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INTERMOLECULAR HYDROAMINATION OF STYRENE CATALYZED BY PALLADIUM(II) N-HETEROCYCLIC CARBENE COMPLEXES IN IONIC LIQUID

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Abstract – $PdCl_2(NHC)_2$ complexes have been synthesized by the reaction of palladium acetate with a series of benzimidazolium and imidazolinium salts and characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectroscopy. These complexes were used as catalysts for the intermolecular hydroamination reactions between styrene with various anilines in ionic liquid at 160 ^oC and corresponding anti-Markovnikov products were obtained with a selectivity of 100% in good yields.

INTRODUCTION

N-Heterocyclic carbenes (NHC) have become one of the most useful and investigated classes of ligands since isolation of the first stable NHC species in 1991 by Arduengo.[1-4] N-Heterocyclic carbenes exhibit good σ-donor and weak π-acceptor properties, and they are very strong nucleophiles. Due to their strong σ-electron-donating properties, NHC ligands form stronger bonds with transition metals than classical ligands such as phosphines, thus giving more stable transition metal complexes that are generally resistant to decomposition[5-8] and can be used as catalysts of various transformations such as C-C and C-N arylation, olefin metathesis, hydrogenation, hydrosilylation and CO-ethylene co-polymerization reactions.[9-20] The transition-metal-catalyzed direct addition of the amines to alkenes and alkynes as known hydroamination represents a potentially expedient and atom-economical route to cyclic and acyclic amines, imines and enamines.[21-27] These compounds are used for the synthesis of pharmaceuticals, agrochemicals, and various bulk and fine chemicals.[28-32] Hydroamination reactions have been catalyzed by a variety of different

metal-based catalysts, including complexes of main group metals, lanthanides, early and late transition metals.[33-50] Metal complexes of N-heterocyclic carbenes have been reported as catalysts for the intermolecular and intramolecular hydroamination reactions.[51-56] Recently, the asymmetric hydroamination of alkenes in the presence of chiral complexes has been reported.[57-60] Numerous methods have developed for the hydroamination of alkenes catalyzed by late transition metals, most of them proceed with Markovnikov selectivity. In contrast, anti-Markovnikov selective methods are less prevalent and often require either a large excess of alkene, strong bases or precious transition metal catalysts. Although considerable progress has been made in intramolecular hydroamination reactions of activated alkenes, intermolecular hydroamination of nonactivated alkenes remains a challenge in this area.

