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PALLADIUM/BENZIMIDAZOLIUM SALT CATALYST SYSTEMS AND N-HETEROCYCLIC CARBENE-PALLADIUM(II)-PYRIDINE (PEPPSI) COMPLEXES FOR ANTI-MARKOVNIKOV HYDROAMINATIONS OF STYRENE IN IONIC LIQUID

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Abstract – Both in situ prepared Pd-NHC and NHC-Pd-PEPPSI complexes were tested as catalysts in the intermolecular hydroamination reactions between styrene with various anilines in ionic liquid. All of the compounds tested here are catalytically active for the intermolecular hydroamination of styrene with aromatic amines. The anti-Markovnikov addition products were obtained selectively by using 1 mol% of the palladium complex.

INTRODUCTION

Since the isolation and characterization of the first stable N-heterocyclic carbene (NHCs) by Arduengo in the early 1990s,[1] N-Heterocyclic carbenes (NHC) have become an important class of the most widely used and studied ligands in organometallic and coordination chemistry in the last few decades due to their readily tunable steric and electronic properties, and their ease of synthesis.[2-4] Steric and electronic properties of NHCs can be tuned by alteration of the substituents on the nitrogen atoms or the carbene ring and backbones.[5-7] N-Heterocyclic carbenes are strong σ-donating and weak π-accepting ligands. Their strong σ-donating properties make them attactive ligands in a variety of metal-catalyzed processes.[8-10] To date, various metal complexes of N-heterocyclic carbenes have been been synthesized and used as catalysts in different organic transformations.[11-16] Among the metal-NHC complexes, owing to their wide applications as catalysts in organic synthesis, palladium-NHC complexes have been extensively studied.[17-20] A new family of NHC-Pd(II) complexes, NHC-PdX_2-Py (Py = pyridine) complexes,

commonly known as the PEPPSI (Pyridine-Enhanced Precatalyst, Preparation, Stabilization and Initiation) complex were first reported by Organ in 2006.[21] The preparative route of PEPPSI complexes reported by Organ involves the heating of imidazolium salts with $PdCl_2$ and K_2CO_3 in neat 3-chloropyridine for 16 h at 80 ºC in air. Since then, a number of study have been made by many groups on the synthesis and catalytic activities of Imy-PdX_2-Py (Imy = imidazol-2-ylidene, X = halogen) and Bimy-PdX_2-Py (Bimy = benzimidazol-2-ylidene) type complexes.[22-28] The PEPPSI complexes are well-defined, userfriendly, easily-prepared, air- and moisture-stable Pd(II) precatalysts that have proven to exhibit excellent reactivity in large number of palladium-catalyzed C-C and C-N bond forming reactions.[29-34]

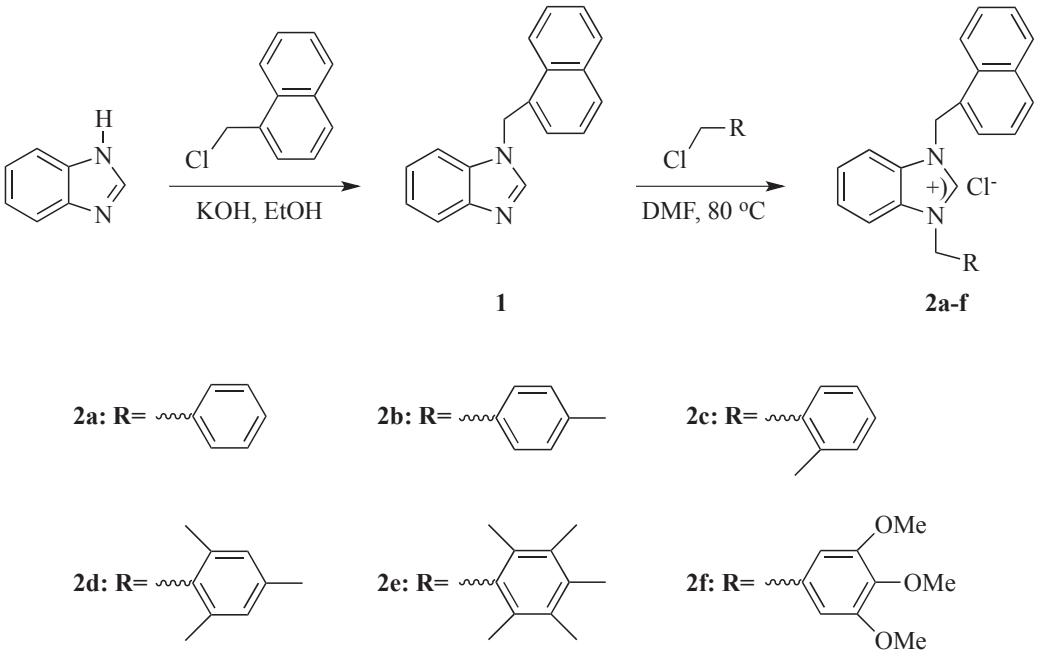
Hydroamination, the addition of N-H bonds across C-C multiple bonds is a simple, useful and atom economical route for making the C-N bonds,[35-38] which have been catalyzed by a variety of different metal-based catalysts, including complexes of main group metals, lanthanides, early and late transition metals.[39-55] The hydroamination of styrenes constitutes the most efficient and atom-economical access to highly valuable phenethylamines, which exhibit a diversity pharmacological activities and also serve as key building blocks in the synthesis of numerous nitrogen containing heterocycles.[56] This transformation proceeds with Markovnikov or anti-Markovnikov selectivity. While the Rh- and Ru-complexes catalyzes the intermolecular hydroamination of vinyarenes with anti-Markovnikov selectivity,[57-59] palladium catalyzed transformations exhibit high Markovnikov selectivity and high yields,[60-62] but suffers from large palladium loading. In stark contrast, Ghosh and co-workers have reported the palladium-N-heterocyclic carbene complexes that catalyzes the anti-Markovnikov addition of secondary amines to activated olefins with good yields.[63] So far, a few example of PEPPSI complexes as catalyst in amination reactions have been reported.[64-66] However, palladium PEPPSI complexes have not yet been employed as catalyst in the hydroamination reactions. We have previously reported the synthesis of $PdCl_2(NHC)_2$ complexes and their catalytic activities in the intermolecular hydroamination reactions.[67,68] Herein we report the use of in situ prepared Pd-NHC and NHC-palladium(II)-PEPPSI complexes as effective catalysts for the anti-Markovnikov hydroamination of styrene with anilines.

