15TH AUSTRALASIAN ORGANOMETALLIC MEETING (OZOM15)

THE UNIVERSITY OF QUEENSLAND
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Welcome Message

We welcome you to the 15th Australasian Organometallics Meeting (OZOM15) and the 3rd Australasian Rare Earths Meeting (OZRE2025). OZOM's inaugural meeting was in 1993 hosted by the University of New England, and OZRE was founded in 2023 with the first meeting at University of Melbourne. However, this is the first time that both of these meetings have been hosted at the University of Queensland and in Brisbane, and we are excited to showcase Brisbane as an excellent location to highlight research and foster bonds (chemical or otherwise).

Given the limited sizes of both organometallic and rare earth chemical communities and the great separation between research groups, OZOM and OZRE meetings serve as excellent opportunities to get to know colleagues and emerging talent in the organometallic and rare earth communities. There are also many chemists who happily fit into both communities and regularly attend both meetings, so we are excited to be able to align the meetings to expose an expanded breadth of chemistry to attendees.
We have followed in the tradition of previous OZOM meetings to focus presentation opportunities towards early career researchers. However, we also feature an exciting line-up of local and international plenary speakers, which ensures that the influence of the research presented at OZOM will have a global impact.

Finally, we wish to acknowledge our sponsors who have made this event possible, namely Rowe Scientific, RSC Publishing (Dalton Transactions and Chemical Communications), the CSIRO (Australian Journal of Chemistry) and the University of Queensland. We hope you enjoy the conference and look forward to learning about all the cutting-edge research that will be shared at this event.

Rowan Young, Masnun Naher and Evan Moore
OZOM15 and OZRE2025 Organising Committee

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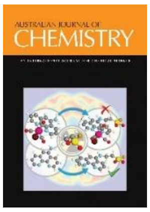

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Program Outline

Time	Sun 22nd June	Mon 23rd June	Tues 24th June	Wed 25th June
		Start 9am	Start 9am	
9:00-9:10		Plenary (OZOM) **Annie Colebatch** (ANU) 9:00-9:40	Plenary (OZOM) **Terrance Hadlington** (TUM) 9:00-9:40	Start 9:30am
9:10-9:20				
9:20-9:30				
9:30-9:40				OZOM26 (**Isabelle M. Dixon**) 9:30-9:50
9:40-9:50		OZOM1 (**Edgar Zander**) 9:40-10:00	OZOM13(**Mani Koodalingam**) 9:40-10:00	
9:50-10:00				OZOM27 (**Marcus Korb**) 9:50-10:10
10:00-10:10		OZOM2 (**Scarlet L. Hopkins**) 10:00-10:20	OZOM14 (**Previati Eleonora**) 10:00-10:20	
10:10-10:20				OZOM28(**Daniel Priebbenowa**) 10:10-10:30
10:20-10:30		OZOM3 (Xin Wu) 10:20-10:40	OZOM15 (**Liam K. Burt**) 10:20-10:40	
10:30-10:40				Awards (OZOM)
10:40-10:50		Morning Tea Break 10:40-11:10	Morning Tea Break 10:40-11:10	Morning Tea Break 10:40-11:10
10:50-11:00				
11:00-11:10				
11:10-11:20		OZOM4 (**Corinna Czernetzki**) 11:10-11:30	OZOM16 (**Max Lapersonne**) 11:10-11:30	Plenary (OZOM/OZRE) **Joy Farnaby** (University of Glasgow) 11:10-11:50
11:20-11:30				
11:30-11:40		OZOM5 (**Dat Tien Nguyen**) 11:30-11:50	OZOM17 (**Pratima Sharma**) 11:30-11:50	
11:40-11:50				
11:50-12:00		OZOM6 (**Nathan Dempsey**) 11:50-12:10	OZOM18 (**Caitlyn Whan**) 11:50-12:10	OZRE1 (**Matthew Anker**) 11:50-12:10
12:00-12:10				
12:10-12:20		OZOM7 (**Miracle I. Ekavhiare**) 12:10-12:30	OZOM19 (**Madeleine Stewart**) 12:10-12:30	OZRE2 (**Jacob M. Neill**) 12:10-12:30
12:20-12:30				
12:30-12:40		OZOM8 (**Ryan Huo**) 12:30-12:50	OZOM20 (**Sumiyyah Hameed**) 12:30-12:50	OZRE3 (**Blake Connolly**) 12:30-12:50
12:40-12:50				
12:50-1:00		Lunch Break 12:50-2:00	Lunch Break 12:50-2:00	Lunch Break 12:50-2:00
1:00-1:10				
1:10-1:20				
1:20-1:30				
1:30-1:40				
1:40-1:50				
1:50-2:00				
2:00-2:10	Registrations 2:00-3:00	Plenary (OZOM) **Erin Leitao** (University of Auckland) 2:00-2:40	Plenary (OZOM) **Shigeyoshi Inoue** (TUM) 2:00-2:40	Plenary (OZRE) **Max Massi** (Curtin University) 2:00-2:40
2:10-2:20				
2:20-2:30				
2:30-2:40				
2:40-2:50		OZOM9 (**Matthew J. Evans**) 2:40-3:00	OZOM21 (**Max S. Coles**) 2:40-3:00	OZRE 4 (**Naveena Y. Salpadoru**) 2:40-3:00
2:50-3:00				
3:00-3:10	Opening Remarks 3:00-3:20	OZOM10 (**Ryan M. Kirka**) 3:00-3:20	OZOM22 (**Andreas Hochholzer**) 3:00-3:20	OZRE 5 (**Ameen Jowhar**) 3:00-3:20
3:10-3:20				
3:20-3:30	Plenary (OZOM) **Stephen Thomas** (University of Edinburgh) 3:20-4:00	OZOM11 (**Marcelo T. de Oliveira**) 3:20-3:40	OZOM23 (**Dean J. O'Brien**) 3:20-3:40	OZRE 6 (**Alex Ireland**) 3:20-3:40
3:30-3:40				
3:40-3:50		OZOM12 (**Charles R. M. Soukup**) 3:40-4:00	OZOM24 (**Thanh Tung Vo**) 3:40-4:00	Awards/Closing 3:40-4:00
3:50-4:00				
4:00-4:10	Welcome Mixer 4:00-6:00 (St Lucy's)	Poster Session 4:00-6:00	OZOM25 (**Emeric Schubert**) 4:00-4:20	
4:10-4:20				
4:20-4:30			Free Time	
4:30-4:40				
4:40-4:50				
4:50-5:00				
5:00-5:10				
5:10-5:20				
5:20-5:30				
5:30-5:40				
5:40-5:50				
5:50-6:00				
6:00-6:10				
6:10-6:20				
6:20-6:30				
6:30-9:30			Conference Dinner 6:30-9:00 (The Ship Inn)	

Conference Venue

The scientific schedule for the conference will take place in the historic Parnell Building, situated within the grounds of the University of Queensland's St Lucia Campus. The St Lucia campus is easily accessed via public transport from South Bank and the Brisbane CBD.

Campus Map

Registration and scientific program

Registration will take place from 2.00 – 3.00 pm on Sunday, the 22nd June in the Foyer of the Parnell Building (Building 7). The registration desk will also be open on Monday morning from 8.30 – 9.00 am for late arriving attendees. Oral presentations will be held in room 7-222 and poster presentations will be held in room 7-326 (both in Parnell Building)

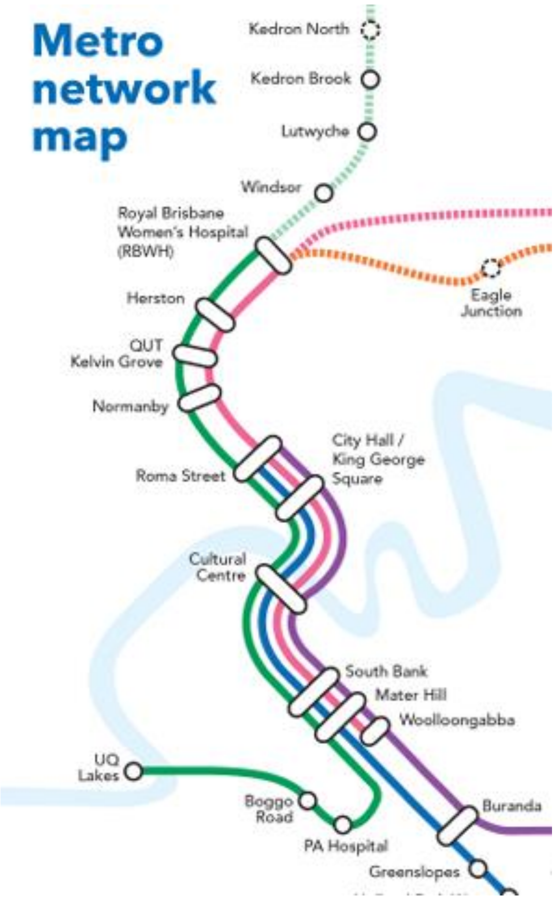
Welcome Mixer and Conference Dinner

The welcome event will take place from 4.00 – 6.00 pm on Sunday 22nd June at Saint Lucy Caffe e Cucina (St Lucy's), University of Queensland, Blair Drive, St Lucia. Ferry Services from UQ to the city will operate every 30 minutes until 10.15 pm on Sunday.

The conference dinner will be held on Tuesday 24th June from 6.30 – 9.30 pm at the upper level of the Ship Inn, Sidon Street, South Bank. This venue is a short stroll from the city, connected via numerous bridges and close to the South Bank Bus and Train Stations.

Transport

Public transport in Brisbane is extremely cheap with 50 cent fares across all routes (if you tap on and off). Ferries, trains and Metro all accept debit and credit card use for tap on/off, or you can purchase a Go Travel Card from UQ Lakes bus station ticketing machines or the UQ News Agency (note: buses only accept travel cards).



Metro

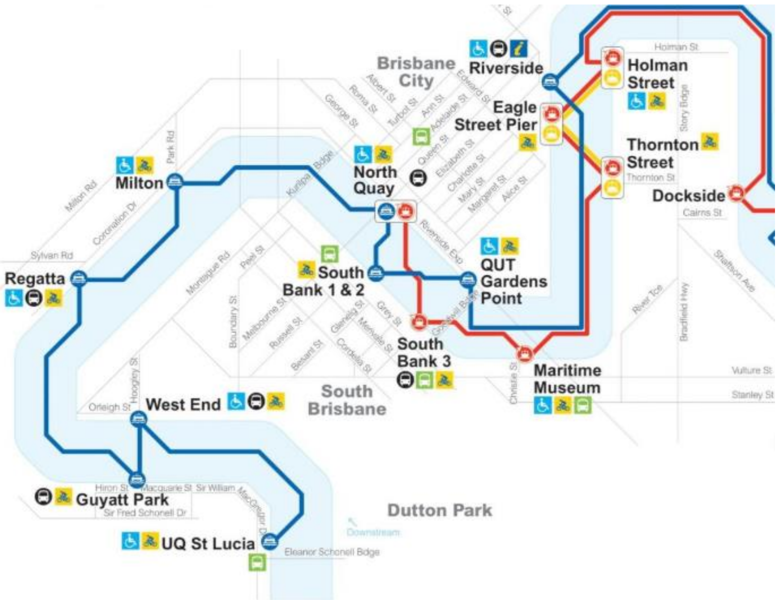
Metro M2 line from UQ Lakes to South Bank and CBD (10-15 min). The metro is an articulated bus with dedicated lanes and not a train!

