UNIVERSITY of York

Chemistry Update

Newsletter 352, 28 February 2023

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Calendar of Events

Chemistry Coffee and Cakes
Date: Thursday 2 March
Time: 1pm
Location: C/B/102

UCAS Visit Days
Dates: 6, 9 & 16 March
Time: 12pm—4pm

Film Screening
Title: LGBTQ+ History Month Event - Screening of Carolyn Bertozzi's Equality Lecture
Date: Tuesday 7 March
Time: 1pm—2pm
Location: C/A/122

Inaugural Lectures
Speakers: Professor Victor Chechik and Professor Neil Hunt
Date: Wednesday 8 March
Time: 4pm—5pm
Location: C/A/101

Research Seminar
Title: Recent Advances in Emitter Design for High Efficiency OLEDs
Speaker: Andrew Danos, Durham University
Date: Wednesday 15 March
Time: 1pm—1.30pm
Location: C/A/101

Research Seminar
Title: Organometallic chemistry using macrocylic pincer ligands: making and breaking C-C bonds through rings
Speaker: Dr Adrian Chaplin, University of Warwick
Date: Wednesday 15 March
Time: 1.30pm—2.30pm
Location: C/A/101

CRCI Launch Event
Date: Thursday 23 March
Time: 10am—3pm
Location: King’s Manor, Exhibition Square

Date of Next Issue:
31 March 2023

Using gels to tame highly reactive chemicals

Scientists from the Department of Chemistry in York have developed an innovative way of using gels to stabilise highly reactive organometallic chemicals. This enhances safety and could transform the way chemical reactions are carried out.

Organometallic reagents are a vital tool in modern chemistry allowing the creation of new carbon-carbon bonds and underpinning the synthesis of vital products such as pharmaceuticals and polymers. However, due to the high reactivity of many organometallics, low temperatures, inert atmospheres and strictly dried solvents are usually necessary. As a result, a high level of training and expertise in specialist methods is required for those who use such reagents, and their storage and transportation are challenging and expensive.

In their newly-published research a team led by Professors David Smith and Peter O'Brien have reported a new encapsulation approach to stabilise sensitive organometallic reagents.

Reactive organometallics based on either lithium or magnesium were mixed with a low-cost hydrocarbon capable of forming a self-assembled gel. As the gel formed, the organometallic reagent became stabilised. The researchers found that reagent lifetime was significantly extended by protection within the gel, which allowed simple handling, delivery and storage, and enabled reproducible reagent portioning. In some cases, the gels could even be held in the hand, exposed to air, before dosing into a reaction vessel.

Team members Dr Petr Slavik and Benjamin Trowse demonstrated the ability of the gels to be used in a wide range of different organic reactions of high value both in industry and in the research community. Reactions proceeded in the absence of all the usual restrictions required for air-sensitive reagents. The purification protocols were simple and gave the desired products in high yields.

Reflecting on the work Professor Smith said: "Storing and using highly-reactive chemicals is one of the most challenging aspects of synthetic chemistry, yet is vital to help produce essential products such as pharmaceuticals. We plan to commercialise this approach to gel-stabilised organometallics so that researchers can benefit from the advantages in terms of safety and handling."

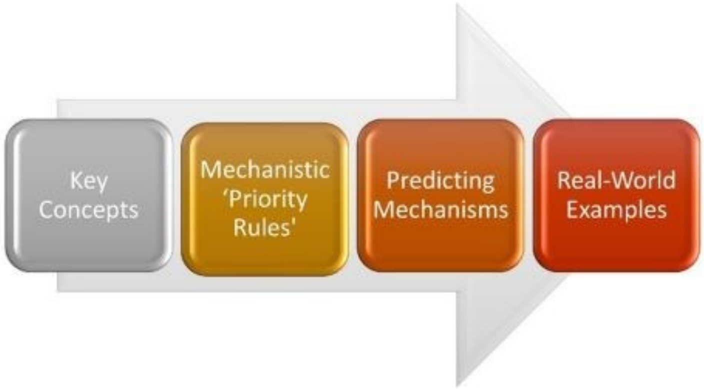
Professor O'Brien added: "By making reaction set-up much more straightforward, these gels have the potential to lower the barrier to doing chemical reactions, making them more accessible to a wider range of researchers. By enhancing storage and lifetime, the use of these reagents becomes more sustainable and cost-effective, which would be attractive in both academic and industrial settings. We are looking forward to extending our approach to organometallics based on different metals, as well as other types of air-sensitive reagents."

In their current work, the team are now extending their approach to organometallics based on different metals, as well as other types of air-sensitive reagents – safe and easy use of a wide range of different reactive chemicals could potentially be enabled using this approach.

The paper is published in *Nature Chemistry*.

