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Dichloropalladium complexes ligated by 4,5-bis(arylimino) pyrenylidenes: Synthesis, characterization, and catalytic behavior towards Heck-reaction

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ABSTRACT

A series of 4,5-bis(arylimino)pyrenylidenylpalladium(II) chloride complexes (**C1**–**C4**) were synthesized and characterized by FT-IR and NMR spectroscopy, elemental analysis as well as by single crystal X-ray diffraction for the representative complexes **C1** and **C3**, which revealed a square planar geometry at the palladium center. All palladium complexes exhibited high activity for the Heck cross-coupling reaction, which were effective when conducted in various solvents. Furthermore, the *in-situ* mixture of palladium dichloride and the ligand (**L1**) provided an effective catalytic system for the Heck-reaction.

1. Introduction

The arylation and vinylation of alkenes with aryl or vinyl halides, known as the Heck reaction, was discovered independently by Heck [1] and Mizoroki [2] in the early 1970s, and has subsequently gained popularity in carbon–carbon formation in synthetic organic syntheses promoted by palladium compounds [3–12]. Moreover, palladium-mediated organic synthesis is also extended to the reactions of Sonogashira–Hagihara [13,14] and Suzuki–Miyaura [15–18]. In order to improve the catalytic efficiency of the palladium system, various complexes have been developed and investigations into the electronic and steric influences exerted by the nature of the substituents on the ligands employed have been reported [19–21]. Moreover, some palladium complex pre-catalysts could promote the coupling reaction of less active haloarenes or alkenes [22–25]. These palladium complex pre-catalysts have often employed ligands derived from phosphine compounds [26–29], for which the toxicity in the application is commonly a concern. Further explorations into other potentially flexible (and efficient) ligands have suggested that palladium complex pre-catalysts bearing *N*,*N*-bidentate ligands such as diimine [30], dipyridine [31–36] and hydrazine are useful [37]. Interestingly, reports on olefin polymerization by *N*,*N*-bidentate palladium complexes have been published [38–42], of which a few were also explored for their application in the Heck reaction [43,44]. During our search for highly active pre-catalysts of α-diiminonickel complexes in ethylene polymerization [45–51], a number of catalytic systems exhibited high activities and enhanced thermal stabilities [49–52]. In addition, the 1,2-bis(arylimino)acenaphthylenylpalladium chlorides were found to be highly active and thermally stable in the Heck reaction [52]. More recently, a series of 4,5-bis(arylimino)pyrenylidenes was developed and successfully used as ligands for their nickel complex pre-catalysts in ethylene polymerization [53]. To broaden the scope of such compounds acting as ligands in catalysis, their palladium complexes have been prepared and were found to be highly active in promoting Heck coupling. Herein, the synthesis and characterization of the title palladium complexes and their catalytic behavior in the Heck reaction are reported.

2. Results and discussion

2.1. Synthesis and characterization of ligands and complexes

The 4,5-bis(arylimino)pyrenylidenes (**L1**–**L4**) were prepared according to the reported method [53]. The α-Diiminopalladium (II)

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chlorides (**C1**–**C4**) were obtained by the reaction of the corresponding ligands with $(CH_3CN)_2PdCl_2$ in dichloromethane at room temperature (Scheme 1). All complexes tended to precipitate from the reaction solution, and optimized yields were obtained by adding excessive amount of Et_2O to the reaction solution. The elemental analysis data confirmed their composition as **L**$PdCl_2$, and the complexes were further identified by FT-IR and NMR spectroscopic measurements.

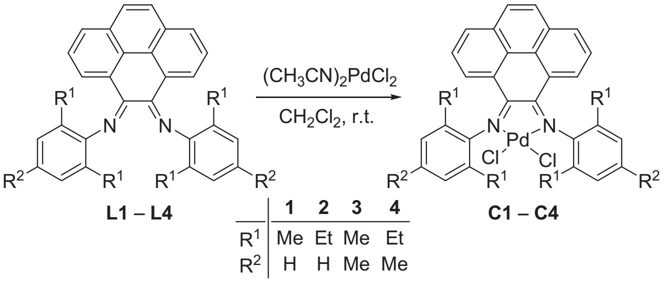
The stoichiometric reaction of $(CH_3CN)_2PdCl_2$ with the α-diimino ligands (**L1**–**L4**) in dichloromethane afforded the corresponding palladium chloride complexes (**C1**–**C4**) in reasonable isolated yields. Moreover, these complexes were characterized by elemental and spectroscopic analysis. Due to the efficient coordination of N_{imino} to Pd, the absorption of the νC=N vibration became quite weak in the IR spectra of the palladium complexes, which is consistent with the observation of the infrared inactive C=N vibration in the palladium complexes [54]. The ^{13}C NMR peaks for the C=N groups in the palladium complexes were shifted to lower field, for example δ 167.1 ppm for **C3** *vs* 159.1 ppm for **L3**, and were indicative of the strong coordination between the N_{imino} atom and the Pd center [55]. To confirm the structures of the palladium complexes, single crystals of complexes **C1** and **C3** were obtained and the molecular structures were determined by single crystal X-ray diffraction.

