In-Crystallo Lattice Adaptivity Triggered by Solid-Gas Reactions of Cationic Group 7 Pincer Complexes

J. C. Goodall, M. Arif Sajjad, E. A. Thompson, Samuel J. Page, Adam M. Kerrigan, H. T. Jenkins, J. M. Lynam, Stuart A. Macgregor and A. S. Weller

The use of organometallic solid-state single-crystal to single-crystal (SC-SC) transformations is an emerging area of synthesis, reactivity and catalysis. A recurring problem with SC-SC transformations is that preservation of crystallinity throughout the transformation is often challenging due to the stress associated with the reaction. Here, the solid-state rearrangements during solid/gas reactions of manganese(I) and rhenium(I) pincer complexes with CO is shown to be highly dependent on the non-covalent interactions between the incoming ligand and the weakly coordinating anion. The reactions cause the crystals to undergo extensive cracking to form micron-sized crystals, which necessitated the use of microcrystal Electron Diffraction (microED) for structural elucidation in the case of the manganese example. This report highlights the extreme plasticity of the solid-state, facilitated by the \([\text{BARF}_4]^{-}\) anions and associated non-covalent interactions, as well as the capability of microED to facilitate structure determination of the products of solid/gas SC-SC reactions where macroscopic crystalline integrity is lost.

Figure 1: Solid-state rearrangement of \([\text{Mn(Pr-PONOP)(THF)(CO)}_2][\text{BARF}_4]\) upon addition of CO in a single-crystal to single-crystal transformation.

References