer ratio, $K_{RI} = \beta/\alpha$ ($\beta = \text{trans-isomer} + \text{cis-isomer}$, $\alpha = \text{gem-isomer}$), ^eTON = mmol of products (conversion)/mmol of Pd catalyst, ^fTOF = TON/time (24 h).

In next step, the Mizoroki-Heck coupling reaction of aryl bromides with styrene was investigated (Table 3). The coupling reaction proceeds smoothly (5 h) with high yield

and selectivity using bromobenzene (93% and 99%, respectively, Table 3, entry 1). Moreover, similar yield and selectivity for the *trans*-isomer coupling products were

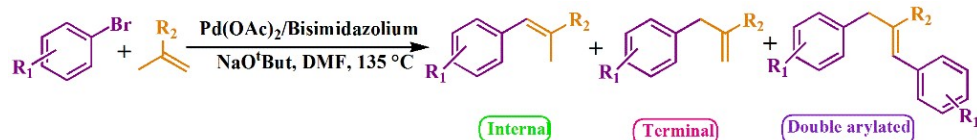
Table 3. The Mizoroki-Heck Coupling Reaction of Styrene with Various Aryl Bromides^a

Entry	Aryl bromide	<i>trans/cis/gem</i> (%) ^b	Time (h)	Conversion (%)	K_{SI}^c, K_{RI}^d	TON/TOF (h ⁻¹)
1		93/0/0	5	93	>99/1, >99/1	3720/155
2		75/0/0	5	75	>99/1, >99/1	3000/125
3		71/0/0	5	71	>99/1, >99/1	2800/117
4		-/-/-	24	0	-/-	-/-
5		55/0/10	9	65	>99/1, 5.5	2600/108
6		52/5/10	9	67	10, 5.5	2600/108
7		50/0/35	9	85	>99/1, 1.43	3400/142
8		23/0/0	9	23	>99/1, >99/1	800/33
9		24/0/0	9 (24)	0 (24)	>99/1, >99/1	1000/42

^aReaction conditions: aryl halide (4 mmol), styrene (6 mmol), NaOtBu (6 mmol), Pd(OAc)₂ (0.025 mol%), Bisimidazolium (0.025 mol%), DMF (4 ml), 135 °C, and N₂ atmosphere, ^bIsolated yield; All products are known and identified by comparing of their spectral data with those of the authentic samples [31,37], ^c*Stereo*-isomer ratio, $K_{SI} = \text{trans-isomer}/\text{cis-isomer}$, ^d*Regio*-isomer ratio, $K_{RI} = \beta/\alpha$ ($\beta = \text{trans-isomer} + \text{cis-isomer}$, $\alpha = \text{gem-isomer}$).

obtained after 5 h for 4-bromotoluene and 3-bromotoluene (Table 2, entries 2,3). However, 4-bromoanisole remained intact even after 24 h (Table 3, entry 4), 4-bromoaniline, 4-bromobenzaldehyde, 4-bromoacetophenone, and 1-bromo-4-nitrobenzene gave the coupling products with moderate yields and low selectivities for the *trans*-isomer coupling products after 9 h (Table 2, entries 5-8). 4-Bromobiphenyl, as a sterically hindered substrate, also showed very low yield

of the *trans*-isomer coupling product after 24 h (Table 3, entry 9). The *regio*- and *stereo*-selectivity, TON, and TOF for all cases are reported in Table 3. Furthermore, the conversions did not change after 24 h for all cases in Table 3 except for 4-bromobiphenyl. The results showed that the yield and selectivity of the coupling products for all aryl bromides remarkably decreased using styrene compared to *n*-butyl acrylate.

Table 4. The Mizoroki-Heck Coupling Reaction of 1,1-Disubstituted Olefins with Aryl Bromides^a

