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Synthesis, characterization and the Suzuki–Miyaura coupling reactions of *N*-heterocyclic carbene–Pd(II)–pyridine (PEPPSI) complexes

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ABSTRACT

N-heterocyclic carbenes (NHCs) are a significant and powerful class of ligands for transition metals. A new series of air and moisture-stable NHC–$PdCl_2$-pyridine complexes, (**2a**–**f**), have been described. With the development of a more efficient catalytic system for the cross-coupling of aryl halides in mind, the catalytic performance of the NHC–$PdCl_2$-pyridine complexes for Suzuki cross-coupling under mild conditions in aqueous *N*,*N*-dimethylformamide (DMF) was investigated. Electron-rich and electron-poor aryl chlorides were facilely coupled with boronic acids by NHC–$PdCl_2$-pyridine complexes.

Introduction

N-heterocyclic carbenes (NHCs) have led to important developments in transition metal chemistry due to their tunable steric and electronic properties. Arduengo et al. isolated and characterized the first stable free NHC in 1991 [1]. Since then, many metal-NHC complexes have been synthesized, leading to many applications in the field of transition metal catalysis such as hydrosilylation [2], Ru-catalyzed furan synthesis [3], transfer hydrogenation [4], olefin metathesis [5], and Pd-catalyzed cross-coupling reactions [6,7].

Herrmann [8], Nolan [9], Beller [10] and Sigman [11] have reported a series of monoligated Pd–NHC complexes that showed high activity in Pd catalyzed reactions.

The reported catalysts were prepared under an inert atmosphere due to the extreme oxygen and water sensitivity of isolated free NHCs that requires rigorously anhydrous reaction conditions [12]. The insitu preparation of active catalysts has proven to be a potent method in overcoming this problem. Organ et al. [13] reported easily-handled, air and moisture stable Pd–NHC complexes through the PEPPSI (**P**yridine-**E**nhanced **P**recatalyst **P**reparation **S**tabilization (and) **I**nitiation) method that featured Pd(II) species bearing an NHC ligand, two halides, and a labile ligand such as 3-chloro pyridine. After Organ's work, Doucet and Matt reported additional monoligated NHC-based palladium pyridine complexes [14,15].

Suzuki coupling, the reaction between boronic acid derivatives and organic electrophiles, is one of the most powerful and widely preferred reactions for C–C bond formation. Carbon–carbon and carbon-heteroatom bond-forming reactions have been catalyzed by structurally different palladium complexes. Recently, significant improvements have been made in the phosphine-ligated palladium catalyzed Suzuki–Miyaura reaction [16]. Fu et al. made a detailed study with alkylboranes and boronic acid derivatives and they took a step forward on the Suzuki–Miyaura reaction [17]. The first NHC-based Suzuki protocol was reported by Capretta et al. [18]. While less reactive and lacking in substrate range, ease of use and handling makes Pd–NHC catalysts attractive. However, preparation of Pd–NHC catalysts and Suzuki–Miyaura reactions require a rigorously inert atmosphere due to the sensitivity of isolated free carbenes [19]. To overcome this difficulty, active catalyst is produced in situ for most NHC-based Suzuki coupling reactions with couple of disadvantages [20]. However, with Organ's PEPPSI method, the synthesis of precatalysts was easily accomplished without air- or water-free conditions. Further studies on this topic have been published by other research groups [14,15].

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The Suzuki coupling reaction plays an important role in the synthesis of fine chemicals [21–26]. Non-toxic, air- and moisture-stable reagents as well as greener solvents are some of its advantages. Mixtures of water and organic solvents in Suzuki coupling promotes the solvation of mineral bases to support the Suzuki reaction by activating the aryl boronic acid and can the dissolve organic substrates and corresponding palladium catalysts. In this respect, water has economical and environmental advantages because it is relatively safe and easily separated from organic compounds. Several organic transformations use water as the solvent [27–43]. In 2010, Ying et al. discovered a novel, highly active pre-catalyst for the coupling of deactivated aryl chlorides and phenyl boronic acid at room temperature by using wet solvents (Dioxane/H_2O, THF/H_2O) in air [33]. Shao et al. reported a study that Pd–NHC complexes showed high catalytic activity in the Suzuki–Miyaura coupling reactions of aryl chlorides in aqueous media [44]. To date, Organ [13] and Cavell [45] groups have published imidazole and ring expanded NHC–Pd pyridine (PEPPSI) complexes and their catalytic activity on C–C, C–N cross coupling transformations. Herein, we would to understand catalytic activity of bezimidazol ligated palladium pyridine complexes on Suzuki reaction because benzimidazole ligands have different σ-donor function and more electrophylic than classical and ring expanded NHC ligands. Results showed that, this catalytic system could be applied to the Suzuki coupling of aryl chlorides in good yields, simply and efficiently.

