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Electronic structure and proton-coupled electron transfer reactivity of cerium oxo clusters.

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Cerium dioxide is an important earth-abundant n-type semiconducting material with rich redox properties and is used in automobile catalytic converters, self-cleaning materials, water purification and (photo)catalysis, with recent interest in the use of ultrasmall (<3 nm) CeO₂ particles. Fascinating nanoscale Ce-oxo clusters (or molecular nanoparticles) have been recently discovered, with up to 100 Ce atoms (2.4 nm Ce-O core diameter).¹⁻³ These nanoscale systems have exceptional surface area, providing opportunity to increase material efficiency in applications. However, the question arises – how are the electronic and redox reactivity properties of these systems affected by size relative to bulk CeO_(2-x)?

This presentation investigates the UV/visible spectra of a range of clusters with the number of Ce atoms ranging from 3-100 providing insight into the electronic structures. The effect of size is discussed within the context of quantum confinement effects and contrasted with other metal oxide semiconductors such as TiO₂. The effects of mixed-valency, including intervalence charge transfer, and ligand design on the optical absorption of Ce-oxo clusters is also considered. Results are compared against bulk and nano ceria and also with cerium metal-organic-frameworks.

The reactivity and reaction mechanism of Ce-oxo clusters with hydrogen atom transfer reagents is explored, providing important information of the thermochemistry ([Ce-oxo]-H bond dissociation free energy) which can then be compared to nanoparticles of ceria.^{4, 5}

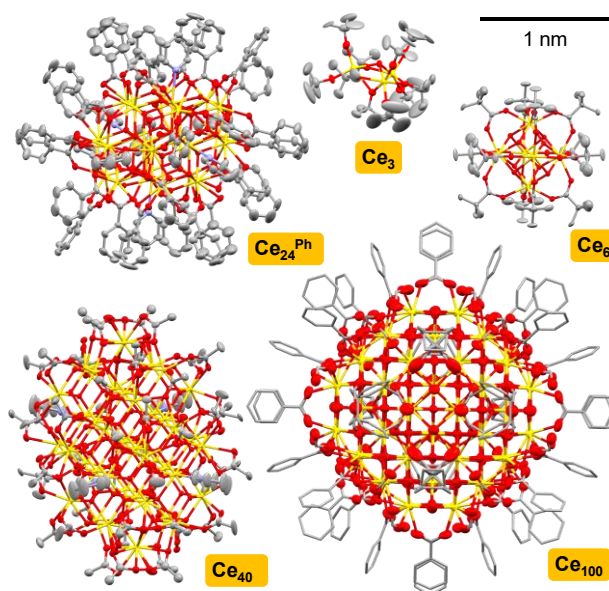


Figure 1. Single crystal X-ray structures of Ce-oxo clusters with nuclearity ranging from 3-100 Ce atoms.

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Single Electron Transfer: EPR Spectroscopy to Explore New Reactivities in 1st row TM and Main Group Catalysis

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1st row transition metals and main group elements have been demonstrated to play an important role in a wide variety of important homogeneous catalytic processes. During the catalytic cycle, many paramagnetic species may be formed either through changes in the redox state of the catalyst, through generation of ligand stabilised radicals or even short-lived excited state species. Herein, we highlight the power of Electron Paramagnetic Resonance spectroscopy as an analytical tool to elucidate reaction mechanisms using exemplar research including: i) mechanistic details of Frustrated Radical Pairs in main-group mediated (site-selective) cross-coupling reactions of aryl esters with terminal alkynes;¹ and ii) the on-cycle oxidation state of iron, and nature of reactive intermediates, formed during Suzuki biaryl coupling² and hydroamination reactions.³

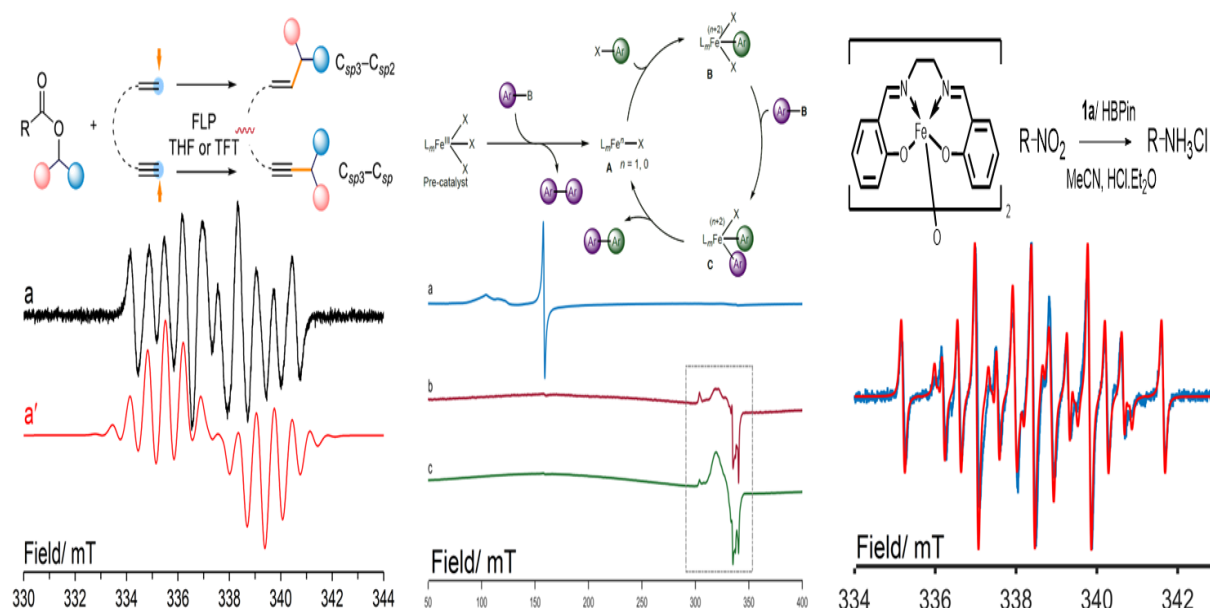


Figure: EPR spectroscopy as a tool for elucidating SET processes in inorganic reaction mechanisms

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Isolated intermediates offer new insights into PRC mechanisms.