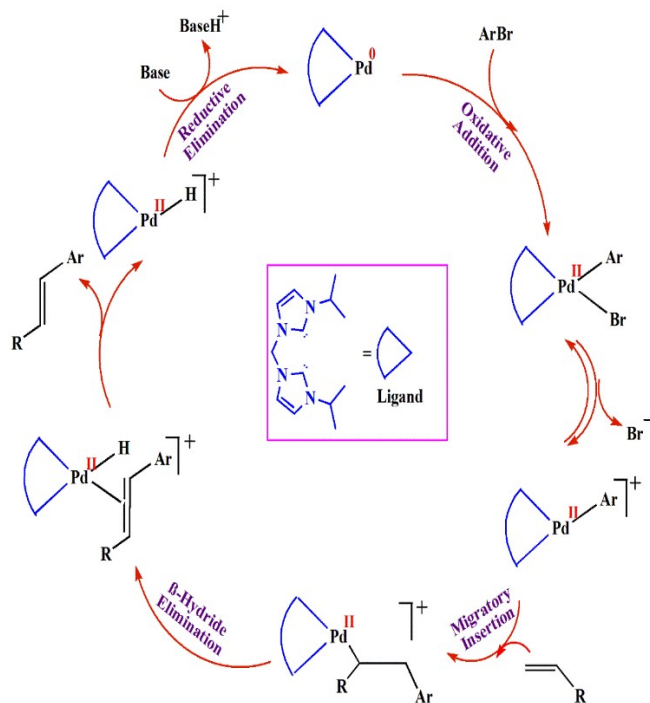
Entry	R ₁	R ₂	Terminal/internal/ double arylated (%) ^b	Conversion (%)	K _{TI} ^c , K _{MD} ^d	TON/TOF (h ⁻¹)
1	H	CO ₂ Bu	92/0/0	92	>99/1, >99/1	3680/153
2	CH ₃	CO ₂ Bu	85/0/0	85	>99/1, >99/1	3400/142
3	NO ₂	CO ₂ Bu	55/8/0	63	5.5, >99/1	2600/108
4	H	Ph	60/11/0	81	6, 7	3200/133
5	CH ₃	Ph	55/10/0	65	5.5, >99/1	2600/108
6	NO ₂	Ph	51/32/0	83	1.67, >99/1	3200/133

^aReaction conditions: aryl halide (4 mmol), 1,1-disubstituted olefins (6 mmol), NaOtBu (6 mmol), Pd(OAc)₂ (0.025 mol%), Bisimidazolium (0.025 mol%), DMF (4 ml), 135 °C, 24 h; and N₂ atmosphere, ^bIsolated yield; All products are known and identified by comparing of their spectral data with those of the authentic samples [38], ^cK_{TI} = terminal-isomer/internal-isomer, ^dK_{MD} = mono aryated/double aryated, (mono aryated = terminal-isomer + internal-isomer).

Generally, the Mizoroki-Heck coupling reaction has been applied to a wide variety of mono-substituted olefins. However, only a few examples of the use of di-substituted olefins have been reported to date. Thus, we then turned our attention to Heck arylation of this class of olefins (*n*-butyl methacrylate and α -methylstyrene) with various aryl bromides (Table 4).

The Heck arylation reactions of bromobenzene or 4-bromotoluene with *n*-butyl methacrylate resulted in terminal coupling products in excellent yields after 24 h (92 and 85%, respectively, Table 4, entries 1,2). Further, 1-bromo-4-nitrobenzene produced both the terminal and internal arylation coupling products after 24 h (55 and 8%, respectively, Table 4, entry 2). The terminal, internal, and double aryated coupling products were obtained using α -methylstyrene as an olefin (Table 4, entries 4-6). According to the results presented in Table 4, the Heck arylation of *n*-butyl methacrylate is more efficient and selective than α -methylstyrene.

Scheme 1 shows the proposed mechanism for the Mizoroki-Heck coupling reaction in the presence of Pd(OAc)₂/Bisimidazolium as a catalyst. Bronsted basic anions on the azolium salt can provide the desired ligand



Scheme 1. Proposed mechanism for the Mizoroki-Heck coupling reactions catalyzed by Pd(OAc)₂/Bisimidazolium catalyst

Table 5. Comparison of the Activity of Pd(OAc)₂/Bisimidazolium Catalyst with some Reported Homogeneous Pd-Catalysts in the Mizoroki-Heck Coupling Reaction of Bromobenzene with *n*-Butyl Acrylate