Results and discussion

Preparation of benzimidazolium salts

According to Scheme 1, **1a**–**f** was synthesized in approximately quantitative yield by quaternization of 1-alkyl-benzimidazole in DMF with corresponding aryl and morpholine chlorides [46]. **1c**, **1d** and **1f** benzimidazolinium salts have already been reported in the literature [47,48]. The ^{1}H- NMR shifts of **1a**, **1b** and **1e** are similar to other characterized benzimidazolium salts [49–54]. In the ^{1}H-NMR spectra of **1a**, **1b** and **1e**, the NC*H*N protons were observed as sharp singlets at 12.15, 11.59, and 11.29 ppm respectively. The imino carbons (NCHN) were detected as typical singlets in the ^{1}H-decoupled mode at 139.5, 142.7, and 156.9 ppm. The IR data of **1a**, **1b** and **1e** clearly support the presence of the C–N group with ν(C–N) vibrations at 1545, 1570 and 1623 cm^{-1}.

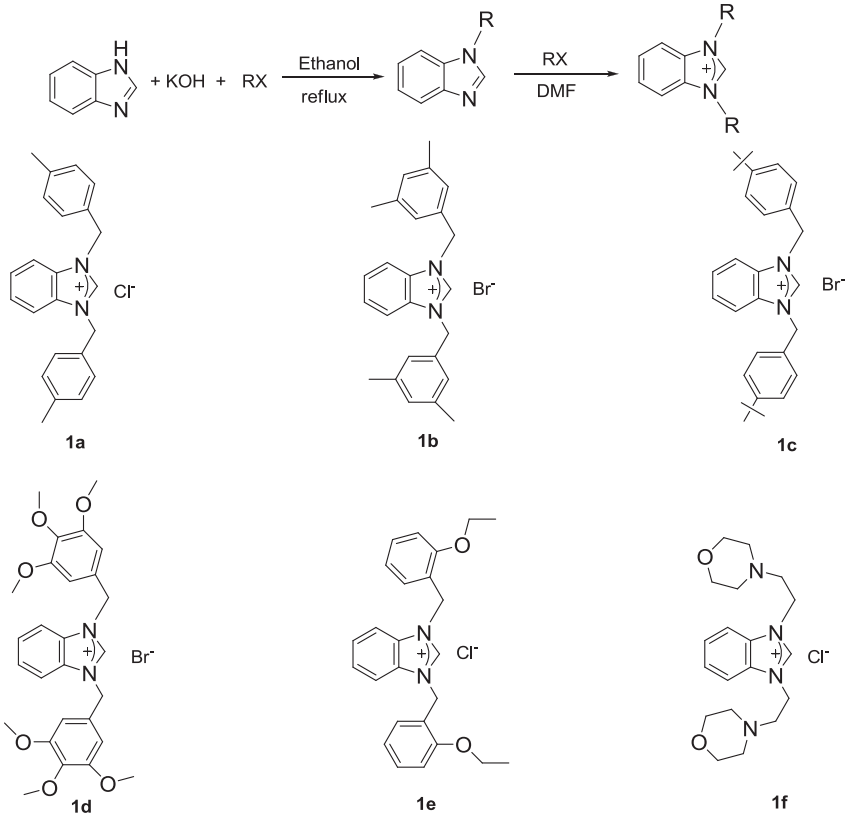
*Preparation of NHC–palladium–pyridine complexes **2a**–**f***

NHC–Pd-pyridine complexes (Scheme 2)were synthesized according to the method described by Organ et al. [13]. Structural definitions of **2a**–**f** were determined by NMR, IR spectroscopy, LC-MS (ESI) spectrometry, and elemental analysis. The ^{1}H NMR spectra for **2a**–**f** reveal disappearance of the distinctive NC*H*N proton signals. Also, ^{13}C{^{1}H} NMR spectra prove a increasing downfield shift of the NCN carbon from **1a**–**f** to **2a**–**f**: for example, the ^{13}C{^{1}H} N–C–N shifts of **1a** and **2a**, which are 139.5 and 162.7 ppm, respectively. This observation is confirmed by previous study [14].

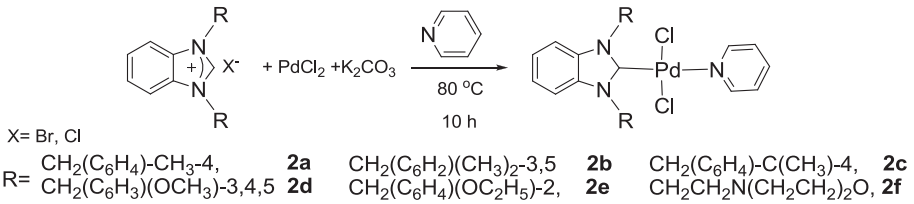
In order to demonstrate the utility of these NHC–$PdCl_2$–pyridine complexes, we used them as co-catalysts in Suzuki–Miyaura coupling reactions, which are common industry-applicable processes.

Suzuki coupling reaction

We performed a series of the Suzuki coupling reactions with 4-chloroacetophenone and phenylboronic acid as a model reaction to



Scheme 1. Synthesis of symmetrical benzimidazole based-NHC ligand precursors, **1a**–**f**.



