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Picolyl substituted *N*-heterocyclic carbene/palladium catalyzed Heck reactions

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Novel 1,3-dialkylimidazolinium and 1,3-dialkyltetrahydropyrimidinium hexafluorophosphate salts as N-heterocyclic carbene precursors were prepared by reacting N,N'-dialkylethandiamine or N,N'-dialkylpropandiamine, triethyl orthoformate, and ammonium hexafluorophosphate. The salts were characterized spectroscopically and tested in homogeneous Heck reactions.

Key Words: Heck reaction, imidazolinium salt, palladium, carbene, catalyst.

Introduction

Palladium-catalyzed C-C bond formation is one of the most fundamental and important reactions in organic synthesis.[1,2] It represents the key step in a wide range of preparative organic processes, from the synthesis of natural products to supramolecular chemistry material science.[3,4] Common methodologies used are the palladium mediated coupling of the organic halides or halide equivalents with Grignard reagents, organotin, or organoboran reagents where monodentate phosphines are usually employed as ancillary ligands.[5−8] However, the major drawback of these is that the phosphine ligands are comparatively difficult to make or rather expensive. Furthermore, most of the phosphine ligands are air- and moisture-sensitive, and P-C bond degradation

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sometimes occurs at elevated temperatures, which poisons the metal, leading to decomposition of the catalyst, which strongly affects conversion and selectivity.[9] The Heck reaction is generally catalyzed by soluble palladium complexes with phosphine ligands. However, the reaction suffers from severe problems related to the separation, recovery, and instability of the homogeneous catalysts at high temperature, which have so far precluded its widespread industrial application. On the other hand, palladium complexes of *N*-heterocyclic carbene (NHC) ligands are suitable catalyst precursors that are more stable to air, moisture, and heat, and are more tolerant toward oxidation than their phosphine counterparts.[10−12] High catalyst and phosphine loading are usually required to produce high yields for unactivated aryl halides using this methodology.

Significant improvements in catalyst performance have recently brought benefits to fine chemistry via simple substitution of a phosphine ligand by a nucleophilic heterocyclic diaminocarbene, such as an imidazolylidene ligand. Illustrative examples are found in cross-coupling or Heck reactions,[13−15] ruthenium catalysts for the formation of furans,[16,17] cyclopropanation,[18] methatesis,[19−21] or hydrogenation,[22−27] and rhodium catalysts for arylation[28−31]or hydrosilylation.[32,33] The ancillary ligand (NHC) coordinated to the metal center has a number of important roles in homogeneous catalysis such as providing a stabilizing effect and controlling activity and selectivity by alteration of steric and electronic parameters. The number, nature, and position of the substituents on the nitrogen atom(s) and/or NHC ring have been found to play a crucial role in tuning the catalytic activity.

We report here on the synthesis and characterization of 1,3-dialkylimidazolinium and 1,3-dialkyltetrahydropyrimidinium salts as N-heterocyclic carbene precursors and the use of the in situ generated catalytic system composed of commercially available $Pd(OAc)_2$ (as the palladium source) and the 1,3-dialkylimidazolinium(**2a-d**) and 1,3-dialkyltetrahydropyrimidinium salts(**3a-c**) (as a carbene precursor) for Heck cross coupling from aryl halides.

Experimental

All reactions for the preparation of 1,3-dialkylimidazolinium salts (**2a-d**) and 1,3-dialkyltetrahydropyrimidinium salts (**3a-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 ^{1}H- and ^{13}C-NMR spectroscopy was performed in DMSO-d_6 using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, with coupling constants (J) in Hertz. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC was performed on a Agilent 6890N gas chromatograph by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed at TÜBİTAK (Ankara, Turkey) Microlab.

1,3-Di(6-methyl-2-picolyl)imidazolinium hexafluorophosphate (**2a**). To a solution of 1,2-bis(6-methyl-2-picolylamino)ethane (2.25 g, 8.33 mmol) were added $CH(OEt)_3$ (3 mL) and NH_4PF_6 (1.36 g, 8.34 mmol), and the reaction mixture was heated for 12 h at 50 °C. A white solid was precipitated and then crystallized from ethanol. Yield: 3.1 g, 87%, mp: 144-145 °C. IR(cm^{-1})ν=1658 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 4.24 (s, 4H, NCH_2CH_2N), 4.64 (s, 4H, $CH_2C_5H_3NCH_3-o$), 2.41 (s, 6H, $CH_2C_5H_3NCH_3-o$), 7.21, 7.24 and 7.70 (m, 6H, $CH_2C_5H_3NCH_3-o$), 8.50 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 50.2 (NCH_2CH_2N), 52.9 ($CH_2C_5H_3NCH_3-o$), 24.1 ($CH_2C_5H_3NCH_3-o$), 123.1, 124.1, 138.9, 150.4, 155.7 ($CH_2C_5H_3NCH_3-o$), 166.5 (2-*C*H). Anal. Calcd for $C_{17}H_{21}N_4PF_6$: C, 47.89, H, 4.96, N, 13.14. Found: C, 47.65, H, 4.80, N, 13.20.

