

N-Functionalized Azolin-2-ylidene-palladium-Catalyzed Heck Reaction

Ismail Özdemir,¹ Nevin Gürbüz,¹ Yetkin Gök,¹ and Bekir Çetinkaya²

¹Department of Chemistry, Faculty of Science and Art, İnönü University, 44280 Malatya, Turkey

²Department of Chemistry, Faculty of Science, Ege University, 35100 Bornova-İzmir, Turkey

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ABSTRACT: Novel 1,3-dialkylimidazolidinium, 1,3-dialkyl-3,4,5,6-tetrahydropyrimidinium, and 1,3-dialkyl-1*H*-4,5,6,7-tetrahydrodiazepinium hexafluorophosphates (**1a–c**, **2a–c**) as *N*-heterocyclic carbene precursors have been synthesized and characterized. The incorporation of saturated *N*-heterocyclic carbenes into palladium precatalysts gives high-catalyst activity in the Heck coupling of aryl bromide substrates in aqueous media. The complexes were generated in the presence of Pd(OAc)₂ by in situ deprotonation of 1,3-dialkylazolinium salts **1**, **2**. © 2008 Wiley Periodicals, Inc. *Heteroatom Chem* 19:82–86, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20415

INTRODUCTION

Palladium-catalyzed C–C coupling reactions have been recognized as power tools in multiple organic transformations, from these the Heck reaction has become a cornerstone in modern organic synthesis [1]. This reaction consists in the coupling of a halo compound with an alkene. The importance of this

reaction has transcended its applications in laboratory and become one of main interest at the industrial level [2].

This reaction is normally performed with 1%–5% mol of Pd catalyst along with phosphine ligands. However, industrial applications of the Heck reaction are still rare, mainly due to the following two problems [3]: First, Pd is expensive, and contamination of the product by Pd has to be tightly controlled. Second, many phosphine ligands are even more expensive, and they are not pleasant to work with as they are poisonous, air sensitive, and subject to P–C bond degradation at the elevated temperature.

The different catalysts employed to carry out this reaction have also evolved to achieve a better understanding of the factors that influence activity, selectivity, and stability. Thus, in recent years, several groups have been involved in the design of ligands that are able to tolerate an oxidizing atmosphere, allowing Heck couplings in a more efficient manner by employing cheap reagent-grade starting materials.

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 [4]. With their phosphine mimic ligating, NHC have attracted the attention of several research

Correspondence to: Ismail Özdemir; e-mail: iozdemir@inonu.edu.tr.

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groups [6]. 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 [7]. Although NHC–palladium complexes used for the Heck reaction were claimed to be air and moisture stable, only a few examples carried out under air were reported by Crabtree and coworkers [8]. Most reactions catalyzed by NHC–palladium complexes are conducted under an inert atmosphere. Therefore, it is easy to handle but highly efficient catalytic processes that are stable toward 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 [9]. There have been a number of reports on the palladium-mediated Heck reaction being performed using water as solvents [10].

We have previously reported the use of in situ formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene, and tetrahydrodiazepin-2-ylidene palladium(II) systems that exhibit high activity of various coupling reactions of aryl bro-

mides and aryl chlorides [11]. To obtain more stable, efficient, and active systems, we have also investigated benzo-annulated derivatives [12].

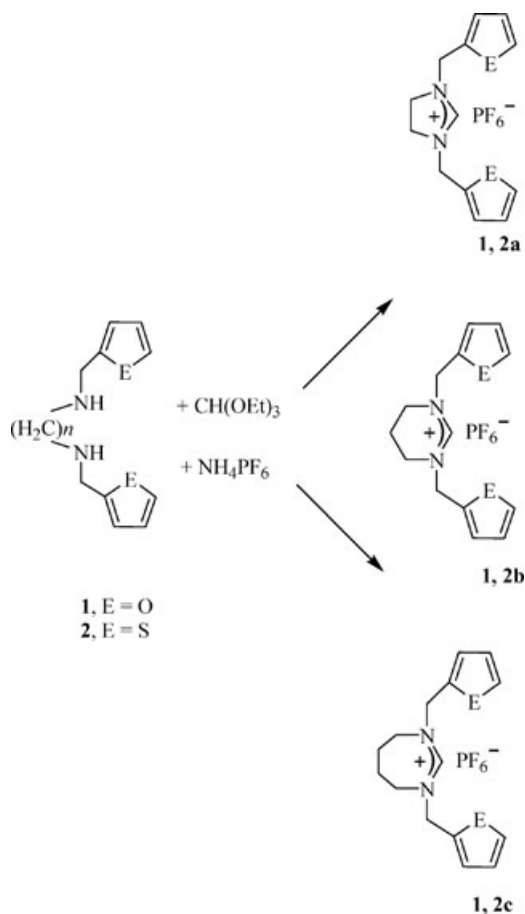
The nature of the NHC ligand has a tremendous influence on the rate of catalyzed reactions. To find more efficient palladium catalysts, we prepared a series of new 1,3-dialkylimidazolidinium, 1,3-dialkyl-3,4,5,6-tetrahydropyrimidinium, and 1,3-dialkyl-1H-4,5,6,7-tetrahydrodiazepinium **1a–c** and **2a–c** compounds (Scheme 1), and we now report the use of the in situ generated catalytic system consisting of Pd(OAc)₂ as palladium source, **1a–c** and **2a–c** as carbene precursors, and KOBu^t as a base for cross coupling of aryl bromides with phenyl styrene in aqueous media.