Scheme 2. Synthesis of NHC-palladium–pyridine complexes, **2a**–**f**.

determine optimum conditions. Next, we investigated the effect of solvent on yield, which is summarized in Table 1. The highest yield was obtained when the DMF/H_2O ratio was equal (1:1). Also, we tested the effect of common mineral bases such as Cs_2CO_3, K_2CO_3, NaOH and KO*t*Bu for the Suzuki coupling reactions of unactivated aryl chlorides. 1 (eq) of KO*t*Bu showed high performance in these catalytic systems. However, 3 eq. of K_2CO_3 was more effective than 1 eq. of KO*t*Bu for the Suzuki coupling reaction in aqueous DMF. Results are summarized in Table 1. The role of NHC–$PdCl_2$-pyridine complex was investigated with control experiments (Table 2, entries 1, 8, 15, 22, 29) in which low or trace yields were obtained. Thus, results showed that palladium complexes are effective for the Suzuki cross-coupling reactions.

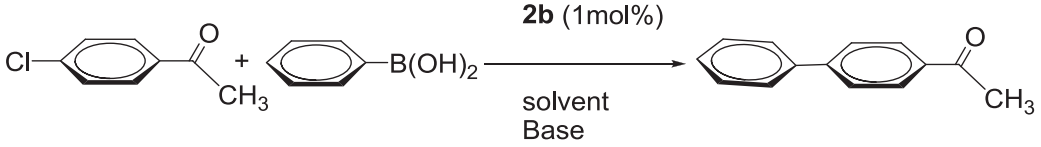
After determining the optimum cross-coupling reaction conditions, we investigated whether electronic properties of the substrate had a significant effect upon the Suzuki coupling reaction with the NHC–Pd-pyridine catalyst. With this catalytic system, unactivated *p*-substituted aryl chlorides and chlorobenzene reacted very cleanly with phenylboronic acid in good yields (Table 2). In all cases, around 10–15% homocoupling of the boronic acid was produced by Pd(0), which results from the reduction of the Pd(II) precatalyst. Both the electron-rich and, especially, the electron-poor un-activated aryl chlorides were coupled successfully with boronic acid in good yields to give desirable products under mild reaction conditions. To date, reviews on these (NHC–Pd(II)-pyridine) type complexes the authors inferred that the catalytic reactivity of these type complexes in C–C or C–N bond formation reaction is originated from both the σ-donor function of NHC ligands and the size of steric hindrance which gives bulky *N*-aryl substituents used systems [55]. Considering the above explanations, the catalytic activity of Pd–NHC complexes strongly depends upon steric bulk and electronic factors of the *N*-heterocyclic carbene ligands. The studies on this issue point out that [45,56], these two factors need to be balanced to create a highly active catalyst system.

Herein, we report the syntheses of benzimidazole-based NHC–$PdCl_2$-pyridine complexes that vary in sterics and electronics. Also we wanted to see the effect of aromatic and non-aromatic bulky cyclic groups on N-substituents. Although results were quite close to each other, sometimes **2f** showed better (Table 2 entries 14 and 28) or worse catalytic activity. From these results, we hypothesize that proper substrate/catalyst matching results in high catalytic activity. These benzimidazolium-based palladium pyridine complexes were found to be useful catalysts for the formation of birayls from un-activated aryl chlorides.

Conclusion

In the last two decade, NHCs have been mostly common used ligand for many transition metals and catalytic transformations. We have been synthesized and well-defined a highly active, easy to producible and environmentally friendly N-heterocyclic carbene precursors and their palladium(II)–pyridine (PEPPSI) complexes. These easily prepared air- and moisture-stable benzimidazolium-based NHC–palladium(II)–pyridine complexes show smooth catalytic activity in the Suzuki–Miyaura coupling reactions of aryl chlorides in aqueous media under mild conditions. Under optimal conditions, the Suzuki–Miyaura reactions with low catalyst loadings (0.01 mol%) resulted in high yields. This catalytic system is simple and efficient for the coupling of various aryl chlorides.

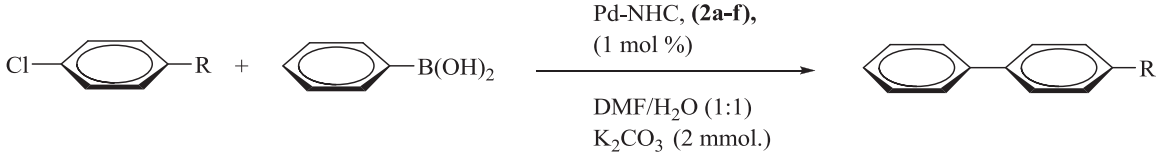
Table 1
The effect of solvent and base on yield in the Suzuki coupling reaction of 4-chloroacetophenone with phenylboronic acid catalyzed by **2b**[a].



