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PII: S0040-4020(18)31176-1

DOI: 10.1016/j.tet.2018.10.003

Reference: TET 29836

To appear in: *Tetrahedron*

Received Date: 26 May 2018

Revised Date: 27 September 2018

Accepted Date: 2 October 2018

Please cite this article as: Gacal E, Denizaltı , Kınal Armağ, Gökçe AytaçGü, Türkmen H, Sterically hindered N-aryl/benzyl substituted piperidoimidazolin-2-ylidene palladium complexes and their catalytic activities, *Tetrahedron* (2018), doi: https://doi.org/10.1016/j.tet.2018.10.003.

Graphical Abstract

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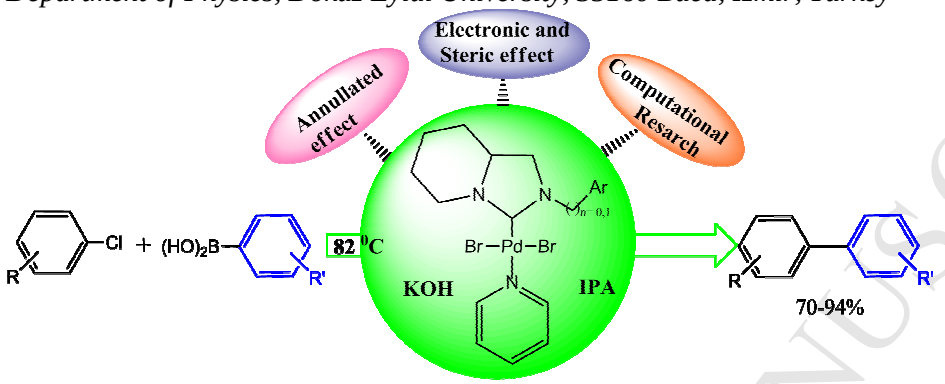

Tetrahedron
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Sterically Hindered N-Aryl/Benzyl Substituted Piperidoimidazolin-2-ylidene Palladium Complexes and Their Catalytic Activities

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Piperidoimidazolin-2-ylidene
Palladium
Suzuki-miyaura coupling
PEPPSI-Pd-NHC
DFT calculations

ABSTRACT

A series of N-aryl (**2a**,**b**) or benzyl (**2c**,**d**) substituted piperidoimidazolinium salts and their palladium complexes (**3a-d**) were prepared and characterized by ^{1}H, ^{13}C NMR, IR spectroscopy and elemental analysis. The crystal structures of **3a** and **3c** have been determined by X-ray crystallography. Thermogravimetric analysis (TGA) was applied to complexes (**3a**–**d**). The palladium complexes have been employed as catalyst for Suzuki-Miyaura cross coupling. The N-aryl substituted complex **3b** was a highly efficient precatalyst and successfully employed in Suzuki-Miyaura cross coupling reactions of (hetero)aryl chlorides with arylboronic acids in air. In addition, the oxidative addition step of the reaction mechanism involving chlorobenzene and the catalysts **3a**, **3b**, **3c** and **3d** were computationally investigated by the DFT-ω-B97X-D method and complete agreement were obtained with the catalytic results. To measure σ-donating and π-acceptor properties of the new ligands, the rhodium carbonyl complexes were also prepared.

1. Introduction

N-heterocyclic carbenes (NHCs) have attracted great interest in various fields of chemistry since the discovery of the first stable NHCs in the late 1980s and early 1990s.[1] Among them, five-membered heterocycles imidazol-2-ylidene and imidazolin-2-ylidene (**A**) and ring expanded analogue tetrahydropyrimidin-2-ylidene (**B**) are now known as normal NHCs (Figure 1).[2] By varying the number and the location of the heteroatoms in the core structure of the NHCs, unsymmetrical NHCs (uNHCs) can be generated. The variation of the substituents bound to the backbone can also lead to uNHCs. Many structural modifications, including steric tuning and changing the ligand backbone structure, had been pursued on uNHC ligands.[3] More recent studies have shown that the annulations of the 1,5- or 3,4-position of the imidazole ring also influence the electronic and steric properties of the resulting complexes.[4,5] Due to their steric demand and the synergy of inductive and mesomeric effects of the heteroatoms in vicinity to the carbenic center, their stability and donating ability is excellent as an uNHCs ligands.[6] For this purpose, herein, we compared NHC ligand (type **C**) with the analogues (**A** and **B**) and also investigated the influence of N-substituents on the catalytic activity of the system.

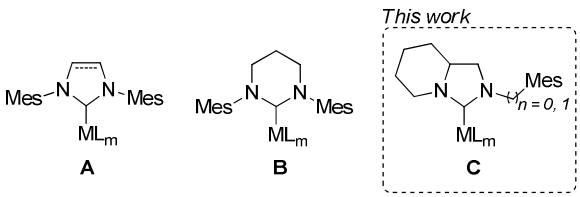


Figure 1.

Organ and co-workers reported pyridine stabilized NHC palladium complexes (PEPPSI-Pd) showing high activity towards C-C and C-N cross-coupling reactions.[7] Extensive studies on the structure and activities of PEPPSI-Pd complexes have been published since 2006.[8-10] Both modification of the NHC moiety and replacement of 3-chloropyridine by other ligands have attracted great interest in order to obtain better catalytic performance.[11]

Imidazol-2-ylidene, 4,5-dihydro-imidazol-2-ylidene or benzimidazol-2-ylidene based NHC systems were used in almost all these studies. In a recent study, Cavell et al. have published ring expanded PEPPSI-Pd complexes and their catalytic activity on cross coupling transformations.[12] They used aryl halides for Suzuki-Miyaura reaction and obtained good yields.

In this work, a series of facile-prepared PEPPSI-Pd-uNHC complexes and their catalytic application in Suzuki-Miyaura cross-coupling aryl chlorides with aryl boronic acid derivatives is reported. Moreover, the present study includes detailed investigations of the sterically hindered N-Aryl substituted piperidoimidazolin-2-ylidene PEPPSI-Pd complex **3b** in terms of catalytic activity on a broad variety of substrates, catalytic conditions (solvent, base, temperature). In comparison with the previously reported studies,[8h,i,12] the complex **3b** (0.01 mol %) gave better yield using aryl chloride in a short time.

2. Results and Discussion

2.1. Synthesis and characterization of Pd(II) and Rh(I) Complexes

Our synthetic strategy was based on the construction of the annulated N-heterocyclic carbene core from readily available building blocks, 2-aminomethyl-piperidine and 2-piperidinemethanol (Figure 2). The benzyl substituted piperidoimidazolinium salts were prepared according to our previous studies.[4a] In the ^{1}H and ^{13}C spectra of N-aryl or benzyl substituted piperidoimidazolinium salts (**2a-d**), the characteristic peaks due to N-CH-N protons and carbons were observed at 8.41 (**2a**), 8.42 (**2b**) and 8.55 (**2d**) ppm and at 156.5 (**2a**), 156.4 (**2b**) and 159.5 (**2d**) ppm in the ^{1}H and ^{13}C NMR spectra, respectively.

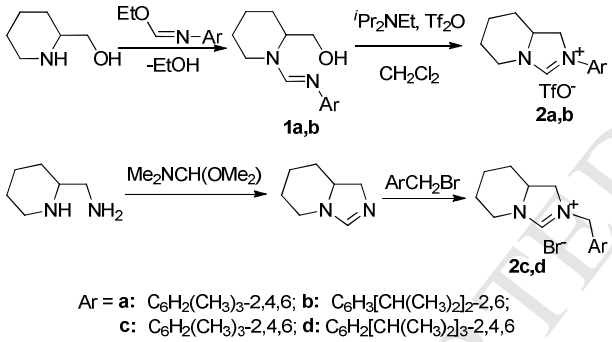


Figure 2. The synthesis of the piperidoimidazolinium salts **2a-d**.

Because the nature of substitution pattern of the employed NHC ligand has great influence on the catalytic activity,[13] PEPPSI-Pd complexes (**3a-d**) with different piperidoimidazolin-2-ylidene were prepared in pyridine. However, Organ showed that an (NHC)$PdCl_2$(pyridine) complex is more active than the (NHC)$PdCl_2$(3-chloropyridine) complex, suggesting that this improved activity could be due either to a higher dissociation rate of the pyridine or to a higher tendency to recoordinate to the species in solution.[14] The reaction of the ligand precursors with excess NaBr and $Pd(OAc)_2$ in neat pyridine under argon atmosphere affords (**3a-d**) in 45 to 80 % yields (Figure 3). The Pd(II) complexes are air and moisture stable yellow solids. The complexes (**3a-d**) were characterized by NMR spectroscopy and exhibit good solubility in CH_2Cl_2, $CHCl_3$ and DMSO. The ^{13}C NMR spectra display the resonance due to the carbene carbon atoms at δ = 179.1, 176.8, 178.4, 179.4 ppm for the complexes **3a-d** respectively. The benzylic protons in N-benzylic piperidoimidazolin-2-ylidene Pd complexes (**3c**, **3d**) display a singlet corresponding to a total of two protons at 5.29 (**3c**) and 5.30 (**3d**) ppm.

