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NC palladacycles in the Heck arylation of ethylene: Synthesis, structure and their reactivity

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ABSTRACT

Monomeric cyclopalladated complexes with NC coordination using ligands 2-phenylpyridine, 2-phenylquinoline, 8-methylquinoline have been synthesized and the structures have been determined by single crystal X-ray structure analysis. The crystal structures of monomeric palladacycles prepared using benzophenone oxime, and 2-phenylpyridine have also been determined. The use of these complexes in the Heck arylation of ethylene with 2-bromo-6-methoxynaphthalne (BMN) to give 2-vinyl-6-methoxynapthalene which is an intermediate for the synthesis of anti-inflammatory drug Naproxen has been examined and also arylation of ethylene with 3-bromo-benzophenone and 4-bromo-isobutylbenzene was investigated. These palladacycles with NC coordination show excellent catalytic activity with a TOF > 4000 h^{-1}.

1. Introduction

Palladium catalyzed Heck reaction is considered as one of the landmark developments in the organic synthesis. During the last decade, homogeneously catalyzed Heck reaction has been investigated extensively and the details are summarized in recent review articles [1]. The palladium catalyzed coupling reaction of organic halides with olefins allows a one step synthesis of aromatic olefins, which are of considerable importance [2] as fine organics, specialty monomers, pharmaceuticals, UV absorbers and precursors of active compounds. Major emphasis of the work during recent times has been on the development of catalysts that are more stable compared to the classical palladium(0) phosphine complexes [3]. Typical examples are palladacycles [4], which remain active at higher temperatures (100–140 °C) leading to higher reaction rates and thus allow lower catalyst loadings and high turnovers (>200 000). There are many types of palladacycles, particularly those with nitrogen [5], phosphorus [6], sulfur [7] and oxygen [8] containing donor ligands. They can also be found in pincer forms [9].

Arylation of ethylene provides an easy and general method for the synthesis of vinyl aromatic compounds. Also, it may allow replacing [10] the classical Friedel and Crafts chemistry and other classical organic chemistry involved in the production of most aromatic compounds and form the basis for environmentally friendly production processes. However, there are very few reports on the arylation of ethylene. Aryl halides [11] and other pseudo-halides [12] (acid chlorides, diazonium salts and triflates) have been used as substrates in the arylation reactions using $Pd(OAc)_2$ as the catalytic system. Activity of the catalyst was generally found to be low (turnover frequency <15 h^{-1}) and high catalyst loading (1–5 mol% of palladium salt based on halide) was essential for good activity. α-Aryl propionic acids such as Ibuprofen, Naproxen, Ketoprofen, Fenoprofen, Indoprofen have emerged as important non-steroidal anti-inflammatory agents during the past three decades [13]. While many synthetic routes [14] for these products are known, a catalytic route involving a two step synthesis [15] (viz Heck reaction followed by carbonylation [16]) is one of the recent developments to achieve an environmentally cleaner route (Scheme 1).

The catalytic systems proposed previously for the arylation of ethylene with 2-bromo-6-methoxynaphthalene (BMN) to produce 2-vinyl-6-methoxynaphthalene (VMN) include the Herrmann palladacycle [17] and $PdCl_2$/NMDP [18] (neomenthyldiphenylphosphine) [19]. However, the activity of these catalysts was found to be very low (TOF: 85 h^{-1} and 444 h^{-1}, respectively). The performance of the colloids $[Pd(CH_3CN)_2Cl_2] \cdot 6Ph_4PCl$ [20] has also been described for these reactions (TOF: 75 h^{-1}). From the literature it was observed that there are very few reports on the arylation of ethylene particularly for the important substrates having potential applications in the synthesis of important drugs such as Ibuprofen,

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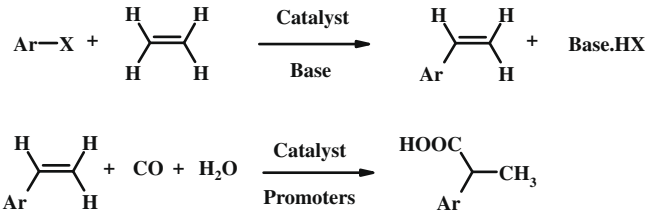


Scheme 1. Synthesis of aryl propionic acids using Heck coupling and carbonylation reaction.

Naproxen. Therefore, there is a need to develop a catalyst system with high activity and selectivity for Heck arylation of ethylene. Palladacycle complexes are stable at higher temperatures, however, catalytic activity was found to be very low [17] for the Heck arylation of ethylene. Also, there are no reports on the use of NC palladacycles for arylation of ethylene.

In the present work, we have prepared new NC palladacycle complexes using cheaper and easily available ligands such as 2-phenylpyridine, 2-phenylquinoline, 8-methylquinoline. Other NC palladacycle complexes containing the ligands benzophenoneoxime [22c] and *N*,*N*-dimethylbenzylamine [22a] already reported in literature have also been tested for their activity in the arylation of ethylene. The palladacycle complexes were characterized in detail and their usefulness as catalysts in Heck arylation of ethylene has been demonstrated.

