

Binuclear palladium complexes bridged by dicarbene with different lengths and their application in Mizoroki–Heck reaction

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ABSTRACT

A series of di-NHC ligands with alkyl bridges of different chain lengths ($n = 2-4$) and their bi-palladium complexes (**4**, **5** and **6**) have been prepared. The molecular structure of **4** and **6** were determined by X-ray diffraction studies. The structures of complex **4** consist of two pseudo-square-planar subunits in a *trans* configuration, however **6** consist of two subunits in a *cis* configuration with π - π stacking between two pyridines. The influence of the different bridges on the structure and reactivity of the complexes has been studied. The catalytic activity of the new binuclear palladium complexes was successfully tested in the Mizoroki–Heck reaction of styrene with bromobenzene. The complex with **2** and **4** carbon linker gave higher yield, while the one with 3 carbon linker gave better regioselectivity.

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1. Introduction

Since the first isolation of a stable, free N-heterocyclic carbene by Arduengo in 1991 [1], NHC has attracted considerable attention as a new class of ligands in organometallic coordination chemistry due to its successful application in homogeneous catalysis [2–4]. The majority of NHC ligands used are monodentate [4], and much fewer complexes are known that involve bidentate di-N-heterocyclic carbene (di-NHC) ligands, in which pairs of NHC groups are joined by an appropriate linker group [5–7]. Most of the complexes containing di-NHC's employ these groups as chelating ligands at a single metal. Investigations of binuclear di-NHC complexes have been limited so far, although some have been reported in which the di-NHC group bridges pairs of metals [8]. On the basis of an extensive chemistry of binuclear, late metal complexes with diphosphine ligand [9], the design and synthesis of binuclear complexes with di-NHC are of considerable interest.

In this paper we describe the synthesis of a series of bi-palladium di-NHC complexes with different length, diagrammed in Scheme 1, and tested them in the C–C coupling reaction of Heck reaction.

2. Results and discussion

2.1. Synthesis of the bisimidazolium chloride salts

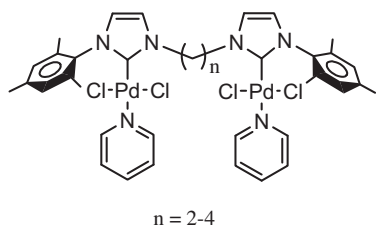
1-Mesitylimidazole was synthesized according to the method reported by Liu et al. (Scheme 2) with a little modification [10]. The product was purified by sublimation instead of column chromatography, giving 65% yield. The synthesis of bisimidazolium salts from imidazoles is accomplished by a substitution reaction of alkyl dihalide with 2 equiv. of imidazoles [11,12]. Usually, the reactions worked well with bromides and iodides, and it generally required high temperature and longer reaction time with chlorides. In addition, hazard organic solvent, such as DME [13], PEG [14] or THF [15] was usually used. We developed a green and easy method to synthesize bisimidazolium chloride salts. As the 1-mesitylimidazole was melted at about 110 °C, the bisimidazolium dichlorides could be prepared in neat condition. As the high concentration of the reaction mixture due to the lack of solvent, the reaction is completed in a shorter time and lower temperature in high yield. The completion of the reaction is easy to monitor by initial colorless solution turning to final white solid. This method is also suitable for synthesis of other bisimidazolium salts [16].

2.2. Synthesis and characterization of the bi-palladium di-NHC complexes

The synthesis of bi-palladium di-NHC complexes **4**, **5** and **6** are achieved by refluxing of the corresponding imidazolium salt, with

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Scheme 1. Bi-palladium di-NHC chloride complexes with different alkyl bridge lengths.

palladium chloride in presence of K_2CO_3 in pyridine, as shown in Scheme 3. These complexes were fully characterized by NMR spectroscopy and gave satisfactory elemental analyses. The complexes are air and moisture stable and can be stored at air atmosphere in solid state for more than 6 months without any noticeable decomposition.

