Palladium-Catalyzed Heck Reaction of Aryl Bromides in Aqueous Media Using Tris(N-Heterocyclic Carbene) Ligands

Ismail Özdemir,*a Serpil Demir,a Bekir Çetinkaya^b

^a Inönü University, Faculty Science and Arts, Chemistry Department, 44280 Malatya, Turkey Fax +90(422)3410212; E-mail: iozdemir@inonu.edu.tr

^b Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey

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Dedicated to Professor Richard F. Heck in great admiration of his scientific work as pioneer of organometallic and organic chemistry

Abstract: A highly effective, easy to handle and environmentally benign process for palladium-mediated Heck reaction was developed. The in situ prepared three-component system composed of palladium(II) acetate, a tris(azolinium) bromide and potassium *tert*-butoxide, quantitatively catalyzes the Heck reaction of aryl bromides in aqueous media.

Key words: Heck reaction, imidazolinium and benzimidazolium salts, C–C coupling, palladium, N-heterocyclic carbene

Palladium-catalyzed arylation of olefins, the Heck reaction, is a powerful tool in organic synthesis.¹ It has found widespread use in the synthesis of natural products, polymers, dendrimers and various conjugated architectures of interest in materials science. The Heck reaction also holds much promise in many industrial processes, especially in the synthesis of fine chemicals and active pharmaceutical intermediates.² In view of these, much attention has been paid in recent years to develop milder and operationally simpler procedures for the Heck reaction. Some important developments include the use of ligand-free palladium catalysts in combination with tetraalkylammonium salts, the use of palladacycles, pincer and supported palladium catalysts and more recently the bulky electron-rich phosphine and N-heterocyclic carbene (NHC) ligands for palladium.³ With their phosphine mimic⁴ ligating, NHC have attracted the attention of several research groups.⁵ Various NHC ligands have been synthesized within a short period of time, and some of them have been successfully used for a variety of palladium-catalyzed transformations.⁶ Although NHC-palladium complexes used for Heck reaction were claimed to be air and moisture stable, only a few examples carried out under air were reported by Crabtree and co-workers.⁷ Most reactions catalyzed by NHC-palladium complexes are conducted under an inert atmosphere. Therefore, easy-to-handle and highly efficient catalysts that are stable towards oxidants and moisture variations are still targets of pursuit. The use of water as a solvent for chemical reactions clearly has both economical and environmental advantages because it is inexpensive, abundant, nontoxic, nonflammable, and readily separable from organic compounds.⁸ There have been a number of reports of the palladium-mediated Heck reaction being performed using water as solvents.⁹

We have previously reported the use of an in situ formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidenepalladium(II) systems that exhibit high activity for various coupling reactions of aryl bromides and aryl chlorides.¹⁰ In order to obtain more stable, efficient and active systems, we have also investigated benzoannelated derivatives.¹¹ Recently, our group reported that novel complexes of rhodium(I) 1,3-dialkylimidazolidin-2-ylidenes gave secondary alcohols in good yields by the addition of phenylboronic acid to aldehydes.¹² In this article, we wish to report an air and water stable, effective tridentate NHC-ligated palladium catalyst that can be used for activation of aryl bromides. Aiming to find novel ligands for palladium-catalyzed transformations, we synthesized a number of tridentate imidazoliniums and benzimidazoliums as depicted in Scheme 1. We report here an in situ Pd-carbene-based catalytic system for the Heck reaction in aqueous media.¹³ The 1-alkylimidazoline and 1-alkylbenzimidazole were prepared according to known method.¹⁴ Tris(imidazolidinium) bromides 2a-c, and tris(benzimidazolium) bromides 3a-c are conventional NHC precursors. N,N-Disubstituted imidazolinium and benzimidazolium bromides 2 and 3 were prepared simply by heating the 2,4,6tris(bromomethyl)mesitylene with 1-substituted imidazolines or benzimidazoles (Scheme 1).^{10,11} It has been found that the in situ formation of the ligand by deprotonation of the bis(imidazolinium) bromides lead to significantly better results than use of the preformed carbene.¹⁵