Empowering students to predict reaction mechanisms

A recent paper presents the innovative teaching approach to organic reaction mechanisms used in the Department of Chemistry at York.



Reaction mechanisms are the language of organic chemistry, providing a detailed insight into how one molecule reacts with another. In recent years, York undergraduates have been taught 'Professor Dave's Rules of Mechanism' in their introductory Year 1 course on the subject. These simple rules, developed by Professor David Smith, aim to empower students to work out reaction mechanisms from basic principles, rather than having to learn them by rote. In this way, it is hoped that students gain a better feel for organic reactions, and why they happen, and can then apply that knowledge in problem-solving exam questions.

In a recent *Journal of Chemical Education* paper, Professor David Smith discusses in detail his approach to teaching introductory reaction mechanisms, and presents the simple priority and selectivity rules that he has developed to assist students with the challenging task of mechanism prediction.

Professor Smith explains: "In many cases, students just try to memorise lots of reaction mechanisms, or simply guess at them based on the expected products. However, reaction mechanisms derive from fundamental principles about electron density, and I therefore wanted to create an approach where students could apply some simple rules to work the mechanisms out, just by looking at the structures of the molecules involved."

Using an analogy from the paper itself, Dave notes: "If curly arrow mechanisms are the language of organic chemistry, it is hoped that these priority rules, rather like the "phonics" approach to breaking down words for reading, will allow students to make the first steps to literacy in a more logical manner, and build their confidence, which ultimately leads to fluency."

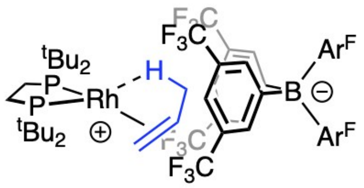
The published paper provides examples of the way in which, alongside the simple rules, Dave's teaching approach present contextualised examples of his rules in action – from the synthesis of dental anaesthetic lidocaine, to the mechanistic chemistry behind the hit TV show 'Breaking Bad'. By bringing the subject to life in this way, Dave hopes that students will be motivated to practice their mechanistic skills and go on to learn more later in the course, when they dive much more deeply into a wide range of organic reactions. It is hoped that this approach encourages students to think like real organic chemists, and better prepares them for jobs, for example in the pharmaceutical industry.

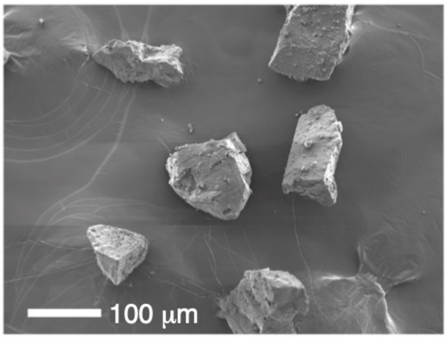
Reflecting on the paper, Dave says: "By publishing the paper, I hope to prompt organic chemists working elsewhere to think about how they teach reaction mechanisms, and why, and perhaps shift the culture away from rewarding rote learning, towards a more concept-led, problem solving approach."

The paper is published in *Journal of Chemical Education*.

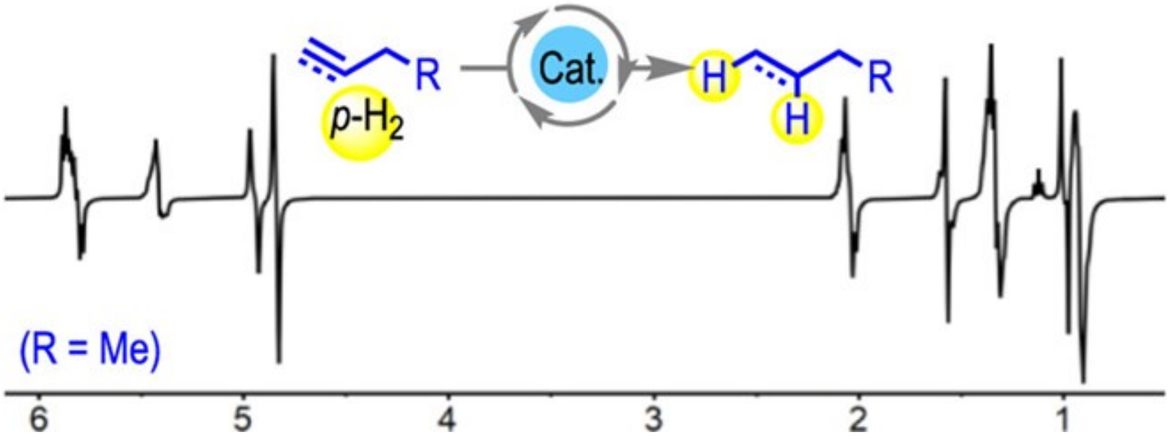
Unlocking the secrets of solid-state molecular catalysis with hyperpolarized hydrogen

Collaborative work between researchers in York has demonstrated a new way to probe the catalytic cycle of molecular heterogeneous catalysts, by combining two areas of expertise in the Department of Chemistry: advanced nuclear magnetic resonance (NMR) methods and new methods for the synthesis and reactivity of organometallic complexes in the crystalline phase.