Ferry

UQ Ferry Terminal to North Quay (CBD) and Southbank (25-30 min)

Buses

Multiple route options. Requires Go Travel Card (10-20 min to city)



Detailed Program

Sunday 22nd June	
2:00 – 3:00	Registration (Parnell, Building 7, UQ)
3:00 – 3:20	Opening remarks
3:20 – 4:00	**Plenary Lecture:** Stephen P. Thomas – Transborylation Enabled Catalysis: From Old Reactivity to New Disconnections and a Cautionary Tale *Chair: Rowan Young*
4:00 – 6:00	Welcome Mixer: Saint Lucy Caffe e Cucina, UQ

Monday 23rd June	
9:00 – 10:40 Session Chair: Masnun Naher	
9:00 – 9:40	**Plenary Lecture:** Annie L. Colebatch – A PNNN dinucleating ligand for heterobimetallic complexation
9:40 – 10:00 OZOM1	Edgar Zander – (EMindNON) – The Synthesis of a Novel Ligand and Its Performance in Low Valent Main Group Chemistry
10:00 – 10:20 OZOM2	Scarlet L. Hopkins – Structural Insights into the Sodium Rhodizonate Test for Lead Detection
10:20 – 10:40 OZOM3	Xin Wu – Anion Coordination Chemistry in Water Using Hydrogen Bonds
10:40 – 11:10 Morning Tea Break	
10:10 – 12:50 Session Chair: Caitlin Lindsay	
10:10 – 11:30 OZOM4	Corinna Czernetzki – Beryllium in Action – Exploring Reductions and Radicals
11:30 – 11:50 OZOM5	Dat Tien Nguyen – Reactivity of an Anionic Magnesium(I) Complex
11:50 – 12:10 OZOM6	Nathan Dempsey – Nicotinamide-Appended Metal Complexes as Luminescent Redox Probes
12:10 – 12:30 OZOM7	Miracle I. Ekavhiare – Through the Ligand: A Mechanistic Twist in Nickel-Catalyzed Double Bond Transposition
12:30 – 12:50 OZOM8	Ryan Huo – Reversible Hydrogen Activation by Trapped Silicon Anions (ANU)
12:50 – 1:00 Lunch	
2:00 – 4:00 Session Chair: Max S. Coles	
2:00 – 2:40	**Plenary Lecture:** Erin M. Leitao – Combining Sulfur with Silicone: A Route to Recyclable Silicone Vitrimers
2:40 – 3:00 OZOM9	Matthew J. Evans – P4 Coordination and Reduction at Alkaline Earth Metal Centres
3:00 – 3:20 OZOM10	Ryan M. Kirka – The Chemistry of Pnictogen-Functionalised Isonitrile and N,P-Heterocyclic Carbene Complexes

3:20 – 3:40 OZOM11	Marcelo T. de Oliveira – Through the Ligand: A Mechanistic Twist in Nickel-Catalyzed Double Bond Transposition
3:40 – 4:00 OZOM12	Charles R. M. Soukup – Indium(III) and bismuth(III) 8-hydroxyquinolinate complexes: enhanced antibacterial activity and selectivity against ESKAPE pathogens
4:00 – 6:00	Poster Session

Tuesday 24th June	
9:00 – 10:40 Session Chair: Liesa Eickhoff	
9:00 – 9:40	**Plenary Lecture:** Terrance J. Hadlington – Leveraging Chemistry at the Molecular p-Block - Transition Metal Interface
9:40 – 10:00 OZOM13	Manikandan Koodalingam – Twisted Carbazole Dendrons for Solution-Processable Green Emissive Phosphorescent Dendrimers
10:00 – 10:20 OZOM14	Previati Eleonora – Phosphorescent Ir(III)-based metallapolymers for UV light harvesting
10:20 – 10:40 OZOM15	Liam K. Burt – Preparation of Alkali-Silanide Nickel(0)-ates and their Intermediacy in Catalytic Silylation of Aryl Ethers
10:40 – 11:10 Morning Tea Break	
11:10 – 12:50 Session Chair: Marcus Korb	
11:10 – 11:30 OZOM16	Max Lapersonne – Electrochemical Synthesis of 3d-Metal Cations stabilised by Weakly
11:30 – 11:50 OZOM17	Pratima Sharma – Nonlinear optical studies of ruthenium alkynyl cruciform compounds
11:50 – 12:10 OZOM18	Caitlyn Whan – Synthesis and characterisation of organogallium complexes with hydroxyanthraquinones
12:10 – 12:30 OZOM19	Madeleine Stewart – The use of the bpp ligand in synthesis and catalysis
12:30 – 12:50 OZOM20	Sumiyyah Hameed – Organo-gallium(III) and bismuth(III) complexes of indeno[1,2]quinoline derivatives as antibacterial agents
12:50 – 2:00 Lunch	
2:00 – 4:20 ***(UQ – TUM Session)*** *Session Chair: Rowan Young*	
2:00 – 2:40	**Plenary Lecture:** Shigeyoshi Inoue – The Power of Earth Abundant Main Group Elements: New Horizons in Bond Activations and Catalysis
2:40 – 3:00 OZOM21	Max S. Coles – A Frustrated Lewis Pair Approach for the Synthesis of Monofluoroallenes
3:00 – 3:20 OZOM22	Andreas Hochholzer – NHC-Stabilized Inorganic Carbamic Acid, (Thio)Urethane and Urea from NHC-Stabilized Heavier Isocyanates
3:20 – 3:40 OZOM23	Dean J. O'Brien – High-Resolution Photocrystallography of Transition Metal Complexes
3:40 – 4:00 OZOM24	Thanh Tung Vo – Electrochemically-mediated copper-catalyzed atom transfer radical addition using polyhaloacetamide derivatives
4:00 – 4:20 OZOM25	Emeric Schubert – Ligand design for modulating Mono- and Bimetallic Ni complexation
6:30 – 9:00	Conference Dinner, The Ship Inn, South Bank, Brisbane

Wednesday 25th June	
9:30 – 10:30 Session Chair: Curtis Ho	
9:30 – 9:50 OZOM26	Isabelle M. Dixon – Counterion effects in photocatalysis: insights from DFT
9:50 – 10:10 OZOM27	Marcus Korb – A revision of the common practice for calculating CH acidities (p*K*a values) of substituted benzenes and ferrocenes
10:10 – 10:30 OZOM28	Daniel L. Priebbenowa – The Influence of Structurally Modified Cyclopentadienyl Ligands in Group-9 Metal Catalysed C-H Functionalisation
10:30 – 10:40	Awards (OZOM)
10:40 – 11:10 Morning Tea Break	
11:10 – 12:50 Session Chair: Evan More	
11:10 – 11:50	**Plenary Lecture:** Joy H. Farnaby – Rediscovering the unsubstituted tris(pyrazolyl)borate ligand on lanthanides: Ln/Al trihydrides, divalents, and radical-bridged heterobimetallics
11:50 – 12:10 OZRE1	Mathew D. Anker – Synthesis and Reactivity of Organolanthanide(II) Hydrides
12:10 – 12:30 OZRE2	Jacob M. Neill – Synthesis, Structure and Properties of 4-Nitrophenylaceto-Rare-Earth (III) Complexes for the Application of Corrosion Inhibition
12:30 – 12:50 OZRE3	Blake Connolly – "Interpreting" Quantum Chemistry with tools of Spectroscopic Analysis
12:50 – 2:00 Lunch	
2:00 – 3:40 Session Chair: William J. Gee	
2:00 – 2:40	**Plenary Lecture:** Max Massi – Sensitisation of Multinuclear Lanthanide Assemblies
2:40 – 3:00 OZRE4	Naveena Y. Salpadoru Thuppahige – Synthesis, and Structural Characterization of Rare-Earth Hydroxyphenylacetate Complexes and Their Corrosion Inhibition Properties
3:00 – 3:20 OZRE5	Ameen Jowhar Eradiparampath – Accessing Lanthanoid Metal Complexes Using Copper (I) Reagents
3:20 – 3:40 OZRE6	Alex Ireland – Sensitised Lanthanoid Luminescence using Bimetallic Cu(I) – Ln(III) Complexes
3:40 – 3:40	Awards (OZRE) and closing remarks (OZOM/ OZRE) (Evan Moore)

Poster Presentations

Poster	Presenter	Presentation Title
P1	Liesa Eickhoff	Stabilisation of Hypervalent Aluminium Hydride Anions in Solution
P2	Jawed El Batti	New investigations on Asymmetric *e*ATRA, Ligand Design and Copper Complex Characterisation
P3	Bahram Ajerloo	Structure-Property Relationships: Metal Complexes in Molecular Junctions
P4	Jeeshma Johny	Synthesis and characterisation of new divalent or trivalent lanthanoid complexes from free metals and pyrazolato ligands
P5	Fabian Kallmeier	Finetuning Ligand Sterics and Electronics for Stabilising Low-Valent Aluminium Species
P6	Mason Lam	Group 13 artificial sweetener complexes as antimicrobials
P7	Li FengLim	Superbasic Calcium Alkyl Complexes: Templated Two-Fold Deprotonation of Benzene
P8	Diego C.	Synthesis of Hemilabile Iron Half-Sandwich Complexes
P9	Caitlin Lindsay	Gotta Trap 'Em All: Capturing Anions for Hydrogen Storage
P10	Rebecca M. Majchrzak	Binuclear Boron Compounds Supported by a Xanthene-Based Scaffold
P11	Emily E. Nahon	C-C Coupling in Late-Stage Ligand Functionalisation Through Low-Oxidation State Group 13 Radicals
P12	Gareth R. Nelmes	Structure and Formation of the Parent Silylone Dianion
P12	Yueer Zhu	Reactivity Study of Silyl-substituted Alanes with Isocyanides
P14	Rebekah N Duffin	Sb(V) aryl anthraquinone complexes: Enhanced stability and antileishmanial activity of a fluorescent anthracycline system
P15	Joseph M. Parr	Carbon-Carbon Bond Activation and Functionalisation by Mg Complexes
P16	Joseph Pearce	Synthesis and Reactivity of Lanthanide (II) Hydrides
P17	Harrison Pinto	Generation of Novel Tellurium Carbyne complexes
P18	Jessica C Reid	Antibiotics revitalised: therapeutic potential of organogallium (III) and organoindium (III) quinolonate complexes
P19	Marie K. Sundin	Selective C–F activation and functionalisation of polyfluorinated 2-phenylpyridines
P20	Sophie Unsworth	Synthesis and Reactivity of a Mg(0) Compound
P21	Joshua Delaney	Copper(II)-Mediated Electrocatalytic Activation of C–X Bonds in Polyhalogenated Compound Synthesis
P22	Max Les	Heavy Metal Molecular Qubits
P23	Peter D. Giang	Enzymes and electrochemistry: A dynamic connection

Abstracts

1. Plenary Lecture Abstracts

2. Oral Presentation Abstracts

3. Poster Presentation Abstracts

1. Plenary Lecture Abstracts

Bio of Stephen P. Thomas

Stephen Thomas is a professor of catalysis at the University of Edinburgh. The Thomas group have published over 60 papers on Earth-abundant element catalysis, including using boron and aluminium catalysts, and pioneered the use of transborylation as a mechanism of catalyst turnover. The group's work has been recognised by prizes including UK Blavatnik Finalist, RSC Merck, Sharpe and Dohme and Hickbottom awards and a Pfizer Green Chemistry Research Grant. The Thomas group currently collaborate with a range of UK-based industrial companies including AZ, GSK, Lubrizol and Johnson-Matthey.

