



Dinuclear macrocyclic palladium complexes having pincer coordinating groups and their catalytic properties in Mizoroki–Heck reactions

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ABSTRACT

An improved synthetic method of palladium(II) dinuclear macrocyclic complexes have been described. Each of the two isomers of the complexes $[\text{Pd}_2\text{LBr}_2]$ has a macrocyclic ligand L in which two 2,6-bis(diaminomethyl)phenyl units coordinate to the Pd(II) centers with N, C, N donor atoms. Substitution of the bromo ligands of one of the isomer of the complexes with acetonitrile ligands affords a new dinuclear complex. Catalytic activities of these complexes were studied for the Mizoroki–Heck type reactions of iodobenzene and styrene. High turnover number up to 30,000 was achieved using one of the isomer of the complexes.

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1. Introduction

A large number of ECE pincer complexes (E = donor atoms or groups such as NR_2 , PR_2 , SR, etc) have been reported due to the potential applications in diverse fields such as catalysis, polymer and dendrimer chemistry, and pharmaceuticals [1–4]. In these studies, palladium complexes have been widely explored because of their activity in many organic reactions [5]. A number of mechanistic studies have been carried out, and there has been controversy on this topic [6].

In 2001, we reported the synthesis and the structure of macrocyclic palladium complexes bearing two pincer ligating groups [7]. The complex has two isomers; U-type (Pd-U) and Z-type (Pd-Z), which are shown in Scheme 1. Overall conformations of the two isomers are different from each other, and the configurations around the coordinated nitrogen atoms are also different for the two isomers. In the original paper, two isomers were obtained by two distinct methods. Pd-Z was prepared by lithiation of the dibromo precursor (LBr_2 , see Scheme 1) followed by the reaction of the lithium complex with $[\text{PdBr}_2(\text{cod})]$, but the yield was very low (<5%). On the other hand, Pd-U was directly obtained by the reaction of LBr_2 with “Pd(dba)₂”. Pure Pd-U was obtained from

chloroform–ether in 10% yield. The low-yield of the compound prevented us to do further study for catalysis etc. Recently, we found a new and easy method to obtain both isomers with improved yields. In this paper, the improved method, the substitution reaction of the bromo ligand, and Mizoroki–Heck-type catalytic reactions mediated by the complexes are presented.

2. Results and discussion

2.1. Synthesis and characterization of Pd-U and Pd-Z

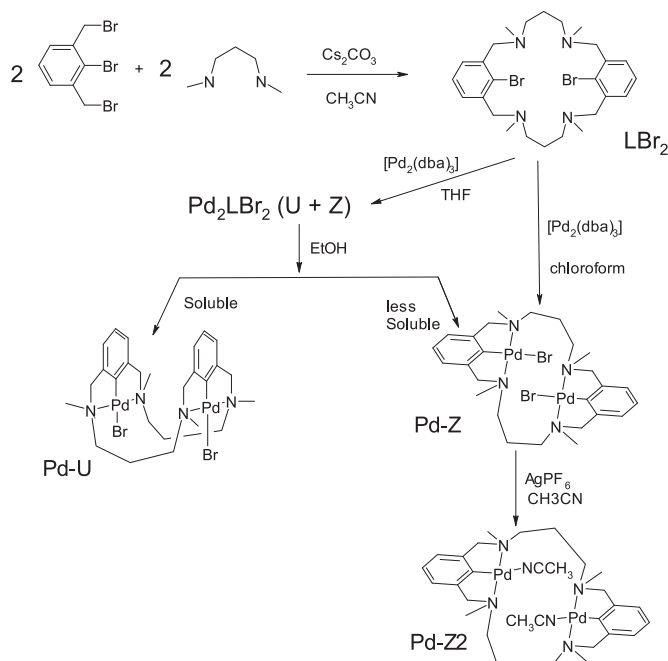
After the publication of the synthetic work of the two isomers of the macrocyclic complexes, we studied more convenient and effective route to synthesize the complexes. Recently, we found that 1) the reaction of the dibromo ligand precursor, LBr_2 , and “Pd(dba)₂” affords a mixture of the two isomers and 2) the two isomers show clearly different solubility in ethanol. Pd-U is far more soluble in ethanol at r.t. than Pd-Z, so that the two isomers can be easily separated from the mixture of the two isomers. The products in the reaction depend on the solvent used in the reaction. The reaction in chloroform and work-up with ethanol gave Pd-Z in 53% yield. The signals due to Pd-U were not detected by ¹H NMR in the filtrate after isolation of Pd-Z when the reaction was performed in chloroform. On the other hand, both the Pd-Z and Pd-U were isolated using THF as the reaction solvent. Separation of the isomers using ethanol gave the Z and U isomers in 10% and 31%, respectively.

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Scheme 1. Preparation of the macrocyclic complexes.

As reported in the previous paper [7], the two isomers can be clearly characterized by ^1H NMR. Aromatic protons of Pd-Z are observed in more low-field region than those of Pd-U. Recently we found that Pd-U slowly changes to Pd-Z in chloroform. In the chloroform-d solution of Pd-U, the NMR signals gradually diminished, and those of Pd-Z appeared. After 50 days kept at room temperature, the signals of both complexes were found with about 1:1 ratio. At 45 °C, Pd-U isomerized almost completely to Pd-Z after 8 days (see Fig. S1(a) in supporting information). On the other hand the NMR spectrum of Pd-Z showed no change even at 45 °C in 8 days (Fig. S1(b)). The result demonstrates that Pd-Z is more thermodynamically stable than the Pd-U complex. Obviously, the synthesis of Pd-U in THF is kinetically controlled.