RESULTS AND DISCUSSION

1,3-Dialkylazolinium salts **1**, **2** (=LHX) are conventional NHC precursors. Their syntheses were achieved by the reaction of *N,N'*-dialkylethan-1,2-diamines, *N,N'*-dialkylpropan-1,3-diamines, and *N,N'*-dialkylbutan-1,4-diamines with triethyl orthoformate and ammonium hexafluorophosphate (Scheme 1) [14].

The structures of **1** and **2** were determined by their spectroscopic data and elemental analyses (see Experimental section). ¹³C NMR chemical shifts were consistent with the proposed structure: the imino carbon appeared as a singlet in the ¹H-decoupled mode at δ = 158.5, 154.7, 159.2, 158.0, 153.7, and 158.9 ppm, respectively, for the azolinium salts **1a–c** and **2a–c**. The ¹H NMR spectra of the imidazolinium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets at δ = 8.70, 10.04, 8.48, 8.71, 8.82, and 8.60 ppm, respectively, for **1a–c** and **2a–c**. The NMR values are similar to those found for other 1,3-dialkylimidazolidinium salts [14]. It has been found that the in situ formation of the ligand by deprotonation of the bis(imidazolidinium) bromides leads to significantly better results than use of the preformed carbene [15].

The Heck reaction [3] 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 phosphine [16] or NHC [17] 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, 2 mol% **1** or **2**, 2 equiv. Cs₂CO₃ or *t*-BuOK, in DMF/H₂O (1:1) at 50°C led to the best



SCHEME 1 Synthesis of 1,3-dialkylazolinium salts (LHX).

TABLE 1 The Heck-Coupling Reaction of Aryl Bromides with Styrene^a


Entry	R	LHX	Yield (%)
1	COCH ₃	1a	92
2	COCH ₃	1b	95
3	COCH ₃	1c	93
4	COCH ₃	2a	94
5	COCH ₃	2b	95
6	COCH ₃	2c	92
7	CHO	1a	84
8	CHO	1b	88
9	CHO	1c	82
10	CHO	2a	79
11	CHO	2b	81
12	CHO	2c	85
13	H	1a	83
14	H	1b	92
15	H	1c	88
16	H	2a	87
17	H	2b	88
18	H	2c	94
19	OCH ₃	1a	87
20	OCH ₃	1b	83
21	OCH ₃	1c	82
22	OCH ₃	2a	74
23	OCH ₃	2b	70
24	OCH ₃	2c	76
25	CH ₃	1a	73
26	CH ₃	1b	81
27	CH ₃	1c	75
28	CH ₃	2a	70
29	CH ₃	2b	72
30	CH ₃	2c	79

^aFor a reaction conditions, see Experimental. Purity of compounds was checked by NMR, and yields are based on aryl bromide. All reactions were monitored by GC.

conversion within 4 h. We initially tested the catalytic activity of Pd(OAc)₂/**1a–c** for the coupling of *p*-bromoacetophenone with styrene (Table 1, entries 1–3).

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 **1** or **2**. 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, such as *p*-bromoacetophenone, *p*-bromobenzaldehyde, bromobenzene, *p*-bromoanisole, and *p*-bromotoluene, were beneficial for the conversions under these conditions. These results indicated that the catalytic system generated in situ from these azolinium

salts and Pd(OAc)₂ has an activity that is superior or comparable to the monodentate imidazolium/Pd(OAc)₂ system [18]. However, chloroarenes basically do not react under standard conditions, and yields are less than 5%.