RESULTS AND DISCUSSION

Synthesis of the benzimidazolium salts

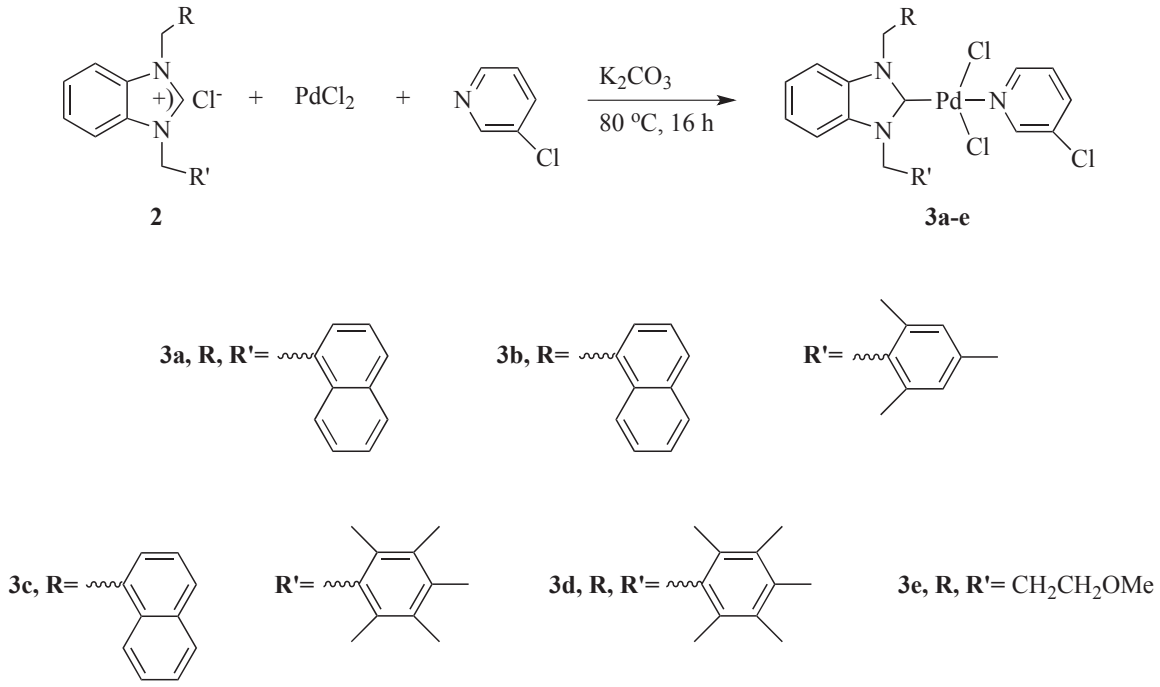
The azolium salts are mostly prepared by the stepwise *N*-alkylation of the parent azoles, which are low cost starting materials. In order to obtain 1,3-dialkylazolium salts by this procedure, firstly, N-H proton of azole removed with a base to obtain an azolate as a stronger nucleophile, subsequent nucleophilic substitution with alkyl halides furnishes the neutral 1-alkylazole, then the other nitrogen alkylated with the same or a different alkyl halides to give the desired 1,3-dialkylazolium salts. In this study,

1-(naphthalen-1-ylmethyl)benzimidazole was synthesized by the reaction of benzimidazole with 1-naphthylmethyl chloride in ethanol at reflux for 24 h in the presence of potassium hydroxide. Treatment of 1-(naphthalen-1-ylmethyl)benzimidazole with benzyl chloride, 4-methylbenzyl chloride, 2-methylbenzyl chloride, 2,4,6-trimethylbenzyl chloride, 2,3,4,5,6-pentamethylbenzyl chloride, 3,4,5-trimethoxybenzyl chloride in DMF at 50 °C for 18 h afforded the expected benzimidazolium salts **2a-f** (Scheme 1). After purification, unsymmetrical salts **2a-f** were obtained in good yields of 72-84%. The salts are soluble in the common polar solvents and are air- and moisture stable both in the solid state and in solution.