Catalytic processes are often conveniently divided into homogeneous or heterogeneous, and while both are important, industrial catalysis often operates using solid-state heterogeneous catalysts due to the benefits associated with catalyst stability, the physical separation of catalyst and substrates/products, operation in flow, and recyclability. Central to optimising both types of catalysis, though, is the ability to define and control the catalytically active site(s); both to optimise the desirable properties of the catalyst (selectivity, rate) and also to stop decomposition of the catalyst. Defining the active catalyst sites in heterogeneous systems is very challenging.



Gas-phase NMR spectrum of butyne hydrogenation that shows intermediate and final products in a single-scan gas phase 1H NMR spectrum at 25ºC.

Solid state Molecular OrganoMetallic (SMOM) chemistry is where molecular organometallic complexes are synthesised and undergo reactivity all in the solid-state, often as single-crystals. This is very different from normal organometallic chemistry where complexes are synthesised and studied in solution. SMOM catalysts offer several benefits of heterogeneous catalysis, such as higher catalyst stability and superior product separation. In addition, their well-defined molecular structures mean it is also possible to gain detailed insight into mechanism and catalyst speciation, that is usually only available for homogeneous catalysts in solution. This provides the opportunity to precisely tune catalyst structure and thus enhance reactivity or resistance to decomposition.

By combining SMOM chemistry (Weller) with expertise in advanced NMR methods that are usually used to analyse solution-based catalysis (Duckett), gas-phase NMR spectroscopy was used to measure the reaction of alkenes and alkynes with hydrogen using a crystalline rhodium-centred catalyst. By using parahydrogen, it is possible to achieve gas-phase NMR signals of the products with enhanced intensity as a result of the parahydrogen-induced polarization effect (PHIP). These enhancements are remarkable, with very high polarisation levels achieved (>85%) that results in signals that are almost 2,000 times stronger than normal. This also results in gas phase $^{13}C\{^1H\}$ NMR spectra of the products of catalysis able to be analysed in a single scan in less than 1 second, an experiment that would normally take many hours to complete.

Typically, PHIP requires the use of ~100% enriched parahydrogen, but with this catalyst, polarisation transfer from the hydrogen to the products is so strong that, when coupled with fast catalytic turnover, the effect could be observed even using hydrogen taken directly from a standard cylinder, at the natural abundance of parahydrogen under standard conditions, resulted in significant enhancements.

Dr Matthew Gyton, the first author on the paper and a PDRA in both Weller and Duckett groups, said: "This study has opened up a simple way of achieving high polarisation levels in hydrocarbon products using solid-state organometallic catalysts. As well as being of fundamental importance in the field of catalysis, this also hints at future use of such catalysts in scenarios where hyperpolarised products are required for applications such as medical diagnostics."

This research was as highlighted as an Editor's Choice paper in the *Journal of the American Chemical Society* and was funded by the Leverhulme Trust and the EPSRC Catalysis Hub.

Welcome to Abigail Frith

Abi completed her Medicinal Chemistry BSc at the University of Leeds. She continued at Leeds to undertake her Chemical Biology and Drug Design MSc. On finishing her undergraduate studies, she joined the group of Dr Charlotte Willans and obtained her PhD (Mary and Alice Smith Scholarship), focusing on the development of silver *N*-heterocyclic carbene complexes for biomedical and catalytic applications, as well as synthesis of such complexes electrochemically.

Abi now works as a postdoctoral researcher for Dr Gerard McGlacken at the University of Cork and has recently started at the University of York as a visiting postdoc for a year supervised by Professor Ian Fairlamb, Professor Jason Lynam and Dr Charlotte Willans focusing on electrochemically-generated Mn catalysts.

When she's not in the lab you can usually find Abi walking around the countryside with her map convincing her friends they are not in fact lost, going for a run or organising Girlguiding events for the county.