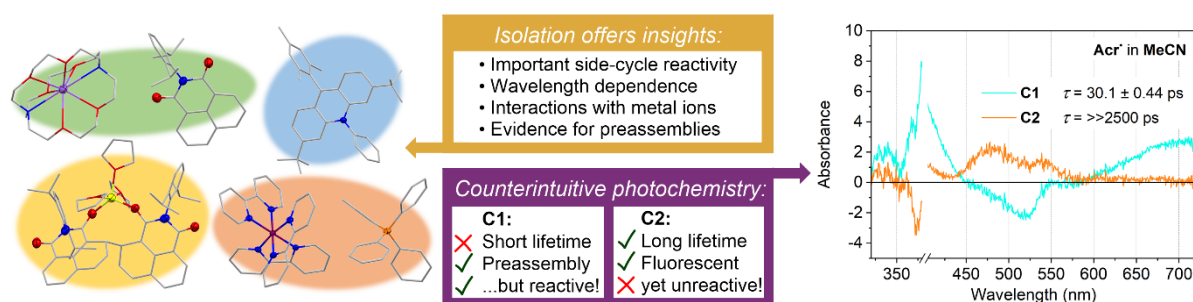
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In photoredox catalysis (PRC), absorption of photons by a photocatalyst (PC) leads to very strong redox agents, which can activate even inert substrates.¹ As an abundant, tunable, and safe energy source, light has many advantages over other options. The wide uptake of PRC and range of transformations developed is therefore unsurprising.² However, the underlying mechanisms and intermediates are challenging to study due to short lifetimes and complex speciation. This has led to significant controversy, particularly around consecutive photo-electron transfer (conPET). We have therefore isolated the key 1 e⁻ reduced intermediates of common PCs ([DCA]⁻, [NpMI]⁻, [Ru(bipy)₃]⁺, Acr[•]) as bottleable species.^{3,4} We can use these as tool compounds to gain insights into PRC mechanisms.

Our studies have revealed examples of unusual side-cycle reactivity and wavelength dependence, as well as the importance of subtle interactions with other components in reaction mixtures, offering new considerations for reaction design. For example, Mg²⁺ ions can couple radical photocatalysts to form closed-shell complexes, significantly impacting electronic structure and reactivity. We have also investigated the unique photochemistry of the fluorescent radical photocatalyst Acr[•] by ultrafast spectroscopy. Counterintuitively, we show that its long-lifetime state previously credited for its conPET photochemistry⁵ does not participate in super-reducing behaviour, and instead it is very short-lived higher excited states that result in electron transfer.⁶ Furthermore, we see direct evidence for formation of the preassembly complex that enables this chemistry to bypass diffusion limits.



Left, isolated radical intermediates of common photocatalysts used for mechanistic studies; and right, transient absorption-observed ESs of Acr[•] species featuring counter-intuitive photochemistry.

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Trivalent metal Lewis acids catalyse the transfer hydrogenation of CO₂

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γ -terpinene can function as a bio-derived H₂ surrogate when using MX₃ (M = Al, Ga, In, Yb, X = Cl, OTf) Lewis acids as catalysts, thereby catalyzing the hydrogenation of CO₂ to formate. A tandem hydrogenation-coupling reaction is also possible wherein amines and diamines can be coupled to formate *in-situ* to produce either N-formamides or heterocycles such as azoles. In which we can achieve yields up to 95% at temperatures of 130°C and pressures as low as 4 bars without the need for additives. The reaction mechanism was then studied in which we found In(OTf)₃ and a Lewis base was unable to abstract a hydride from γ -terpinene. DFT calculations show that, for the synthesis of formate from CO₂, the reaction proceeds *via* CO₂ activation where CO₂ directly accepts a hydride from γ -terpinene. This contrasts with the more commonly reported mechanism of LA hydride abstraction from the 1,4-cyclohexadiene hydride source commonly reported for Lewis acids such as B(C₆F₅)₃. This study represents an avenue to hydrogenate CO₂ using biomass to produce value-added products under relatively mild conditions ¹

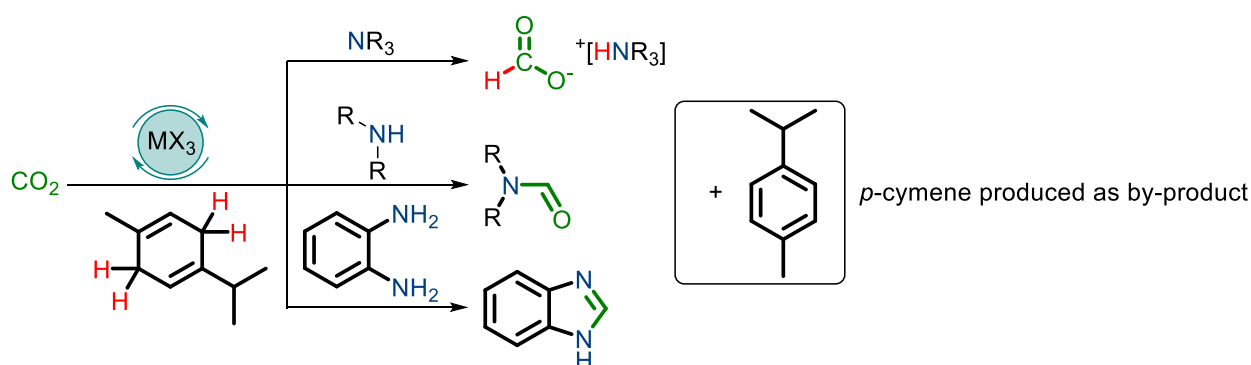


Figure 1: Lewis acid CO₂TH to formate and the tandem condensation to formamides and azoles.

