APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 187–192 **Materials, Nanoscience and Catalysis** **AOC**

Synthesis of novel palladium *N*-heterocyclic-carbene complexes as catalysts for Heck and Suzuki cross-coupling reactions

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Received 7 July 2005; Revised 22 August 2005; Accepted 22 August 2005

Novel palladium-1,3-dialkylperhydrobenzimidazolin-2-ylidene (2a–c) and palladium-1,3-dialkylimidazolin-2-ylidene complexes (4a,b) have been prepared and characterized by C, H, N analysis, ^{1}H-NMR and ^{13}C-NMR. Styrene or phenylboronic acid reacts with aryl halide derivatives in the presence of catalytic amounts of the new palladium-carbene complexes, $PdCl_2$(1,3-dialkylperhydrobenzimidazolin-2-ylidene) or $PdCl_2$(1,3-dialkylimidazolin-2-ylidene) to give the corresponding C–C coupling products in good yields. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Heck; Suzuki; palladium; perhydrobenzimidazolin-2-ylidene; imidazolin-2-ylidene; *N*-heterocyclic carbene

INTRODUCTION

Palladium-catalyzed couplings have become an indispensable tool for organic synthesis and there is a wide range of synthetically valuable transformations which can be catalyzed by palladium.[1,2] We are interested in palladium-catalyzed carbon–carbon bond-forming reactions,[3–9] and in this regard seek to understand and exploit the unique features of novel ligand systems to generate catalyst systems exhibiting broad scope and high efficiency.

The first metal complexes of *N*-heterocyclic carbenes (NHCs) were reported independently in 1968 by Wanzlick[10] and Öfele,[11] although Lappert and co-workers continued investigations in this area.[12–14] Since the isolation and crystallographic characterization of stable *N*-heterocyclic carbenes by Arduengo,[15–19] increasing attention has focused on using these compounds as ancillary ligands for transition–metal complexes. Interestingly, most studies focusing on catalysts incorporating NHC ligands have revolved around the platinum group metals. In numerous instances simple substitution reaction routes involving replacement of phosphines by NHC ligands lead to higher catalytic activity as well as improved thermal stability of the resulting organometallic complexes. The working hypothesis is that NHCs are strong σ-donors with negligible π-accepting ability, and so they resemble donor phosphine ligands rather than the classical Fischer- or Schrock-type carbenes[20] and thereby also lead to electron-rich metal centers.[21] In contrast to metal–phosphine complexes, they form metal complexes that have higher stability towards heat, moisture and oxygen. Numerous publications related to their metal coordination chemistry and catalytic properties have been reported in the past 10 years.[22–27]

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 governing 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. Recently, it was shown that palladium complexes of *N*-heterocyclic carbene ligands offer distinctive advantages as possible alternatives for palladium/phosphine systems in the C–C coupling reactions.[23,28,29]

Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of palladium-1,3-dialkylperhydrobenzimidazolin-2-ylidene (**2a–c**) and palladium-1,3-dialkylimidazolin-2-ylidene com-

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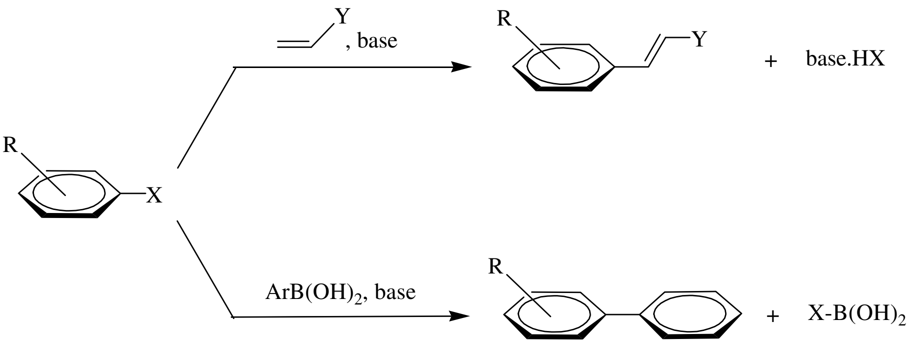
Contract/grant sponsor: TÜBİTAK; Contract/grant numbers: COST D17; TBAG-2474 (104T085).
Contract/grant sponsor: Inönü University Research Fund; Contract/grant number: I.Ü. B.A.P. 2005/42.



