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Amido-functionalized N-Heterocyclic carbene ligands and corresponding PalladiumComplexes: Synthesis, characterization and catalytic activity

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ABSTRACT

Thirteen amido functionalized N-heterocyclic carbene ligands were synthesized via a simple synthetic procedure. The synthesized ligands were characterized by NMR, FAB-MS and single crystal X-ray analysis, unanimously confirming the proposed structures. Subsequent complexation with a palladium precursor allowed the synthesis of four new complexes. The molecules structures of all four complexes were confirmed by single crystal X-ray diffraction. The catalytic activity of the synthesized ligands and complexes was tested for the Heck alkenylation of aryl iodide readily allowing the synthesis of cinnamic acids esterin yields ranging from 67 to 93% for ligands and 69–95% for complexes while turn-over-numbers of up to 75000 was observed for the complexes.

1. Introduction

The introduction of palladium-catalyzed cross-coupling reactions as powerful C–C bond forming synthetic methodologies in the late 70s revolutionized the way syntheses were carried out in academia as well as industries [1,2].Tremendous amount of research in the past few decades focusing on the development of highly electron-rich and rationally designed ligand systems have led to an exponential rise in popularity of such processes. To meet the challenges of modern day synthetic chemistry, strongly σ-donating phosphines [3] and N-heterocyclic carbenes (NHC) [4,5] as coordinating/activating ligands were introduced. The ease of synthesis and possibility of fine tuning the electronic properties of phosphines although, promoted their dominance over other ligand systems, but their sensitivity towards moisture or oxygen as well as difficulty in non-trivial handling and storage have hindered an unrestricted applicability in catalytic processes [6]. NHCs in this regard provide a useful alternative to overcoming the problems associated with phosphines while their strongly electron-donating ability allows the efficient activation even of the less reactive C–Cl bonds[7] (see Scheme 1)

N-Heterocyclic carbenes as efficient donor ligands have provided modular flexibility over steric and electronic factors and have been exploited extensively by research groups such as those of Organ [8],Hermann [9],Nolan [10], and many others [11]. In recent years, our research group has also contributed towards the development of NHC ligand systems in combination with palladium precursor for the regioselective Suzuki-Miyaura coupling of chloropyridines as well as for the preparation of phenanthrene-based OLED-type molecules [12]. In most of these examples, the coordination of the ligating NHC is via the carbene providing thus, excellent control over the reactivity towards chemically inert C–X bonds (C–O and C–Cl).The stability of the synthesized complexes was found to be lower though, an improved stability of Pd-NHC complexes could be achieved using carbene ligands possessing extra coordination sites leading to the formation of NHC complexes [13] (chelate formation) exhibiting higher thermal and moisture stability.

Amido-functionalized NHCs offer both, mono and dual coordination potential, i.e. binding via the carbene carbon (most commonly) and/or nitrogen atom of the amido-linkage [14]. Monoligated amido-functionalized NHC complexes (binding through

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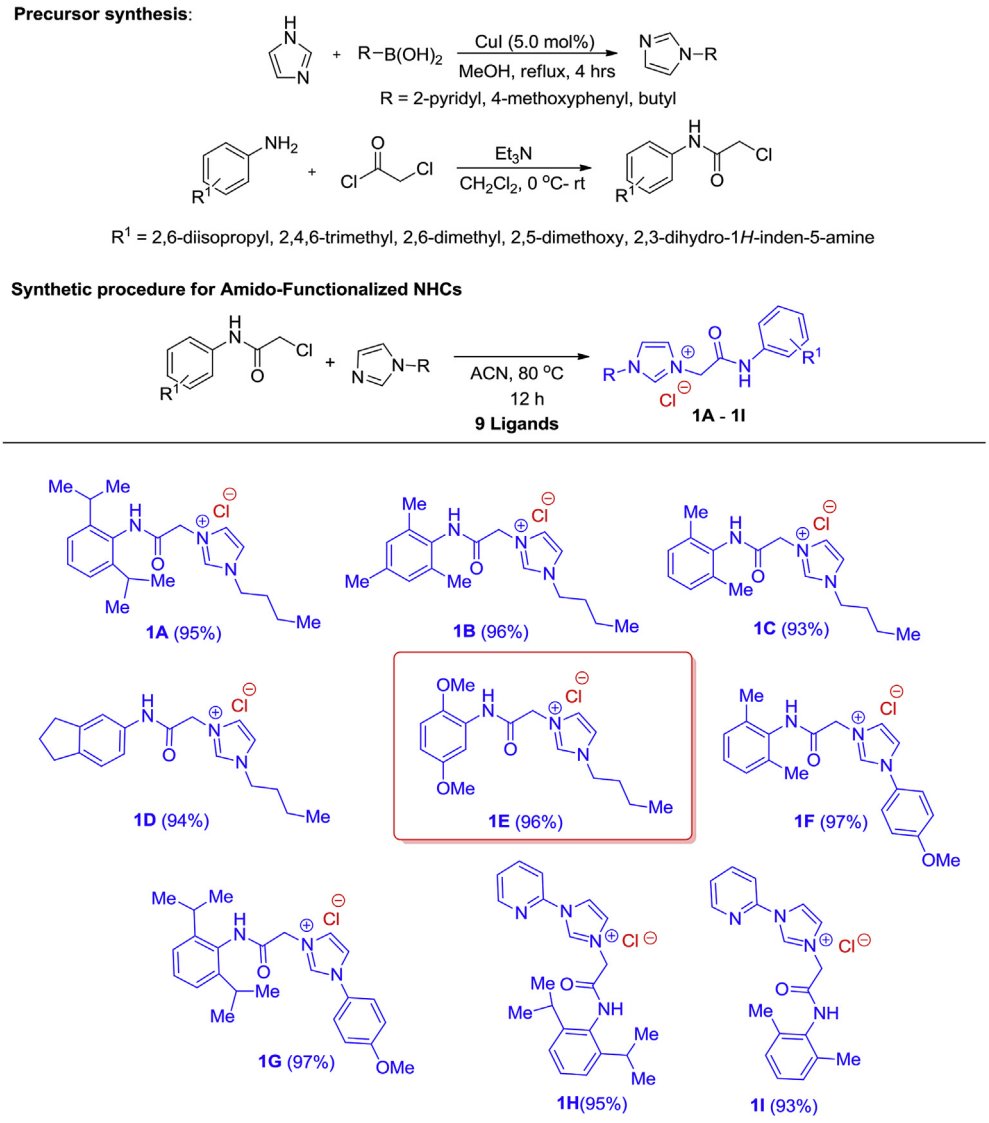


Scheme 1. Synthesis of N-heterocyclic carbene salts.

carbene carbon) are known and have been applied in catalytic processes with lowcatalytic activity observed for such copmplexes. However, reports on dual coordinated amido-functionalized NHC derived complexes are again very rare. In one such example, Lee and co-workers have demonstrated the applicability of amido-functionalized NHCs to synthesize several complexes via the dual coordination mode [15]. Lee's ligand system, however exhibits poor catalytic performance due to the lack of throw away ligand. Amido-functionalized NHCs have also been employed by Ghosh and co-workers for the synthesis of gold or silver dimeric complexes [16] (rather than palladium).

