

# Structural Peculiarities and Catalytic Activity of Dibenzobarrelene-Based PC<sub>sp3</sub>P Pincer Iridium Complexes

*N.V. Belkova*<sup>1</sup>, *G.A. Silantjev*<sup>1</sup>, *O.A. Filippov*<sup>1</sup>, *S. Musa*<sup>2</sup>, *D. Gelman*<sup>2</sup>, *L.M. Epstein*<sup>1</sup>,  
*K. Weisz*<sup>3</sup>, *E.S. Shubina*<sup>1</sup>

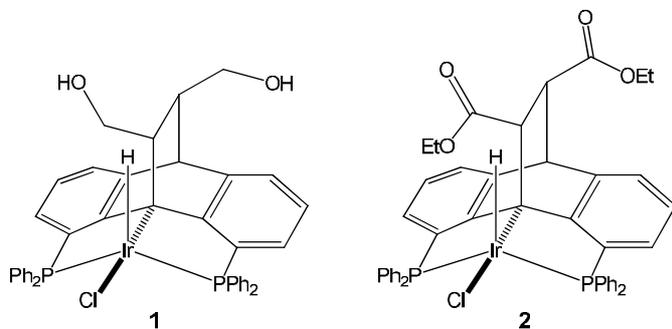
1 - A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia

2 - The Hebrew University of Jerusalem, Jerusalem, Israel

3 - Ernst Moritz Arndt University of Greifswald, Greifswald, Germany

[nataliabelk@ineos.ac.ru](mailto:nataliabelk@ineos.ac.ru)

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<sub>sp3</sub>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<sub>sp3</sub>-metalated pincer compounds based on the dibenzobarrelene scaffold and the role of CH<sub>2</sub>OH 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 H<sub>2</sub> activation and C-H bond formation involves intramolecular cooperation between the structurally remote CH<sub>2</sub>OH 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