

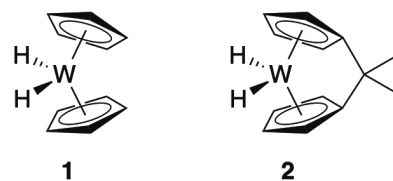
Mobley Group Research

Investigations in Transition Metal Hydride Structures: Refining Hydride Locations in X-ray Structures with Heteronuclear Magnetic Resonance Corroborated Density Functional Theory

The proposed research will investigate the fundamental nature of the transition metal hydride bond utilizing solution state indirect spin-spin coupling constants to corroborate the density functional theory (DFT) calculated position of hydrides in X-ray structures. Because X-ray crystallography relies on the diffraction of photons by the electron density within the crystal lattice, light atoms (*i.e.* hydrogen) are inherently difficult to locate accurately in the presence of heavy atoms. While *ab initio* calculations have been utilized to augment X-ray structures to provide more accurate transition metal hydride locations, these estimations would be improved by utilizing additional experimental data to corroborate the placements. Advances in relativistic density functional theory (DFT) calculations of nuclear magnetic resonance parameters of indirect spin-spin coupling constants make it likely that for some transition metal hydride species these solution state NMR parameters could be utilized to corroborate the DFT calculations. While the focus of the experiments is to “locate” the hydrogen atoms accurately in X-ray structures and confirm those positions utilizing neutron diffraction, the core results from this study will stem from the comparison of the experimental data to the theoretical predictions, leading to greater understanding in the metal hydrogen bonding interaction. As knowledge in metal hydrogen bonding has been critical in the development of catalytic processes such as olefin hydrogenation, carbon-hydrogen bond activation and functionalization, and hydrodesulfurization, fundamental research in transition metal structures such as the proposed study have played an enormous role in the development of catalytic processes important to the petrochemical industry.

Tungsten Project

We have recently been investigating the one-bond coupling between the NMR-active tungsten nucleus and the proton nucleus of the hydride ligands ($^1J_{WH}$) in the tungstenocene dihydride complex, Cp_2WH_2 (**1**). The theoretical studies have shown that the $^1J_{WH}$ is highly dependent on bonding of the cyclopentadienyl ligands to the tungsten center. This



project will explore two aspects that remain unresolved by our previous study: (1) solvent effects on the structure and NMR coupling in Cp_2WH_2 (an extension on a study by Claudia Viquez-Rojas '15) and (2) effects of geometry changes on the coupling constant due to modifications of cyclopentadienyl structure when tying the Cp rings together, so-called ansa-metallocenes (**2**).

Platinum Project

Recent work in my group by Linqing Peng ('19) and Daniel Somorov ('19) (following up careful work by both Serena Hocharoen ('17) and Alex Schmiechen ('17)), has explored an unusual behavior in the coupling patterns of the platinum satellites of the hydride signals from the complexes (dppe)PtHSnPh₃ and

(dppp)PtHSnPh₃ (dppe and dppp are bis-diphenylphosphino ligands ligated by either a ethane (e) or propane (p) chain). This behavior is explained by two different mechanisms, one involving a fluxional process in which the two phosphorus atoms become equivalent and a second process in which chemical shift changes in the phosphorus atoms causes them to become magnetically equivalent. Because both things are happening at once, this can provide an opportunity to examine how the two react differently in NMR experiments that detect this behavior. We have been in contact with Timothy Claridge at Oxford University and are exploring a potential collaboration to investigate the platinum and tin satellites of these complexes.