2. Results and discussion

2.1. Synthesis of NC palladacycle complexes

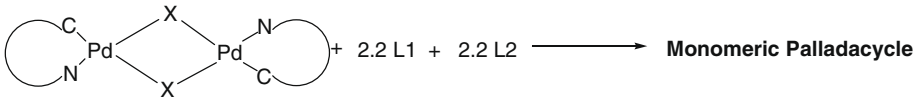
The NC palladacycle complexes were prepared in two steps using literature procedures [21]. The first step involves the reaction of palladium salts (or palladating agent, $Pd(OAc)_2$ or Li_2PdCl_4) and the ligands to form dinuclear molecules with acetate or halide bridged NC palladacycle [21]. In the second step, the obtained palladacycle is treated with triphenylphosphine ligand and *p*-toluenesulfonic acid (for chloro bridged complex only triphenylphosphine is used) to get the appropriate mononuclear palladacycle (Table 1). Attempts to prepare the palladacycle in a single step by reacting concomitantly the palladating agent and the ligands, e.g., in the case of **1**, ($Pd(OAc)_2$ + ppy(2-phenylpyridine) + PPh_3 + TsOH); resulted in the precipitation of palladium black. So the complexes were prepared in two steps. The crystal structures of the monomeric palladacycles (**1**–**5**) have been solved unequivocally by X-ray diffraction studies (Figs. 1 and 2). The monomeric NC palladacycles having monophosphine and sulphanato ligands (**1**, **2** and **3**) are described for the first time. Whereas the monomeric palladacycle complexes bearing monophosphine and chloride ligands (**4**, **5** and **6**) are already known and were synthesized as per the literature procedures [22]. However, the crystal structures of **4** [22b,d] and **5** [22c] have not been reported, hence the structures of these complexes were determined by single crystal X-ray diffraction studies (Fig. 2).

2.2. Characterization and molecular structures of NC palladacycle complexes

The ^{31}P NMR spectra of the complexes **1**, **2** and **3** show signals at δ 39.9, 41.98 and 32.42 ppm, respectively. When an extra aromatic ring as in the case of 2-phenylquinoline compared to 2-phenylpyridine is present in the complex, a downfield shift in the ^{31}P NMR spectra from δ at 39.9–41.98 ppm takes place. In these cases the metallated carbon is a sp^2 centre. Changing the metallated carbon from sp^2 to sp^3 (complex **3**) showed ^{31}P signals at δ = 32.4 ppm, this can be attributed to the increased electron density at the palladium centre by methylene protons thereby showing ^{31}P signals at high field. The occurrence of a single peak in the ^{31}P NMR indicates the formation of one isomer. Further single crystal structure determination confirmed the *trans* isomer, i.e., the phosphorus is *trans* to the N-donor. The ^1H NMR spectra of the complexes **1** and **3** reveal that the proton being ortho to the nitrogen atom appears at the low field at δ 9.14 and 9.68 ppm, respectively. 2-Phenylquinoline does not show a signal in this region due to the absence of the ortho proton to the nitrogen. It is reported that the proton on the carbon ortho to the palladated carbon appears at the low field in the range 6.18–6.44 ppm [22a]. However, we do not observe a characteristic peak associated with the said proton because of the presence of other phenyl rings. The respective methyl group for the complexes **1**, **2** and **3** from the sulphanato group shows a singlet at δ 2.3, 2.14 and 2.24 ppm. The methylene protons for the complex **3** appear as doublet at δ 2.93–2.95 ppm.

From X-ray crystallographic data it can be seen that the palladacyclic complexes adopt distorted square planar geometries at the palladium atom and the phosphorus atom is in *trans* position to the donor N atom. The angle P–Pd–N varies from 168.94° to 177.92°. The Pd–N bond length for **2** is longer compared to the rest of the compounds (Table 2). When the bulkiness of the ligand is more as in complex **2** with respect to **1**, there is an increase in the P–Pd–O bond angles and a decrease in the N–Pd–O bond angles (Table 2). The crystallographic data for the palladium complexes are summarized in Table 8. For the complexes **1**, **2** and **3** having similar PPh_3, OTs motifs differing in the NC coordination, the C–Pd–N bond angles are as follows: 81.25° (**1**), 80.95° (**2**) and 83.53° (**3**). Kim et al. [23] have reported crystal structure of Pd complex with 2-phenylpyridine, PPh_3, and $SP(=O)(OCH_3)_2$ as a ligand, which is structurally very close to complexes [Pd(κ^2-N,C-

Table 1
Synthesis of various NC palladacycles.



CN coordination ligand	X	L 1	L 2	Monomeric palladacycle	Yield (%)
2-Phenylpyridine	OAc	PPh_3	$TsOH \cdot H_2O$	**1**	92
2-Phenylquinoline	OAc	PPh_3	$TsOH \cdot H_2O$	**2**	95
8-Methylquinoline	OAc	PPh_3	$TsOH \cdot H_2O$	**3**	90
2-Phenylpyridine	Cl	PPh_3	–	**4**	86
Benzophenone oxime	Cl	PPh_3	–	**5**	90
N,*N*-Dimethylbenzylamine	Cl	PPh_3	–	**6**	90

The reaction was carried out with the cyclopalladated dimer (1 equiv.) and the ligands (2.2 equiv.) in chloroform at room temperature.

