Novel Ag(I), Pd(II), Ni(II) complexes of N,N'-bis-(2,2-diethoxyethyl)imidazole-2-ylidene: Synthesis, structures, and their catalytic activity towards Heck reaction

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ARTICLE INFO

ABSTRACT

Tetra-ether substituted imidazolium salts, LHX (where LH = N,N'-bis(2,2-diethoxyethyl)imidazolium cation and X = Br, BF_4, PF_6, BPh_4, NO_3 and NTf_2 anions) were derived from imidazole. Attempts to produce aldehyde functionalized imidazolium salt through acid hydrolysis of LHBr resulted an unexpected tetra-hydroxy compound L_AHBr and the dialdehyde compound L_BHBr. Reaction of LHBr with Ag_2O afforded $[L_2Ag][AgBr_2]$ (**1**). Mononuclear Pd-complex trans-$[L_2PdCl_2]$ (**2**) and dinuclear Pd-complex $[(LPdCl_2)_2]$ (**3**) were obtained by 1:1 and 1:2 reaction of in situ generated Ag-carbene with $Pd(CH_3CN)_2Cl_2$. cis-$[LPdPPh_3Cl_2]$ (**4**) was synthesized from reaction of PPh_3 with dinuclear complex **3**. Hydrolysis of **3** under acidic conditions also generates a hydroxy derivative **3A** and the aldehyde derivative **3B**. Direct heating of LHBr with $Ni(OAc)_2 \cdot 4H_2O$ at 120 °C under vacuum generated trans-$[L_2NiBr_2]$ (**5**). These complexes were characterized by NMR, mass, elemental analysis, and X-ray single crystal diffraction analysis. Pd–Pd interaction was observed in **3**. All the Pd complexes exhibited excellent catalytic activity in Heck reaction.

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1. Introduction

Ancillary ligands coordinated to the transition metal center influence the performance of homogenous catalysts [1]. Recently, N-heterocyclic carbenes (NHCs) have been employed as alternative or better ancillary ligands than phosphine. NHCs are stronger σ-donor ligands than widely used phosphines and are easy to be derivatized; therefore, stable NHC complexes [2] with various properties can be synthesized. Notably, metal–NHC complexes show better catalytic activity in various chemical transformations such as C–C bond formations [3,4], olefin metathesis [5], hydrosilylation [6], CO–ethylene co-polymerization [7], and hydrogenation [8] reactions. Pd–NHC complexes are the choice to be regarded as versatile and robust catalysts for C–C bond formation reactions; reactions could be conducted under mild conditions and with low catalyst loading [9].

Imidazole, benzimidazole, imidazoline derived NHC's [4b,4i,4j, 5i,7,10] with functional groups such as alkyl, aryl, pyridyl, amide, carboxylate, nitrile have been incorporated to N-side arms of NHCs for specific requirements. We became interested in ether substituted imidazolium salts and their metal complexes. While been less studied, ether substituted imidazolium salts may extend the availability of functionalized ionic liquids (ILs), and have the potential to be used as Task Specific IL [11]. The tetra ether groups presented in NHC may stabilize the Pd(0) formed during the C–C coupling reactions and may expect to facilitate the reactions. We have also targeted to synthesize the aldehyde functionalized NHC via acid hydrolysis of the acetal protected aldehyde containing LHBr ligand. The synthesis of a Ni(II)–NHC [12] was also attempted to explore the validity of the synthetic method.

Herein, we report the preparation of a series of new tetra-ether substituted ionic liquids (ILs) of imidazolium salts, N,N'-bis-(2,2-diethoxyethyl)imidazolium salts with different anions (Scheme 1). Among them, LHBr was used to prepare Ag(I) and Pd(II), Ni(II) complexes and to study the reaction hydrolysis. We also report the use of Pd(II)–NHC complexes as catalyst in Heck coupling reaction of aryl halides with styrene.

2. Results and discussion

2.1. Synthesis and characterization of the tetra-ether substituted imidazolium salts

Symmetrical 1,3-disubstituted imidazolium salts were usually prepared in two steps; mono substituted imidazole was first synthesized, further alkylation was then followed [3i]. Recently, one step synthesis of symmetrical 1,3-disubstituted benzimidazolium salts have also been reported [13]. In this work, N,N'-bis-(2,2-diethoxyethyl)imidazolium bromide (LHBr) was synthesized as

X = Br, BF$_4$, PF$_6$, NO$_3$, NTf$_2$, BPh$_4$
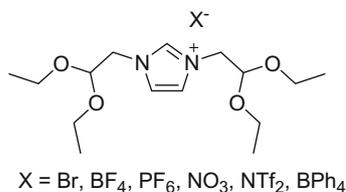
Scheme 1. Tetraether substituted imidazolium salts.

viscous liquid in 80% yield by reaction of imidazole with excess 2,2-diethoxyethylbromide in the presence of Na$_2$CO$_3$ in dimethyl-formamide (DMF) for 3 days at 120 °C. This salt is soluble in most of the common organic solvents and water but not in ether and hexane.

The mass spectrum of this salt is in agreement with its formulation; a peak corresponding to m/z 301 [M$^+$] is observed. ^{1}H NMR spectrum of LHBr shows characteristic downfield-shift at 10.28 ppm for the NCHN proton, indicating the formation of an imidazolium salt. A triplet of CH(OO) proton at 4.82 ppm and a doublet of NCH_2 protons at 4.44 ppm indicate the presence of ether substituents. In addition, elemental analysis and ^{13}C NMR for NCN carbon at 138.5 ppm also indicate the formation of imidazolium salt. The exchange of anion of LHBr was done by using different ammonium, sodium or lithium salts in acetone or water.

The thermal stability of the salts was examined by thermal gravimetric analyzer. The thermal stability of the imidazolium salts containing various anions is almost equal except LHBF$_4$. The lower thermal stability for the LHBF$_4$ salt is probably due to the thermal lability of the anion [14]. The low temperature physical behaviors of these ether substituted imidazolium salts were also examined in DSC in the temperature range −100 °C to 100 °C. On heating, the compounds showed a glass-transition (T_g), which is the midpoint of a small heat capacity change on heating from the amorphous glass state to a liquid state, in the range −72 °C to −49 °C.

2.2. Synthesis and characterization of complexes

The Ag–NHC complex bis(N,N′-bis-(2,2-diethoxyethyl)imidazo-lin-2-ylidene)silver(I) dibromoargentate(I), [L$_2$Ag][AgBr$_2$] (**1**), was prepared as a white solid by the treatment of LHBr with Ag$_2$O in dichloromethane at room temperature in 85% yield. This silver complex is soluble in common organic solvents and insoluble in water. The formation of Ag-carbene was preliminarily confirmed by the absence of C^2 proton in ^{1}H NMR spectrum. All the resonance signals in ^{1}H NMR and ^{13}C NMR spectra were upfield-shifted upon coordination to Ag metal as compared to those corresponding signals in imidazolium salt. For example, the resonance observed at 4.82 ppm and 4.44 ppm for CH(OO) and NCH_2 protons in LHBr were upfield-shifted [15] to 4.65 ppm and 4.17 ppm, respectively, in **1**. Elemental analysis data suggested the stoichiometry and formula as [L$_2$Ag][AgBr$_2$] (**1**). Whereas, single crystals grown by the slow evaporation of dichloromethane solution produced [L$_2$Ag]Br (**1A**), which were confirmed by X-ray diffraction analysis. We have observed the formation of AgBr at the bottom of the crystal tube. Probably during crystallization, the [AgBr$_2$]$^-$ anion disintegrates to AgBr and Br$^-$.

Various synthetic procedures have been described in the literature for the preparation of Pd(II) and Ni(II) complexes of NHC ligands [1c,4k,4r,4x,16]. We employed the silver carbene transferring technique [17] to prepare the Pd(II) complexes (**2**, **3**) whereas direct heating of basic Ni(II) acetate with LHBr was employed to synthesize Ni(II)-NHC complex (**5**). The synthetic reaction procedures, reagents and abbreviation of the complexes are presented in Scheme 2.

