

Determination Of Hydrogen Atom Position in Stryker's Reagent Through the Application Of Quantum Crystallographic Methods On Microed Data

Dr. Kunal K Jha¹, Professor Hosea M Nelson¹

¹*Division of Chemistry & Chemical Engineering, California Institute of Technology*

kunaljha@caltech.edu

Metal-hydride catalysts are widely used in synthetic organic chemistry for the preparation of molecules with applications ranging from pharmaceuticals to plastics. Regioselective hydro functionalization of olefins and reductions of carbonyl derivatives are well established.

Despite this prominent role in chemical synthesis for metal hydrides, the position of the hydrogen atoms in their structures is often a mystery. A representative example is "Stryker's" reagent¹. While single crystal neutron diffraction data collected from the derivative of Stryker's reagent showed the hydrogen atoms occupying the face bridging position², recent work based on Neutron scattering and vibrational spectroscopy supports the hydrides bridging Cu-Cu edge positions³. Compelling empirical evidence for the exact positions of hydrides in Stryker's reagent is still lacking. Beyond this reagent, there are numerous published X-ray diffraction structures of metal-hydride complexes without definitive hydride positions. The exact position of hydrogen atoms in metal-hydrides is imperative to understand the mechanism of reactions mediated by these catalysts.

Microcrystal electron diffraction (microED) is a powerful tool for structural determination that has become increasingly accessible with recent hardware and method developments driven by its usage of small crystals. When light atoms are bonded to heavier atoms, the electron densities or the electrostatic potential are strongly influenced and hence their position become ambiguous. With the independent atom model (IAM), information about bonding between the atoms or lone pairs is lost and light atoms (such as hydrogen) can be positioned incorrectly. Atoms in molecules are aspherical; they are bonded covalently or non-covalently and the electrons are shared unevenly. Quantum crystallographic methods that use Aspherical atom refinements, such as Hirshfeld atom refinement (HAR) and transferable aspherical atom model (TAAM), have been widely used for small molecules and successfully achieved better refinement statistics, accurate and precise hydrogen atom positions both for X-ray and electron diffraction data^{4,5}. Recently, a hybrid method has been developed utilizing combined HAR-TAAM approach⁶. In the hybrid HAR-TAAM approach, the refinement of metal-organic complex structures is much faster and the accuracy of hydrogen atom position is comparable to HAR and Neutron bond distances. Quantum crystallographic approaches (HAR and hybrid HAR-TAAM refinements) will be applied on the structure obtained from electron diffraction data on Stryker's reagent, thus the hydrogen atom position will be determined.

References:

- {1} Bezman, S. A., Churchill, M. R., Osborn, J. A. & Wormald, J. J. *Am. Chem. Soc.* 93 (8), 2063-2065 (1971).
- {2} Stevens, R. C., McLean, M. R., Bau, R., Koetzle, T. F. *J. Am. Chem. Soc.* 111, 3472-3473 (1989).
- {3} Bennett, E. L., Murphy, P. J., Imberti, S. & Parker, S. F. *Inorg. Chem.* 53 (6), 2963-2967 (2014).
- {4} Woińska, M., Grabowsky, S., Dominiak, P. M., Woźniak, K. & Jayatilaka, D. *Sci. Adv.* 2, e1600192 (2016).
- {5} Jha, K. K., Gruza, B., Chodkiewicz, M. L. Jelsch, C. & Dominiak, P. M. *J. Appl. Cryst.* 54, 1234-1243 (2021).
- {6} Jha, K. K., Kleemiss, F., Chodkiewicz, M. L. Jelsch, C. & Dominiak, P. M. *J. Appl. Cryst.* 56, (2023).