Transborylation Enabled Catalysis: From Old Reactivity to New Disconnections and a Cautionary Tale

Stephen P. Thomas[a]
[a]EAStCHEM School of Chemistry, The University of Edinburgh, Edinburgh, UK
Email: *stephen.thomas@ed.ac.uk*

The main-group offers a sustainable and underutilised alternative to transition metal catalysis; however, the redox chemistry of transition metals is not readily translated to main-group species.[1] This talk will discuss our use of a redox-neutral turnover strategy tailored to p-block elements; transborylation.[2] The potential of this turnover mechanism will be demonstrated through catalytic, enantioselective[3] and carbon-carbon bond forming[4] reactions, and role in 'hidden borane' catalysis.[5]

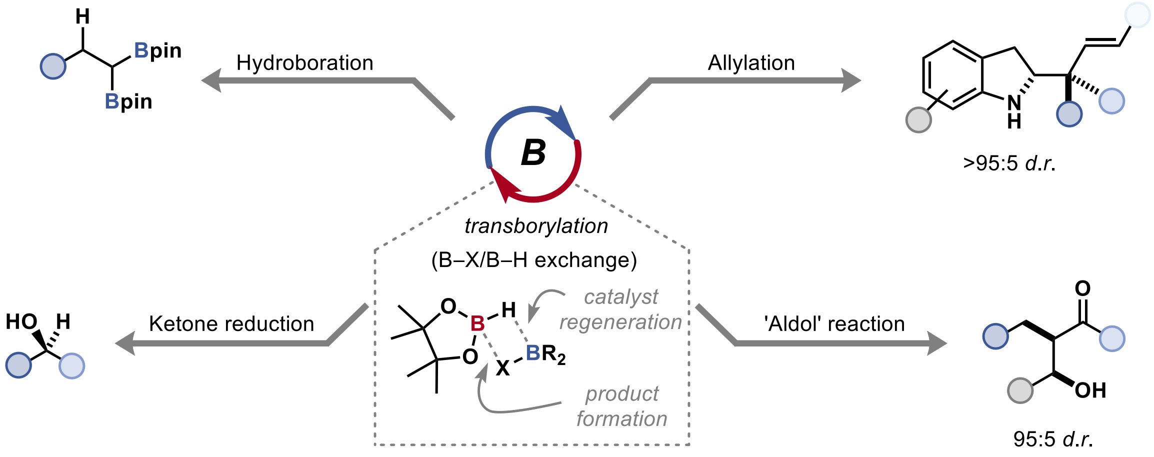


Figure 1. Examples of transborylation catalysis.

References

[1] T. Chu, G. I. Nikonov, *Chem. Rev.,* 2018, **118**, 3608–3680.
[2] (a) D. Willcox, S, P. Thomas, Beilstein *J. Org. Chem.,* 2023, **19**, 325–348; (b) A. D. Bage, K. Nicholson, T. A. Hunt, T. Langer, S. P. Thomas, *Synthesis*, 2023, **55**, 62–74.
[3] (a) K. Nicholson, J. Dunne, P. DaBell, A, Beaton Garcia, A. D. Bage, J. H. Docherty, T. A. Hunt, T. Langer, S. P. Thomas, *ACS Catal.*, 2021, *11*, 2034–2040; (b) K. Nicholson, T. S. McOnie, T. Langer, G; S. Nichol, Langer, S. P. Thomas, *Chem Commun.*, 2024, **60**, 10748–10751.
[4] (a) A. Moreno González, K. Nicholson, N. Llopis, G. S. Nichol, T. Langer, A. Baeza, S. P. Thomas, *Angew. Chem. Int. Ed.*, 2022, **61**, e202209584; (b) D. R. Willcox, E. Cocco, G. S. Nichol, A. Carlone, S. P. Thomas, *Angew. Chem. Int. Ed.*, 2024, **63**, e202401737.
[5] (a) J. MacLeod, A. D. Bage, L. M. Meyer, S. P. Thomas, *Org. Lett.*, 2024, **26**, 9564–9567; (b) A. D. Bage, T. A. Hunt, S. P. Thomas, *Org. Lett.*, 2020, **22**, 4107–4112.

Bio of Annie L. Colebatch

Annie completed her undergraduate degree and PhD at the Australian National University. She received an Endeavour Research Fellowship to work at the University of Bath (2015) with Prof Michael Hill, followed by postdoctoral appointments at the University of Oxford (2015-2017) with Prof Andrew Weller and the University of Cambridge (2017-2019) with Prof Dominic Wright. She returned to the ANU in 2019 as a Rita Cornforth Fellow, and was awarded an Australian Research Council Discovery Early Career Researcher Award (2020 - 2023). She was awarded the J. G. Russell Award in 2020, the RACI Rita Cornforth Lectureship in 2022 and the RACI Organometallics Prize in 2024.

A PNNN Dinucleating Ligand for Heterobimetallic Complexation

Jingyun Wu,[a] Michael A. Stevens,[a] Michael G. Gardiner,[a] Annie L. Colebatch[a]
[a]Research School of Chemistry, Australian National University, Canberra, ACT, Australia
Email: annie.colebatch@anu.edu.au

While metal-ligand cooperativity is a well-established approach in transition metal catalysis, metal-metal cooperativity remains an emerging strategy.[1-2] Work in this field has shown that catalysts that operate via cooperative bimetallic mechanisms can lead to differing reactivity and selectivity profiles compared to conventional monometallic catalysts. Heterobimetallic complexes provide an additional handle with which to tailor reactivity, but this comes at the expense of added synthetic complexity. Success in bond activation and catalysis depends not only on the nature of the metal-metal pairing but also on the steric and electronic relationship between the two metal centres.[3-5] Ligand design plays an important role; unsymmetrical ligands can be employed to target heterobimetallic complexes and control the relative positioning of the two metals.

This presentation will describe our work on heterobimetallic complexes of a PNNN unsymmetrical dinucleating ligand of the 1,8-naphthyridine expanded pincer ligand family.[6] The proton-responsive ligand design allows for metal-metal-ligand cooperativity via dearomatisation (Figure 1). Applications of these complexes in catalytic hydrogenation will also be discussed.

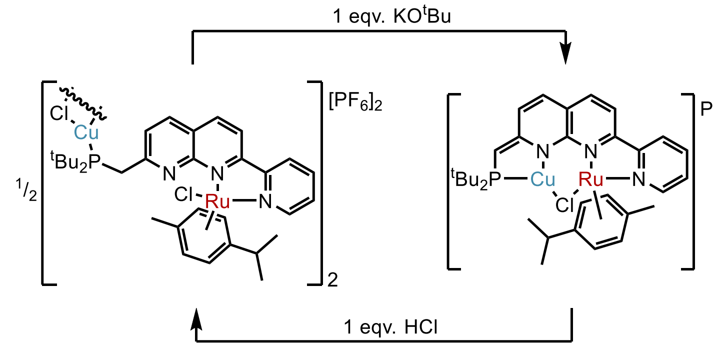


Figure 1. Reversible aromatisation-dearomatisation in ruthenium-copper complexes of an unsymmetrical PNNN dinucleating ligand.

References

[1] M. A. Stevens, A. L. Colebatch *Chem. Soc. Rev.,* 2022, **51**, 1881-1898.
[2] R. Maity, B. S. Birenheide F. Breher, B. Sarkar *ChemCatChem,* 2021, **13**, 2337-2370.
[3] Z. Fickenscher, E. Hey-Hawkins *Molecules,* 2023, **28**, 4233.
[4] R. Govindarajan, S. Deolka, J. R. Khusnutdinova *Chem. Sci.*, 2022, **13**, 14008-14031.
[5] P. C. Abhyankar, C. M. Thomas *Angew. Chem. Int. Ed.*, 2024, **63**, e202416100.
[6] J. Wu, M. A. Stevens, M. G. Gardiner, A. L. Colebatch, *Dalton Trans.,* 2024, **53**, 18037-18046.

Bio of Erin Leitao

Erin joined the University of Auckland in late 2015 after a Marie Skłodowska-Curie Postdoctoral Research Fellowship at the University of Bristol (UK). Her research group is interested in efficiently synthesizing safe-by-design functional inorganic molecules and polymers, ideally using catalysis. Where possible, renewable feedstocks are used, green chemistry principles are applied, and the degradation and fate of the materials are considered. Erin's research projects include understanding catalytic mechanisms to improve the selectivity of forming of main-group/main-group bonds, polymer recycling (plastics, silicone), and the synthesis of replacements for PFAS, flame-retardants, pesticides as well as new materials to be used as sorbents.

Combining Sulfur with Silicone: A Route to Recyclable Silicone Vitrimers

Erin M. Leitao,[a,b] Mahsa Rokni[a,b]
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[b]The MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand
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Sulfur, a waste by-product of petroleum and gas refining, accumulates at a rate of tens of millions of tons annually.[1] In 2013, Pyun and coworkers discovered that sulfur could be used as a feedstock to make polymeric materials.[2] Polysulfide, formed via thermal ring opening polymerisation of elemental sulfur, is stabilised when copolymerised with a variety of diene crosslinkers and has shown promise in a number of applications. In our group, we are exploiting this same chemistry to combine sulfur with silicone. Inspired by the fact that the properties exhibited by polysulfides and silicones are similar (*e.g.* hydrophobicity, flexibility, thermal and chemical resistance), we have incorporated both small molecule silicones into polysulfides[3],[4] and sulfides into silicone via crosslinking.[5] When sulfur is combined with commercial grade silicone, the hydrosilylation crosslinking reaction is intentionally halted as sulfur poisons the Pt catalyst and sulfide crosslinks are installed in their place (Figure, blue chains with linked orange dots). This results in the production of a silicone vitrimer. The presence of the dynamic sulfur-sulfur bonds provide the ability for the silicone to be healed after being damaged (orange arrows). Our current work is focused on transferring this chemistry to other silicone formulations, and tuning the functionality towards developing a completely reconfigurable material (green arrows) that is commercially applicable.

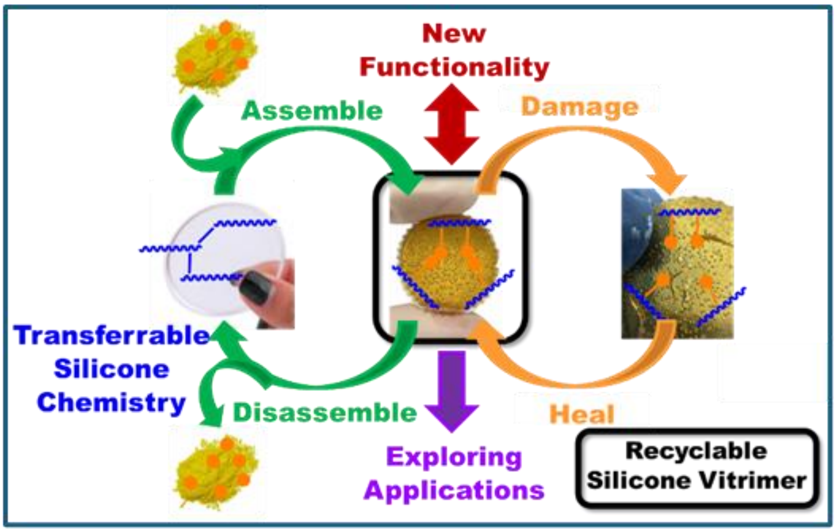

Figure 1. The development of a reconfigurable silicone vitrimer

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Bio of Terrance J. Hadlington

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Terry grew up in the UK, and received his MChem degree from the University of Bath in 2011. He then moved to Melbourne, Australia, where he conducted his PhD research with Prof. Cameron Jones at Monash University, utilizing heavier tetrylenes in catalysis and exploring low-valent group 14 chemistry more broadly. During this time, he also spent four months at the University of Oxford, working with Prof. Simon Aldridge. He then relocated to Berlin as a UniCat Postdoctoral Fellow with Prof. Matthias Driess. In late 2019, Terry started his independent research career at the TU Munich, supported by a Liebig Fellowship of the FCI. Here his fascination regarding the synergistic reactivity between low-valent main group ligands, such as gallylenes and stannylenes, and low-valent first row transition metals is a major topic of research. His team additionally develops chelating polyphosphinidene ligands, and as well as investigating unexplored hydride chemistry of the alkaline earth metals, including beryllium.