All above reports suggest a certain deficiency in literature with regards to the synthesis and applicability of chelating amido-based NHCs in palladium-catalyzed coupling processes. Lower applicability of the amide-functionalized NHC's in catalytic processes could be attributed to the less reactivity of the palladium centre. Subtle variation in the electronics around the metal centre could help improve the catalytic activity and provide solutions to synthetically challenging problems such as selective C—I activation vs C—X (X = Br or Cl). Herein we therefore report the synthesis of thirteen new amido-functionalized NHC ligands and their corresponding four square planar palladium complexes. Structural characterization by single crystal X-ray analysis ofthree ligands and all synthesized complexes evidences their chemical composition. The application of amido-functionalized NHC ligands and complexes in catalytic Heck alkenylation of aryl iodides was studied offering an insight into their respective reactivity compared to other active NHC ligand systems.

2. Results and discussion

2.1. Synthesis and characterization of amido-functionalized N-heterocyclic carbene salts

Previous reports by Lee and co-workers [15] indicated a drastic reduction in catalytic activity brought about by the amido-

functionalized NHC ligands that were found to chelate the palladium centre via tetra-coordination through two carbene carbons and two amidic N atoms. It is therefore important to note that the overcrowding of the palladium centre by amido-functionalized NHC (via tetra-coordination) likely the reason for a reduction in the catalytic activity. Keeping this in mind, we envisaged the development of amido-functionalized NHCs with bidentate coordination which would provide the necessary flexibility required for obtaining better catalytic efficiency.

Accordingly, various differently substituted imidazoles were prepared via simple alkylation or arylation of imidazole following reported literature protocols [17]. Then the synthesis of substituted 2-chloro-N-arylacetamides was achieved by the reaction between differently substituted anilines with chloroacetyl chloride (refer to experimental section for exact procedure to obtain N-arylacetamides). The choice of substituents on aniline is crucial as it would allow the assessment of the effect of bulky substituents on the subsequent reactivity in catalytic processes and also on the stability of the synthesized ligands as well as the corresponding palladium complexes. With the precursors in hand, the reaction between substituted 2-chloro-N-arylacetamides and N-substituted imidazoles was performed to furnish the desired amido-functionalized NHC ligands containing chloride as the counter anion in good to excellent yields.

The synthesized ligands were characterized in bulk using standard characterization techniques such as NMR and Elemental analysis, while in some cases (**1D**, **1E** and **1F**) it was also possible to obtain single crystals suitable for X-ray analysis (Fig. 1). Compounds **1D**, **1E** and **1F** were crystallized in space groups *C*2/*c* (monoclinic, **1D**), $P2_1/c$ (monoclinic, **1E**), and $P2_12_12_1$ (orthorhombic, **1F**), respectively. All three crystallographic structures are compromised quality wise due to twinning, multi-domain crystal samples and/or disorder so that they are merely taken as evidence for the respective chemical structures but not discussed with regard to their crystallographic features (see Fig. 2) (see Scheme 2).

To assess the effect of change in the anionic counterpart on the properties and catalytic activity of the synthesized ligands, a simple anion exchange reaction was performed on four amido-functionalized NHC ligands originally synthesized as chloride salts. The reaction was performed with ligands **1A**-**1C** and **1G** using sodium hexafluorophosphate in water at room temperature resulting in the formation of crystalline salts of NHC-hexafluorophosphates **1J**-**1M** in excellent yields (Scheme 3).

2.2. Synthesis and characterization of amido-functionalized N-heterocyclic carbene complexes

Next, the palladium complexes were synthesized with some of the amido-functionalized NHCs to assess the accuracy of our proposal of obtaining such complexes. This was achieved by mixing NHC ligands **1A**-**D** under inert gas atmosphere (N_2) with K_2CO_3as the added base for the deprotonation of the NHC.HCl salt. A palladium precursor such as palladium chloride was then added along with freshly powdered 3 Å molecular sieves and the whole mixture dissolved in freshly distilled pyridine as solvent and potentially coordinating ligand (stabiling the metal centre as in the case of PEPPSI complexes[8a]). On stirring the reaction mixture for 12 h at 60 °C, typical work-up provided crude solids that were recrystallized from ethanol. Pure crystalline palladium (II) complexes **2A-D** were obtained in good to excellent yields and were characterized using standard characterization techniques such as NMR and Elemental analysis. It was also possible to obtain single crystals suitable for all the synthesized complexes for X-ray analysis. The crystal structures of N-heterocyclic carbene complexes which bind Pd in a chelating fashion with only one carbene donor

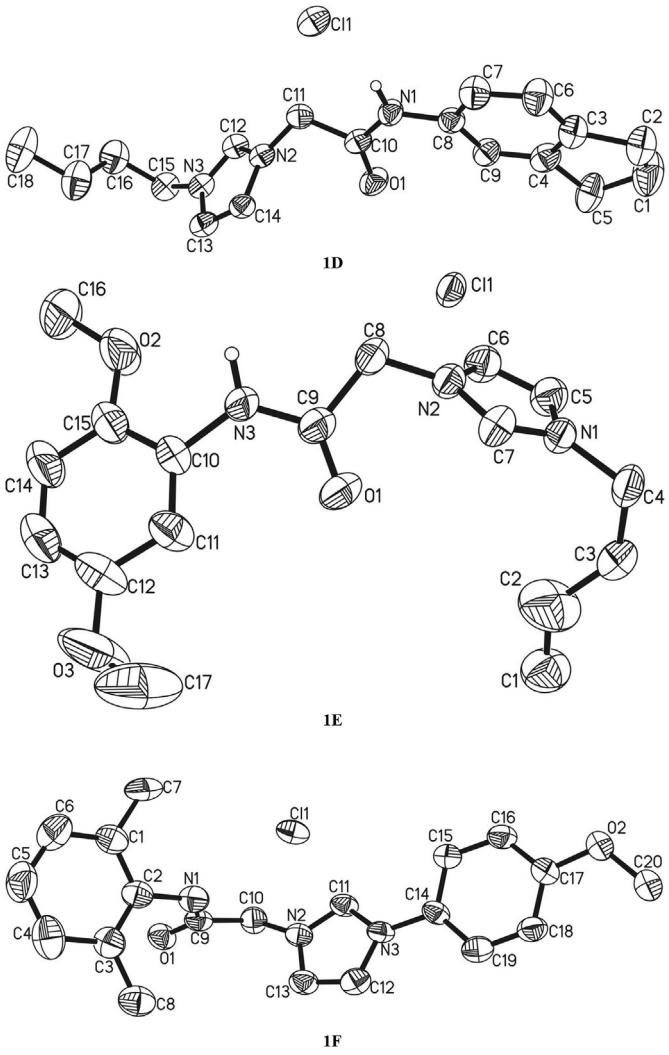


Fig. 1. The molecular structure of **1D** [18b], **1E** and **1F** [18]. Ellipsoids are shown at the 50% probability level. Disorder and H atoms (except those on nitrogen) were omitted for clarity reasons.

atom (in contrast to slightly more common *bis*-carbene structures) are only very rarely reported [19]. On analyzing these crystals it was observed that the complexes **2A-D** crystallized in space groups *P*-1 (triclinic; **2A**), $P6_5$ (hexagonal; **2B**) and $P2_1/c$ (monoclinic; **2C** and **2D**) respectively. All complexes were found to be mononuclear with palladium being fourfold coordinated in a square planar geometry.