Scheme 1. Synthesis of benzimidazolium salts

PEPPSI complexes **3a-e** were prepared by the treatment of benzimidazolium salts with $PdCl_2$ in 3-chloropyridine at 80 °C in the presence of K_2CO_3 for 16 h in air via a one-pot process (Scheme 2).[16] All PEPPSI complexes were purified by passage through a short silica gel column using dichloromethane as eluent and subsequent crystallisation. These complexes were obtained in high yields and appeared to be stable both in solution and in solid states against air, light and moisture.

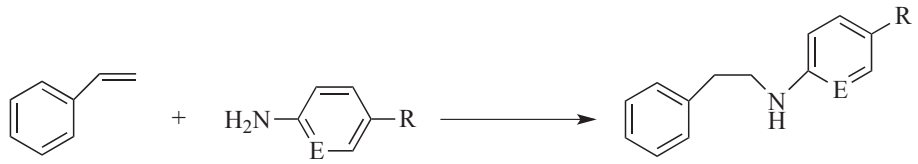


Scheme 2. NHC-$PdCl_2$-3-chloropyridine complexes

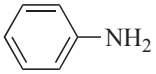
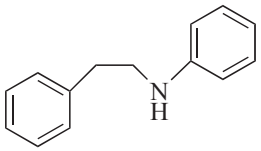
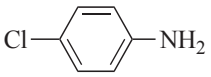
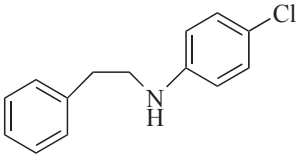
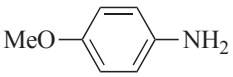
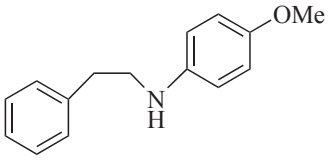
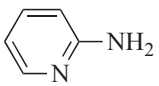
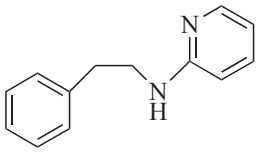
Catalytic studies

Using our previously reported reaction conditions, we examined the intermolecular hydroamination reactions between styrene and aromatic amines. In this study, potassium *tert*-butoxide (*t*-BuOK) and *N*-butylpyridinium hexafluorophosphate were selected as the base and ionic liquid. The catalytic reactions were carried out using 1 mol% of palladium complex ($Pd(OAc)_2$/**2a-f** or NHC-$PdCl_2$-3-chloropyridine complexes **3a-e**), 1.10 mmol *t*-BuOK, 1.10 mmol styrene and 1.00 mmol aniline in 1 mL *N*-butylpyridinium hexafluorophosphate at 160-190 °C for 1-2 h. In the absence of palladium(II) N-heterocyclic carbene complex, the reactions of styrene with aromatic amines resulted in very low yields. Under these reaction conditions, the palladium catalyzed hydroamination of styrene with various aromatic amines bearing electron-withdrawing or electron-donating groups at the *para* position to prepare diverse phenethylamines were examined. The hydroamination reactions of styrene with aromatic amines are fast and high-yielding reactions under these reaction conditions. All substrates gave complete anti-Markovnikov regioselectivity, and in all cases, only the anti-Markovnikov products were formed. The chemical characterizations of the products were made by NMR. The conversions were screened by GC analysis and results were summarized in Tables 1 and 2.

Table 1. Intermolecular hydroamination of styrene with anilines by $Pd(OAc)_2$/**2a-f**[a-d]



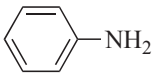
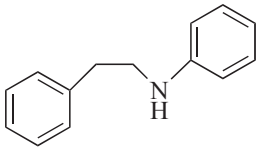
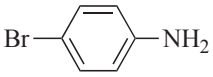
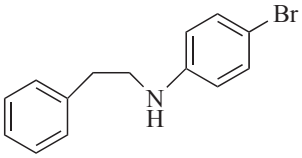
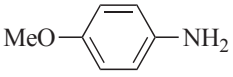
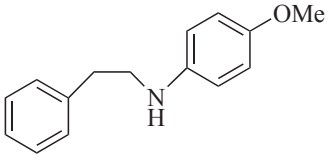
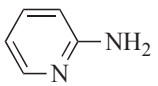
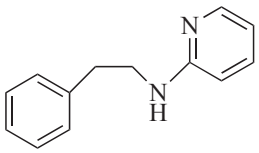
4 **5-8** **9-12**