Thermogravimetric analysis (TGA) was applied to complexes

3a-d. TGA measurements of the complexes showed a significant weight loss, occurring in different steps in the range 180-450 °C (see ESI). This is attributed to decomposition of pyridine and piperidoimidazolin-2-ylidene. Metallic Pd or Pd salts (PdBr, $PdBr_2$) remained thermally intact under an inert gas atmosphere. The thermal decompositions of N-Aryl substituted complexes (**3a**,**b**) occur in one step whereas N- benzyl substituted complexes (**3c**,**d**) occur in multiple steps. The lower thermal stability of **3c, d** may be attributed to the benzyl substitution on NHC ligand. The thermal stability of the complexes played an important role on catalytic activity.

In recent studies of PEPPSI-Pd-NHC complexes,[8] the authors report that the catalytic properties of this type complexes in cross-coupling reactions can changeable with both the large σ- donating of NHC ligands and steric hindrance imported by the bulky N-aryl substituents employed systems.

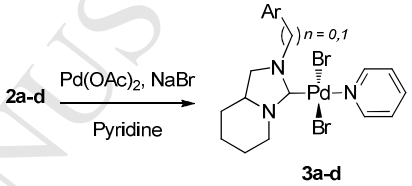


Figure 3. The synthesis of the palladium complexes **3a-d**.

With this in mind, the rhodium complexes (**4a-c**) were prepared by reaction of the rhodium dimer [Rh(μ-OMe)(COD)]$_2$ with two equivalents of the piperidoimidazolinium salts **2a-c** (Figure 4). They were purified by chromatography on silica gel. These complexes were observed to be stable towards air and moisture. They exhibit characteristic ^{13}C chemical shift, which provide a useful diagnostic tool for metal carbene complexes. The most significant resonance in the ^{13}C NMR spectra of **4a-c** is assigned to the metal carbene carbon at 209.1 (**4a**), 209.5 (**4b**) and 211.2 (**4c**) ppm. Coupling constant *J* (^{103}Rh-^{13}C) for the new complexes (**4a-c**) are comparable to those found for rhodium-NHC complexes that have been described previously.[4a,15]

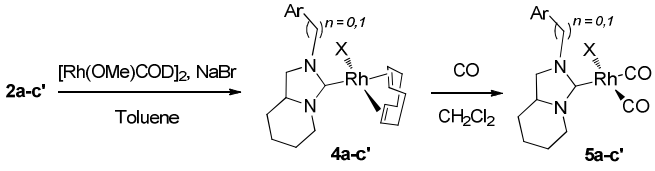


Figure 4. The synthesis of the rhodium complexes.

The *ν*(CO) measurement of [MCl(NHC)$(CO)_2$], (M = Rh, Ir) is the most commonly used method to determine electron donor ability of NHCs.[15,16] The [Ni(NHC)$(CO)_3$] complexes are also used but rhodium or iridium preferred because of the toxicity of [$Ni(CO)_3$] used as starting material in this case. To determine σ-donating ability of piperidoimidazolin-2-ylidene ligand, the COD complexes (**4a**, **4c**) were converted straight forwardly to the corresponding carbonyl derivatives **5a** and **5c**, which

allowed the electronic nature of the aryl or benzyl substituted piperidoimidazolin-2-ylidene ligand to be inferred from the IR spectra. The N-aryl substituted carbene complex **5a** exhibited lower wave numbers (**5a**: 2071.0 and 1992 cm-1, ν_{av}(CO) cm^{-1}= 2032; **5c:** 2072 and 1993 cm^{-1}, ν_{av}(CO) cm^{-1} = 2033). Additionally, the complex **5c´** did not give rise to difference when it was compared to **5c** (Figure 5).

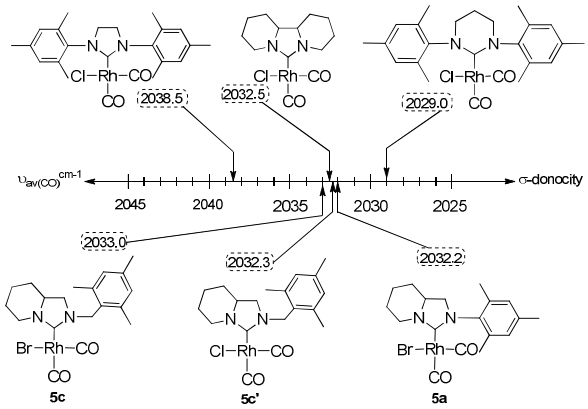


Figure 5. The carbonyl stretching frequencies of [Rh(NHC)X(CO)$_2$] complexes (X: Cl, Br).

This observation is in accordance with earlier report by Hahn.[16] The aryl substituted piperidoimidazolin-2-ylidene (**5a**) was found to be relatively better electron donor than benzyl-analogues (**5c**, **5c´**). Moreover, it is seen obviously that the values of carbonyl frequencies of the complexes (**5a**, **5c**, **5c´**) fall into between the types of NHC **A** and **B**. This observation indicates that the electronic and steric influences of the N-substituents are contributed to some extent on the electron donating property of the NHC ligand.

2.2. Structural Studies

The molecular structures of complexes **3a** and **3c** were determined by single crystal X-ray diffraction analysis. Details of data collection and refinement are presented as Supporting Information (Table S1, ESI). The structural analysis display the presence of slightly distorted square-planar coordination environments defined by the coordination of the metal to the pyridine ligand, the NHC ligand and the bromine atoms in a *trans* arrangement as shown in Figure 6. In **3a**, the asymmetric unit contains two symmetry independent molecules, denoted *A* and *B*, which do not differ significantly except disordered NHC ring appeared in molecule *B* (Figure S1, ESI). The palladium-NHC bond lengths in **3a** and **3c** are in agreement with the values found in our previously characterized Pd-NHC complexes.[10a,b,17] The NHC ring of **3a** adopts an envelope conformation in molecule *A* and also in the minor component of molecule *B*, and a twisted conformation in the minor component of molecule *B*. In **3c**, the conformation of disordered NHC ring is envelope and twisted for the major and minor components, respectively. In molecule *A* of **3a**, NHC ring is rotated with respect to the coordination plane by 88.3(4). In molecule *B* of **3a**, NHC ring with major and minor components are oriented at dihedral angles of 68.7(5)° and 77.5(6)°, respectively, with the coordination plane, whereas corresponding angles are 73.8(6)° and 78.8(6)° in **3c**. Following atoms in NHC rings are chiral centers with the absolute configurations: C3 (S), C24A (S) and C24B (R) in **3a**, and C3A (S) and C3B (R) in **3c**. Four C-H…Br and a C-H..N type intramolecular interactions are present in the crystal structure of **3a** (Figures S2 and Table S2, ESI). The molecular packing of the complexes are stabilized by a combination of two C−H…Br and two C-H…π type intermolecular interactions for 3a and two C−H…Br, a C-H…π and a π…π type intermolecular interactions for 3c (Figures S3-6 and Table S3, ESI). For both structures, these interactions those Br atoms involved may cause a departure from the ideal value of 180° for *trans* angles of Br-Pd-Br.

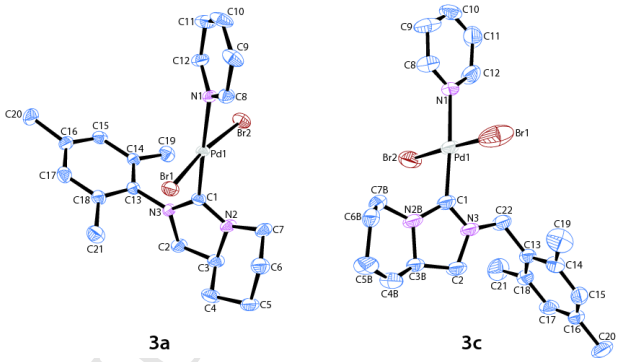


Figure 6. The molecular structures of **3a** and **3c** with displacement ellipsoids drawn at the 30% probability level. Only molecule A of **3a** and the major components of the disordered atoms of **3c** are shown for clarity. Selected bond lengths (Å) and angles (°):Complex **3a**; Pd1-C1 1.949(7), Pd1-N1 2.089(6), Pd1-Br2 2.4301(11), Pd1-Br1 2.4506(10), C1-Pd1-N1 177.9(3), Br2-Pd1-Br1 171.78(4), Complex **3c**; Pd1-C1 1.962(7), Pd1-N1 2.095(6), Pd1-Br2 2.4178(15), Pd1-Br1 2.4112(16), C1-Pd1-N1 176.5(3), Br2-Pd1-Br1 176.23(7).