The Heck reaction¹⁶ has been shown to be very useful for the preparation of disubstituted olefins in particular. The rate of the coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, Heck reactions conducted with tertiary phosphine¹⁷ or NHC ¹⁸ complexes required high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we surveyed Cs₂CO₃, K₂CO₃, *t*-BuOK, and K₃PO₄. Finally, we found that use of 1% mol Pd(OAc)₂, 0.7% mol **2** or **3**, 2 equivalents Cs₂CO₃ or *t*-BuOK, in DMF–H₂O (1:1) at 50 °C led to the best conversion within 5 hours. We initially tested the catalytic activity of Pd(OAc)₂/**2a–c** for the coupling of *p*-bromoacetophenone with styrene (Table 1, entries 1–3).

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Scheme 1 The synthesis of tris(azolinium) salts

In addition, the reactions were performed in air and without degassing the water and DMF prior to use.

Control experiment indicated that the coupling reaction did not occur in the absence of **2a**. Under the determined reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups can react with styrene affording the coupled products in excellent yields. As expected, electron-deficient bromides were beneficial for the conversions.

Under those conditions, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromoanisole, and *p*-bromotoluene react very cleanly with styrene in goods yields (Table 1, entries 1, 2, 4, 10, 11, 16 and 19). The higher performance of the tridentateazolium salts 2 and 3 are thought to be due to its better electron-donating ability and more steric hindrance.

These results indicated that the catalytic system generated in situ from tridentateazolinium salts and $Pd(OAc)_2$ have an activity, which is superior or comparable to the monodentate imidazolinium/ $Pd(OAc)_2$ system.¹⁹ However, chloroarenes basically do not react under standard conditions, and yields are lower than 4%.

In conclusion, the tridentate carbene-ligand-palladiumcatalyst system disclosed herein represents an easy to han-

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dle, robust, and high-yielding procedure for Heck couplings. The procedure is simple and efficient towards various aryl bromides and does not require an induction period. The advantage of the catalyst is the low loading capabilities and it is use in air. The ligands are also easily accessible. Further study is underway to optimize the reactivity of these N-heterocyclic carbene precursors for C– C and C–N coupling with Pd(OAc)₂, and transition-metal complexes of Ru, Pd, and Rh to explore their catalytic activity.

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+ Br R			
	Pd(OAc) ₂ , 2 or 3, <i>t</i> -BuOK		
	DMF–H ₂ O, 50 °C, 5 h	*	
Entry	Catalyst	R	Yield (%) ^a
1	2a	СОМе	97
2	2b	COMe	97
3	2c	COMe	91
4	3 a	COMe	93
5	3b	COMe	88
6	3c	COMe	86
7	2a	СНО	94
8	2b	СНО	92
9	2c	СНО	91
10	3 a	СНО	96
11	3b	СНО	96
12	3c	СНО	90
13	2a	OMe	87
14	2b	OMe	84
15	2c	OMe	79
16	3 a	OMe	89
17	3b	OMe	85
18	3c	OMe	81
19	2a	Me	84
20	2b	Me	81
21	2c	Me	79
22	3 a	Me	83
23	3b	Me	81
24	3c	Me	78

^a *Reaction conditions:* p-BrC₆H₄R (1.0 mmol), styrene (1.5 mmol), *t*-BuOK (2 mmol), Pd(OAc)₂ (1.0%), **2** or **3** (0.7 mmol%), H₂O–DMF (6 ml, 1:1), 50 °C, 5 h. Purity of compounds was checked by NMR and yields are based on aryl bromide.