Entry	Solvent	Base(eq)	Yield[b] (%)
1	Dioxane (6 mL)	KO*t*Bu (1)	66
2	Dioxane (6 mL)	K_2CO_3 (2)	75
3	Dioxane (6 mL)	Cs_2CO_3 (2)	40
4	i-PrOH	KO*t*Bu (1)	55
5	i-PrOH	K_2CO_3 (2)	52
6	i-PrOH	Cs_2CO_3 (2)	40
7	DMF (6 mL)	K_2CO_3 (2)	60
8	DMF/H_2O (4/2 mL)	K_2CO_3 (2)	66
9	DMF/H_2O (3/3 mL)	K_2CO_3 (2)	96
10	DMF/H_2O (2/4 mL)	K_2CO_3 (2)	85
11	H_2O (6 mL)	K_2CO_3 (2)	22

[a] Reaction conditions: complex **2b** (1 mol %), 4-chloroacetophenone (1 mmol), $Ph(OH)_2$ (1.5 mmol), 80 °C, 3 h.
[b] Isolated yields.

Table 2
The Suzuki coupling reaction of aryl chlorides with phenylboronic acid catalyzed by Pd–NHC (PEPSSI) complexes, (**2a**–**f**).



Entry	R	Product	Pd–NHC	Yield[a,b,c,d] (%)
1	COMe	Ph–Ph-p-COMe	–	1[e]
2			**2a**	80
3			**2b**	96
4			**2c**	94
5			**2d**	85
6			**2e**	84
7			**2f**	81
8	COH	Ph–Ph-p-COH	–	3[e]
9			**2a**	92
10			**2b**	95
11			**2c**	82
12			**2d**	84
13			**2e**	99
14			**2f**	93
15	OMe	Ph–Ph-p-OMe	–	0[e]
16			**2a**	75
17			**2b**	83
18			**2c**	71
19			**2d**	62
20			**2e**	68
21			**2f**	56
22	Me	Ph–Ph-p-Me	–	1[e]
23			**2a**	55
24			**2b**	69
25			**2c**	59
26			**2d**	60
27			**2e**	55
28			**2f**	72
29	–H	Ph–Ph	–	2[e]
30			**2a**	64
31			**2b**	85
32			**2c**	83
33			**2d**	84
34			**2e**	69
35			**2f**	60

[a] Reaction conditions: 1.0 mmol of *p*-R–C_6H_4Cl, 1.5 mmol of phenylboronic acid, 2 mmol K_2CO_3, 1 mmol% Pd–NHC (**2a**–**f**), water (3 ml)–DMF (3 ml).
[b] Purity of compounds was checked by NMR and yields are based on arylchloride.
[c] All reactions were monitored by thin-layer chromatography (TLC).
[d] Temperature 80 °C, 3 h.
[e] No Pd–NHC(**2a**–**f**).

Experimental

Materials and methods

Unless stated otherwise, all procedures were carried out under a normal atmosphere. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK) and used directly. Elemental analyses were performed by Turkish Research Council (Ankara, Turkey) Microlab.

NMR and IR spectroscopy

^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkurspectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer, wave numbers in cm^{-1}.

General preparation of 1,3-dialkylbenzlimidazolium salts

Diaryl/alkylbenzimidazolium salts **1a**–**f** were prepared according to known methods [46,52]. Symmetric benzimidazolium salts **1a**–**f** were obtained upon reaction of alkyl/aryl halides with 1-alkyl/arylbenzimidazole in DMF and isolated in 80–92% yields (Scheme 1).

1,3-Bis(4-methylbenzyl)benzimidazolium chloride, ***1a***

m.p: 218–219 °C. Yield: % 90 (3.26 g). $\nu_{(CN)} = 1545\ cm^{-1}$. ^{1}H NMR (399.9 MHz, $CDCl_3$, 25 °C): $\delta = 2.31$ [s, 6H, $CH_2C_6H_4(CH_3)$-4], 5.82 [s, 4H, $CH_2C_6H_4(CH_3)$-4], 7.16–7.55 [m, 12H, $C_6H_4(CH_3)$-4 and C_6H_4], 12.15 [s, 1H, NC*H*N]. ^{13}C NMR (100 MHz $CDCl_3$, 25 °C): $\delta = 19.8$, 50.3, 114.1, 128.5, 131.6, 127.2, 127.3, 129.9, 130.5, 139.5. Anal. Calcd. for

$C_{23}H_{23}N_2Cl$: C,76.12; H, 6.39; N, 7.72 Found: C, 76.14; H, 6.42, N, 7.75.

1,3-Bis(3,5-dimethylbenzyl)benzimidazolium bromide, ***1b***

m.p: 254–255 °C. Yield: % 89 (3.48 g). $\nu_{(CN)}$ = 1570 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 2.52 [s, 12H, $CH_2C_6H_4(CH_3)_2$-3,5], 5.78 [s, 4H, $CH_2C_6H_3(CH_3)_2$-3,5], 6.93–7.60 [m, 10H, $C_6H_3(CH_3)_2$-3,5 and C_6H_4], 11.59 [s, 1H, NC*H*N]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.2, 51.5, 113.9, 125.9, 131.0, 127.2, 132.0, 132.5, 139.9, 142.7. Anal. Calcd. for $C_{25}H_{27}N_2Br$: C, 68.96; H, 6.25; N, 6.43. Found: C, 69.00; H, 6.28; N, 6.47.