References

1. Alexandros Paparakis,^a Leandro Imena,^b Daniel Shirwani,^a Jorge G. Uranga,^{*b} and Martin Hulla^{*a} (manuscript under review).

A combined kinetic and computational analysis of the palladium-catalysed formylation of aryl bromides

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Aryl aldehydes are integral building blocks in the syntheses of many active pharmaceutical ingredients, and therefore their efficient production on a large scale is important. Currently aryl aldehydes are made industrially using aryl halides however these transformations are often multi-step, involve stoichiometric halogen/metal exchange, and have limited functional group tolerance.

An attractive alternative process is palladium-catalysed formylation of aryl bromides using syngas (CO:H₂, 1:1) as a CO and hydride source. Beller and coworkers' best-in-class catalyst system, applied on >1000 kg scale, employs di-1-adamantyl-n-butylphosphine (cataCXium® A), palladium(II) acetate, and tetramethylethylenediamine, under mild conditions of 5 bar and 100 °C.¹⁻³

Herein, we present a detailed experimental and computational mechanistic study of Beller's catalytic formylation, accelerated using automated platforms (Unchained Laboratories Optimisation Sampling Reactor and Opentrons OT-2).⁴ A general workflow for kinetic investigations into catalytic formylation reactions at elevated pressures has been developed. Kinetic studies (orders of reaction, kinetic isotope effect) provide new evidence that base-assisted dihydrogen cleavage is likely turnover-limiting. A Hammett analysis reveals that the CO migratory insertion step contributes to the turnover-limiting sequence for electron deficient substrates, whereas electron-rich substrates react faster and more selectively. Density functional theory (DFT) calculations of each elementary step support these findings, including the elucidation of the key base-assisted dihydrogen activation step.

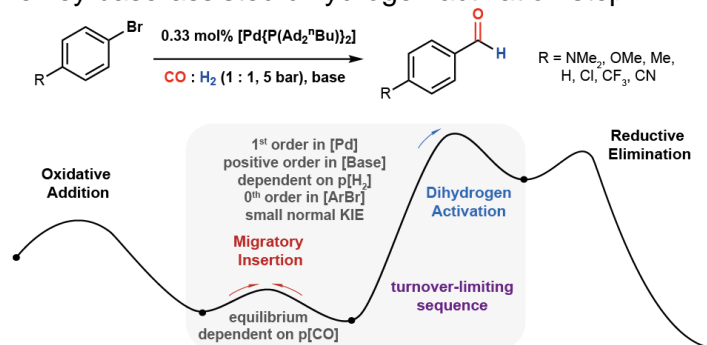


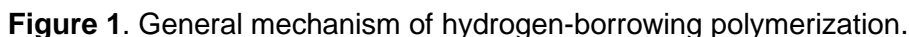
Figure 1. Overview of the updated mechanistic model for the best-in-class catalytic formylation system.

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This presentation will describe the synthesis of new polymers using the approach of hydrogen borrowing polymerisation. Hydrogen borrowing catalysis has been used in the past to functionalise small molecules. Recently, we have demonstrated the application of this concept to make polyethylenimines,¹ polyketones,² and polyesterethers³ using renewable feedstock based on diols and diamines. Mechanistic studies based on experiments and DFT computation will also be discussed (Figure 1).



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Selective transesterification mediated by lanthanum complexes in the copolymerization of lactide with various lactones

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Sustainable polymers continue to generate a high level of interest.¹ Metal-mediated ring-opening polymerization (ROP) is an efficient method to prepare biodegradable polymers; catalyst design is a key influence in the resulting copolymer microstructure.² However, controlling copolymer sequence with the same catalyst across different monomer combinations is challenging.

A series of novel lanthanum amido complexes, supported by ligands designed around the salan framework (salan = *N,N'*-bis(*o*-hydroxy, *m*-di-*tert*-butylbenzyl)-1,2-diaminoethane) are reported.³ The ligands incorporate benzyl or 2-pyridyl substituents at each tertiary amine centre. The complexes are active and selective catalysts in the copolymerization of lactide with ϵ -caprolactone, δ -valerolactone and β -butyrolactone. Solvent and the number of 2-pyridyl groups in the complex influence catalyst selectivity and the resulting copolymer microstructure. Experiments reveal rapid ROP of lactide initially, then incorporation of the second lactone into the copolymer through transesterification. The mode of transesterification (T_I or T_{II}) is determined by the structure of the metal complex and reaction solvent. Similar microstructures are obtained with different comonomers demonstrating the broad applicability of the catalysts and precise control over the microstructure of a range of copolymers through catalyst design.

