**University of Leicester**

**Chemistry GTA Studentship Project 2022**

**Section 1 – *Supervisor Information***

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**Section 2 – *Project Information***

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| **Project Title** | **Manganese catalysis in the 21st century** |
| **Project Highlights:** | 1. | Development of highly active catalysts based on inexpensive and earth-abundant manganese for industrially significant chemical transformations. |
| 2. | The associated atom-economy, sustainability and environmental benefits will be a step change in the field. |
| 3. | The discovery of new and desirable reactivity patterns not accessible by current catalyst technology. |
| **Project Overview**  |
| **Introduction** Of paramount importance to catalysis in the 21st century is atom-economy, sustainability and environmental considerations. In this regard, the conversion of hydrogen-rich alcohols to give aldehydes (and ketones) *via* a process known as acceptorless dehydrogenation (AAD) represents a transformation that has seen transition-metal complexes emerge as effective catalysts. In the past, hazardous oxidants have been used to promote the dehydrogenation of an alcohol leading to wasteful by-product generation. In an acceptorless approach, no oxidant is necessary and molecular hydrogen is generated as the only by-product, underlining its desirability in terms of atom-economy and environmental considerations. Perhaps more significantly, the products from the dehydrogenation can be used upstream in a process allowing access to a plethora of pharmaceutically relevant organic materials such as acetals, esters, amides, imines, amines and heterocycles. However to date, the types of transition metals employed to promote AAD are largely limited to precious metals; *the replacement with base metals would be transformative to the chemical industry*.**Project outline**This PhD project will achieve exciting and ground-breaking advances in the development of novel catalytic materials based on earth-abundant manganese. The capacity of these materials to mediate fundamentally significant chemical transformations will be investigated *via* an AAD strategy. The drive for increasingly greener and more cost-effective approaches has sparked international interest in the replacement of well-established precious metal catalysts (*e.g.* ruthenium, iridium and rhodium) for cheaper and more available ones based on base metals (*e.g.* iron and cobalt). In this programme, we focus on the application of the third most abundant transition metal, manganese, which has received relatively little attention in this area. Nevertheless, the potential is there to enable industrially important organic reactions to be conducted with greater efficiency, lower cost and in a more sustainable manner. Moreover, the amenability of these catalysts to promote transformations currently inaccessible by their noble metal counterparts offers an intriguing challenge. Two aims are outlined:(i) Synthesis & reactivity of functionalised dipyridylimine-manganese pincer complexes.Based on ligand systems developed in the group, a range of well-defined molecular complexes will be prepared based on OH-functionalised *N,N,N* ligands. The fundamental reactivity patterns of these complexes will be established.(ii) Evaluation of the new complexes in AAD reactions.These new complexes will systematically evaluated for their ability to mediate AAD reactions. As a key preliminary result to support this proposal, a previous PhD student has demonstrated that mixtures of an OH-functionalised dipyridylimine *N,N,N*-pincer ligand and Mn(CO)5Br in neat 1-hexanol can catalyse the formation of hexanal and hexyl caproate. This *in-situ* finding, though not optimised, shows the huge promise of our catalysts in acceptorless alcohol dehydrogenation (AAD) reactions. In short, these novel molecular manganese catalysts offer not only a greener approach to promote known reaction pathways, but *also permit new and unexplored organic reactivity patterns*. |
| **Methodology**  |
| This cutting-edge project will make use of state-of-the-art approaches to ligand design, metal complexation and catalytic evaluation. In collaboration with Dr Ortu, considerable structural expertise will be added to the project which will be supported by our new X-ray facility and soon to be purchased NMR instrument (as part of a successful EPSRC Strategic Equipment bid). Hence the student will not only gain experience in multiple synthetic techniques but also develop important skills in structural characterization. In each stage of the project, the student will undergo a comprehensive training programme to allow them to perform the various tasks. The synthetic work will be supported by a wide range of characterisation techniques including 500 and 400 MHz NMR spectrometers, GC-MS and ESI-MS, HPLC, GC, and UV/Vis and IR spectrophotometers. These analytical facilities are supported by dedicated technical staff who can provide training and perform routine measurements as required. In addition, the Synthesis and Catalysis section hold weekly joint group meetings where the student will present their research across multiple disciplines. |