2.3. Catalytic Suzuki-Miyaura Coupling Reaction with Pd(II) Complexes

We investigated the activity of complexes **3a-d** as catalysts for the coupling of 4-chloroacetophenone with phenylboronic acid under air and argon atmosphere (Figure 7). The complex **3b** was found to be the most active catalyst among all of these complexes tested. The sequence of the activity is **3b** > **3a** > **3c** > **3d**. The aryl-substituted complexes (**3a**, **3b**) were more efficient than their benzyl analogues (**3c**, **3d**). To confirm the decomposition of complexes (**3a**, **3c**) to Pd nanoparticles, the complexes (**3a**, **3c**) were investigated (initial, with the addition of KOH and at 65 ^{0}C) in $CDCl_3$. A direct comparison between catalysts **3a** and **3c** was performed by ^{1}H NMR analysis, which revealed different catalytic behavior for two complexes (see ESI). The catalyst **3a** also proved to be competent in this transformation, giving yields comparable those for the catalyst **3c.** A shorter induction period was present for **3a** relative to **3c,** which may be related to the reduction to the active Pd^0 species. The performance of the catalytic activity of the complexes revealed that improvement in activity could be reached not only by using the rigid architecture of the NHC ligand, but also by changing the substituents on the nitrogen atoms in NHC ligands.

The catalytic activities have impressed by both the rigid architecture of the NHC ligand and the substituents on the nitrogen atoms in NHC ligands. Moreover, the thermal stability of the complexes played an important role on catalytic activity. Because of the higher thermal stability and lower energy barriers, **3a** and **3b** exhibit higher catalytic activity. The above experimental results stabilities of **3c** to comparison **3a**, which

prompted us to investigate the mechanism by the density functional theory (DFT) method.

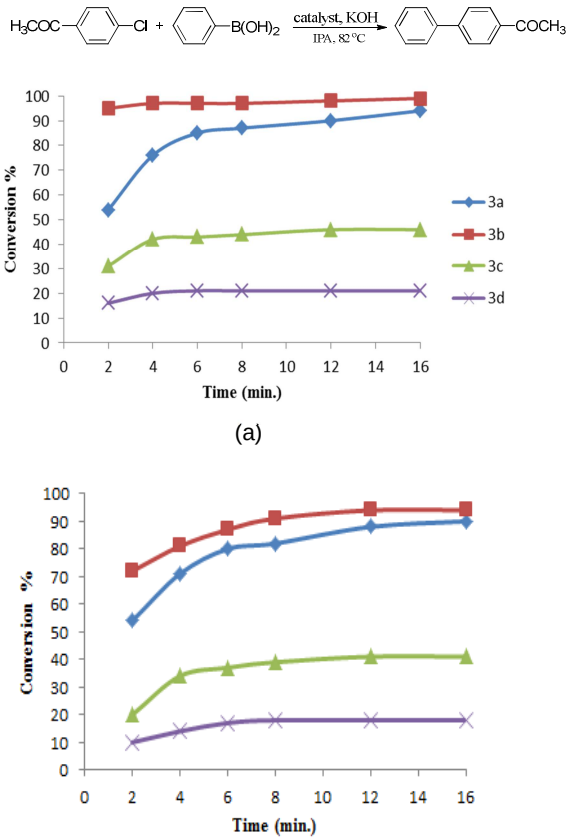


Figure 7. Time dependency of catalytic Suzuki-Miyaura coupling reaction by complexes **3a-d** under in air (a) and argon atmosphere (b).

The mechanism of Suzuki-Miyaura coupling reaction with Pd(II) complexes includes oxidative addition, transmetallation steps and reductive elimination.[18,19] The first step (the oxidation step) of this coupling reaction is generally the slowest step that determined the reaction rate. Recently, it is shown that the [Pd(NHC)(R-allyl)Cl] type catalysts are rather active in the Suzuki−Miyaura coupling reaction[20] and their activity comes from monoligated [NHC-Pd^0] complexes which serves as active catalytic species.[21] In the light of these information, we proposed a mechanism for the oxidative addition step (accepting as the rate determining step) involving the monoligated [NHC-Pd^0] complex (Figure 8). Specifically, we computationally determined the activation energy barriers of oxidative addition step involving benzene chloride and active catalysts, **3a'**, **3b'**, **3c'** and **3d'**, with DFT-ω-B97X-D method that gives better accuracy than the commonly used DFT-B3LYP due to inclusion of dispersion interactions.

Table 2. Activation free energy barriers of oxidative addition paths of the **3a′**, **3b′**, **3c′** and **3d′** active catalysts with benzene chloride.

Active catalysts	$\Delta G^{\#}$ (kcal/mol)	$\Delta\Delta G^{\#}$ (kcal/mol)	%Prob [a]	%Initial Conversion rate (theo)	%Initial Conversion rate (exp)[b]
3b'	11.26	0.00	100.00	67.24	48.72
3a'	11.96	0.71	34.90	23.47	28.21
3c'	12.86	1.61	9.13	6.14	15.38
3d'	13.31	2.06	4.68	3.15	7.69

[a]Prob = 100 exp(-$\Delta\Delta G^{\#}$/RT) at 298 K. [b]Conversion percent under air atmosphere within 2 min.

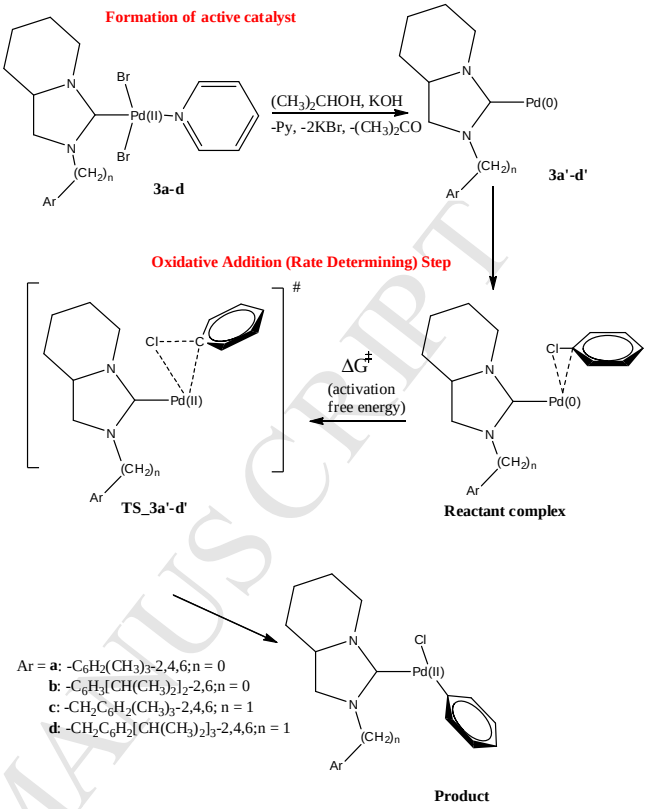
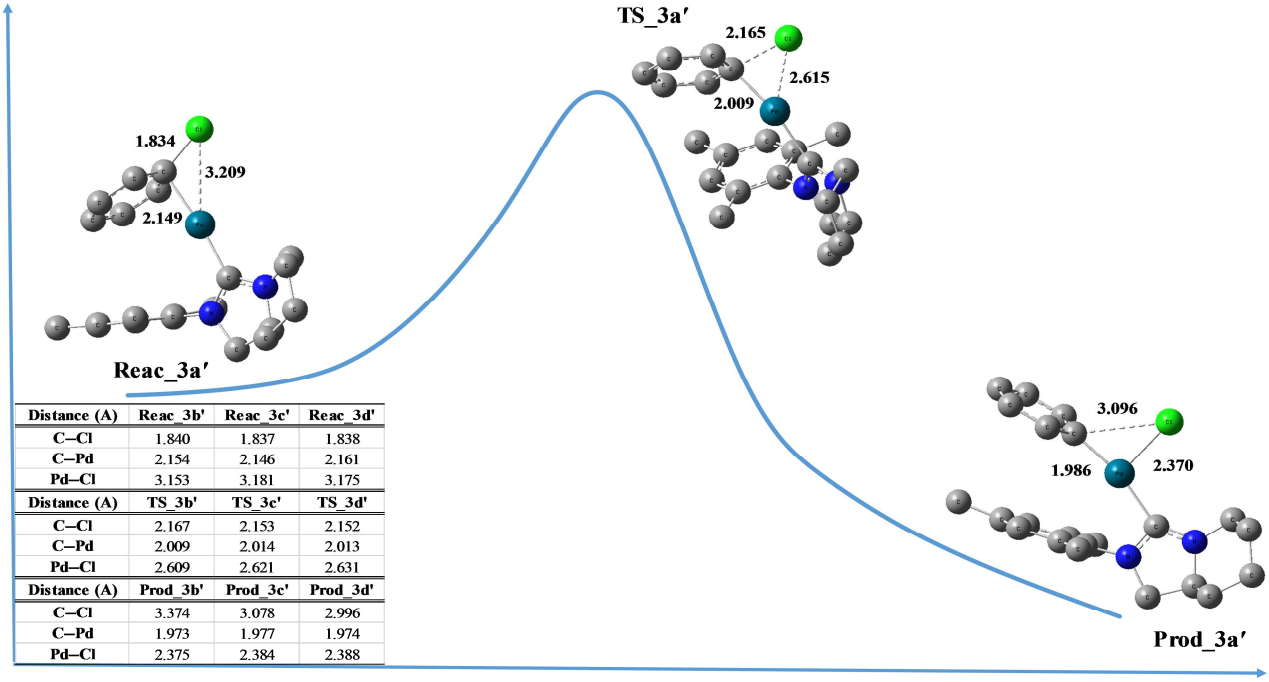