The mononuclear and dinuclear palladium complexes trans-bis-(N,N′-di(2,2-diethoxyethyl)imidazolin-2-ylidene)dichloropalla-dium(II), trans-[L$_2$PdCl$_2$] (**2**), and di-μ-dichlorobis-(N,N′-bis-(2,2-diethoxyethyl)imidazolin-2-ylidene)dichlorodipalladium(II), [(LPdCl$_2$)$_2$] (**3**), were obtained by the reaction of LHBr with Ag$_2$O, followed by the addition of Pd(CH$_3$CN)$_2$Cl$_2$ in 1:1 and 1:2 mole ratio in CH$_2$Cl$_2$ at room temperature, respectively. The pale yellow mononuclear complex **2** and orange yellow dinuclear complex **3** were obtained as air stable solid in 65% and 91% yield, respectively. Both complexes are soluble in common organic solvents. Similar type of dimeric Pd-NHC complexes derived from imidazole and benzimidazole precursors have been reported [4k,4r,4x,13,16,18].

Complexes **2** and **3** were characterized spectrally. The ^{1}H NMR spectra show an upfield-shift of the NHC C^4 and C^5 proton resonances with respect to the imidazolium salt whereas NCH_2 and CH(OO) proton resonances show downfield-shift [2b,19]. In the ^{13}C NMR spectra the coordinated carbene resonance was downfield-shifted to 170.3 ppm for mononuclear and 141.3 ppm for dinuclear as expected, an indication of lower electron density on the carbene carbon atom in mononuclear complex than that in the dinuclear one. All other peaks are also slightly downfield shifted or almost no change. Both complexes were characterized structurally by single crystal X-ray diffraction.

The mixed NHC/phosphine ligand complex cis-N,N′-bis-(2,2-diethoxyethyl) imidazolin-2-ylidene)dichlorotriphenylphosphine-palladium(II), cis-[LPdPPh$_3$Cl$_2$] (**4**), was prepared by stirring 1 equiv. of **3** in dichloromethane with 2 equiv. of PPh$_3$ at room temperature; the color change from orange yellow to pale yellow. Removal of solvent after 1 h afforded 90% yield. cis and trans NHC/phosphine isomers have been reported by Herrmann et al. [1c,3i]. The authors have crystallized cis-isomer from dichloromethane, whereas trans-isomer from coordinating solvent acetonitrile. Margado et al. also reported cis-isomer from benzene [20]. The coordinated carbene carbon (NCN) resonance of **4** was downfield shifted as compared to that of mother complex **3**, as has been noted [1c].

Initial attempts to prepare Ni(II)–carbene complex via silver carbene transfer to NiCl$_2$ in dichloromethane at various temperatures were unsuccessful. Surprisingly, the general method for the synthesis of Ni(II) complex involving the reaction of Ni(OAc)$_2$ with imidazolium salt in MeOH also failed. Direct heating [21] of imidazolium salt (LHBr) with Ni(OAc)$_2$ · 4H$_2$O at 120 °C with stirring under vacuum gave satisfactory result. After purification by column chromatography, red color trans-bis-(N,N′-bis-(2,2-diethoxy-ethyl) imidazolin-2-ylidene)dibromonickel(II), trans-[L$_2$NiBr$_2$] (**5**), was obtained in 50% yield. The complex is insoluble in water but soluble in other common organic solvents. The absence of NCHN proton resonance at 10.28 ppm in the imidazolium salt and the downfield-shift of ^{13}C NMR resonance of carbene carbon confirmed the formation of Ni complex. Furthermore, a significant downfield-shift of the NCH_2 and CH(OO) proton resonances was observed upon coordination: from 4.82 ppm to 5.37 ppm and from 4.44 ppm to 5.03 ppm for the two, respectively. Single crystals of Ni complex for X-ray diffraction were grown by the diffusion of ether into a saturated dichloromethane solution of the complex.

2.3. Hydrolysis of LHBr and 3

Hydrolysis of acetal is a common practice to produce aldehyde. To have aldehyde functional groups in the ligand side arms from the acetal protected aldehyde and to extend our work to more hydrophilic imine derivative, we investigated the acid hydrolysis of LHBr with dil. HCl. A brown hygroscopic amorphous solid which contains two species, L$_A$HBr (N,N′-bis-(2,2-dihydroxyethyl)imi-dazolium bromide) and L$_B$HBr (N,N′-di-(ethanaldehyde)imidazoli-um bromide), was obtained from LHBr after drying under vacuum at room temperature for 24 h. The formation of only one
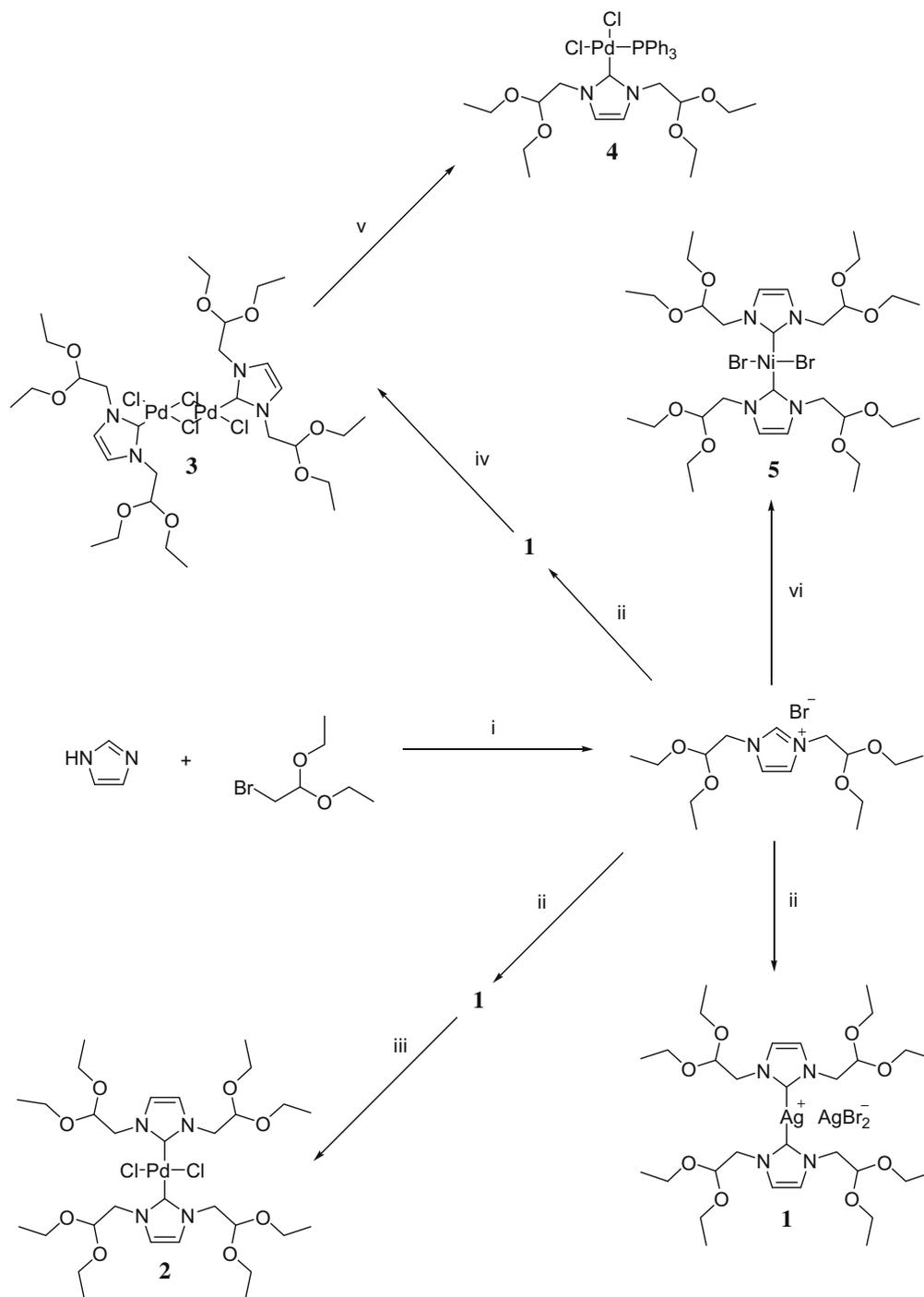
Reagents and Conditions : (i) Na$_2$CO$_3$, DMF, 120°C, 3d (ii) Ag$_2$O, CH$_2$Cl$_2$, RT, 1h, Dark
(iii) PdCl$_2$(CH$_3$CN)$_2$, RT, 1h, Dark (iv) PdCl$_2$(CH$_3$CN)$_2$, RT, 1h, Dark (v) PPh$_3$, CH$_2$Cl$_2$, RT, 1h
(vi) Ni(OAc)$_2$ 4H$_2$O, in vacuum, 120°C, 4h.