Scheme 1.

plexes (**4a,b**) for the Heck and Suzuki cross coupling of aryl halides (Scheme 1).

We now report: (i) the straightforward preparation of new [$PdCl_2$(1,3-dialkylperhydrobenzimidazolin-2-ylidene)$_2$] and [$PdCl_2$(1,3-dialkylimidazolin-2-ylidene)$_2$] complexes and (ii) their efficient catalysis for the Heck and Suzuki cross coupling of aryl halides.

EXPERIMENTAL

All reactions for the preparation of **1–4** were carried out under argon in flame-dried glassware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane and toluene (Na). For flash chromatography Merck silica gel 60 (230–400 mesh) was used and the eluent was ethylacetate–hexane (1 : 5). The 1,3-dialkylperhydrobenzimidazolinium (**1**) and 1,3-dialkylimidazolinium salts (**3**) were prepared according to known methods.[30] All reagents were purchased from Aldrich Chemical Co. All ^1H and ^{13}C-NMR were performed in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab.

Synthesis of bis{1,3-di(2,4,6-trimethylbenzyl)perhydrobenzimidazolin-2-ylidene} dichloropalladium(II) (2a)

A stirred DMSO solution (10 ml) of 1,3-bis(2,4,6-trimethylbenzyl)perhydrobenzimidazolinium chloride (0.849 g, 2 mmol; **1a**; 2 mmol) and $Pd(OAc)_2$ (0.224 g, 1 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, **2** and **4**. Recrystallization from CH_2Cl_2–Et_2O was carried out. The crystals were filtered, washed with diethyl ether (3 × 10 ml) and dried under vacuum. The melting point was 274–275 °C; yield 0.82 g, 87%; $\nu_{(NCN)} = 1493\ cm^{-1}$. Anal. found: C, 67.99; H, 7.48; N, 5.95. Calcd for $C_{54}H_{72}N_4PdCI_2$: C, 67.96; H, 7.55; N, 5.87%.

^1H NMR (δ948; $CDCI_3$): 0.74–0.83, 1.21–1.37 and 2.89–2.91 [m, 20H, $\mathrm{NC}\mathit{H}(\mathrm{C}\mathit{H}_2)_4\mathrm{C}\mathit{H}\mathrm{N}$]; 6.77 [s, 8H, $\mathrm{CH_2C_6}\mathit{H}_2(Me)_3$-2,4,6]; 5.03 and 6.05 [d, 8H, J = 14.8 Hz $\mathrm{C}\mathit{H}_2\mathrm{C_6H_2(Me)_3}$-2,4,6]; 2.22 and 2.44 [s, 36H, $\mathrm{CH_2C_6H_2}(\mathit{Me})_3$-2,4,6]. ^{13}C {H} NMR (δ, $CDCI_3$): 206.93 [$C_{carb.}$]; 24.66, 29.51 and 49.98 [$NCH(CH_2)_4CHN$]; 125.82, 129.31, 130.23 and 137.39 [$CH_2C_6H_2(Me)_3$-2,4,6]; 69.64 [$CH_2C_6H_2(Me)_3$-2,4,6]; 21.10 and 21.37 [$\mathrm{CH_2C_6H_2}(\mathit{Me})_3$-2,4,6].