Since establishing his independent research group in Munich, Terry has been awarded the Liebig Stipendium of the FCI (2019), two Independent Research grants from the DFG (2021, 2023), an Exploration Grant of the Boehringer Ingelheim Foundation (2022), as well as an ERC Starting Grant (2022). He was also the recipient of the 2022 Wöhler-BASF-Nachwuchs Preis of the GDCh, and the 2023 ADUC Preis.

Leveraging Chemistry at the Molecular *p*-Block - Transition Metal Interface

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The Renaissance in main group chemistry over recent decades has given us a huge depth in understanding the electronic characteristics of low-valent *p*-block species.[1,2] The importance of developing sustainable chemical technologies, in conjunction with the impressive reactive capacity of the abundant *p*-block elements in non-classical oxidation states, has firmly established this chemistry as a cornerstone in modern synthesis, albeit in a largely fundamental capacity. In taking such species from laboratory curiosities to utility, our research focuses on developing the Single-Centre Ambiphile ligand concept.[3] This concept utilises the ambiphilic frontier orbitals of now well established low-valent group 13 and 14 species, incorporating these elements into chelating ligands and thus forming a bespoke family of non-innocent ligand systems. These have the capacity to bind a transition metal centre through a lone electron pair, whilst the same binding centre remains highly Lewis acidic (Fig. 1). This, in turn, promotes nucleophile binding at the ligand centre, even in complexes containing sub-18-electron transition metal centres. This opens a new mechanistic pathway for accessing hitherto unknown bond activation processes, moving towards catalysis.

Utilizing Single-Centre Ambiphile ligands, we have shown that stable complexes of Fe^0, Co^0, and Ni^0 are readily accessible, with each transition metal displaying a unique reactive capacity. This is also dependent on the ligand's binding centre (*e.g.* Ge^{II} vs. Sn^{II}), giving a high degree of control over these reactive systems. This and subsequent chemistry of these complexes will be discussed, including site-selective nucleophile binding, Lewis super-acidity, reversible small-molecule activation, and (switchable) alkene functionalisation catalysis in Ga^I, Ge^{II}, and Sn^{II} systems.[4]

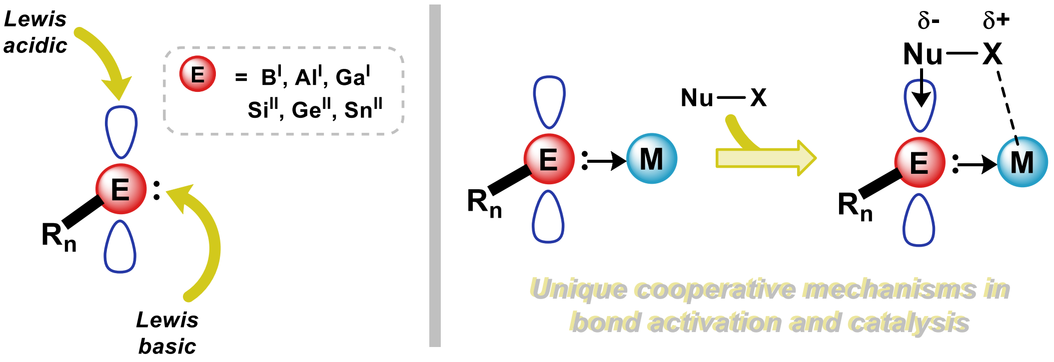

Figure 1. The Single-Centre Ambiphile concept.

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Bio of Shigeyoshi Inoue

Shigeyoshi studied at the University of Tsukuba, earning B.Sc. and M.Sc. under the supervision of Prof. Dr. Akira Sekiguchi. He remained in the Sekiguchi group to carry out his doctoral studies, obtaining his Ph.D. in 2008. As an Alexander von Humboldt grantee and a JSPS grantee, he spent the academic year 2008-2010 at the Technical University of Berlin in the group of Prof. Dr. Matthias Drieß. In 2010 he established an independent research group as a Sofja Kovalevskaja Professor at the Technical University of Berlin. Since 2015 he has been on the faculty at the Technical University of Munich, where he holds a chair of silicon chemistry.

The Power of Earth Abundant Main Group Elements: New Horizons in Bond Activations and Catalysis

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Recent developments in main group chemistry are largely attributed to the isolation of stable low-valent/oxidation state main group compounds capable of catalyzing chemical transformations, as well as exhibiting transition-metal-like behavior and bonding modes. The use of reactive main group compounds (i.e. silicon and aluminium) may offer a cost-efficient and non-toxic alternative to many current transition metal-based industrial processes. Recently, we have successfully synthesized silyl-substituted low-valent silicon and aluminium compounds. These compounds show unique reactivity and are capable of activating various small molecules under very mild reaction conditions, and can also act as (pre)catalysts. In addition, we employed N-heterocyclic imines (NHIs) and N-heterocyclic-phosphinidene-carbenes (NHCPs) as ligands to isolate novel low-valent silicon and aluminium complexes and found their intriguing reactivity towards various small molecules. This presentation will discuss the synthesis, isolation, and reactivity of selected silicon and aluminum compounds. Unique bond activation of various small molecules, bottom-up synthesis of clusters, and homogeneous catalysis using earth-abundant main group compounds will be presented.

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Bio of J. H. Farnaby

Joy did her DPhil at the University of Sussex in Organometallic Uranium Chemistry with Professor Geoff Cloke. This was followed by three postdoctoral research positions, in the USA with Professors N. Hazari and W. J. Evans, and in the UK with Prof. P. L. Arnold. Joy was then awarded a Junior Research Fellowship at Imperial College London under the mentorship of Professor N. J. Long, before moving to the University of Glasgow to take up a lectureship and start her group in 2016. In 2023, she was awarded a UKRI Future Leaders Fellowship to address challenges in the nuclear industry and related knowledge gaps in actinide chemistry.

Rediscovering The Unsubstituted Tris(pyrazolyl)borate Ligand on Lanthanides: Ln/Al Trihydrides, Divalents, and Radical-bridged Heterobimetallics

J. H. Farnaby,[a] T. Chowdhury,[a] S. J. Horsewill,[a] J. R. Hickson,[a] A. G. Bailey,[a] L. W. Stewart,[a] C. Wilson,[a] W. J. Peveler,[a] G. J. Hedley,[a] F. Murphy,[b] A. R. Kennedy,[b] C. E. Weetman,[b] M. J. Evans,[c] M. P. Coles,[c]

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The *bis*-tris(pyrazolyl)borate (Tp) ligand environment on lanthanides (Ln) has enabled the synthesis of: Ln/Al heterobimetallic trihydrides, Ln(II) for Eu, Yb and Sm, and radical-bridged Ln/Ln′ complexes (**Fig. 1**).[1-4] Complexes $[Ln(Tp)_2(\mu\text{-}H)_2Al(H)(N'')]$ (**Fig. 1(a)**; Ln = Y, Sm, Dy, Yb; N″ = $N(SiMe_3)_2$) were synthesised by insertion of aminoalane $[Me_3N{\bullet}AlH_3]$ into the Ln–amide bonds of $[Ln(Tp)_2(N'')]$.[1] Reduction of $[Ln(Tp)_2(OTf)]$ (OTf = triflate) with either an aluminyl(I) anion or KC_8 yielded the Ln(II) complexes $[\{Eu(Tp)(\mu\text{-}\kappa^1\text{:}\eta^5\text{-}Tp)\}_2]$, $[Yb(Tp)_2]$ and $[Sm(Tp)_2(DME)]$ **Fig. 1(b)**.[2,3] Reduction chemistry of either the metal or the neutral ligand resulted in $[Ln(Tp)_2(O,O'\text{-}pd^{\bullet-})]$ (Ln = Dy, Yb; $pd^{\bullet-}$ = 1,10-phenanthroline-5,6-semiquinone) and reaction with $[Ln'(hfac)_3(THF)_2]$ (Ln′ = Eu, Yb; hfac = hexafluroacetylacetonate) yielded the radical-bridged heterobimetallic complexes $[Ln(Tp)_2(O,O'\text{-}N,N'\text{-}\ pd^{\bullet-})Ln'(hfac)_3]$ (**Fig. 1(c)**; Ln,Ln′ = Yb,Eu or Dy,Yb).[4]

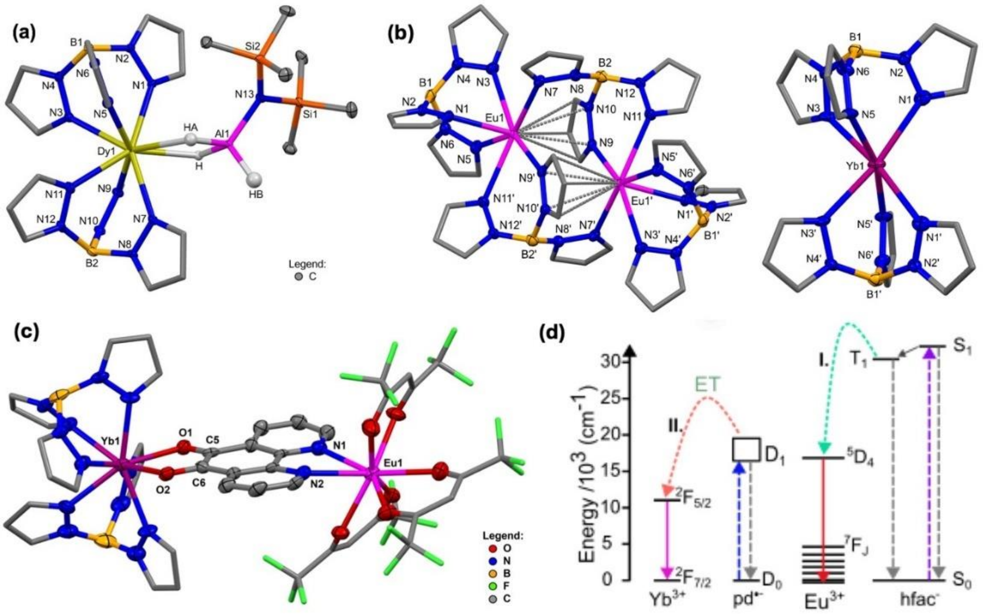

Figure 1. Crystal structures of ***(a)*** *the Dy/Al trihydride,* ***(b)*** *divalent Eu and Yb,* ***(c)*** *the Yb,Eu radical-bridged complex;* ***(d)*** *Energy level diagram depicting either hfac (I) or radical (II) sensitization of Ln photoluminescence.*

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Bio of Max Massi

Max completed his PhD in chemistry at the University of Bologna in 2005. He then joined the groups of Profs Phil Andrews and Peter Junk at Monash University as a postdoctoral researcher, working on the synthesis of multinuclear lanthanoid clusters for diagnostic imaging. In 2009, he commenced his independent academic career as a Lecturer at Curtin University, where is currently employed as a Full Professor. During this period, he was awarded a Postdoctoral Research Fellowship and a Future Fellowship from the ARC. Between 2018 and 2024, he acted as a Chemistry Discipline Lead and Head of the School of Molecular and Life Sciences. Max's research group focuses on the synthesis of luminescent metal complexes, based on both transition and lanthanoid elements, and the study of their photophysical properties at a fundamental level and in view of their potential application in materials and life sciences.