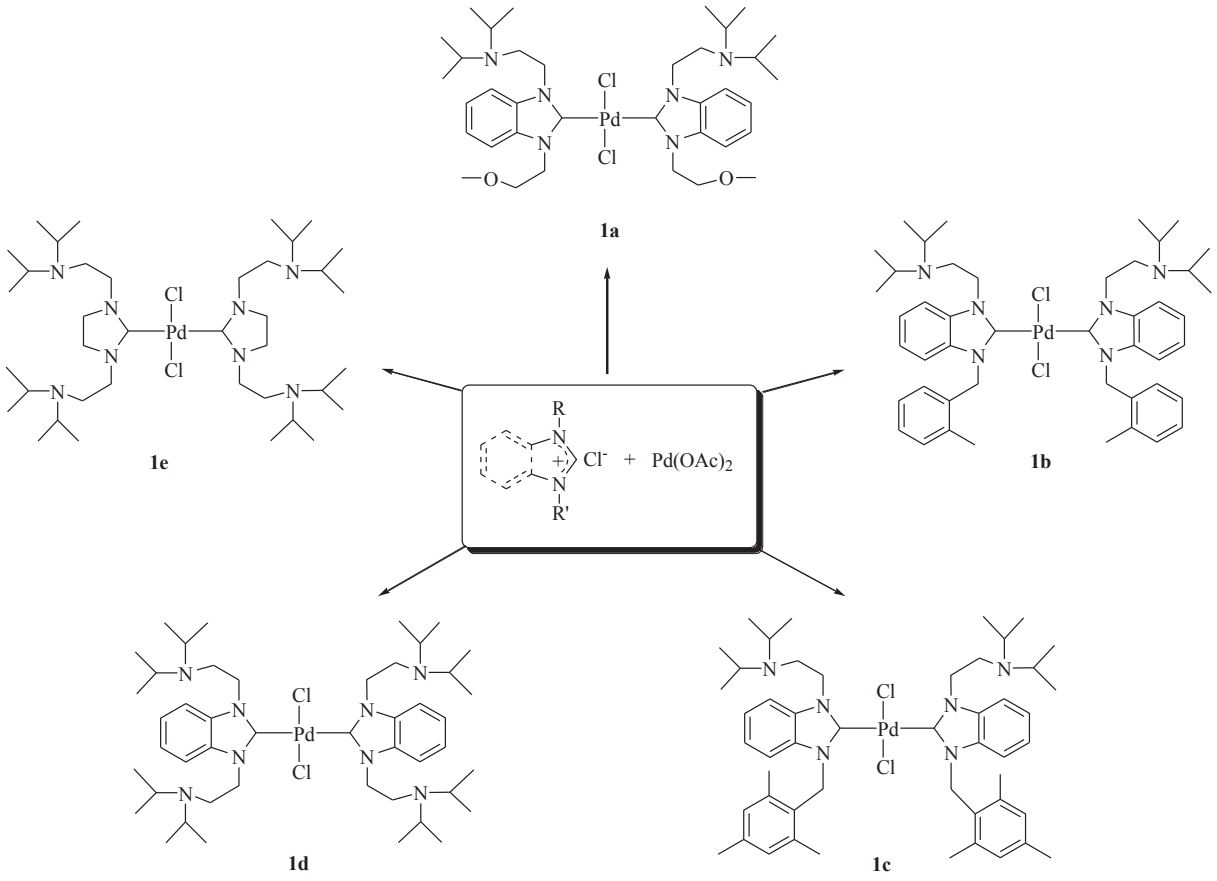
Ionic liquids (ILs) are a broad group of organic salts that are generally defined as salts with a melting point below 100 ^{o}C. They are usually composed of large organic cations and either smaller organic or inorganic anions. Recently, ionic liquids have atracted much attention in many different areas of chemistry due to their valuable properties such as chemical and thermal stability, structure and property tunabilities, negligible vapor pressure, non-flammability, good dissolving ability and recyclability. However, ionic liquids have been used as solvent or catalysts in different chemical reactions. Reactions performed in ionic liquids as solvent often show rate enhancement, selectivity and higher yields with respect to traditional solvents.[61-64]

In this paper, we report the synthesis and characterization of palladium(II) complexes with N-heterocyclic carbene ligand derived from benzimidazolium and imidazolinium salts, and their application as catalysts for the intermolecular hydroamination of styrene with anilines**.**

RESULTS AND DISCUSSION

Generally, palladium(II) carbene complexes can be easily prepared by the reaction of palladium(II) acetate with two molar equivalents of azolium salts[65] or transmetalation of the carbene from silver carbene complexes to a species such as [$PdCl_2$(MeCN)].[66-68] As shown in Scheme 1. the palladium complexes **1a-c** were synthesized by direct reaction of the 1,3-dialkylbenzimidazolium chlorides with palladium(II) acetate in DMSO, in moderate yields (50-70%). The crude products were recrystallized from dichloromethane : diethyl ether (1 : 2) at room temperature. Palladium carbene complexes (**1a-e**) were soluble in halogenated solvents and are air- and moisture stable both in the solid state and in solution. Compounds **1d** and **1e** have been previously reported,[69] however, for a comparison of catalytic activity of imidazolin-2-ylidene and benzimidazol-2-ylidene complexes, **1d** and **1e** were also used in this study. The new complexes were characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis techniques, which support the proposed structures. The formation of the Pd-NHC complexes was confirmed by the absence of the NCHN proton in ^{1}H NMR and NCHN carbon in ^{13}C NMR spectra. The ^{13}C NMR spectra

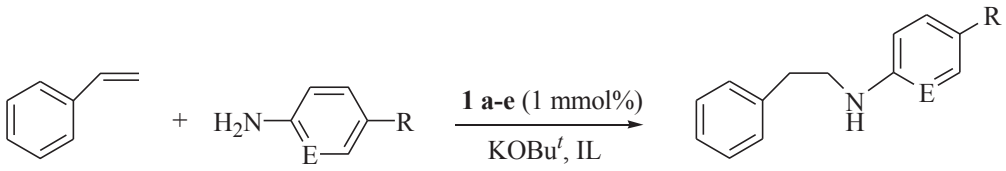
of the Pd-NHC complexes exhibit the NCN resonances between 181.7 and 182.6 ppm, which are consistent with reported values for $[PdCl_2(NHC)_2]$ complexes.