No.	Catalytic system	Pd (mol%)	Base/Solvent/Additive	Yield (%)	Ref.
1	Pd(OAc) ₂ /Quinoline-8-carboxylate	0.01	K ₂ CO ₃ /DMF/-	91	[46]
2	Pd(dba) ₂ /Bis(thiourea)	0.1	NaOAc/NMP/TBAB	92	[47]
3	Pd(OAc) ₂ / <i>N,N</i> -Dimethyl-β-alanine	1.0	K ₂ CO ₃ /NMP/-	98	[48]
4	PdCl ₂ /5,6-Dibutoxy- <i>N,N</i> -dibutylbenzimidazolium bromide	0.1	NaOAc/DMF/TBAB	96	[49]
5	<i>Trans</i> -[PdCl ₂ (MPI) ₂]	0.1	K ₂ CO ₃ /DMF/-	92	[50]
6	Cyclopalladated ferrocenylimine/NHC	5.0	K ₃ PO ₄ /DMF/TBAB	83	[51]
7	Pd ^{II} bis(thiosemicarbazone)	0.1	K ₂ CO ₃ /DMF/-	89	[52]
8	[PdCl(PC(CH ₂) ₅ CP)(CH ₃ CN)]BF ₄	0.1	K ₂ CO ₃ /DMF/-	95	[53]
9	Di-μ-bromo-bis{2-[(Diisopropylphosphano)methyl]-3,6-difluorophenyl-C ¹ ,P} dipalladium(II)	0.1	Cs ₂ CO ₃ /DMF/-	81	[54]
10	Di-μ-bromo-bis{2-[(Diphenylphosphano)methyl]phenyl-C ¹ ,P} dipalladium(II)	0.1	Cs ₂ CO ₃ /DMF/-	90	[54]
11	[LPd ₂ (pz)], L = 2-(<i>N,N</i> -dimethylthiocarbamato)-5-methylisophthalaldehyde di-2'-hydroxy 5'-methylanyl	2.0	K ₂ CO ₃ /DMF/-	99	[55]
12	[PdCl(ppy){(CN) ₂ IMes}]	0.1	Na ₂ CO ₃ /DMF/TBAB	73	[56]
13	PdCl ₂ / <i>N</i> -(diphenylphosphino)triethylammonium chloride	3.0	NaOH/DMF/-	82	[57]
14	Pd(OAc) ₂ /1,1'-Methylene-3,3'-bis[(<i>N</i> -(<i>tert</i> -butyl)imidazol-2-ylidene)]	0.025	K ₂ CO ₃ /DMF/-	97	[28]
15	Pd(OAc) ₂ /Bisimidazolium	0.025	NaOtBu/DMF/-	99	-

through their *in situ* deprotonation by a base (NaOtBu) under heat. In the case of coordinating anion on the azolium salt, this anion is incorporated into Pd(OAc)₂. The palladium complex with bridged methylene and chelating NHCs is accessible only through this route [39,40]. The Pd(II) precursor in Pd(OAc)₂/Bisimidazolium complex reduces to active Pd(0) species in the presence of olefin substrates. The lower amount of active Pd(0) species is stabilized by coordination of olefin substrates in Mizoroki-Heck reactions [41] as previously confirmed by DFT calculations [42]. The lower relative concentration of complex against olefin can

lead to the higher TONs [43].

As can be seen in Scheme 1, the C–Br bond of an aryl halide is oxidative added to the active Pd(0)–NHC species. After oxidative addition, the dissociation of a ligand (Br⁻) is proposed to occur prior to coordination of the olefin. In the Mizoroki-Heck coupling reactions catalyzed by Pd(0)–phosphine complexes, a phosphine ligand is substituted by an alkene. However, for the Pd(0)–NHC complexes, where the binding energy calculated for a NHC is higher than that of the halide anion, the situation could be different [44]. In the next step, the olefin molecule is inserted to the Pd–Ar bond,

which is followed by the formation of a new coordinated alkene by β -hydride elimination through a C–H agostic interaction with the Pd, which then gives a hydride-Pd(II) complex and a free new alkene. Finally, the reductive elimination of the hydride-Pd(II) complex, which is favored by the steric effects of the bulky *N*-substituents on carbene ligand [45], provides a Pd(0)–NHC complex as the active species restarting the catalytic cycle.

Several goals must be achieved in the Mizoroki-Heck coupling. One of the most important goals is the use of stable and inexpensive starting materials and ligands with low palladium loading to obtain high TONs. However, the high palladium loading and long reaction time for some reported systems are not favorable to the synthetic and industrial applications. Moreover, some catalyst systems are associated with the practical problems such as multistep synthesis procedures or high sensitivity of ligand toward air and moisture. Comparison of our results with some other catalytic systems indicates that Pd(OAc)₂/Bisimidazolium catalyst gives a higher yield with a very low catalyst loading in a shorter reaction time (Table 5).

CONCLUSIONS

The Pd(OAc)₂/Bisimidazolium catalyst was used in the Mizoroki-Heck coupling reaction. This homogeneous catalyst catalyzed the coupling reaction of a broad range of aryl halides, less reactive chlorobenzene as well as aryl bromides, with mono- and di-substituted olefins. In the presence of our catalytic system, the Heck arylation reactions of aryl halides with *n*-butyl acrylate and *n*-butyl methacrylate had high yield and selectivity for the *trans*-isomer coupling and terminal coupling products, respectively.

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