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The imidazo{[4,5-f][1,10]-phenanthrolin}l-2-ylidene and its palladium complexes: Synthesis, characterization, and application in C-C cross-coupling reactions

Lütfiye Gök [a], Salih Günnaz [a], Zarife Sibel Şahin [b], Levent Pelit [a], Hayati Türkmen [a, *]

[a] Department of Chemistry, Ege University, 35100 Bornova, Izmir, Turkey
[b] Department of Energy Systems Engineering, Faculty of Engineering and Architecture, Sinop University, Sinop, Turkey

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ABSTRACT

1,3-dibutyl-1*H*-imidazo[4,5-f][1,10]phenanthrolinium iodide, **L_5.2HI** ligand and their mono-, di-, tri-, tetra-nuclear palladium(II) complexes (**5.HPF_6**, **6**–**8**) were synthesized and characterized by elemental analysis, FTIR, UV–visible and NMR spectroscopy. In addition, the complexes (**5.HPF_6**, **6**–**8**) were determined by mass spectrometry (MALDI). The ligand **L_5.2HI** was determined by X-ray diffraction. The complexes (**5.HPF_6**, **6**–**8**) were tested in Suzuki-Miyaura and Mizoroki-Heck reactions at elevated temperatures. The activities of the catalysts were monitored by NMR and GC analysis. We found that the poly-nuclear complexes display better activities compared to the mono-nuclear derivatives, thus proposing that an increase in metal moieties which leads to an increase in activity in cross-coupling reaction.

1. Introduction

Transition metal N-heterocyclic carbene (NHC) complexes were documented in 1968 [1]. But the isolation of the first stable NHC was discovered by Arduengo in 1991 [2]. Since that time, their derivatives and complexes have been comprehensively explored [3]. Many theoretical and experimental studies have been focused on σ-donation and π-accepting properties of NHCs [4]. These have been achieved by variation of both the groups attached to the nitrogen atoms and the backbone structure on imidazole ring. The latter approach includes variations in ring size and the backbone topology by attaching functional groups or heteroatoms into the backbone. Annulation and carbonylation of NHC decrease the σ-donation and increase π-accepting abilities [5]. Heinicke et al. have observed that the extension of the π system of NHCs by annulation increases their π accepting ability [6]. We found that the less intensively studied ylidenes derived benzimidazolium or other π-extended arylimidazolium salts behave differently [7]. We also reported synthesis of Palladium(II) complexes containing piperidoimidazolin-2-ylidene and their catalytic properties were studied in the Suzuki-Miyaura(SM), Kumada–Tamao–Corriu (KTC) and Mizoroki-Heck(MH) cross-coupling reactions [8]. On the other hand, the transition metal complexes of 1,10-phenanthroline showed interesting catalytic properties in C-heteroatom coupling reactions [9] and C–C bond formation reactions such as fluoroalkylation [10], direct arylation of heterocycles [11], and decarboxylation reactions [12]. Chen et al. have reported that 1-butyl-3-(1,10-phenanthrolin-2-yl)imidazolylidene as a pincer NNC ligand forms nikel and palladium complexes which exhibit good activity in the Sonogashira and KTC coupling reactions [13]. Most recently, we synthesized a series of ruthenium complexes bearing 1-alkyl-imidazo[4,5-f][1,10]-phenanthroline and the catalytic activity of complexes for the hydrogen transfer reaction of ketones was examined [14].

The imidazo{[4,5-f][1,10]-phenanthroline}linium ligands having large π-conjugated electron systems were prepared [15]. Their dinuclear complexes were synthesized and investigated in photophysical properties [15a], visible-light induced hydrogen-evolving systems [15b], electrochemical properties [15c], photocatalytic hydrogen formation [15d], Prolonged Excited-State Lifetimes [15e], spectroscopic studies [15f]. It is known that polyaromatic linker ligands can support catalytic reaction due to their π–π stacking capability between substrates and ligands [16]. However, the

* Corresponding author. Tel.: +90 2323111713; fax: +90 2323888264.
E-mail address: hayatiturkmen@hotmail.com (H. Türkmen).

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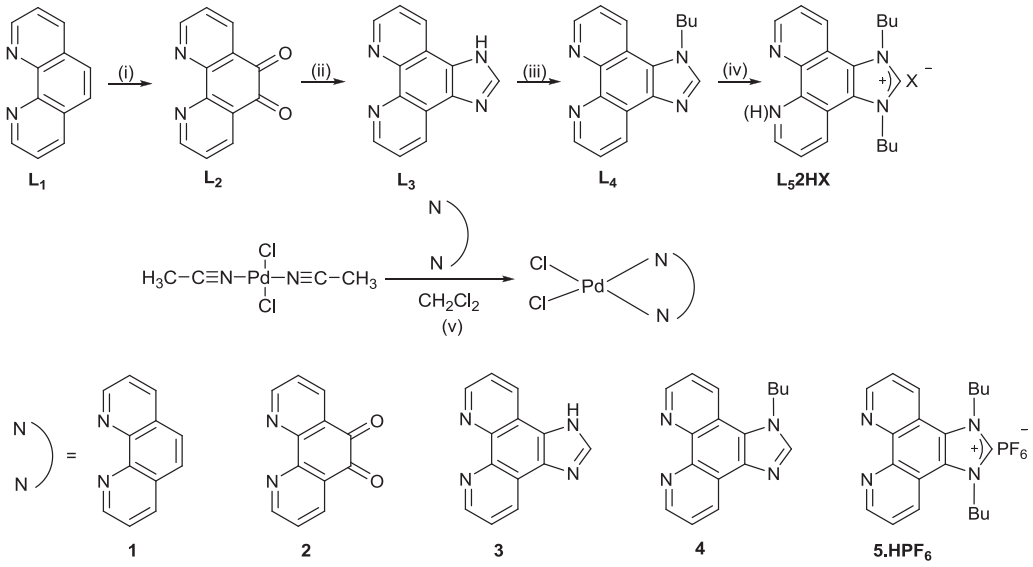
mono-Pd(II) complexes bearing imidazo{ [4,5-f] [1,10]-phenanthrolin}l-2-ylidene and its derivatives were not studied in detail. We now report the palladium complexes of the 1,10-phenanthroline annulated NHCs and their catalytic application to Suzuki-Miyaura, Mizoroki-Heck cross-coupling reactions.