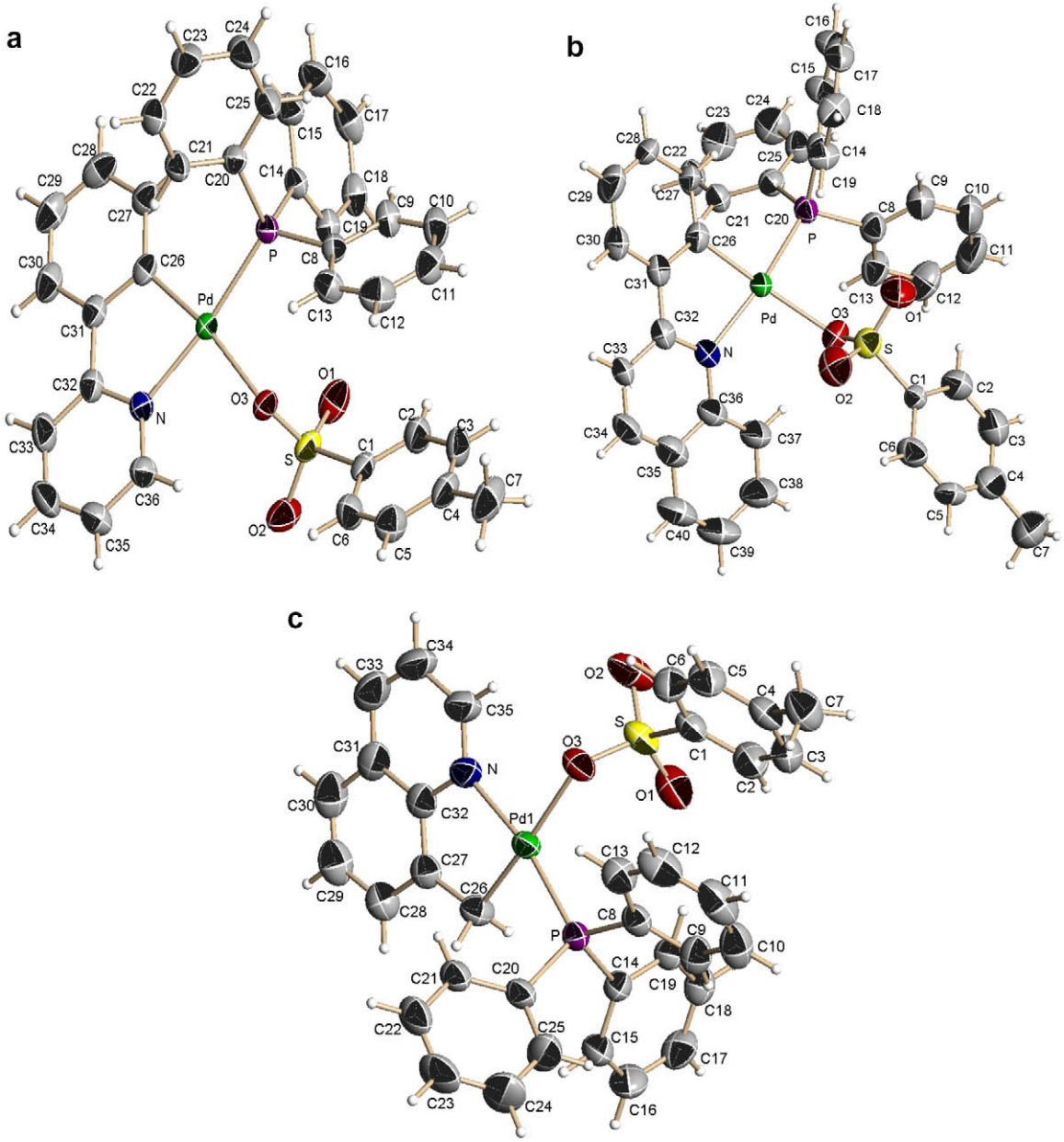


Fig. 1. ORTEP drawing of the palladium complexes with 50% probability: (a) [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] (**1**), (b) [Pd(κ^2-N,C-$C_{15}H_{10}N$)(PPh_3)(OTs)] (**2**) and (c) [Pd(κ^2-N,C-$C_{10}H_8N$)(PPh_3)(OTs)] (**3**).

$C_{11}H_8N$)(PPh_3)(OTs)] (**1**) and [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(Cl)] (**4**) reported in the present work. The average bond lengths (Å) for all the three complexes for Pd–P, Pd–N and Pd–C are comparable and are in the range 2.251–2.276, 2.080–2.095 and 1.985–2.026, respectively. In complexes **1** and **4** the Pd center adopts a distorted square planar configuration with PPh_3 and N atom of 2-phenylpyridine having *trans* configuration while that with C of 2-phenylpyridine is in *cis* arrangement. Kim et al. [23] have observed similar structure for the complex [Pd(κ^2-N,C-$C_{11}H_8N$)(SP(=O)(OCH_3)$_2$)(PPh_3)] having two molecules in the asymmetric unit. This observation agrees with the documented tendency of phosphine to avoid coordinating *trans* to carbon donor ligands [24]. In the present work, crystal structure of [Pd(κ^2-N,C-$C_{10}H_8N$)(PPh_3)(OTs)] (**3**) was determined, while there are reports [25] on similar complexes with Br as a ligand instead of OTs. In both of the reported structures there are two molecules in asymmetric unit along with benzene molecule as a solvent of crystallization. Comparison of these structures with complex **3** from present work showed that the Pd–C, Pd–P and Pd–N bond lengths (Å) are in the range 2.019–2.064, 2.240–2.277 and 2.084–2.124, respectively. Because of the presence of OTs group in the present work in place of Br in the reported structure, the square planar geometry around palladium is more distorted compared to literature reports.

2.3. Catalytic activities of NC palladium complexes for the arylation of ethylene with 2-bromo-6-methoxynaphthalene

To investigate the new NC palladacycles in catalysis, Heck reaction *viz*. the arylation of ethylene with 2-bromo-6-methoxynaphthalene (BMN) was chosen as this yields 2-vinyl-6-methoxynaphthalene (VMN) which is an intermediate for the synthesis of anti-inflammatory drug Naproxen. The reaction was carried out in a 50 cm^3 Parr Autoclave made of Hastelloy-C-276.

