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THE SYNTHESIS OF NOVEL PALLADIUM(II) CARBENE COMPLEXES, AZOLIUM SALTS AND THEIR CATALYTIC PROPERTIES

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Abstract- Novel three 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium, 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium and 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazolium chloride salts (**1**, **3a-b**) and two palladium complex (**2**, **4**) have been prepared and characterized by C, H, N analysis, ¹H NMR and ¹³C NMR and they have been investigated their catalytic activity in the Heck and Suzuki coupling reactions.

INTRODUCTION

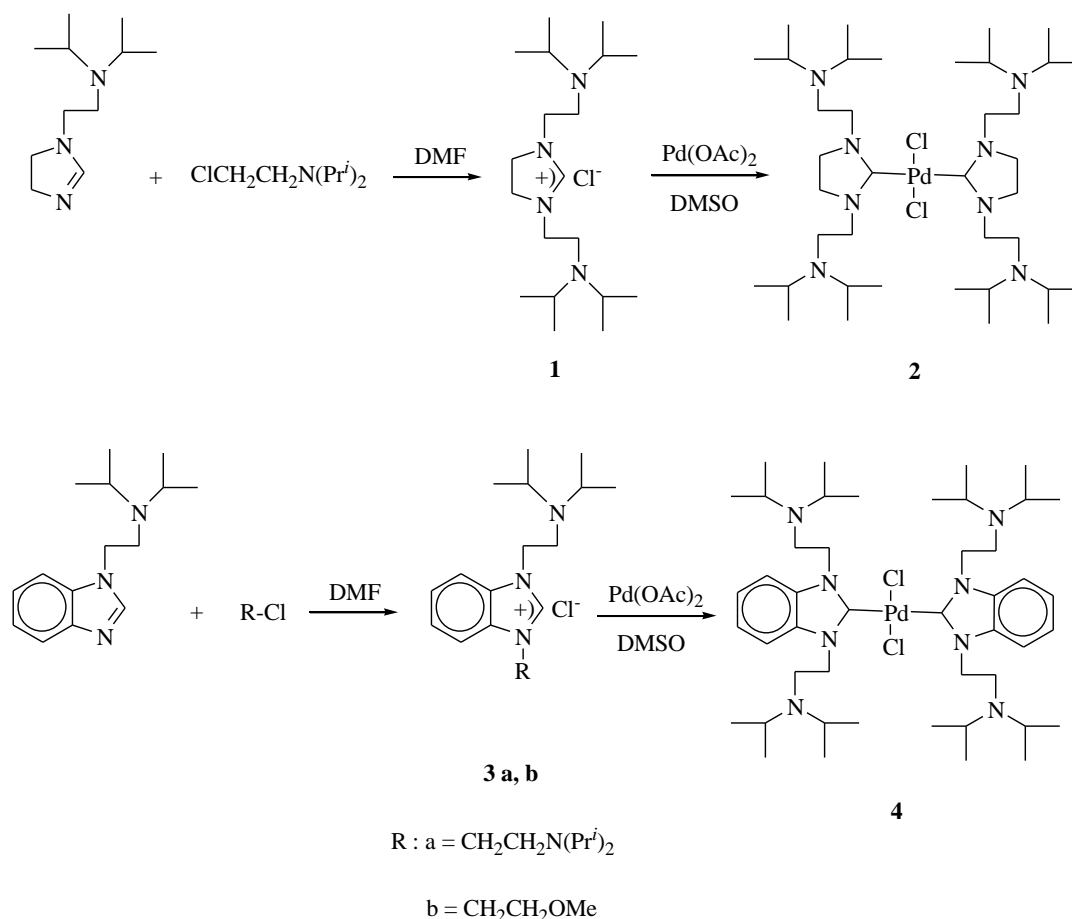
Palladium-catalyzed cross-coupling reactions have become an extremely important tool for organic synthesis and there is a wide range of synthetically valuable transformations which can be catalyzed by palladium.^{1,2} For many years, phosphines have been the most commonly used as ligands for these reactions. The phosphine ligands are expensive, toxic and unrecoverable, which needs high temperatures and bases, and have limited substrate generality and selectivity.³⁻⁶ *N*-Heterocyclic carbenes have proven to be electron rich donors which provide higher reactivity and stability toward heat, air and moisture than phosphines. Transition metal complexes containing *N*-heterocyclic carbenes have been used as effective catalyst for Heck and Suzuki cross-coupling, amination, olefin metathesis, hydrogenation, arylation and hydrosilylation reactions.⁷⁻¹⁹ Among them, palladium-catalyzed Heck and Suzuki reaction have to be