Entry	$ArNH_2$	Salt	Product	Yield (%)
1	 **5**	**2a**	 **9**	94
2		**2b**		89
3		**2c**		92
4		**2d**		85
5		**2e**		90
6		**2f**		93
7	 **6**	**2a**	 **10**	97
8		**2b**		86
9		**2c**		93
10		**2d**		89
11		**2e**		87
12		**2f**		95
13	 **7**	**2a**	 **11**	81
14		**2b**		79
15		**2c**		83
16		**2d**		86
17		**2e**		82
18		**2f**		85
19	 **8**	**2a**	 **12**	90
20		**2b**		92
21		**2c**		90
22		**2d**		88
23		**2e**		94
24		**2f**		95
25	**5**	**none**	**9**	7[d]
26	**6**	**none**	**10**	5[d]
27	**7**	**none**	**11**	trace[d]
28	**8**	**none**	**12**	trace[d]

[a]Reaction conditions: $Pd(OAc)_2$/**2a-f** (0.01 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol), *t*-BuOK (1.10 mmol), *N*-butylpyridinium hexafluorophosphate (1 mL). [b]Yields were determined GC, dodecane was used as internal standard, products were characterized by NMR. [c]160 °C, 1 h. [d]No catalyst.

Initially, we examined the reactions of styrene with aniline, *p*-chloroaniline, 2-aminopyridine or *p*-methoxyaniline in the presence of $Pd(OAc)_2$/**2a-f** catalyst system, which proceeds with anti-Markovnikov addition. From reaction of styrene with aniline (**5**), only the anti-Markovnikov hydroamination product, *N*-(2-phenylethyl)aniline (**9**) were obtained selectively in high yields for all six $Pd(OAc)_2$/**2** catalyst systems (Table 1, entries 1-6). The best yield were achieved with catalyst $Pd(OAc)_2$/**2a**. No formation of Markovnikov product was detected. The reaction of styrene with *p*-chloroaniline (**6**) and 2-aminopyridine (**8**) provided the desired products with anti-Markovnikov selectivity in high yields in the presence of $Pd(OAc)_2$/**2a-f** catalyst system under the same reaction conditions (Table 1, entries 7-24), but the reaction with *p*-methoxyaniline (**7**) gave slightly lower yields of the desired product (**11**) when compared others.

Table 2. Intermolecular hydroamination of styrene with anilines by **3a-e**[a-f]

Entry	$ArNH_2$	Complex	Product	Yield (%)
1		**3a**		97
2		**3b**		96
3		**3c**		93
4	**5**	**3d**		92
5		**3e**	**9**	90
7		**3a**		87[d]
8		**3b**		94[d]
9		**3c**		97[d]
10	**6**	**3d**		80[d]
11		**3e**	**10**	82[d]
13		**3a**		79[e]
14		**3b**		85[e]
15		**3c**		81[e]
16	**7**	**3d**		87[e]
17		**3e**	**11**	83[e]
19		**3a**		82[f]
20		**3b**		89[f]
21		**3c**		87[f]
22	**8**	**3d**		91[f]
24		**3e**	**12**	88[f]

[a]Reaction conditions: **3a-e** (0.01 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol), *t*-BuOK (1.10 mmol), *N*-butylpyridinium hexafluorophosphate (1 mL). [b]Yields were determined GC, dodecane was used as internal standard, products were characterized by NMR. [c]160 °C, 1 h. [d]180 °C, 2 h. [e]190 °C, 2 h. [f]185 °C, 2 h.

Next, NHC-$PdCl_2$-3-chloropyridine complexes **3a-e** were also investigated for the intermolecular hydroamination of styrene with same amines under the similar reaction conditions. The aniline provide excellent yields of *N*-(2-phenylethyl)aniline for all five catalysts (Table 2, entries 1-6). The treatment of styrene with *p*-bromoaniline (**6**), *p*-methoxyaniline (**7**) and 2-aminopyridine (**8**) (Table 2, entries 1-15) gave corresponding secondary amines in high yields under these conditions. These results clearly show that the electron-withdrawing (4-chloro) and electron-donating substituent (4-methoxy) on aniline gave slightly lower yield when compared that of aniline. We observed that the *para*-chloro or methoxy substitution on the *N*-aryl fragment was decreased the activity for the intermolecular hydroamination of styrene is similar with trends documented by Zhou and Hartwig.[69] These results indicates that both $Pd(OAc)_2$/**2a-f** catalyst systems and NHC-$PdCl_2$-3-chloropyridine complexes **3a-e** are active species for the intermolecular hydroamination of styrene with aromatic amines, but as expected, in situ prepared palladium complexes led to significantly better results than the use of the preformed palladium complexes.