2. Results and discussion

2.1. Synthesis, characterization of ligands and their complexes

Phenanthroline (phen) used as a ligand in coordination chemistry forms strong complexes with most metal ions [17]. Starting from phenanthroline (**L_1**), their derivatives (**$L_{2\text{-}4}$**) were synthesized according to the literature [14]. The reaction of 1-butyl-imidazo [4,5-f][1,10]-phenanthroline derivative (**L_4**) with excess butyl iodides gave 1,3-dibutyl-1*H*-imidazo[4,5-f][1,10]phenanthrolinium iodide (**L_5.2HI**) (Scheme 1). Because of solvating problems of **L_5.2HI**, an anion exchange was performed replacing the iode ions with hexafluorophospate (PF_6^-) ions and **L_5.HPF$_6$** salt was prepared. The 1,3-dibutyl-1*H*-imidazo[4,5-f][1,10]phenanthroline-2-ylidene (**L_5**) have large conjugated electron system and they can serve as co-chelating and co-sensitizing ligand. Ligands have been isolated as colourful and air stable solids. The ^{1}H and ^{13}C resonance for **L_5.2HI** moiety NCHN were detected at 9.89 and 150.5 ppm. In the case of the anion effect, the resonance for the proton on the imidazole ring in **L_5.2HI** with iodide as an anion (δ 9.89 ppm) shifts downfield



Scheme 1. (i) H_2SO_4, $KBrO_3$, 25 °C; (ii)AcOH, NH_4OAC, HCHO, 120 °C; (iii) $(CH_3)COCH_3$, KOH, BuI, 80 °C; (iv) BuI, 140 °C; (v) CH_2Cl_2, $PdCl_2(MeCN)_2$, 25 °C.

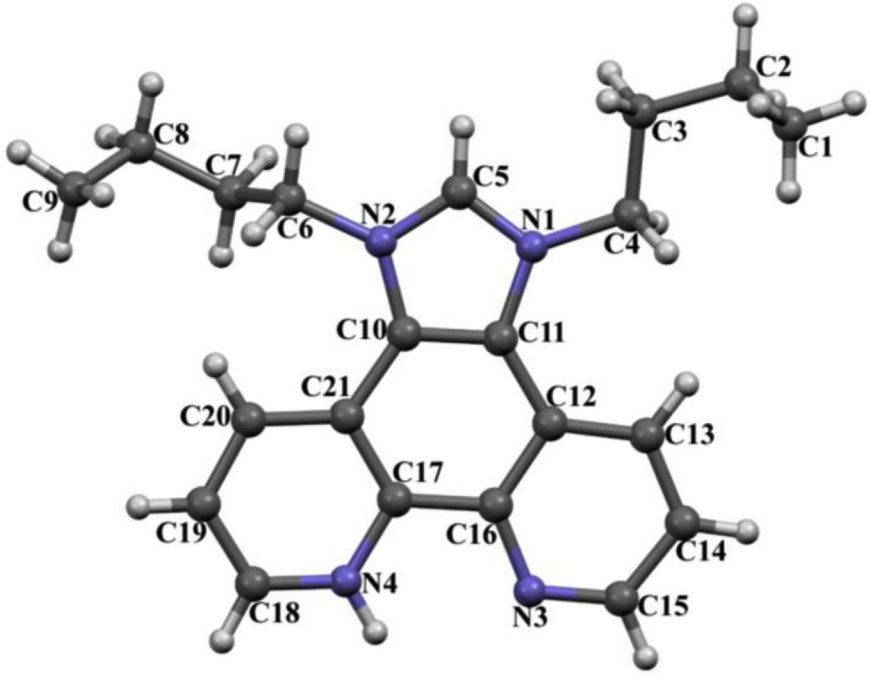


Fig. 1. The molecular structure of **L5.2HI** showing the atom numbering scheme.

compared to that for the **L_5.HPF$_6$** with PF_6 (δ 10.17 ppm). To learn solvating problem of **L_5.2HI**, the salt was crystallized beautifully out of an acetonitrile solution using Et_2O diffusion, and the structure was confirmed by single-crystal X-ray diffraction. The molecular structure of **L_5.2HI** was depicted in Fig. 1. The molecule was entirely flat and its bond lengths and angles were comparable to those in related carbene precursors (see Fig. 2).

In order to evaluate the differences between the mono- and poly-metallic complexes, monometallic complexes (**1**–**4**) were prepared and characterized by spectroscopic methods. But monometallic complexes **1** and **2** have been known in literature [18a,b]. The reaction of **L_5.HPF$_6$** with $PdCl_2(MeCN)_2$ in CH_2Cl_2 gave **5.HPF$_6$** complex (Scheme 2). For the synthesis of tri- (**6**) and tetra-nuclear (**7**) Pd(II) complexes, **5.HPF$_6$**, $Pd(OAc)_2$ and NaBr were used in different proportions. Pyridine-derived PEPPSI (Pyridine Enhanced Precatalysts Preparation, Stabilization and Initiation) type Pd(II) complex (**8**) was synthesized from cleavage reaction of dimeric Pd complex (**7**) with pyridine [19].

Reverse solubility ordering of complexes (**5.HPF$_6$**, **6**–**8**) in acetone or chlorinated solvents were observed **7** < **6** < **5.HPF$_6$** < **8** (mg/L). The complex **5.HPF$_6$** can be also soluble in aqueous solution. All complexes are stable toward air and moisture. The new complexes were characterized by elemental analysis and spectroscopic methods. ^{1}H NMR signal of the NCHN of **5.HPF$_6$** (δ 10.23 ppm) was observed to shift slightly to lower field as compared to its signal in the **5.HPF$_6$** salt (δ 10.17 ppm). The ^{31}P NMR spectrum for complex **5.HPF$_6$** in deuterated DMSO (−144.3 ppm) remains unchanged for up to one month.

In the polymetallic complexes (**6**–**8**), the coordination of the NHC ligands to the palladium is confirmed by the appearance of a downfield shifted in the ^{13}C NMR spectra for the carbenic carbon (δ 150.4, 154.5 and 171.9 ppm, respectively). Crystallization attempts were unsuccessful with the mono- and poly-metallic complexes.

The IR spectra of ligands and complexes showed many bands of varying intensities within 4000-400 cm^{-1}. The assignment of each individual band to a specific vibration has not been attempted. The presence of the −C═N- group in complexes was verified with υ (C═N) vibrations between 1561 and 1407 cm^{-1}.

The electronic spectra of the salts **L_5.2HI**, **1.PF$_6$**, the monometallic complexes (**1**–**4**, **5.HPF$_6$**) and polymetallic complexes (**6**–**8**) in dimethyl sulfoxide at room temperature showed medium-intensity bands around 406-383 nm range due to metal to-ligand charge transfer transitions (MLCT) and intense n-π*, π-π* ligand-centred transitions bands with maxima in the 358-224 nm range.