perhaps the most widespread and successful application of carbene complexes. Initially, water-soluble phosphines were used as ligands for the cross-coupling reactions in aqueous media,²⁰ but in recent years, other hydrophilic phosphine-free systems²¹ and soluble palladium nanoparticles²²⁻²⁴ have also been found to be highly efficient catalysts for this transformation. Palladium(II) carbene complexes can be easily prepared by the reaction of palladium(II) acetate with two equiv. of azolium salts²⁵ or the use of silver carbene complexes as carben transfer reagent.²⁶⁻²⁹ Generally, Silver NHC complexes are prepared by treatment of silver oxide, silver carbonate or silver acetate with the corresponding azolium salts.³⁰⁻³² In general, NHC chemistry is dominated by imidazole and imidazoline based carbene ligands. On the other hand, catalytic applications of carbenes and carbene complexes derived from benzimidazole have received less attention.³³⁻³⁸ We have previously reported the synthesis of *N*-heterocyclic carbene derivative ligands and their palladium(II) carbene complexes and investigated for catalytic activity in Heck and Suzuki reactions.³⁹⁻⁴² Herein we wish to report the synthesis of new imidazolium and benzimidazolium chlorides, **1**, **3a-b** and their palladium (II) complexes, **2**, **4** (scheme 1), and their application in Heck and Suzuki cross-coupling from aryl halides.

RESULTS AND DISCUSSION

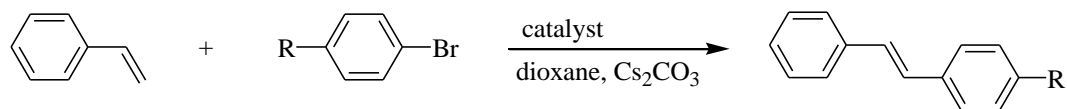
As shown in Scheme 1 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium (**1**), 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium and 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)-benzimidazolium salts (**3a-b**) were readily prepared by quaternization of 1-(2-diisopropylaminoethyl)-imidazolin and 1-(2-diisopropylaminoethyl)benzimidazole in DMF with alkyl halides. After purification, the salts (**1** and **3a-b**) were obtained in good yields of 58-82%. The salts are soluble in common polar solvents. Although the **3a-b** are stable under air and in the presence of moisture, compound **1** is very hygroscopic. The structures of **1** and **3** were determined by their spectroscopic data and elemental analyses (see experimental section). The ¹³C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet at 159.0, 144.1 and 143.7 ppm respectively for **1** and **3a-b**. The ¹H NMR spectra of imidazolium and benzimidazolium salts further supported the assigned structures. The resonances of the C(2)-H were observed as sharp singlets at $\delta = 9.23, 11.09$ and 10.67 ppm for **1** and **3a-b**, respectively. The IR data for **1** and **3a-b** salts clearly indicate the presence of the -C=N- group with a $\nu(\text{C=N})$ vibration at $1650, 1560$ and 1564 cm^{-1} for **1** and **3a-b**, respectively. These NMR and IR values were similar to other 1,3-dialkylbenzimidazolium and 1,3-dialkylimidazolium salts.^{41,43} The palladium complexes **2** and **4** were prepared by the reaction of 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium chloride (**1**) and 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium (**3a**) with the Pd(OAc)₂ in DMSO (Scheme 1). Each palladium compound was fully characterized by ¹H and ¹³C NMR spectroscopy, FT-IR, and elemental analysis. The

palladium complexes exhibit a characteristic $\nu_{(\text{NCN})}$ band typically at 1529 and 1415 cm^{-1} . ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}\text{C}_{\text{carb}})$ are in the 198.8 and 181.8 ppm and are similar to those found in other carbene complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for $[\text{PdCl}_2(\text{NHC})_2]$ complexes.⁴⁴