2.2. Crystal and molecular structures

Single crystals of the representative complexes **C1** and **C3** were obtained by slow diffusion of diethyl ether into dichloromethane solutions at ambient temperature. The molecular structures of each are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles tabulated in Table 1. As shown in Figs. 1 and 2, the complexes **C1** and **C3** possess similar structures, that is, with a square planar geometry at the palladium center comprised of two nitrogen atoms (of the chelate) and two chloride atoms. For the complexes **C1** and **C3**, the double bonding features are illustrated by N1–C1 1.301(5) Å and N2–C14 1.310(5) Å in **C1** and 1.306(6) Å and 1.308(6) Å in **C3**, whilst the single bonds for N1–C17 and N2–C23 are 1.431(5) Å and 1.448(5) Å in **C1** and 1.439(6) Å and 1.433(6) Å in **C3**. The dihedral angles formed by the C17–C18–C22 and C1–N1–Pd1 are 89.3° in **C1** and 80.3° in **C3**. In addition, the dihedral angles formed by the two imino-phenyl rings connected to the nitrogen atoms are 24.8° in **C1** and 18.6° in **C3**, respectively. Compared to the crystal structure of **L3** [53], there are obvious changes of the dihedral angles involving the two imino-phenyl rings at 72.67° in **L3** and 18.6° in **C3**, the difference being attributed to more efficient coordination to the palladium center in **C3**.

2.3. Catalytic behavior

With regard to the use of these palladium complexes as pre-catalysts in ethylene polymerization, the complexes **C1**–**C4** exhibited poor catalytic activities in the range 10^3 g(PE)·mol^{-1}(Pd)·h^{-1}, with the assistance of MAO (co-catalyst) and with an Al/Pd ratio at 2000. Therefore, trials of their potential in Heck coupling became the focus of our studies here.



Scheme 1. Synthetic procedure for the palladium complexes (**C1**–**C4**).

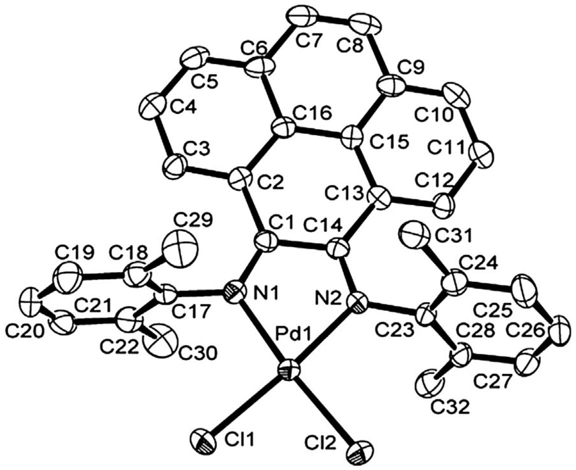


Fig. 1. ORTEP drawing of **C1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The complex **C1** was explored for the Heck reaction of bromobenzene with styrene to ascertain the optimum conditions for producing 1,2-diphenylethene. Besides the palladium complex pre-catalyst, in principle, the catalytic behavior can also be significantly affected by the inorganic base and organic solvent used. The trial conditions were fixed at a slight excess (1.2 equivalent) of styrene and 1.1 equivalents of inorganic base to bromobenzene with a catalytic amount of **C1** ([Pd]/[bromobenzene] = 4 × 10^{-5}); the conversion of bromobenzene was monitored and results are tabulated in Table 2. According to our previous experience [52], the *N*,*N*'-dimethylacetamide (DMA) is the preferred solvent and this was utilized in the presence of different inorganic bases (entries 1–9, Table 2). As shown by entries 1 to 5 with the base as Na_2CO_3, it is necessary to activate the catalytic system by elevating the reaction temperature. Trace amounts of bromobenzene were converted over 12 h at 120 °C (entry 1, Table 2); meanwhile, at 150 °C, 70% of bromobenzene was converted over 3 h (entry 2, Table 2), and more bromobenzene was converted on further prolonging the reaction time (entries 3 and 4, Table 2); more than 99% of bromobenzene was converted over 12 h at 150 °C (entry 5, Table 2) without

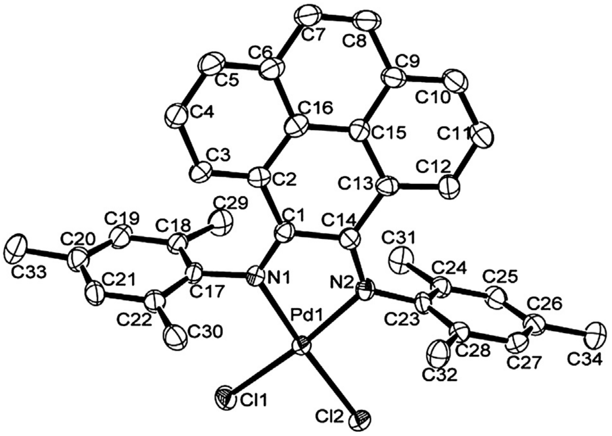


Fig. 2. ORTEP drawing of **C3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.