

Centre for Sustainable and Circular Technologies; University of Bath

Project Title:	Catalysis <sup>2</sup> : Synergistic Cooperativity within Bimetallic Pentalenide Complexes
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Industrial Partner:	N.A.

#### Project Summary

Molecular transition metal catalysts typically rely on the use of platinum group metals, whose availability and toxicity are increasing concerns in the context of sustainability. The much more benign and available base metals represent appealing alternatives if we had strategies available for imparting 2 electron redox chemistry on them to effect selective element-element bond rearrangements without free radical intermediates. Current focus on achieving this lies on functional organic ligands that either actively participate in a step of the catalytic cycle (e.g. proton relays) or function as electron buffers (redox-active ligands). These strategies have been derived from observing such effects on noble metals, and only in few cases have been successfully transferred to base metals. A general difficulty with this functional ligand design is that the ligand electronics and sterics have to be precisely tailored to a-priori unknown intermediates to effect the desired cooperativity.

The successful candidate will join another PhD student currently working on pentalenide synthesis in our lab and synthesize novel homo- and hetero-dinuclear pentalenide complexes of Mn, Fe, Co, Ni and Cu with a variety of ancillary ligands. We will then investigate their redox and ligand substitution chemistry with the aim of using them in reductive catalysis (hydrogenations, hydrogen-borrowing, proton reduction, carbonylations, etc.) following a mechanism-guided approach based on operando spectroscopy and electrochemistry.

#### Sustainability issues addressed

In this project, we will explore an alternative approach based on intermetallic cooperativity in precisely engineered dinuclear base metal complexes. Natural metalloenzymes have evolved to use a flexible ensemble of base metals for multi-electron catalysis at their active sites, so with the right ligand scaffold this must be feasible in synthetic systems too. Based on encouraging literature precedence and our recent work on pentalenides, we will develop synthetic methodologies to syn-dinuclear half-sandwich complexes of bridging pi ligands that hold two base metals in the right position for synergistic cooperativity in catalysis. These compounds hold great potential for replacing precious metals - whose availability and toxicity are increasing concerns in the context of sustainability - in existing applications and promise new catalytic methodologies that are impossible with existing mononuclear catalysts.