Synthesis of bis{1,3-di(*p*-dimethylaminobenzyl)perhydrobenzimidazolin-2-ylidene} dichloropalladium(II) (2b)

Compound **2b** was prepared in a similar way to **2a**, from 1,3-bis(4-dimethylaminobenzyl)perhydrobenzimidazolinium chloride (**1b**; 0.853 g, 2 mmol) and $Pd(OAc)_2$ (0.224 g, 1 mmol). The melting point was 295–296 °C; yield 0.85 g, 89%; $\nu_{(NCN)} = 1523\ cm^{-1}$. Anal. found: C, 62.75; H, 7.01; N, 11.78. Calcd for $C_{50}H_{68}N_8PdCI_2$: C, 62.66; H, 7.10; N, 11.69%.

^1H NMR (δ, $CDCI_3$): 0.95–1.00, 1.56–1.82 and 2.82–2.83 [m, 20H, $\mathrm{NC}\mathit{H}(\mathrm{C}\mathit{H}_2)_4\mathrm{C}\mathit{H}\mathrm{N}$]; 6.63 and 7.46 [d, 16H, J = 8.8 Hz, $\mathrm{CH_2C_6}\mathit{H}_4\mathrm{NMe_2}$-*p*]; 5.02 and 5.43 [d, 8H, J = 14.8 Hz $\mathrm{C}\mathit{H}_2\mathrm{C_6H_2NMe_2}$-*p*]; 2.84 [s, 24H, $\mathrm{CH_2C_6H_2N}\mathit{Me}_2$-*p*]. ^{13}C {H} NMR (δ, $CDCI_3$): 203.81 [$C_{carb.}$]; 24.45, 28.74 and 52.73 [$NCH(CH_2)_4CHN$]; 113.50, 128.98, 129.96 and 150.05 [$CH_2C_6H_2NMe_2$-*p*]; 66.82 [$CH_2C_6H_2NMe_2$-*p*]; 41.17 [$\mathrm{CH_2C_6H_2N}\mathit{Me}_2$-*p*].

Synthesis of bis{1,3-di(*p*-methoxybenzyl)perhydrobenzimidazolin-2-ylidene} dichloropalladium(II) (2c)

Compound **2c** was prepared in a similar way to **2a**, from 1,3-bis(4-methoxybenzyl)perhydrobenzimidazolinium chloride (**1c**; 0.801 g, 2 mmol) and $Pd(OAc)_2$ (0.224 g, 1 mmol). The melting point was 285–286 °C; yield 0.76 g, 84%;

$\nu_{(NCN)} = 1513\ cm^{-1}$. Anal. found: C, 60.90; H, 6.25; N, 6.07. Calcd for $C_{46}H_{56}N_4O_4PdCl_2$: C, 60.96; H, 6.18; N, 6.18%.

^1H NMR (δ, $CDCl_3$): 0.93–1.09, 1.58–1.78 and 2.84–2.86 [m, 20H, $NC\mathit{H}(C\mathit{H}_2)_4C\mathit{H}N$]; 6.76 and 7.47 [d, 16H, $J = 8.4$ Hz, $CH_2C_6\mathit{H}_4\mathit{OMe}\text{-}p$]; 5.07 and 5.35 [d, 8H, $J = 15.2$ Hz $C\mathit{H}_2C_6H_2OMe\text{-}p$]; 3.74 [s, 12H, $CH_2C_6H_2O\mathit{Me}\text{-}p$]. ^{13}C {H} NMR (δ, $CDCl_3$): 204.07 [$C_{carb.}$]; 24.19, 28.51 and 51.89 [$NCH(CH_2)_4CHN$]; 113.93, 128.81, 129.79 and 159.06 [$CH_2C_6H_2OMe\text{-}p$]; 66.89 [$CH_2C_6H_2OMe\text{-}p$]; 55.34 [$CH_2C_6H_2O\mathit{Me}\text{-}p$].

Synthesis of bis{1,3-di(2,4,6-trimethylbenzyl)-4-methylimidazolin-2-ylidene} dichloropalladium(II) (4a)

Compound **4a** was prepared in a similar way to **2a**, from 1,3-bis(2,4,6-trimethylbenzyl)-4-methylimidazolinium chloride (**3a**) (0.769 g, 2 mmol) and $Pd(OAc)_2$ (0.224 g, 1 mmol). The melting point was 308–309 °C; yield 0.78 g, 90%; $\nu_{(NCN)} = 1498\ cm^{-1}$. Anal. found: C, 65.98; H, 7.41; N, 6.50. Calcd for $C_{48}H_{64}N_4PdCl_2$: C, 65.94; H, 7.32; N, 6.41%.