Figure 8. Representative initial steps of the mechanism of Suzuki-Miyaura coupling reaction with Pd(II) complexes (**3a-d**).

Figure 8 depicts the representative initial steps of the Suzuki-Miyaura coupling reaction mechanism, the oxidative addition paths of the **3a′, 3b′, 3c′** and **3d′** active catalysts with chlorobenzene while the corresponding activation Gibbs free energy barrier values of these paths obtained with ω-B97X-D method, % probability based on Boltzmann distribution formula, the calculated and experimental percent initial conversion rates are given in the Table 2. The ω-B97X-D barrier height order is **3b** < **3a** < **3c** < **3d**, leading to the theoretical activity sequence of **3b** > **3a** > **3c** > **3d**. The difference in activation free energy barriers let us calculate %probability of molecules passing through these barriers. % initial conversion rate, which can be defined as number of molecules passing through activation barrier under exactly the same conditions out of 100 molecules, is calculated using % probabilities. The last column gives experimental conversion percent under air atmosphere within 2 min. As seen from the table, theoretical and experimental initial conversion rates well agree with each other.

Figure 9 displays the important geometrical parameters of all species involved the oxidative addition paths of the **3a′, 3b′, 3c′** and **3d′** active catalysts. As seen from the figure, chlorobenzene approaches to active catalyst from its C atom attached to the Cl atom, hence each oxidative addition step starts with an active-catalyst-chlorobenzene complex (**reac_3a', reac_3b', reac_3c', reac_3d'**). Then, both the C and Cl atoms continue to approach Pd atom of the active catalyst (see TS structures), finally the C and Cl atoms completely separate from each other producing the oxidized active catalyst-chlorobenzene complex.



Distance (A)	Reac_3b'	Reac_3c'	Reac_3d'
C–Cl	1.840	1.837	1.838
C–Pd	2.154	2.146	2.161
Pd–Cl	3.153	3.181	3.175
Distance (A)	**TS_3b'**	**TS_3c'**	**TS_3d'**
C–Cl	2.167	2.153	2.152
C–Pd	2.009	2.014	2.013
Pd–Cl	2.609	2.621	2.631
Distance (A)	**Prod_3b'**	**Prod_3c'**	**Prod_3d'**
C–Cl	3.374	3.078	2.996
C–Pd	1.973	1.977	1.974
Pd–Cl	2.375	2.384	2.388

Figure 9. Important geometrical parameters of species in the oxidative addition path (the distances given are in Å units)

The conditions employed for the catalytic experiments are depicted on Table 3. In order to improve the reactivity of our catalytic system, we examined the influence of the base. We used Cs_2CO_3, KOH, K_3PO_4, NaOH and KO^{t}Bu (entries 1-5). The highest yield of the desired product was obtained with KOH as the base (entry 1). Preferred solvent for Suzuki-Miyaura cross-coupling reactions was *i*-PrOH as MeOH and EtOH solvents lowered the catalytic activity. The decrease of the reaction temperature from 82 to 25 ^{o}C led to decrease the yield (entries 8, 9). If the loading catalyst **3b** was further reduced to 0.01 to 0.001 mol%, the cross-coupling product was obtained in satisfying yields of 95 and 70 % (entries 1, 10).

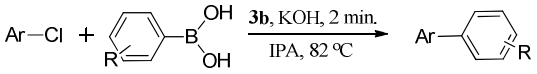
Table 3. Different reaction conditions for Suzuki-Miyaura Coupling with complex **3b** for 2 min.

Entry	Solvent	Base	Loading **3b**(mol%)	T [^{o}C]	Yield[%]
1	*i*-PrOH	KOH	0.01	82	95
2	*i*-PrOH	K_3PO_4	0.01	82	70
3	*i*-PrOH	Cs_2CO_3	0.01	82	53
4	*i*-PrOH	NaOH	0.01	82	33
5	*i*-PrOH	*t*BuOK	0.01	82	31
6	EtOH	KOH	0.01	78	54
7	MeOH	KOH	0.01	65	22
8	*i*-PrOH	KOH	0.01	50	35
9	*i*-PrOH	KOH	0.01	25	12
10	*i*-PrOH	KOH	0.001	82	70
11	*i*-PrOH	KOH	0.0001	82	28

After optimizing the reaction conditions, the palladium complex (**3b**) was also tested for various substrates in Suzuki-Miyaura reaction (Table 4). Generally, moderate to good conversions 70-93% were obtained (Table 3). For arylboronic acids with electron-withdrawing or electron donating groups, such as fluorine, methyl, methoxy and formyl groups, the reactions could afford the corresponding biaryls in moderate to good yields. Apart from the electronic features, the impact of steric hindrance aryl chlorides with 2,6-dimethylphenylboronic acid was also investigated (Table 4, entries 11-13). *para*-substituted chloride was compared with *ortho*-substituted ones, the former gave the 85% yield (Table 4, entry 11). When the aryl chloride had multiple substituents, the reaction yield exceeded 75% (Table 4, entries 1, 13) over 2 minutes.

Cavell group's synthesized various Pd-PEPPSI complexes and obtained 96% yield at 80 ^{o}C within 1 h for coupling reaction of phenyl chloride with the phenylboronic acid.[12] Lee and co-workers performed the Suzuki-Miyaura reaction using aryl bromides at 80 ^{o}C and the yield's up to 100 after 2 h.[8i] The Pd-PEPPSI complexes were synthesized by Organ's group showed 95% yield at 65 ^{o}C within 24 h using aryl chlorides.[8b] In comparison with these studies, our results are acceptable.

Table 4. The Suzuki-Miyaura reaction of aryl chlorides with phenylboronic acids using catalyst



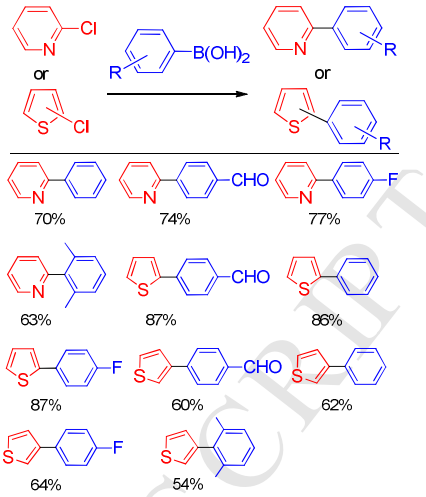
Entry	Ar	R	Yield (%)
1	2,5-Me-Ph	H	75
2	4-CN-Ph	H	89
3	4-CHO-Ph	H	93
4	2-Me-Ph	H	77
5	4-Me-Ph	H	70
6	4-MeO-Ph	H	71
7	Ph	H	80
8	4-CN-Ph	4-MeO	82
9	Ph	4-MeO	77
10	4-Me-Ph	4-MeO	74
11	4-Me-Ph	2,6-Me	85
12	2-Me-Ph	2,6-Me	73
13	2,4-Me-Ph	2,6-Me	71
14	4-Me-Ph	4-F	77
15	2-Me-Ph	4-F	74
16	4-Me-Ph	4-CHO	73
17	4-MeO-Ph	4-CHO	72
18	4-CN-Ph	4-CHO	71
19	2-Me-Ph	4-CHO	75
20	Ph	4-CHO	72
21	4-NO_2-Ph	4-CHO	85

Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), KOH (2.0 mmol), catalyst (0.01 mol %), IPA (1 mL).

