MS32 Advanced techniques to disclose Structure-Property Relationships

MS32-03
Quantum crystallography of titanium amides with agostic interactions
L. A. Malaspina [1], S. Grabowsky [1]
[1]University of Bern - Bern (Switzerland)

Abstract
C-H bond activation by metal-hydrogen bonding (agostic interactions) plays a central role in catalytic processes [1]. These processes are directly dependent on metal-hydrogen bond energies. The versatility of the coordination modes of the heavy metals allows wide structure and topology variations of the complexes. Therefore, it is of major importance to accurately describe these chemical bonds.
One important drawback is the difficulty of deriving accurate and precise hydrogen atom positions by any kind of experiment. Neutron-diffraction experiments would be the only reliable source of such information, but there is a lack of available accurate X-H bond distances with X being a transition metal from neutron diffraction. Therefore, it would be desirable to determine the elongation of the C-H bonds in agostic interactions and the metal-hydrogen bonding parameters from standard X-ray diffraction experiments. In this context, the capabilities of Hirshfeld Atom Refinement [2] to obtain precise and accurate C-H/C-H…Ti bond parameters in a series of titanium amides are tested. The compounds were synthesized in the group of Prof. Beckhaus, University of Oldenburg, Germany.
Experimental and theoretical charge densities of agostic interactions involving transition metal compounds have been determined and analysed in the past [3]. Here, we use a combination of HAR with subsequent X-ray constrained wavefunction fitting [4] and purely theoretical calculations on the accurate HAR geometries to analyse the related chemical bonding beyond a charge-density analysis. We discuss how signatures of agostic interactions manifest themselves in the classical C-H…Ti agostic interactions found in titanium amides (Figure 1).[5]

References
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Investigated titanium amide compounds