Sensitisation of Multinuclear Lanthanide Assemblies

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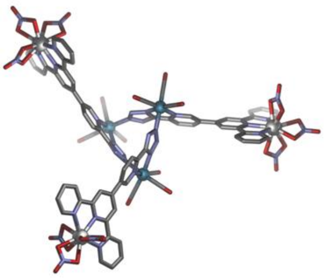
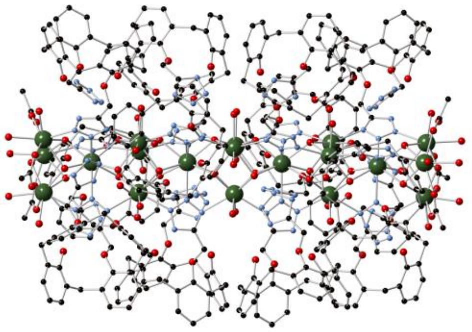
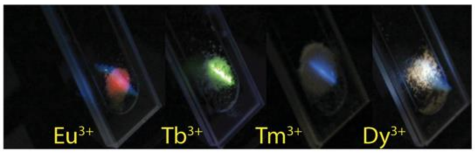
The antenna effect is the strategy of choice for the synthesis of highly luminescent lanthanoid complexes with emission in the visible or near-infrared region.[1] The most common approach to sensitise lanthanoid luminescence is the use of p-conjugated organic chromophores. However, energy transfer to lanthanoid excited states can also be achieved from transition metal complexes, which has been particularly investigated for the sensitisation of near-infrared lanthanoids such as Yb(III) and Nd(III).[2] This presentation will showcase our ongoing research focused on the investigation of the luminescence proprties of multinuclear lanthanoid assemblies.[3-5]







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2. Oral Presentation Abstracts

($^{\mathrm{EMind}}$NON) – The Synthesis of a Novel Ligand and Its Performance in Low Valent Main Group Chemistry

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Increasing steric demand is a powerful tool for the isolation and characterisation of highly reactive main group element compounds.

Recent investigations of our group have focused on using di-anionic diaminoxanthene-based ligands of the type **($^{\mathrm{R}}$NON)$^{2-}$** to protect unusual structure motifs (Figure 1). The usage of the **($^{\mathrm{Dipp}}$NON)** ligand in particular has allowed the isolation of a series of highly reactive anions, like the first aluminyl anion[1] or germanium(I) and tin(I) radical anions.[2] However, the isolation of some species remained unachieved, due to insufficient steric protection: group 13 radicals form stable dimers,[1] and a lead radical anion could be only characterised in solution at low temperatures.[2]

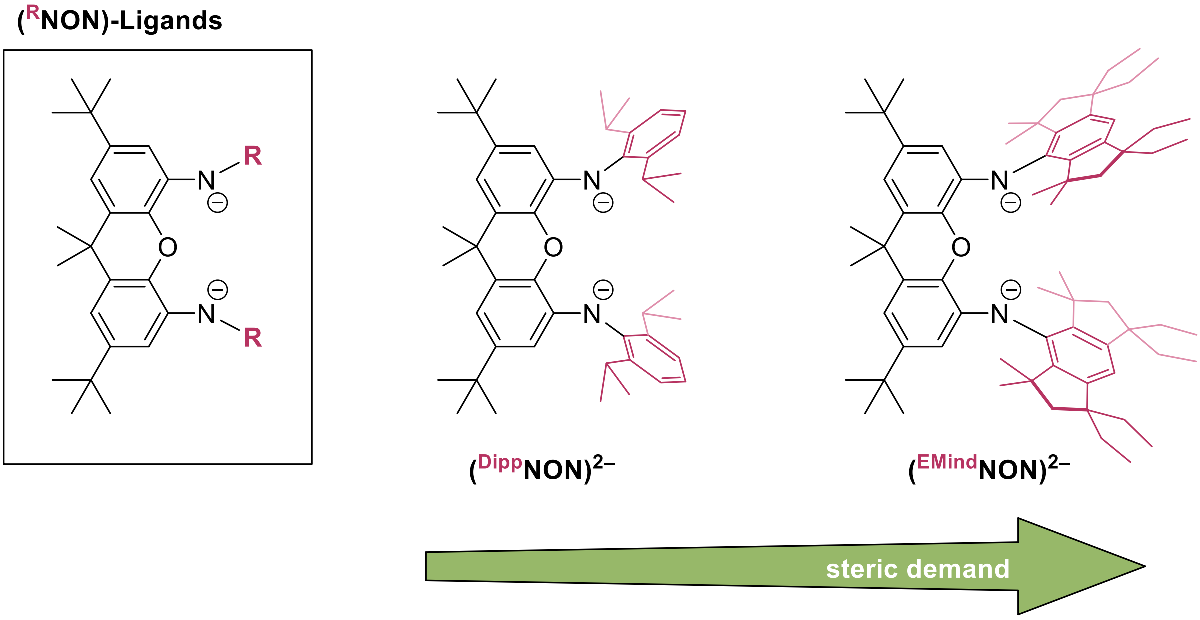

*Figure 1. The **($^{\mathrm{EMind}}$NON)** ligand has been designed to stabilise structure motifs that could not be achieved with other known **($^{\mathrm{R}}$NON)** ligands, such as **($^{\mathrm{Dipp}}$NON)$^{2-}$**.*

Within this project, we designed a new ligand **($^{\mathrm{EMind}}$NON)$^{2-}$**, which has a significantly increased steric profile to protect reactive compounds from dimerisation. The synthesis of this new ligand and its performance in low valent main group chemistry will be presented with a focus on synthetic targets that could not be isolated by using known **($^{\mathrm{R}}$NON)**-type ligands.

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Structural Insights into the Sodium Rhodizonate Test for Lead Detection

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Sodium rhodizonate is a colourimetric reagent commonly used for the detection of lead in gunshot residue analysis. Colourimetric reagents are applied to trace evidence and will react positively in the presence of the target compound by producing a colour change, enabling the trace to be visualised. They have the advantage over instrumental techniques by being cost-effective, efficient, accessible, and easy to apply. Forensic scientists utilise the sodium rhodizonate reagent for shooting distance determination and bullet hole identification. However, the products formed from the reaction between sodium rhodizonate and lead are poorly understood. Previous attempts at understanding the chemistry underpinning this reaction have been restricted by the limited solubility of sodium rhodizonate in solvents other than water, the instability of the reagent in water, as well as the rapid precipitation of the product. These factors have prevented the use of X-ray diffraction techniques for characterisation of the products. By developing an understanding of the reaction pathway, we hope to improve forensic methodologies and public confidence in forensic techniques.

This research investigated the products formed in the sodium rhodizonate test using X-ray diffraction techniques. The results provided previously unknown structural insights into the reaction and explored the influence of the reagent formulation on the products formed.

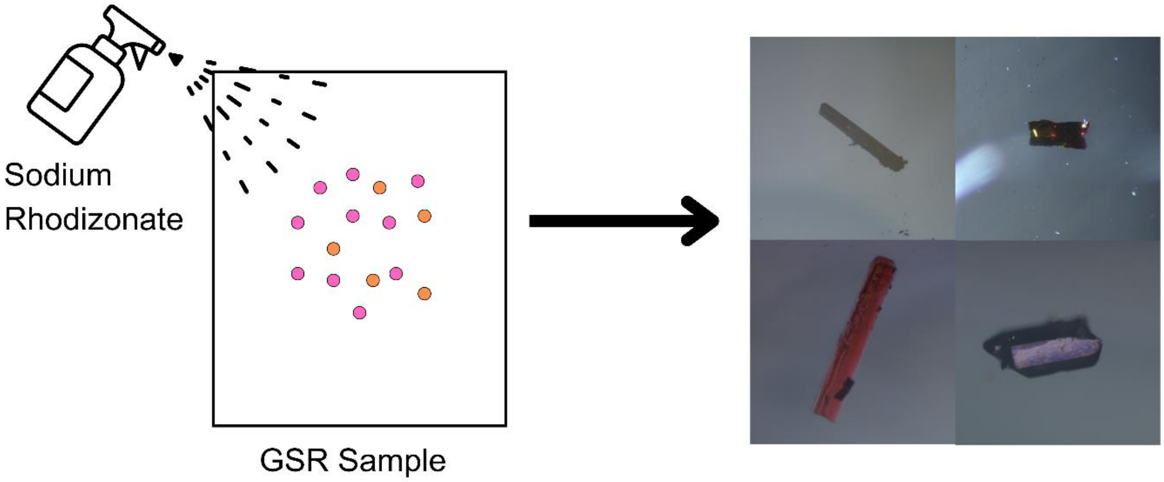

Figure 1. Schematic representation of a gunshot residue sample being treated with sodium rhodizonate and crystal images of the products.

Anion Coordination Chemistry in Water Using Hydrogen Bonds

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[b]School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland, Australia
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Hydrogen bonding plays a central role in molecular recognition by biological receptors. A well-known example is the sulfate-binding protein, which achieves sub-micromolar affinity for sulfate anions through a network of neutral NH and OH hydrogen bond donors.[1] In contrast, synthetic receptors face significant challenges in using hydrogen bonding for molecular recognition in water, as both hydrogen bond donor and acceptor groups are heavily solvated. In this presentation, I will focus on our molecular design strategies that overcome this limitation, enabling high-affinity binding of hydrophilic anions in water by solely relying on hydrogen bonds.[2]

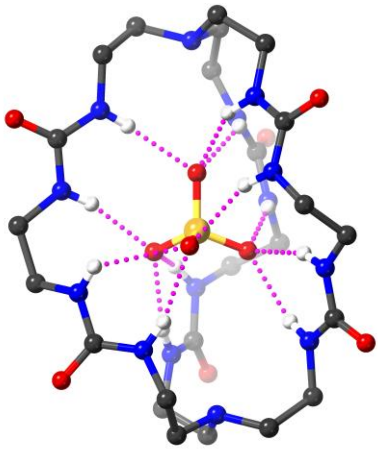

Figure 1. Crystal structure of a sulfate-binding organic cage.

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Beryllium in Action – Exploring Reductions and Radicals

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Due to its presumed toxicity, beryllium remains one of the least investigated non-radioactive elements.[1] While its heavier analogues and neighbouring elements are well explored and widely utilised, many questions remain unanswered for the lightest group 2 element.[2] Over the last decade, however, extensive research has led to the isolation of a diverse array of compounds featuring beryllium in exceptional electronic states. Recent seminal reports of stable Be-Be and Be-Mg bonded compounds,[3],[4] paired with the first example of a cationic beryllium radical,[5] highlights the rich and unusual chemistry of organoberyllium compounds.

Herein, we present the synthesis of the first neutral beryllium radicals *via* reduction of halogenated precursors. Investigations using single crystal X-ray diffraction measurements, DFT studies, and EPR spectroscopy, have unveiled the unique structural and electronic properties of these compounds. , while reactivity studies yielded the first structurally authenticated Be-Se and Be-Te bonds, as well as other unexpected beryllium-centred reaction patterns. Furthermore, new and promising beryllium complexes using N,N-containing ligands and their reactivity are presented.

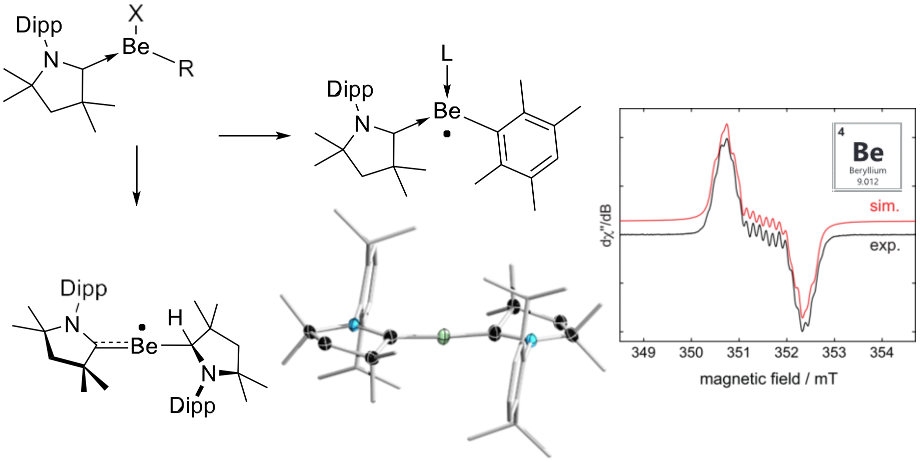

Figure 1. Synthesis of neutral beryllium radicals (CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, Dur = 2,3,5,6-tetramethylphenyl, X = Cl or Br, L = Lewis base).