CONCLUSION

In summary, the benzimidazolium salts and NHC-$PdCl_2$-3-chloropyridine complexes were prepared. The catalytic activity of these compounds was investigated in the intermolecular hydroamination reaction of styrene with anilines in ionic liquid. Both in situ prepared Pd-NHC complexes and NHC-Pd-PEPPSI complexes catalyzed the hydroamination of styrene with aniline, *p*-chloroaniline, 2-aminopyridine and *p*-methoxyaniline with very high anti-Markovnikov selectivity. The hydroamination reactions proceeded in good to excellent yield with regioselectivity and in all cases, only the anti-Markovnikov addition products were obtained.

EXPERIMENTAL

All reactions for the preparation of the benzimidazolium salts and NHC-palladium(II)-PEPPSI complexes were carried out under air. All reagents were purchased from Sigma-Aldrich and used obtained. Benzimidazolium salts **2a-f** were used for the synthesis of silver complexes,[70] but their characterizations were not published. PEPPSI complexes **3a-e**[16] were synthesized according to published procedures. ^{1}H NMR and ^{13}C NMR were recorded 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, 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 by GC-FID on a Agilent 6890N gas chromatograph equipped 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 by LECO CHNS-932 elemental analyzer.

Synthesis of 1-(naphthalen-1-ylmethyl)benzimidazole 1

To a solution of benzimidazole (10.00 g, 84.74 mmol) in EtOH (60 mL), potassium hydroxide (4.80 g, 85.71 mmol) was added and stirred at room temperature for 1 h. After this time, 1-naphthylmethyl chloride (14.98 g, 84.80 mmol) was added slowly and the resulting mixture was refluxed for 6 h. After reaction completed, the reaction mixture was cooled to room temperature. The formed inorganic salt was filtered through filter paper and the solvent was removed under reduced pressure to give the product **1**. The crude product was purified by distillation, and product was obtained as a white solid. Yield: 19.78 g, 90%, mp 92-93 ºC.

Synthesis of benzimidazolium salts 2

To a solution of 1-(naphthalen-1-ylmethyl)benzimidazole (1.69 g, 6.55 mmol) in DMF (5 mL), alkyl chloride (6.55 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and heated at 50 ºC for 18 h. After reaction completed, the reaction mixture was cooled to room temperature. Et_2O (10 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et_2O and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O.

1-Benzyl-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2a

Yield: 2.40 g, 95%; mp 142-143 ºC, IR, υ: 1561 cm^{-1} (NCN). ^{1}H NMR (DMSO-d_6) δ: 5.82 (s, 2H, CH_2C$_6$H$_5$), 6.35 (s, 2H, CH_2C$_{10}$H$_7$), 7.36-8.19 (m, 16H, Ar-*H*), 10.20 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-d_6) δ: 48.8 (*C*H$_2$C$_6$H$_5$), 50.4 (*C*H$_2$C$_{10}$H$_7$), 114.6, 123.4, 126.1, 126.9, 127.3, 127.8, 128.1, 128.6, 128.9, 129.2, 129.4, 129.5, 130.1, 130.9, 131.5, 131.9, 133.9 and 134.6 (Ar-*C*), 143.4 (N*C*HN). Anal. Calcd for $C_{25}H_{21}N_2Cl$: C, 78.01; H, 5.50; N, 7.28. Found: C, 78.02; H, 5.51; N, 7.28.

1-(4-Methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2b

Yield: 1.55 g, 91%; mp 175-176 ºC, IR, υ: 1561 cm^{-1} (NCN). ^{1}H NMR (DMSO-d_6) δ: 2.28 (s, 3H, CH$_2$C$_6$H$_4$CH_3-4), 5.78 (s, 2H, CH_2C$_6$H$_4$CH$_3$-4), 6.35 (s, 2H, CH_2C$_{10}$H$_7$), 7.17-8.19 (m, 15H, Ar-*H*), 10.17 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-d_6) δ: 21.2 (CH$_2$C$_6$H$_4$*C*H$_3$-4), 48.7 (*C*H$_2$C$_6$H$_4$CH$_3$-4), 50.2 (*C*H$_2$C$_{10}$H$_7$), 114.6, 123.4, 126.1, 126.9, 127.3, 127.4, 127.6, 127.7, 128.7, 129.4, 129.6, 129.9, 130.1, 130.9, 131.4, 131.5, 131.9, 133.9 and 138.6 (Ar-*C*), 143.3 (N*C*HN). Anal. Calcd for $C_{26}H_{23}N_2Cl$: C, 78.28; H, 5.81; N, 7.02. Found: C, 78.27; H, 5.80; N, 7.02.