The molecular structure of **L_5.2HI** with the atom numbering scheme is shown in Fig. 1. Molecules of **L_5.2HI** are linked into sheets by a combination of O–H···I hydrogen bonds and π … π interactions. The details of these interactions are given in Supplementary material.

2.2. Electrochemistry

The electrochemical behaviors of the Pd complexes were investigated by cyclic voltammetry. Fig. 3 shows the cyclic voltammograms of 1.0×10^{-3} M of Pd-complexes recorded at a platinum electrode. Responses of the complexes were qualitatively similar except **5.HPF6**. The cyclic voltammogram of **5.HPF6** displayed two irreversible oxidation peaks at −1.14 V and +0.56 V and a quasi-reversible reduction peaks at −0.60 V. The irreversible oxidation peak at +0.56 V can be attributed to the oxidation of Pd(II) to Pd(IV). The quasi-irreversible reduction peak at −0.60 V

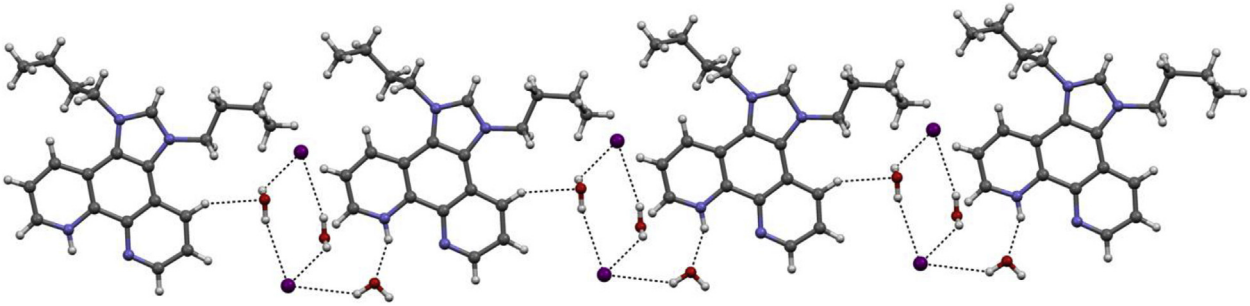
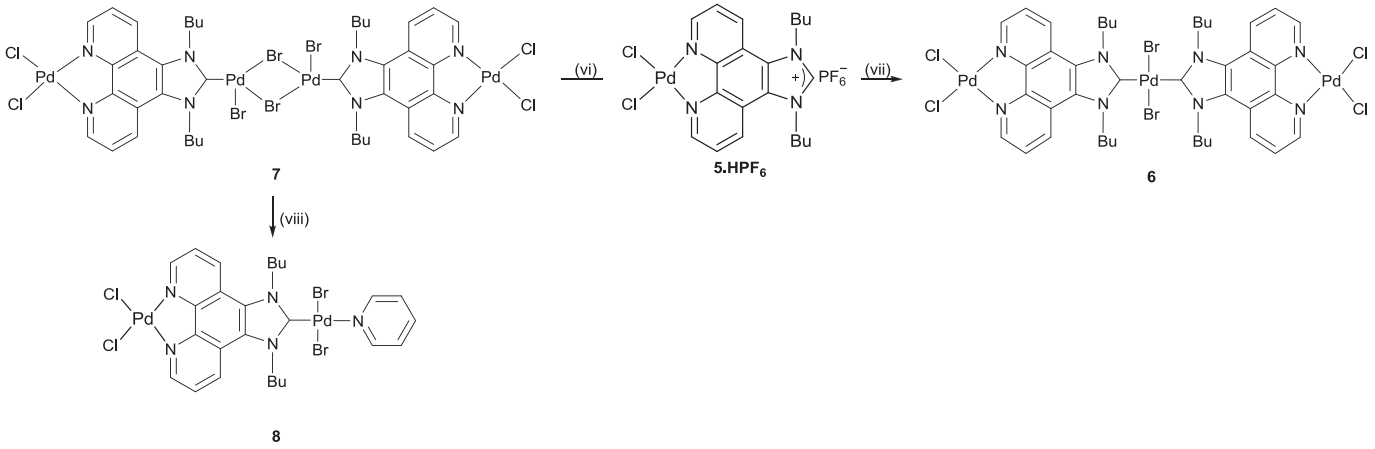


Fig. 2. The O–H···I, N–H···O and C–H···O hydrogen bonds of **L_5.2HI**.



Scheme 2. (vi) $Pd(OAc)_2$, DMSO, NaBr, 80 °C; (vii) $Pd(OAc)_2$, DMSO, NaBr, 80 °C; (viii) Pyridine, CH_2Cl_2, 25 °C.

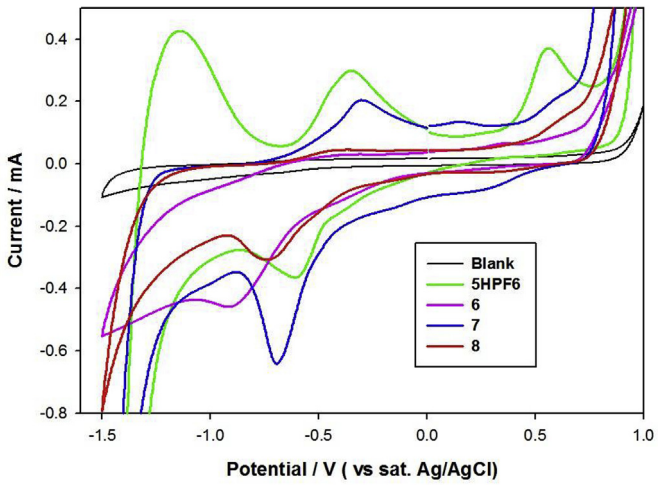
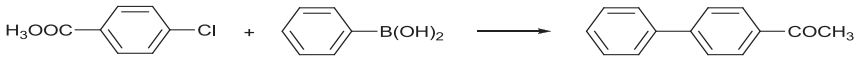


Fig. 3. Cyclic voltammogram of the complexes (**5.HPF$_6$**, **6**–**8**).