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Reactivity of an Anionic Magnesium(I) Complex

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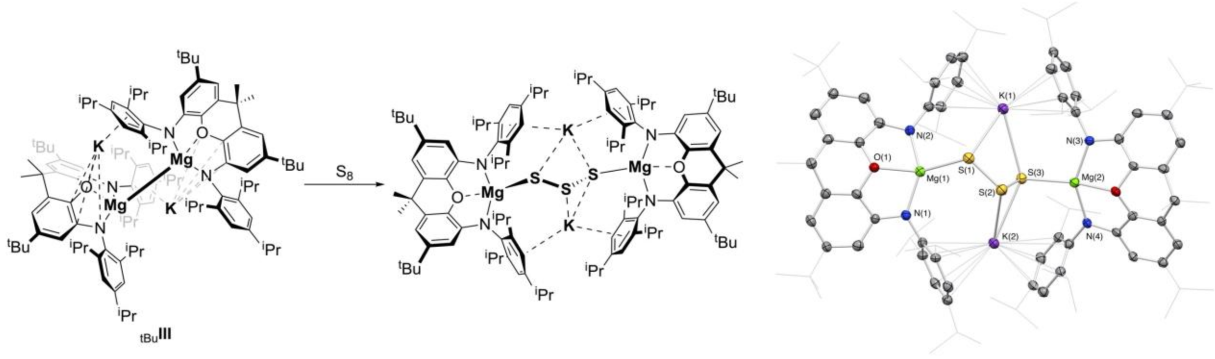
Low-oxidation state group 2 metal chemistry has flourished since the first isolation of a neutral dimagnesium(I) compound, LMg–MgL (**I**, L = bulky κ^2-diketiminate and guanidianate), in 2007.[1] Since then, dimagnesium(I) species have been widely employed as a versatile reductants in organometallic chemistry.[2] By 'upgrading' the ligands in **I** from a monoanionic scaffold to a dianionic scaffold, anionic dimagnesium(I) systems, M_2[LMg–MgL] (**II**, M = alkali metal cations, L = bulky chelating diamide), can be isolated that are charge-balanced by alkali metal cations.[3] In the quest for bulky diamide ligands to stabilise low-oxidation state group 2 metals species,[4] the rigid, pincer xanthene-bridged diamide ligand ($_{R}$NON^{Ar}) has emerged, proven by its capacity to support several other unprecendented p-block species.[5] Through the utilisation of these xanthene-bridged diamide ligands, we have reported that the potassium reduction of a moderately bulky Mg(II) precursor, [Mg($_{Et}$NON^{Trip})] (Trip = 2,4,6- triisopropylphenyl), produces a K/Mg(I) complex, [{K($_{Et}$NON^{Trip})Mg}$_2$] ($_{Et}$**III**), featuring a long Mg–Mg bond.[6] Interestingly, using a bulkier [Mg($_{Et}$NON^{TCHP})] (TCHP = 2,4,6-tricyclohexylphenyl) for the reduction frustrates the Mg–Mg bond formation, which instead gives rise to the reductive capture of dinitrogen to afford the first N_2-fixed magnesium complex [{K($_{Et}$NON^{TCHP})Mg}$_2$(N_2)] (**IV**).[7] The reaction chemistry of **III** and **IV** has recently been studied and their reactivity towards small molecules investigated.[7,8] In this presentation, we highlight the solid-state structures and potassium reductions of the precursor [Mg($_{R}$NON^{Ar})] (R = Et, tBu; Ar = 2,6-disubstitutedphenyl or 2,4,6-trisubstitutedphenyl) as well as the reducing capabilities of [{K($_{R}$NON^{Trip})Mg}$_2$] ($_{R}$**III**, R = Et, tBu) with inorganic substrates (e.g. S_8, Figure 1) and transition metal carbonyl species.



X-ray Structure of [{K($_{tBu}$NON^{Trip})Mg}$_2$(S_3)]

Figure 1. Representative reactivity of anionic Mg(I) complex with elemental sulfur.

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Nicotinamide-Appended Metal Complexes as Luminescent Redox Probes

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Despite the essential roles of reactive oxygen species (ROS) in cellular function, chronic imbalance in ROS levels has been implicated in the pathology of cancer and neurodegenerative diseases.[1] Luminescent redox probes that respond to changing oxidative capacity of live cells in real time, may enable study of the roles of ROS, and associated pathologies. Many redox probes have been developed[2–4]; however, most respond in a concentration-dependent manner. Further, being predominantly organic molecules, interference from endogenous cellular luminophores may hinder their detection. While ratiometric probes have been developed to address these drawbacks,[2,5] organometallic probes for luminescence lifetime-based detection (FLIM/PLIM) may offer an alternative solution. However, lifetime-based redox probes remain unexplored. This presentation will showcase our synthesis and preliminary investigation of nicotinamide-appended Re(I) and Ir(III) complexes, as potential lifetime-based redox probes (Figure 1). Preliminary photophysical investigation revealed that the reduced and oxidised forms of these complexes exhibit distinct luminescence lifetimes and are reversibly interconvertible *in vitro*.

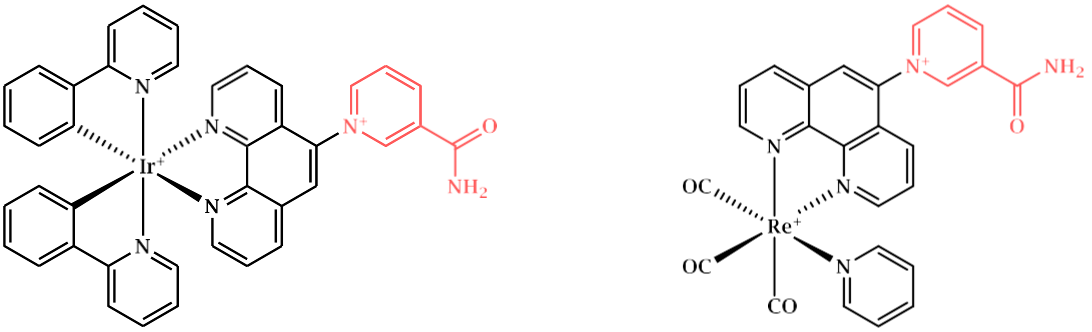

Figure 1. Two Ir(III) (left) and Re(I) (right) complexes discussed in this presentation. The redox-active nicotinamide appendage has been emphasised (pink).

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Radical Induced Cyclisation of Perfluoro Aryl Imines

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The selective activation of carbon-fluorine (C-F) bonds has become increasingly significant due to the widespread presence of fluorinated motifs in pharmaceuticals and agrochemicals. [1] Imines (Schiff bases) are important in synthetic chemistry due to their ease of preparation and use as ligand precursors. [2] Fluorinated imine-type scaffolds generally undergo four reactions; metalation, addition, C-F activation and cyclisation. [2]

Recent advances highlight the superior performance of bimetallic systems — such as lithium magnesiates and lithium zincates, over their monometallic moieties. [3] These bimetallic reagents leverage cooperative effects to access reactivities which its individual moieties are incapable of reproducing. Thus, two different metals would possess synergistic capabilities whereby they can promote charge separation or participate in the transition states of reaction intermediates. [3]

Herein we present the reactivity of perfluoro aryl imines with a sodium magnesiate base resulting in an unusual cascade reaction involving; C-F activation, 1,2-addition, C-N coupling and cyclisation. DFT studies and EPR measurements provide strong evidence to support a biradical mechanistic pathway.

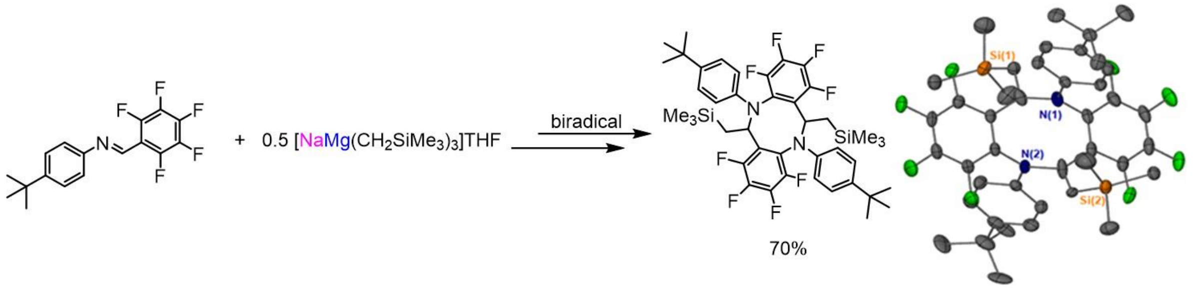

Figure 1. Cyclisation of perfluoro aryl imine

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Reversible Hydrogen Activation by Trapped Silicon Anions

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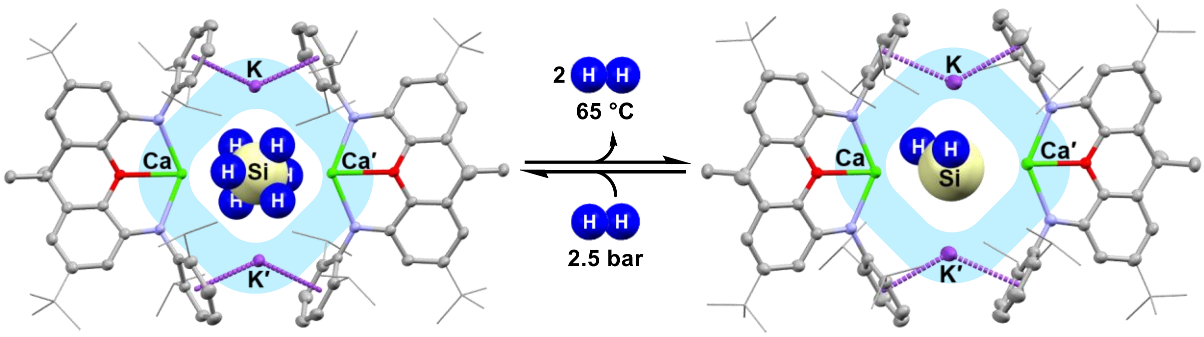
Metal hydrides have been deemed a green and safer approach for hydrogen storage compared to storing hydrogen under excessive pressure. Main group hydrides in particular have shown great potential in practical applications as they are considered more abundant and economical.[1] However, as metal hydrides demand excessive heating for hydrogen liberation and lack reversibility for further hydrogen capture, their efficiency is currently limited.[2]

Recently, we reported the first room temperature stable hexahydridosilicate complex $[\{KCa(NON)(OEt_2)\}_2][SiH_6]$ (Scheme 1, left; NON = the diamido xanthene-based ligand).[3] This was achieved by encapsulating the $[SiH_6]^{2-}$ anion within a supramolecular assembly, which is decorated on the inside with four Lewis acidic metal centres (two Ca^{2+} and two K^+ cations), mimicking the surrounding environment of an anion in a solid-state lattice.[4] Remarkably, heating a solution of the complex above 65 °C leads to the evolution of two equivalents of H_2 to give the novel $[SiH_2]^{2-}$ anion through a spontaneous four-electron reduction of the silicon centre (Scheme 1, right). Placing $[\{KCa(NON)(OEt_2)\}_2][SiH_2]$ under an atmosphere of H_2 (2.5 bar) reverses this process, with the anion taking up two equivalents of H_2 and reverting to the $[SiH_6]^{2-}$ complex. These exciting results demonstrate the potential for silicon anions to be used in hydrogen storage materials.