Thanks for the memories

After 18 years as Admissions Tutor for the Department, recruiting well over 3,000 well-qualified undergraduate chemists, I would like to thank everyone for their help and support. I have been involved in over 50 open days and more than 500 visit days, and I thank you for delivering a talk, leading a tour, interviewing applicants, chatting to visitors, and/or prepping for our open days. During this time, we have had to deal with several recruitment challenges, from the introduction of fees, to a fire in B-block (during a visit day in 2012), a steep drop in chemistry applications nationally, and some ‘bumper’ intakes (e.g. I had many sleepless nights when we went from an intake of 148 students in 2009 to 202 in 2010). Coupled with this, we have had many changes to our admissions policy, from increasing offer grades, to introducing widening participation initiatives, and most notably, moving away from applicant interviewing in 2018. At that time, the department had always interviewed applicants, and so it was a big decision to not interview. But we made it work and as most members of academic staff were involved in interviewing, we saved many hundreds of hours of time. The admissions team has also been required to operate in various locations, including running admissions events in two different portacabins (one nice, one not so nice).

Our intake targets have also changed – when I started, we recruited around 110-120 students, and this increased to the 180-mark in 2011. The fact that we have always met or exceeded our undergraduate home targets, over 18 years, is due to enthusiastic colleagues and students working together as a highly effective team. I have been especially lucky to work with Katrina, Lisa and Nick, a talented team of administrators, who always went above and beyond to showcase the Department and ensure our visitors and incoming students received all the help and support they needed. This team introduced many initiatives to aid our recruitment, from launching undergraduate vacation bursaries, and a teaching pack, to instigating a new starters VLE site, a stepping-up website, introducing admissions scholarships and a scheme enabling our students to deliver talks at our top feeder schools. We were viewed as a beacon of good practice by the central admissions team, and often asked to discuss what we do and why we do it with other departments. The feedback from our visitors has always been excellent, who have valued the time and effort that we invested, and we regularly scored

the highest satisfaction marks in university open day surveys. In recent years, our student ambassadors (in orange tee-shirts) have played a significant role in our recruitment, and they have been a pleasure to work with. On the subject of orange, the choice of orange publicity came from a photo of a firefly experiment used in our early admissions publicity – we have been proud of the range of admissions publicity that we have produced, from departmental booklets, to posters, banners, videos, screencasts, parent and guest leaflets, newsletters and sponsorship booklets. Our distinctive range of publicity and merchandise (not to mention our orange clothing) ensured we always stood out positively at highly competitive recruitment events, such as the Meet the Universities RSC events in London. The significant impact and achievements of the undergraduate admissions team was recognised in 2011 when it was nominated for a Times Higher Education Award.

Our growth in undergraduate student numbers has allowed the department to expand, creating many new jobs, and it has enabled new building projects, principally the teaching laboratory and green chemistry building in 2014. Perhaps the most impressive outcome of our admissions efforts has been the quality of our intakes – over the last 5-10 years, we have had the highest grade-point-average, or one of the highest, of any department at York. Our intakes have regularly been in the top 10 nationally, for entry tariff for chemistry. In 2022, we were ranked 4th in England (behind Imperial, Oxford, and Durham).

I will certainly not miss the difficult decision-making that takes place in August (responsible for the change in my hair colour!) and my anxieties over national league table and NSS positions (I am highly competitive!). But I will miss giving admissions presentations and talking to prospective students about our teaching and research excellence, and particularly, being part of such an effective, committed, and innovative admissions team.

Andy Parsons

Congratulations to Harry Maslen

Huge congratulations to Green Chemistry PhD student Harry Maslen who was selected to represent England at the World Athletics Combined Events Tour in February. The high-level meeting attracts some of the best combined eventers in the world. Harry ranked 18th at the event and hopes to build on this at the British Indoor Championships at the end of the month!

Great work Harry!

Event: Chemistry Coffee and Cakes (C^3)

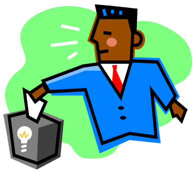
Thursday 2nd March • C/B/102 • 13.00

Warm up with a cuppa and a chat at the next Chemistry Coffee and Cakes (C^3) event. Bring your own mug please! Organised by the newly re-formed Chemistry Postdoc Society Committee, and sponsored by Research England's Enhancing Research Culture fund, awarded by University of York, and ThermoFisher Scientific. Staff welcome - see you then!

Decolonisation and Diversification of the Curriculum (DDC) Working Group

Message from Sam Furfari: We would welcome any undergraduates, postgraduates or members of staff who are interested in becoming part of our Decolonisation and Diversification of the Curriculum (DDC) Working Group to please fill in this Google form. We have our next meeting on **Friday 3 March, 1-2.30pm in C/B/102** as a hybrid event (Zoom link). Any questions, please contact sam.furfari@york.ac.uk.

Online Department suggestion box



The online Equality and Diversity suggestion box has been extended to be a suggestion box for the whole Department. You can submit your thoughts/suggestions/ideas for general Departmental matters as well as matters relating to Equality and Diversity. You can find the Google form at this link.