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(13) General Procedure for the Synthesis of Tridentateazolinium Bromides

To a solution of 1-alkylimidazoline or 1-alkylbenzimidazole (15 mmol) in DMF (15 mL) was added slowly 2,4,6-tris(bromomethyl)mesitylene (5 mmol) at 25 °C and the resulting mixture was heated for 5 h at 60 °C. Then, Et₂O (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et₂O (3×15 mL), dried under vacuum. The crude product was crystallized from EtOH–Et₂O (2:1). 2,4,6-Tris[3-(2,4,6-trimethylbenzyl)imidazolinium]methylmesitylene bromide (**2a**): yield 4.67 g (93%); mp 86–287 °C. IR: $v_{(CN)} = 1650$ cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.16$ and 2.22 [s, 27 H, CH₂C₆H₂(CH₃)₃-2,4,6], 2.49 [s, 9 H,

 $C_6(CH_{3)3}(CH_{2)3}-2,4,6]$, 3.64 and 4.29 [t, J = 10.8, 10.4 Hz, 12 H, NCH₂CH₂N], 4.69 [s, 6 H, $C_6(CH_{3})_3(CH_{2})_3-2,4,6]$, 4.91 [s, 6 H, $CH_2C_6H_2(CH_{3})_3-2,4,6]$, 6.76 [s, 6 H,