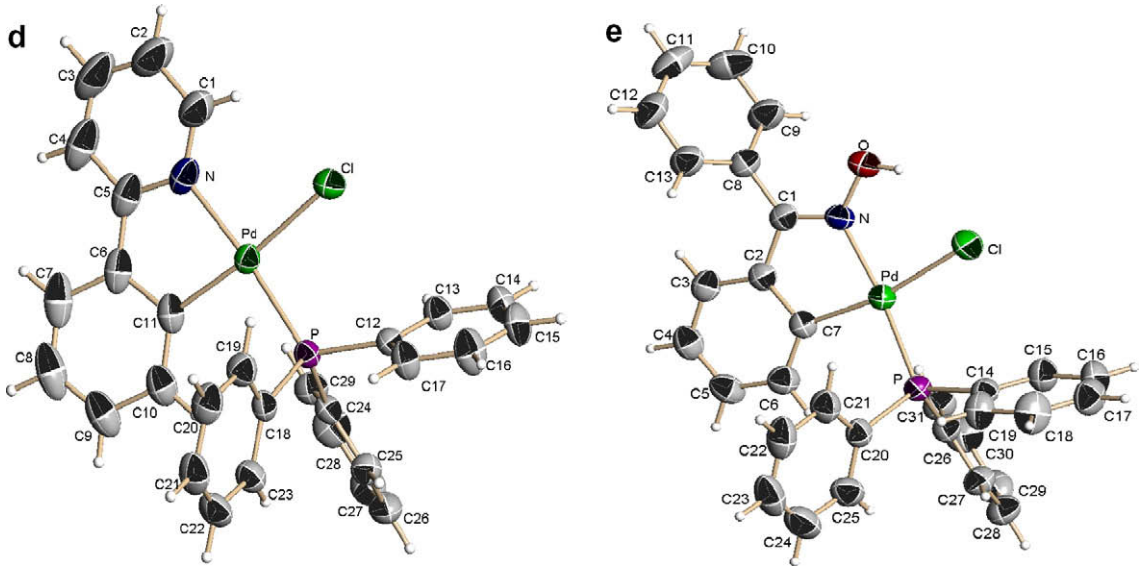


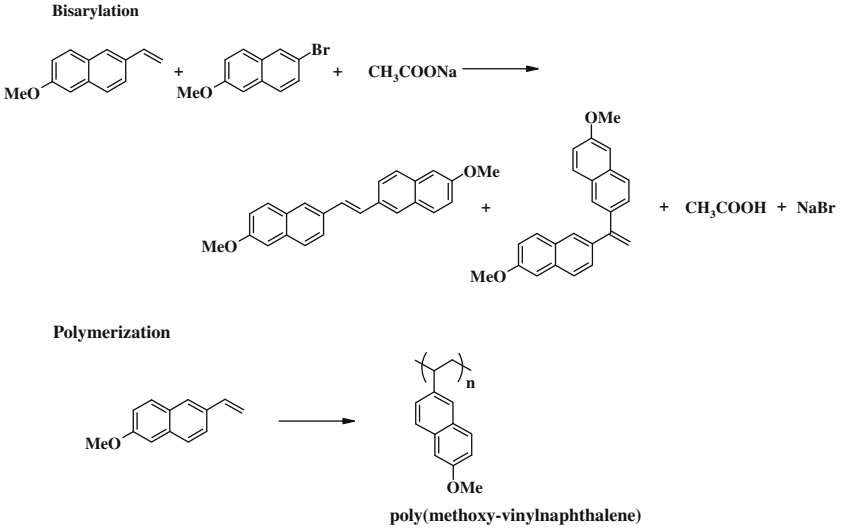
Fig. 2. ORTEP drawing of the palladium complexes with 50% probability (d) [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(Cl)] (**4**) and (e) [Pd(κ^2-N,C-$C_{13}H_{11}NO$)(PPh_3)(Cl)] (**5**).

Table 2
Selected bond lengths (Å) and angles (deg) for NC palladacycles.

	1	2	3	4	5
Pd–C	1.985(3)	1.987(3)	2.025(2)	2.020(2)	2.017(2)
Pd–P	2.2758(7)	2.2749(7)	2.2403(6)	2.2510(5)	2.2523(7)
Pd–N	2.085(2)	2.143(2)	2.0836(18)	2.0950(18)	2.060(2)
Pd–X	2.1351(19)	2.167(2)	2.1702(15)	2.3706(6)	2.3839(7)
C–Pd–N	81.25(11)	80.95(11)	83.53(8)	80.90(9)	79.69(9)
C–Pd–P	95.50(9)	94.95(9)	87.16(7)	94.53(7)	95.51(7)
P–Pd–X	94.87(6)	88.44(6)	99.59(5)	91.468(18)	96.33(3)
N–Pd–X	89.10(8)	97.94(9)	90.16(7)	93.05(6)	88.51(6)
C–Pd–X	169.07(10)	166.42(10)	171.64(8)	173.84(7)	168.17(7)
N–Pd–P	169.74(7)	168.94(7)	169.30(5)	174.92(5)	173.60(6)

X = O for **1**, **2**, and **3**; X = Cl for **4** and **5**.