In all four cases the complex arrangement is identical with the pyridine N donor atom and the carbene ligand carbon in *trans* position to each other. Notable crystallographic features comprise i) intermolecular hydrogen bonding interactions in **2A** (which crystallizes with two independent molecules in the unit cell) between the coordinated chloride ligands and a methylene proton of a second complex by which dimers of two complexes are formed; ii) hydrogen bonding interactions in **2B** between coordinated chloride ligands and a methyl proton of an adjacent molecule forming indefinite chains protruding in the crystallographic a/b plane.

For the combination of chelating carbene carbon atoms and amide nitrogens atom only two precedence's are available in the literature [15,20]. The ligand used by Tan et al. [20] is again tetradentate (similar to that employed by Lee and co-workers [15]) with two coordinating carbene functions and two amide nitrogen donor atoms. Crystallographically, the now reported complexes are,

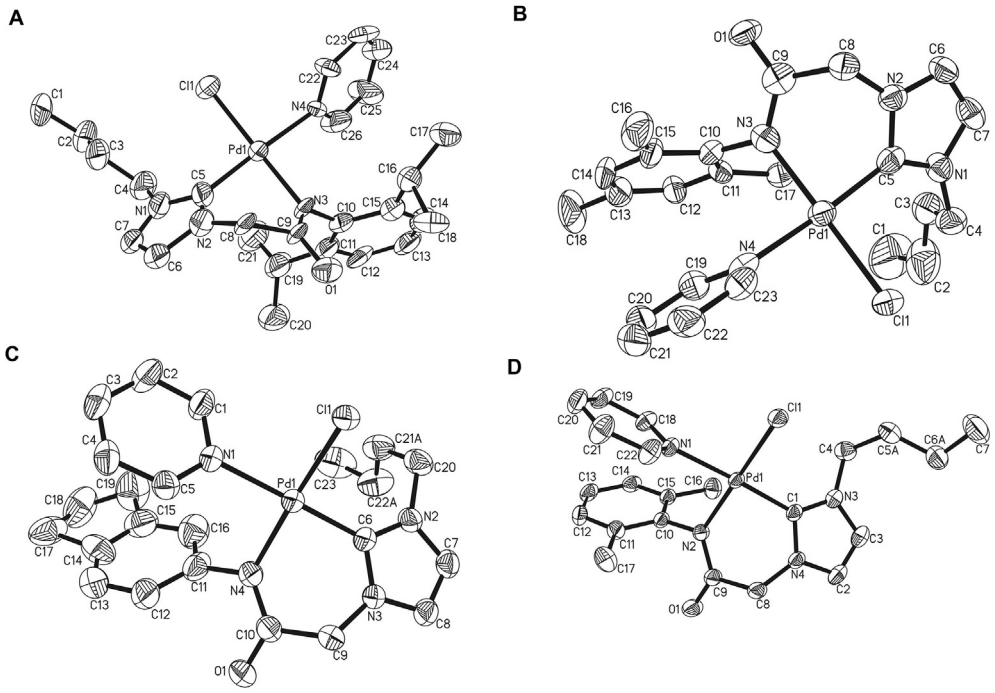
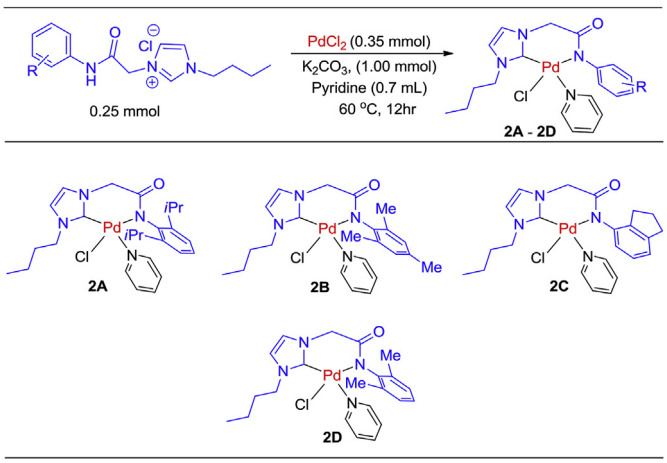


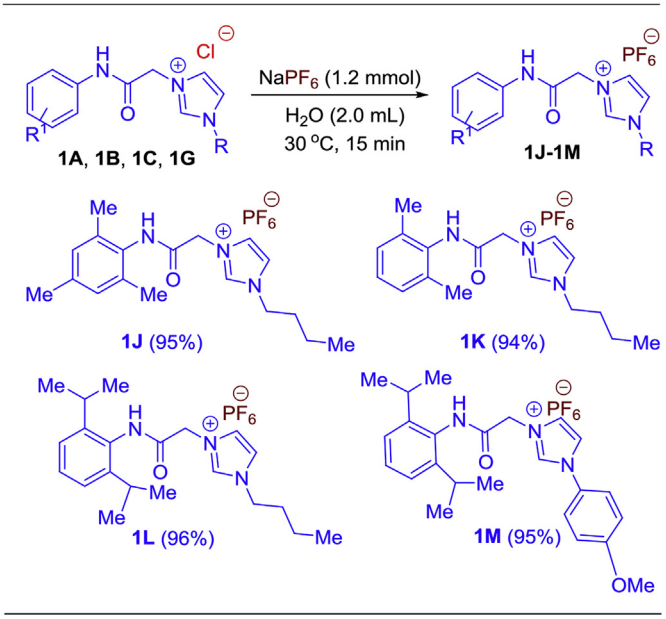
Fig. 2. Molecular structures of **2A-D** [21].Ellipsoids are shown at the 50% probability level. Disorder and H atoms (except those on nitrogen) were omitted for clarity reasons.

hence, unprecedented with one carbene carbon, one amide nitrogen, one chloride and one pyridine nitrogen donor atom. Tan's complex is also to some extent distorted from the ideal square planar geometry due to the steric strain of the tetra-dentate binding mode of the ligand. The ligand atom to the C, N, N, C, Pd plane distances range from 0.162 to 1.185 Å (both amide nitrogen atoms) with a Pd-plane distance of 0.016 Å. In case of the four novel complexes of this study the range of Pd to C, N, Cl, N, Pd plane distances are 0.011 Å (**2A**) to 0.043 Å (**2B**) while the shortest and longest donor atom to plane distances are 0.008 Å (**2A**) and 0.100 Å (**2C**), respectively. Therefore no significant distortion from nearly ideal square planar geometry was observed here.

It was also possible to analyze the Pd–C bond lengths between the Pd centre and carbene carbon. This provides us with an insight into the potential effect of steric bulk on the Pd–C bond strength and respective electronic factors (Table 1). From Table 1A, it is evident that the variation in electronics as well as steric bulk on the amide-functionalized NHCs affects the strength of the **Pd–C** bond. Lengthening of the bond can be observed in the case of complex **2A** possibly due to the presence of sterically bulky isopropyl groups (complex **2C** and **2D** show intermediate values), while complex **2B** shows bond strengthening. Metal coordination would also have a direct effect on the characteristics of the amidic bond. **Pd–N** bond lengths obtained from the crystal data suggests no significant variation, however a definite effect could be observed on the **C–O** bond length. A steady reduction in bond length could be observed from **2A** to **2D**evidencing a strengthening of the **C–O** bond. These



Scheme 2. Synthesis of N-heterocyclic carbene-palladium complexes.