 $CH_2C_6H_2(CH_3)_3-2,4,6], 9.54 (s, 3 H, NCHN).$ ¹³C{¹H}NMR $(CDCl_3): \delta = 20.6 \text{ and } 21.3 [CH_2C_6H_2(CH_3)_3-2,4,6], 18.0$ [C₆(CH₃)₃(CH₂)₃-2,4,6], 46.5 [C₆(CH₃)₃(CH₂)₃-2,4,6], 47.9 and 48.0 (NCH₂CH₂N), 50.3 [CH₂C₆H₂(CH₃)₃-2,4,6], 126.0, 130.1, 138.2 and 139.0 [CH₂C₆H₂(CH₃)₃-2,4,6], 129.4, 141.4 and 156.8 [C₆(CH₃)₃(CH₂)₃-2,4,6], 162.9 (NCHN). Anal. Calcd for C₅₁H₆₉N₆Br₃: C, 60.90; H, 6.91; N, 8.36. Found: C, 60.92; H, 6.88; N, 8.35. 2,4,6-Tris[3-(methoxyethyl)imidazolinium]methylmesitylene bromide (2b): yield 3.16 g (81%); mp 156-157 °C. IR: $v_{(CN)} = 1660 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): $\delta = 2.44 \text{ [s,}$ 9 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 3.28 (s, 9 H, NCH₂CH₂OCH₃), 3.41 and 3.52 (t, J = 4.8 Hz, 12 H, NCH₂CH₂N), 4.14 (t, J = 11.0 Hz, 6 H, NC H_2 CH $_2$ OCH $_3$), 4.38 (t, J = 11.2 Hz, 6 H, NCH₂CH₂OCH₃), 4.65 [s, 6 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 9.14 (s, 3 H, NCHN). ${}^{13}C{}^{1}H$ NMR (CDCl₃): $\delta = 17.7$ [C₆(CH₃)₃(CH₂)₃-2,4,6], 59.0 (NCH₂CH₂OCH₃), 47.7 (NCH₂CH₂OCH₃), 47.9 (NCH₂CH₂OCH₃), 50.1 and 50.6 (NCH₂CH₂N), 69.9 [C₆(CH₃)₃(CH₂)₃-2,4,6], 129.1, 141.0 and 157.1 [C₆(CH₃)₃(CH₂)₃-2,4,6], 162.6 (NCHN). Anal. Calcd for C₃₀H₅₁N₆O₃Br₃: C, 45.99; H, 6.56; N, 10.73. Found: C, 46.00; H, 6.55; N, 10.75. 2,4,6-Tris[3-(ethoxyethyl)imidazolinium]methylmesitylene bromide (2c): yield 3.54 g (86%); mp 123-124 °C. IR: $v_{(CN)} = 1659 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): $\delta = 0.96 \text{ [t, } J = 6.9 \text{ Hz,}$ 9 H, NCH₂CH₂OCH₂CH₃], 2.31 [s, 9 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 3.30 (q, J = 6.9 Hz, 6 H, NCH₂CH₂OCH₂CH₃), 3.42 and 3.68 (m, 12 H, NCH₂CH₂N), 4.06 (t, J = 10.4 Hz, 6 H, $NCH_2CH_2OCH_2CH_3$, 4.25 (t, J = 10.6 Hz, 6 H, NCH₂CH₂OCH₂CH₃), 4.50 [s, 6 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 9.03 (s, 3 H, NCHN). ${}^{13}C{}^{1}H}NMR$ (CDCl₃): $\delta = 17.5$ [C₆(CH₃)₃(CH₂)₃-2,4,6], 15.5 (NCH₂CH₂OCH₂CH₃), 66.7 (NCH₂CH₂OCH₂CH₃), 47.9 (NCH₂CH₂OCH₂CH₃), 48.4 (NCH₂CH₂OCH₂CH₃), 50.5 and 50.8 (NCH₂CH₂N), 68.3 [C₆(CH₃)₃(CH₂)₃-2,4,6], 129.2, 141.2 and 157.2 [C₆(CH₃)₃(CH₂)₃-2,4,6], 162.7 [NCHN]. Anal. Calcd for $C_{33}H_{57}N_6O_3Br_{3:}$ C, 48.01; H, 6.96; N, 10.18. Found: C, 48.03; H, 6.99; N: 10.15. 2,4,6-Tris[3-(2,4,6-trimethylbenzyl)benzimidazolium]methylmesitylene bromide (**3a**): yield 5.00 g (87%); mp 214–215 °C. IR: $v_{(CN)} = 1562 \text{ cm}^{-1}$. ¹H NMR (DMSO d_6): $\delta = 2.22$ and 2.24 [s, 27 H, CH₂C₆H₂(CH₃)₃-2,4,6], 2.39 [s, 9 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 5.94 and 5.95 [s, 12 H, $C_6(CH_3)_3(CH_2)_3$ -2,4,6 and $CH_2C_6H_2(CH_3)_3$ -2,4,6], 6.93 [s, 6 H, $CH_2C_6H_2(CH_3)_3$ -2,4,6], 7.16 [d, J = 8.0 Hz, 3 H, NC₆H₄N], 7.56 and 7.67 (t, *J* = 7.6 Hz, 6 H, NC₆H₄N), 8.13 $(d, J = 8.4 \text{ Hz}, 3 \text{ H}, \text{NC}_6\text{H}_4\text{N}), 10.33 (s, 3 \text{ H}, \text{NCHN}).$ ¹³C{¹H}NMR (DMSO- d_6): $\delta = 20.4$ and 21.3 [CH₂C₆H₂(CH₃)₃-2,4,6], 17.2 [C₆(CH₃)₃(CH₂)₃-2,4,6], 47.1 [C₆(CH₃)₃(CH₂)₃-2,4,6], 47.4 [CH₂C₆H₂(CH₃)₃-2,4,6], 126.8, 130.4, 138.6 and 139.1 [CH₂C₆H₂(CH₃)₃-2,4,6], 129.5, 141.9 and 142.9 $[C_6(CH_3)_3(CH_2)_3-2,4,6]$, 114.3, 115.2, 127.3, 127.8, 132.1 and 132.4 (NC₆H₄N), 163.1 (NCHN). Anal. Calcd for C₆₃H₆₉N₆Br₃: C, 65.80; H, 6.05; N, 7.31. Found: C, 65.83; H, 6.02; N, 7.30. 2,4,6-Tris[3-(3,4,5-trimethoxybenzyl)benzimidazolium]methylmesitylene bromide (**3b**): yield 5.81 g (90%); mp 195–196 °C. IR $v_{(CN)} = 1596 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): $\delta = 2.44$ [s, 9 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 3.72 and 3.77 [s, 27 H, CH₂C₆H₂(OCH₃)₃-3,4,5], 5.84 [s, 6 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 5.90 [s, 6 H, CH₂C₆H₂(OCH₃)₃-3,4,5], 6.82 [s, 6 H, CH₂C₆*H*₂(OCH₃)₃-3,4,5], 7.56 (m, 9 H, NC₆H₄N), 8.25 (d, J = 8.1 Hz, 3 H, NC₆H₄N), 10.59 (s, 3 H, NCHN). ¹³C{¹H}NMR (CDCl₃): $\delta = 18.5 [C_6(CH_3)_3(CH_2)_3 - 2, 4, 6],$ 47.5 [C₆(CH₃)₃(CH₂)₃-2,4,6], 52.7 [CH₂C₆H₂(OCH₃)₃-