Scheme 2. Synthesis of complexes **1–5**.

species, L$_A$HBr in presence of water was evidenced by NMR and Mass spectra. The ^{1}H NMR spectrum in D$_2$O shows the absence of all the protons signals of CH(OCH_2CH_3)$_2$. Instead a new signal at δ 5.30 ppm was appeared corresponding to CH(OH)$_2$. However, the aldehyde proton signal and carbonyl carbon resonance expected for an aldehyde were also absent in NMR (D$_2$O). The mass spectrum of the compound in H$_2$O matrix shows a peak at m/z

189 corresponding to [L$_A$+1]$^+$, which suggests the formation of tetra-hydroxy species, L$_A$HBr. The ^{1}H NMR spectrum of the same product in DMSO-d^6, on the other hand, shows two sets of proton signals corresponding to the hydroxy species, L$_A$HBr and aldehyde species, L$_B$HBr. The peak ratio indicates the presence of hydroxy species with small amount of aldehyde species. The Mass spectrum in DMSO matrix also indicates two molecular ion peaks at m/z 189

and 153 corresponding to $[L_A+1]^+$ and $[L_B+1]^+$, respectively. Infrared spectroscopy performed on the solid also shows absorption peak at 1733 cm^{-1}, which disappears in methanol solution, indicating the presence of a mixture of L$_A$HBr and L$_B$HBr in the solid state. Heating the compound at 100 °C under vacuum produced an insoluble material in all common solvents including DMF and DMSO. So we treated the compound at 80 °C for 24 h under vacuum and prepared the sample in glove box. The ^{1}H NMR (DMSO-d^6) spectrum shows the characteristic aldehyde resonance in the speculated region and the peak ratio indicates the presence of aldehyde species, L$_B$HBr with small amount of tetrahydroxy species, L$_A$HBr. This observation is opposite to that observed for the sample dried at room temperature condition. We believe that the acid hydrolysis of LHBr produced aldehyde groups. However, the electron withdrawing and extreme hygroscopic nature of the imidazolium salt activates carbonyl carbon and facilitates the formation of tetrahydroxy derivative L$_A$HBr (Scheme 3).

Next hydrolysis of the complex **3** was examined. The hydrolysis of dinuclear complex **3** with dil. HCl produced a hygroscopic orange solid which also contains two species (L$_A$PdCl$_2$)$_2$, **3A** and (L$_B$PdCl$_2$)$_2$, **3B**. The NMR spectra of the solid in D$_2$O and in DMSO-d^6 as well as the Mass and IR spectra showed the similar observation like hydrolyzed imidazolium salt LHBr. Upon treatment of the orange solid at 80 °C for 24 h under vacuum, the ^{1}H NMR spectrum (DMSO-d^6) also exhibits more conversion towards aldehyde substituted complex **3B** which indicates the existence of equilibrium between aldehyde and hydroxyl species. The ratio of **3A** and **3B** depends on the temperature and vacuum applied. Although complexes **2** and **3** are insoluble in water, the sister complexes **3A** and **3B** are quite soluble in water. In recent years, the water soluble organometallic compounds have received particular attention in catalysis for environmental reason [22].

2.4. Structural description

The molecular structure of the crystallized Ag-carbene complex **1A,** as determined by means of single-crystal X-ray diffraction analysis, is shown in Fig. 1. The crystal parameters are tabulated in Table 1. Structural diversity of Ag(I)–NHC complexes [23] has been realized; five forms of halide bonding motifs were identified in the solid state: coordinating, bridging, staircase, halogens counter ion and Ag–NHC with Ag–Ag interaction. Complex **1A** provides an alternative bonding mode. The Ag atom was coordinated by two carbene moieties and partially coordinated by a bromide ion. The Ag–Br distance of 2.906 Å is longer than the Ag–Br covalent radii
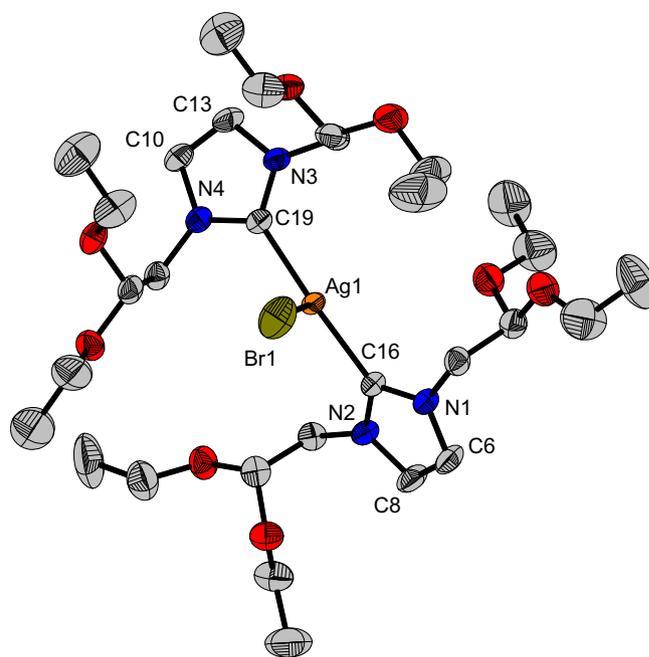
Fig. 1. ORTEP view of complex **1A** showing 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Ag1–C16, 2.108(6); Ag1–C19, 2.110(6); Ag1–Br1, 2.906(14), C16–Ag1–C19, 159.03(2).

(2.80 Å) and much shorter than the van der Waals radii (3.57 Å). This weak interaction has changed the geometrical parameters of the metal center as revealed by the bent C–Ag–C angle (159.03(2) Å). The dihedral angle between the two planes, defined by the imidazole rings, is 36.35°. The complex shows no evidence of Ag–Ag interaction. The average Ag–C$_{carb}$ bond distance 2.109 Å, is comparable to those observed in literature [23].

Two protons of the imidazole ring involve in weak hydrogen–hydrogen interactions with other imidazole protons of adjacent complex molecule and other two protons of another imidazole ring involve in hydrogen bonding interactions with ether oxygen atoms of other two different complex molecule. NCH$_2$ protons and ether oxygen atoms also suffer hydrogen bonding interactions in different ways in crystal lattice. Thus in the crystal lattice, the molecules are interconnected to give a network through moderate hydrogen bonding interactions (for packing, interaction and distance see Supplementary material file S-1a, S-1b, S-1c and Table a).
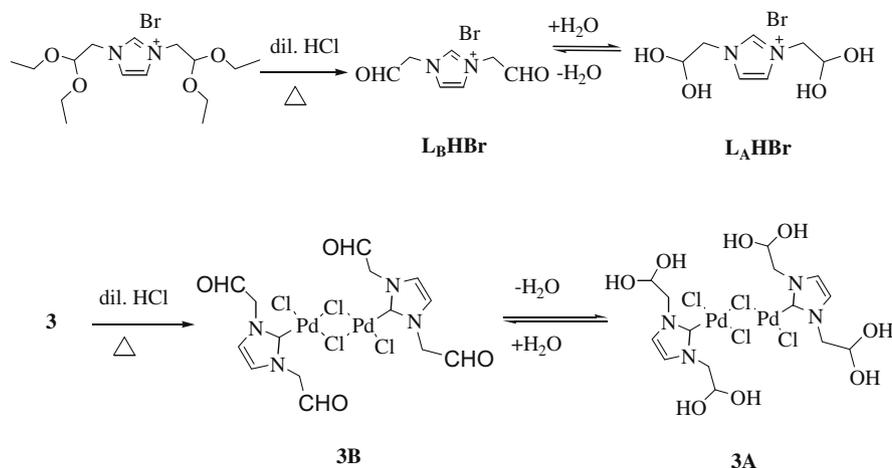
Scheme 3. Hydrolysis of LHBr and complex **3.**