Scheme 3. Synthesis of NHC hexafluorophosphate salts.

Table 1
A)Pd–C bond lengths, Pd–N bond lengths and C–O bond lengths for the synthesized complexes. **B)** Infrared frequencies for synthesized complexes and ligands.

Complex	2A	2B	2C	2D
Pd–C bond length (Å)	1.982	1.951	1.959	1.967
Pd–N bond length (Pd-amide N) (Å)	2.038	2.034	2.037	2.034
C–O bond length (amide C=O) (Å)	1.270	1.253	1.232	1.236

Complex	Complex C=O stretching (cm^{-1})	Ligand C=O stretching (cm^{-1})
2A	1601.62	1684.92 (**1A**)
2B	1596.34	1685.87 (**1B**)
2C	1613.04	1685 (**1C**)
2D	1611.02	1700.23 (**1D**)

results give an insight into the coordination chemistry of the synthesized complexes and also strongly indicate that the substituents on the N-heterocyclic carbene do affect the Pd–C bond strength, which consequently allowsa rationale for future fine-tuning of the respective catalytic properties.

Infrared spectral analysis of the synthesized complexes and a comparison with the amide-functionalized NHC ligand precursors reveal an expected reduction in the C=O stretching frequenciescompared to the ligand C=O stretching frequencies due to the palladium coordination to the amidic N atom, thus having an influence on the carbonyl bond strength according to the values represented by Table 1B.

2.3. Analysis of catalytic activity of amido-functionalized NHCs and complexes for Heck alkenylation reactions

The synthesized amido-functionalized NHCs along with the Pd-NHC complexes were next tested for catalytic activity. The Heck alkenylation [22] of aryl halides has for the past several decades served as a sharpening tool for testing active palladium catalysts delivering in turn synthetically useful molecules. Given the lower reactivity of amido-functionalized Pd-NHC complexes suggested in the literature by Lee and co-workers [15], we decided to test our catalytic systems against aryl halides under Heck alkenylation conditions with butyl acrylate using $PdCl_2$ as the catalyst precursor (for *in situ* generation of catalytically active Pd(0)-NHC species).

Initially, the coupling reaction between aryl bromide (4-bromoanisole) or aryl chloride and butyl acrylate failed to furnish any of the coupled product and therefore it was decided to test the catalytic systems against aryl iodides. The reaction of 4-iodoanisole with butyl acrylate in acetonitrile using trimethylamine as the base at 70 °C was monitored using GCMS (Gas Chromatograph coupled Mass Spectrometry) and yields were compared for the various catalytic systems after 20 h. Subsequently, a plot of %Yield for the different catalytic systems was plotted to help demonstrate the potential of the synthesized ligands and complexes in catalyzing the given transformation (with dodecane used as an internal standard).

First the Heck alkenylation reaction was carried out using only a Pd(II) precursor($PdCl_2$) under ligand-free conditions [23](usually associated with the formation of palladium nanoparticles). The reaction was continued for 20 h and an aliquot of the reaction mixture was injected into a Gas Chromatograph-Mass Spectrometer. The reaction with $PdCl_2$ (ligand-free) proceeded at a comparably slower rate providing only 41% of the desired cross-coupled product. To test the synthesized ligand's ability to further enhance the catalytic activity, a catalytic ratio of $PdCl_2$ (1.0 mol%) and Ligand (**1A-1M**, 1.0 mol%) was employed. It could be observed from Fig. 3 that in most cases an appreciable enhancement in catalytic activity takes place. In comparison to the *in situ* generated catalytic systems, preformed complexes exhibit higher catalytic activity as

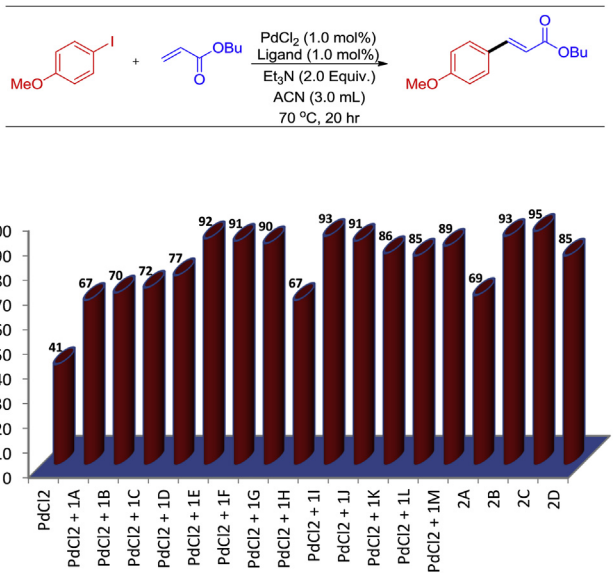


Fig. 3. Comparison of %yield of Heck coupled product for different catalytic system.

the time required for the formation of the catalytically active species is reduced. With this in mind, preformed Pd-NHC complexes **2A-D** (1.0 mol%), were subjected to the Heck alkenylation conditions as described above with aliquots injected after 20 h. As predicted, the preformed complexes showed comparable or comparably better performance to that of the *in situ* generated catalytic systems ($PdCl_2$ + Ligand) with complexes**2B** and **2C** proceeding smoothly towards the complete conversion of the substrate to the product (93% and 95% respectively).

Encouraged by the catalytic activity of the preformed catalysts, catalyst loading studies were subsequently performed to assess the catalytic ability of the Pd-NHC complexes at lower concentrations. Catalytic reactions were carried out under identical conditions for complex **2B** and **2C** at concentrations of 1.0 mol%, 0.5 mol%, 0.1 mol %, 0.01 mol% and 0.001 mol% with results represented in Table 2. It was observed that the reactivity of the preformed complexes **2B** and **2C** is retained even at lower catalyst loading up to a Pd concentration of 0.001 mol%. Accordingly, the catalysts exhibit impressive turn over numbers for the Heck alkenylation of aryl iodides upto 75000 and 69000 respectively for **2B** and **2C**. Similarly, when turn-over-frequency (TOF = TON/hr) was calculated it was observed that an appreciable TOF value was obtained for complexes 2B and 2C, respectively at 0.001 mol% catalyst concentration (3750 and 3450).

A comparative of the literature reports on the catalytic activity of amide-based Pd-NHC complexes suggests that either comparable or better reactivity is observed for the synthesized ligands and complexes.

Table 2
Catalyst loading experiments for complexes **2B** and **2C**.

