RSC INTEREST GROUP
INORGANIC REACTION
MECHANISMS

RSC Inorganic Reaction Mechanisms Group

50th Anniversary Virtual Symposium

10th September 2020

12.30-12.40	Introduction	Sam de Visser, IRMG Chair
12.40-13.15	***Adventures in Homogeneous Water Oxidation Catalysis***	**Robert Crabtree,** **Yale University**
13.15-13.30	*Mechanistic Investigation of the Nickel-Catalyzed Carbonylation of Alcohols*	Maximilian Menche, CaRLa (Catalysis Research Laboratory), Heidelberg
13.30-13.45	*The Role of Porphyrin Peripheral Substituents in Determining the Reactivities of Ferrous Nitrosyl Species*	Sk Amanullah, IACS Kolkata
13.45-14.00	*Catalyst Seeking Substrate: Computational Prediction in Homogeneous Catalysis*	Derek Durand, University of Bristol
14.00-14.35	***Nucleophilic Boryls: Magnesium Complexes Exhibiting Oxy Moronic Boron Behaviour***	**Claire McMullin,** **2020 IRMG Young Investigator,** **University of Bath**
14.35-14.45	Break	
14.45-15.00	*Alkene Epoxidation Catalysed by Ru-Porphyrin Catalysts using Molecular Oxygen as the Oxidant*	Qun Cao, University of Bath
15.00-15.15	*Ab initio calculations in non-heme iron reactivity*	Carlos Martin-Fernandez, KU Leuven
15.15-15.30	*In-Crystal Reactions of Chemisorbed NO and* O_2	Mads Sondrup Møller, University of Southern Denmark
15.30-16.05	***Solid-state Molecular Organometallic Chemistry (SMOM): Reactivity, Catalysis and Substrate Mobility in Single-Crystals***	**Andrew Weller,** **University of York**
16.05-16.10	Break	
16.10-16.25	*Mechanistic insights into the ortho-defluorination-hydroxylation of 2-halophenolates promoted by a bis(μ-oxo)dicopper(III) complex*	Pau Besalú-Sala, Universitat de Girona
16.25-16.40	*An exploration of paramagnetic hydride complexes' acidity and electrochemistry*	Benjamin E. Rennie, University of Toronto
16.40-16.55	*A Molecular Mediator for Electrocatalytic Concerted-Proton Electron Transfers*	Matthew Chalkley, Caltech
16.55-17.30	***Tailoring Transition Metal Ates for Chemical Cooperativity***	**Eva Hevia,** **University of Bern**
17.30-17.35	Close	Sam de Visser, IRMG Chair

Short presentation abstracts

1. **Mechanistic Investigation of the Nickel-Catalyzed Carbonylation of Alcohols**
Maximilian Menche, CaRLa (Catalysis Research Laboratory), Heidelberg
The carbonylation of alcohols employing carbon monoxide represents an atom-efficient methodology for the preparation of carboxylic acids. Current processes either rely on harsh reaction conditions or precious metals. Here, we present a detailed mechanistic study of a catalytic system based on NiI_2, which can carbonylate benzylic alcohols in a highly regioselective manner to the corresponding branched carboxylic acids. Quantum-chemical computations were used to evaluate the underlying mechanistic processes. They revealed that the combination of two mechanisms is responsible for the experimentally observed reactivity and that the oxidative addition of alkyl halides to the Ni(0) species follows a radical oxidation pathway via two one-electron steps.

2. **The Role of Porphyrin Peripheral Substituents in Determining the Reactivities of Ferrous Nitrosyl Species**
Sk Amanullah, IACS Kolkata, (Dey Group)
$\{FeNO\}_7$ species are intermediate common to the catalytic cycles of Cd_1NiR (NO2 – to NO) and CcNiR (NO_2 – to NH_4^+). The major difference is the structure of the heme d_1 (Cd_1NiR), relative to heme *c* (CcNiR). A series of iron porphyrinoids, designed to model heme d_1 and heme *c*, and their NO adducts were synthesized. The weakening of the Fe–NO bonding biases the $\{FeNO\}_7$ species of heme d_1 mimic for NO dissociation, as in Cd_1NiR, which is otherwise set-up for a proton-coupled electron transfer (PCET) to form an $\{FeHNO\}_8$ species eventually leading to its further reduction to NH_4^+.

