

Structural Peculiarities and Catalytic Activity of Dibenzobarrelene-Based PC_{sp3}P Pincer Iridium Complexes

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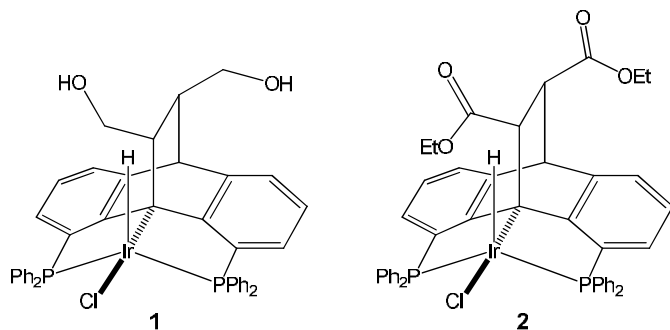
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During the last decade there is a steadily growing interest to so-called “ligand-metal cooperating” catalysts bearing “non-innocent” ligands. The intramolecular hydride-proton interaction that leads to facile hydrogen release was hypothesized as the origin of high catalytic activity of the bifunctional dibenzobarrelene-based PC_{sp3}P pincer iridium complex **1** in acceptorless dehydrogenation of alcohols.[1] Most recent results of our studies showed the catalytic activity of **1** in hydroformylation based on metal-ligand cooperation and presumably taking place without a change in the metal oxidation state. In order to shed more light on the peculiarities of the geometry of the C_{sp3}-metalated pincer compounds based on the dibenzobarrelene scaffold and the role of CH₂OH group in catalysis, the detailed structural investigation was carried out for complexes **1-2**. For this purpose variable temperature IR and NMR spectroscopic studies were combined with the DFT/B3PW91 calculations.



It was established that the structural transformations between *fac*- or *mer*-isomers of **1** and **2** become possible in the presence of bases/coordinating reagents such as DMSO, pyridine, acetonitrile and triethylamine, some of which have been used as auxiliary base in catalytic alcohols dehydrogenation [1]. The mechanism of the H₂ activation and C-H bond formation involves intramolecular cooperation between the structurally remote CH₂OH functionality and the metal center and proceeds without the change of the oxidation state of the metal.

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1. S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem. Int. Ed.* **2011**, 50, 3533