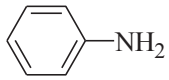
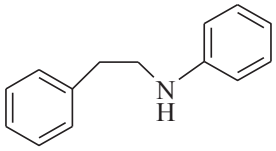
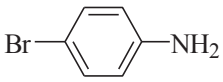
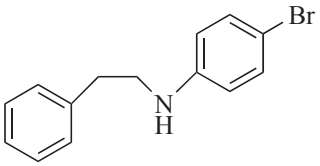
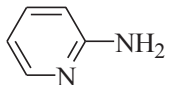
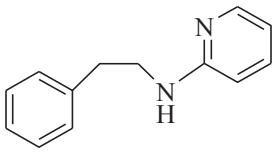
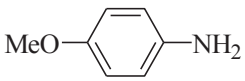
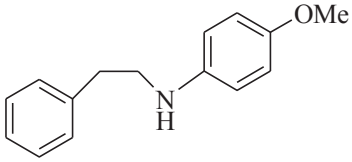
Scheme 1. The synthesis of palladium complexes

Catalytic intermolecular hydroaminations of sytrene with aniline derivatives were initially investigated using palladium(II) N-heterocyclic carbene complexes (**1a**, **1b**, **1c**) as catalyst in ionic liquid. Also included in this study were the previously reported complexes (**1d**, **1e**). The imidazolium based ionic liquids which contain acidic hydrogen are converted to N-heterocyclic carbenes by the strong bases. Therefore, the *N*-butylpyridinium hexafluorophosphate was used as ionic liquid. The catalytic reactions were carried out using 1 mol% of palladium complex, 1.10 mmol *t*-BuOK, 1.10 mmol styrene and 1.00 mmol aniline in 1 mL ionic liquid at 160 °C for 1 h. Under this reaction conditions, styrene was allowed to react with four aromatic amines (aniline, *p*-bromoaniline, 2-aminopyridine and *p*-methoxyaniline) to furnish the intermolecular hydroamination products in moderate to good yields (Table 1). In the absence of palladium(II) N-heterocyclic carbene complex, the reactions of styrene with aniline, *p*-bromoaniline, 2-aminopyridine or *p*-methoxyaniline resulted in very low yields under these reaction conditions. The conversions of the products were screened by GC analysis and results were summarized in Table 1.

Table1. Intermolecular hydroamination of styrene with anilines in ionic liquid



E : C or N

Entry	$ArNH_2$	Product	Catalyst	Yield[a-c] (%)
1			**1a**	74
2			**1b**	60
3			**1c**	82
4			**1d**	78
5			**1e**	60
6			**1a**	98
7			**1b**	93
8			**1c**	99
9			**1d**	90
10			**1e**	80
11			**1a**	79
12			**1b**	73
13			**1c**	87
14			**1d**	69
15			**1e**	65
16			**1a**	71
17			**1b**	56
18			**1c**	78
19			**1d**	74
20			**1e**	58

Reaction conditions: [a] Isolated yield (purity of yield checked by NMR and GC). [b] All reactions were monitored by TLC. [c] 160 °C, 1 h.