3,4,5], 57.1 and 61.2 [CH₂C₆H₂(OCH₃)₃-3,4,5], 106.5, 138.6, 141.5 and 153.9 $[CH_2C_6H_2(OCH_3)_3-3,4,5]$, 129.2, 142.4 and 142.7 [*C*₆(CH₃)₃(CH₂)₃-2,4,6], 114.2, 114.7, 127.5, 127.8, 132.0 and 132.1 (NC₆H₄N), 190.1 (NCHN). Anal. Calcd for C₆₃H₆₉N₆O₉Br₃: C, 58.48; H, 5.37; N, 6.49. Found: C, 58.45; H, 5.36; N, 6.50. 2,4,6-Tris[3-(ethoxtethyl)benzimidazolium]methylmesitylene bromide (3c): yield 4.01 g (83%); mp 282-283 °C. IR $v_{(CN)} = 1563 \text{ cm}^{-1}$. ¹H NMR (CDCl₃): $\delta = 0.79 \text{ (t,}$ J = 6.8 Hz, 9 H, NCH₂CH₂OCH₂CH₃), 2.48 [s, 9 H, C₆ $(CH_3)_3(CH_2)_3$ -2,4,6], 3.76 (quart, J = 7.2 Hz, 6 H, NCH₂CH₂OCH₂CH₃), 3.79 (t, J = 12.0 Hz, 6 H, NCH₂CH₂OCH₂CH₃), 4.85 (t, J = 12.0 Hz, 6 H, NCH₂CH₂OCH₂CH₃), 5.90 [s, 6 H, C₆(CH₃)₃(CH₂)₃-2,4,6], 8.12 (d, J = 7.6 Hz, 3 H, NC₆H₄N), 8.29 (d, J = 8.0 Hz, 3 H, NC₆H₄N), 7.76 (m, 6 H, NC₆H₄N), 10.09 (s, 3 H, NCHN). ¹³C{¹H}NMR (CDCl₃): $\delta = 17.1 [C_6(CH_3)_3(CH_2)_3 - 2, 4, 6],$ 15.4 (NCH₂CH₂OCH₂CH₃), 46.7 (NCH₂CH₂OCH₂CH₃), 47.3 (NCH₂CH₂OCH₂CH₃), 66.2 (NCH₂CH₂OCH₂CH₃), 68.2 [C₆(CH₃)₃(CH₂)₃-2,4,6], 129.4, 142.0 and 142.8 [C₆(CH₃)₃(CH₂)₃-2,4,6], 114.8, 114.9, 127.4, 127.6, 131.8 and 132.4 (NC₆H₄N), 171.2 (NCHN). Anal. Calcd for C₄₅H₅₇N₆O₃Br₃: C, 55.74; H, 5.92; N, 8.67. Found: C, 55.75; H, 5.90; N: 8.66.

General Procedure for the Heck Coupling Reaction Pd(OAc)₂ (1.0 mmol%), 2,4,6-tris[(3-alkyl)azolinium]methylmesitylene bromide **2** or **3** (0.7 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), *t*-BuOK (2 mmol), H₂O–DMF (6 mL, 1:1) were added to a small Schlenk tube and the mixture was heated at 50 °C for 5 h. Finally, the mixture was cooled, extracted with EtOAc–hexane (1:5), 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, yields are based on aryl bromide.

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