1,3-Di(2-picolyl)imidazolinium hexafluorophosphate (**2b**). This compound was prepared in the same way as **2a** from 1,2-bis(2-picolylamino)ethane (2.40 g, 9.91 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (1.62 g, 9.93 mmol) to give white crystals of **2b**. Yield: 3.4 g, 86%, mp: 132-133 °C. IR(cm^{-1})ν=1664.3 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 3.86 (s, 4H, NCH_2CH_2N), 4.85 (s, 4H, $CH_2C_5H_4N$), 7.39, 7.48, 7.87 and 8.60 (m, 8H, $CH_2C_5H_4N$), 8.89 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 49.3 (NCH_2CH_2N), 52.5 ($CH_2C_5H_4N$), 123.5, 124.1, 138.1, 150.3, 154.1 ($CH_2C_5H_4N$), 160.6 (2-*C*H). Anal. Calcd for $C_{15}H_{17}N_4PF_6$: C, 45.22, H, 4.27, N, 14.07. Found: C, 45.31, H, 4.35, N, 14.20.

1,3-Di(3-picolyl)imidazolinium hexafluorophosphate (**2c**). This compound was prepared in the same way as **2a** from 1,2-bis(3-picolylamino)ethane (2.30 g, 9.50 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (1.55 g, 9.51 mmol) to give white crystals of **2c**.

Yield: 3.4 g, 90%, mp: 207-208 °C. IR(cm^{-1})ν=1664.0 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 3.76 (s, 4H, NCH_2CH_2N), 4.72 (s, 4H, $CH_2C_5H_4N$), 7.46, 7.84, 8.58 and 8.63 (m, 8H, $CH_2C_5H_4N$), 8.74 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 48.7 (NCH_2CH_2N), 49.2 ($CH_2C_5H_4N$), 124.5, 130.2, 137.1, 150.4, 150.5 ($CH_2C_5H_4N$), 159.1 (2-*C*H). Anal. Calcd for $C_{15}H_{17}N_4PF_6$: C, 45.22, H, 4.27, N, 14.07. Found: C, 44.87, H, 4.32, N, 13.24.

1,3-Di(4-picolyl)imidazolinium hexafluorophosphate (**2d**). This compound was prepared in the same way as **2a** from 1,2-bis(4-picolylamino)ethane (2.60 g, 10.74 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (1.75 g, 10.74 mmol) to give white crystals of **2d**.

Yield: 3.7 g, 86%, mp: 199-200 °C. IR(cm^{-1})ν=1666 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 3.81 (s, 4H, NCH_2CH_2N), 4.76 (s, 4H, $CH_2C_5H_4N$), 7.44 and 8.63 (d, 8H, J=4.4 Hz, $CH_2C_5H_4N$), 8.78 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 49.1 (NCH_2CH_2N), 50.5 ($CH_2C_5H_4N$), 123.7, 143.6, 150.8 ($CH_2C_5H_4N$), 160.1 (2-*C*H). Anal. Calcd for $C_{15}H_{17}N_4PF_6$: C, 45.22, H, 4.27, N, 14.07. Found: C, 45.30, H, 4.16, N, 14.20.

1,3-Di(2-picolyl)tetrahydropyrimidinium hexafluorophosphate (**3a**). This compound was prepared in the same way as **2a** from 1,2-bis(2-picolylamino)propane (3.10 g, 12.10 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (1.97 g, 12.08 mmol) to give white crystals of **3a**. Yield: 4.2 g, 84%, mp: 124-125 °C. IR(cm^{-1})ν=1697 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 1.94 (quin., 2H, J=4.2 Hz, $NCH_2CH_2CH_2N$), 3.31 (t, 4H, J=4.5 Hz, $NCH_2CH_2CH_2N$), 4.81 (s, 4H, $CH_2C_5H_4N$), 7.38, 7.47, 7.88 and 8.61 (m, 8H, $CH_2C_5H_4N$), 8.79 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 19.0 and 43.7 ($NCH_2CH_2CH_2N$), 59.3 ($CH_2C_5H_4N$), 123.6, 124.1, 138.1, 150.3, 154.5 ($CH_2C_5H_4N$), 155.7 (2-*C*H). Anal. Calcd for $C_{16}H_{19}N_4PF_6$: C, 46.60, H, 4.61, N, 13.59. Found: C, 46.33, H, 4.65, N, 13.28.

