Bifunctional metal-pyridonate complexes as acceptorless dehydrogenation catalysts

Highlights
- Improved catalytic performance: more highly prized hydrogen for less catalyst
- Atom economy: no wasteful and hazardous by-product information
- Use of earth abundant metals: more cost effective and industrially relevant catalysts

Overview
Bifunctional transition-metal complexes bearing two or more active sites (e.g., a metal center and a functional group that can synergistically participate), have proved versatile homogeneous catalysts for a broad range of organic transformations. The ligands not only influence the steric and electronic properties of transition metal complexes but also affect the mechanistic pathway through chemical interactions with substrates and products. Conceptually, there are two different classes of bifunctional complexes namely those involving a functional group participating in the primary coordination sphere of the metal centre, and those in which this functional group is not directly bound to the metal centre. In this programme we focus on the less studied, but with exceptional potential, second type which leads to so-called remote metal–ligand cooperation (MLC).

The acceptorless dehydrogenation (AD) of hydrogen-rich secondary alcohols to give carbonyl compounds represents a process that has seen bifunctional complexes emerge as promising catalysts. Traditionally such transformations make use of stoichiometric or excess quantities of hazardous oxidants that lead to wasteful by-product generation. In the AD approach, molecular hydrogen is generated as the only by-product highlighting its desirability in terms of atom-economy and environmental considerations. Moreover, the liberated hydrogen can be potentially used in situ to hydrogenate unsaturated intermediates generated upstream in a process. While both heterogeneous and homogeneous AD processes have been developed, the catalytic efficiency of the homogeneous variant remains insufficiently high to merit industrial application and hence needs improvement. Nevertheless, recent developments using pincer complexes have, however, shown the potential of ligand cooperativity as a means of enhancing catalyst turnover. Perhaps more importantly, the potential to use earth abundant metals in place of traditional precious metals highlights the enormous scope of this strategy.

In this research programme we develop the concept of remote MLC to enhance the performance of an AD catalyst. In particular, we will be targeting metal catalysts that incorporate the biologically relevant 2-pyridonate functionality.
within the multidentate ligand frame. Both precious metals (e.g., Ir, Pd, Ru) and earth abundant metal centres (e.g., Fe, Co, Mn) will be investigated while bi- and tridentate ligands will be prepared using routes developed in our group. Comprehensive screening of their complexes as AD catalysts will be performed with a range of hydrogen rich substrates (e.g., and alcohols and amines) to ascertain their versatility and performance characteristics.

Methodology

A broad range of synthetic chemistry will be employed to generate the ligands and complexes that will be used for the investigation. Indeed, our group has considerable expertise in ligand design with some approaches already in place to develop such metal functionalised complexes. To drive the equilibrium toward the products in an AD reaction, molecular hydrogen must be effectively removed with the result that the reactions need to be conducted under more forcing conditions. To enhance the thermal stability of the catalyst the functional pyridonate moiety will be incorporated within a multidentate ligand. Indeed, the synthesis of three target ligands, makes use of approaches developed and refined within the PI’s group.

Further Reading


Funding

This research project is one of a number of projects in the Department. It is in competition for funding with one or more of these projects. Usually the project which receives the best applicant will be awarded the funding.

Home/EU Applicants

This project is eligible for a fully funded Graduate Teaching Assistant studentship which includes:

- A full UK/EU fee waiver for 4 years
- A stipend/salary package at UKRI rates

International Applicants

This project does not have any funding for international students.

Application Instructions

The online application and supporting documents are due by Thursday 25th April 2019.

Any applications submitted after the deadline will not be accepted for the studentship scheme.

References should arrive no later than Monday 29th April 2019.

Applicants are advised to apply well in advance of the deadline, so that we can let you know if anything is missing from your application.
Required Materials

1. Online application form
2. Two academic references
3. Transcripts
4. Degree certificate/s (if awarded)
5. Curriculum Vitae
6. English language qualification (if English is not your first language)

Applications which are not complete by the deadline will not be considered for the studentship scheme. It is the responsibility of the applicant to ensure the application form and documents are received by the relevant deadlines.

All applications must be submitted online, along with the supporting documents as per the instructions on the website.

Please ensure that all email addresses, for yourself and your referees, are correct on the application form.