S. No.	Catalyst concentration (mol%)	%Yield		TON (TOF)	
		2B	2C	2B	2C
1.	1.0	93	95	93 (4.65)	95 (4.75)
2.	0.5	90	88	450 (22.5)	440 (22)
3.	0.1	90	87	900 (45)	870 (43.5)
4.	0.01	80	74	8000 (400)	7400 (375)
5.	0.001	75	69	75000 (3750)	69000 (3450)

3. Conclusion

In conclusion, the synthesis and characterization of thirteen amide-functionalized NHC ligands has been reported herein. The uniqueness of the synthesized ligands is to offer dual coordination possibility with metals such as Pd resulting into the formation of four Pd-NHC complexes. An unprecedented bidentate coordination of the amide-functionalized NHC ligand with the palladium centre involving the carbenic carbon and amidic N atom as the sites of attachment is a feature that has been reported first time. Catalytic activity of all the synthesized ligands and complexes was tested against a Heck alkenylation protocol revealing an improved activity on the part of the complexes. The pre-formed complexes due to their enhanced stability reinforced by the bidentate coordination also performed efficiently at a concentration of 0.001 mol%, providing TON of >70000 and TOF of >3000. These results provide an insight into the effect of the presence of an amide-functionality (on the carbene backbone) on the coordination mode with the metal centre (bidentate) as well as the catalytic activity. Such a strategy could provide an ideal solution for obtaining improved stability of the catalyst and at the same time enhance its efficiency towards catalyzing a variety of synthetic transformations.

4. Experimental section

All the reactions were performed under nitrogen atmosphere using oven dried standard schlenk glassware. Solvents and chemicals were obtained from commercial sources and were used without further purification.1-(4-Methoxyphenyl)-1H-imidazole,2-(1H-imidazole-1-yl)pyridine and N-butyl imidazole were obtained from commercial sources. ^{1}H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance II-300 spectrometer. Chemical shifts δ are given in ppm and the solvent residual peak ($CDCl_3$: ^{1}H, $\delta = 7.27$; ^{13}C, $\delta = 77.0$ and DMSO-d6: ^{1}H, $\delta = 2.50$; ^{13}C, $\delta = 40$) was used as an internal standard. Peak multiplicities are specified as followed: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. APCI-MS (m/z) spectra were recorded on a Advion MS. Mechenary-Nagel silica gel 60 F254 plates were used for thin layer chromatography (TLC) and detection was achieved by UV light. Column chromatography was performed on silica gel 60 (40–63 μm) or on Acros Organics silica gel 60 (35–70 μm). "Elementar Vario MICRO cube" was used for the experimental determination of elemental configurations of final pure products.

Single crystal x-ray analysis: Crystals of **2A**,**2B**,**2C**,**2D**,**1D**,**1E**and**1F**were mounted on a glass fiber in inert paraffin oil. Data were recorded at 170 K on a STOE-IPDS 2 T diffractometer with graphite-monochromated Mo-*Kα*-radiation ($\lambda = 0.71073$ A). The structures were solved by direct methods (SHELXT-2016 [24]; or Superflip [25]; and refined by full-matrix least-squares techniques (SHELXL-2016 [26]; using the WingX GUI [27]. All non-hydrogen-atoms were refined with anisotropic displacement parameters. Unless otherwise stated, all hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} in case of methyl groups and to 1.2 U_{eq} of their pivot atoms in case of all other hydrogen atoms.

The measured crystal of **2A** was a multidomain platelet. It was not possible to cut a single-domain piece from it. The data are comparably poor, accordingly. It was tested whether the problem could be solved by applying a twin law as well as to integrate various domains separately. Both attempts were unsuccessful as aside from the major domain the others generated essentially noise. In order to improve the data to noise ratio the hkl file was cut at 1.0 Å resolution. As **2A** crystallized in triclinic space group P-1, this negatively affected the number of unique reflections, sine(-theta_max)/wavelength ratio etc. yielding A, B and C-Alerts in the checkcif file.

In the crystal lattice co-crystallized solvent was heavily disordered except for one water which is located directly in between and in rather close proximity to two complex molecules connecting them via hydrogen bonding (as acceptor only; the water hydrogen atoms could neither be located nor fixed; the oxygen atom (O3) was refined isotropically). Approximately four other water molecules or alternatively one ethanol and one water molecule per formula were removed from the refinement/hkl file using the SQUEEZE/PLATON routine and hence treated as a diffuse contribution to the overall scattering (152 electrons and 649 Å3 void volume per unit cell) [28]. All ligand molecules (except chloride) showed some kind of disorder in particular the iso-propyl substituents. In order to obtain ellipsoids with scientifically sound displacement parameters all ligand atoms (except chloride) were sorted into different groups and refined with constraints (SIMU/DELU and in case of the peptide link between the two aromatic systems of mole 1 even EADP was used for the respective three atoms, N3, C8, C9). As a consequence of the poor data quality, metrical parameters cannot be discussed for this compound but its composition is proven by the obtained data plus the similarity with the three related complexes, regardless.

The structure of **2B**crystallized together with one water solvent, the hydrogen atoms of which could not be located. The water was refined as isolated oxygen atom. The butyl chain in the structure of **2C** is disordered over two positions, which was modelled using SADI, SIMU and DELU constraints.In **2D** the butyl chain is disordered similarly over two positions, which was modelled using SADI, SIMU and DELU constraints. Three reflexes were omitted from the data set as they were far too intense.All amide structures are significantly problem ridden regarding disorder and/or twinning which seriously compromised data quality. Therefore metrical parameters should be taken with caution and are not discussed here. The structures nevertheless unanimously confirm the compounds' compositions.

The structure of **1E** is heavily disordered with over 50% of atoms appearing in two positions. The hydrogen atom on the amide nitrogen (N3) was located in ideal position but could not be refined freely because it tended to be sucked up by one of the two chlorine positions (Cl^- being disordered over two positions).The crystal of **1D** was twinned. The amide hydrogen atom on N1 was found and refined freely (no constraints or restraints).The crystal of **1F** was a multiply twinned crystal comprising *inter allia* merohedral twinning plus racemic twinning, for which the respective twin law could be applied. The remaining twinning could not be treated. The amide hydrogen atom was fixed as aromatic hydrogen atom using HFIX 43.

Selected crystal and refinement data are summarized in Table 3. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. These data can be obtained free of charge on quoting the depository numbers CCDC **1832439**–**1832445** by FAX (+44-1223-336-033), email (deposit@ccdc.cam.ac.uk) or their web interface (at http://www.ccdc.cam.ac.uk).

Synthesis of Ligand (1A-1E): Under nitrogen atmosphere, a schlenk tube was charged with a strring bar, 1.00 mmol of 2-chloro-N-arylacetamide, 1.5 mmol of N-butylimidazole, and 2 mL of dry acetonitrile. The reaction mixture was stirred for 12 h at 80 °C temperature. Subsequently, the reaction mixture was cooled and diethyl ether was added in it and during stirring precipitate of product was formed. The precipitate was isolated by decanting off the solvent, and washed with acetone (2 X 5 mL) and Hexane (2 X 5 mL), and dried in a vacuum.