Scheme 1. Synthesis of salts and palladium-carbene complexes

The Heck reaction has been shown to be very useful for the preparation of disubstituted olefins. The Heck C-C coupling reactions of aryl halides with styrene were carried out homogeneously with $\text{Pd}(\text{OAc})_2/\mathbf{1}$, $\mathbf{3a-b}$ or palladium complexes $\mathbf{2}$, $\mathbf{4}$ as catalysts in the presence of a base in air. For optimal reaction conditions, the $\text{Pd}(\text{OAc})_2$ -catalyzed cross coupling of bromobenzene with styrene was employed as the model reaction using ligand $\mathbf{1}$ at 80 °C, as the base commonly used bases Cs_2CO_3 , K_2CO_3 , K_3PO_4 and *t*-BuOK were tested. The coupling reactions of aryl bromides and styrene were carried out in dioxane (3 mL) with 1 mol% $\text{Pd}(\text{OAc})_2$, 2 mol% $\mathbf{1}$, $\mathbf{3}$ or 1.5 mol% $\mathbf{2}$, $\mathbf{4}$ and 2 equiv. Cs_2CO_3 for 8 h at 80 °C. The reactions in this conditions gave the coupling products in good yields (81-96%) and the coupling reaction did not occur in the absence of salt or palladium complex. The results are summarized in Table 1.

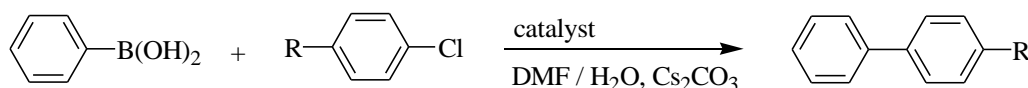
Table 1. The Heck coupling reaction of aryl bromides with styrene

Entry	R	Catalyst	Yield ^{a,b,c,d} (%)
1	COMe	1	96
2	COMe	3a	93
3	COMe	3b	94
4	COMe	2	92
5	COMe	4	90
6	Me	1	89
7	Me	3a	84
8	Me	3b	87
9	Me	2	83
10	Me	4	81
11	CHO	1	92
12	CHO	3a	95
13	CHO	3b	95
14	CHO	2	90
15	CHO	4	88
16	OMe	1	89
17	OMe	3a	87
18	OMe	3b	90
19	OMe	2	85
20	OMe	4	81
21	H	1	90
22	H	3a	83
23	H	3b	88
24	H	2	86
25	H	4	83

^a Reaction conditions: 1.0 mmol of R-C₆H₄Br-*p*, 1.5 mmol of styrene, 2.0 mmol Cs₂CO₃, 1.0 mmol Pd(OAc)₂, 2.0 mol% **1** or **3a-b**. ^b 1.5 mol% **2** or **4**. ^c Purity of compounds is checked by NMR and isolated yields are based on aryl halide. ^d All reactions were monitored by GC.

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 1, entries 1, 6, 13, 18 and 21). Enhancements in activity, although less significant, are also observed employing 4-bromobenzaldehyde instead of 4-bromoacetophenone (entries 1-5 and 11-15, respectively). However, chloroarenes do not react under standard conditions, and yields are typically < 6%. We observed that the imidazolium salt (**1**) was the more effective than benzimidazolium salts (**3a-b**) for the Heck reactions. It was expected that in situ formation of the azolium salts led to significantly better results than the use of the palladium complexes. The Suzuki coupling of phenylboronic acid with aryl chlorides to form biaryls were undertaken with Pd(OAc)₂/**1**, **3a-b** or **2**, **4** as catalysts. Similar reaction conditions were employed to the Suzuki reactions. As the base Cs₂CO₃ was used. The coupling reactions of aryl chlorides and phenylboronic acid were carried out in DMF/H₂O (3:3 mL) with 1.0 mol% Pd(OAc)₂, 2.0 mol% **1**, **3a-b** or 1,5 mol% **2**, **4** and 2 equiv. Cs₂CO₃ for 5 h at 80 °C. We started our investigation on the coupling of 4-chloroacetophenone and phenylboronic acid in the presence of Pd(OAc)₂/**1**. The results are summarized in Table 2.