2.3. Catalytic activity

Peris at al. were prepared di- and tri-metallic complexes with polyaromatic–NHC-based ligands, and observed that the use of these complexes as catalysts enhanced catalytic activity compared to that offered by the related monometallic analogues [16]. This catalytic enhancement may be a catalytic cooperativity between the metals and a consequence of the π–π interaction between the substrate and the ligands. In their other study, a series of mono- and dimetallic complexes of palladium with N-methylene–pyrene substituents were described and proved that their activity in the Suzuki–Miyaura C-C coupling was highly influenced by the presence of π-stacking additives (pyrene and anthracene) in the reaction media [16c]. Transition metal-catalyzed coupling reactions are extremely powerful tools for carbon-carbon bond formation and have been widely utilized in a great number of syntheses. In particular, palladium-catalyzed C-C cross coupling reactions (Mizoroki-Heck, Suzuki-Miyaura, and Stille) have become classical vehicles to occur various carbon-carbon bonds.



was attributed to Pd(II) to Pd(0). The irreversible oxidation peak at −1.14 can be attributed the oxidation of electrochemically reduced imidazolium group [20]. On the other hand, the complex **6** displayed two quasi-reversible reduction peaks at −0.91 V and +0.20 V respectively. Similarly, complex **7** and **8** displayed two quasi-reversible reduction peaks at −0.69, +0.26 V and −0.73, +0.38 V respectively. In the same manner, the first quasi-reversible peaks about 0.3 V can be attributed to the reduction of Pd(IV) to Pd(II) and the second irreversible peaks about −0.7 V can be attributed to the reduction of Pd(II) to Pd(0) of complex **7** and **8** respectively.

The ease in reduction of Pd(IV) to Pd(II) in complexes was investigated and was sorted as **8** > **7** > **6** > **5HPF6**. The reduction potential of the complex is related to the charge density on metal. Thus, stronger electron-donor ligands will form Pd complexes with a smaller positive charge density on the metal [21]. As a result, the reduction potential will shift to more positive potential values. Therefore, the complex **8** bearing electron-donating pyridine group has the smallest positive charge density and the highest catalytic activity.

The activities of mono-metallic complexes (**1**–**4**, **5.HPF$_6$**) and poly-metallic complexes (**6**–**8**) toward the Suzuki-Miyaura coupling reactions of chloroacetophenone with phenyl boronic acid in the presences of Cs_2CO_3 as base in DMF-H_2O mixture (1:1, 4 mL) yielding the corresponding biphenyl products are given in Fig. 4. In order to evaluate the differences between the mono-, di-tri-and tetra-metallic complexes, we applied a low catalyst loading at 100 °C, 1.5 h.

The mol% of palladium was an important parameter to keep constant catalytic reaction while carrying out reactions of 1 mol% mono-nuclear complex (**1**–**4**, **5.HPF$_6$**), 0.5 mol% di-nuclear complex (**8**), 0.33 mol% for tri-nuclear complex (**6**) and 0.25 mol% tetra-nuclear complex (**7**). In the course of the Suzuki–Miyaura coupling reaction, black particles appear, which suggest that catalysts (**5.HPF$_6$**, **6**–**8**) are probably precursors to a catalytically active complex which is formed during the reaction. A direct comparision between mono-metallic (**1**–**4**, **5.HPF$_6$**) and poly-metallic complexes (**6**–**8**) was performed by GC analysis, which revealed nearly identical catalytic behavior for complexes. The poly-metallic catalysts are often substantially more efficient than a monometallic

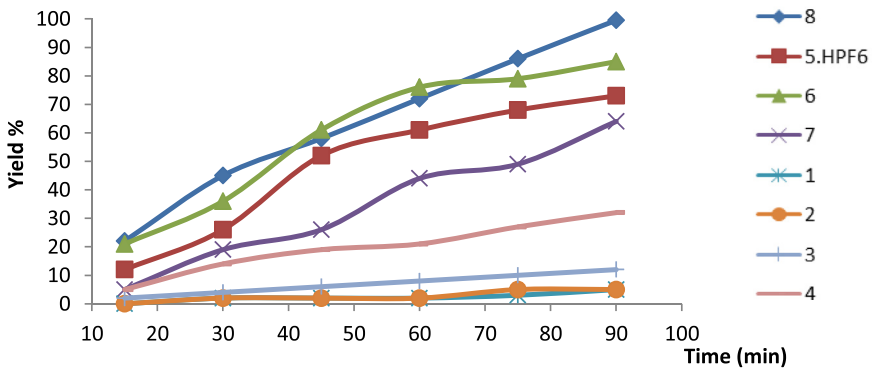


Fig. 4. The Suzuki–Miyaura reaction of 4-chloroacetophenone (1.0 mmol),and phenylboronic acid(1.5 mmol), Cs_2CO_3 (2.0 mmol), 1 mol % Pd., solvent DMF- H_2O (1:1, 4 mL), 100 °C, 90 min.

Table 1
Selected UV–visible, IR and NMR spectroscopic data.

Entry	Complex	IR (ν-cm^{-1})	UV–visible (nm)	$\delta C_{carbene}$ (ppm)
1	**L_5.2HI**	1580, 1408, 842	359, 285, 265, 236	–
2	**L_5.HPF$_6$**	1561, 1411, 842	383, 334, 291, 224	–
3	**1**	1580, 1423, 840	330, 305, 230, 205	–
4	**2**	1573, 1424, 817	385, 370, 320, 230	–
5	**3**	1537, 1445, 807	390, 355, 330, 305	–
6	**4**	1525, 1403, 804	405, 370, 345, 330	–
7	**5.HPF$_6$**	1530, 1416, 828	413, 374, 301, 245	–
8	**6**	1560, 1408, 750	401, 351, 304, 268	171.9
9	**7**	1550, 1407, 802	396, 347, 300, 257,	150.4
10	**8**	1515, 1407, 847	406, 358, 307, 262	154.5

catalyst of similar structure with the increase in catalyst performance attributed to "cooperative" interactions between the two metals and the substrate of the reaction [22]. The highest catalytic activity was observed with complex **8** bearing pyridine. Recently, Pd(NHC) complexes with PEPPSI have been used in the Suzuki-Miyaura coupling reaction with high activities [19,23]. Control experiment indicated that the coupling reaction did not occur in the absence of the complex. In order to improve the reactivity of our catalytic system, we firstly started to examine the influence of solvent. Among the various solvents explored; IPA, DMF, H_2O, DMF-H_2O, the best result were obtained with DMF-H_2O mixture (1:1, 4 mL). Catalyst **8** demonstrated very low activity with NaOH and KOH (Table 3). Na_2CO_3 was somewhat more effective than K_3PO_4. We also performed an additional experiment with mercury to assess whether the reaction system is homogeneous or heterogeneous. The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst [24]. It was found that the our system was homogenous by Hg(0) which did not influence suppression of the catalysis (Entry 9) (see Table 1).