Scheme 1. Reversible hydrogen uptake and release by trapped silicon anions.

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P4 Coordination and Reduction at Alkaline Earth Metal Centres

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Molecular phosphorus, P_4, does not occur naturally, yet it remains the primary resource for the production of phosphorus-containing fine-chemicals.[1] The pyrophoricity of P_4, paired with its toxicity, presents many industrial challenges and is the reason safe approaches to store, handle and functionalise P_4 have received considerable attention over recent years.[2]–[4] In this presentation, we detail the first examples of P_4 coordination to environmentally benign main-group metal centres (Figure 1).[5] This was made possible through the use of coordinatively unsaturated and Lewis acidic magnesium(II) complexes, "$[Mg(^{Et}NON^{Ar})]$" ($^{Et}NON^{Ar}$; Ar = DCHP, 4,5-bis(2,6-dicyclohexylanilido)-2,7- diethyl-9,9-dimethyl-xanthene or Ar = TCHP, 4,5-bis(2,4,6-tricyclohexylanilido)-2,7-diethyl-9,9- dimethyl-xanthene). Extension of this to the heavier alkaline earth metals, calcium and strontium, was achieved through the utilisation of their arene capped complexes, $[\mathbf{M}(^{Et}NON^{TCHP})(\eta^6\text{-}C_7H_8)]$ (**M** = Ca and Sr). By invoking low oxidation state magnesium(I) complexes, we show that P_4 can be reduced by magnesium-based reductants and subsequently hydrolysed to give phosphine (PH_3) – a useful building block to access organophosphorus species. This work demonstrates opportunities for P_4 storage, reduction and functionalisation using earth-abundant alkaline earth metal-based reagents.

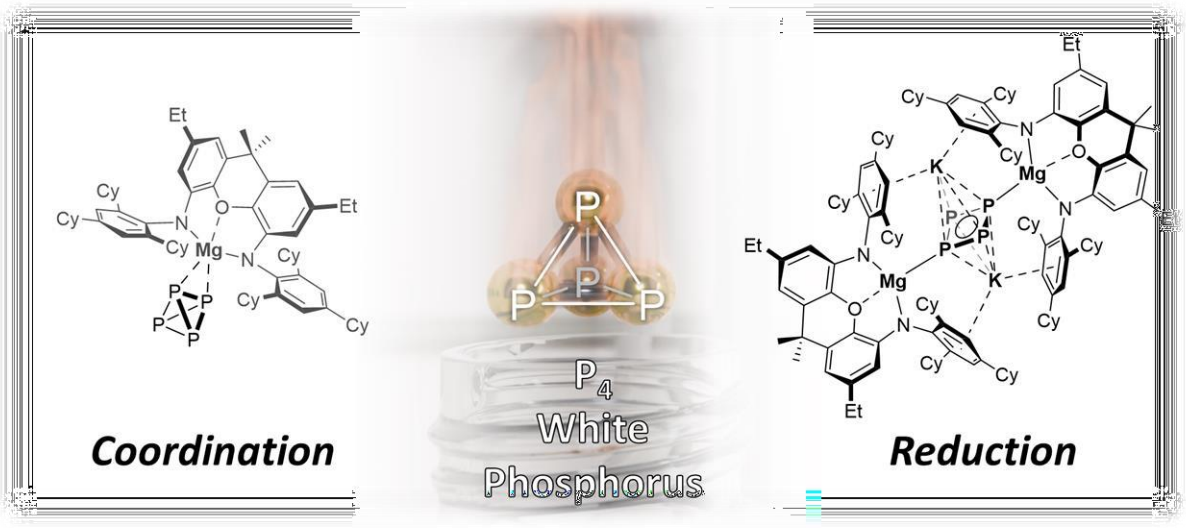

Figure 1. Coordination of P_4 to an alkaline earth metal centre (left) and reduction of P_4 by a low oxidation state magnesium complex (right).

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The Chemistry of Pnictogen-Functionalised Isonitrile and *N*,*P*-Heterocyclic Carbene Complexes

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The action of $[N(SiMe_3)_2]^-$ upon CO proceeds in a stepwise and irreversible manner to CN^- and $O(SiMe_3)_2$.[1] If performed within the coordination environment of a transition metal centre,[2] the resultant anionic cyanometallates are nucleophilic at the nitrogen terminus, a reaction with obvious synthetic utility since it avoids the need for nocuous cyanide salts. Thereby, a series of new pnictogen-functionalised isonitrile complexes $[M(C{\equiv}NPn{}^tBu_2)\{L_n\}]$ have been prepared[3] from low-valent anionic cyanometallates $[M(C{\equiv}N)\{L_n\}]^-$ (M = Cr, Mo, W, Fe, Mn, Re; L = CO, PR_3, $[NO]^+$, $[C_5H_5]^-$ *etc.*) and ${}^tBu_2PnCl$ (Pn = P, As, Sb), which augment the sparse handful of examples reported previously.[4] These species enter into a variety of reactions with electrophilic substrates[5] leading to, *inter alia*, metal coordination, N-Pn bond scission, C≡N linkage inversion, and [3+2]-cyclisation. The latter reaction (where Pn = P) is a remarkably facile entry point into a novel class of deeply coloured, unsymmetric *N*,*P*-heterocyclic carbene complexes $[M\{CNP{}^tBu_2C(R){=}C(R)\}\{L_n\}]$ featuring heretofore unknown 2,3-azaphospholyl-1-idene ring systems.[6] These are readily transferred to later transition metals although in contrast to conventional Fischer-type carbenes or NHC's, these NPHC's are unusually strong π-acceptors and are prone to nucleophilic addition at the ring system.[5]

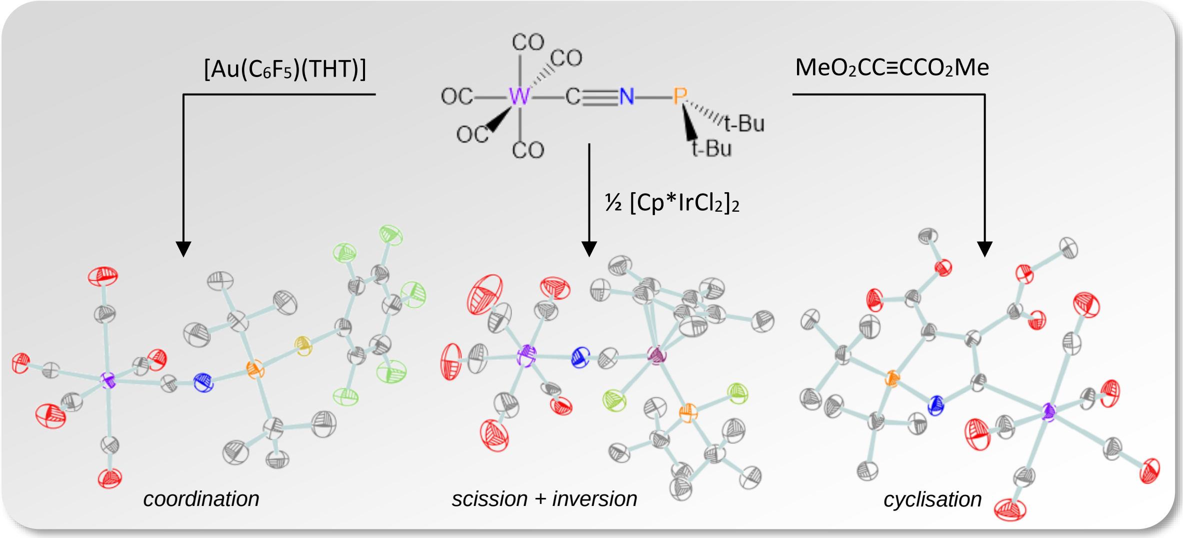

Figure 1. Representative transformations of the phosphinoisonitrile complex $[W(C{\equiv}NP{}^tBu_2)(CO)_5]$.

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Through the Ligand: A Mechanistic Twist in Nickel-Catalyzed Double Bond Transposition

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A nickel(0)/Lewis acid catalytic system was developed to achieve stereoselective monotransposition of terminal alkenes via allylic C–H activation, without the need for external hydride sources.[1] By modulating ligand structure, the method provides divergent access to either *E*- or *Z*-olefins and was further applied in diastereodivergent allylboration and desymmetrization reactions. These experiments aim to establish a kinetically controlled, ligand-directed platform for precise alkene migration and downstream stereoselective transformations.

To uncover the underlying mechanistic basis of the 1,3-hydrogen migration pathway, we performed a detailed computational investigation using ωB97X-D3(BJ) and revDOD-PBEP86-D4 functionals, alongside a cost-efficient hybrid basis set protocol [def2-QZVPP/def2-TZVP(-f)//def2-SVP], recently developed by one of our groups.[2] A previously unreported "flip" transition state (TS-flip) was identified, in which the hydrogen atom migrates through the ligand cavity – facilitated by a wide bite angle and intramolecular hydrogen bonding. The Lewis acid $Mg(OTf)_2$ lowers the activation barrier by stabilizing the developing positive charge in the allyl intermediate.

Microkinetic simulations reproduce the experimentally observed ligand-dependent stereoselectivity, demonstrating that both kinetic and thermodynamic factors contribute to product distributions. To our knowledge, this is the first mechanistic proposal involving ligand-cavity-mediated hydrogen migration in a nickel system. These findings not only rationalize observed experimental trends but also highlight how ligand architecture can guide nonclassical pathways and offer new design principles for selective metal-catalyzed transformations.

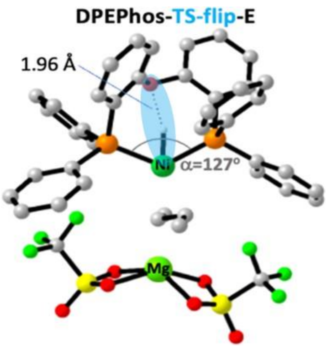

Figure 1. Structure of TS-flip showing the hydrogen migration through the ligand cavity (highlighted in blue).

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Indium(III) and bismuth(III) 8-hydroxyquinolinate complexes: enhanced antibacterial activity and selectivity against ESKAPE pathogens

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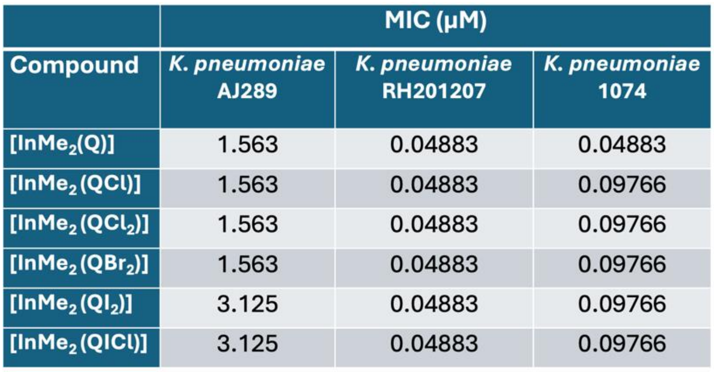
Antimicrobial resistance (AMR) — defined as the reduced efficacy of previously effective antibiotics for the treatment of viral, bacterial, fungal, and parasitic infections — is an urgent global crisis.[1] The dramatic reduction of novel antibiotic development over the past half-century further exacerbates the increasing prevalence of AMR.[2] Life-threatening bacterial infections among immunocompromised and critically ill patients are often caused by a group of nosocomial pathogens termed 'ESKAPE pathogens' (*Enterococcus faecium, Staphylococcus aureus, Klebsiella pneumoniae, Acinetobacter baumannii, Pseudomonas aeruginosa,* and *Enterobacteriaceae* species), which are known to possess drug resistance mechanisms.[3] As bacteria continue to acquire resistance against organic-based therapeutics, there has been renewed interest in the development of metal-based therapeutics — which often possess greater resilience against AMR.[4, 5] Previously, a series of dimethyl gallium(III) 8-hydroxyquinolinates were synthesised and demonstrated marked antibacterial activity and selectivity against drug-resistant *Klebsiella pneumoniae.*[6] In order to assess if these trends continue for other biologically relevant main group M(III) metal complexes, a series of In(III) and Bi(III) 8-hydroxyquinolinate complexes were synthesised and assessed for their antibacterial activity.



