

Experimental evaluation of ligand electronic effects on cyclopentadienyl iron complexes

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In organometallic chemistry, and especially in the catalysis area, accessing the finest tuning of a catalytic reaction pathway requires a detailed knowledge of the steric and electronic influence of the ligands bound to the metal center. Usually, the M-L bond between a ligand and a metal is depicted by the Dewar-Chatt-Duncanson¹ model involving two opposite interactions, a σ -donor and a π -acceptor effect of the ligand. Various experimental approaches have been devoted to the exploration of these ligand effects, as, for instance, the Tolman Electronic Parameter.² The development of new experimental methodologies is interesting in order to overcome the limitations that may be encountered by the existing methods. In the recent years, our group has thus worked on the development of new experimental approaches to evaluate these ligands effects, using either mass spectrometry (MS) or photoelectron spectroscopy (PES) with synchrotron radiation. Model systems were first tested in order to probe the validity of the approaches.^{3,4} Series of cyclopentadienyl iron complexes developed by the group of J.-L. Renaud in Caen University have thus been studied using photoelectron spectroscopy. The results obtained will be presented and discussed in light of modelization results based on DFT and energy decomposition analysis (EDA) calculations combined with the natural orbitals for chemical valence (NOCV) analysis.⁵

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