1,3-Bis(4-ter-buthylbenzyl)benzimidazolium bromide, 1c

This known compound was synthesized and characterized by m.p, IR, ^1H and ^{13}C NMR and micro analyses. Results, which we found, are consistent with the literature [47].

1,3-Bis(3,4,5-trimethoxybenzyl)benzimidazolium bromide, 1d

This known compound was synthesized and characterized by m.p, IR, ^1H and ^{13}C NMR and micro analyses. Results, which we found, are consistent with the literature [48a].

1,3-Bis(2-ethoxybenzyl)benzimidazolium chloride, ***1e***

m.p: 232–233 °C. Yield: % 85 (3.59 g). $\nu_{(CN)}$ = 1623 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 1.27 [t, J = 8 Hz, 6H, $CH_2C_6H_3(OCH_2CH_3)$-2], 3.99 [q, J = 8 Hz, 4H, $CH_2C_6H_3(OCH_2CH_3)$-2], 5.79 [s, 4H, $CH_2C_6H_3(OCH_2CH_3)$-2], 6.80–7.60 [m, 10H, $CH_2C_6H_3(OCH_2CH_3)$-2 and C_6H_4], 11.29 [s, 1H, NC*H*N]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.0, 46.8, 64.2, 111.9, 121.4, 131.1, 113.9126.7, 131.2, 131.6, 132.3, 132.9156.9. Anal. Calcd. for $C_{23}H_{27}N_2O_2Cl$: C,69.25; H, 6.82; N, 7.02. Found: C, 69.29; H, 6.86; N, 7.06.

1,3-Bis(2-morpholinethyl)benzimidazolium chloride, ***1f***

This known compound was synthesized and characterized by m.p, IR, ^1H and ^{13}C NMR and micro analyses. Results, which we found, are consistent with the literature [48b].

*General method for the preparation of the NHC-palladium-pyridine complexes (**2a**–**f**)*

The palladium-NHC complexes (**2a**–**f**) were synthesized with method reported by Organ [13]. In air, a pressure tube was charged with $PdCl_2$ (87 mg, 0.5 mmol), NHC·HCl (0.55 mmol), and K_2CO_3 (345 mg, 2.5 mmol). 3 mL of pyridine was added. The reaction mixture was heated with vigorous stirring for 10 h at 80 °C. The reaction mixture was then diluted with sufficiently dichloromethane (DCM) until the product was recovered. The DCM was evaporated, and the pyridine was vacuum-distilled. Residue solid was washed with hexane (2 × 10 mL) and diethyl ether (2 × 10 mL) and then dried in vacuo. Molecular structures of NHC–Pd-pyridine complexes were determined by NMR, LC- MS(ESI), IR and micro analyses.

Dichloro[1,3-bis-(4-methylbenzyl)benzimidazole-2-ylidene]pyridine palladium(II), ***2a***

m.p: 200–201 °C. Yield: % 90 (0.52 g). $\nu_{(CN)}$ = 1444 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 2.34 [s, 3H, $CH_2C_6H_4(CH_3)$-4], 2.36 [s, 3H, $CH_2C_6H_4(CH_3)$-4], 5.10 [s, 2H, $CH_2C_6H_4(CH_3)$-4], 6.26 [s, 2H, $CH_2C_6H_4(CH_3)$-4],6.90–7.79 [m, 15H, $C_6H_4(CH_3)$-4 and NC_5H_5], 9.04 [d, J = 5.6 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 19.6, 50.5, 114.2, 124.1, 124.6, 125.5, 128.6, 131.9, 134.7, 138.4, 152.2, 152.8, 162.7. Anal. Calcd. for $C_{28}H_{27}Cl_2N_3Pd$: C,57.70; H, 4.67; N, 7.21 Found: C, 57.77; H, 4.76, N, 7.33. LC-MS (ESI): m/z 581.5 [MH^-].

Dichloro[1,3-bis-(3,5-dimethylbenzyl)benzimidazole-2-ylidene] pyridine palladium(II), 2b

m.p: 240–242 °C. Yield: % 85 (0.52 g). $\nu_{(CN)}$ = 1462 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 2.33 [s, 12H, $CH_2C_6H_4(CH_3)_2$-3,5], 6.17 [s, 4H, $CH_2C_6H_3(CH_3)_2$-3,5], 6.97–7.77 [m, 13H, $C_6H_3(CH_3)_2$-3,5 and NC_5H_5], 9.04 [d, J = 5.6 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.3, 53.3, 111.4, 123.8, 124.4, 125.9, 129.8, 132.0, 134.8, 138.4, 152.0, 152.7, 164.2. Anal. Calcd. for $C_{30}H_{31}Cl_2N_3Pd$: C, 58.98; H, 5.11; N, 6.88. Found: C, 59.03; H, 5.17; N, 6.96. LC-MS (ESI): m/z 609.0 [MH^-].

