

Paramagnetic NMR and EPR parameters of Iridium complexes with pincer PNP ligands: Effects of Structure and Relativity

Pankaj Lochan Bora,^{†,‡} Jan Novotný,^{†,§} Michal Repisky,^Δ Kenneth Ruud,^Δ Stanislav Komorovsky,^{||}
and Radek Marek^{*†,‡,§}

[†] CEITEC - Central European Institute of Technology, Masaryk University, Brno, Czechia

[‡] Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czechia

[§] National Center for Biomolecular Research, Faculty of Science, Masaryk University, Brno, Czechia

^Δ Center for Theoretical and Computational Chemistry, Department of Chemistry, UiT – The Arctic University of Norway, Tromsø, Norway

^{||} Institute of Inorganic Chemistry, Slovak Academy of Science, Bratislava, Slovakia

Relativistic effects play an important role in the study of molecules containing heavy atoms, because in those systems the electrons move very fast near the nucleus. It significantly affects the intermolecular interaction, various spectroscopic properties etc. of compounds containing heavy elements. Particularly in Nuclear Magnetic Resonance (NMR) spectroscopy, the heavy atoms strongly influence the NMR shielding constants of neighboring light atoms. We have studied the effect of relativity on the response parameters of open-shell iridium complexes with pincer PNP ligands. We optimized methodology to calculate the EPR parameters and the paramagnetic NMR chemical shifts in iridium pincer PNP complexes by using Density-Functional theory (DFT). As the electronic structure of compounds containing 5d transition metal is heavily affected by spin-orbit coupling, the evaluation of relativistic effects and the validation of density functional used to calculate magnetic response properties have to be performed. We used new implementation of the fully-relativistic Dirac-Kohn-Sham (DKS) method in the program ReSpect, employing hybrid GGA functional (mainly PBE0 and B3LYP with user-defined amount of exact-exchange admixture) and the GIAO approach to the NMR chemical shifts. The performance of the four-component (4c) DKS approach to calculate the NMR and EPR parameters is compared with that of the two-component (2c) spin-orbit zeroth-order relativistic approximation (SO-ZORA). Although the effects of non-polar solvents (e.g., CH₂Cl₂) are shown to be quite marginal, the relativistic effects and the selection of functional and basis sets are crucial in reproducing or predicting the paramagnetic NMR chemical shifts. Particularly the hyperfine coupling constant of some atoms is demonstrated to change its sign upon the effect of spin-orbit coupling. The chemical interpretations of hyperfine (HF) contributions, particularly paramagnetic spin-orbit (PSO) term for the directly bonded nitrogen and chlorine ligand atoms and Fermi-contact term for more distant hydrogen and carbon atoms, are based on the molecular-orbitals (MO) theory and chemical bond concepts. The electronic structure around the central transition-metal atom and the nature of metal-ligand bond is reflected in the ligand hyperfine coupling constant (A^{FC}) and ligand hyperfine NMR chemical shift (δ^{FC}). These magnetic resonance observables are related to the visualized molecular spin density.

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