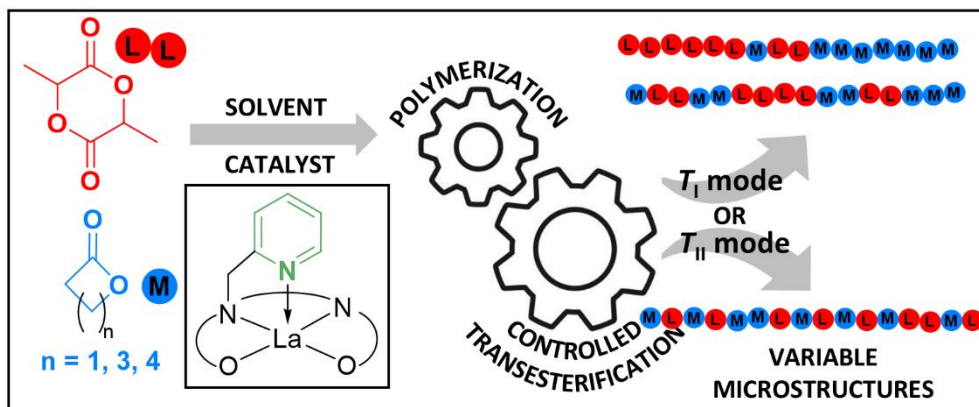


Figure 1. Variable microstructure copolymers by selective transesterification in ROP.

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In control: A kinetics and mechanistic study of an Ir(POCOP) catalyst for the controlled synthesis of polyaminoboranes.

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Polyaminoboranes (PABs) are isosteres of polyolefins by the isoelectronic relationship between the C—C and B—N units.¹ These polymeric materials have potential use as precursors to B,N-based pre-ceramics, such as hexagonal boron nitride (*h*-BN) an isostere of graphene. The mechanical properties of *h*-BN rival that of carbon fibres and *h*-BN has high chemical stability, low electrical conductivity, excellent heat conductivity, as well as being superhydrophobic.^{2,3} These properties make *h*-BN a material of interest, and in particular PABs a potential pre-ceramic precursor for the synthesis of 1-, 2- and 3-D *h*-BN materials.

This contribution describes the use of transition metal-based catalyst, Ir(POCOP)H₂ (POCOP = [κ³-1,3-(OP^{*t*}Bu₂)₂C₆H₃])⁴, to produce high molecular weight PAB polymer, selectively and with fine control over molecular weight. In this contribution we report a detailed kinetics, speciation, and mechanistic study carried out that provides a thorough understanding of catalysis and allows rationalisation of the reaction behaviour and mechanism. Ultimately delivering fine control over the polyaminoborane, allowing for their use in the production of 1- and 2-D BN materials.

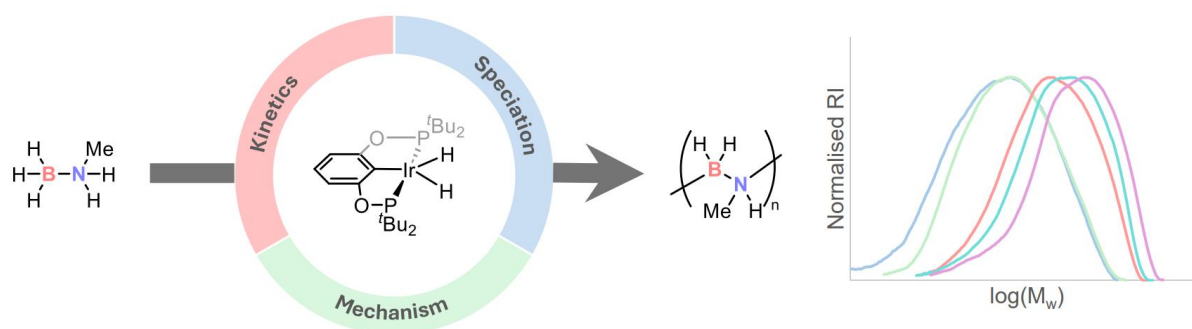


Figure 1: Amine-borane dehydropolymerisation.

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Photochemistry and New Time-resolved Studies with Metal Carbonyls

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This presentation will cover two recent activities at Nottingham in the areas of:

(i) **Organometallic Alkane and Silane Complexes** where we will show how a combination of fast IR spectroscopy and time-resolved XAFs provides new insight into bonding and reactivity. We recently reported results obtained following irradiation of $W(CO)_6$, we were able to structurally characterize the formation of an organometallic alkane complex, $W(CO)_5(alkane)$ and determine the W–C distances, and monitor the reactivity with silane to form an organometallic silane complex. Experiments in perfluorosolvents doped with xenon afford a solvated complex, which is sufficiently reactive in the presence of Xe that we could then provide a unique insight into the metal–xenon bonding [1]. Here we will report XAFs results obtained following UV irradiation of $CpMn(CO)_3$ in alkane and silane solution.

(ii) **Synthetic Methods to Generate IR Probes of DNA Damage** where we exploit results from our research on photochemistry as potentially very powerful tools for manufacturing. As recent advances in simple reactor designs using both visible and UV irradiation particularly focussed on continuous photo-redox processes enabling 10 kg/day [2]. Here we will report a new synthetic route to $cis-[Re(diimine)(dimimine')(CO)_2]^+$ where the mono and mix diimines can be produced at relatively low temperatures and be a simple method with the ability to make mixed diimine complexes.

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Artificial Force Induced Reaction Pathway Determination: A Case Study in Group-1 Organometallic Chemistry

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Computational modelling has been applied to chemical reactions to improve mechanistic understanding in several areas of chemistry. One primary drawback of this approach is that it requires pre-requisite knowledge of the reaction mechanism in the form of ‘guess structures’ for the various minima and transition state (TS) structures featured on the pathway, the chemical accuracy of which is integral to their success. As such, investigation of reaction pathways which are not well-understand pose a unique challenge and can incur significant computational cost. One such methodology developed to address this problem is the Artificial Force Induced Reaction Methodology (AFIR), which is an automated reaction pathway sampling program.¹ AFIR samples a force-modulated potential energy surface which is subsequently relaxed to yield approximate minima and TS structures without the need for in-depth *a priori* knowledge of the reaction system.