1,3-Di(3-picolyl) tetrahydropyrimidinium hexafluorophosphate (**3b**). This compound was prepared in the same way as **2a** from 1,2-bis(3-picolylamino)propane (3.33 g, 13.00 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (2.12 g, 13.00 mmol) to give white crystals of **3b**.

Yield: 4.7 g, 88%, mp: 245-246 °C. IR(cm^{-1})ν=1670 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 1.89 (quin., 2H, J=4.5 Hz, $NCH_2CH_2CH_2N$), 3.22 (t, 4H, J=4.5 Hz, $NCH_2CH_2CH_2N$), 4.71 (s, 4H, $CH_2C_5H_4N$), 7.45, 7.86, 8.58 and 8.65 (m, 8H, $CH_2C_5H_4N$), 8.82 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 18.8 and 42.8 (N*C*H$_2$*C*H$_2$*C*H$_2$N), 55.9 (*C*H$_2$C$_5$H$_4$N), 124.5, 130.5, 136.8, 150.3, 150.4 (CH$_2$*C*$_5$H$_4$N), 154.7 (2-*C*H). Anal. Calcd for $C_{16}H_{19}N_4PF_6$: C, 46.60, H, 4.61, N, 13.59. Found: C, 46.47, H, 4.44, N, 13.24.

1,3-Di(4-picolyl) tetrahydropyrimidinium hexafluorophosphate (**3c**). This compound was prepared in the same way as **2a** from 1,2-bis(4-picolylamino)propane (3.04 g, 11.87 mmol), $CH(OEt)_3$ (3 mL), and NH_4PF_6 (1.93 g, 11.84 mmol) to give white crystals of **3c**.

Yield: 4.4 g, 90%, mp: 209-210 °C. IR(cm^{-1})ν=1702 (NCN), ^{1}H-NMR (DMSO-d$_6$)δ: 1.97 (quin., 2H, J=4.2 Hz, NCH$_2$C*H*$_2$CH$_2$N), 3.26 (t, 4H, J=4.5 Hz, NC*H*$_2$CH$_2$C*H*$_2$N), 4.73 (s, 4H, C*H*$_2$C$_5$H$_4$N), 7.43 and 8.62 (d, 8H, J=4.5 Hz, CH$_2$C$_5$*H*$_4$N), 8.79 (s, 1H, 2-C*H*). ^{13}C-NMR (DMSO-d$_6$)δ: 18.8 and 43.3 (N*C*H$_2$*C*H$_2$*C*H$_2$N), 57.1 (*C*H$_2$C$_5$H$_4$N), 123.5, 143.8, 150.7 (CH$_2$*C*$_5$H$_4$N), 155.6 (2-*C*H). Anal. Calcd for $C_{16}H_{19}N_4PF_6$: C, 46.60, H, 4.61, N, 13.59. Found: C, 46.30, H, 4.56, N, 13.43.