Table 1
Selected X-ray crystallographic data for complexes **1A**, **2–5**

	1A	**2**	**3**	**4**	**5**
Formula	$C_{30}H_{56}AgBrN_4O_8$	$C_{30}H_{56}Cl_2N_4O_8Pd$	$C_{30}H_{56}N_4Cl_4O_8Pd_2$	$C_{34}H_{45}N_2PCl_4O_4Pd$	$C_{30}H_{28}Br_2N_4O_8Ni$
Formula weight	788.57	778.09	955.39	824.89	819.65
Crystal size (mm)	$0.1 \times 0.1 \times 0.09$	$0.51 \times 0.20 \times 0.16$	$0.1 \times 0.1 \times 0.09$	$0.5 \times 0.5 \times 0.4$	$0.1 \times 0.1 \times 0.09$
T (K)	273(2)	273(2)	273(2)	273(2)	273(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/m$	$P\bar{1}$	$P2(1)/n$	$C2/m$
a (Å)	9.2307(10)	15.4212(9)	10.8615(6)	14.1394(5)	15.4395(18)
b (Å)	13.8839(15)	15.9352(9)	14.3307(9)	14.0754(5)	15.8881(19)
c (Å)	16.4360(18)	8.8322(6)	14.5826(9)	19.4267(7)	8.9224(14)
α (°)	99.015(2)	90	87.5770(10)	90	90
β (°)	103.143(2)	115.2660(10)	78.4230(10)	99.4020(10)	115.2920(10)
γ (°)	103.558(2)	90	89.0150(10)	90	90
V (Å³)	1944.4(4)	1962.8(2)	2221.6(2)	3814.3(2)	1978.9(5)
Z	2	2	2	4	2
D_{calc} (g cm⁻³)	1.347	1.317	1.428	1.436	0.737
μ (mm⁻¹)	1.592	0.656	1.094	0.846	1.509
θ Range/°	1.30–25.03	1.94–25.04	1.42–25.03	1.66–28.72	1.94–25.10
Number of reflections unique/collected	6845/16880	1736/10503	7529/11849	9850/33971	1836/6505
R_1/wR_2 ($I > 2\sigma(I)$)	0.0807/0.2637	0.0523/0.1201	0.0412/0.1190	0.0386/0.11290	0.0435/0.1027
Goodness-of-fit	1.031	1.032	1.031	1.035	1.793

Molecular structures of complexes **2**, **3** and **4** are depicted in Figs. 2–4, respectively, and crystal parameters are summarized in Table 1. The square planar Pd(II) center is coordinated by two NHC's and two chloro ligands in a *trans*-arrangement in complex **2**. Although *cis* geometry is preferable due to *trans*-influence of NHC [24], bulky substituents in NHC's probably enforce the molecule in a *trans*-geometry [25]. Both of the *trans* angles C–Pd–C and Cl–Pd–Cl are 180°. The two NHC ligands approach Pd center in the same plane (dihedral angle = 0.00°). The imidazole ring plane of the NHC ligands is almost perpendicular to the coordination plane of the Pd(II) center (dihedral angle = 86.09°), a characteristic feature of carbene complexes [25] to relieve steric strain. The Pd–C_{carb} and Pd–Cl bond lengths are within the expected range [2b,19,16a,25]. The O–CH_2–CH_3 branches in side arms of the complex are highly disordered.

Complex **3** exists as a dimer with two bridging chloro ligands in the solid state. Each of the Pd (II) center is coordinated by one terminal chloro, two bridging chloro and one carbene ligands in a

Fig. 3. ORTEP view of complex **3** showing 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Pd1–Pd2, 3.222; Pd1–C5, 1.951(5); Pd2–C1, 1.941(4); Pd1–Cl3, 2.420(12); Pd1–Cl4, 2.334(12); Pd1–Cl5, 2.296(14); Pd2–Cl1, 2.281(12); Pd2–Cl3, 2.320(12); Pd2–Cl4, 2.424(11). C5–Pd1–Cl3, 176.70(13); C5–Pd1–Cl5 88.70(14); Pd1–Cl3–Pd2, 85.65(4); Pd1–Cl4–Pd2, 85.23(4).

square planar fashion. The two carbene ligands are anti to each other. The dinuclear frame (Pd_2Cl_2) formed by two Pd(II) center and two bridging chloro is twisted due to Pd–Pd interaction or steric crowding by N-substituents. The Pd1-Pd2 distance of 3.222 Å is shorter than the sum of van der Waals radii of two Pd centers of 3.26 Å. The dihedral angle between the two imidazole ring planes is 35.70°. Among the three types of Pd–Cl bonds in the complex, Pd–Cl bridge bonds *trans* to the terminal chloro is significantly longer than other bridge bonds *trans* to carbene. This observation is opposite to the other reported bromobridged dinuclear complexes from benzimidazole [13,18a]. The Pd–C_{carb} bond lengths are shorter than our mononuclear complexes **2** and **4** (*vide infra*) and comparable to that reported complexes [16a,16d].

Hydrogen bonding interactions among protons at imidazole ring, NCH_2 and oxygen of ether made a network structure in

Fig. 2. ORTEP view of complex **2** showing 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Pd1–C1, 2.013(7); Pd1–Cl1, 2.3437(17). C1–Pd1–C1(i) 180.0; C1–Pd1–Cl1, 90.0. Symmetry transformations $i = -x + 1, -y + 1, -z + 1$.
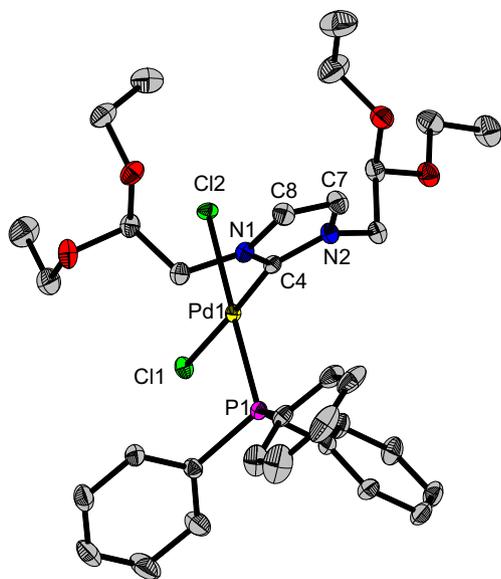
Fig. 4. ORTEP view of complex **4** showing 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Pd1–C4, 1.975(3); Pd1–P1, 2.268(7); Pd1–Cl1 2.355(6); Pd1–Cl2, 2.393(6). Cl1–Pd1–P1, 88.62(2); Cl1–Pd1–Cl2, 90.75(2); Cl2–Pd1–C4, 87.05(7); C4–Pd1–P1, 93.59(7); Cl2–Pd1–P1, 178.63(2); Cl1–Pd1–C4 177.75(7).

Fig. 5. ORTEP view of complex **5** showing 30% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Ni1–C1(i), 1.916(5); Ni1–Br1, 2.3118(6). C1(i)–Ni1–C1, 180.0; C1(i)–Ni1–Br1, 90.0. Symmetry transformations $i = -x + 1, -y + 1, -z + 1$.

complex **3** (for packing, interaction and distance see Supplementary file S-2a, S-2b, 2c and Table a).

NHC and phosphine ligands in complex **4** are *cis* to each other (Fig. 4). Both *cis* coordination and *trans*-coordination of NHC and phosphine have been reported earlier [1c,3i]. The Pd–C_{carb} and Pd–P bond lengths are comparable with similar *cis* isomer [1c] but shorter than that of reported for *trans*-isomer [3i]. The distance between Pd and chloride *trans* to the phosphine [Pd–Cl2 = 2.393(6) Å)] is slightly longer than the distance between the Pd and chloride *trans* to carbene [Pd–Cl1 = 2.355(6) Å)]. This observation shows that phosphine is slightly stronger *trans* influencing

ligand than this carbene. Again the imidazole ring plane of NHC is almost perpendicular to the square plane formed by the Pd(II) center (dihedral angle = 79.45°). In this type of arrangement the N-substituents of imidazole ring reduce the steric interaction with triphenyl phosphine ligand. More interestingly the two N-substituents in imidazole ring are faced away from the phenyl ring of triphenyl phosphine.