In this work, we report the reaction between carbon monoxide (CO) and two monomeric Group-1 organometallic complexes, namely, $[M(CHSiMe_3Ph)(Me_6Tren)]$ where **M** can be either Li or Na - **1Li** and **1Na** respectively.² The reactions, detailed in Figure 1, have different products, suggesting that the metal identity plays a key role in the reaction outcome. The AFIR method has been utilised to determine the reaction pathways for the formation of the three unique products (**2**, **3** and **4**) in an attempt to rationalise the influence of the metal identity on the reactivity of **1Li** and **1Na** with CO.

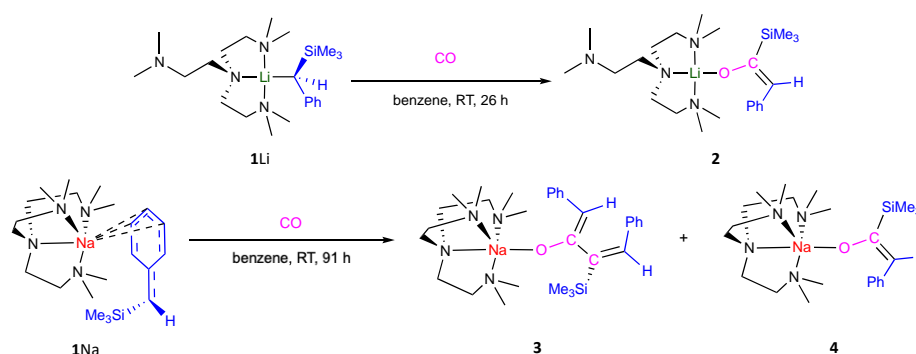


Figure 1: Shows the reaction between both **1Li** and **1Na** with CO detailing the products formed.

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Catalytic Applications of Iron (II) PCP Alkyl Pincer Complexes

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Transition metal alkyl complexes have gained significant attention in recent years, as they present themselves as bench stable pre-catalysts, that feature a variety of catalytic reactivities, such as hydrogenation, reduction and hydro-functionalisations.¹ Examples of catalytically active and bench stable Iron PCP Pincer complexes are scarce.²⁻³ We discovered a simple methodology to generate stable iron pre-catalysts. Upon activation an unsaturated hydride-species is formed which is catalytically active for various transformations such as hydroboration and hydrosilylation of alkynes and alkenes.

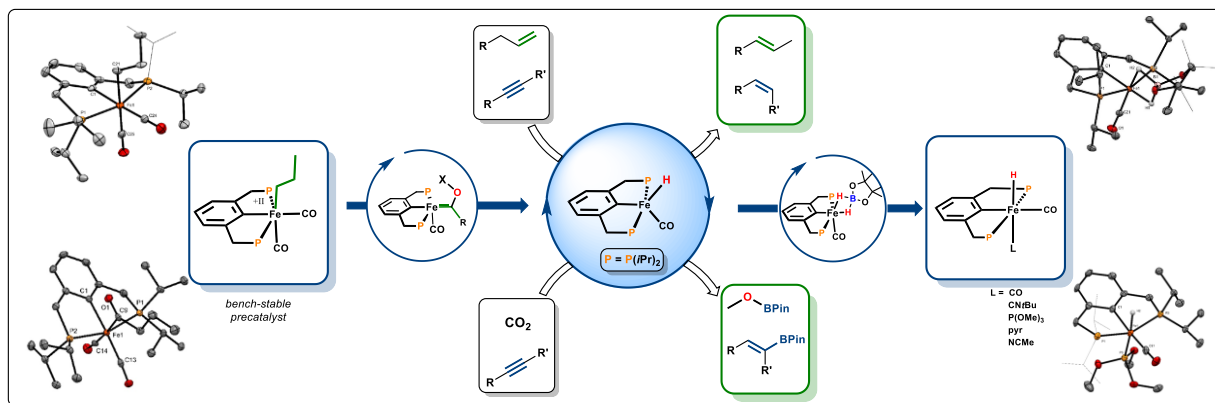


Figure 1: Diverse Reactivity of Bench Stable Iron PCP Pincer complexes.

In this presentation, details about the reactivity of these unsaturated hydrides in hydroboration of C≡C triple bonds and the isomerization of C=C double bonds will be highlighted, which are scarcely reported for iron pincer complexes. Based on kinetic studies, supported by DFT calculations, mechanistic aspects of the unusual activation pathway of the pre-catalyst as well as the unusual reactivity in alkene isomerization will be described.⁴⁻⁵

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Understanding C–C bond formation by migratory insertion in manganacycles – A combined time-resolved spectroscopy, computational chemistry and data science study

Stefan Flesch, Chris Horbaczewskyj, Barnabas Franklin, Ian J. S. Fairlamb, Jason M. Lynam^a