1-(2-Methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2c

Yield: 2.15 g, 84%; mp 120-121 °C, IR, υ: 1561 cm^{-1} (NCN). ^{1}H NMR (DMSO-*d*$_6$) δ: 2.33 (s, 3H, $CH_2C_6H_4CH_3$-2), 5.93 (s, 2H, $CH_2C_6H_4CH_3$-2), 6.42 (s, 2H, $CH_2C_{10}H_7$), 7.18-8.49 (m, 15H, Ar-*H*), 10.96 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-*d*$_6$) δ: 19.6 ($CH_2C_6H_4CH_3$-2), 49.9 ($CH_2C_6H_4CH_3$-2), 50.3 ($CH_2C_{10}H_7$), 113.8, 114.1, 122.6, 125.3, 126.6, 127.0, 127.1, 127.3, 127.4, 127.7 128.0, 128.2, 129.2, 129.3, 130.2, 130.5, 130.6, 131.3, 131.6, 131.7, 133.9 and 136.6 (Ar-*C*), 144.8 (N*C*HN). Anal. Calcd for $C_{26}H_{23}N_2Cl$: C, 78.28; H, 5.81; N, 7.02. Found: C, 78.29; H, 5.82; N, 7.03.

1-(2,4,6-Trimethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2d

Yield: 1.30 g, 88%; mp 205-206 °C, IR, υ: 1569 cm^{-1} (NCN). ^{1}H NMR (DMSO-*d*$_6$) δ: 2.21 and 2.22 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.88 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.35 (s, 2H, $CH_2C_{10}H_7$), 6.90 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.28-8.21 (m, 11H, Ar-*H*), 11.70 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-*d*$_6$) δ: 20.3 and 21.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 47.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 49.8 ($CH_2C_{10}H_7$), 113.7, 113.9, 122.6, 125.1, 125.2, 126.5, 126.9, 127.0, 127.1, 127.6, 128.1, 129.1, 130.1, 130.2, 130.6, 131.4, 131.7, 133.8, 137.9 and 139.6 (Ar-*C*), 144.4 (N*C*HN). Anal. Calcd for $C_{28}H_{27}N_2Cl$: C, 78.76; H, 6.37; N, 6.56. Found: C, 78.75; H, 6.37; N, 6.57.

1-(2,3,4,5,6-Pentamethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2e

Yield: 1.24 g, 78%; mp 165-166 °C, IR, υ: 1561 cm^{-1} (NCN). ^{1}H NMR (DMSO-*d*$_6$) δ: 2.18, 2.21 and 2.23 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 5.83 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 6.41 (s, 2H, $CH_2C_{10}H_7$), 7.28-8.14 (m, 11H, Ar-*H*), 10.93 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-*d*$_6$) δ: 16.9, 17.1 and 18.4 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 48.3 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 49.8 ($CH_2C_{10}H_7$), 113.6, 114.0, 122.6, 124.9, 125.2, 126.5, 126.9, 127.0, 127.5, 128.4, 129.1, 129.9, 130.6, 131.5, 131.9, 133.8, 133.7 and 137.3 (Ar-*C*), 143.8 (N*C*HN). Anal. Calcd for $C_{30}H_{31}N_2Cl$: C, 79.19; H, 6.87; N, 6.16. Found: C, 79.18; H, 6.87; N, 6.17.

1-(2,3,4-Trimethoxybenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride 2f

Yield: 1.72 g, 92%; mp 224-225 °C, IR, υ: 1592 cm^{-1} (NCN). ^{1}H NMR (DMSO-*d*$_6$) δ: 3.62 and 3.73 (s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.69 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.36 (s, 2H, $CH_2C_{10}H_7$), 6.96 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 7.52-8.23 (m, 11H, Ar-*H*), 11.29 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-*d*$_6$) δ: 56.5 and 60.4 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 48.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 50.6 ($CH_2C_{10}H_7$), 106.7, 114.6, 114.7, 123.6, 126.0, 126.9, 127.3, 127.6, 127.7, 129.4, 129.7, 129.8, 130.1, 130.9, 131.4, 131.9, 132.0, 133.9, 138.0, 143.3 (Ar-*C*), 153.4 (N*C*HN). Anal. Calcd for $C_{28}H_{27}N_2O_3Cl$: C, 70.80; H, 5.73; N, 5.90. Found: C, 70.81; H, 5.72; N, 5.90.

Synthesis of the NHC-$PdCl_2$-3-chloropyridine complexes 3

A mixture of benzimidazolium chloride (1.1 mmol), $PdCl_2$ (1.0 mmol) and K_2CO_3 (5 mmol) in 3-chloropyridine (4 mL) was heated with vigorous stirring at 80 ºC for 16 h. The 3-chloropyridine was removed in vacuo. CH_2Cl_2 (20 mL) was added to the reaction mixture. The obtained mixture was filtered into a silica gel columm and then the solvent was removed under reduced pressure. The product was recrystallized from CH_2Cl_2/Et_2O (1:2) at room temperature. The resulting bright yellow crystals was isolated by filtration and dried in vacuum.

General procedure for the hydroamination of styrene

The $Pd(OAc)_2$/**2** or NHC-$PdCl_2$-PEPPSI complexes **3** (1.0 mol%), *t*-BuOK (1.10 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol) and *N*-butylpyridinium hexafluorophosphate (1 mL) were added to a small Schlenk tube and the mixture was heated at 160-190 ºC for 1-2 h. At the end of reaction, the mixture was cooled to room temperature, and water (5 mL) was added. The mixture was extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4 and filtered through a short silica column. The filtrate was concentrated under reduced pressure, and purified by flash chromatography on silica gel (EtOAc/hexane; 1/5). The yields were calculated by GC analysis based on aromatic amines.