A variety anilines and 2-aminopyridine reacted efficiently with styrene affording the anti-Markovnikov products in moderate to good yields. The anti-Markovnikov product *N*-(2-phenylethyl)aniline was synthesized with a selectivity of 100% in 60-78% yields from styrene (entry 1-4) at 160 °C using all

catalysts. Müller et al. reported that the Markovnikov izomer *N*-(1-phenylethyl)aniline was formed exclusively at lower temperature from reacted styrene with aniline using immobilized palladium catalysts, whereas at higher temperatures the corresponding anti-Markovnikov izomer *N*-(2-phenylethyl)aniline was also formed.[70,71] The *p*-bromoaniline provide excellent yields of *N*-(2-phenylethyl)-*p*-bromoaniline by catalyzed complexes (**1a** and **1c**). The treatment of styrene with aniline, *p*-bromoaniline and 2-aminopyridine (Table 1, entries 1-15) gave corresponding secondary amines in high yields under these conditions. Use of aniline bearing electron-donating group such as OMe slightly decreased the yields under the same conditions (entries 16-20). Among the tested complexes, complex **1c** bearing NHC ligand with methyl substituents on phenyl group exhibited better catalytic activity than the others. When compared with the benzimidazol-2-ylidene liganded complexes with imidazolin-2-ylidene liganded complex, the benzimidazol-2-ylidene containing complexes (**1a-d**) in intermolecular hydroamination reactions were showed significantly better catalytic activity than the imidazolin-2-ylidene containing complex (**1e**). This catalytic intermolecular hydroamination provides the direct access to *N*-(2-phenylethyl)anilines from styrene and anilines as it is free of co-catalyst.

CONCLUSION

In summary, Pd-NHC complexes have been readily prepared from the reaction between palladium acetate and benzimidazolium or imidazolinium salts in DMSO and their catalytic activities in intermolecular hydroamination reactions were investigated. These complexes showed excellent activity and selectivity for *N*-(2-phenylethyl)anilines in the intermolecular hydroamination reaction of styrene with anilines in ionic liquid. Among them, complex **1c** is the most active complex. Further studies on the reacivity of benzimidazole derived rhodium complexes in intermolecular hydroamination reactions are in progress.

EXPERIMENTAL

The syntheses were carried out by using standart Schlenk techniques under an inert argon atmosphere with previously dried solvents. ^{1}H and ^{13}C NMR spectra were recorded by using a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. GC spectra were recorded on an Agilent 6890 N GC system 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 Inönü University research center.

Dichlorobis[1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]palladium(II)

(**1a)**

A mixture of 1-(2-diisopropylaminoethyl)-3-(2-methoxyethyl)benzimidazolium chloride (1 mmol) and $Pd(OAc)_2$ (0.5 mmol) in DMSO (5 mL) was stirred at 60 ºC for 3 h and then at 110 ºC for a further 2 h. The DMSO was removed in vacuo and the remaining solid was washed with Et_2O. The residue was crystallized from CH_2Cl_2-Et_2O. The crystals were washed with Et_2O (3 x 15 mL) and dried under vacuum. Yield: 0.11 g, 65%, mp 188-190 ºC. ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 4H, C_6H_4), 7.47 (m, 4H, C_6H_4), 4.84 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.26 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.11 (sep, J = 6.4 Hz, 4H, $NCH(CH_3)_2$), 1.02 (d, J = 2.4 Hz, 12H, $NCH(CH_3)_2$), 1.04 (d, J = 2.4 Hz, 12H, $NCH(CH_3)_2$), 4.19 (m, 4H, $CH_2CH_2OCH_3$), 5.08 (t, J = 6.4 Hz, 4H, $CH_2CH_2OCH_3$), 3.35 (s, 3H, $CH_2CH_2OCH_3$), 3.37 (s, 3H, $CH_2CH_2OCH_3$). ^{13}C NMR ($CDCl_3$): δ 111.3; 111.4; 111.5; 122.7; 122.8; 135.0; 135.1; 135.2 and 135.3 (Ar-*C*), 49.9 ($CH_2CH_2N(Pr^i)_2$), 45.6 ($CH_2CH_2N(Pr^i)_2$), 48.2 ($NCH(CH_3)_2$), 21.2 ($NCH(CH_3)_2$), 49.0 ($CH_2CH_2OCH_3$), 72.2 ($CH_2CH_2OCH_3$), 59.4 ($CH_2CH_2OCH_3$), 181.7 (*C*-Pd). Anal. Calcd for $C_{36}H_{62}N_6O_2PdCl_2$: C, 55.21; H, 7.42; N, 10.58. Found: C, 55.14; H, 7.47; N, 10.54.