Table 3
Crystal data for **2A-D** and **1D-F**.

parameters	2A	2B	2C	2D	1D	1E	1F
Formula	C52H70Cl2N8 O3Pd2	C23H29ClN4 O2Pd	C23H27ClN4 OPd	C22H27ClN4 OPd	C18H24Cl N3O	C17H24Cl N3O3	C20H21Cl N3O2
CCDC Number formula weight	1832442	1832441	1832445	1832444	1832439	1832443	1832440
	1138.86	535.35	517.33	505.32	333.85	353.84	370.85
Crystal system	Triclinic	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P-1	P 65	P 21/c	P 21/c	C 2/c	P 21/c	P 21 21 21
Z	2	6	4	4	8	4	4
a, Å	13.823(3)	20.245(3)	12.7565(6)	10.9687(5)	36.270(8)	16.755(3)	7.5480(15)
b, Å	15.221(3)	20.245(3)	11.5594(4)	14.2474(4)	5.3986(11)	8.1954(16)	8.5862(17)
c, Å	15.271(3)	10.100(2)	16.1082(7)	14.4388(7)	18.620(4)	14.232(3)	28.796(6)
A, deg	101.71(3)	90	90	90	90	90	90
β, deg	91.36(3)	90	109.905	95.463(4)	103.34(3)	94.97(3)	90
γ, deg	103.32(3)	120	90	90	90	90	90
V, Å^3	3052.9 (12)	3584.9(12)	2233.37(17)	2246.18(16)	3547.6(14)	1946.9(7)	1866.2(6)
T, K	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)	170(2)
$\lambda(Mo_{k\alpha})$,Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ,mm^{-1}	0.719	0.915	0.973	0.965	0.224	0.215	0.224
D_{calcd},mg/cm^3	1.239	1.488	1.539	1.494	1.250	1.207	1.320
F (000)	1176	1644	1056	1032	1424	752	780
Unique reflections	6337	4190	6163	6177	3620	5366	5144
Measured reflections	13327	26457	24824	24604	14282	20894	23514
R_{int}	0.1890	0.1200	0.1159	0.0437	0.1273	0.0577	0.0633
GOF on F^2	1.018	1.017	0.988	1.058	1.026	1.149	1.746
R_1[a],[$I>2\sigma(I)$]	0.1365	0.0466	0.0550	0.0274	0.0698	0.0913	0.1485
R_w[b] [$I>2\sigma(I)$]	0.3208	0.0875	0.1418	0.0742	0.1757	0.2646	0.3922
R_1, R_w (all data)	0.2172, 0.3713	0.0764,0.0975	0.0779,0.1542	0.0337,0.0772	0.1236,0.2123	0.1111,0.2858	0.1645, 0.4099
$\Delta\rho$ max/min [e Å^{-3}]	2.299/−1.418	0.498/-0.652	1.430/-1.717	0.888/-0.973	0.534/-0.460	1.456/-0.435	1.820/-1.082

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.
[b] .$R_w = [\sum\{w(Fo^2 - Fc^2)^2\}/\sum\{w(Fo^2)^2\}]^{1/2}$

Ligand 1A: white solid, Yield: 95%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.23 (s, 1H), 9.29 (s, 1H), 7.80 (dd, *J* = 3.4, 1.4 Hz, 2H), 7.26–7.20 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 5.32 (s, 2H), 4.21 (t, *J* = 7.1 Hz, 2H), 3.03 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.78–1.69 (m, 2H), 1.21 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.16–0.97 (m, 12H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 165.2, 146.2, 137.7, 131.8, 128.2, 124.2, 123.4, 122.3, 51.0, 49.0, 31.8, 28.3, 24.3, 23.6, 19.1, 13.6. Anal. Calcd for $C_{21}H_{32}ClN_3O$: C, 66.73; H, 8.53; N, 11.12. Found: C, 66.58; H, 8.65; N, 11.21.

Ligand 1B: white solid, Yield: 96%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.09 (s, 1H), 9.28 (s, 1H), 7.79 (d, *J* = 0.8 Hz, 2H), 6.84 (s, 2H), 5.27 (s, 2H), 4.19 (t, *J* = 7.1 Hz, 2H), 2.17 (s, 3H), 2.08 (s, 6H), 1.78–1.70 (m, 2H), 1.21 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d6): δ 164.0, 137.8, 136.1, 135.1, 131.9, 128.7, 124.3, 122.3, 51.0, 49.0, 31.7, 20.9, 19.1, 18.4, 13.7. Anal. Calcd for $C_{18}H_{26}ClN_3O$: C, 64.37; H, 7.80; N, 12.51. Found: C, 64.21; H, 7.73; N, 12.59.

Ligand 1C: white solid, Yield: 93%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.35 (s, 1H), 9.32 (s, 1H), 7.81 (d, *J* = 0.5 Hz, 2H), 7.03 (s, 3H), 5.32 (s, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 2.13 (s, 6H), 1.78–1.69 (m, 2H), 1.21 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 163.9, 137.8, 135.4, 134.6, 128.1, 127.1, 124.3, 122.3, 51.0, 49.0, 31.7, 19.1, 18.6, 13.7. Anal. Calcd for $C_{17}H_{24}ClN_3O$: C, 63.44; H, 7.52; N, 13.06. Found: C, 63.53; H, 7.43; N, 13.18.

Ligand 1D: white solid, Yield: 94%,^{1}H NMR (400 MHz, DMSO-d6): δ 10.99 (s, 1H), 9.26 (s, 1H), 7.79 (d, *J* = 10.5 Hz, 2H), 7.50 (s, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 5.24 (s, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 2.77 (q, *J* = 7.7 Hz, 4H), 1.95 (qui, *J* = 7.4 Hz, 2H), 1.79–1.70 (m, 2H), 1.28–1.18 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 163.8, 144.6, 139.3, 137.8, 137.1, 124.7, 124.4, 122.1, 117.6, 115.7, 51.7, 49.0, 32.9, 32.1, 31.7, 25.5, 19.1, 13.7. Anal. Calcd for $C_{17}H_{24}ClN_3O$: C, 64.76; H, 7.25; N, 12.59. Found: C, 64.59; H, 7.12; N, 12.48.

Ligand 1E: white solid, Yield: 96%,^{1}H NMR (400 MHz, DMSO-d6): δ 9.90 (s, 1H), 9.25 (d, J = 8.3 Hz, 1H), 7.77 (d, *J* = 16.5 Hz, 2H), 7.60 (s, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 5.26 (s, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.62 (s, 3H), 1.79–1.70 (m, 2H), 1.28–1.18 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.6, 153.2, 143.9, 137.8, 127.6, 124.4, 122.2, 112.5, 109.1, 108.5, 56.6, 55.7, 51.8, 49.0, 31.7, 19.1, 13.7. Anal. Calcd for $C_{17}H_{24}ClN_3O$: C, 57.70; H, 6.84; N, 11.88. Found: C, 57.53; H, 6.99; N, 11.71.

Synthesis of Ligand (1F-1G): Under nitrogen atmosphere, a schlenk tube was charged with a strring bar, 1.00 mmol of 2-chloro-N-arylacetamide, 1.5 mmol of 1-(4-Methoxyphenyl)-1H-imidazole, and 2 mL of dry acetonitrile. The reaction mixture was stirred for 12 h at 80 °C temperature. Subsequently, the reaction mixture was cooled and diethyl ether was added in it and during stirring precipitate of product was formed. The precipitate was isolated by decanting off the solvent, and washed with acetone (2 X 5 mL) and Hexane (2 X 5 mL), and dried in a vacuum.