^1H NMR (δ, $CDCl_3$): 3.61–3.67 [m, 2H, $NC\mathit{H}(CH_3)CH_2N$]; 2.85 and 3.45 [t, 4H, $J = 10.4$ Hz, $NCH(CH_3)C\mathit{H}_2N$]; 1.14 [d, 6H, $J = 7.2$ Hz, $NCH(C\mathit{H}_3)CH_2N$]; 6.83 [s, 8H, $CH_2C_6\mathit{H}_2(Me)_3$-2,4,6]; 5.18 and 5.64 [d, 8H, $J = 14.4$ Hz, $C\mathit{H}_2C_6H_2(Me)_3$-2,4,6]; 2.24 and 2.45 [s, 36H, $CH_2C_6H_2(\mathit{Me})_3$-2,4,6]. ^{13}C {H} NMR (δ, $CDCl_3$): 198.74 [$C_{carb.}$]; 19.59, 47.37 and 48.53 [$NCH(CH_3)CH_2N$]; 124.95; 129.26; 129.56; 137.43; 137.62; 138.57 and 138.61 [$CH_2C_6H_2(Me)_3$-2,4,6]; 54.38 and 55.13 [$CH_2C_6H_2(Me)_3$-2,4,6]; 21.05 and 21.24 [$CH_2C_6H_2(\mathit{Me})_3$-2,4,6].

Synthesis of bis{1,3-di(*p*-methoxybenzyl)-4-methylimidazolin-2-ylidene}dichloro palladium(II) (4b)

Compound **4b** was prepared in a similar way to **2a**, from 1,3-bis(*p*-dimethylaminobenzyl)-4-methylimidazolinium chloride (**3b**) (0.773 g, 2 mmol) and $Pd(OAc)_2$ (0.224 g, 1 mmol). The melting point was 236–237 °C; yield 0.81 g, 93%; $\nu_{(NCN)} = 1517\ cm^{-1}$. Anal. found: C, 60.30; H, 6.75; N, 12.88. Calcd for $C_{44}H_{60}N_8PdCl_2$: C, 60.17; H, 6.83; N, 12.76%.

^1H NMR (δ, $CDCl_3$): 3.58–3.67 [m, 2H, $NC\mathit{H}(CH_3)CH_2N$]; 3.26 and 3.47 [t, 4H, $J = 10.4$ Hz, $NCH(CH_3)C\mathit{H}_2N$]; 1.26 [d, 6H, $J = 6.4$ Hz, $NCH(C\mathit{H}_3)CH_2N$]; 6.62 and 7.35 [d, 16H, $J = 7.2$ Hz, $CH_2C_6\mathit{H}_4NMe_2\text{-}p$]; 5.07 and 5.30 [d, 8H, $J = 14.2$ Hz, $C\mathit{H}_2C_6H_2NMe_2\text{-}p$]; 3.05 [s, 24H, $CH_2C_6H_2N\mathit{Me}_2\text{-}p$]. ^{13}C {H} NMR (δ, $CDCl_3$): 197.68 [$C_{carb.}$]; 18.86, 50.86 and 53.76 [$NCH(CH_3)CH_2N$]; 113.07, 130.03, 130.06 and 150.15 [$CH_2C_6H_2NMe_2\text{-}p$]; 54.28 and 55.15 [$CH_2C_6H_2NMe_2\text{-}p$]; 40.39 [$CH_2C_6H_2N\mathit{Me}_2\text{-}p$].

General procedure for the Heck coupling reactions

[$PdCl_2(NHC)_2$], (**2** or **4**), (1 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), Cs_2CO_3 (2 mmol) and dioxane (3 ml) were added to a small Schlenk tube and the mixture was heated at 80 °C for 15 h under Ar. 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.