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REFERENCES

1. A. J. Arduengo III, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
2. D. Jansenn-Müller, C. Schlepphorst, and F. Glorius, *Chem. Soc. Rev*., 2017, **46**, 4845.
3. S. Diez-Gonzalez, N-Heterocyclic Carbenes, Royal Society of Chemistry, 2017.
4. M. N. Hopkinson, C. Richter, M. Schedler, and F. Glorius, *Nature*, 2014, **510**, 485.
5. L. Jafarpour and S. P. Nolan, *Adv. Organomet. Chem*., 2000, **46**, 181.
6. E. Peris and R. H. Crabtree, *Coord. Chem. Rev*., 2004, **248**, 2239.
7. P. De Frémont, N. Marion, and S. P. Nolan, *Coord. Chem. Rev*., 2009, **253**, 862.
8. W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl*., 1997, **36**, 2162.
9. L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, and V. César, *Chem. Rev*., 2011, **111**, 2705.
10. E. Levin, E. Ivry, C. E. Diesendruck, and N. G. Lemcoff, *Chem. Rev.*, 2015, **115**, 4607.
11. J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, and L. M. Alcazar-Roman, *J. Org.*

Chem., 1999, **64**, 5575.

12. A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, and S. P. Nolan, *J. Organomet. Chem.*, 2002, **653**, 69.
13. G. Occhipinti, H.-R. Bjørsvik, and V. R. Jensen, *J. Am. Chem. Soc*., 2006, **128**, 6952.
14. M. Yiğit, B. Yiğit, İ. Özdemir, E. Çetinkaya, and B. Çetinkaya, *Appl. Organometal. Chem.*, 2006, **20**, 322.
15. M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz, and M. Spiegler, *J. Organomet. Chem*., 1999, **572**, 239.
16. İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, and C. Bruneau, *Eur. J. Inorg. Chem*., 2010, 1798.
17. F. Li, J. J. Hu, L. L. Koh, and T. S. A. Hor, *Dalton Trans*., 2010, **39**, 5231.
18. F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, and T. Pape, *Organometallics*, 2005, **24**, 6458.
19. B. Yiğit, M. Yiğit, Z. Dağdeviren, and İ. Özdemir, *Transition Met. Chem*., 2016, **41**, 751.
20. E. Ö. Karaca, N. Gürbüz, İ. Özdemir, H. Doucet, O. Şahin, O. Büyükgüngör, and B. Çetinkaya, *Organometallics*, 2015, **34**, 2487.
21. C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, and M. G. Organ, *Chem. Eur. J*., 2006, **12**, 4743.
22. L. Benhamou, C. Besnard, and E. P. Kündig, *Organometallics*, 2014, **33**, 260.
23. J. Zhao, L. Yang, K. Ge, Q. Chen, Y. Zhuang, C. Cao, and Y. Shi, *Inorg. Chem. Commun*., 2012, **20**, 326.
24. M. G. Organ, G. A. Chass, D.-C. Fang, A. C. Hopkinson, and C. Valente, *Synthesis*, 2008, 2776.
25. L. Ray, M. M. Shaikh, and P. Ghosh, *Dalton Trans*., 2007, 4546.
26. A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, and S. P. Nolan, *Organometallics*, 2012, **31**, 6947.
27. M. Teci, E. Brenner, D. Matt, C. Gourlaouen, and L. Toupet, *Dalton Trans*., 2015, **44**, 9260.
28. S. Yaşar, Ç. Şahin, M. Arslan, and İ. Özdemir, *J. Organomet. Chem*., 2015, **776**, 107.
29. C. Valente, S. Çalimsiz, K. H. Hoi, D. Mallik, M. Sayah, and M. G. Organ, *Angew. Chem. Int. Ed*., 2012, **51**, 3314.
30. P. Nun, J. Martinez, and F. Lamaty, *Synlett*, 2009, 1761.
31. F. Martínez-Olid, R. Andrés, J. C. Flores, and P. Gómez-Sal, *Eur. J. Inorg. Chem*., 2015, 4076.
32. J. Huang, J.-T. Hong, and S. H. Hong, *Eur. J. Org. Chem*., 2012, 6630.
33. Y. Zhang, V. César, and G. Lavigne, *Eur. J. Org. Chem*., 2015, 2042.
34. F. Wang, L. Zhu, Y. Zhou, X. Bao, and H. F. Schaefer, III, *Chem. Eur. J*., 2015, **21**, 4153.