Dichloro[1,3-bis-(4-ter-butylbenzyl)benzimidazole-2-ylidene] pyridine palladium(II), ***2c***

m.p: 235–237 °C.Yield: % 85 (0.56 g). $\nu_{(CN)}$ = 1489 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 2.34 [s, 18H, $CH_2C_6H_4(C(CH_3)_3)$-4], 6.22 [s, 2H, $CH_2C_6H_4(C(CH_3)_3)$-4], 6.26 [s, 2H, $CH_2C_6H_4(C(CH_3)_3)$-4], 7.08–7.78 [m, 15H, $CH_2C_6H_4(C(CH_3)_3)$-4], C_6H_4andNC_5H_5], 9.05 [d, J = 5.6 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.3, 34.4, 53.0, 111.6, 123.0, 124.5, 125.8, 132.0, 134.7, 137.9, 149.9, 152.1, 152.6, 164.1. Anal. Calcd. for $C_{34}H_{39}Cl_2N_3Pd$: C, 61.22, H, 5.89, N, 6.30. Found: C, 61.27; H, 5.94; N, 6.40. LC-MS (ESI): m/z 666.6 [MH^-].

Dichloro[1,3-bis-(3,4,5-methoxybenzyl)benzimidazole-2-ylidene] pyridine palladium(II), 2d

m.p: 253–254 °C.Yield: % 93 (0,68 g). $\nu_{(CN)}$ = 1489 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 3.84 [s, 6H, $CH_2C_6H_2(OCH_3)_3$-4], 3.86 [s, 12H, $CH_2C_6H_2(OCH_3)_3$-3,5], 6.20 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 6.94 [s, 4H, $C_6H_2(OCH_3)_3$-3,4,5] 6.96–7.80 [m, 7H, $C_6H_4$and NC_5H_5], 9.01 [d, J = 5.6 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 49.4, 50.3, 62.5, 111.4, 120.6, 123.6, 124.3, 130.0, 130.5, 134.8, 138.5, 151.3, 156.4, 164.6. Anal. Calcd. for $C_{32}H_{35}Cl_2N_3O_6Pd$: C, 52.29; H, 4.80; N, 5.72. Found: C, 52.34; H, 4.86; N, 5.86. LC-MS (ESI): m/z 733.0 [MH^-].

Dichloro[1,3-bis-(2-ethoxybenzyl)benzimidazole-2-ylidene] pyridine palladium(II), ***2e***

m.p: 225–226 °C.Yield: % 83 (0.5 g). $\nu_{(CN)}$ = 1456 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 1.41 [t, J = 6.8 Hz, 6H, $CH_2C_6H_3(OCH_2CH_3)$-2], 4.16 [q, J = 6.8 Hz, 4H, $CH_2C_6H_3(OCH_2CH_3)$-2], 6.25 [s, 4H, $CH_2C_6H_3(OCH_2CH_3)$-2], 6.89–7.77 [m, 15H, $CH_2C_6H_3(OCH_2CH_3)$-2, $C_6H_4$and NC_5H_5], 8.95 [d, J = 4.8 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.9, 46.7, 63.6, 111.3, 120.7, 123.2, 123.7, 124.3, 129.1, 130.1, 134.5, 138.0, 151.4, 156.5, 164.0. Anal. Calcd. for $C_{30}H_{31}Cl_2N_3O_2Pd$: C,56.05; H, 4.86; N, 6.54. Found: C, 56.09; H, 4.89; N, 6.60.LC-MS (ESI): m/z 641.5 [MH^-].

Dichloro ([1,3-bis-(2-morpholinoethyl)benzimidazole-2-ylidene] pyridine palladium(II), ***2f***

m.p: 250–251 °C.Yield: % 84 (0.5 g). $\nu_{(CN)}$ = 1448 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 2.71 [bs, 4H, $CH_2CH_2N(CH_2CH_2)_2O$], 3.25 [t, J = 7.2 Hz, 2H, $CH_2CH_2N(CH_2CH_2)_2O$], 3.72 [bs, 4H, $CH_2CH_2N(CH_2CH_2)_2O$], 5.01 [t, J = 7.2 Hz, 2H, $CH_2CH_2N(CH_2CH_2)_2O$], 7.30–7.85 [m, 7H, NC_5H_5 and C_6H_4], 9.03 [d, J = 7.2 Hz, 2H, NC_5H_5]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 45.7, 54.1, 57.6, 67.0, 110.6, 123.2, 124.8, 134.5, 138.6, 151.1, 163.7. Anal. Calcd. for $C_{24}H_{33}Cl_2N_5O_2Pd$: C, 47.97; H, 5.54; N, 11.66. Found: C, 48.01; H, 5.59; N, 11.78. LC-MS (ESI): m/z 617.7 [MH^+].

General procedure for Suzuki cross-coupling reactions

NHC–$PdCl_2$-pyridine (**2a**–**f**) (1.0 mmol %), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), and 6 mL of a 1:1 mixture of water and DMF were added to a small round bottom flask under argon gas, and the mixture was heated at 80 °C for 4 h. The reaction mixture was then cooled to room

temperature and extracted with Et_2O, filtered through a pad of silica with copious washings of diethyl ether, concentrated, and purified by flash chromatography on silica. The purity of the compounds was checked by NMR. The yields are based on aryl chloride.