General procedure for the Suzuki coupling reaction

[$PdCl_2(NHC)_2$], (**2** or **4**), (1 mmol%), aryl chloride (1.0 mmol), phenyl boronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 ml) were added to a small Schlenk tube and the mixture was heated at 80 °C for 5 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, 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 GC and yields are based on aryl chloride.

RESULTS AND DISCUSSION

In the following sections we discuss the synthesis and characterization of the [$PdCl_2$(1,3-dialkylperhydrobenzimidazolin-2-ylidene)$_2$] (**2**) and [$PdCl_2$(1,3-dialkylimidazolin-2-ylidene)$_2$] (**4**) complexes, their use in the Heck and Suzuki coupling reactions, and the results of these studies.

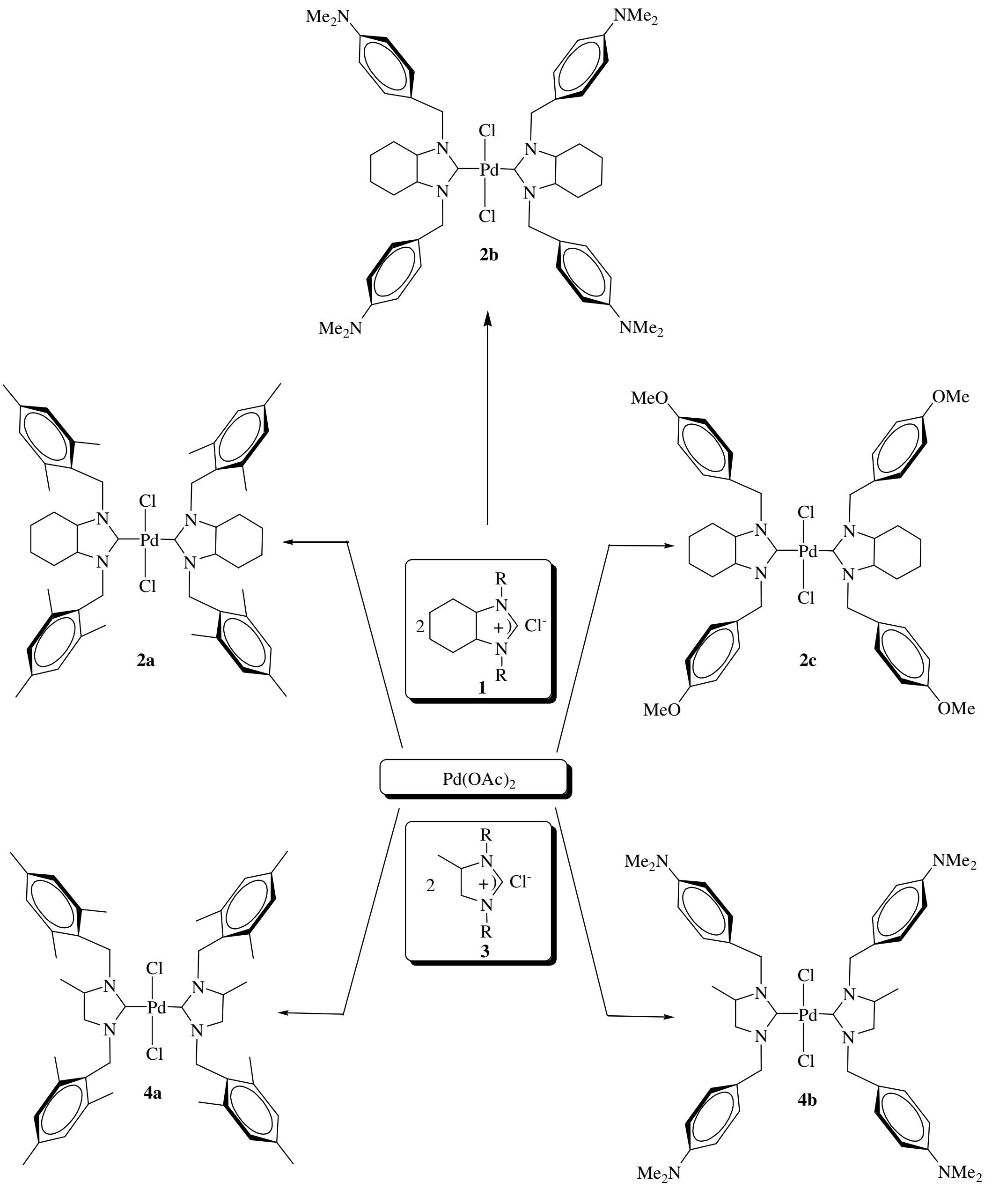
Synthesis and characterization of [$PdCl_2(NHC)_2$]