The complex **1** [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] was examined in the arylation of ethylene with the reaction conditions as described in the US Patent 6005151. The patent describes the arylation of ethylene using BMN (100 mmol) and a dimeric complex (0.05 mmol) in *N*,*N*-dimethylacetamide solvent at 140 °C for a period of 10–16 h. In contrast, our reactions were carried at lower BMN (10.5 mmol) charge in *N*-methyl-2-pyrrolidone (NMP) solvent. The following reaction conditions were used for our reaction: BMN = 10.5 mmol, Cat = 0.05 mol%, NMP = 23 ml, NaOAc = 15.75 mmol, T = 140° C, ethylene pressure = 290 psi. To our surprise we found more than 96% of BMN was converted to the product in a very short time (<10 min). Thus, achieving the reaction completion in a much shorter time than described previously. One important point to be noted is the product VMN is a highly reactive compound and polymerizes at higher temperatures (Scheme 2), and the polymerized product is not detected by GC and an indirect proof of its formation is seen in the decreased area percent of VMN with time in samples withdrawn by GC analysis. For the optimized usage of the catalyst and reaction temperature, the reactions were carried at a lower catalyst loading of 0.013 mol% and in the temperature range of 90–120 °C. The results in the Fig. 3 show the percent conversion with the reaction time. The figure clearly reflects that at a temperature of 120 °C the rate of arylation is very fast. The reaction at 110 °C showed perfect mass balance with >99% conversion for the reactant consumed and the



Scheme 2. Side products in the arylation of ethylene with BMN.

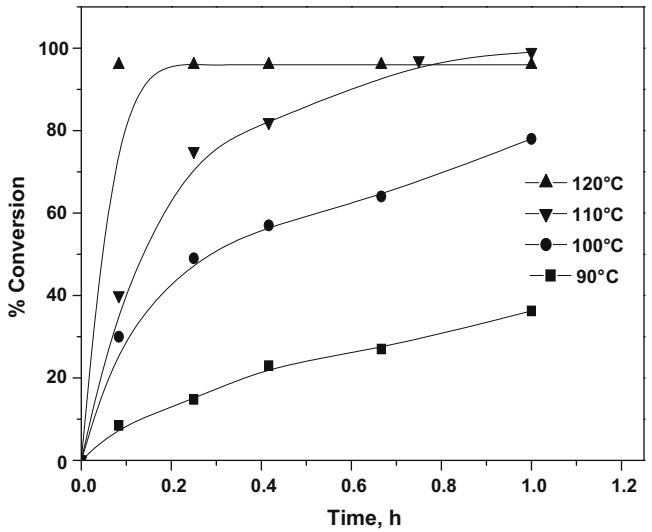


Fig. 3. Plots of conversion versus time for the arylation of ethylene with BMN at various temperatures.

product formed. Based on this observation further reactions were done at this temperature. The reaction showed a high selectivity towards VMN (>97%) and the dehalogenated product 2-methoxynaphthalene (MN) was also observed (<2%) during the reaction.

Few solvents were screened to find the best solvent system for this reaction and the results are presented in the Table 3.

N-methyl-2-pyrrollidone (NMP) was found to be the most suitable solvent for this reaction among the solvents screened. Using acetonitrile as solvent did not produce any results. Probably it acts as a ligand and coordinates with the palladium thus inhibiting it to enter the catalytic cycle. Applying diethylketone as solvent gave poor conversions. The polar solvents *viz. N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide also yield good conversions for the reaction. Since the Heck reaction mainly involves ionic components, and the exclusion of an acid in each catalytic step, polar aprotic solvents are the most desirable. Further experiments were conducted with NMP varying some reaction parameters at 90 °C to understand the selectivity pattern of the reaction. The results of these experiments are presented in Table 4. At 90 °C the reaction is slow and helps to understand details of mechanism more precisely. For this purpose higher catalyst loading of 0.068 mol% was used.

The results in Table 4 demonstrate that when the reaction is carried out at lower ethylene pressure, the selectivity towards the desired product VMN is low (73%). However, increasing the ethylene pressure leads to an increase of the selectivity towards VMN to 98%. Such behavior has also been observed by De Vries and Mendoza [11c] in the arylation of ethylene with 2-bromo-toluene as substrate (the formation of *trans*-1,2-bis(*ortho*-tolyl) ethylene and *gem*-1,1′-bis(*ortho*-tolyl)ethylene at lower ethylene pressure). In our experiments at lower ethylene pressure other products were obtained which could not be detected by GC. We believe that side reactions such as bisarylations arylations take place in the reaction, which is shown in Scheme 2 assuming the formation of by-products as described by De Vries. No attempt was made to isolate the side products. However, no side reaction takes place at an ethylene pressure of 290 psi. With increasing BMN concentration the TOF increases initially but dropped down with further increase: the TOF increases from 282 h^{-1} to 944 h^{-1} for BMN concentrations in the range 2.63–10.54 mmol, but for a further increase of BMN to 21.09 mmol the TOF decreases to 770 h^{-1}.

The choice of a base can have a crucial effect on the rate and product distribution of Heck reactions. The role of the base is to regenerate the active palladium complex by capturing the acid HBr and to complete the catalytic cycle [1b]. A number of organic and inorganic bases were tested in the arylation reactions, and we indeed observed a strong base dependence. The results are summarized in the Table 5. The use of organic bases gave low conversions entry 8–10 as compared to inorganic salts; organic bases such as triethylamine can act as ligands and they are strongly bond to Pd thereby making the catalytically active centre less accessible for the activation of the arylbromides [26]. The use of calcium oxide as a base yields a lower conversion of 35%. Sodium and potassium acetate which are less expensive and nonflammable are found to be the best base systems for these reactions.

A reaction was also carried out to compare the NC palladacycle catalysts with the Herrmann palladacycle under our reaction conditions. It was found that both the complexes exhibit similar activities, which was confirmed by concentration–time profiles displayed in Fig. 4. The concentration–time profile shows the perfect mass balance between the reactant (BMN) consumed and the product (VMN) formed.