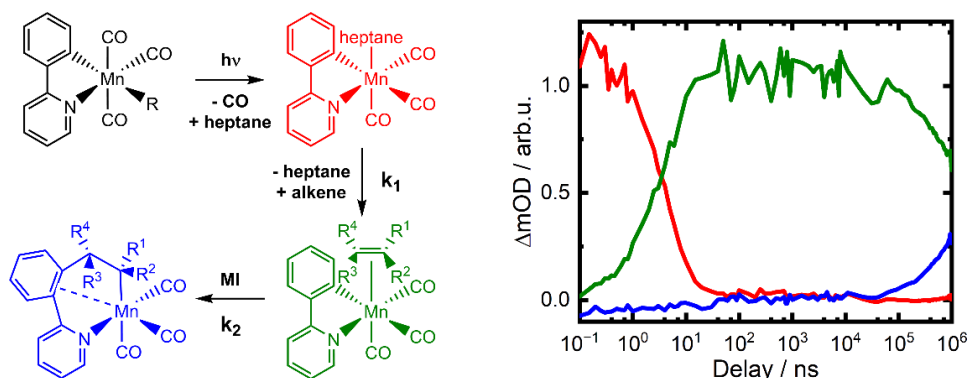
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The development of new versatile synthetic routes requires the determination of the substrate scope for which the given method yields the desired product and hence involves a screening of numerous reactants. Yet, even after extensive investigations, the applicability to a new substrate to a given reaction can often not be predicted reliably.

Developing a profound understanding of the mechanism and driving forces behind chemical conversions can help the *a priori* prediction of the result of a reaction thus saving the time and resources required to test every substrate explicitly. In this case study, we explored the migratory insertion of alkenes into a Mn–C bond following the photo-induced activation of pre-catalyst [Mn(ppy)(CO)₄] (ppy = metalated 2-phenylpyridine) in heptane solution. Catalytically, this reaction forms a new C–C single bond in analogy to the related reactivity of alkynes.¹⁻³

The sequential reaction steps, CO release, formation of a solvent coordinated complex, ligand exchange and migratory insertion (see figure) have been tracked by means of time-resolved multiple probe infrared spectroscopy (ps-ms timescale) for a set of more than twenty exemplary alkenes. These experiments demonstrate that the migratory insertion is only feasible for activated alkenes. Subsequently, the results of the spectroscopic measurements – rate constants and vibrational frequencies – have been combined with a series of parameters obtained by computational chemistry (density functional theory) and subjected to a data science evaluation. This procedure allows a determination of properties which are pivotal for the occurrence of migratory insertion of an alkene in the given catalytic system.



Reaction scheme of the processes following the photoexcitation of [Mn(ppy)(CO)₄] (left) and kinetic traces of signals associated with the occurring intermediates extracted from the time-resolved infrared measurements (right, alkene = bicyclo[2.2.1]hept-2-ene).

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Innocent until proven guilty: DFT investigation into the mechanism of NacNacZn catalysed C–H functionalisation

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Direct C–H functionalisation offers an atom-economic route to install a variety of synthetically useful functional groups, which can be further transformed to increase molecular complexity. One prominent example is C–H metalation affording organonucleophiles, which are of particular interest as cross coupling partners.¹ We have recently developed a novel catalytic transition metal-free protocol to form C(arene)–[M] bonds, where [M] = ZnNacNac, Al(Me)NacNac (NacNac = {(Ar)N(CH₃)C}₂CH).² This talk will present our DFT investigations of the reaction mechanism which revealed that combining an endergonic C–H metalation step with a sufficiently exergonic dehydrocoupling step is key for enabling experimentally observed reactivity. Expanding this work, we achieved a main group catalysed C–H borylation of heteroarenes using 9-borabicyclo-[3.3.1]-nonane, (H–BBN)₂ (**Figure 1**).³ This borane is under-explored in C–H borylation but exists as a dimer, in contrast to ubiquitous dioxaborolanes (e.g. BPin, BCat).

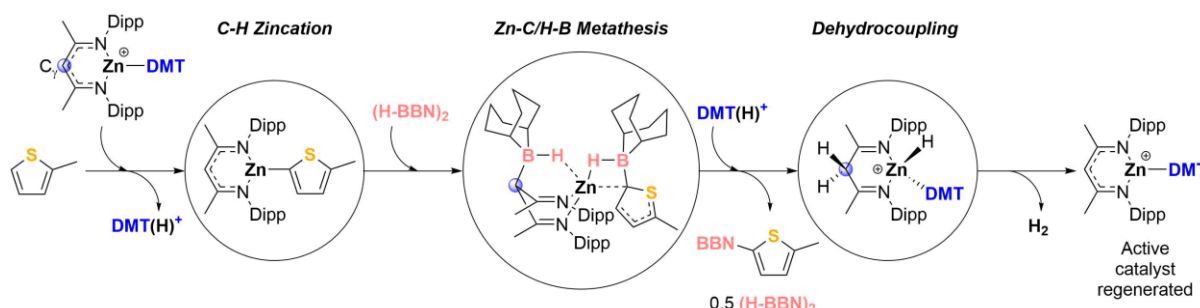


Figure 1 Overview of the computed reaction mechanism for C–H borylation including structural representatives of three key steps: C–H zincation, Zn–C/H–B metathesis and dehydrocoupling.

We will show that in both processes,^{2,3} ligand non-innocence proved vital. Our results indicate that the C_γ-position on the NacNac ligand backbone assists with both the σ -bond metathesis between NacNacZn–Aryl and the hydroborane, as well as in the dehydrocoupling step required to complete the catalytic cycle and regenerate the active catalyst, [NacNacZn–DMT]⁺.

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Catalytic H/D Exchange of Aluminium Hydrides by Cobalt–Aluminium Complexes

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Here we present the catalytic deuteration of aluminium hydrides promoted by a cobalt(I) hydride complex (Figure 1). This simple yet effective method can be applied to a series of β -diketiminato stabilised aluminium dihydrides and appears to be synthetically widely relevant given the frequent utilisation of these reagents.

