

## Poster Presentation

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### Heterolytic Cleavage of H<sub>2</sub> Revealed by Neutron Single Crystal Diffraction

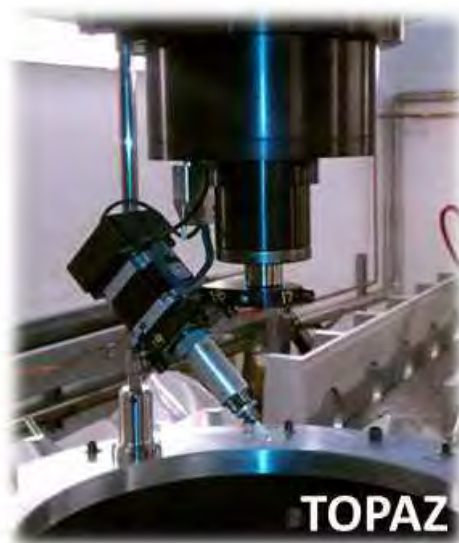
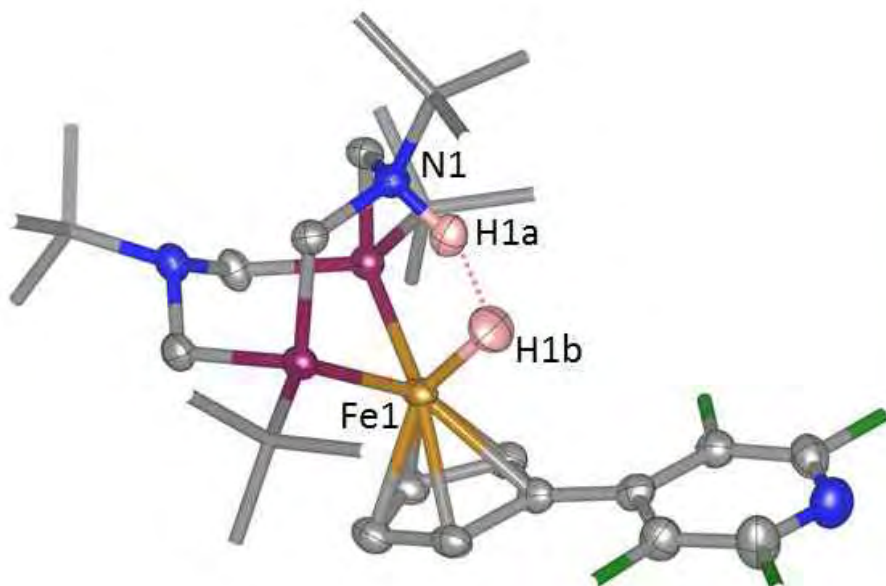
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Synthetic biologically inspired complexes exhibiting reactivity similar to hydrogenase enzymes have provided evidence of hydride transfer to the metal and proton transfer to an amine, but key structural information about the intermediate is not readily discernible with X-rays. The greater sensitivity of neutron to hydrogen makes it ideal for studying the structure and dynamics of catalytic materials. The newly commissioned TOPAZ neutron single crystal diffractometer at the SNS is capable of continuous 3D diffraction space mapping from a small stationary crystal, permitting detailed structural study at atomic resolution. The structure measured on TOPAZ for an Fe-based mononuclear electrocatalyst confirms that reaction of [CpFeN-L])(BARF) [1] with H<sub>2</sub> under mild conditions leads to heterolytic cleavage of the H-H bond into a proton and hydride[1]. The precise location of H atoms in [Fe-H...H-N]<sup>+</sup> reveals an unconventional H-bonding interaction, where the ferrous hydridic site {Fe(II)-H} acts as the H-bond acceptor and the nitrogen of the protic pendant amine {L-N-H<sup>+</sup>} as the H-bond donor. The neutron structure provides clear evidence of a crucial intermediate involving an Fe-H...H-N interaction in the oxidation of H<sub>2</sub>. The result clarifies the key role of the pendant amine in the iron complex and provides insights into the design of synthetic electrocatalysts sought as cost-effective alternatives to platinum in fuel cells. The reaction is also a critical step in homogeneous catalysts for hydrogenation of C=O and C=N bonds. A preliminary result from TOPAZ measurement shows that **1** undergoes further single-crystal to single-crystal chemical reaction with moisture in the air, leading to a Fe(H<sub>2</sub>O)<sup>+</sup> complex.

Abbreviations: Cp = pentafluoropyridylcyclopentadienide; N-L= 1, 5-di(tert-butyl)-3,7-di(tert-butyl)-1,5-diaza-3,7-diphosphacyclooctane; BARF = [B[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub>]<sup>-</sup>

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