The new complexes have been demonstrated to be significantly different from those of the related five- and six-membered NHC-Pd-PEPPSI systems in cross-coupling reactions. Overall, this procedure is suitable for this synthesis of diverse biaryls through the cross-coupling reaction of different aryl electrophiles and aryl boronic acids.

Heteroaryl chlorides (3-chloropyridine, 2-chlorothiophene, 3-chlorothiophene) were also tested under our optimized conditions using different aryl boronic acids (benzeneboronic acid, 4-formylphenylboronic acid, 2,6-dimethylphenylboronic acid, 4- fluorophenylboronic acid) and were produced in 63-77% yield, demonstrating the applicability of heterocyclic substrates in this procedure (Table 5). Initially, 3-chloropyridine was explored. Reacting 4-formylphenylboronic acid with 3-chloropyridine formed 74% of the expected product. The arylboronic acids in combination with 2-chlorothiophene gave the cross-coupling products in very good yields. Having chloride at the 3-position of thiophene ring, the decreasing the yields of the products was observed compared to its 2-position analogue.

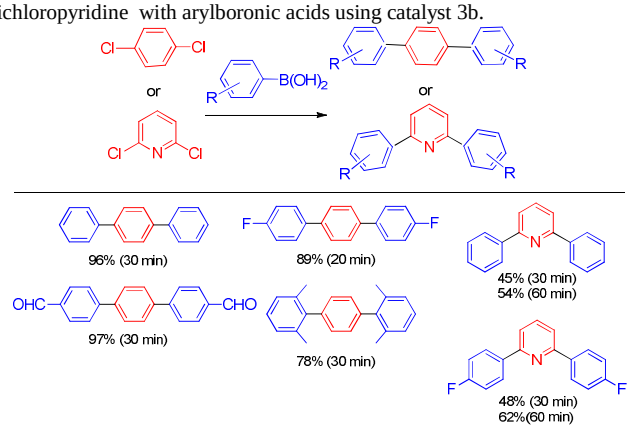
Table 5. The Suzuki-Miyaura reaction of heteroaryl chlorides with arylboronic acids using catalyst **3b**.



Reaction conditions: heteroaryl halide (1.0 mmol), arylboronic acid (1.2 mmol), KOH (2.0 mmol), catalyst **3b** (0.01 mol %), IPA (1 mL), 10 min, in air.

Double coupling of 1,4-dichlorobenzene and 2,6-dichloropyridine with arylboronic acid derivatives was also performed efficiently to give dicoupling products (Table 6). The efficiency and selectivity towards diarylated product were obtained in higher times. Phenylboronic acid, 4-Formylphenylboronic acid, 2,6-dimethylphenylboronic acid, 4-fluorophenylboronic acid were all successfully treated with 1,4-dichlorobenzene to provide products in high yields (78-97%). Encouraged by the very good results obtained with the catalyst 3b for 1,4-dichlorobenzene, we decided to focus our research on a more difficult substrate 2,6- dichloropyridine. As expected, the double couplings of benzeneboronic acid, 4-fluorophenylboronic acid with 2,6- dichloropyridine afforded corresponding heteropolyarenes. An increase of the reaction time to 1 h resulted in increase of the yield to 62 %.

Table 6. The Suzuki-Miyaura reaction of 1,4-dichlorobenzene or 2,6-dichloropyridine with arylboronic acids using catalyst 3b.



Reaction conditions for double coupling: aryl halide (1.0 mmol), arylboronic acid (2.4 mmol), KOH (4.0 mmol), catalyst **3b** (0.01 mol %), IPA (1 mL), in air.

3. Conclusions

New ligands and eleven metal complexes related with our previously reported piperidoimidazolin-2-ylidene system were

prepared and fully characterized. The molecular structures of the complexes **3a** and **3c** were determined by X-ray crystallography. The catalytic activities of the palladium complexes (**3a-d**) were investigated in the Suzuki-Miyaura coupling between aryl chlorides and arylboronic acids. In this transformation, aryl-substituted pre-catalysts significantly surpassed benzyl substituted pre-catalysts in efficiency. Pre-catalyst **3d** with a 2,4,6-tri(isopropyl)benzyl arm showed lower activity; however the catalytic activity of 2,6-di(isopropyl) substituted pre-catalyst (**3b**) was higher than that of 2,4,6-mesityl substituted (**3a**). Moreover, the DFT calculations revealed that catalysts **3a** and **3b** exhibit higher catalytic activity than catalysts **3c** and **3d** due to having lower energy barriers.

4. Experimental Section

The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (toluene, diethyl ether, hexane, tetrahydrofuran), P_2O_5 (dichloromethane). Toluene, tetrahydrofuran, dichloromethane, ethanol, hexane, pentane, diethyl ether, acetonitrile, and methanol were obtained from J. T. Baker and Merck. All reagents were purchased from commercial sources and used as received. Ethyl N-2,6-di-iso-propyl-phenylformamidinate, ethyl N-mesityl-formamidinate[22] and **2c**[23] were prepared according to literature. ^{1}H and ^{13}C NMR spectra were taken with Varian AS 400 Mercury instrument operating at 400 MHz (1H), 100.56 (^{13}C). $CDCl_3$ was employed as solvent. Chemical shifts (δ) are given in ppm relative to TMS; coupling constants (J) in Hz. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a Perkin–Elmer Pyris 6 analyzer in the range 50–950 ^{0}C in alumina crucibles under nitrogen (flux rate: 20 cm^3 min^{-1}) at a heating rate of 20 ^{0}C min $^{-1}$ using alumina as reference. The yields of catalytic experiments were measured by GC Agilent brand (7890A series) on a HP-5 capillary column and with a FID detector) in Ege University in Faculty of Science at Department of Chemistry.

*4.1. Synthesis of **1a-b***

A neat mixture of 2-piperidine methanol (3.2 g, 28.0 mmol) and ethyl N-(2,6-diisopropylphenyl)formamidinate (6.37 g, 28.0 mmol) was stirred at 160 °C for 3 h in a flask equipped with a Dean-Stark condenser to remove ethanol. The residue was dried under high vacuum, and the resulting orange oil (**1a**) was used without further purification. By using the same procedure as above, but with ethyl N-mesityl-formimidate (2.8 g, 28.0 mmol) and 2-piperidinemethanol (3.2 g, 28.0 mmol) was obtained as a orange oil (**1b**). But the compounds were not isolated exactly.

*4.2. Synthesis of aryl substituted piperidoimidazol-2-ylidene derivatives salts, **2a-b***

Amidine **1a-b** (42.5 mmol) was dissolved in 20 mL of dried CH_2Cl_2 and cooled to -78 ^{o}C. Diisopropylethylamine (8.9 mL, 51.0 mmol) was added to the solution, followed by the dropwise addition of trifluoromethanesulfonicanhydride (7.1 mL, 42.5 mmol). The solution was stirred for 30 min at -78 ^{o}C and then warmed to room temperature. The volatiles were removed under reduced pressure to afford an orange solid, which was washed with diethylether until no colored impurities remained. The resulting white powder was washed with water (3x50.0 mL), and with technical grade diethyl ether (3x30.0 mL), dissolved in CH_2Cl_2, and the solution was dried with sodium sulfate. After filtration, the concentrated solution was layered with hexane, and the triflate salt **2a-b** was isolated as colorless crystals upon cooling at -10 ^{o}C overnight.