The 1,3-dialkylperhydrobenzimidazolinium chloride (**1**) and 1,3-dialkylimidazolinium chloride (**3**), were synthesized using a method similar to that reported by Arduengo *et al.*[30] The reaction of 1,3-dialkylperhydrobenzimidazolinium chloride (**1**) and 1,3-dialkylimidazolinium chloride (**3**), with the [$Pd(OAc)_2$] complex proceeded smoothly on heating at 60 °C for 3 h and then at 110 °C for a further 2 h. The remaining DMSO was then removed *in vacuo* to give [$PdCl_2$(1,3-dialkylperhydrobenzimidazolin-2-ylidene)$_2$] (**2a–c**) and [$PdCl_2$(1, 3-dialkylimidazolin-2-ylidene)$_2$] complexes (**4a,b**) as crystalline solids in 84–93% yields (Scheme 2). Each palladium compound was fully characterized by ^1H and ^{13}C NMR spectroscopy, FT-IR and elemental analysis.

The palladium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1493–1523 cm^{-1}.[31] ^{13}C chemical shifts, which provide a useful diagnostic tool for metal–carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 197.7–206.9 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 [$PdCl_2(NHC)_2$] complexes.[31]

The Heck reaction

The Heck reaction[32] has been shown to be very useful for the preparation of disubstituted olefins. The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, Heck reactions conducted with tertiary phosphine[2] or NHC[33] complexes



Scheme 2. Synthesis of palladium-carbene complexes (**2a–c** and **4a,b**).

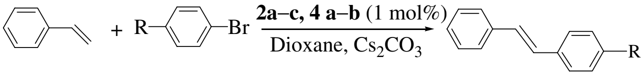
require high temperatures (higher than 120 °C) and polar solvents. For the base, we chose to use Cs_2CO_3, K_2CO_3 and K_3PO_4. Finally, use of 1 mmol% mol $[PdCl_2(NHC)_2]$ and 2 equiv. Cs_2CO_3 in dioxane at 80 °C led to the best conversion within 15 h. We initially evaluated the catalytic activity of $[PdCl_2(NHC)_2]$, (**2a**), for the coupling of 4-bromoacetophenone with styrene (Table 1, entry 1).

Control experiments indicate 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 1, entries 1, 6 and 9). 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%.

The Suzuki coupling

Suzuki cross-coupling reaction, which is the palladium-catalyzed cross-coupling reaction of organic halides with organoboron compounds, represents one of the most important methods of forming sp^2–sp^2 carbon–carbon bonds in synthetic chemistry, as well as in industrial

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

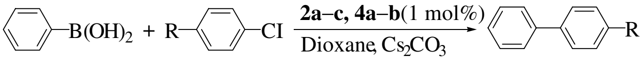


Entry	R	Catalyst	Yield[a] (%)
1	$COCH_3$	**2a**	97
2	$COCH_3$	**2b**	95
3	$COCH_3$	**2c**	93
4	$COCH_3$	**4a**	94
5	$COCH_3$	**4b**	93
6	CHO	**2a**	95
7	CHO	**2b**	92
8	CHO	**2c**	90
9	CHO	**4a**	93
10	CHO	**4b**	91
11	H	**2a**	95
12	H	**2b**	93
13	H	**2c**	88
14	H	**4a**	92
15	H	**4b**	90