Table 2. The Suzuki coupling reaction of aryl chlorides with phenylboronic acid



Entry	R	Catalyst	Yield ^{a,b,c,d} (%)
1	COMe	1	95
2	COMe	3a	90
3	COMe	3b	93
4	COMe	2	92
5	COMe	4	90
6	Me	1	87
7	Me	3a	83
8	Me	3b	85
9	Me	2	83
10	Me	4	80
11	CHO	1	92
12	CHO	3a	88
13	CHO	3b	90

14	CHO	2	91
15	CHO	4	87
16	OMe	1	80
17	OMe	3a	75
18	OMe	3b	76
19	OMe	2	78
20	OMe	4	75
21	H	1	85
22	H	3a	73
23	H	3b	78
24	H	2	76
25	H	4	74

^a Reaction conditions: 1.0 mmol of R-C₆H₄Cl-*p*, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs₂CO₃, 1.0 mmol Pd(OAc)₂, 2.0 mol% **1** or **3a-b**. ^b 1.5 mol% **2** or **4**. ^c Purity of compounds is checked by NMR and isolated yields are based on aryl chloride. ^d All reactions were monitored by GC.

As seen the Heck reactions, the **1** catalyst system is most effective for the Suzuki reactions. It can be shown these salts are an effective ligand precursor for the coupling of unactivated, activated and deactivated chlorides. These results are similar to other Pd-NHC complexes^{11,45} or in situ prepared Pd(OAc)₂/NHC systems⁴⁶⁻⁴⁸ and are in agreement with other reports.^{10,49-52}

CONCLUSION

In conclusion, we have synthesized three 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium, 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium and 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazolium chloride salts and their two palladium complexes and have investigated their catalytic activity in the Heck and Suzuki coupling reactions. In this study, in situ catalytic system is seen to be more effective than palladium complex system in both the Heck reactions of aryl bromides with styrene and the Suzuki reactions of aryl chlorides with phenylboronic acid. The procedure is simple and efficient toward various types of aryl halides and does not require an induction period. The advantage of the catalyst is that it has low-loading capabilities, and it is usable 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.

EXPERIMENTAL

All reactions for the preparation of 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium (**1**),

1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium and 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazolium salts (**3a-b**) and palladium complexes (**2, 4**) were carried out under argon using standart Schlenk-type flasks. Heck and Suzuki coupling reactions were carried out in air. All reagents were purchased from Aldrich Chemical Co., Turkey. All ^1H and ^{13}C NMR were performed in CDCl_3 using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. FT-IR spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC were measured 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 uncorrected. Elemental analyses were performed at İnönü University research center.

Synthesis of 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolium chloride (**1**)

To a solution of 1-(2-diisopropylaminoethyl)imidazoline (1.21 g, 6.14 mmol) in DMF (4 mL) was added slowly 2-diisopropylaminoethyl chloride (1.05 g, 6.41 mmol) at 25 °C and the resulting mixture was stirred at rt for 5 h. Et_2O (20 mL) was added to obtain a white crystalline solid, which was filtered off. White hygroscopic crystals were washed with Et_2O (3x15 mL) and dried under vacuum. Yield: 1.78 g, 82%, mp 100-102 °C. IR, ν : 1650.7 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ : 9.23 (s, 1H, C-2 H); 3.81 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$); 3.28 (m, 4H, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.41 (m, 4H, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.72 (septet, 4H, $J = 6.4$ Hz, $\text{NCH}(\text{CH}_3)_2$); 0.68 (d, 24H, $J = 6.0$ Hz, $\text{NCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) δ : 159.0 (C-2); 49.5 ($\text{NCH}_2\text{CH}_2\text{N}$); 47.8 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 43.1 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 47.6 ($\text{NCH}(\text{CH}_3)_2$); 20.8 ($\text{NCH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{19}\text{H}_{41}\text{N}_4\text{Cl}$: C, 63.21; H, 11.45; N, 15.52. Found: C, 63.30; H, 11.40; N, 15.62.

