

Spectroscopic, Diffraction, and Computational Studies on Iridium Dihydride Complexes

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Since it was first developed, Nuclear Magnetic Resonance (NMR) has become a powerful analytical tool. One way to overcome its intrinsic insensitivity is to use hyperpolarization techniques to produce non-Boltzmann spin-state distributions. As illustrated in the Figure, transfer of hyperpolarization (yellow stars) can be achieved by the temporary association of parahydrogen and a substrate in the coordination sphere of a transition metal [1]. The best catalyst for polarization transfer [2] is based on IMes (**1**), which gives a transient six-coordinate iridium N-heterocyclic carbene complex with three substrates and two hydrides (**2**), in which the exchange rate of substrate and parahydrogen at the metal centre and the scalar coupling constant J determine the efficiency of the hyperpolarization of the substrate, pyridine (Py) in this case.

There is a X-ray crystallographic structure available of $[\text{Ir}(\text{IMes})(\text{pyr})_3\text{H}_2]\text{Cl}$ complex (**2**) [3], which has also been studied by Density Functional Theory (DFT) calculations and Extended X-ray Absorption Fine Structure (EXAFS) [4]. It is found that there is agreement to within 0.01-0.02 Å between most Ir–ligand distances derived from EXAFS and XRD, but that those derived from DFT can be up to 0.1 Å larger. The strongest disagreement between the structures for **2** is on the Ir-H distances which are 0.2 and 0.1 Å longer in DFT than in XRD and EXAFS, respectively. We have recently found that an analogue of **2**, $[\text{SiMe}_3\text{H}_2\text{PyBpy}]\text{BF}_4$ (**3**) gives stable crystals so that it is amenable to accurate structural studies. Single crystal neutron diffraction [5] takes advantage of the relatively strong neutron scattering by H as compared to other nuclei and is therefore a more suitable experimental technique to validate the Ir-H distances derived from DFT than X-ray techniques such as XRD and EXAFS where the contributions of H are only weak.

We have calculated the structure of **3** by DFT and experimentally validated it by spectroscopy (EXAFS) of the solid, and X-ray and neutron diffraction of the crystals, in order to get accurate structural information, in particular on the Ir-H distances.

The results of spectroscopic, diffraction, and computational studies of iridium dihydride complexes are complementary.

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