CONCLUSION

1,3-Dialkylazolinium ligands palladium-catalyst system disclosed herein represents an easy to handle, robust, and high-yielding procedure for the Heck couplings. The procedure is simple and efficient toward various types of aryl bromides and does not require induction period. The advantage of the catalyst is that it has the low-loading capabilities, and it is useable 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.

EXPERIMENTAL

All reactions for the preparation of 1,3-dialkylazolinium salts **1a–c** and **2a–c** were carried out under argon using standard Schlenk-type flasks. Heck-coupling reactions were carried out in air. All reagents were purchased from Aldrich Chemical Co., Turkey. All ¹H and ¹³C NMR were performed in DMSO-*d*₆ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 75.47 MHz (¹³C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in hertz. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at TUBITAK (Ankara, Turkey) Microlab.

1,3-Difurfurylimidazolidinium Hexafluorophosphate (**1a**)

To a solution of 1,2-bisfurfurylaminoethane (3.21 g, 14.59 mmol), CH(OEt)₃ (5 mL) and NH₄PF₆ (2.37 g, 14.54 mmol) were added, and the reaction mixture was heated for 12 h at 60°C. A white solid was precipitated. The precipitate was then crystallized from EtOH/Et₂O (1:2). Yield: 4.85 g, 88%, mp 117–118°C. ¹H NMR (DMSO) δ: 3.79 (s, 8H, NCH₂CH₂N), 4.73 (s, 4H, CH₂C₄H₃O), 6.48, 6.54 and 7.71 (m, 6H, C₄H₃O), 8.70 (s, 1H, 2-CH). ¹³C NMR (DMSO) δ: 44.3 (NCH₂CH₂N), 48.8 (CH₂C₄H₃O), 111.3, 111.6, 144.8, and 147.7 (C₄H₃O), 158.5 (2-CH). Anal. Calcd for C₁₃H₁₅N₂O₂PF₆: C, 41.50, H, 4.02, N, 7.45. Found: C, 41.49, H, 3.99, N, 7.46.

1,3-Difurfuryltetrahydropyrimidinium Hexafluorophosphate (1b)

This compound was prepared from 1,3-bisfurfurylaminopropane (2.17 g, 9.27 mmol) $\text{CH}(\text{OEt})_3$ (5 mL) and NH_4PF_6 (1.51 g, 9.27 mmol). Yield: 3.21, 89%, mp 210–211°C. ^1H NMR (DMSO) δ : 1.94 (quin., 4H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.26 (t, 8H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.82 (s, 4H, $\text{CH}_2\text{C}_4\text{H}_3\text{O}$), 6.22, 6.45, and 7.28 (m, 6H, $\text{C}_4\text{H}_3\text{O}$), 10.04 (s, 1H, 2-CH). ^{13}C NMR (DMSO) δ : 19 and 42.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 50.9 ($\text{CH}_2\text{C}_4\text{H}_3\text{O}$), 110.9, 111.5, 143.9, and 146.9 ($\text{C}_4\text{H}_3\text{O}$), 154.7 (2-CH). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2\text{PF}_6$: C, 43.09, H, 4.39, N, 7.18. Found: C, 49.09, H, 4.38, N, 7.16.

1,3-Difurfuryltetrahydrodiazepinium hexafluorophosphate (1c)

This compound was prepared from 1,4-bisfurfurylaminobutane (0.92 g, 3.70 mmol) $\text{CH}(\text{OEt})_3$ (5 mL) and NH_4PF_6 (0.60 g, 3.68 mmol). Yield: 1.20 g, 81%, mp 107–108°C. ^1H NMR (DMSO) δ : 1.78 (quin., 8H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.65 (t, 8H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.68 (s, 4H, $\text{CH}_2\text{C}_4\text{H}_3\text{O}$), 6.49, 6.59, and 7.73 (m, 6H, $\text{C}_4\text{H}_3\text{O}$), 8.48 (s, 1H, 2-CH). ^{13}C NMR (DMSO) δ : 24.7 and 49.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 53.3 ($\text{CH}_2\text{C}_4\text{H}_3\text{O}$), 111.4, 111.6, 144.9, and 148.4 ($\text{C}_4\text{H}_3\text{O}$), 159.2 (2-CH). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_2\text{PF}_6$: C, 44.56, H, 4.74, N, 6.93. Found: C, 44.55, H, 4.74, N, 6.95.