3. **Catalyst Seeking Substrate: Computational Prediction in Homogeneous Catalysis**
Derek Durand, University of Bristol (Fey Group)
The computational optimisation and design of homogenous TM catalysts using mechanistic studies based on density functional theory calculations has been previously demonstrated.[1] Such studies can be supplemented and guided using calculated chemical descriptor databases, such as Bristol's Ligand Knowledge Bases (LKBs).[2]
Utilising cationic rhodium complexes bearing bisphosphine ligands,[3-4] we present the initial phase of a dual-purpose approach, suitable for both mechanistically exploring a range of additions to multiple bond substrates and constructing a database of calculated catalyst descriptors, which can be used with the LKB's to guide both catalyst optimisation and novel substrate discovery.

1. S. Ahn, M. Hong, M. Sundararajan, D. H. Ess and M.-H. Baik, *Chem. Rev.*, 2019, **119**, 6509-6560.
2. D. J. Durand and N. Fey, *Chem. Rev.*, 2019, **119**, 6561-6594.
3. R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2134-2143.
4. J. A. Osborn and R. R. Schrock, *J. Am. Chem. Soc.*, 1971, **93**, 2397-2407.

4. **Alkene Epoxidation Catalysed by Ru-Porphyrin Catalysts using Molecular Oxygen as the Oxidant**
Qun Cao, University of Bath (Hintermair/Muldoon Groups)
We developed a Ru-porphyrin catalysed epoxidation method using O_2 as direct oxidant without using any sacrificial reductant. We found that the addition of water and ethyl acetate could significantly improve the conversion and yield of aerobic epoxidation with di-oxo-Ru^{VI}(TMP) (1a) as catalyst. Utilising 0.5 mol% catalyst 1a, the addition of water and EtOAc could improve the catalyst turnover numbers (TONs) from 23 to 166. Using our improved protocol, we have also

seen an increased substrate scope that now includes aliphatic and cyclic alkenes in addition to aromatic ones with up to 100% conversion and 96% selectivity. Preliminarily kinetic studies carried out using in-situ (Flow)NMR and ESI-MS. We found that the addition of water and EtOAc significantly increase the life time of the catalyst by stabilizing the key mono-oxo-Ru^{IV}(TMP) complex which can be monitored by ^{1}H FlowNMR. Besides, the catalyst intermediates mono-oxo-Ru^{IV}(TMP)(H_2O), di-oxo-Ru^{VI}(TMP)(H_2O), Ru^{VI}(TMP)(H_2O) and the deactivated form (CO)Ru^{II}(TMP) could be identified using ESI-MS, which indicated the potential of water coordinated to the Ru complexes could be involved in the reaction mechanism.

5. ***Ab initio calculations in non-heme iron reactivity***

Carlos Martin-Fernandez, KU Leuven (Harvey Group)

The theoretical study of inorganic reaction mechanisms is traditionally done using DFT methods. However, this might not always be the best choice. We have used as a study case the reaction between cyclohexene and a non-heme iron(IV)-oxo complex, which can follow two reaction paths (HAT or epoxidation) and potentially show two-state reactivity. We have compared the DFT results with different ab initio methods (CASPT2 and two flavours of local coupled cluster) and shown that in order to explain the experimental observations we need ab initio calculations which can take both static and dynamic correlation into account.