2a: Yield: 60%; m.p = 210-212 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.35 (s, 1 H, NC*H*), 6.91 (s, 2 H, $NC_6H_2(CH_3)_3$), 4.43-4.46 (m, 1 H, piperidine-*H*), 4.26-4.32 (m, 2 H, piperidine-*H*), 3.41-3.47(m, 1 H, NCH_2CH), 3.62-3.66 (m, 1 H, NCH_2CH), 1.62-2.15 (m, 6 H, piperidine-*H*), 2.28, 2.24 (s, 9 H, $NC_6H_2(CH_3)_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 156.4 (N*C*H), 140.4, 135.6, 130.6, 130.1 (Ar-*C*), 120.1 (CF_3SO_3), 60.2 (NCH_2CH), 56.8, 46.4, 32.5, 25.9, 22.3 (piperidine-*C*), 21.2, 17.7 ($NC_6H_2(CH_3)_3$). Anal.Calc. for $C_{17}H_{23}F_3N_2O_3S$: C, 52.03; H, 5.91; N, 7.14. Found: C, 52.15; H, 6.03; N, 7.33.

2b: Yield: 62%; m.p = 170-172 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.44 (s, 1 H, NC*H*), 7.43 (t, *J* = 4.0 Hz, 1 H, $NC_6H_3[CH(CH_3)_2]_2$), 7.21 (d, *J* = 4.0 Hz, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 4.37-4.49 (m, 1 H, piperidine-*H*), 4.27-4.33 (m, 2 H, piperidine-*H*), 3.64-3.70 (m, 2 H, NCH_2CH), 2.82-2.88 (m, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 1.67-2.22 (m, 6 H, piperidine-H), 1.37, 1.41 (d, *J* = 4.0 Hz, 12 H, ^{i}*Pr*-H). ^{13}C NMR ($CDCl_3$, δ, ppm): 156.4 (N*C*H), 147.1, 146.6, 131.3, 129.9 (Ar-*C*), 125.1 (CF_3SO_3), 60.2 (NCH_2CH), 55.2, 46.6, 32.8, 28.8, 26.2 (piperidine-*C*), 18.7 ($NC_6H_3[CH(CH_3)_2]_2$). Anal. Calc. for $C_{20}H_{29}F_3N_2O_3S$: C, 55.28; H, 6.73; N, 6.45. Found: C, 55.21; H, 6.63; N, 6.88.

2d: Different benzylbromides (15.0 mmol) and piperidoimidazole (1.86 g, 15.0 mmol) were refluxed in toluene (15.0 mL) for 4 h. The volume of the solution was reduced to 5.0 mL, and diethyl ether was added to the remaining solution, which was vigorously stirred and then decantated. The solid residue was washed with diethyl ether (3 × 20.0 mL) to obtain an orange solid, which was recrystallized from methanol/diethyl ether (3 mL/20.0 mL). Yield: 52%; m.p= 209-211 ^{o}C. ^{1}H NMR (DMSO, δ, ppm): 8.10 (s, 1 H, NC*H*), 7.07 (s, 2 H, $NCH_2C_6H_2[CH(CH_3)_2]_3$), 2.78-3.32 (m, 5 H, piperidine-*H*, $NCH_2C_6H_2[CH(CH_3)_2]_3$), 1.35-1.73 (m, 6 H, piperidine-*H*), 1.12-1.19 (m, 18 H, $NCH_2C_6H_3[CH(CH_3)_2]_3$). ^{13}C NMR (DMSO, δ, ppm): 160.2 (N*C*H), 149.3, 148.2, 132.6, 130.1 (Ar-*C*), 77.8 (NCH_2CH), 64.5 (NCH_2CH), 60.9, ($NCH_2C_6H_3[CH(CH_3)_2]_3$), 55.2, 46.6, 32.8, 28.8, 26.2 (piperidine-*C*), 18.7 ($NC_6H_2[CH(CH_3)_2]_3$). Anal. Calc. for $C_{23}H_{37}BrN_2$: C, 65.55; H, 8.85; N, 6.65. Found: C, 66.74; H, 8.88; N, 6.80.

4.3. General procedure of [PdBr$_2$(NHC)Py] complexes

The $Pd(OAc)_2$ (65.0 mg, 0.3 mmol) was added to **2a** (125.0 mg, 0.3 mmol) and NaBr (60.0 mg, 0.6 mmol) which was dissolved in pyridine (5.0 mL) under argon atmosphere. The reaction mixture was stirred 1 h at RT and then refluxed for 48 h. Meanwhile the reaction progress was controlled with layer chromatography. After removal of the solvent under vacuum, the precipitate was purified by column chromatography on silica gel using CH_2Cl_2 to give a yellow solid. The residue was recrystallized from CH_2Cl_2 / $(C_2H_5)_2O$ (v/v = 3:10 mL)

3a: Yield: 45%; m.p = 296-298 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.69-8.71 (m, 2 H, Py-*H*), 7.58-7.62 (m, 1 H, Py-*H*), 7.14-7.18 (m, 2 H, Py-*H*), 6.95 (s, 2 H, $NC_6H_2(CH_3)_3$), 5.32 (dd,

J = 16 Hz, 1 H, piperidine-*H*), 3.91-3.96 (m, 2H, NCH_2CH), 3.35-3.48 (m, 2 H, piperidine-*H*), 2.31, 2.47, 2.50 (s, 9 H, $NC_6H_2(CH_3)_3$), 1.18-2.00 (m, 6 H, piperidine-*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 179.1 (N*C*N), 152.6, 138.5, 137.7 (Py-*C*), 134.6, 129.8, 129.7, 124.4 (Ar-*C*), 59.9 (NH*C*H_2CH), 57.6, 49.1, 32.8, 25.9, 23.7 (piperidine-*C*), 21.3, 20.2 ($NC_6H_2(CH_3)_3$). Anal. Calc. for $C_{21}H_{27}Br_2N_3Pd$: C, 42.92; H, 4.63; N, 7.15. Found: C, 42.88; H, 4.52; N, 7.30.

3b: Yield: 50%; m.p = 328-330 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.73-8.75 (m, 2 H, Py-*H*), 7.59-7.64 (m, 1 H, Py-*H*), 7.39 (t, *J* = 8.0 Hz, 2 H, Py-*H*), 7.30 (d, *J* = 12.5 Hz, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 7.16-7.19 (m, 1 H, $NC_6H_3[CH(CH_3)_2]_2$), 5.47 (dd, *J* = 4.4, 12.8 Hz, 1 H, piperidine-*H*), 3.43-4.04 (m, 6 H, NCH_2CH, piperidine-*H*, $NC_6H_3[CH(CH_3)_2]_2$), 1.59-2.09 (m, 6 H, piperidine-*H*), 1.46, 1.16 (t, *J* = 12.0 Hz, 12 H, $NC_6H_3[CH(CH_3)_2]_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 179.6 (N*C*N), 152.3, 148.3, 137.4 (Py*C*), 134.2, 129.4, 124.5, 124.2 (Ar-*C*), 60.1 (NCH_2CH), 59.5 ($NC_6H_3[CH(CH_3)_2]_2$), 49.3, 32.3, 28.3, 26.9, 26.8 (piperidine-*C*), 25.6, 24.4, 23.4 ($NC_6H_3[CH(CH_3)_2]_2$). Anal. Calc. for $C_{24}H_{33}Br_2N_3Pd$: C, 45.77; H, 5.28; N, 6.67. Found: C, 45.79; H, 5.53; N, 6.84.

3c: Yield: 80%; m.p= 272-274 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.02-9.04 (m, 2H, Py-*H*), 7.12-7.76 (m, 1 H, Py-*H*), 7.29-7.33 (m, 2 H, Py-*H*), 6.87 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.25 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.08-5.12 (dd, *J* = 4.4, 13.2 Hz, 1 H, piperidine-*H*), 3.66-3.71 (m, 1 H, NCH_2CH), 3.26-3.35 (m, 2 H, NCH_2CH, piperidine-*H*), 2.73-2.77 (m, 1 H, piperidine-*H*), 2.27, 2.41 (s, 9 H, $NCH_2C_6H_2(CH_3)_3$), 1.36-1.96 (m, 6 H, piperidine-*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 178.4 (N*C*N), 152.4, 138.4, 137.8 (Py*C*), 137.7, 129.2, 128.3, 124.5 (Ar-*C*), 59.2 (NCH_2CH), 53.8 ($NCH_2C_6H_2(CH_3)_3$), 48.6, 48.3, 31.9, 25.5, 23.2 (piperidine-*C*), 20.8, 20.9 ($NCH_2C_6H_2(CH_3)_3$). Anal. Calc. for $C_{22}H_{29}Br_2N_3Pd$: C, 43.91; H, 4.86; N, 6.98. Found: C, 44.01; H, 4.81; N, 7.11.