Each imidazole proton is connected *via* hydrogen bonding interaction with ether oxygen atoms of adjacent complex molecule while each ether oxygen atom is connected either with imidazole proton or with NCH_2 protons of adjacent complex (for packing and interaction see Supplementary file S-4).

In complex **5**, square planar Ni(II) center is coordinated by two NHCs and two bromo ligands in a *trans*-arrangement (Fig. 5) and

Table 2
Coupling of aryl bromide and styrene in different bases catalyzed by **2**, **3**, and **4**[a]

Entry	Catalyst	Base	Time (h)	Yield [b] (%)
1	**3**	NaOAc	4	47 (21)
2	**3**	K_2CO_3	4	97 (99)
3	**3**	Na_2CO_3	4	39 (84)
4	**3**	Et_3N	4	17 (11)
5	**3**	K_3PO_4	4	53 (93)
6	**3**	Cs_2CO_3	4	6 (42)
7	**3**	$Ba(OH)_2$	4	72 (83)
8	**3**	KOH	4	56 (42)
9	**3**	NaOH	4	42 (72)
10	**3**	K_2CO_3	2	61 (91)
11	**3**	K_2CO_3	2	95[c]
12	**2**	K_2CO_3	2	64 (91[c])
13	**4**	K_2CO_3	2	79 (99[c])

[a] Reaction conditions: 1 mmol bromobenzene, 1.5 mmol styrene, 2 mmol base, 0.5 mol% for (**3**), 1 mol% for (**2**) and (**4**), 1.5 mL DMF, 140 °C. All are isolated yields, average of two runs.

[b] 1 mmol of TBAB was added.

[c] 0.5 mmol of TBAB was added.

the complex is isostructural with mononuclear Pd-complex **2**. The side arms are also highly disordered in complex **5**. The bond length between C_{carb} and Ni(II) [Ni–C = 1.916(5) Å] is in good agreement with values reported for similar Ni–NHC [12,26] but is longer than that reported Ni–NHC of benzimidazol-2-ylidene [21a].

2.5. Heck catalysis

Pd-catalyzed Heck reaction is one of the most useful methods of forming natural products, drug design and organic synthesis [3f,10a,27]. A variety of parameters such as solvent, catalyst loading, temperature can influence the reactivity of Heck coupling [28]. The benefits of DMF as a solvent or solvating ligands are well known [18a,24,27b,29] and the presence of TBAB (tetra-*n*-butylammonium bromide) can increase the conversion rate by stabilization of Pd colloids or nanoparticles [30]. So initially, the reactions were performed in DMF as solvent with different bases at 140 °C in the presence or absence of TBAB using complex **3** as catalyst (Table 2). Excellent yield was found with base K_2CO_3 (Table 2, entry 2) at 140 °C for 4 h with or without the use of TBAB. Decreasing the reaction time to 2 h, better results were obtained in the presence of TBAB (entries 10 and 11). K_3PO_4 and $Ba(OH)_2$ also gave very good yield in the presence of TBAB after 4 h (entries 5 and 7). The most effective catalytic conditions for **3** is 0.5 mol% catalyst loading with 0.5 mmol of TBAB, base K_2CO_3 at 140 °C in DMF. Using the same optimized condition, complexes **2** and **4** gave >90% yield (entries 12 and 13) with 1 mol% of catalyst loading for each. So it is clearly discerned that all the Pd-complexes are useful precatalysts for Heck reaction. It was also observed that the mixed ligated complex **4** was most active with or without TBAB in comparison to **2** and **3**.

When DMF was replaced by H_2O as solvent (Table 3, entries 2, 3 and 4) the conversion decreases markedly and for complex **2** only

Table 3
Coupling of aryl bromide and styrene in different condition catalyzed by **2, 3, 4**[a]
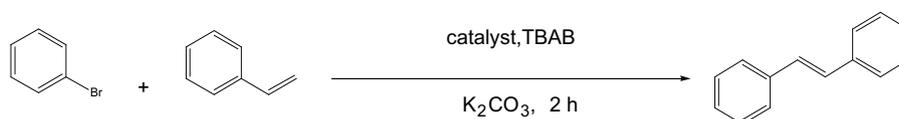
Entry	Catalyst	Temperature (°C)	Solvent	Yield[b] (%)
1	**3**	140	DMF	0[c]
2	**3**	140	H_2O	52
3	**2**	140	H_2O	Trace
4	**4**	140	H_2O	36
5	**3**	120	DMF	43
6	**4**	120	DMF	95
7	**3**	140	$LHBr/H_2O$	0
8	**4**	140	$LHBr/H_2O$	0

[a] Reaction conditions: 1 mmol bromobenzene, 1.5 mmol styrene, 2 mmol potassium carbonate, 0.5 mmol TBAB, 0.5 mol% for **3**, 1 mol% for **2** and **4**.
[b] All are isolated yields, average of two runs.
[c] TBAB was replaced by 0.5 mmol LHBr.

Table 4
Heck reaction of substituted aryl bromide and styrene catalyzed by **3, 4**[a]
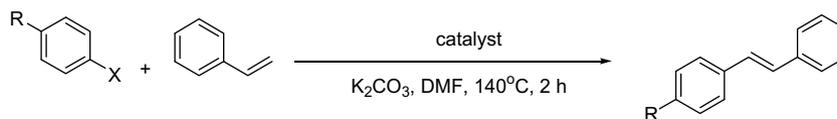
Entry	Catalyst	X	R	Yield[b] (%)
1	**3**	Br	H	94
2	**3**	Br	Me	87
3	**3**	Br	OMe	94
4	**3**	Br	C(O)Me	88
5	**3**	Br	CN	89
6	**4**	Br	H	99
7	**4**	Br	Me	100
8	**4**	Br	OMe	100
9	**4**	Br	C(O)Me	100
10	**4**	Br	CN	100
11	**4**	Cl	H	Trace
12	**4**	Cl	C(O)Me	92
13	**4**	Cl	NO_2	75

[a] Reaction conditions: 1 mmol substituted aryl bromide, 1.5 mmol styrene, 2 mmol potassium carbonate, 0.5 mol% for **3**, 1 mol% for **4**, 0.5 mmol TBAB, 1.5 mL DMF.
[b] All are isolated yields, average of two runs.

Table 5
Heck reaction of aryl bromide and styrene catalyzed by **4** in different catalyst loading[a]
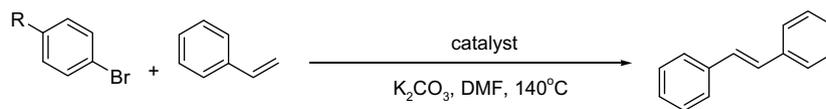
Entry	R	Amount of catalyst (mol%)	Time (h)	Yield[b] (%)	Ton
1	H	1	2	99	99
2	H	0.1	2	89	890
3	H	0.01	2	39	3900
4	H	0.01	12	100	10 000
5	H	0.001	24	29	29 000
6	H	1×10^{-5}	36	9	900 000
7	OMe	0.01	12	100	10 000

[a] Reaction conditions: 1 mmol bromobenzene, 1.5 mmol styrene, 2 mmol potassium carbonate, 0.5 mmol TBAB, 1.5 mL DMF, 140 °C.
[b] All are isolated yields, average of two runs.

trace amount of product was isolated (entry 3). The use of LHBr/H_2O as solvent (entries 7 and 8) or the use of LHBr instead of TBAB (entry 1) completely suppressed the Heck reaction. Note that, in all the cases Pd-black were formed during the catalytic reactions. Decreasing reaction temperature to 120 °C, complex **3** (Table 3, entry 5) failed to promote the reaction to obtain a good yield whereas complex **4** (Table 3, entry 6) activated the coupling reaction as well. In both cases the Pd-black formation was not observed. The *cis* coupling product was not found at all for all catalysts. So the catalysts are highly selective and that is their advantage. In all cases only trace gem-isomer formed was confirmed by NMR spectra.

Complexes **3** and **4** were further used to examine their activities toward substituted aryl halides (Table 4). The results showed that both complexes promoted the coupling reaction very well and for complex **4** we got 100% yields (entries 7, 8, 9 and 10) [1c]. Activated aryl chlorides also produced good yields by mixed ligated complex **4**.