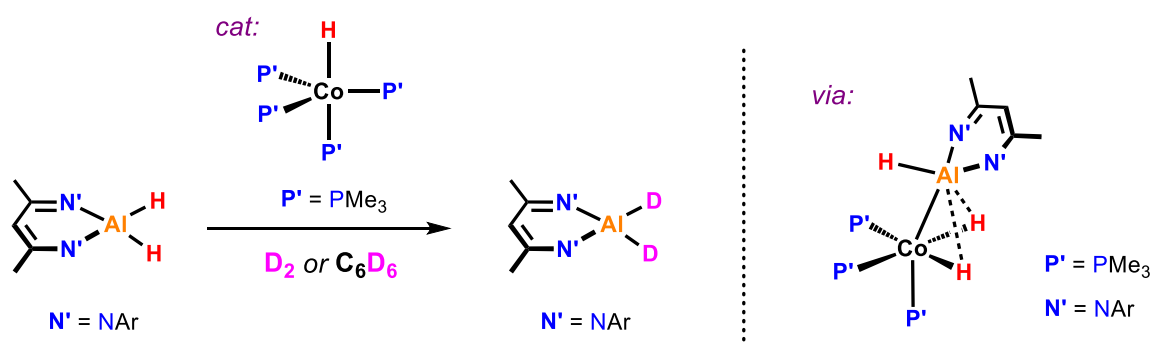


Figure 1. Cobalt catalysed H/D exchange of bis(ketiminato) aluminium hydrides.

Reactions are typically performed at 80-100 °C in presence of 1-5 mol% of the cobalt catalyst using benzene- d_6 or D_2 as deuterium source. After reaction times of 18-24 h deuterium incorporation of >99 % into the Al–H bonds is obtained. Key to this reactivity is the reversible formation of well-defined bimetallic cobalt–aluminium complexes some of which have been isolated and structurally characterised by single crystal X-ray diffraction. The structures of these species possess a distorted octahedral geometry reminiscent of related iron/aluminium complexes described previously.¹ We will give insight into the bonding of these bimetallic species as well as into the underlying mechanism of the H/D exchange process.

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The Active Encounter Complex in Frustrated Lewis Pair Chemistry

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Formed of sterically hindered Lewis acids and bases, frustrated Lewis pairs (FLPs) are able to activate small molecules, and show excellent catalytic activity.^{1, 2} The encounter complex is the pre-association of the bulky acid and base, which we use to rationalise the termolecular reactivity of these systems; understanding the formation and stability of this encounter complex is vital to rationalising and improving FLP reactivity.^{3, 4} Our research seeks to build upon existing literature to probe and quantify the interactions that hold these compounds together as an encounter complex.⁵⁻⁷ By using UV-vis spectroscopy we exploit the charge-transfer band to calculate the association constant (K_a) using supramolecular chemistry techniques. Through our research, we aim to develop our understanding of this encounter complex; expanding our understanding of the mechanism of complexation, where fine tuning the Lewis acid and base substituents can allow us to maximise and control their reactivity.

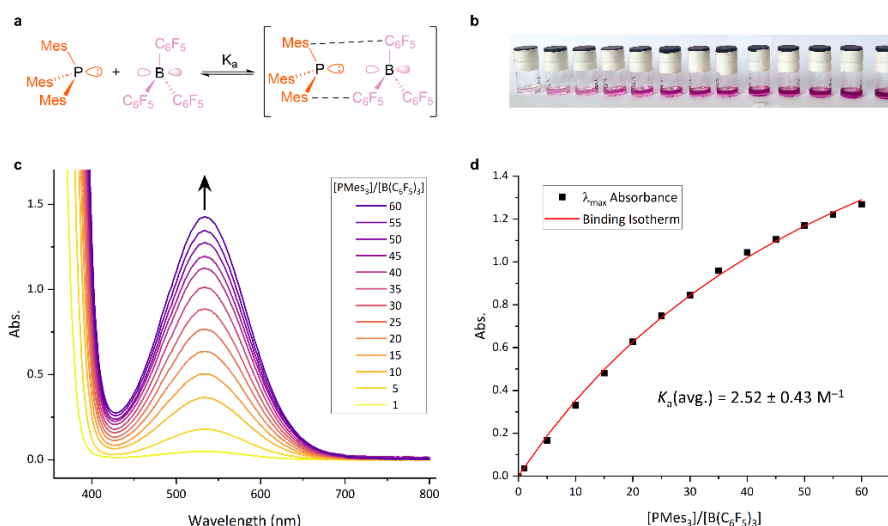


Fig. : **a:** Complexation for which K_a is being determined. **b:** Solutions used in titration experiments; increasing magenta colour with increasing ratios of phosphine:borane. **c:** Increasing λ_{max} of charge-transfer band with increasing Lewis base concentration. **d:** plot of λ_{max} absorbance as a function of phosphine:borane ratio, and the binding isotherm that has been modelled to fit these data.