After a brief catalyst **8** optimization study, the initial substrate range to **8** was tested in the cross-coupling of a number of aryl chloride substrate from reactive (electron-deficient) to unreactive (electron rich) with phenyl boronic acid (Table 4). This conditions allowed for the coupling of unactivated (entries 3, 4, 6), activated (entries1, 2, 5, 7) aryl chlorides in short reaction times.

The coupling of 4-bromoacetophenone with styrene (in DMF at 100 °C, Na_2CO_3 as base) was used as the model reaction in order to highlight the influence of complexes (**5.HPF$_6$**, **6**–**8**) on the catalytic activity. As shown in Table 5, the complex **8** bearing the pyridine shows a significantly higher activity compared to dimer complex **7**. Tri-nuclear complex **6** showed no difference in activity compared to the mono-nuclear complex **5.HPF$_6$**.

We explored the effectiveness of catalyst **8** on other aryl bromides (Table 6). The catalyst **8** gave good results when electron-donating (OMe, Me) and electron withdrawing (NO_2, CHO) substituents were present at the *para*-position of the arylbromide. It should be noted that in all cases only the *trans* products were selectively obtained as confirmed by ^{1}H NMR.

In an additional series of experiments we also studied the coupling reactions between aryl bromides and *n*-butyl acrylate. A methodology similar to that described for styrene was also employed for this purpose. Again, activated aryl bromides (4-bromoacetophenone, 4-bromonitrobenzene, 4-bromobenzaldhyde) provide the corresponding cinnamic esters in plausible yields (35–69%), while 4-bromoanisole yields 29% of the desired product. 4-bromotoluene gave lower yield; 22% in the presence of 0.33 mol % catalyst.

Both catalytic reactions indicate that the presence of the dimetallic structure in the catalyst introduces some benefits to the catalytic outcomes of the reactions. This study reveals several important implications regarding the influence of metal-metal interactions and ligand-substrate interactions in the performance of the catalysts used. Comparison of our results with those based on the use of monometallic complexes in other reaction systems show the advantages of the present method [25a,b].

Table 2
Crystal data and structure refinement parameters for compound **L_5.2HI**.

Empirical formula	$C_{21}H_{30}N_4I_2O_2$
Formula weight	624.29
Crystal system	Triclinic
Space group	P-1
a (Å)	8.3747 (5)
b (Å)	10.6876 (6)
c (Å)	13.9932 (8)
α (°)	91.687 (5)
β (°)	99.713 (4)
γ (°)	96.391 (4)
V (Å^3)	1225.35 (12)
Z	2
D_c (g cm^{-3})	1.692
μ (mm^{-1})	2.59
θ range (°)	1.5–27.2
Measured refls.	16786
Independent refls.	5157
R_{int}	0.076
S	1.06
R/w*R*	0.052/0.134
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	2.20/-1.47

3. Conclusion

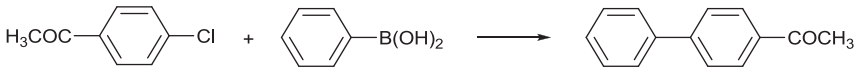
In this work, the preparation and characterization of Pd(II) complexes containing imidazo{ [4,5-f] [1,10]-phenanthrolin}l-2-ylidene were investigated. The complexes were successfully used as catalysts in the C-C coupling reactions such as Suzuki-Miyaura and Mizoroki-Heck reactions. The poly-nuclear complexes display better activities compared to the mono-nuclear derivatives, thus proposing that an increase in metal moieties leading to an increase in activity in cross-coupling reaction. The most active complex was **8**. This activity of **8** may be a consequence of the lability of pyridine ligands in the PEPPSI type complex. We believe that the unique topological properties of palladium complexes derived from imidazo{ [4,5-f] [1,10]-phenanthrolin}l-2-ylidene, that migh have facilitated the interaction between aromatic substrate and the catalyst through π stacking. The systems reported here are likely to be appropriate synthons for generating supramolecular assemblies and catalytic properties. Current research in our laboratory is focused in synthesis heterobimetalic complexes and their different cross-coupling reactions.

4. Experimental

All manipulations were performed in air. The solvents were used as received. The reagents were purchased from Sigma-Aldrich, Merck, Alfa Aesar and Acros Organics. The compound **L_{1-4}** were prepared according to the literature methods [14]. ^{1}H, ^{13}C NMR spectra were recorded with a Varian AS 400 Mercury instrument. As solvent, $CDCl_3$ and DMSO was employed. Chemical shifts (δ) were given in ppm and coupling constants (J) in Hz. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 series and UV spectra were on PG T60 UV–visible spectrophotometer. Elemental analyses were performed on Perkin Elmer PE 2400 elemental analyzer.

Mass spectrometry analysis was performed on an autoflex III MALDI TOF/TOF MS system (Bruker Daltonics, Bremen, Germany). The instrument was operated in positive ion reflectron mode with a reflectron acceleration voltage of 21 keV. The ions were generated

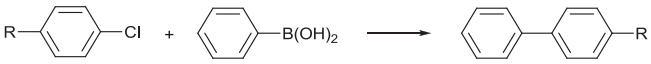
Table 3
Screening of bases and reaction conditions.



Entry	Base	Solvent	Yield (%)
1	Cs_2CO_3	*i*PrOH	21
2	Cs_2CO_3	DMF	44
3	Cs_2CO_3	H_2O	15
4	KOH	DMF/H_2O	52
5	Na_2CO_3	DMF/H_2O	67
6	K_2CO_3	DMF/H_2O	59
7	Cs_2CO_3	DMF/H_2O	99
8	K_3PO_4	DMF/H_2O	63
9	NaOH	DMF/H_2O	52
10	Cs_2CO_3	DMF/H_2O	89[a]

The Suzuki–Miyaura reaction of 4-chloroacetophenone (1.0 mmol), and phenylboronic acid (1.5 mmol), base (2.0 mmol), solvent (1:1, 4 mL), % 0.5 mol of cat. (**8**). Yields were determined by gas chromatography for an average of 2 runs.
[a] The reaction was carried out in the presence of a drop of Hg(0).

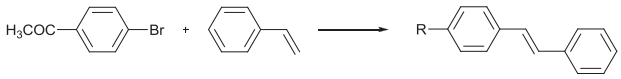
Table 4
Suzuki-Miyaura reaction of aryl chlorides.



