Modelling the Structure and Reactivity of Rhodium σ-Alkane Complexes in the Solid State.

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Transition metal σ-alkane complexes are key intermediates in mechanisms of C–H bond activation and have been extensively characterized in solution using spectroscopic methods. However, these species are notoriously unstable in solution and this has frustrated attempts at their crystallographic characterization. A step-change in this area was provided by Andrew Weller's group, who used single crystal-to-single crystal (SC-SC) transformations to permit both the structure and the reactivity of σ-alkanes complexes to be studied in the solid state.[1]

This presentation will describe the computational modelling of Rh σ-alkane complexes in the solid state, performed in collaboration with the Weller group. Using electronic structure analyses a continuum of σ-alkane binding modes has been defined that aligns with the mechanism of C–H oxidative addition first predicted by Crabtree in 1985.[2] These σ-alkane complexes also show remarkable reactivity in the solid state, including fluxional processes and room temperature dehydrogenation reactions, as exemplified by the $[(Cy_2PCH_2CH_2PCy_2)Rh(c\text{-}C_6H_{12})][BAr^F{}_4]$ and $[(Cy_2PCH_2CH_2PCy_2)Rh(i\text{-}C_4H_{10})][BAr^F{}_4]$ systems (Ar^F = 3,5-$(CF_3)_2C_6H_3$).[3] The modelling of these systems highlights the importance of including the solid-state environment via periodic DFT calculations to capture their structure and reactivity correctly. The factors contributing to the stability of the σ-alkane complexes in the solid state will also be discussed.

References.

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