Low catalyst loading tests were performed for complex **4** with aryl bromide and styrene in the optimized condition. The catalyst proceeded to complete the reaction up to 89% in 2 h using 0.1 mol% of catalyst (Table 5, entry 2). Further lowering of catalyst loading decreased the yield enormously (entry 3) within 2 h. But running longer reaction time up to 12 h we got 100% yield (entry 4). It has been reported [31] that the full conversion for the reaction of bromoanisole with styrene in Heck catalysis is difficult to achieve. Only a few examples are present for good yields [30,32]. Using 0.01 mol% of catalyst loading and running the reaction in a longer time period (12 h) we have got 100% yield with a good ton (1×10^4) in case of catalyst **4**. It is also important to note that by lowering the catalyst loading the Pd-black formation was not observed. It had been reported that low concentration of Pd-catalyst is required to prevent agglomeration and Pd-black formation [27f,30b,30d]. Therefore, these Pd–NHCs and more importantly complex **4** showed excellent activity in the Heck coupling of bromoanisole and styrene. Moreover, the observed catalytic activity of our pre-catalyst is also better than reported ether linked chelate and alkyl chain substituted benzimidazole pre-catalyst [33].

Ni complex is unstable in protic solvents like MeOH, EtOH and isopropanol. So Heck reactions were performed using DMF and other solvents in N_2 atmosphere. Using several bases and solvents we detected only 15–20% yield for coupling of phenyl iodide with styrene using 1–3 mol% of catalyst. Hydrolyzed product **3A** showed better result and found to give 89% yield for the coupling of phenyl iodide and styrene in DMF at 140 °C using 0.1 mol% of catalyst and K_2CO_3 as base.

3. Conclusion

We have presented the synthesis and structures of imidazole *N*-ether substituted Ag(I), Pd(II), Ni(II) complexes. Structure of Pd(II) complex of mixed NHC and phosphine has also been solved. Acid hydrolysis of the tetraethoxy substituted imidazolium salt and dinuclear Pd-complex (**3**) results an equilibrium mixture of hydroxy group and aldehyde group in the side arms. The ratio of the mixture depends on the temperature and vacuum applied. All the Pd(II) complexes demonstrated good catalytic activity in Heck reaction. Specially Pd(II) complex with mixed NHC and phosphine ligands (**4**) provided an excellent activity and high TON in Heck coupling of bromoanisole with styrene. Further studies on the activity of the hydrolyzed product and its derivatives in water are ongoing in our laboratory.

4. Experimental section

4.1. General

All the reactions were carried out in air. The solvents and reagents were purchased from general sources and were used without further purification. NMR spectra were recorded on a Bruker DX-300 NMR spectrometer (^{1}H, 300 MHz; ^{13}C, 75.46 MHz; ^{31}P, 121.49 MHz). IR spectra were recorded using Jasco FTIR 410 instrument. Mass Spectra were measured on a Micromass Platform II spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400, 2400II elemental analyzer. TGA of the imidazolium salts were examined by means of Mettler-Toledo TGA 851 thermal gravimetric analyzer. An average sample weight of 5–10 mg was placed in an aluminum pan and heated at 10 °C min^{-1} from 25 °C to 500 °C under a flow of nitrogen. The onset of decomposition was defined as the decomposition temperature (T_d). Differential Scanning Calorimeter (DSC) measurements were performed for imidazolium salts using TA 2920 DSC in the temperature range −100 °C to 100 °C.

4.2. Synthesis of N,N′-bis-(2,2-diethoxyethyl)imidazolium salt (LHX)

4.2.1. LHBr

A mixture of imidazole (1.00 g, 14.7 mmol), bromoacetaldehyde diethylacetal (8.68 g, 44.1 mmol) and sodium carbonate (3.11 g,

29.4 mmol) in 50 ml of DMF was stirred at 120 °C for 3 days. After the filtration, the solvents were removed under reduced pressure and a minimum amount of dry dichloromethane was added to filter out the remnant sodium carbonate. The organic part was extracted with water and the water layer was dried in a rotavapor and finally dried in vacuo to get a yellow color oily liquid (yield 4.48 g, 80% yield). The liquid is soluble in most of the common solvents except ether and hexane. ^{1}H NMR (CDCl$_3$): δ 10.28 (s, 1H, NCHN), 7.36 (d, J_{H-H} = 1.5 Hz, 2H, imi-H), 4.82 (t, J_{H-H} = 4.5 Hz, 2H, CHOO), 4.44 (d, J_{H-H} = 4.5 Hz, 4H, NCH_2), 3.74 (m, 4H, OCH_a), 3.62 (m, 4H, OCH_b) 1.17 (t, J_{H-H} = 6.9 Hz, 12H, CH_3). ^{13}C NMR (CDCl$_3$): δ 138.5 (NCHN), 122.8 (imi-C), 99.5 (CHOO), 64.4 (NCH$_2$), 52.0 (OCH$_2$), 15.1 (CH$_3$). MS (MALDI): m/z 301 [M–Br$^-$]$^+$. Anal. Calc. for C$_{15}$H$_{29}$N$_2$O$_4$Br.1H$_2$O: C, 45.11, H, 7.77, N, 7.01. Found: C, 44.98, H, 7.48, N, 6.79%. T_d = 270 °C, T_g = −58.72 °C.

4.2.2. LHX (X = BF$_4$ and PF$_6$)

A mixture of LHBr (1 mmol) and NH$_4$X (X = BF$_4$ and PF$_6$, 1.2 mmol) in 20 ml acetone was stirred at 45 °C (BF$_4$) or room temperature (PF$_6$) for 1–2 h. The mixture was filtered through Celite 545 and the solvent was removed under reduced pressure. The light brown color liquid obtained was finally dried in vacuo (yield 80% for LHBF$_4$ and 85% for LHPF$_6$). Both the salts are soluble in dichloromethane, acetonitrile and water.

LHBF$_4$: ^{1}H NMR (CDCl$_3$): δ 8.91 (s, 1H, NCHN), 7.30 (s, 2H, imi-H), 4.78 (t, J_{H-H} = 3.9 Hz, 2H, CHOO), 4.28 (d, J_{H-H} = 4.2 Hz, 4H, NCH_2), 3.77 (m, 4H, OCH_a), 3.56 (m, 4H, OCH_b) 1.19 (t, J_{H-H} = 6.9 Hz, 12H, CH_3). ^{13}C NMR (75.43 MHz, CDCl$_3$): δ 137.6 (NCHN), 122.8 (imi-C), 99.3 (CHOO), 64.0 (NCH$_2$), 51.8 (OCH$_2$), 14.9 (CH$_3$). MS (MALDI): m/z 301 [M–BF$_4^-$]$^+$. T_d = 130 °C, T_g = -67.85 °C.

LHPF$_6$: ^{1}H NMR (CDCl$_3$): δ 8.5 (s, 1H, NCHN), 7.30 (s, 2H, imi-H), 4.76 (t, J_{H-H} = 4.2 Hz, 2H, CHOO), 4.23 (d, J_{H-H} = 3.9 Hz, 4H, NCH_2), 3.76 (m, 4H, OCH_a), 3.58 (m, 4H, OCH_b) 1.19 (t, J_{H-H} = 6.9 Hz, 12H, CH_3). ^{13}C NMR (CDCl$_3$): δ 137 (NCHN), 123 (imi-C), 99.3 (CHOO), 64.1 (NCH$_2$), 51.0 (OCH$_2$), 14.9 (CH$_3$). MS (MALDI): m/z 301 [M–PF$_6^-$]$^+$. T_d = 260 °C, T_g = −49.59 °C.

4.2.3. LHBPh$_4$

A mixture of LHBr (1 mmol) and NaBPh$_4$ (1.2 mmol) in 10 ml water was stirred at room temperature for 2 h. The white solid was filtered and washed with cold water thoroughly and dried in vacuo (yield 80%). LHBPh$_4$ is soluble in dichloromethane, acetonitrile but insoluble in water. ^{1}H NMR (CDCl$_3$): δ 8.37 (s, 1H, NCHN), 7.33 (s, 2H, imi-H), 7.28 (m), 7.00 (m), 6.85 (m) (Ph–H), 4.73 (t, J_{H-H} = 4.2 Hz, 2H, CHOO), 4.19 (d, J_{H-H} = 4.2 Hz, 4H, NCH_2), 3.70 (m, 4H, OCH_a), 3.54 (m, 4H, OCH_b), 1.15 (m, 12H, CH_3). ^{13}C NMR (CDCl$_3$): δ 164.2 9(Ph–C), 136.0 (NCHN), 125.9 (imi-C), 99.1 (CHOO), 64.0 (NCH$_2$), 51.5 (OCH$_2$), 15.1 (CH$_3$). MS (MALDI): m/z 301 [M–BPh$_4^-$]$^+$. T_d = 280 °C, T_m = 93 °C.