The results for the arylation reaction using the synthesized palladacycles are summarized in Table 6 and progress of the reactions with time in Fig. 5. From Fig. 5, it can be seen that complete conversion with high selectivity to VMN is obtained in 1.5 h for all

Table 3
Effect of the solvent in the arylation of ethylene with BMN.

Entry	Solvent	Time (h)	Conversion (%)
1	*N*-methyl-2-pyrollidone	1.5	98
2	*N*,*N*-dimethylformamide	1.5	80
3	*N*,*N*-dimethylacetamide	1.5	90
4	Diethylketone	1.5	17
6	Acetonitrile	2	–

Reaction conditions: BMN (10.54 mmol), base (15.81 mmol), T = 110 °C, $P_{Ethylene}$ = 290 psi, solvent (~23 ml), [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] = 0.013 mol%.

Table 4
Effect of substrate concentration and ethylene pressure in arylation at 90 °C.

S. no.	BMN (mmol)	Conversion (%)	Ethylene pressure (psi)	Time (h)	VMN selectivity	Turnover no.	Turnover frequency (h^{-1})
1	10.54	75	290	1	98	944	944
2	5.27	95	290	1	98	566	566
3	2.63	95	290	1	98	282	282
4	21.09	35	290	1	98	770	770
5	10.54	100	35	2	73	1014	507
6	10.54	100	70	2	85	1136	568
7	10.54	74	150	2	90	958	479

Reaction conditions: base (15.81 mmol), T = 90 °C, NMP (~23 ml), [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] = 0.068 mol%.

Table 5
Effect of the base on the [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] catalyzed reaction of BMN and ethylene.

Entry	Base	Conversion (%)	Time (h)	TOF (h^{-1})
1	Sodium acetate	98	1.5	4629
2	Sodium carbonate	35	1.5	1391
3	Calcium oxide	35	1.5	1408
4	Sodium orthophosphate hydrate	84	1.5	3413
5	Cesium carbonate	70	1.5	3695
6	Potassium acetate	97	1.5	4272
7	Potassium carbonate	77	1.5	3326
8	Dicyclohexylamine	60	1.5	3087
9	Diisopropylamine	68	1.5	3316
10	Triethylamine	38	1.5	1711

Reaction conditions: BMN (10.54 mmol), base (15.81 mmol), T = 110 °C, $P_{Ethylene}$ = 290 psi, solvent (NMP ~23 ml), Pd-complex = 0.013 mol%.

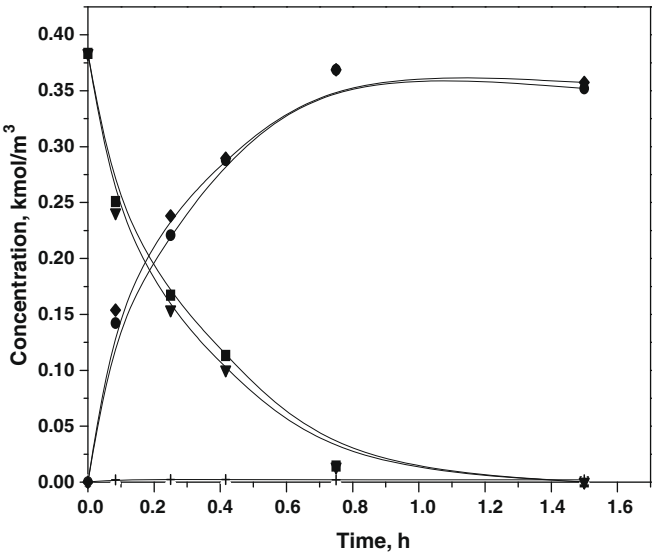


Fig. 4. Diagram of concentration versus reaction time for the arylation of ethylene with BMN using the complex [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] (**1**) and *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium (hc palladacycle).

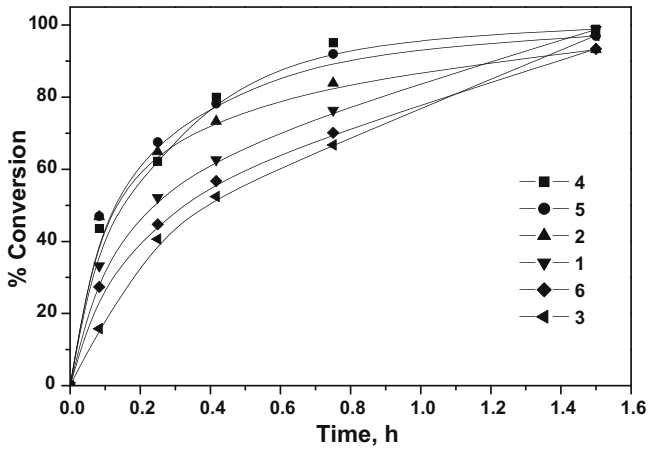


Fig. 5. Reaction profiles using various complexes.

Table 7
Arylation of ethylene with industrially important substrates.