Entry	Ar-Cl	Ar-Ph	Yield (%) 0.5 h	Yield (%) 1.0 h	Yield (%) 1.5 h
1	$CH_3(O)C$-C_6H_4-4-Cl	$CH_3(O)C$-C_6H_4-4-Ph	49	76	99
2	$CH_3(O)C$-C_6H_4-2-Cl	$CH_3(O)C$-C_6H_4-2-Ph	37	68	89
3	Me-C_6H_4-4-Cl	Me-C_6H_4-4-Ph	35	65	80
4	CH_3O-C_6H_4-4-Cl	CH_3OC-C_6H_4-4-Ph	30	71	82
5	OHC-C_6H_4-4-Cl	OHC-C_6H_4-4-Ph	34	69	82
6	CH_3O-C_6H_4-2-Cl	CH_3O-C_6H_4-2-Ph	21	47	54
7	NO_2-C_6H_4-4-Cl	NO_2-C_6H_4-4-Ph	29	56	83
8	2,4-$(Me)_2$ -C_6H_3-Cl	2,4-$(Me)_2$ -C_6H_3- Ph	32	65	73
9	2,3-$(Me)_2$ -C_6H_3-Cl	2,3-$(Me)_2$ -C_6H_3-Ph	38	59	69
10	2,4,6-$(Me)_3$ -C_6H_2-Cl	2,4,6-$(Me)_3$ -C_6H_2-Ph	17	38	51

The Suzuki–Miyaura reaction of Aryl chlorides (1.0 mmol), and phenylboronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol), DMF/H_2O (4 mL), % 0,5 mol of cat. (**8**), 100 °C.

Table 5
Palladium-catalyzed C-C coupling reaction of styrene with 4-bromoacetophenone.



Entry	Catalyst	Cat. loading (mol%)	Yield (%) 0.5 h	Yield (%) 1.0 h	Yield (%) 2.0 h	Yield (%) 4.0 h
1	**5**.HPF_6	1.00	12	26	38	45
2	**7**	0.25	25	38	51	65
3	**8**	0.33	34	45	66	84
4	**6**	0.50	13	30	46	54

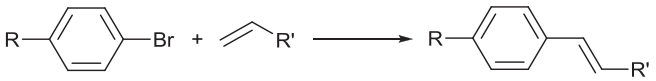
The 4-bromoacetophenone (1.0 mmol), styrene (1.2 mmol), Na_2CO_3 (2.0 mmol), DMF (4 mL), 100 °C.

using 337-nm nitrogen laser and the spectra were acquired over a 400–5000 *m*/*z* mass range. For each spectrum, at least 1000 laser shots were averaged at a laser frequency of 100 Hz and the system was externally calibrated using peptide calibration mixture (Bruker Daltonics, Peptide Calibration mixture).

The all-trans retinoic acid (RA) was used as a matrix throughout the analysis. The matrix was prepared at a concentration of 0.1 M in THF. The small amounts of samples were dissolved in the DMSO solvent. Each sample were mixed separately with an RA matrix as a ratio of 2:5 and, 1 μL, of final solution was deposited onto the stainless MALDI target and allowed to dry under ambient conditions based on dried droplet method.

Synthesis of the L_5.2HI: A mixture of **L_4** (2.0 g, 7.23 mmol), in 1-Iodobutane (10 mL) was refluxed for 48 h with stirring. The reaction mixture is allowed to cool down to room temperature and the 1-Iodobutane was distilled under reduced pressure. The dark red residue was washed with diethyl ether (3 × 10 mL) and dried in vacuum. Dark red crystals were obtained from slow evaporation of acetonitrile. Yield 3.00 g, 90%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.89 (s, 1 H, C_2-*H*), 9.20 (d, J = 4.2 Hz, 2 H, phen-*H*), 8.92 (d, J = 8.4 Hz, 2 H, phen-*H*), 7.96 (dd, J = 8.4, 4.4 Hz, 2 H, phen-*H*), 4.92 (t, J = 7.1 Hz, 4 H, butyl-C*H*$_2$), 1.99 (m, 4 H, butyl-C*H*$_2$), 1.48 (m, 4 H,

Table 6
Palladium-catalyzed C-C coupling reaction of styrene and *n*-butyl acrylate with aryl bromides.



Entry	R-Br	R'	Yield (%) 0.5 h	Yield (%) 1.0 h	Yield (%) 2.0 h	Yield (%) 4.0 h
1	$CH_3(O)C$-C_6H_4-4-Br	C_6H_5	29	44	63	84
2	NO_2-C_6H_4-4-Br	C_6H_5	41	50	65	71
3	Me-C_6H_4-4-Br	C_6H_5	25	38	54	65
4	CH_3O-C_6H_4-4-Br	C_6H_5	38	45	66	76
5	OHC-C_6H_4-4-Br	C_6H_5	42	58	78	92
6	$CH_3(O)C$-C_6H_4-4-Br	COO*n*Bu	9	17	21	35
7	NO_2-C_6H_4-4-Br	COO*n*Bu	10	19	28	46
8	Me-C_6H_4-4-Br	COO*n*Bu	4	11	15	22
9	CH_3O-C_6H_4-4-Br	COO*n*Bu	5	13	18	29
10	OHC-C_6H_4-4-Br	COO*n*Bu	15	27	42	69

Aryl bromide (0.50 mmol), styrene/*n*-butyl acrylate (0.75 mmol), Na_2CO_3 (2.00 mmol), **8** (0.33% mol), DMF (4 mL). Yields were determined by gas chromatography for an average of 2 runs.

butyl-CH_2), 0.98 (t, J = 7.3 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.5, 144.8, 142.1, 130.8, 125.4, 124.9, 118.4, 50.3, 30.9, 19.3, 13.9. Anal. Calc. for $C_{21}H_{26}N_4I_2$ (M = 588.27): C, 42.88; H, 4.45; N, 9.52; Found: C, 42.78, H, 4.40, N, 9.58%.

L_5.HPF$_6$: Yield: 1.80 g, 72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1 H, C_2-*H*), 9.21 (m, 2 H, phen-*H*), 8.43 (d, J = 8.0 Hz, 2 H, phen-*H*), 7.94 (m, 2 H, phen-*H*), 4.95 (t, J = 8.0 Hz, 4 H, butyl-CH_2), 2.03 (m, 4 H, butyl-CH_2), 1.50 (m, 4 H, butyl-CH_2), 1.02 (m, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.1, 144.7, 144.0, 135.6, 127.1, 126.5, 120.8, 50.7, 30.3, 19.5, 14.0.^{19}F NMR (376 MHz, DMSO-d_6): δ −70.5 (d, J = 639.2 Hz). ^{31}P NMR (161 MHz, DMSO-d_6): δ −144.1 (septet, J = 709.7 Hz). Anal. Calc. for $C_{21}H_{27}N_4F_6P$ (M = 480.43): C, 52.50; H, 5.66; N, 11.66; Found: C, 52.68, H, 5.80, N, 11.42%.

