“Chiral-at-metal” inert octahedral Co(III) complexes as “organocatalysts in disguise” for asymmetric transformations

Vladimir A. Larionov,1,2 Victor I. Maleev,1 Yuri N. Belokon1
1 - Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Vavilov Str. 28, 119991 Moscow, Russian Federation
2 - Department of Inorganic Chemistry, People’s Friendship University of Russia (RUDN University), Miklukho-Maklaya Str. 6, 117198 Moscow, Russian Federation
vldmr.larionov@gmail.com

By the end of the last century, the main development focused on the asymmetric metal complex catalysis, where the metal ion was directly involved in a catalytic process by interacting with the substrates.1 Now days, the most popular area of research is so-called chiral organocatalytic systems, where no metal ions are involved in catalysis.2 However, for the last 10 years there appeared several papers reported use of kinetically-inert chiral, coordinatively saturated stereogenic-at-metal complexes for the asymmetric catalysis.3 In those complexes the metal center serve, mainly, a structural role as a "scaffold" for the participating ligands, keeping them in space in an asymmetrically designed manner. An additional role of the metal is the activation of the acidic groups (OH or NH) of the ligands. As a result, the catalytic activity of the complexes originated not from metal/substrate relations but from the ligand/substrate multiple cooperative hydrogen-bonding interactions in a chiral environment.3

Herewith, we report the synthesis of a novel type of chiral coordinatevely saturated Co(III) complexes, featuring chirality centered both at metal and ligands (Figure). Additionally, their application as “organocatalysts in disguise” is disclosed for many asymmetric transformations such as asymmetric alkylation, Michael addition, epoxidation, trimethylsilylation and etc.4

This work has been supported by the Russian Science Foundation (RSF grant 17-73-10016).