Rare Earth organometallic reagents for C-H activation chemistry

**Project Description**

Electrophilic Aromatic Substitution (EAS) reactions are one of the pillars of organic synthesis and are widely used to functionalise arenes. Amongst these, the Friedel-Crafts alkylation is one the most popular reactions used in synthetic chemistry, but its scope is limited by the difficulties in controlling the reactivity and stopping the formation of undesired by-products. To tackle this, other approaches have been investigated, such as the employment of nucleophilic reagents. However, such pathways are impeded by a significant thermodynamic barrier and the use of electron-withdrawing groups (EWGs) is normally required. Recently, Hill and co-workers have recently shown that highly nucleophilic calcium-alkyl reagents are capable of performing Nucleophilic Aromatic Substitution (NAS) of benzene and other simple arenes in the absence of EWGs. Inspired by this discovery, we plan on discovering even more powerful NAS reagents by employing Rare Earth (RE) metals.

Our research group studies the fundamental chemistry of main group and f-block elements and their application in sustainable synthesis. Several RE metals share many similarities with the heavy Group 2 elements, such as low-toxicity, ionic radii and coordination chemistry. Therefore, REs offer great scope for developing a new class of NAS reagents to be employed in new synthetic methodologies. In particular, we will develop organometallic reagents with selected REs (Sc, Y, La, Ce, Nd, Sm, Yb, Lu) stabilised using sterically demanding nitrogen ligands. The target reagents will be highly reactive hydride and alkyl reagents and will perform facile NAS reactivity with simple arenes (e.g. benzene, toluene) in mild conditions. These new species will provide an innovative approach towards NAS reactivity and provide a valid alternative to EAS methodologies currently used in synthetic chemistry.

**Methodology**

All the compounds will be synthesised following advanced anaerobic synthetic protocols used in organometallic and inorganic chemistry, including Schlenk line and glovebox techniques. As part of the project, the student will develop extensive knowledge of ligand design and its application in coordination chemistry, together with a good
understanding of organic chemistry. In conjunction with standard synthetic work, the successful candidate will also perform kinetic studies to probe the reactivity profile of new reagents.

The synthetic work will be complemented by hands-on experience of a wide range of analytical and spectroscopic techniques, including single crystal X-ray crystallography, multinuclear NMR spectroscopy, UV/vis/NIR and EPR.

Further Reading


Application Instructions

When applying, please ensure we have received all of the following required documents by Tuesday 4th February 2020:

- Application Form
- 2 academic references
- CV
- Undergraduate transcripts
  - If you have completed your undergraduate degree, we will also require your undergraduate degree certificate
  - If you have completed a postgraduate degree, we will also require your transcripts and degree certificate

If we do not have the required documents by the closing date, your application may not be considered for the studentship.