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EXAFS and DFT studies on iridium catalysts for SABRE

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Since it was first developed, Nuclear Magnetic Resonance (NMR) has become a powerful analytical tool that is now used widely in the fields of chemistry, materials science, and medicine. One way to overcome the intrinsic insensitivity of NMR is to use hyperpolarization techniques to produce non-Boltzmann spin-state distributions. One of these techniques is Signal Amplification By Reversible Exchange (SABRE),[1] in which hyperpolarization is achieved by the temporary association of parahydrogen and a substrate in the coordination sphere of a transition metal. The polarization can be transferred from the parahydrogen-derived hydride ligands to the bound substrate via scalar coupling, followed by dissociation of the hyperpolarized substrate into the bulk solution. We have investigated the efficiency of various iridium NHC complexes with aliphatic and aromatic R groups as SABRE catalysts.[2] The used metal centre is a six-coordinate iridium N-heterocyclic carbene complex, with three substrates and two hydrides, in which the exchange rate of substrate and parahydrogen at the metal centre determines the efficiency of the hyperpolarization. As solvent molecules compete with pyridine for coordination to iridium, the sensitivity of SABRE can be enhanced by displacement of solvent molecules by cosubstrates, i.e. proton-poor ligands such as methyltriazole.[3] In this exchange process, several mixed iridium complexes can be considered to exist, which were not all observed by NMR. Therefore, Density Functional Theory (DFT) calculations were performed on these complexes to better understand this phenomenon. While NMR itself is the best source of information on protons and dynamic processes involved in SABRE, we have found that Extended X-ray Absorption Fine Structure (EXAFS) studies in organic solutions provide interesting complimentary information on the complexes involved.

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