3d: Yield: 68%; m.p = 322-324 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.04 (dd, *J* = 5.6 Hz, 2 H, Py-*H*), 7.35 (t, *J* = 7.6 Hz, 1 H, Py-*H*), 7.32 (t, *J* = 5.6 Hz, 2 H, Py-*H*), 7.03 (s, 2 H, $NCH_2C_6H_2[CH(CH_3)_2]_3$), 5.27-5.35 (m, 2 H, $NCH_2C_6H_2[CH(CH_3)_2]_3$), 5.07-5.10 (m, 1 H, piperidine-*H*), 3.28-3.68-9 (m, 5 H, NCH_2CH, $NCH_2C_6H_2[CH(CH_3)_2]_3$), 2.79-2.90 (m, 2 H, piperidine-*H*), 1.37-1.95 (m, 6 H, piperidin-*H*), 1.23-1.27 (m, 18 H, $NCH_2C_6H_2[CH(CH_3)_2]_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 178.2 (N*C*N), 152.5, 149.1, 148.9 (Py*C*), 137.7, 125.5, 124.4, 121.3 (Ar-*C*), 59.3 (NCH_2CH), 53.9 ($NCH_2C_6H_2[CH(CH_3)_2]_3$), 48.4, 46.5, 34.2, 31.6, 29.2 (piperidine-C), 25.5, 24.4, 24.3, 23.9, 23.2 ($NCH_2C_6H_2[CH(CH_3)_2]_3$). Anal. Calc. for $C_{28}H_{41}Br_2N_3Pd$: C, 49.03; H, 6.03; N, 6.13. Found: C, 49.19; H, 6.12; N, 5.99.

4.4. General procedure of [RhBr(NHC)COD] complexes

$[Rh(\mu\text{-}OMe)COD]_2$ (54.0 mg, 0.12 mmol) was added to **2a** (100.0 mg, 0.24 mmol) and NaBr (46.0 mg, 0.48 mmol) which was dissolved in dry toluene (6.0 ml) under argon atmosphere. The reaction mixture was stirred 1 h at 25 °C and then refluxed for 48 h. Meanwhile the reaction progress was controlled with layer chromatography. After removal of the solvent under vacuum, the rhodium compound was purified by column chromatography on silica gel using CH_2Cl_2 to give a yellow solid. The residue was recrystallized from CH_2Cl_2 / $(C_2H_5)_2O$ (v/v = 3:10 mL)

4a: Yield: 57.7 mg, 45%; m.p = 190-192 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.00, 6.87 (s, 2 H, $NC_6H_2(CH_3)_3$), 5.41-5.50 (m, 1 H, piperidine-*H*), 4.79-4.93 (m, 2 H, piperidine-*H*), 3.73-3.83 (m, 2 H, NCH_2CH, COD-C*H*), 3.56-3.61 (m, 1 H, COD-C*H*), 3.18-3.28 (m, 2 H, NCH_2CH, COD-C*H*), 3.11-3.16 (m, 1 H, COD-C*H*), 2.52, 2.05 (d, *J* = 4.0 Hz, 6 H, $NC_6H_2(CH_3)_3$), 2.34-2.39 (m, 2 H, piperidine-*H*), 2.32 (s, 3 H, $NC_6H_2(CH_3)_3$), 1.81-1.95 (m, 8 H, piperidine-*H*, COD-CH_2), 1.39-1.65 (m, 8 H, piperidine-*H*, COD-CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm): 208.3 (d, $^1J_{Rh\text{-}C}$ = 57.7, Rh-$C_{carbene}$), 138.2, 138.1, 137.6, 137.5, 136.1, 135.1 (Ar-*C*), 97.2 (d, *J* = 9.2 Hz, COD-*C*H), 69.4 (d, *J* = 14.0 Hz, COD-*C*H), 59.6 (NCH_2CH), 57.4, 49.5, 34.3, 32.9, 30.8, 30.6, 29.7, 27.6, 27.1, 23.7 (piperidine-*C*, COD-*C*H_2), 21.0 20.4 ($NC_6H_2(CH_3)_3$). Anal.Calc. for $C_{24}H_{34}BrN_2Rh$: C, 54.05; H, 6.43; N, 5.25. Found: C, 54.12; H, 6.51; N, 5.34.

4b: Yield: 75.2 mg, 45%; m.p= 201-203 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.29-7.34 (m, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 7.11-7.14 (m, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 5.43-5.54 (m, 1 H, piperidine-*H*), 4.83-4.94 (m, 2 H, piperidine-*H*), 3.71-3.88 (m, 3 H, NCH_2CH, COD-C*H*), 3.55-3.60 (m, 1 H, COD-C*H*), 3.33-3.45, 2.88-2.97 (m, 2 H, COD-C*H*), 2.69-2.80, 2.27-2.39 (m, 2 H, $NC_6H_3[CH(CH_3)_2]_2$), 1.72-2.14, 1.62-1.55, 1.31-1.38 (m, 10 H, piperidine-*H*, COD-CH_2), 1.09, 1.20, 1.49 (m, 12 H, $NC_6H_3[CH(CH_3)_2]_2$). ^{13}C NMR (CDC_{l3}, δ, ppm): 208.9 (dd, $J_{Rh\text{-}C}$ = 46.0, Rh-$C_{carbene}$), 149.3, 146.1, 135.9, 128.7, 124.9, 123.5 (Ar-*C*), 97.6 (d, *J* = 6.0 Hz, COD-*C*H), 68.2 (dd, *J* = 14.0 Hz, COD-*C*H), 60.4, 60.1, 59.5, 59.1, 50.0, 48.6, 34.6, 32.6, 30.3, 29.7, 28.1, 27.2, 26.6, 25.2, 23.1 ($NC_6H_3[CH(CH_3)_2]_2$). Anal.Calc. for $C_{27}H_{40}BrN_2Rh$: C, 56.36; H, 7.01; N, 4.87. Found: C, 56.41; H, 7.19; N, 5.02.

4c: Yield: 447.2 mg, 68%; m.p= 168-170 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.85 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.25-5.48 (m, 1 H, $NCH_2C_6H_2(CH_3)_3$), 4.87-5.12 (m, 3 H, COD-C*H*, $NCH_2C_6H_2(CH_3)_3$, 3.45-3.56 (m, 4 H, COD-C*H*, piperidine-*H*), 3.09-3.21 (m, 2H, NCH_2CH), 2.57-2.64 (m, 2 H, piperidine-*H*), 2.36, 2.26 (s, 9 H, $NCH_2C_6H_2(CH_3)_3$), 2.25-2.49 (m, 4 H, piperidine-*H*), 1.86-1.97, 1.29-1.50 (m, 8 H, COD-CH_2). ^{13}C NMR (CDC_{l3}, δ, ppm): 208.9 (dd, $J_{Rh\text{-}C}$ = 46.0, Rh-$C_{carbene}$), 138..2, 137.5, 129.2, 129.1 ($CH_2C_6H_2(CH_3)$, 98.5, 98.4, 98.1, 98.0 (COD-CH), 70.1, 69.5, 67.8, 67.4 (COD-CH), 59.1 (NCH_2CH), 54.1 ($NCH_2C_6H_2(CH_3)_3$), 48.3, 33.1, 32.2, 31.9, 31.7, 29.5, 28.4, 26.6, 26.1 (piperidine-C, CODCH_2), 22.6 ($C_6H_2(CH_3)_3$-*o*-CH_3), 20.7 ($C_6H_2(CH_3)_3$-*p*-CH_3). Anal. Calc. for $C_{25}H_{36}BrN_2Rh$: C, 54.86; H, 6.63; N, 5.12. Found: C, 54.93; H, 6.59; N, 5.25.