1,3-Di(2-thiophenemethyl)imidazolidinium Hexafluorophosphate (2a)

This compound was prepared from 1,2-bis(2-thiophenemethyl)aminoethane (2.3 g, 91.16 mmol) $\text{CH}(\text{OEt})_3$ (5 mL) and NH_4PF_6 (1.48 g, 9.10 mmol). Yield: 3.08, 83%, mp 125–126°C. ^1H NMR (DMSO) δ : 3.79 (s, 8H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.89 (s, 4H, $\text{CH}_2\text{C}_4\text{H}_3\text{S}$), 7.01, 7.19 and 7.60 (m, 6H, $\text{C}_4\text{H}_3\text{S}$), 8.71 (s, 1H, 2-CH). ^{13}C NMR (DMSO) δ : 46 ($\text{NCH}_2\text{CH}_2\text{N}$), 48.4 ($\text{CH}_2\text{C}_4\text{H}_3\text{S}$), 128.2, 128.3, 129.6 and 136.2 ($\text{C}_4\text{H}_3\text{S}$), 158.0 (2-CH). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{S}_2\text{PF}_6$: C, 38.24, H, 3.70, N, 6.86. Found: C, 38.25, H, 3.71, N, 6.86.

1,3-Di(2-thiophenemethyl)tetrahydropyrimidinium Hexafluorophosphate (2b)

This compound was prepared from 1,3-bis(2-thiophenemethyl)aminopropane (4.42 g, 16.58 mmol) $\text{CH}(\text{OEt})_3$ (5 mL) and NH_4PF_6 (2.70 g, 16.56 mmol). Yield: 6.1 g, 87%, mp 171–172°C. ^1H NMR (DMSO) δ : 1.88 (quin., 4H, $J = 6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.27

(t, 8H, $J = 6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.88 (s, 4H, $\text{CH}_2\text{C}_4\text{H}_3\text{O}$), 7.07, 7.21, and 7.60 (m, 6H, $\text{C}_4\text{H}_3\text{O}$), 8.82 (s, 1H, 2-CH). ^{13}C NMR (DMSO) δ : 19.1 and 42.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 52.9 ($\text{CH}_2\text{C}_4\text{H}_3\text{S}$), 128.1, 128.2, 129.4, and 136.9 ($\text{C}_4\text{H}_3\text{S}$), 153.7 (2-CH). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{S}_2\text{PF}_6$: C, 39.81, H, 4.06, N, 6.63. Found: C, 39.81, H, 4.07, N, 6.63.

1,3-Di(2-thiophenemethyl)terahydrodiazepinium Hexafluorophosphate (2c)

This compound was prepared from 1,4-bis(2-thiophenemethyl)aminobutane (1.90 g, 6.77 mmol) $\text{CH}(\text{OEt})_3$ (5 mL) and NH_4PF_6 (1.10 g, 6.74 mmol). Yield: 2.24 g, 76%, mp 156–157°C. ^1H NMR (DMSO) δ : 1.78 (quin., 8H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.66 (t, 8H, $J = 5.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.86 (s, 4H, $\text{CH}_2\text{C}_4\text{H}_3\text{S}$), 7.07, 7.25, and 7.60 (m, 6H, $\text{C}_4\text{H}_3\text{S}$), 8.60 (s, 1H, 2-CH). ^{13}C NMR (DMSO) δ : 24.9 and 49.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 55.3 ($\text{CH}_2\text{C}_4\text{H}_3\text{S}$), 128.1, 128.3, 129.4, and 137.6 ($\text{C}_4\text{H}_3\text{S}$), 158.9 (2-CH). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{S}_2\text{PF}_6$: C, 41.28, H, 4.39, N, 6.42. Found: C, 41.30, H, 4.38, N, 6.43.

General Procedure for the Heck-Coupling reaction

$\text{Pd}(\text{OAc})_2$ (1.0 mmol%), 1,3-dialkylazolinium salts **1** or **2** (= LHX, 2 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), *t*-BuOK (2 mmol), water (3 mL) and DMF (3 mL) were added to a small Schlenk tube, and the mixture was heated to 50°C for 4 h. At the conclusion of the reaction, the mixture was cooled, extracted with ethylacetate/hexane (1:5), filtered through a pad of silicagel with copious washings, concentrated, and purified by flash chromatography on silicagel. The purity of the compounds was checked by NMR and GC, and yields are based on arylbromide.

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