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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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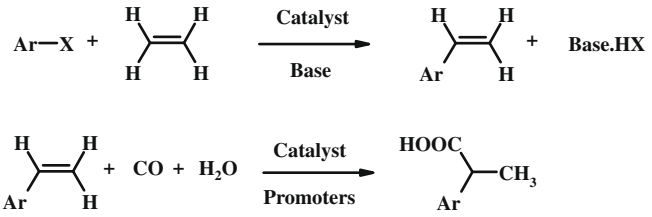


Scheme 1. Synthesis of aryl propionic acids using Heck coupling and carbonylation reaction.

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

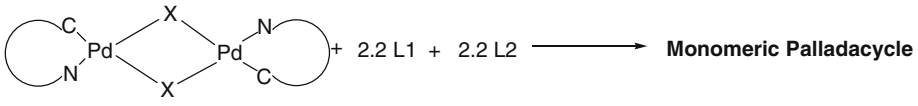
The NC palladacycle complexes were prepared in two steps using literature procedures [21]. The first step involves the reaction of palladium salts (or palladating agent, $Pd(OAc)_2$ or Li_2PdCl_4) and the ligands to form dinuclear molecules with acetate or halide bridged NC palladacycle [21]. In the 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.