1: A mixture of Pd(MeCN)$_2$Cl$_2$ (52 mg, 0.2 mmol) and 1,10-phenanthroline (36 mg, 0.2 mmol) in MeCN (5 mL), stirred for 24 h at room temperature. The resulting cream precipitates were filtered. The crude product was washed with diethyl ether (2 × 5 mL), dried under vacuum. Yield 61 mg, 86%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.30 (dd, J = 5.0, 1.2 Hz, 2 H, phen-*H*), 9.07 (dd, J = 8.2, 1.6 Hz, 2 H, phen-*H*), 8.35 (s, 2 H, phen-*H*), 8.22 (dd, J = 8.2, 4.4 Hz, 2 H, phen-*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.2, 142.4, 138.0, 130.1, 128.0, 126.2. Anal. Calc. for $C_{12}H_8Cl_2N_2Pd$ (M = 357.53): C, 40.31; H, 2.26; N, 7.84; Found: C, 40.27; H, 2.18; N,7.83.

2: A mixture of Pd(MeCN)$_2$Cl$_2$ (52 mg, 0.2 mmol) and 1,10-phenanthroline-5,6-dione (42 mg, 0.2 mmol) in MeCN (5 mL), stirred for 24 h at room temperature. The resulting cream precipitates were filtered. The crude product was washed with diethyl ether (2 × 5 mL), dried under vacuum. Yield 64 mg, 89%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 (d, J = 5.2 Hz, 2 H, phen-*H*), 8.76 (dd, J = 8.4, 1.2 Hz, 2 H, phen-*H*), 8.02 (dd, J = 8.0, 5.4 Hz, 2 H, phen-*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.2, 150.6, 140.6, 128.1, 126.4, 109.4. Anal. Calc. for $C_{12}H_6Cl_2N_2O_2Pd$ (M = 387.51): C, 37.19; H, 1.56; N, 7.23; O, 8.26; Found: C, 37.16; H, 1.49; N, 7.21; O, 8.23.

3: A mixture of Pd(MeCN)$_2$Cl$_2$ (52 mg, 0.2 mmol) and 1*H*-imidazo[4,5-*f*] [1,10]phenanthroline (44 mg, 0.2 mmol) in MeCN (5 mL), stirred for 24 h at room temperature. The resulting cream precipitates were filtered. The crude product was washed with diethyl ether (2 × 5 mL), dried under vacuum. Yield 68 mg, 85%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (d, J = 6.4 Hz, 2 H, phen-*H*), 9.09 (d, J = 8.4 Hz, 2 H, phen-*H*), 8.66 (s, 1 H, C_2-*H*), 8.11 (dd, J = 8.2, 5.4 Hz, 2 H, phen-*H*). Anal. Calc. for $C_{13}H_8Cl_2N_4Pd$ (M = 397.56): C, 39.27; H, 2.03; N, 14.09; Found: C, 39.17; H, 2.00; N, 14.03.

4: A mixture of Pd(MeCN)$_2$Cl$_2$ (52 mg, 0.2 mmol) and 1-butyl-1*H*-imidazo[4,5-*f*] [1,10]phenanthroline (55 mg, 0.2 mmol) in MeCN (5 mL), stirred for 24 h at room temperature. The resulting cream precipitates were filtered. The crude product was washed with diethyl ether (2 × 5 mL), dried under vacuum. Yield 79 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (m, 2 H, phen-*H*), 8.98 (dd, J = 8.0, 1.6 Hz, 1 H, phen-*H*), 8.54 (dd, J = 8.0, 1.8 Hz, 1 H, phen-*H*), 7.99 (s, 1 H, C_2-*H*), 7.71 (m, 2 H, phen-*H*), 4.61 (t, J = 7.2 Hz, 2 H, butyl-CH_2), 2.03 (m, 2 H, butyl-CH_2), 1.51 (m, 2 H, butyl-CH_2), 0.98 (t, J = 6.8 Hz, 3 H, butyl-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 148.9, 147.9, 142.8, 130.4, 128.1, 123.6, 122.2, 47.9, 32.0, 22.6, 19.8. Anal. Calc. for $C_{17}H_{16}Cl_2N_4Pd$ (M = 453.66): C, 45.01; H, 3.55; N, 12.35; Found: C, 44.98; H, 3.49; N, 12.31.

5.HPF$_6$: A mixture of Pd(MeCN)$_2$Cl$_2$ (26 mg, 0.1 mmol) and **L_5.HPF$_6$** as a ligand (48 mg, 0.1 mmol) in MeCN (5 mL), stirred for 2 h at room temperature. The resulting cream precipitates were filtered. The crude product was washed with diethyl ether (2 × 5 mL), dried under vacuum. Yield: 58 mg, 88%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.23 (s, 1 H, C_2-*H*), 9.32 (m, 2 H, phen-*H*), 8.74 (d, J = 8.0 Hz, 2 H, phen-*H*), 8.09 (m, 2 H, phen-*H*), 5.03 (t, J = 8.0 Hz, 4 H, butyl-CH_2), 2.11 (m, 4 H, butyl-CH_2), 1.56 (m, 4 H, butyl-CH_2), 1.05 (m, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.8, 145.0, 143.6, 135.1, 126.9, 126.8, 120.3, 50.2, 30.0, 19.0, 13.5.^{19}F NMR (376 MHz, DMSO-d_6): δ −70.2 (d, J = 564.0 Hz). ^{31}P NMR (161 MHz, DMSO-d_6): δ −144.3 (septet, J = 709.9 Hz). Anal. Calc. for $C_{21}H_{25}Cl_2F_6N_4PPd$ (M = 655.74): C, 38.46; H, 3.84; N, 8.54; Found: C, 38.41, H, 3.79, N, 8.48%.%. MS (MALDI): m/z = 736.88 [M+2 + DMSO]$^+$.