Substrate	Catalyst (mol%)	Time (h)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
3-Bromo-benzophenone	0.013	1	97	98	4842
4-Bromo-isobutylbenzene	0.013	3	95	75	1874

Reaction conditions: BIBB (10.54 mmol), BBP (7.63 mmol), catalyst = [Pd(κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)], NaOAc (15.81 mmol), T = 110 °C, $P_{Ethylene}$=290 psi, solvent (NMP ~23 ml); BIBB = 4-bromo-isobutylbenzene, BBP = 3-bromo-benzophenone.

the complexes investigated. However, at 0.75 h, the catalytic activity was found to be different for the various complexes investigated. According to these results the complexes can be arranged in decreasing order of activity as follows: **4** > **5** > **2** > **1** > **6** > **3**. Complexes **1**, **2** and **3** have different NC ligands, while other ligands *viz.* PPh_3 and OTs are common. The X-ray structure analysis demonstrates that the bite angle N–Pd–C decreases in the order **3** > **1** > **2**, and the catalytic activity on the contrary increased in the order **3** < **1** < **2**. It is likely that various geometrical and electronic factors may be responsible for the observed trends in catalytic activity for Heck arylation reaction.

Arylation of ethylene was also carried out with industrially important substrates such as 3-bromo-benzophenone (BBP) and 4-bromo-isobutylbenzene (BIBB), and the results are presented in Table 7. It can be seen that the selectivity of the product using BIBB as a substrate is low. More detailed studies are needed for the improvement in the selectivity for this reaction. The selectivity of the product using BBP was found to be 98%.

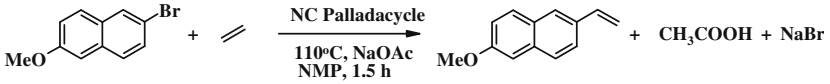
2.4. Concluding remarks

NC palladacycle complexes were prepared using inexpensive ligands and they were characterized in detail. The NC palladacycles show an excellent performance for arylation reactions with high turnover frequencies (TOF > 4000 h^{-1}) for the first time. The reaction requires less catalyst, lower temperature, and was found to be effective in the arylation of ethylene with industrially important substrates such as 3-bromo-benzophenone and 4-bromo-isobutylbenzene. All the six NC palladacycle are potential candidates for the arylation reactions. Further studies on arylation and carbonylation reactions to synthesize Naproxen and Ketoprofen are in progress in our Laboratory.

3. Experimental

Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ as an internal standard (δ 77.0). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C. Commercially available reagents were used without purification.

Table 6
Arylation of ethylene with 2-bromo-6-methoxynaphthalene using various NC palladacycle complexes.



Palladacycle	Catalyst (mol%)	Conversion (%)	TOF (h^{-1})
1	0.013	98	4629
2	0.013	93	4457
3	0.013	97	4634
4	0.013	98	4636
5	0.013	96	4729
6	0.013	93	4628

Reaction conditions: BMN (10.54 mmol), NaOAc (15.81 mmol), T = 110 °C, $P_{Ethylene}$ = 290 psi, time = 1.5 h, solvent (NMP ~23 ml).

3.1. General method for the synthesis of NC palladacycles

A mixture of the appropriate dimeric complex and triarlyphosphine/*p*-toluenesulfonic acid in chloroform was stirred at room temperature for 15 min. The solution was filtered through celite and hexanes were added to induce precipitation. The product was collected by filtration and recrystallized from either CH_2Cl_2/hexane or $CHCl_3$/hexane. (The complex **4** is known so the characterization details are not given).

3.2. [Pd (κ^2-N,C-$C_{11}H_8N$)(PPh_3)(OTs)] (**1**)

Yield 92%, Dec. pt. 205 °C (capillary, gradual darkening without melting); Elemental Anal.: found: C, 62.07; H, 4.27; N, 2.14; S, 4.14%; $C_{36}H_{30}NO_3PPdS$ (694.04) Calc.: C, 62.29; H, 4.32; N, 2.01; S, 4.61; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 6.46–7.81 (m, 26H), 9.14(m, 1H); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ = (163.10, 151.16, 148.11, 147.35, 139.59, 139.3, 139.2 135.47(d, J = 11.52 Hz), 134.74(d, J = 11.51 Hz), 130.68, 130.48, 130.09, 128.93, 128.74(d, J = 5.76 Hz), 128.21(d, J = 11.51 Hz), 126.24, 124.83, 123.98, 122.47, 118.04, 21.24); $^{31}P\{^1H\}$ NMR (202.46 MHz, CDCl3): δ = 39.92; IR (KBr): ν(O═S═O) 1255 cm^{-1} and 1150 cm^{-1}.

3.3. [Pd (κ^2-N,C-$C_{15}H_{10}N$)(PPh_3)(OTs)] (**2**)

Yield 95%, Dec. pt. 190 °C (capillary, gradual darkening without melting); Elemental Anal.: found: C, 59.07; H, 4.27; N, 1.44; S, 3.44%; $C_{40}H_{32}NO_3PPdS.CH_2Cl_2$ (829.02) Calc.: C, 59.4; H, 4.13; N, 1.69; S, 3.85; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 3H), 5.29 (s, 2H), 6.47–8.59 (m, 29H); $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 162.82(d, J = 3.66 Hz), 150.83, 147.51(d, J = 1.83 Hz), 146.85, 141.14, 139.51, 139.28, 138.74, 135.55(d, J = 12.08 Hz), 130.79(d, J = 2.56 Hz), 130.48, 130.34, 129.47, 128.18(d, J = 10.98 Hz), 127.7, 127.36, 126.93, 126.57, 125.78, 125.69, 124.75, 116.22, 53.40, 21.10; $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): δ = 41.98; IR (KBR): ν(O═S═O) 1260 cm^{-1} and 1152 cm^{-1}.