Synthesis of 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium chloride (**3a**)

To a solution of 1-(2-diisopropylaminoethyl)benzimidazole (1.5 g, 6.11 mmol) in DMF (2 mL), 2-diisopropylaminoethyl chloride (1.03 g, 6.11 mmol) was added; the resulting solution was stirred for 1 h at room temperature and heated for 12 h at 80 °C. Et_2O (10 mL) was added to the reaction mixture. A white solid was precipitated in this period. The precipitate was then crystallized from $\text{EtOH}/\text{Et}_2\text{O}$ (1:2). Yield: 2.11 g, 63%, mp 194-195 °C. IR, ν : 1560 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ : 11.09 (s, 1H, C-2 H); 7.62 (m, 4H, C_6H_4); 4.53 (t, 4H, $J = 6.0$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.93 (t, 4H, $J = 6.4$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 3.00 (m, 4H, $\text{NCH}(\text{CH}_3)_2$); 0.82 (d, 24H, $J = 6.8$ Hz, $\text{NCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) δ : 144.1 (C-2); 113.5, 126.8, 131.7 (C_6H_4); 47.9 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 44.8 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 48.4 ($\text{NCH}(\text{CH}_3)_2$); 20.9 ($\text{NCH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{23}\text{H}_{41}\text{N}_4\text{Cl}$: C, 67.53; H, 10.10; N, 13.70. Found: C, 67.41; H, 10.16; N, 13.85.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazolium chloride (3b)

This compound was prepared in same way as **3a** from 1-(2-diisopropylaminoethyl)benzimidazole (1.18 g, 4.81 mmol) and 2-methoxyethyl chloride (0.68 g, 4.81 mmol) in DMF (2 mL) to give white crystals of **3b**. Yield: 2.55 g, 58%, mp 223-224 °C. IR, ν : 1564 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ : 10.67 (s, 1H, C-2 H); 7.62 (m, 4H, C_6H_4); 4.51 (m, 2H, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.82 (d, 2H, $J = 12.8$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.94 (m, 2H, $\text{NCH}(\text{CH}_3)_2$); 0.71 (d, 12H, $J = 6.0$ Hz, $\text{NCH}(\text{CH}_3)_2$); 3.81 (t, 2H, $J = 4.8$ Hz, $\text{CH}_2\text{CH}_2\text{OCH}_3$); 4.78 (t, 2H, $J = 5.2$ Hz, $\text{CH}_2\text{CH}_2\text{OCH}_3$); 3.21 (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$). $^{13}\text{C}\{1\text{H}\}$ -NMR (CDCl_3) δ : 143.7 (C-2); 112.9, 114.1, 126.9, 131.3, 131.9 (C_6H_4); 47.4 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 44.1 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 47.7 ($\text{NCH}(\text{CH}_3)_2$); 20.7 ($\text{NCH}(\text{CH}_3)_2$); 47.9 ($\text{CH}_2\text{CH}_2\text{OCH}_3$); 70.6 ($\text{CH}_2\text{CH}_2\text{OCH}_3$); 59.0 ($\text{CH}_2\text{CH}_2\text{OCH}_3$). Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{N}_3\text{OCl}$: C, 63.60; H, 8.90; N, 12.36. Found: C, 63.61; H, 8.94; N, 12.45.