6: The salt **5.HPF$_6$** (66 mg, 0.1 mmol), Pd(OAc)$_2$ (12 mg, 0.05 mmol), KBr (120 mg, 0.1 mmol) ve NaOAc (33 mg, 0.40 mmol) were suspended in DMSO (10 mL) and stirred at 90 C for 48 h. After the solution was cooled, DMSO was distilled in vacuum. The product was purified by column chromatography on silica gel. Elution with CH_2Cl_2 gave a product. Yield: 106 mg, 82%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.37 (d, J = 8.0 Hz, 4 H, phen-*H*), 9.10 (d, J = 8.0 Hz, 4 H, phen-*H*), 8.17 (m, 4 H, phen-*H*),5.42 (t, J = 8.0 Hz, 8 H, butyl-CH_2), 2.12 (m, 8 H, butyl-CH_2), 1.73 (m, 8 H, butyl-CH_2), 1.10 (m, 12 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.9, 150.3, 144.2, 133.7, 126.8, 126.7, 118.9, 50.9, 29.9, 19.2, 13.7. Anal. Calc. for $C_{42}H_{52}N_8Br_2Cl_4Pd_3$ (M = 1287.78): C, 39.17; H, 3.91; N, 8.70; Found: C, 39.28, H, 3.76, N, 8.64%. MS (MALDI): m/z = 1072.86 [M+2-2Br-Bu]$^+$.

7: The salt **5.HPF$_6$** (66 mg, 0.1 mmol), Pd(OAc)$_2$ (23 mg, 0.1 mmol), KBr (240 mg, 0.60 mmol) and NaOAc (33 mg, 0.40 mmol) were suspended in DMSO (10 mL) and stirred at 90 C for 48 h. The solvent was removed under vacuum. The product was purified by

column chromatography on silica gel. Elution with CH_2Cl_2 gave a product. Yield: 127.0 mg, 82%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.45 (d, J = 4.0 Hz, 4 H, phen-*H*), 9.10 (d, J = 4.0 Hz, 4 H, phen-*H*), 8.18 (m, 4 H, phen-*H*),5.42 (m, 8 H, butyl-CH_2), 2.13 (m, 8 H, butyl-CH_2), 1.73 (m, 8 H, butyl-CH_2), 1.11 (m, 12 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.4, 144.3, 133.7, 126.8, 126.6, 118.9, 50.9, 29.9, 19.2, 13.7. Anal. Calc. for $C_{42}H_{52}N_8Br_4Cl_4Pd_4$ (M = 1554.01): C, 32.46; H, 3.24; N, 7.21; Found: C, 32.14, H, 3.19, N, 7.17%. MS (MALDI): m/z = 855.98 [M/2+DMSO]$^+$.

8: A sample of compound **7** (100 mg, 0.07 mmol) and pyridine (13 mg, 0.10 mmol) were dissolved in 10 mL of CH_2Cl_2. The mixture was stirred at ambient temperature for 1 h. The volume of the solution was reduced to about 5 mL in vacuo. Diethyl ether (10 mL) was added to the solution to obtain a bright cream precipitate, which was collected by filtration, washed with 10 mL of diethyl ether, and dried in vacuo. Yield: 44 mg, 74%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.46 (d, J = 5.2 Hz, 2 H, py-*H*), 9.13 (d, J = 8.2 Hz, 2 H, Py-*H*), 8.93 (m, 2H, phen-*H*), 8.19 (m, 2 H, phen-*H*), 8.04 (m, 1 H, Py-*H*), 7.63 (m, 2 H, phen-*H*), 5.49 (br, 4 H, butyl-CH_2), 2.18 (m, 4 H, butyl-CH_2), 1.76 (m, 4 H, butyl-CH_2), 1.12 (m, 12 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.5, 150.9, 144.9, 134.2, 127.3, 127,0, 125.8, 119,5, 51.4, 30.6, 19.8, 14.1. Anal. Calc. for $C_{26}H_{30}Br_2Cl_2N_5Pd_2$ (M = 856.10): C, 36.48; H, 3.53; N, 8.18; Found: C, 36.88, H, 3.49, N, 8.26%. MS (MALDI): m/z = 856.90 [M]+.

4.1. Crystallographic data collection and refinement

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [26]. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods [26]. The parameters for data collection and structure refinement of compound **L$_5$.2HI** are listed in Table 2. Water H atoms were located in a difference map refined subject to a DFIX restraint. All hydrogen atoms bonded to C atoms were refined using a riding model with C–H = 0.93–0.97. The constraint U_{iso}(H) = 1.2U_{eq}(C and CH_2) or 1.5U_{eq}(CH_3) was applied. The following procedures were implemented in our analysis: data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [27]; program(s) used for molecular graphics were as follows: Mercury programs [28] software used to prepare material for publication: WinGX [29].

4.2. Electrochemical measurements

The cyclic voltammetry (CV) studies were carried out with Autolab 204 electrochemical system with three electrode assemblies. The three electrode system consisted of platinum disk as working electrode, platinum wire as a counter electrode and Ag/AgCl as reference electrodes. The voltammograms recorded at DMSO in the presence of 0.1 M of tetrabutil ammonium hexaflouro phosphate solution. The electrochemical responses of the complexes were studied by recording the cyclic voltammogram in the potential range between +1.0 V and −1.5 V at a scan rate of 0.1 V/s.

4.3. General procedure for the Suzuki coupling reactions

A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl chlorides (1.0 mmol), 2 mmol Cs_2CO_3, phenylboronic acid (1.5 mmol), diethyleneglycol-di-*n*-butylether (0.6 mmol, internal standard), 1 mol% for **1**–**4** and **5.HPF$_6$**; 0.5 mol % for **8**; 0.33 mol % for **6**; 0.25 mol % for **7** in 4 mL of DMF- H_2O (1:1, 4 mL). The flask was placed in a preheated oil bath (80 °C), under air atmosphere for 1.5 h. The conversion was monitored by gas chromatography following filtration. Yields were determined by gas chromatography for an average of two runs. Products were purified by column chromatography on silica gel using a mixture of hexane and EtOAc (4:1) as eluent.

4.4. General procedure for the Heck coupling reactions

A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl chlorides (1.0 mmol), 2 mmol Na_2CO_3, styrene (1.5 mmol), diethyleneglycol-di-*n*-butylether (0.6 mmol, internal standard), 1 mol% for **5.HPF$_6$**; 0.5 mol % for **8**; 0.33 mol % for **6**; 0.25 mol % for **7** in 4 mL of DMF. The flask was placed in a preheated oil bath (100 °C) under argon atmosphere for 4 h. After the required reaction time, the solution was allowed to cool down to room temperature and then extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent evaporated. The residue was purified by column chromatography on silica gel using a mixture of hexane and EtOAc (4:1) as eluent. Yields were determined by gas chromatography for an average of two runs.

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Supplementary material

CCDC 937867 contains the supplementary crystallographic data for **L$_5$.2HI**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.htmL (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data contain NMR spectra and Mass data for new complexes.

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