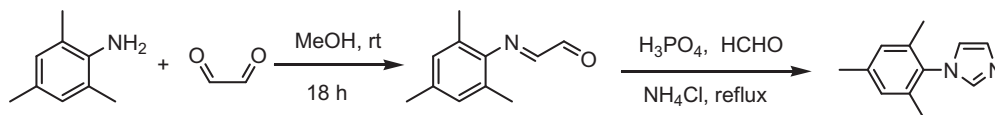
The formation of the metal complexes was evident from the distinctive metal-bound carbene peak, which appeared at 152.5 and 151.3 ppm for complex **4**, 152.5 and 151.2 ppm for **5**, and 153.3 and 150.1 ppm for **6**. It is noteworthy that the 1H NMR patterns of four methyl groups from 2, 6-dimethyl on mesityl group of the imidazolylidene ligand in complexes **4**, **5** and **6** are very different. The 1H NMR of **6** which has longer linker between two Pd centers showed only one signal (2.25 ppm) for the four methyl groups on the phenyl group meaning the molecule has a binary symmetry and methyl groups and phenyl rings could rotate rapidly within NMR time scale in the solution at room temperature, so there is almost no steric hindrance around Pd center in complex **6**. However,

the 1H NMR of **5** having one carbon shorter linkage between two palladium compared to **6** showed two distinctive signals for the four CH_3 (2.29 ppm and 2.25 ppm), and the 1H NMR of **4** with two carbon shorter linkage showed multiple peaks from 2.30 to 2.25 ppm.

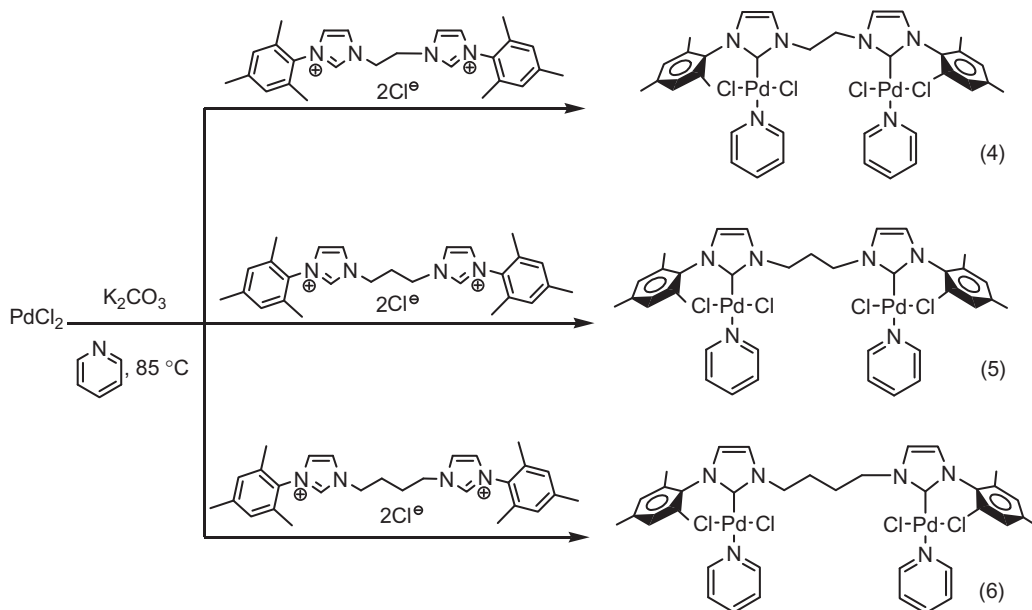
The molecular structures of **4** and **6** were determined by means of X-ray diffraction studies. The molecular diagrams of **4** and **6** are shown in Figs. 1 and 2 and selected crystallographic data are shown in Table 1. The structures of complex **4** consist of two pseudo-square-planar subunits in a *trans* configuration bridged with ethylene. The structures of complex **6** consist of two pseudo-square-planar subunits in a *cis* configuration bridged with butylene, and there is probably a face-to-face π - π stacking between two pyridine rings. The distance of the centers of the two pyridines is 3.913 Å and the shortest atom distance on the two pyridines is 3.525 Å. Two complexes show slightly distorted square-planar geometries around two palladium centers, which are surrounded by imidazolylidene, two chloro ligands in a *trans* configuration, and a pyridine. The Pd- C_{carbene} distance is 1.951(18) Å and 1.988(17) Å for **4** and 1.965(5) Å for **6** (Table 2), similar to that shown by other palladium-related species [17,18]. The Pd- N_{pyridine} distance in complex **6** [2.094(4) Å], **4** [2.070(9) Å, 2.075(14) Å] was comparable to that of its related saturated mono-palladium carbene analogues [17]. All other distances and angles lie in the expected range (Table 2).

3. Heck reaction

The palladium-catalyzed arylation of olefins has found wide application in organic synthesis. The activity of complexes **4–6** in



Scheme 2. Synthesis of 1-mesitylimidazole.



Scheme 3. Synthesis of the bi-palladium di-NHC complexes **4**, **5** and **6**.

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