35. M. Beller, J. Seayad, A. Tillack, and H. Jiao, *Angew. Chem. Int. Ed*., 2004, **43**, 3368.
36. J. Hannedouche and E. Schulz, *Chem. Eur. J*., 2013, **19**, 4972.
37. J. C.-H. Yim and L. L. Schafer, *Eur. J. Org. Chem*., 2014, 6825.
38. L. Huang M. Arndt, K. Gooßen, H. Heydt, and L. J. Gooßen, *Chem. Rev*., 2015, **115**, 2596.
39. F. Hild and S. Dagorne, *Organometallics*, 2012, **31**, 1189.
40. D. Jaspers, R. Kubiak, and S. Doye, *Synlett*, 2010, 1268.
41. M. Khandelwal and R. J. Wehmschulte, *J. Organomet. Chem*., 2012, **696**, 4179.
42. J.-M. Huang, C.-M. Wong, F.-X. Xu, and T.-P. Loh, *Tetrahedron Lett*., 2007, **48**, 3375.
43. M. Arrowsmith, M. S. Hill, and G. Kociok-Köhn, *Organometallics*, 2009, **28**, 1730.
44. N. Romero, S.-C. Roşca, Y. Sarazin, J.-F. Carpentier, L. Vendier, S. Mallet-Ladeira, C. Dinoi, and M. Etienne, *Chem. Eur. J*., 2015, **21**, 4115.
45. S. Hong and T. J. Marks, *Acc. Chem. Re*s., 2004, **37**, 673.
46. S. Datta, M. T. Gamer, and P. W. Roesky, *Organometallics*, 2008, **27**, 1207.
47. X. Yu and T. J. Marks, *Organometallics*, 2007, **26**, 365.
48. A. Heutling, F. Pohlki, and S. Doye, *Chem. Eur. J*., 2004, **10**, 3059.
49. K. Born and S. Doye, *Eur. J. Org. Chem*., 2012, 764.
50. D. M. Lyubov, L. Luconi, A. Rossin, G. Tuci, A. V. Cherkasov, G. K. Fukin, G. Giambastiani, and A. A. Trifonov, *Chem. Eur. J*., 2014, **20**, 3487
51. F. Schroeter, S. Lerch, M. Kaliner, and T. Strassner, *Org. Lett*., 2018, **20**, 6215.
52. K. D. Hesp, *Angew. Chem. Int. Ed*., 2014, **53**, 2034.
53. S. D. Lee, J. C. Timmerman, and R. A. Widenhoefer, *Adv. Synth. Catal*., 2014, **356**, 3187.
54. S. R. Beeren, S. L. Dabb, and B. A. Messerle, *J. Organomet. Chem*., 2009, **694**, 309.
55. M. A. Chilleck, L. Hartenstein, T. Braun, P. W. Roesky, and B. Braun, *Chem. Eur. J*., 2015, **21**, 2594.
56. K. W. Bentley, *Nat. Prod. Rep*., 1999, **16**, 367.
57. A. Couce-Rios, A. Lledós, and G. Ujaque, *Chem. Eur. J*., 2016, **22**, 9311.
58. M. Utsunomiya, R. Kuwano, M. Kawatsura, and J. F. Hartwig, *J. Am. Chem. Soc*., 2003, **125**, 5608.
59. M. Utsunomiya and J. F. Hartwig, *J. Am. Chem. Soc*., 2004, **126**, 2702.
60. A. M. Johns, M. Utsunomiya, C. D. Incarvito, and J. F. Hartwig, *J. Am. Chem. Soc*., 2006, **128**, 1828.
61. M. Utsunomiya and J. F. Hartwig, *J. Am. Chem. Soc*., 2003, **125**, 14286.
62. M. Kawatsura and J. F. Hartwig, *J. Am. Chem. Soc*., 2000, **122**, 9546.
63. C. Dash, M. M. Shaikh, R. J. Butcher, and P. Ghosh, *Dalton Trans*., 2010, **39**, 2515.
64. D. Mendoza-Espinosa, R. González-Olvera, C. Osornio, G. E. Negrón-Silva, A. Álvarez-Hernández,

C. I. Bautista-Hernández, and O. R. Suárez-Castillo, *J. Organomet. Chem*., 2016, **803**, 142.

65. K. H. Hoi, S. Çalimsiz, R. D. J. Froese, A. C. Hopkinson, and M. G. Organ, *Chem. Eur. J*., 2011, **17**, 3086.
66. K. H. Hoi, J. A. Coggan, and M. G. Organ, *Chem. Eur. J*., 2013, **19**, 843.
67. B. Yiğit, M. Yiğit, Y. Gök, and Ö. Özeroğlu Çelikal, *Heterocycles*, 2016, **92**, 1994.
68. Y. Gök, B. Yiğit, Ö. Özeroğlu Çelikal, and M. Yiğit, *Transition Met. Chem*., 2018, **43**, 591.
69. J. S. Zhou and J. F. Hartwig, *J. Am. Chem. Soc*., 2008, **130**, 12220.
70. Y. Gök, S. Akkoç, Ö. Özeroğlu Çelikal, İ. Özdemir, and S. Günal, *Arab. J. Chem.*, 2015, DOI: 10.1016/j.arabjc.2015.04.019.