3.4. [Pd (κ^2-N,C-$C_{10}H_8N$)(PPh_3)(OTs)] (**3**)

Yield 90%, Dec. pt. 220 °C (capillary, gradual darkening without melting); Elemental Anal.: found: C, 61.21; H, 4.37; N, 2.37; S, 4.35%; $C_{35}H_{30}NO_3PPdS$ (682.03) Calc.: C, 61.6; H, 4.4; N, 2.05; S, 4.69; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.93–2.95 (d, 2H), 6.84–8.29 (m, 25H); $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = (154.53, 151.47, 150.50(d, J = 2.93 Hz), 146.85, 141.57, 139.34, 137.92, 134.35(d, J = 12.07 Hz), 130.53(d, J = 2.56 Hz), 129.62, 128.83, 128.24(d, J = 10.61 Hz), 128.15, 128.05, 127.4, 126, 124.13, 122.11(d, J = 3.66 Hz), 122.03, 28.44, 21.16); $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ = 32.42; IR (KBr): ν(O═S═O) 1216 cm^{-1} and 1154 cm^{-1}.

3.5. [Pd (κ^2-N,C-$C_{13}H_{11}NO$)(PPh_3)(Cl)] (**5**)

Yield 90%, Dec. pt. 215 °C (capillary, gradual darkening without melting); Elemental Anal.: found: C, 62.04; H, 4.07; N, 2.34; Cl, 6.13%; $C_{31}H_{25}ClNOPPd$ (600.34) Calc.: C, 62.0; H, 4.16; N, 2.33; Cl, 5.91; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.39–7.81 (m, 25H), 10.73 (s, 1H); 13C$\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = (166.01, 153.35, 144.75, 137.70(d, J = 10.61 Hz), 135.09(d, J = 12.08 Hz), 131.01(d, J = 12.08 Hz), 130.75, 129.87, 129.74, 129.37, 128.76, 128.37, 128.23, 128.15, 124.24; $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ = 42.12.

3.6. General procedure for the heck arylation of ethylene with BMN

In a typical Heck reaction, a mixture of BMN (10.54 mmol), sodium acetate (15.8 mmol), solvent (NMP-23 ml) and NC palladacycle catalyst (required amount, a stock solution of the catalyst in NMP solvent was used) to make the total volume 25 cm^3 were charged into a 50 cm^3 Parr Autoclave made of Hastelloy-C-276. The reactor was purged with nitrogen to remove the traces of air inside the reactor at room temperature and the mixtures were heated to the desired temperature. After the temperature was attained, the reactor was pressurized to 290 psi of ethylene and the reaction was started at the agitation of 1000 rpm. The reaction was monitored by taking aliquot samples at regular intervals and analyzed by GC immediately. (Precaution: special care should be taken while sampling the reaction mixtures; inorganic salts can block the sampling tube).

3.7. X-ray structure determination

The X-ray data of all the compounds were collected at room temperature on a SMART APEX CCD single crystal X-ray diffractometer with omega and phi scan mode and different number of

Table 8
Crystallographic data for palladium complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{36}H_{30}NO_3PPdS$	$C_{41}H_{34}Cl_2NO_3PPdS$	$C_{35}H_{30}NO_3PPdS$	$C_{29}H_{23}ClNPPd$	$C_{31}H_{25}ClNOPPd$
Formula weight	694.04	829.02	682.03	558.30	600.34
Crystal size (mm)	0.42 × 0.17 × 0.10	0.43 × 0.39 × 0.24	0.38 × 0.24 × 0.17	0.50 × 0.47 × 0.33	0.13 × 0.09 × 0.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.7329(4)	10.6960(5)	10.6375(4)	9.9575(4)	9.8861(6)
b (Å)	16.7366(7)	16.8380(8)	15.9797(6)	10.3204(4)	10.5028(6)
c (Å)	17.2684(7)	22.2180(9)	18.0061(7)	13.5965(5)	14.0789(8)
α (°)				78.847(1)	75.252(1)
β (°)	101.608(10)	113.500(1)	95.578(1)	70.540(1)	74.277(1)
γ (°)				67.960	79.892(1)
V (Å^3)	3038.5(2)	3669.6(3)	3046.3(2)	1217.41(8)	1351.84(14)
Z	4	4	4	2	2
μ (mm^{-1})	0.770	0.792	0.767	0.955	0.869
F_{000}	1416	1688	1392	564	608
D_{calc} (g cm^{-3})	1.517	1.501	1.487	1.523	1.475
Number of unique reflections	5356	6462	5351	4280	4759
Number of variables	389	452	380	300	326
R	0.0320	0.0340	0.0255	0.0214	0.0278
R_w	0.0803	0.0897	0.0635	0.0600	0.0655
Goodness-of-fit	1.065	1.062	1.056	1.119	1.053
Maximum/minimum $\Delta\rho$, e Å^{-3}	0.694, −0.203	0.849, −0.694	0.435, −0.171	0.302, −0.652	0.352, −0.225

scans and exposure times for different crystals using λ Mo Kα = 0.71073 Å radiation, at T = 293(2) K with oscillation/frame −0.3°, maximum detector swing angle = −30.0°, beam center = (260.2, 252.5), in plane spot width = 1.24. All the crystals were yellow colored and were grown by slow evaporation of a solution mixture in chloroform/dichloromethane and hexane. The data for all the compounds were corrected for Lorentz, polarization and absorption effects using SAINT and SADABS programs. The crystal structures were solved by direct method using SHELXS-97 and the refinement was performed by full matrix least squares of F^2 using SHELXL-97 (G.M. Sheldrick, SHELX-97 Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997). The structures were elucidated by single crystal X-ray analysis and the stereochemistry of the molecules was confirmed. Crystallographic data and details of structure refinement are summarized in Table 8.

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Appendix A. Supplementary material

CCDC 686824, 686825, 686826, 686827 and 686829 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.065.

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