Synthesis of bis[1,3-bis(2-diisopropylaminoethyl)imidazolidin-2-ylidene]dichloro palladium(II) (2)

A stirred DMSO solution (10 mL) of 1,3-bis[2-(N,N' -diisopropylamino)ethyl]imidazolium chloride (0.17 g, 0.48 mmol) and $\text{Pd}(\text{OAc})_2$ (0.054 g, 0.24 mmol) was heated 60 °C for 3 h and then at 110 °C for a further 2 h, during which time the reaction solution changed from being initially orange. The remaining DMSO was then removed in vacuo to give a pale yellow solid. Recrystallization from CH_2Cl_2 - Et_2O was carried out. The crystals were washed with diethyl ether (3x15 mL) and dried under vacuum. Yield: 0.14 g, 70%, mp 224-225 °C. IR, ν : 1529.0 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ : 3.68 (s, 8H, $\text{NCH}_2\text{CH}_2\text{N}$); 3.96 (t, 8H, $J = 6.4$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 2.88 (t, 8H, $J = 6.4$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 3.03 (m, 8H, $\text{NCH}(\text{CH}_3)_2$); 1.02 (d, 48H, $J = 6.4$ Hz, $\text{NCH}(\text{CH}_3)_2$). $^{13}\text{C}\{1\text{H}\}$ -NMR (CDCl_3) δ : 198.8 (C-2); 50.2 ($\text{NCH}_2\text{CH}_2\text{N}$); 50.5 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 44.9 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 48.7 ($\text{NCH}(\text{CH}_3)_2$); 21.1 ($\text{NCH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{38}\text{H}_{80}\text{N}_8\text{PdCl}_2$: C, 55.23; H, 9.76; N, 13.56. Found: C, 55.11; H, 9.71; N, 13.45.

Synthesis of bis[1,3-bis(2-diisopropylaminoethyl)benzimidazoline-2-ylidene]dichloro palladium(II) (4)

This compound was prepared in same way as **2** from 1,3-bis[2-(N,N' -diisopropylamino)ethyl]benzimidazolium chloride (0.22 g, 0.54 mmol) and $\text{Pd}(\text{OAc})_2$ (0.060 g, 0.27 mmol) in DMSO (2 mL) to give yellow crystals of **4**. Yield: 0.16 g, 64%, mp 196-197 °C. IR, ν : 1415.6 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ : 7.23-7.46 (m, 8H, C_6H_4); 4.88 (t, 8H, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 3.25 (t, 8H, $J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 3.11 (m, 8H, $\text{NCH}(\text{CH}_3)_2$); 1.03 (d, 48H, $J = 6.8$ Hz, $\text{NCH}(\text{CH}_3)_2$). $^{13}\text{C}\{1\text{H}\}$ -NMR (CDCl_3) δ : 181.8 (C-2); 111.4, 122.5, 135.2 (C_6H_4); 50.1 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 45.5 ($\text{CH}_2\text{CH}_2\text{N}(\text{Pr}^i)_2$); 49.0 ($\text{NCH}(\text{CH}_3)_2$); 21.3 ($\text{NCH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{46}\text{H}_{80}\text{N}_8\text{PdCl}_2$: C, 59.89; H, 8.74; N, 12.15. Found: C, 59.92; H, 8.65; N, 12.30.

General Procedure for the Heck-Type Coupling Reactions

Pd(OAc)₂ (1.0 mmol%), salts **1**, **3a-b** (2.0 mmol%) or **2**, **4** (1.5 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), Cs₂CO₃ (2.0 mmol) and dioxane (3 mL) were added in a Schlenk tube under argon and mixture was heated at 80 °C for 8 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et₂O, filtered through a pad of silicagel with copious washings, concentrated, and purified by flash chromatography on silicagel. Purity of compounds was checked by NMR and GC. The yields are based on aryl bromide.

General Procedure for the Suzuki-Type Coupling Reactions

Pd(OAc)₂ (1.0 mmol%), salts **1**, **3a-b** (2.0 mmol%) or **2**, **4** (1.5 mmol%), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), Cs₂CO₃ (2.0 mmol) and water (3 mL)-DMF (3 mL) were added in a Schlenk tube under argon and mixture was heated at 80 °C for 5 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et₂O, filtered through a pad of silicagel with copious washings, concentrated, and purified by flash chromatography on silicagel. Purity of compounds was checked by NMR and GC. The yields are based on aryl chloride.

ACKNOWLEDGEMENTS

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