Ligand 1F: white solid, Yield: 97%,^{1}H NMR (400 MHz, DMSO-d6): δ 10.29 (s, 1H), 9.93 (s, 1H), 8.25 (s, 1H), 8.01 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.04 (s, 3H), 5.38 (s, 2H), 3.80 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d6): δ 163.7, 160.4, 136.8, 135.5, 134.5, 128.1, 128.1, 127.2, 125.0, 123.8, 121.3, 115.6, 56.1, 51.3, 18.6. Anal. Calcd for $C_{20}H_{22}ClN_3O_2$: C, 64.60; H, 5.96; N, 11.30. Found: C, 64.53; H, 5.78; N, 11.42.

Ligand 1G: white solid, Yield: 97%,^{1}H NMR (400 MHz, DMSO-d6): δ 10.23 (s, 1H), 9.94 (s, 1H), 8.25 (s, 1H), 7.99 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.26–7.21 (m, 1H), 7.15 (dd, *J* = 15.5, 8.3 Hz, 4H), 5.38 (s, 2H), 3.81 (s, 3H), 3.06 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.09 (d, *J* = 17.1 Hz, 12H).^{13}C NMR (101 MHz, DMSO-d6): 164.9, 160.4, 146.3, 136.7, 131.8, 128.3, 128.1, 124.9, 123.8, 123.4, 121.5, 115.6, 56.1, 51.3, 28.3, 24.3, 23.7. Anal. Calcd for $C_{24}H_{30}ClN_2O_2$: C, 67.35; H, 7.07; N, 9.82. Found: C, 67.38; H, 7.16; N, 9.95.

Synthesis of Ligand (1H-1I): Under nitrogen atmosphere, a Schlenk tube was charged with a strring bar, 1.00 mmol of 2-chloro-N-arylacetamide, 1.5 mmol of 2-(1H-imidazole-1-yl)pyridine, and 2 mL of dry acetonitrile. The reaction mixture was stirred for 12 h at 80 °C temperature. Subsequently, the reaction mixture was cooled and diethyl ether was added in it and during stirring precipitate of

product was formed. The precipitate was isolated by decanting off the solvent, and washed with acetone (2 X 5 mL) and Hexane (2 X 5 mL), and dried in a vacuum.

Ligand 1H: white solid, Yield: 95%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.24 (s, 1H), 10.09 (s, 1H), 8.66 (ddd, J = 4.9, 1.7, 0.7 Hz, 1H), 8.58 (t, J = 1.9 Hz, 1H), 8.21 (ddd, J = 8.2, 7.6, 1.8 Hz, 1H), 8.09–8.04 (m, 2H), 7.65 (ddd, J = 7.5, 4.8, 0.7 Hz, 1H), 7.29–7.25 (m, 1H), 7.16 (d, J = 7.7 Hz, 2H), 5.46 (s, 2H), 3.13–3.07 (m, 2H), 1.12 (dd, J = 26.9, 5.3 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.8, 149.7, 146.6, 146.3, 141.1, 136.6, 131.6, 128.4, 125.8, 125.4, 123.5, 119.3, 114.7, 28.3, 24.8, 24.0. Anal. Calcd for $C_{22}H_{27}N_4OCl$: C, 66.24; H, 6.82; N, 14.04. Found: C, 66.38; H, 6.63; N, 13.87.

Ligand 1I: white solid, Yield: 93%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.21 (s, 1H), 10.01 (s, 1H), 8.66–8.64 (m, 1H), 8.56 (t, J = 1.9 Hz, 1H), 8.23–8.19 (m, 1H), 8.06 (dd, J = 5.7, 3.6 Hz, 2H), 7.65 (ddd, J = 7.5, 4.9, 0.7 Hz, 1H), 6.87 (s, 2H), 5.41 (s, 2H), 2.20 (s, 3H), 2.14 (s, 6H).^{13}C NMR (101 MHz, DMSO-d6): δ 163.7, 149.7, 146.6, 141.1, 136.6, 136.3, 135.2, 131.7, 128.7, 125.5, 119.2, 114.6, 51.5, 20.8, 18.4. Anal. Calcd for $C_{18}H_{19}N_4OCl$: C, 63.06; H, 5.59; N, 16.34. Found: C, 63.21; H, 5.40; N, 16.11.

Synthesis of Ligand (1J-1M): A schlenk tube was charged with a strring bar, 1.2 mmol of sodiumhexafluorophosphate, and 2 mL of water. After 2 min stirring 1.00 mmol of ligand with chloride anion (**1A, 1B, 1C, 1G**) was added in it and reaction mixture was stirred at 30 °C. After 15 min reaction mixture was filtered and product was washed by water and dried in a vacuum.

Ligand 1J: white solid, Yield: 95%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.09 (s, 1H), 9.28 (s, 1H), 7.79 (d, J = 0.8 Hz, 2H), 6.84 (s, 2H), 5.27 (s, 2H), 4.19 (t, J = 7.1 Hz, 2H), 2.17 (s, 3H), 2.08 (s, 6H), 1.78–1.70 (m, 2H), 1.21 (dq, J = 14.6, 7.3 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.0, 137.8, 136.1, 135.1, 131.9, 128.7, 124.3, 122.3, 51.0, 49.0, 31.7, 20.9, 19.1, 18.4, 13.7. ^{31}P NMR (DMSO-d6): δ −144.21. ^{19}F (470 MHz, DMSO-d6): δ −69.39 (s), −70.91 (s). Anal. Calcd for $C_{18}H_{26}N_3OPF_6$: C, 48.54; H, 5.88; N, 9.43. Found: C, 48.64; H, 6.05; N, 9.30.

Ligand 1K: white solid, Yield: 94%, ^{1}H NMR (400 MHz, DMSO-d6): δ 10.35 (s, 1H), 9.32 (s, 1H), 7.81 (d, J = 0.5 Hz, 2H), 7.03 (s, 3H), 5.32 (s, 2H), 4.20 (t, J = 7.1 Hz, 2H), 2.13 (s, 6H), 1.78–1.69 (m, 2H), 1.21 (dq, J = 14.7, 7.4 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d6): δ 163.9, 137.8, 135.4, 134.6, 128.1, 127.1, 124.3, 122.3, 51.0, 49.0, 31.7, 19.1, 18.6, 13.7. ^{31}P NMR (DMSO-d6): δ −144.23. ^{19}F (470 MHz, DMSO-d6): δ −69.39 (s), −70.91 (s). Anal. Calcd for $C_{17}H_{24}N_3OPF_6$: C, 47.33; H, 5.61; N, 9.74. Found: C, 47.38; H, 5.61; N, 9.42.

Ligand 1L: white solid, Yield: 96%, 1H NMR (400 MHz, DMSO-d6): δ 10.23 (s, 1H), 9.29 (s, 1H), 7.80 (dd, J = 3.4, 1.4 Hz, 2H), 7.26–7.20 (m, 1H), 7.12 (d, J = 7.6 Hz, 2H), 5.32 (s, 2H), 4.21 (t, J = 7.1 Hz, 2H), 3.03 (dt, J = 13.6, 6.8 Hz, 2H), 1.78–1.69 (m, 2H), 1.21 (dq, J = 14.7, 7.4 Hz, 2H), 1.16–0.97 (m, 12H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 165.2, 146.2, 137.7, 131.8, 128.2, 124.2, 123.4, 122.3, 51.0, 49.0, 31.8, 28.3, 24.3, 23.6, 19.1, 13.6. ^{31}P NMR (DMSO-d6): δ −144.25. ^{19}F (470 MHz, DMSO-d6): δ −69.39 (s), −70.91 (s). Anal. Calcd for $C_{21}H_{32}N_3OPF_6$: C, 51.74; H, 6.62; N, 8.62. Found: C, 51.59; H, 6.45; N, 8.51.