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References

[1] a) A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361;
b) A.J. Arduengo, Acc. Chem. Res. 32 (1999) 913.
[2] W.A. Herrmann, L.T. Goosen, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 35 (1996) 2805.
[3] H. Küçükbay, B. Çetinkaya, G. Salaheddine, P.H. Dixneuf, Organometallics 15 (1996) 2434.
[4] a) S. Yaşar, K.J. Cavell, B.D. Ward, B. Kariuki, Appl. Organomet. Chem. 25 (2011) 374;
b) N. Gürbüz, İ. Özdemir, S. Demir, B. Çetinkaya, J. Mol. Catal. A. Chem. 209 (2004) 23.
[5] a) T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. Int. Ed. 37 (1998) 2490;
b) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674.
[6] a) C.W.K. Gstöttmayr, V.P.W. Böhm, E. Herdtweck, M. Grosche, W.A. Hermann, Angew. Chem. Int. Ed. 41 (2002) 1363;
b) M.F. Lappert, J. Organomet. Chem. 358 (1988) 185;
c) C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804;
d) A. Fürstner, A. Leitner, Synlett (2001) 290.
[7] a) D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39;
b) W.A. Herrmann, T. Wescamp, V.P.W. Böhm, Adv. Organomet. Chem. 48 (2001) 1.
[8] a) G.D. Frey, J. Schvtz, E. Herdtweck, W.A. Herrmann, Organometallics 24 (2005) 4416;
b) W.A. Herrmann, C.-P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.
[9] a) O. Navarro, N. Marion, N.M. Scott, J. Gonzalez, D. Amoroso, A. Bell, S.P. Nolan, Tetrahedron 61 (2005) 9716;
b) R. Singh, M.S. Viciu, N. Kramareva, O. Navarro, S.P. Nolan, Org. Lett. 7 (2005) 1829;
c) M.S. Viciu, E.D. Stevens, J.L. Petersen, S.P. Nolan, Organometallics 23 (2004) 3752;
d) M.S. Viciu, O. Navarro, R.F. Germaneau, R.A. Kelly, W. Sommer, N. Marion, E.D. Stevens, C. Luigi, S.P. Nolan, Organometallics 23 (2004) 1629;
e) M.S. Viciu, R.A. Kelly, E.D. Stevens, F. Naud, M. Studer, S.P. Nolan, Org. Lett. 5 (2003) 1479.
[10] R. Jackstell, M.G. Andreu, A.C. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, Angew. Chem. 114 (2002) 1028. Angew. Chem. Int. Ed. 41 (2002) 986.
[11] D.R. Jensen, M.J. Schultz, J.A. Mueller, M.S. Sigman, Angew. Chem. 115 (2003) 3940. Angew. Chem. Int. Ed. 42 (2003) 3810.
[12] V. Nair, S. Bindu, V. Sreekumar, Angew. Chem. 116 (2004) 5240. Angew. Chem. Int. Ed. 43 (2004) 5130.
[13] C.J. O'Brien, E.A.B. Kantchev, C. Valente, N. Hadei, G.A. Chass, A. Lough, A.C. Hopkinson, M.G. Organ, Chem. Eur. J. 12 (2006) 4743.
[14] İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, C. Bruneau, Eur. J. Inorg. Chem. (2010) 1798.
[15] M. Teci, E. Brenner, D. Matt, L. Toupet, Eur. J. Inorg. Chem. (2013) 2841.
[16] a) A. Meijere, F. Diederich, Metal-Catalyzed Cross-Coupling Reactions, second ed., Wiley-VCH, Weinheim, 2004;
b) E. Negishi, Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, New York, 2002.
[17] J.H. Kirchhoff, M.R. Netherton, I.D. Hills, G.C. Fu, J. Am. Chem. Soc. 124 (2002) 13662.
[18] T. Brenstrum, D.A. Gerristma, G.M. Adjabeng, C.S. Frampton, J. Britten, A.J. Robertson, J. McNulty, A. Capretta, J. Org. Chem. 69 (2004) 7635.
[19] a) K. Arentsen, S. Caddick, F.G.N. Cloke, Tetrahedron 61 (2005) 9710;
b) G.A. Grasa, M.S. Viciu, J. Huang, C. Zhang, M.L. Trudell, S.P. Nolan, Organometallics 21 (2002) 2866.
[20] C.J. O'CBrien, E.A.B. Kantchev, G.A. Chass, N. Hadei, A.C. Hopkinson, M.G. Organ, D.H. Setiadi, T.-H. Tang, D.-C. Fang, Tetrahedron 61 (2005) 9723.
[21] a) H. Doucet, J. Eur. Org. Chem. (2008) 2013;
b) V.L. Budarin, J.H. Clark, R. Luque, D.J. Macquarrie, R.J. White, Green. Chem. 10 (2008) 382;
c) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633.
[22] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[23] A.J. Suzuki, J. Organomet. Chem. 576 (1999) 147.
[24] S.P. Stanforth, Tetrahedron 54 (1998) 263.
[25] N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449.
[26] G.T. Crisp, Chem. Soc. Rev. 27 (1998) 427.
[27] a) A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176;
b) A. Suzuki, J. Organomet. Chem. 653 (2002) 83;
c) L. Xu, W. Chen, J. Xiao, Mol. Catal. A 187 (2002) 189;
d) J. Yin, M.P. Rainka, X.X. Zhang, S.L. Buchwald, J. Am. Chem. Soc. 124 (7) (2002) 1162.
[28] a) S.D. Walker, T.E. Barder, J.R. Martinelli, S. L Buchwald, Angew. Chem. Int. Ed. Engl. 43 (2004) 1871;
b) A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020;
c) G.R. Rosa, G. Ebeling, J. Dupont, A.L. Monteiro, Synthesis (2003) 2894;
d) W.A. Herrmann, T. Wescamp, V.P.W. Bohm, Adv. Organomet. Chem. 48 (2001) 1;
e) C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.
[29] G.R. Peh, E.A.B. Kantchev, J.C. Er, J.Y. Ying, Chem. Eur. J. 16 (2010) 4010.
[30] Y.Q. Tang, H. Lv, J.M. Lu, L.X. Shao, J. Organomet. Chem. 696 (2011) 2576.
[31] a) J.P. Genet, M. Savignac, J. Organomet. Chem. 576 (1999) 305;
b) H. Sakurai, T. Sukuda, T. Hirao, J. Org. Chem. 67 (2002) 2721;
c) S. Parisot, R. Kolodziuk, C.G. Henry, A. Iourtchenko, D. Sinou, Tetrahedron. Lett. 43 (2002) 7397.
[32] D. Dallinger, C.O. Kappe, Chem. Rev. 107 (2007) 2563.
[33] C.-J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68.
[34] C.-J. Li, Chem. Rev. 93 (1993) 2023.
[35] C.-J. Li, Chem. Rev. 105 (2005) 3095.
[36] U.M. Lindström, Chem. Rev. 102 (2002) 2751.
[37] U.M. Lindström (Ed.), Organic Reactions in Water, Blackwell Publishing, Oxford, 2007.
[38] C.-J. Li, T.H. Chan, Organic Reactions in Aqueous Media, Wiley, New York, 1997.
[39] C.I. Herrerias, X.-Q. Yao, Z.-P. Li, C.-J. Li, Chem. Rev. 107 (2007) 2546.
[40] S. Kobayashi, C. Ogawa, Chem. Eur. J. 12 (2006) 5954.
[41] P.A. Grieco (Ed.), Organic Synthesis in Water, Blackie, London, 1998.
[42] R.N. Butler, A.G. Coyne, Chem. Rev. 110 (2010) 6302.
[43] J. Mlynarski, J. Paradowska, Chem. Soc. Rev. 37 (2008) 1502.
[44] Y.Q. Tang, J.M. Lu, L.X. Shao, J. Organomet. Chem. 696 (2011) 3741.
[45] J.J. Dunsford, K.J. Cavell, Organometallics 33 (2014) 2902.
[46] F. Demirhan, O. Yildirim, B. Cetinkaya, Trans. Metal. Chem. 28 (2003) 558.
[47] N. Gürbüz, S. Yasar, E.Ö. Özcan, I. Özdemir, B. Çetinkaya, Eur. J. Inorg. Chem. (2010) 3051.
[48] a) S. Yasar, I. Özdemir, B. Cetinkaya, J.L. Renaud, C. Bruneau, Eur. J. Org. Chem. (2008) 2142;
b) İ. Özdemir, Y. Gök, N. Gürbüz, E. Çetinkaya, B. Çetinkaya, J. Heterocycl. Chem. 42 (2005) 303.
[49] Y. Gök, N. Gürbüz, İ. Özdemir, B. Çetinkaya, E. Çetinkaya, Appl. Organometal. Chem. 19 (2005) 870.
[50] S. Köytepe, T. Seçkin, S. Yaşar, I. Özdemir, Des. Monomers Polym. 11 (2008) 409.
[51] S. Demir, İ. Özdemir, B. Çetinkaya, Appl. Organomet. Chem. 23 (2009) 520.
[52] İ. Özdemir, Y. Gök, N. Gürbüz, E. Çetinkaya, B. Çetinkaya, J. Heterocycl. Chem. 42 (2005) 303.
[53] S. Grupta, B. Basu, S. Das, Tetrahedron 69 (2013) 122.
[54] F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122.
[55] (a) J. Nasielski, N. Hadei, G. Achonduh, E.A.B. Kantchev, C.J. O'Brien, A. Lough, M.G. Organ, Chem. Eur. J. 16 (2010) 10844;
(b) C. Valente, S. Calimsiz, K.H. Hoi, D. Mallik, M. Sayah, M.G. Organ, Angew. Chem. Int. Ed. 51 (2012) 3314.
[56] E. Negishi, Hand-book of Organopalladium Chemistry for Organic Synthesis and York, 2002 Synthesis, Wiley, New York, 2002.