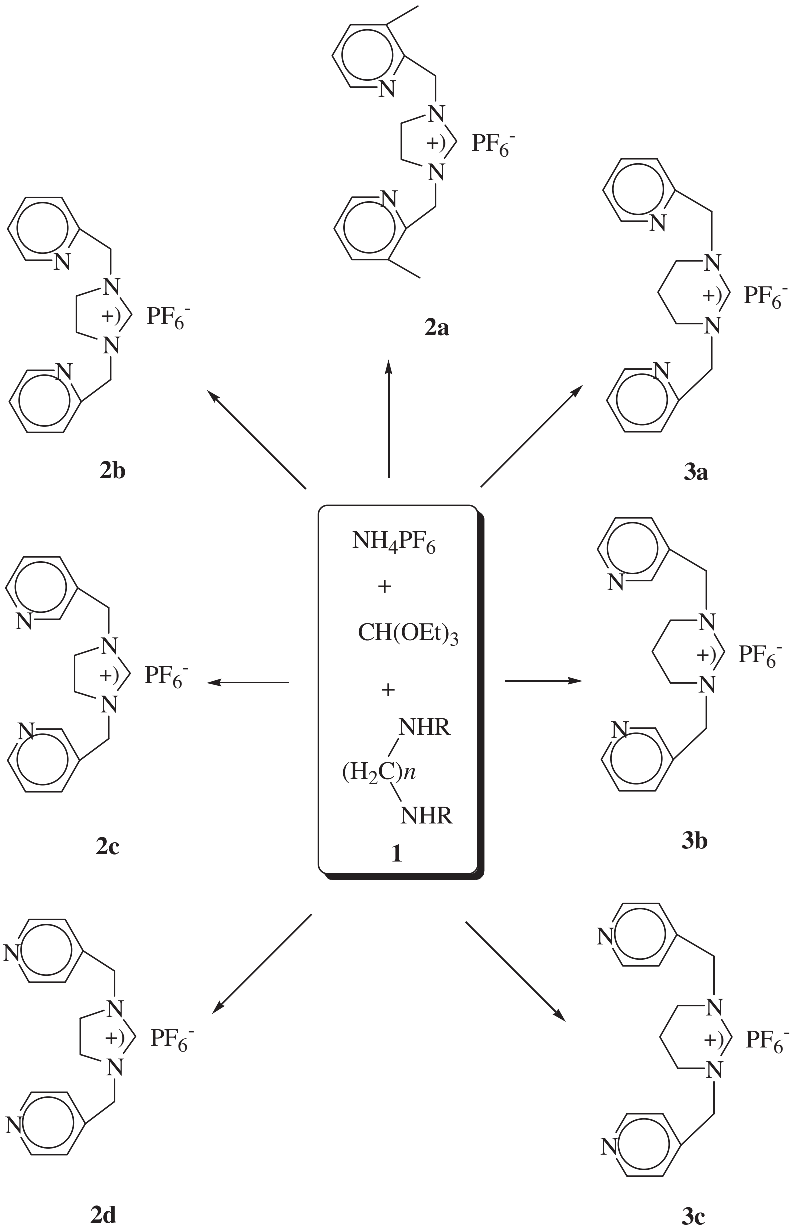
General procedure for the Heck coupling reactions

$Pd(OAc)_2$ (1.0 mmol%), 1,3-dialkylimidazolinium salts **2a-d**, or 1,3-dialkyltetrahydropyrimidinium salts **3a-c** (2 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), water (3 mL), and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated at 90 °C for 3 h. At the conclusion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and yields are based on aryl bromide.

Results and discussion

Condensation of ethylendiamine or 1,3-propandiamine with aldehydes in ethanol gave Schiff bases in high yields. Reduction of the resulting Schiff bases with $NaBH_4$ leads to N,N'-dialkylethan-1,2-diamines and N,N'-dialkylpropan-1,3-diamines.

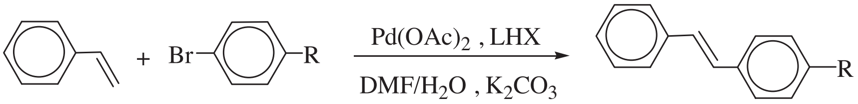
As shown in the Scheme, 1,3-dialkylimidazolinium salts **2** and 1,3-dialkyltetrahydropyrimidinium salts **3** were easily synthesized in high yields from N,N'-dialkylethan-1,2-diamines, N,N'-dialkylpropan-1,3-diamines, triethyl ortoformate, and ammonium hexafluorophosphate. The salts are soluble in the common polar solvents ethanol and dichloromethane and are stable under air and in the presence of moisture. The structures of **2** and **3** were determined by their spectroscopic data and elemental analyses (see Experimental section). The ^{13}C-NMR spectra of **2a-d** and **3a-c** show only a singlet (165.5 ppm(**2a**), 160.6 ppm(**2b**), 159.1 ppm(**2c**), 160.1 ppm(**2d**), 155.7 ppm(**3a**), 157.7 ppm(**3b**), and 155.6 ppm(**3c**)) for the imino carbon and (52.9 ppm(**2a**), 52.5 ppm(**2b**), 49.2 ppm(**2c**), 50.5 ppm(**2d**), 59.3 ppm(**3a**), 55.9 ppm(**3b**), and 57.1 ppm(**3c**)) for benzylic carbon. The ^{1}H-NMR spectra of imidazolinium and tetrahydropyrimidinium salts further supported the assigned structures. The resonances of the C(2)-H were observed as a sharp singlets at δ= 8.50, 8.89, 8.74, 8.78, 8.79, 8.82, 8.79 ppm for **2a-d** and **3a-c**, respectively. The IR data for imidazolinium **2a-d** and tetrahydropyrimidinium **3a-c** salts clearly indicate the presence of the –C=N- group with a ν(C=N) vibration at 1658, 1664.3, 1664.0, 1666, 1679, 1670, and 1702 cm^{-1} for **2a-d** and **3a-c**, respectively. These NMR and IR values were similar to other 1,3-dialkylimidazolinium and 1,3-dialkyltetrahydropyrimidinium salts.[34]



