Project title: Metal-mediated alkyne activation reactions in catalyst selective synthesis  
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Project Description:
Catalysts have the power to profoundly alter the outcome of chemical transformations. This is well illustrated by recent research in York, in which the preparation of up to 6 products can be achieved from the same starting material by the judicious choice of catalyst and reaction conditions.\textsuperscript{1-3} This is exemplified below, in which the nature of the key reactive intermediates 2 and 3 have a major bearing on the reaction outcome (forming up to 4 products 4a–d from a single starting material 1). To date, this research program has been almost exclusively concerned with synthesis, but despite many of the reactions discovered during this work being completely novel processes, very little research into their mechanism, or the nature of the key reactive intermediates, has been performed.

It is planned to address this during this project, which will focus on reactions promoted by the activation of alkynes with metal-based catalysts. A multi-disciplinary approach will be adopted in which a range of kinetic, physical organic and computational methods will be employed, including (but not limited to) traditional organic synthesis, organometallic chemistry, kinetic analysis, real-time reaction monitoring (e.g. using ReactIR and NMR) and DFT calculations, to attain a detailed picture of the divergent reaction pathways. The fundamental mechanistic insight gleaned from this research is likely to be of much interest from a purely theoretical standpoint, but also, it is expected to be useful in directing the development of entirely new catalyst selective synthesis methods. Key project goals are summarised below:

1) To perform a detailed study on the mechanism of the divergent reaction pathways of ynones 1, as outlined in the Figure above. Particular attention will be paid to how fundamental interactions between metal and substrate in reactive intermediates 2 and 3 influences the reaction outcomes.

2) To examine whether transient reactive intermediates of the form 3 can be intercepted and participate in reactions with additional reagents, e.g. cross coupling reactions.

3) To develop novel catalyst selective synthesis systems, by varying the ‘R group’ or aromatic portion of the starting material (e.g. pyrroles, phenols, azaindoles and benzofurans). In contrast to previous work in catalyst synthesis programs, we hope to more rationally predict the reaction outcomes and ideal catalysts/conditions using the information accrued by in part 1, rather than relying on more ‘random’ screening.

4) To examine more novel catalyst selective synthesis processes via completely different activation modes, e.g. via metal carbenoids and/or alkene activation.
Training:

All research students follow our innovative Doctoral Training in Chemistry (iDTC): cohort-based training to support the development of scientific, transferable and employability skills. All research students take the core training package which provides both a grounding in the skills required for their research, and transferable skills to enhance employability opportunities following graduation. Core training is progressive and takes place at appropriate points throughout a student’s higher degree programme, with the majority of training taking place in Year 1. In conjunction with the Core training, students, in consultation with their supervisor(s), select training related to the area of their research.

Training in synthetic organic chemistry will be provided to ensure the student has a strong overall knowledge of organic chemistry as well as the synthesis of other small molecules and the associated practical techniques that all synthetic chemists need to master, i.e. anhydrous techniques, chromatographic purification, compound characterisation etc. This will be supplemented by attendance at the organic section problem classes. The student will also be trained in spectroscopy, especially NMR characterisation of complex compounds and mass spectrometry. The student will also be trained in how to run and interpret DFT calculations as well the preparation of organometallic compounds and how to perform kinetic analysis. Attending the group meetings of both supervisors will allow regular opportunities to develop skills in presenting and discussing scientific ideas, and will provide a broader grounding in both organic and inorganic chemistry.

References


Equality and Diversity:

The Department of Chemistry holds an Athena SWAN Gold Award and is committed to supporting equality and diversity for all staff and students. The Department strives to provide a working environment which allows all staff and students to contribute fully, to flourish, and to excel. Chemistry at York was the first academic department in the UK to receive the Athena SWAN Gold award, first attained in 2007 and then renewed in October 2010 and in April 2015. This PhD project is available to study full-time or part-time (50%).

Funding:

Value: Studentships are fully funded either by (1) the EPSRC for 3 years (2) a Department of Chemistry Teaching Studentship for 3 years or (3) a Department of Chemistry NMR Studentship for 4 years, and cover: (i) a tax-free annual stipend at the standard Research Council rate (£14,553 for 2017-18), (ii) tuition fees at the UK/EU rate.

Eligibility: EPSRC studentships are available to UK and EU students who meet the UK residency requirements. Students from EU countries who do not meet the residency requirements may still be eligible for a fees-only award. Chemistry Teaching Studentships are available to any student who is eligible to pay tuition fees at the home rate. Further information about eligibility for Research Council UK funding can be found at the following website: http://www.bbsrc.ac.uk/documents/studentship-eligibility-pdf/.

Candidate selection process:

- Applicants should submit an application for a PhD in Chemistry by 17:00 on Wednesday 10 January 2018
- Supervisors will interview their preferred candidates either by email, telephone, web-chat or in person
- Supervisors may nominate up to two candidates to the assessment panel
- The assessment panel will shortlist candidates for interview from all those nominated
- Shortlisted candidates will be invited to a panel interview at the University of York on 13 or 15 February 2018
- The Chemistry Graduate Awards Panel will award studentships following the panel interviews
- Candidates will be notified of the outcome of the panel’s decision by email

For more information contact chemgrad@york.ac.uk or see our web page: http://www.york.ac.uk/chemistry/postgraduate/