6. **In-Crystal Reactions of Chemisorbed NO and O_2**

Mads Sondrup Møller, University of Southern Denmark (McKenzie Group)

The reactivity of nitric oxide (NO) with transition metal complexes in solution state is well developed, and its non-innocence as a ligand is a classic in coordination chemistry. Its reactivity with solid-state metal-organic materials is, however, far less explored. We can show that NO is chemisorbed by the crystalline solid-state of complexes containing tuneable[1,2] dicobalt(II) or dicobalt(III) sites[3,4] with an impressive cascade of in-crystal reactions. These comprise the in-crystal syntheses of a coordinated bridging $\eta1$–N:$\eta1$–O-nitrite, a nitrate counteranion, and the stepwise oxidation of an aryl amine group on the ligand scaffold, all this observable via a single-crystal to single-crystal transformation.[5]

1. F. B. Johansson, A. D. Bond, C. J. McKenzie, *Inorg. Chem*. **2007**, *46*, 2224–2236.
2. M. S. Vad, F. B. Johansson, R. K. Seidler-Egdal, J. E. McGrady, S. M. Novikov, S. I. Bozhevolnyi, A. D. Bond, C. J. McKenzie, *Dalton Trans.* **2013**, *42*, 9921–9929.
3. J. Sundberg, L. J. Cameron, P. D. Southon, C. J. Kepert, C. J. McKenzie, *Chem. Sci.* **2014**, *5*, 4017–4025.
4. P. D. Southon, D. J. Price, P. K. Nielsen, C. J. McKenzie, C. J. Kepert, *J. Am. Chem. Soc*. **2011**, *133*, 10885–10891.
5. M. S. Møller, A. Haag, V. McKee, C. J. McKenzie, *Chem. Commun*. **2019**, *55*, 10551-10554.

7. **Mechanistic insights into the ortho-defluorination-hydroxylation of 2-halophenolates promoted by a bis(μ-oxo)dicopper(III) complex**

Pau Besalú-Sala, Universitat de Girona (Costas/Company Group)

C–F bonds are one of the most inert functionalities in organic chemistry. Nevertheless, some $[Cu_2O_2]^{2+}$ species are able to defluorinate-hydroxylate orthofluorophenolates in a chemoselective manner.[1,2] We present a combined theoretical and experimental mechanistic study to unravel the origin of the chemo-selectivity of the *ortho*-defluorination-hydroxylation of 2-halophenolates by the $[Cu_2(O)_2(DBED)_2]^{2+}$ complex.[2] Our results show that the equilibria between (side-on)peroxo and bis(μ-oxo) isomers plays a key role in the mechanism, being the latter the reactive species. Furthermore, we have been able to rationalize the chemoselectivity of $[Cu_2(O)_2(DBED)_2]^{2+}$ for the C–F activation over C–Cl and C–H activations.

1. Serrano-Plana, J.; Garcia-Bosch, I.; Miyake, R.; Costas, M.; Company, A. *Angew. Chem. Int. Ed*. **2014**, *53*, 9608-9612.
2. Mirica, L. M.; Vance, M.; Rudd, D. J.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; Stack, T. D. P., *Science* **2005**, *308*, 1890-1892.

8. **An exploration of paramagnetic hydride complexes' acidity and electrochemistry**
Benjamin E. Rennie, University of Toronto (Morris Group)
The thermodynamics of paramagnetic transition metal hydride complexes are explored. The pK_a of these paramagnetic hydrides are estimated using an empirically derived formula called the ligand acidity constant (LAC), in acetonitrile. Alongside the $pK_a^{\text{LAC-MeCN}}$, the electrochemistry of over 200 transition metal hydrides has been tabulated. In many cases, the electrochemical reversibility could be predicted based on the $pK_a^{\text{LAC-MeCN}}$ of the oxidized complex: if acidic enough, proton loss is expected. The redox potential is used with the $pKa^{\text{LAC-MeCN}}$ of the oxidized complex to calculate the bond dissociation free energies (BDFEs) of all of the complexes studied.

9. **A Molecular Mediator for Electrocatalytic Concerted-Proton Electron Transfers**
Matthew Chalkley, Caltech (Peters Group)
CPET approaches to the reduction of small molecules are useful due to the lowered required potential compared to approaches based on initial electron transfer. Such approaches are, however, challenging due to the dual requirement to form a thermodynamically weak X-H bond that does not undergo hydrogen evolution. We demonstrate the first example of an electrochemical approach to reductive CPET via synthetic integration of a Brønsted acid with a cobaltocenium redox mediator. Synthetic integration both facilitates reduction-triggered weakening of the Brønsted acidic X-H bond resulting in controlled CPET reaction to a model substrate and minimizes H_2 formation.