4c´: Yield: 423.4 mg, 70 %; m.p = 160-162 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.80 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.29-5.42 (m, 1 H, $NCH_2C_6H_2(CH_3)_3$), 4.80-5.08 (m, 3 H, COD-C*H*, $NCH_2C_6H_2(CH_3)_3$, piperidine-*H*), 3.39-3.54 (m, 4 H, COD-C*H*, piperidine-*H*), 3.05-3.18 (m, 2H, NCH_2CH), 2.51-2.61 (m, 2 H, piperidine-*H*), 2.32, 2.21 (s, 9 H, $NCH_2C_6H_2(CH_3)_3$), 2.24-2.42 (m, 4 H, piperidine-*H*), 1.76-1.95, 1.47-1.21 (m, 8 H, COD-CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm): 211.0 (dd, $J_{Rh\text{-}C}$ = 45.0, Rh-$C_{carbene}$), 138.1, 137.4, 129.1, 128.9 (Ar-*C*), 98.2, 97.8 (d, *J* = 6.0 Hz, COD-*C*H), 70.0, 67.5, (d, *J* = 14.0 Hz, COD-*C*H), 58.1 ($NCH_2C_6H_2(CH_3)_3$), 54.1 (NCH_2CH), 48.0, 47.8, 33.2, 32.2, 32.1, 31.9, 29.4, 28.5, 26.1, 23.3, (piperidine-*C*, COD-*C*H_2), 20.7 20.8 ($NCH_2C_6H_2(CH_3)_3$). Anal.Calc. for $C_{25}H_{36}ClN_2Rh$: C, 59.70; H, 7.21; N, 5.57. Found: C, 59.87; H, 7.75; N, 5.49.

4.5. General procedure of [RhX(NHC)(CO)$_2$] complexes

The complex (**4a**) (120.0 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (6.0 mL) and carbon monoxide was passed through the solution for 3 h. After the completion of the time, volatiles were removed in vacuo and residue was washed with cold *n*-pentane to give a yellow solid.

5a: Yield: 85.6 mg, 79%; m.p= 182 ^oC; ν_{av}(CO) cm^{-1}: 2032.2. ^1H NMR ($CDCl_3$, δ, ppm): 6.91 (s, 2 H, $NC_6H_2(CH_3)_3$), 4.72 (d, *J* = 12 Hz, 1 H, piperidine-*H*), 3.89-3.99 (m, 2 H, NCH_2CH, piperidine-*H*), 3.39-3.43 (m, 1 H, NCH_2CH), 3.18-3.27 (m, 1 H, piperidine-*H*), 2.17-2.34 (m, 2 H, piperidine-*H*), 2.29 (s, 9 H, $NC_6H_2(CH_3)_3$), 1.89-2.00 (m, 2 H, piperidine-*H*), 157-1.64 (m, 2 H, piperidine-*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 200.1 (d, J_{Rh-C} = 39.0 Hz, Rh-$C_{carbene}$), 185.9 (d, *J* = 52.0 Hz, *C*O), 182.8 (d, *J* = 60.0 Hz, *C*O), 138.4, 134.9, 129.9, 128.9 (Ar-*C*), 60.3, 57.4, 48.6, 34.1, 32.8, 23.3 (piperidine-*C*), 21.1, 22.3 ($NC_6H_2(CH_3)_3$). Anal. Calc. for $C_{18}H_{24}BrN_2O_2Rh$: C, 44.74; H, 5.01; N, 5.80. Found: C, 44.82; H, 5.13; N, 5.88.

5c: Yield: 74.2 mg, 82%; m.p= 168-170 ^oC; ν_{av}(CO) cm^{-1}: 2033.0. ^1H NMR ($CDCl_3$, δ, ppm): 6.86 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.05-5.11 (m, 1 H, $NCH_2C_6H_2(CH_3)_3$), 4.55-4.71 (m, 2 H, piperidine-*H*, $NCH_2C_6H_2(CH_3)_3$), 3.67-3.71, 3.13-3.41, 2.77-2.87 (m, 4 H, piperidine-*H*, NCH_2CH), 2.33, 2.26 (s, 9 H, $NCH_2C_6H_2(CH_3)_3$), 2.24-2.41 (m, 2 H, piperidine-*H*), 1.44-1.89 (m, 4 H, piperidine-*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 199.3 (d, J_{Rh-C} = 45.0 Hz, Rh-$C_{carbene}$), 186.7 (d, *J* = 70.0 Hz, *C*O), 182.8 (d, *J* = 77.0, *C*O), 137.8, 129.4, 129.3, 128.3 (Ar-*C*), 59.9, 59.4, 54.1, 48.8, 32.3, 25.5, 23.1 (piperidine-*C*, $NCH_2C_6H_2(CH_3)_3$), 20.5, 20.9 ($NCH_2C_6H_2(CH_3)_3$). Anal.Calc. for $C_{19}H_{26}BrN_2O_2Rh$: C, 45.89; H, 5.27; N, 5.63. Found: C, 45.93; H, 5.25; N, 5.68.

5c´: Yield: 59.7 mg, 74%; m.p= 162-164 ^oC; ν_{av}(CO) cm^{-1}: 2032.3. ^1H NMR ($CDCl_3$, δ, ppm): 6.84 (s, 2 H, $NCH_2C_6H_2(CH_3)_3$), 5.02-5.09 (m, 1 H, $NCH_2C_6H_2(CH_3)_3$), 4.53-4.69 (m, 2 H, piperidine-*H*, $NCH_2C_6H_2(CH_3)_3$), 3.64-3.75, 3.12-3.42, 2.76-2.85 (m, 4 H, piperidine-*H*, NCH_2CH), 2.32, 2.26 (s, 9 H, $NCH_2C_6H_2(CH_3)_3$), 2.24-2.37 (m, 2 H, piperidine-*H*), 1.37-1.87 (m, 4 H, piperidine-*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 199.2 (dd, J_{Rh-C} = 40.0 Hz, Rh-$C_{carbene}$), 186.3 (dd, *J* = 16.0 Hz, *C*O), 182.7 (d, *J* = 76.0, *C*O), 137.8, 129.4, 128.6, 128.3 (Ar-*C*), 59.9, 59.4, 54.1, 48.9, 32.4, 26.2, 23.1 (piperidine-*C*, $NCH_2C_6H_2(CH_3)_3$), 20.5, 20.9 ($NCH_2C_6H_2(CH_3)_3$). Anal. Calc. for $C_{19}H_{26}ClN_2O_2Rh$: C, 50.40; H, 5.79; N, 6.19. Found: C, 50,62; H, 5.63; N, 6.35.

4.6. General procedure for the Suzuki coupling reaction

A two-necked 25.0 mL flask fitted with a reflux condenser and septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), KOH (2.0 mmol), diethyleneglycol-di-n-butylether (0.6 mmol, internal standard), and the palladium-pyridine catalyst (0.01 mol %) in isopropyl alcohol (1.0 mL) was added. The mixture was heated to 82 ^oC under an air atmosphere. The conversion was monitored by gas chromatography.

4.7. Computational details

The geometrical parameters of all stationary points on the oxidative addition steps were optimized and the structures were characterized with the *ω*-B97X-D method[25] (which gives better accuracy due to inclusion of dispersion interactions) employing LANL2DZ basis set[26] for all atoms. The transition state structures were also verified with IRC calculations at the level of optimization. To be able to obtain better energy values, single point energy calculations were performed with ω-B97X-D employing the triple split valence basis set 6-311+G(d,p) was used for C, H, O, N, and Cl atoms, while LANL2TZ+ECP[26,27] was employed for the Pd center in isopropyl alcohol medium through integral equation formalism polarized continuum model (IEFPCM).[28] All calculations were performed utilizing Gaussian 09 quantum chemistry program suite.[29]

4.8. X-ray Crystallography

Single crystal X-ray diffraction data for **3a** and **3c** were collected on an Agilent Diffraction Xcalibur diffractometer with an Eos CCD area detector using graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at room temperature. The data collection, cell refinement, and data reduction were executed using the CrysAlisPro[28] program. The absorption corrections were done analytically using a multifaceted crystal model.[29] The crystal structures were solved by direct methods using SHELXS-97[30] and the refinement (on F2) was carried out by full-matrix least square techniques using SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms (C-H= 0.95 to 0.99 Å). Molecular graphics are prepared using ORTEP-3[31] and PLATON[32] software. In both structures, some of the atoms of the NHC rings (N5, C24, C25, C26, C27, C28 in **3a** and N2, C3, C4, C5, C6, C7 in **3c**) were disordered over two different orientations (letters A and B for minor and major components, respectively). The refinements converged to final occupancies of 0.521(6)/0.479(6) in **3a** and 0.514(8)/0.486(8) in **3c**. Equal Uij constraints (EADP) were used for all of the disordered atom pairs.

CCDC 1053359 (**3a**) and 1053360 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

Acknowledgements

All calculations reported in this paper were performed at High Performance and Grid Computing Center (TRUBA resources), ULAKBIM. The authors also acknowledge Dokuz Eylül University for the use of the Agilent Xcalibur Eos diffractometer (purchased under University Research Grant no. 2010.KB.FEN.13). Financial support from Ege University (project 2010-FEN -046 and 2010- Fen-076) is gratefully acknowledged.

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