2.2. Synthesis and structure of the acetonitrile complex Pd-Z2

Considering that an acetonitrile ligand is generally more labile than a halogeno ligand [8], we thought that the macrocycle complex bearing acetonitrile ligands may be more suitable as a catalyst. Therefore substitution of the bromo ligands of the macrocyclic complex with acetonitrile ligands has been studied. Reaction of Pd-Z with silver hexafluorophosphate in acetonitrile gave the bis(acetonitrile)-substituted complex, $[\text{Pd}_2\text{L}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, Pd-Z2, with a moderate yield. In the aromatic region in the ^1H NMR spectrum, a triplet at 7.05 ppm and a doublet at 6.85 ppm are observed, which is similar to Pd-Z. One more characteristic feature of the NMR signals of these macrocyclic complexes is the presence of AB doublet of doublets at ca. 4 ppm, which is assigned to the inequivalent methylene protons adjacent to the aromatic groups. The difference in the chemical shifts between the two doublets for Pd-U and Pd-Z are 0.10 and 0.37 ppm [7], respectively. For Pd-Z2, the difference is 0.23 ppm, which is in the middle of the value of Pd-Z and Pd-U.

The crystal structure of the Pd-Z2, $[\text{Pd}_2\text{L}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot (\text{C}_6\text{H}_6)_2$, was clarified by X-ray crystallography. The structure of the complex cation is shown in Fig. 1 and the important structural parameters are listed in Table 1. The triclinic unit cell contains one

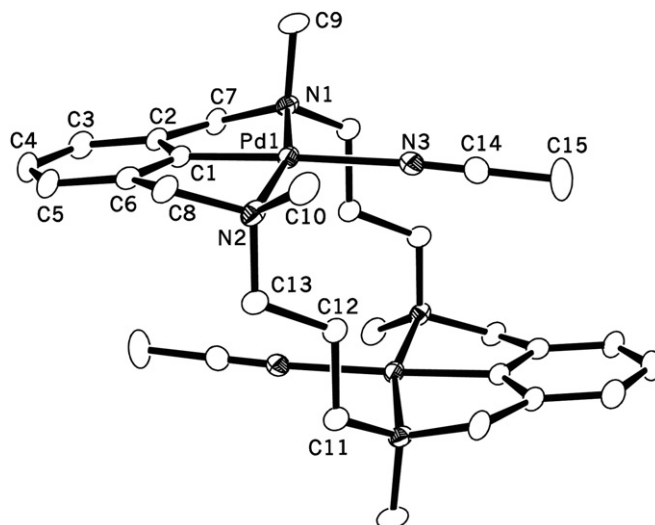


Fig. 1. The structure of Pd-Z2 showing the numbering scheme of the atoms. Thermal ellipsoids are drawn at 50% probability level.

$[\text{Pd}_2\text{L}(\text{CH}_3\text{CN})_2]^{2+}$ cation, two hexafluorophosphate anions, and two benzene molecules of solvation. The complex cation has a crystallographic center of inversion at the central position of the complex, as found in the crystal structure of the Pd-Z complex. N1 and N2 are asymmetric nitrogen atoms, however, the complex cation itself shows an achiral meso-type structure. For the coordination of the macrocyclic ligand, the average Pd–N (pincer ligand) bond length for Pd-Z2 (2.11 Å) is somewhat shorter than that of Pd-Z and Pd-U but the differences are very small (see Table 1). Pd–C1 (1.924(4) Å) length is slightly longer than the other two complexes. The two previous complexes have bromo ligands located at the *trans* position of the C atoms, which may be the main reason of the shorter Pd–C bonds (1.924(4) Å). Pd–N (acetonitrile) bond length (2.149(4) Å) is somewhat longer than those in the previously reported similar $\text{N}^+\text{C}\equiv\text{N}$ pincer Pd(II) complexes with an acetonitrile ligand [9]. The bond angle, C1–Pd–N3, is almost linear (176.9(2)°).

2.3. Catalytic activity

In order to examine the catalytic activity of the complexes, Mizoroki–Heck type reaction was studied (Scheme 2). The reaction of iodobenzene (2 mmol) and styrene (3 mmol) were investigated. The results under various reaction conditions are shown in Table 2. The reaction products are *trans*-stilbene and 1,1-diphenylethylene (*gem*-stilbene), and the ratio of the two products was almost always constant, ca. 6:1 (Fig. 2). It should be noted that oxygen-free condition is not necessary for the reaction although dry solvent is necessary to drive the reaction (see run 1 and 2).

Almost no difference has been found in the catalytic activities of the Pd-U and Pd-Z complexes (compare runs 2 vs. 3, 5 vs. 6 and 7 vs. 8). One possible interpretation of the result was that, in the heated

Table 1
Comparison of the structural parameters of palladium macrocycles.

	$[\text{Pd}_2\text{L}(\text{CH}_3\text{CN})_2]^{2+}$, (Pd-Z2)	$[\text{Pd}_2\text{LBr}_2]$ (Pd-Z)	$[\text{Pd}_2\text{LBr}_2]$ (Pd-U)
Pd–N	2.109(4), 2.116(4)	2.131(4), 2.122(4)	2.104(6), 2.136(6)
Pd–C	1.924(4)	1.919(5)	1.914(6)
Pd–X	2.149(4) X = N	2.569(1) X = Br	2.562(2) X = Br
N1–Pd–N2	163.6(2)	162.5(2)	164.8(2)
C1–Pd–X	176.9(2) X = N	173.7(2) X = Br	173.9(2) X = Br

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