[a] *Reaction conditions*: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2 mmol Cs_2CO_3, 1 mmol% **2a–c** or **4a,b**, dioxane (3 ml); purity of compounds is checked by NMR and yields are based on arylhalide. All reactions were monitored by GC; temperature 80 °C, 15 h.

applications.[34–37] Recently, the Suzuki reaction of aryl chlorides catalyzed by palladium–tertiary phosphine[2] and palladium–NHC[23,38–40] systems was studied extensively due to the economically attractive nature of the starting materials and the production of the less toxic salt by-products, e.g. NaCl as opposed to NaBr. Here, various $[PdCl_2(NHC)_2]$, (**2a–c** or **4a,b**) complexes were compared under the same reaction conditions. To survey the parameters for the Suzuki reaction, we chose to examine Cs_2CO_3, K_2CO_3 and K_3PO_4 as base and DMF or dioxane as the solvent. We found that the reactions performed in dioxane with Cs_2CO_3 at 80 °C appeared to be best. We started our investigation with the coupling of 4-chloroacetophenone and phenylboronic acid, in the presence of $[PdCl_2(NHC)_2]$. Table 2 summarizes the results obtained in the presence of **2a–c** and **4a,b** (Table 2, entries 1–5). The scope of the cross-coupling reaction with respect to the aryl chloride component was also investigated. It can be seen that **2a** and **4a** are effective palladium–carbene complexes for coupling unactivated with activated chlorides (Table 2, entries 1–25).

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



Entry	R	Catalyst	Yield[a] (%)
1	$COCH_3$	**2a**	96
2	$COCH_3$	**2b**	95
3	$COCH_3$	**2c**	86
4	$COCH_3$	**4a**	97
5	$COCH_3$	**4b**	93
6	CH_3	**2a**	87
7	CH_3	**2b**	83
8	CH_3	**2c**	86
9	CH_3	**4a**	82
10	CH_3	**4b**	80
11	CHO	**2a**	94
12	CHO	**2b**	92
13	CHO	**2c**	87
14	CHO	**4a**	93
15	CHO	**4b**	90
16	OCH_3	**2a**	83
17	OCH_3	**2b**	80
18	OCH_3	**2c**	75
19	OCH_3	**4a**	77
20	OCH_3	**4b**	74
21	H	**2a**	90
22	H	**2b**	83
23	H	**2c**	86
24	H	**4a**	85
25	H	**4b**	80

[a] *Reaction conditions*: 1.0 mmol of R-C_6H_4Cl-*p*, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1 mmol% **2a–c** or **4a,b,** dioxane (3 ml); purity of compounds is checked by NMR and yields are based on arylchloride. All reactions were monitored by GC; temperature 80 °C, 5 h.

CONCLUSIONS

In summary, from readily available starting materials, such as 1,3-dialkylperhydrobenzimidazolinium and 1,3-dialkylimidazolinium chloride, five novel palladium–carbenes (**2a–c** and **4a,b**) have been prepared and characterized. We are pleased to find that among the various palladium-NHC complexes (**2,4**) are excellent catalysts for the different functionalization of aryl halides, in particular aryl chlorides, for the Suzuki reaction. Depending on the type of coupling reaction, excellent yields of the desired products were obtained. In general, **2a-** and **4a**-based catalysts appear to be more efficient for the Heck reactions of aryl bromides, but their activity is much lower for the coupling of aryl chlorides. Detailed investigations, focusing on palladium-imidazolidin-2-ylidene and palladium-benzimidazolin-2-ylidene complex substituent effects, functional group tolerance and catalytic activity in this and other coupling reactions, are ongoing.

Acknowledgments

This work was financially supported by the Technological and Scientific Research Council of Turkey, TÜBİTAK [TÜBITAK COST D17 and TBAG-2474 (104T085)] and Inönü University Research Fund (I.Ü. B.A.P. 2005/42).

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