Scheme. Synthesis of 1,3-dialkylimidazolinium and 1,3-dialkyltetrahydropyrimidinium salts.

The Pd-catalyzed Heck reaction between aryl halides and alkenes is a very useful method for forming natural products, drug design, and organic synthesis.[35,36] The choice of bases and solvents is usually important for achieving an efficient cross coupling reaction. The widely used solvents such as DMF, DMSO, toluene, dioxane, THF, and CH_3CN had remarkable effects on the coupling reaction. For optimal reaction conditions, the $Pd(OAc)_2$-catalyzed cross coupling of bromobenzene with styrene was employed as the model reaction using ligand **2a** at 90 °C, as the bases $CsCO_3$, K_2CO_3, K_3PO_4, and *t*-BuOK were tested. The coupling reactions of aryl bromides and styrene were carried out in DMF/H_2O (3:3 mL) with 1 mol% $Pd(OAc)_2$, 2 mol% **2** or **3**, and 2 equiv. K_2CO_3 for 3 h at 90 °C. The results are summarized in Table. Control experiments indicate

Table. The Heck coupling reaction of aryl bromides with styrene.



Entry	R	LHX	Yield (%)
1	$COCH_3$	**2a**	92
2	$COCH_3$	**2b**	98
3	$COCH_3$	**2c**	96
4	$COCH_3$	**2d**	97
5	$COCH_3$	**3a**	97
6	$COCH_3$	**3b**	94
7	$COCH_3$	**3c**	95
8	CHO	**2a**	85
9	CHO	**2b**	94
10	CHO	**2c**	89
11	CHO	**2d**	92
12	CHO	**3a**	96
13	CHO	**3b**	91
14	CHO	**3c**	88
15	H	**2a**	83
16	H	**2b**	80
17	H	**2c**	89
18	H	**2d**	82
19	H	**3a**	90
20	H	**3b**	84
21	H	**3c**	91
22	OCH_3	**2a**	72
23	OCH_3	**2b**	74
24	OCH_3	**2c**	81
25	OCH_3	**2d**	79
26	OCH_3	**3a**	71
27	OCH_3	**3b**	73
28	OCH_3	**3c**	75
29	CH_3	**2a**	82
30	CH_3	**2b**	79
31	CH_3	**2c**	80
32	CH_3	**2d**	74
33	CH_3	**3a**	76
34	CH_3	**3b**	73
35	CH_3	**3c**	75

Reaction conditions: R-C_6H_4Br-*p*1.0 mmol, styrene 1.5 mmol, K_2CO_3 2.0 mmol, $Pd(OAc)_2$ 1% (molar ratio), **2a-d**, **3a-c** 2% (molar ratio), water (3 mL)/DMF (3 mL), 90 °C, 3 h. Yields are based on aryl bromide. All reactions were monitored by GC, and the compound purity was checked by NMR.

that the coupling reaction did not occur in the absence of **2a**. Under these reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups react with styrene, affording the coupled products in excellent yields (Table, entries 2, 12, 21, 24 and 29). Enhancements in activity, although less significant, are also observed employing 4-bromobenzaldehyde instead of 4-bromoacetophenone (entries 1-7 and 8-14, respectively). However, chloroarenes do not react under standard conditions, and yields are typically $<6\%$.

Conclusion

We synthesized 1,3-dialkylimidazolinium and 1,3-dialkyltetrahydropyrimidinium hexafluorophosphate salts and investigated their catalytic activity in Heck coupling reactions. The procedure is simple and efficient for various types of aryl bromides and does not require an induction period. The advantage of the catalyst is that it has low-loading capabilities, and it is useable in air. Detailed investigations focusing on imidazolidin-2-ylidene and benzimidazolin-2-ylidene substituent effects, functional group tolerance, and catalytic activity in this and other coupling reactions are ongoing.

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