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Hypervalent Iodine Oxidation of Alcohols: A Mechanistic Puzzle Hiding in Plain Sight

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The oxidation of alcohols to their corresponding aldehydes or ketones is a fundamentally important transformation. Nitroxides or aminoxyl radicals, such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), are a prominent and important class of catalysts for alcohol oxidation and have been subject to numerous studies and reviews.^{1,2} A very popular terminal oxidant for TEMPO mediated alcohol oxidations is the hypervalent iodine reagent phenyliodine(III) diacetate (PIDA), developed by Piancatelli and co-workers in 1997 (Figure 1).³ Hypervalent iodine (V) reagents have their own rich history as alcohol oxidants, although there are significantly fewer examples of direct alcohol oxidation using iodine (III) reagents. TEMPO/PIDA oxidation proceeds rapidly under mild conditions with no need for exclusion of air or water, is exceptionally functional group tolerant, can oxidise a wide range of structurally diverse alcohols, is highly selective towards primary alcohols, and displays no over-oxidation of aldehydes. Since inception, the role of PIDA has been assumed simply as that of a terminal oxidant, with the mechanism supposedly proceeding via an oxoammonium/hydroxylamine cycle common to TEMPO systems (Figure 1).^{1,3} However, simple kinetic experiments in our lab have shown zero order behaviour in TEMPO; TEMPO cannot be involved in a rate determining step so disproving the assumed mechanism.

Herein, we report a full reappraisal of the PIDA/TEMPO reaction mechanism, including kinetic, electrochemical, spectroscopic, and computational studies. We demonstrate that the hydroxylamine/oxoammonium pathway of Figure 1 cannot be in operation and, instead, propose an updated mechanism of redox relay cooperativity. We find that water plays a central role in the mechanism with PIDA unusually acting as both terminal oxidant and co-catalyst through accessing the I(V) oxidation state.

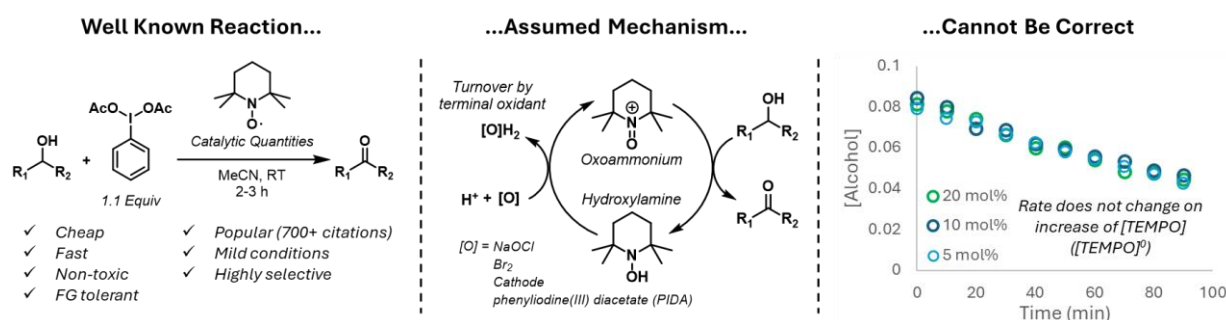


Figure 1: Piancatelli's and co-worker's TEMPO/PIDA oxidation reaction,³ the assumed mechanism, kinetic experiments disproving this assumption.

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Oxidation States and Inverted Ligand Fields: Facts or Artefacts?

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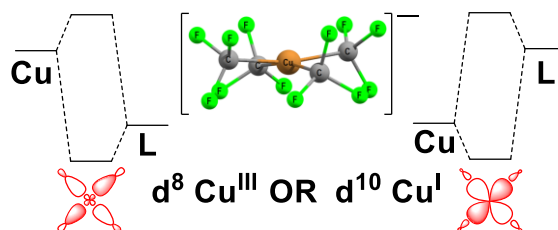
In transition-metal systems, the metal's d^n configuration and oxidation state are often easy to define but much harder to corroborate. Even more so when the M-L bonding is highly covalent. $[\text{Cu}(\text{CF}_3)_4]^-$ is a prime example. Formally, this is a low-spin d^8 Cu^{III} species but molecular orbital (MO) calculations yield Cu 3d populations much closer to 10 than 8. The copper is thus reformulated as Cu^{I} with a d^{10} configuration since the high energy of the ligand orbitals results in the mostly $d_{x^2-y^2}$ MO being bonding, and thus filled, and lying at the bottom of the d-orbital stack instead of the top. The ligand field is said to be 'inverted' (See figure below).

The inverted ligand field (ILF) is a widespread feature of LCAO-type methods such as those based on DFT. It also enjoys strong support from x-ray spectroscopy to the extent that the 'experimental' Cu 3d percentage in the acceptor orbital of nominally Cu^{III} species is so low that d^8 Cu^{III} is suggested to be largely a myth.¹

However, orbitals are not observables and the percentage $d_{x^2-y^2}$ in the b_{1g} LUMO of a planar complex cannot be measured directly. Also, MO theory only defines the total electron count: how the density is divided up amongst individual atomic orbitals is model dependent and 3d populations and metal oxidation states derived from MO calculations have limited significance.

In contrast, both are well defined in classical ligand field theory (LFT). Classical LFT uses the crystal field Hamiltonian and has completely different physics to the MO version of LFT we teach currently. However, this version is both conceptually and numerically deficient. The reference states of MO energy-level diagrams are unphysical and the underlying Wolfsberg-Helmholtz approximation is flawed. The orbital overlap model is poorly suited for describing the role of the d electrons in metal-ligand bonding.

A better conceptual picture is a crystal-field-like set of localised d electrons which interacts with the potential field of all the others. In this picture, which is supported by high-level quantum chemistry, the 'true' ligand field cannot invert but the d configuration can be compromised. $[\text{Cu}(\text{CF}_3)_4]^-$ happens to lie below the internal electron-transfer threshold and is a 'normal' low-spin d^8 Cu^{III} system but there remain limitations on the maximum oxidation state a given ligand set can support. Compared to the ILF of MO theory, LFT provides a different take on the conditions and, more significantly, the *consequences* of exceeding these limits.



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