4.2.4. LHNO$_3$

A mixture of LHBr (1 mmol) and AgNO$_3$ (1 mmol) in 10 ml water was stirred at room temperature for 2 h. The light yellow precipitate was filtered off through celite and the filtrate was dried in a rotavapor. The light brown liquid was finally dried in vacuo to give LHNO$_3$ (yield 84%). The liquid is soluble in dichloromethane, acetonitrile and water. ^{1}H NMR (CDCl$_3$): δ 9.9 (s, 1H, NCHN), 7.29 (s, 2H, imi-H), 4.76 (t, J_{H-H} = 4.2 Hz, 2H, CHOO), 4.33 (d, J_{H-H} = 3.9 Hz, 4H, NCH_2), 3.76 (m, 4H, OCH_a), 3.59 (m, 4H, OCH_b), 1.19 (t, J_{H-H} = 7.2 Hz, 12H, CH_3). ^{13}C NMR (CDCl$_3$): δ 138.6 (NCHN), 122.8 (imi-C), 99.5 (CHOO), 64.0 (NCH$_2$), 51.7 (OCH$_2$), 14.9 (CH$_3$). MS (MALDI): m/z 301 [M–NO$_3^-$]$^+$. T_d = 257 °C, T_g = −71.68 °C.

4.2.5. LHNTf$_2$

A mixture of LHBr (1 mmol) and LiNTf$_2$ (1.2 mmol) in 10 ml water was stirred at room temperature for 2 h. The reaction mixture was then extracted with dichloromethane three times (5 ml each). The organic part was dried over MgSO$_4$ and filtered. The solvent was evaporated and dried to get a brown liquid LHNTf$_2$ (yield 80%). The liquid is soluble in dichloromethane, acetonitrile but insoluble in water. ^{1}H NMR (CDCl$_3$): δ 8.9 (s, 1H, NCHN), 7.29 (s, 2H, imi-H), 4.75 (t, J_{H-H} = 3.9 Hz, 2H, CHOO), 4.29 (d, J_{H-H} = 3.9 Hz, 4H, NCH_2), 3.75 (m, 4H, OCH_a), 3.59 (m, 4H, OCH_b) 1.20 (t, J_{H-H} = 7.2 Hz, 12H, CH_3). ^{13}C NMR (CDCl$_3$): δ 137 (NCHN), 123 (imi-C), 99.3 (CHOO), 64.2 (NCH$_2$), 52.1 (OCH$_2$), 14.9 (CH$_3$). MS (MALDI): m/z 301 [M–NTf$^-_2$]$^+$. T_d = 267 °C, T_g = −64.37 °C.

4.3. Synthesis the complexes

4.3.1. Synthesis of [L$_2$Ag][AgBr$_2$] (1)

A suspension of LHBr (1.00 g, 2.62 mmol) and silver oxide (0.33 g, 1.4 mmol) in dichloromethane was stirred at room temperature for 1 h in dark. The mixture was then filtered through celite and the filtrate was concentrated to ~5 ml. The concentrated solution was added dropwise into a large volume of hexane. The resulting white solid was isolated by filtration and dried in vacuum (yield 1.27 g, 85%). The compound is soluble in ether, dichloromethane, chloroform and acetone. The X-ray quality crystals were grown after a long time by the slow evaporation of dichloromethane solution of the compound. ^{1}H NMR (CDCl$_3$): δ 7.05 (s, 4H, imi-H), 4.65 (t, J_{H-H} = 5.1 Hz, 4H, CHOO), 4.17 (d, J_{H-H} = 5.1 Hz, 8H, NCH_2), 3.70 (m, 8H, OCHa), 3.49 (m, 8H, OCHb), 1.16 (t, J_{H-H} = 6.9 Hz, 24H, CH_3). ^{13}C NMR (CDCl$_3$): δ 122.3 (imi-C), 101.7 (CHOO), 64.0 (NCH$_2$), 52.4 (OCH$_2$), 15.2 (CH$_3$). MS (MALDI): m/z 709 [L$_2$Ag]$^+$, 407 [L$_2$Ag–L–1]$^+$, 301 [L]$^+$. Anal. Calc. for C$_{30}$H$_{56}$Ag$_2$Br$_2$N$_4$O$_8$: C, 36.91; H, 5.78; N, 5.74. Found: C, 37.02; H, 5.64; N, 5.78%.

4.3.2. Synthesis of L$_2$PdCl$_2$ (2)

A suspension of LHBr (3.00 g, 7.87 mmol) and silver oxide (1.00 g, 4.3 mmol) in dichloromethane was stirred at room temperature for 1 h in dark. To this reaction mixture Pd(CH$_3$CN)$_2$Cl$_2$ (1.00 g, 3.90 mmol) was added and stirred for additional 1 h. The mixture was then filtered through celite and the filtrate was dried in vacuum. The pale yellow color solid was further purified by silica gel column using ethyl acetate as eluent (yield 1.98 g, 65%). The compound is soluble in dichloromethane, chloroform, acetone, ethyl acetate, and slightly soluble in methanol but insoluble in water. The X-ray quality crystals were grown by the slow evaporation of chloroform solution of the compound. ^{1}H NMR (CDCl$_3$): δ 6.99 (s, 4H, imi-H), 5.21 (m, 4H, CHOO), 4.58 (dd, J_{H-H} = 8.1, 6.0 Hz, 8H, NCH_2), 3.79 (m, 8H, OCHa), 3.59 (m, 8H, OCHb), 1.20 (t, J_{H-H} = 6.9 Hz, 24H, CH_3). ^{13}C NMR (CDCl$_3$): δ 170.3 (NCN), 122.1 (imi-C), 102.3 (CHOO), 64.5 (NCH$_2$), 53.5 (OCH$_2$), 15.3 (CH$_3$). MS (MALDI): m/z 741 [M–Cl]$^+$, 441 [M–L–Cl]$^+$, 301 [L]$^+$. Anal. Calc. for C$_{30}$H$_{56}$Cl$_2$N$_4$O$_8$Pd: C, 46.31; H, 7.25; N, 7.20. Found: C, 46.23; H, 7.09; N, 6.96%.

4.3.3. Synthesis of (LPdCl$_2$)$_2$ (3)

The chlorobridged binuclear palladium complex was prepared in analogy to the above mononuclear complex using LHBr and Pd(CH$_3$CN)$_2$Cl$_2$ in 1:1 molar ratio instead 2:1 for mononuclear one. Upon chromatographic purification an orange color solid was obtained (yield 91%). The compound is slightly soluble in water and soluble in other solvents like mononuclear one. ^{1}H NMR (CDCl$_3$): δ 7.06 (s, 4H, imi-H), 5.13 (t, J_{H-H} = 5.7 Hz, 4H, CHOO), 4.72 (br, 4H, NCH_2), 4.63 (br, 4H, NCH_2), 3.86 (t, 8H, OCHa), 3.64 (br, 8H, OCHb), 1.24 (s, 24H, CH_3). ^{13}C NMR (CDCl$_3$): δ 141.3 (NCN), 123.8 (imi-C), 101.5 (CHOO), 64.6 (NCH$_2$), 53.6 (OCH$_2$), 15.3 (CH$_3$). MS (MALDI): m/z 743 [M–3Cl–Pd]$^+$, 301 [L]$^+$. Anal. Calc. for C$_{30}$H$_{56}$Cl$_2$N$_4$O$_8$Pd$_2$: C, 37.71; H, 5.91; N, 5.86. Found: C, 37.59; H, 5.74; N, 5.74%.