Dichlorobis[1-(2-diisopropylaminoethyl)-3-(2-methylbenzyl)benzimidazol-2-ylidene]palladium(II) (1b)

The complex was prepared as described for **1a** by using 1-(2-diisopropylaminoethyl)-3-(2-methylbenzyl)benzimidazolium chloride. Yield: 0.28 g, 50%, mp 175-176 ºC. ^{1}H NMR ($CDCl_3$): δ 4.72 (t, J = 6.4 Hz, 4H, $CH_2CH_2N(Pr^i)_2$), 3.35 (t, J = 6.8 Hz, 4H, $CH_2CH_2N(Pr^i)_2$), 3.13 (m, 4H, $NCH(CH_3)_2$), 1.04 (d, J = 6.4 Hz, 24H, $NCH(CH_3)_2$), 2.17 (s, 6H, $CH_2C_6H_4CH_3$-2), 5.83 (s, 4H, $CH_2C_6H_4CH_3$-2), 6.8-7.4 (m, 16H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 110.9; 111.7; 122.9; 126.5; 127.4; 127.8; 128.1; 130.0; 133.8; 134.1; 135.0 and 135.1 (Ar-*C*), 49.13 ($CH_2CH_2N(Pr^i)_2$), 45.9 ($CH_2CH_2N(Pr^i)_2$), 49.9 ($NCH(CH_3)_2$), 19.9 ($NCH(CH_3)_2$), 21.3 ($CH_2C_6H_4CH_3$-2), 50.2 ($CH_2C_6H_4CH_3$-2), 182.6 (*C*-Pd). Anal. Calcd for $C_{46}H_{62}N_6PdCl_2$: C, 63.76; H, 7.17; N, 9.23. Found: C, 63.73; H, 7.12; N, 9.28.

Dichlorobis[1-(2-diisopropylaminoethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]-palladium(II) (1c)

The complex was prepared as described for **1a** by using 1-(2-diisopropylaminoethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride. Yield: 0.31 g, 70%, mp 226-227 ºC. ^{1}H NMR ($CDCl_3$): δ 3.57 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.08 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.30 (m, 4H, $NCH(CH_3)_2$), 0.96 (d, J = 6.6 Hz, 24H, $NCH(CH_3)_2$), 2.28; 2.37 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.97 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.21 (s, 2H); 6.37 (s, 2H); 6.89-7.41 (m, 8H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 110.7; 122.6; 128.0; 129.5; 134.2; 134.3; 135.2; 135.4; 138.1; 138.2; 138.6 and 138.7 (Ar-*C*), 48.8

($CH_2CH_2N(Pr^i)_2$), 45.3 ($CH_2CH_2N(Pr^i)_2$), 59.1 ($NCH(CH_3)_2$), 20.9 ($NCH(CH_3)_2$), 20.8; 21.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 65.8 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 181.9 (*C*-Pd). Anal. Calcd for $C_{50}H_{70}N_6PdCl_2$: C, 64.42; H, 7.52; N, 9.02. Found: C, 64.48; H, 7.48; N, 9.08.

Dichlorobis[1,3-bis(2-diisopropylaminoethyl)benzimidazol-2-ylidene]palladium(ll) (1d)

This compound was prepared as described for **1a** by using 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]benzimidazolium chloride.[69]

Dichlorobis[1,3-bis(2-diisopropylaminoethyl)imidazolin-2-ylidene]palladium(ll) (1e)

This compound was prepared as described for **1a** by using 1,3-bis[2-(*N,N'*-diisopropylamino)ethyl]imidazolinium chloride.[69]

General Procedure for Catalytic Hydroamination

The NHC-Pd(II) catalyst **1** (1.0 mol%), *t*-BuOK (1.10 mmol), styrene (1.10 mmol), aniline (1.00 mmol) and *N*-butylpyridinium hexafluorophosphate (1 mL) were added to a small Schlenk tube and the mixture was heated at 160 ºC for 1 h. The reaction mixture was allowed to cool 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 anilines.

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