Ligand 1M: white solid, Yield: 95%, 1H NMR (400 MHz, DMSO-d6 δ 10.23 (s, 1H), 9.94 (s, 1H), 8.25 (s, 1H), 7.99 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.26–7.21 (m, 1H), 7.15 (dd, J = 15.5, 8.3 Hz, 4H), 5.38 (s, 2H), 3.81 (s, 3H), 3.06 (dt, J = 13.6, 6.8 Hz, 2H), 1.09 (d, J = 17.1 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.9, 160.4, 146.3, 136.7, 131.8, 128.3, 128.1, 124.9, 123.8, 123.4, 121.5, 115.6, 56.1, 51.3, 28.3, 24.3, 23.7. ^{31}P NMR (DMSO-d6): δ −144.23. ^{19}F (470 MHz, DMSO-d6): δ −69.39 (s), −70.91 (s). Anal. Calcd for $C_{24}H_{30}N_3O_2PF_6$: C, 53.63; H, 5.63; N, 7.82. Found: C, 53.41; H, 5.47; N, 7.60.

Synthesis of complex (2A-2D): A Schlenk tube was charged with a stirring bar, ligand **1A-1D** (0.25 mmol), K_2CO_3 (1.00 mmol), Palladium (II) chloride (0.35 mmol), freshly powdered 3 Å molecular sieves (40 mg) under nitrogen atmosphere. Dry pyridine (0.7 mL) was added and mixture was stirred for 12 h at 60 °C temperature. The mixture was then filtered using celite bed and the filtrate was dried under vacuum. The crude solid was recrystallized from hot ethanol.

Complex 2A:Yield: 65%, ^{1}H NMR (400 MHz, DMSO) δ 8.52 (d, J = 5.5 Hz, 1H), 8.40 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.79 (ddd, J = 8.2, 7.1, 1.7 Hz, 3H), 7.39 (s, 1H), 7.20–7.14 (m, 3H), 4.87 (d, J = 5.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.87 (dd, J = 13.3, 4.8 Hz, 1H), 2.39 (dd, J = 13.3, 8.2 Hz, 1H), 1.88 (d, J = 8.6 Hz, 3H), 1.69–1.60 (m, 3H), 1.21 (dd, J = 14.6, 7.5 Hz, 9H), 0.87 (d, J = 6.3 Hz, 3H), 0.79 (d, J = 14.2 Hz, 2H).^{13}C NMR (75 MHz, MeOD) δ 170.1, 152.0, 151.7, 142.3, 139.3, 127.1, 125.8, 124.4, 123.3, 123.0, 57.6, 51.5, 34.7, 29.5, 24.8, 23.4, 21.0, 14.1.Anal. Calcd for $C_{26}H_{36}N_4OPdCl$: C, 55.52; H, 6.45; N, 9.96. Found: C, 55.41; H, 6.34; N, 9.82.

Complex 2B: Yield: 72%, ^{1}H NMR (400 MHz, DMSO) δ 7.90 (d, J = 5.0 Hz, 2H), 7.73 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 19.5 Hz, 1H), 7.41 (d, J = 17.4 Hz, 1H), 7.18–7.11 (m, 2H), 6.71 (s, 1H), 6.52 (d, J = 14.6 Hz, 1H), 4.77 (d, 2H), 4.44 (s, 2H), 2.14 (d, J = 5.1 Hz, 1H), 2.08 (s, 3H),1.99 (s, 3H), 1.92 (dd, J = 15.0, 7.5 Hz, 1H), 1.77 (s, 3H), 1.32 (dt, J = 14.4, 7.3 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 165.90, 150.65, 150.51, 142.67, 138.34, 132.97, 128.11, 124.47, 122.64, 122.52, 56.58, 49.72, 33.43, 20.87, 19.71, 19.26, 18.92, 14.11.

Anal. Calcd for $C_{23}H_{30}N_4OPdCl$: C, 53.09; H, 5.81; N, 10.77. Found: C, 53.15; H, 5.75; N, 10.63.

Complex 2C: Yield: 58%, ^{1}H NMR (300 MHz, MeOD) δ 8.36 (d, J = 5.0 Hz, 2H), 7.69 (t, J = 7.7 Hz, 1H), 7.39 (s, 1H), 7.27 (d, J = 1.8 Hz, 1H), 7.23–7.13 (m, 2H), 6.84 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 8.6 Hz, 2H), 4.58 (s, 2H), 2.74–2.58 (m, 4H), 2.17–2.05 (m, 2H), 1.93 (p, J = 7.4 Hz, 2H), 1.54 (dt, J = 14.6, 7.4 Hz, 2H), 1.15 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, MeOD) δ 170.3, 151.8, 151.7, 146.1, 145.0, 141.0, 139.0, 125.7, 125.2, 124.5, 123.6, 123.3, 123.2, 58.0, 50.8, 34.8, 33.4, 33.1, 26.7, 20.8, 14.2.Anal. Calcd for $C_{23}H_{28}N_4OPdCl$: C, 53.29; H, 5.44; N, 10.81. Found: C, 53.19; H, 5.49; N, 10.93.

Complex 2D: Yield: 69%, ^{1}H NMR (400 MHz, DMSO) δ 7.89 (d, J = 7.71 Hz, 2H), 7.69 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 1.92 Hz, 1H), 7.40 (d, J = 1.9 Hz, 1H), 7.17–7.00 (m, 2H), 6.87 (s, 1H), 6.76–6.61 (m, 2H), 4.77 (s, J = , 2H), 4.44 (s, 2H), 2.10 (d, 2H), 1.89 (s, 6H), 1.32 (m, 2H), 0.94 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, MeOD) δ 168.8, 151.7, 144.8, 139.1, 135.2, 128.9, 126.2, 125.4, 123.3, 123.3, 57.3, 51.4, 34.7, 20.9, 19.0, 14.1.Anal. Calcd for $C_{22}H_{28}N_4OPdCl$: C, 52.18; H, 5.57; N, 11.06. Found: C, 52.27; H, 5.41; N, 10.98.

General procedure for heck coupling reaction: A dry Schlenk tube was charged with a strring bar, ligand (0.01 mmol), palladium(II) chloride (0.01 mmol), triethylamine (1.00 mmol), and 0.5 mL of dry acetonitrile under nitrogen atmosphere. The reaction mixture was stirred for 10 min at 50 °C temperature. To this 4-iodoanisole (0.5 mmol) was added and was stirred for 5 min at 50 °C temperature. In same reaction mass butyl acrylate (1.5 mmol) was added and the resultant mixture was stirred for 20 h at 70 °C temperature. At the end of the reaction an aliquot was quenched and injected into GCMS.

Author contributions

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