4.3.4. Synthesis of LPdPPh$_3$Cl$_2$ (4)

The dinuclear Pd complex **3** (0.10 g, 0.1 mmol) was dissolved in 5 ml dichloromethane and triphenylphosphine (0.06 g, 0.2 mmol) was added to it. The mixture was stirred at room temperature for 1 h and than the solvent was removed to yield a pale yellow powder (yield 0.15 g, 90%). The compound is insoluble in water. X-ray quality crystals were grown by slow diffusion of ether into a dichloromethane solution of the compound. ^{1}H NMR (CDCl$_3$): δ 7.62–7.31 (m, 15H, PPh$_3$-H), 6.71 (d, J_{H-H} = 5.7 Hz, 2H, imi-H), 5.13 (dd, J_{H-H} = 8.1, 3.0 Hz, 2H, CHOO), 4.48 (dd, J_{H-H} = 13.5, 3.0 Hz, 2H, NCH_a), 3.82 (m, 2H, NCH_b), 3.67 (m, 4H, OCH_c, OCH_d), 3.45 (m, 4H, OCH_e, OCH_f), 1.30 (m, 6H, CH_3), 1.04 (m, 6H, CH_3). ^{13}C NMR (CDCl$_3$): δ 162.5 (NCN), 134.1(Ph-C), 131.2 (Ph-C), 130.0(imi-C), 129.3 (imi-C), 128.6 (Ph-C), 122.9 (Ph-C), 101.0 (CHOO), 65.4 (NCH_2), 64.3 (OCH_2), 53.6 (OCH_2), 15.5(CH_3), 15.1(CH_3). ^{31}P NMR (CDCl$_3$): δ 28.6 (major), 27.7. MS (MALDI): m/z 703 [M]$^+$, 441 [M–PPh$_3$]$^+$, 301 [L]$^+$. Anal. Calc. for C$_{33}$H$_{43}$Cl$_2$N$_2$O$_4$Pd: C, 52.29; H, 5.98; N, 3.70. Found: C, 52.50; H, 5.76; N, 3.62%.

4.3.5. Synthesis of L$_2$NiBr$_2$ (5)

LHBr (3.00 g, 7.9 mmol) and Ni(OAc)$_2$ · 4H$_2$O (0.75 g, 2.6 mmol) were heated slowly with stirring under vacuum. The mixture was kept at 120 °C for 4 h. After slow cooling to room temperature the mixture was purified by SiO$_2$ column using ethyl acetate as eluent. The compound was isolated as red powder (yield 2.13 g, 50%). The compound is insoluble in water. The X-ray quality crystals were grown by the slow evaporation of ethyl acetate solution of the compound. ^{1}H NMR (CDCl$_3$): δ 6.87 (s, 4H, imi-H), 5.37 (t, J_{H-H} = 5.4 Hz, 4H, CHOO), 5.03 (d, J_{H-H} = 5.7 Hz, 8H, NCH_2), 3.80 (m, 8H, OCH_a), 3.61 (m, 8H, OCH_b), 1.20 (t, J_{H-H} = 6.9 Hz, 24H, CH_3). ^{13}C NMR (CDCl$_3$): δ 169.9 (NCN), 122.6 (imi-C), 101.7 (CHOO), 64.5 (NCH_2), 53.5 (OCH_2), 15.3 (CH_3). MS (MALDI): m/z 739 [M−Br]$^+$, 737 [M−Br]$^+$, 658 [M−2Br]$^+$, 439 [M−L]$^+$, 437 [M−L]$^+$, 301 [L]$^+$. Anal. Calc. for C$_{30}$H$_{56}$Cl$_2$N$_4$ NiO$_8$: C, 43.98; H, 6.89; N, 6.84. Found: C, 43.98; H, 6.88; N, 6.78%.

4.4. Hydrolysis of LHBr

LHBr (0.5 g, 1.31 mmol) was dissolved in HCl (1.5 M, 10 ml) in 50 ml flask and was stirred for 4 h at 60 °C in air. After the solvent was removed in vacuo, the residue was dissolved in 1.5 ml water and the solution was added dropwise into acetone (40 ml) with vigorous stirring. The sticky solid was collected and the procedure was repeated three times. Finally the hygroscopic brown solid which contains two species L$_A$HBr and L$_B$HBr was obtained after drying under vacuum (0.2 g). The solid is soluble in water, DMF and DMSO. In presence of water only L$_A$HBr was found. ^{1}H NMR (D$_2$O): δ 8.76 (s, 1H, NCHN), 7.45 (d, J_{H-H} = 1.5 Hz, 2H, imi-H), 5.30 (t, J_{H-H} = 4.5 Hz, 2H, CHOO), 4.20 (d, J_{H-H} = 4.5 Hz, 4H, NCH_2). ^{13}C NMR (D$_2$O): δ 137.2 (NCHN), 123.0 (imi-C), 87.29 (CHOO), 54.3 (NCH_2). MS (MALDI, D$_2$O): m/z 189 [L$_A$+1]$^+$. In DMSO two sets of proton signals for L$_A$HBr and L$_B$HBr were found. ^{1}H NMR (DMSO-d^6) L$_A$HBr: δ 7.65 (d, J_{H-H} = 1.8 Hz, 2H, imi-H), δ 7.05 (br, 4H, C–O–H), 5.48 (t, J_{H-H} = 4.5 Hz, 2H, CHOO), 4.28 (m, 4H, NCH_2); L$_B$HBr: δ 9.62 (t, J_{H-H} = 2.4 Hz, 2H, CHO), 7.77 (d, J_{H-H} = 1.8 Hz, 2H, imi-H), 5.22 (br, 4H, NCH_2). MS (MALDI, DMSO): m/z 189 [L$_A$+1]$^+$, 153 [L$_B$+1]$^+$. IR (KBr film): ν_{max} (CO) 1733 cm^{-1}.

4.5. Hydrolysis of 3

Complex **3** (0.2 g, 0.21 mmol) was dissolved in 5 ml CH$_3$CN in a 50 ml flask. Then HCl (3 M, 1 ml) was added and stirred for 4 h at 60 °C in air. The solvent was removed in a rotavapor. Finally the orange hygroscopic solid was dried in vacuo (0.15 g). The solid is soluble in water, DMF and DMSO. In presence of water only **3A** was found. ^{1}H NMR (D$_2$O): δ 7.15 (d, J_{H-H} = 1.5 Hz, 2H, imi-H), 5.66 (t, J_{H-H} = 5.4 Hz, 2H, CHOO), 4.47 (d, J_{H-H} = 5.4 Hz, 4H, NCH_2). ^{13}C NMR (D$_2$O): δ 124.51 (imi-C), 88.75 (CHOO), 55.34 (NCH_2). MS (MALDI, D$_2$O): m/z 329, 331 [L$_A$+Pd+1]$^+$, 189 [L$_A$+1]$^+$. In DMSO a mixture of **3A** and **3B** were obtained. ^{1}H NMR (DMSO-d^6): δ 9.65 (CHO), 7.47 (imi-H), 5.41 (CHOO), 4.50 (NCH_2). MS (MALDI, DMSO): m/z 295, 293 [L$_B$+Pd+1]$^+$, 189 [L$_A$+1]$^+$, 153 [L$_B$+1]$^+$. IR (KBr film): ν_{max} (CO) 1731 cm^{-1}.

4.6. General procedure for Heck coupling

A mixture of aryl halide or substituted aryl halide (1.0 mmol), styrene (1.5 mmol), solvent (1.5 ml), Pd(II) catalyst (0.5 mol%), TBAB (0.5 mmol) and base (2 mmol) was charged in a vial under air, locked up with a screw cap and then heated at 140 °C in a pre-heated oil bath. After 2 h, the mixture was extracted with diethyl ether or dichloromethane/H$_2$O (5 mL/2 mL) three times. The organic phase was separated and dried in vacuo. The crude product was purified by column chromatography using 5:1 n-hexane:EA (V/V).

4.7. X-ray crystallography

Single crystals were mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Bruker Smart APEXII CCD XRD. The intensity data were collected at 273 K. All data were collected with ω scan technique using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). All Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included at calculated positions. The structures were solved by direct methods using the SHELXS-97 computer program and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [34].

Acknowledgements

Appendix A. Supplementary material

SCCDC Nos. 640680 (for **1A**), 648302 (for **2**), 648301 (for **3**), 640679 (for **4**), and 668115 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.017.

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