	MIC (µM)		
Compound	***K. pneumoniae*** **AJ289**	***K. pneumoniae*** **RH201207**	***K. pneumoniae*** **1074**
[InMe$_2$(Q)]	1.563	0.04883	0.04883
[InMe$_2$(QCl)]	1.563	0.04883	0.09766
[InMe$_2$(QCl$_2$)]	1.563	0.04883	0.09766
[InMe$_2$(QBr$_2$)]	1.563	0.04883	0.09766
[InMe$_2$(QI$_2$)]	3.125	0.04883	0.09766
[InMe$_2$(QICl)]	3.125	0.04883	0.09766

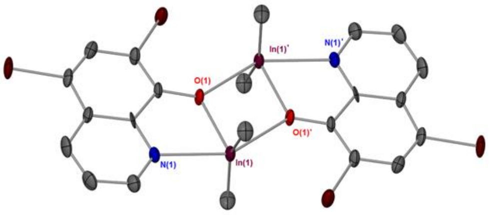


Figure 1. Minimum inhibitory concentrations (MIC) (µM) of dimethyl In(III) 8-hydroxyquinolinate complexes against multi-drug resistant strains of Klebsiella pneumoniae (left), and an X-ray crystal structure of a dimethyl In(III) 8-hydroxyquinolinate complex (right).

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Twisted Carbazole Dendrons for Solution-Processable Green Emissive Phosphorescent Dendrimers

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Organic light-emitting diodes (OLEDs) have been intensively studied as a key technology for next- generation displays and lighting. The efficiency of OLEDs has improved in the last 15 years by employing phosphorescent emitters. Phosphorescent emitters can give rise to OLEDs with a 100% internal quantum efficiency (IQE) by utilizing both singlet and triplet excitons produced in the device. Iridium(III) complexes have proved an attractive choice for incorporation into OLEDs due to their short excited state lifetimes, color tunability, and high photoluminescence quantum yield (PLQY) at ambient temperature.

In the fabrication of large area OLEDs for lighting applications, solution processability is a desirable trait as it is conducive to low-embedded energy manufacturing. However, most iridium(III) complexes used in evaporative fabrication of OLEDs are simply too insoluble to solution process. To overcome this limitation solution processed dendrimers have been developed with substantial performance improvements over their small molecule counterparts.

In this work, carbazole based dendrons were chosen because their hole-transporting properties may improve charge transport, and *tert*-butyl surface groups were added to further increase the size of the dendrons, improve solubility and prevent the oxidation of the carbazole moiety in devices. Lastly, the methyl group on the central ring was included to rotate the carbazole moieties out of plane, further shielding the chromophore and increasing the molecule's triplet energy, thus preventing the dendron quenching the chromophore. The synthesis and characterization of different generations of dendronized tris-bidentate based iridium(III) complexes will be described in this presentation. Their thermal, electrical, photophysical, and device properties will also be discussed.

Phosphorescent Ir(III)-based metallapolymers for UV light harvesting

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With the growing global demand for sustainable energy solutions, the development of new materials for efficient solar light harvesting is of crucial importance. To overcome the limited efficiency of traditional Si-based solar cells towards the UV part of the solar radiation, Luminescent Solar Concentrators (LSCs) have been developed. These devices embed UV-absorbing luminophores within polymeric waveguides, down-converting higher-energy to lower-energy photons.[1] In this context, we proposed a first example of colourless LSCs obtained by physical dispersion of Ir(III) phosphors into different acrylic matrices.[2] In fact, Ir(III) cyclometalated complexes exhibit advantageous photophysical properties – *i.e.* strong UV light absorption and intense colour tuneable phosphorescent emissions with high quantum yields. Attachment of the emissive species to the polymer network was then accomplished by designing a set of "polymerizable ligands" capable of coordinating the metal center and, at the same time, being able to copolymerize with methacrylic monomers. The resulting metallapolymers were obtained either by the complexation of a pre-formed MMA-L copolymer with different amounts of appropriate Ir fragments, or by the copolymerization of the mononuclear Ir(III) complexes with MMA. The new hybrid materials displayed intense phosphorescence in the solid state, with high PLQY and Ir(III)-centred emission colors spanning from green to red, and were therefore assessed for their application in the LSCs technology.

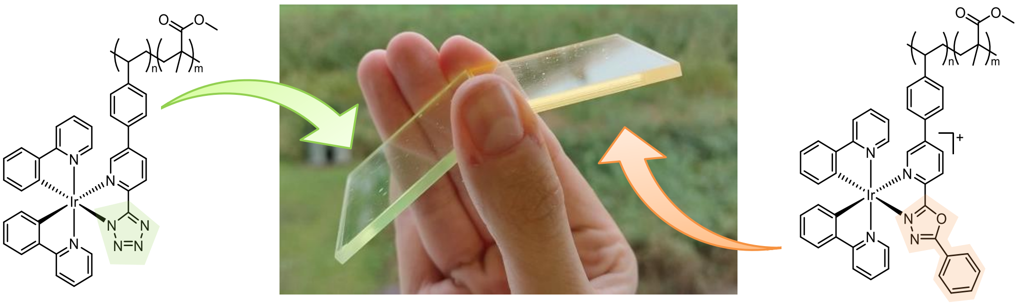

Figure 1. LSCs prototypes exposed to solar light and relative materials structure.

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Preparation of Alkali-Silanide Nickel(0)-ates and their Intermediacy in Catalytic Silylation of Aryl Ethers

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Organosilicon motifs are important in small molecule synthesis,[1] however, they often arise from abundant electrophilic reagents, rather than nucleophilic silanide species, which remain less generalisable and challenging to prepare.[2] Silylboranes have emerged as ‘masked’ sources of sensitive nucleophilic silicon,[3] which can undergo Ni-catalysed cross-coupling of challenging C–O and C–F bonds.[4] In the catalytic silylation of aryl ethers, a non-classical mechanism of oxidative addition was proposed involving bimetallic nickel(0)-ate species,[4a,b] sensitive complexes that have enjoyed several recent advances,[5] but are yet to be observed bearing silicon groups.

This presentation will describe the synthesis of previously unknown alkali-silanide nickel(0)-ate (*AM*NiSi) complexes through co-complexation techniques. With recourse to detailed solution- and solid-state studies to discern their behaviour, a diverse range of bonding will be discussed and how this may relate to the cooperative activation of aryl ethers, before evaluation of their relevance in catalytic silylation reactions.

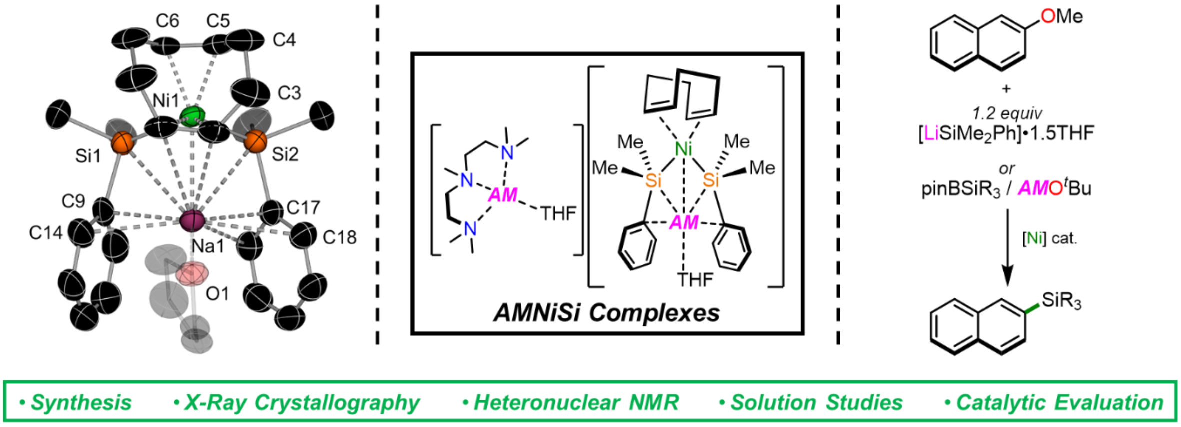

Figure 1. (a) Molecular structures of alkali-silanide nickel(0)-ate (AMNiSi) complexes. (b) Catalytic silylation of aryl ethers speculated to be catalysed by AMNiSi species.

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Electrochemical Synthesis of 3*d*-Metal Cations Stabilised by Weakly Coordinating Anions

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The controlled oxidation—or "deelectronation"—of transition metal complexes to their corresponding cations is a fundamental transformation in inorganic and organometallic chemistry.[1],[2] Traditionally, this is achieved chemically using strong oxidants such as $[Fe(\eta^5\text{-}C_5H_5)_2][Al(OR^F)_4]$[3], $[Ag][Al(OR^F)_4]$[4], or $[NO][F(Al(OR^F)_3)_2]$[2],[5] ($R^F=C(CF_3)_3$). However, these classical approaches can suffer from limitations such as overoxidation, lack of selectivity, or incompatibility with sensitive ligands.

To address these challenges, we investigated the electrochemical synthesis of 3*d*-metal cations—specifically nickel, iron, and cobalt— starting from their elemental metals. Critical to the success of this and similar works is the utilisation of weakly coordinating anions, such as the fluorinated alkoxyaluminate $[Al(OR^F)_4]^-$, which act to minimize ion pairing to afford the high-valent metal cations in solution or as a solid. A variety of solvents and ligands were investigated to probe their influence on complex formation and stability.

This presentation will highlight the use of electrochemical methods to enable cleaner one electron oxidations through fine-tuning the redox potential applied in the reaction. We will also briefly explore the design of new ligand systems to stabilise magnesium in unusual oxidation states.

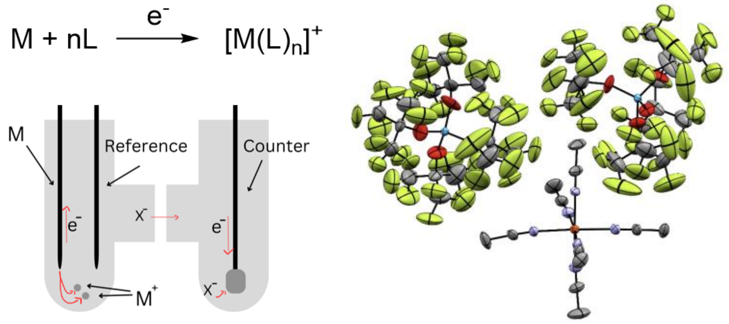

Figure 1. Electrochemical reaction and setup for different Chronoamperometric experiments(left). Molecular structure of synthesised $[Fe(MeCN)_6][Al(OR^F)_4]_2$ complex. (right).

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Nonlinear Optical Studies of RRuthenium Alkynyl Cruciform Compounds

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The role of organometallics in nonlinear optics is quite promising and has attracted significant attention for higher-order NLO activity.[1] Ruthenium-containing phenylalkynyl complexes are of great interest due to their facile syntheses and excellent balance between reactivity and optical stability, with large NLO coefficients reported.[1,2] Here, we describe the structure-property relationship of ruthenium alkynyl cruciform compounds and their cubic, quintic, and septic NLO coefficients (**2PA**, **3PA**, and **4PA** respectively), measured by the Z-scan technique. Measurements were performed over a wide range of wavelengths (600-2100 nm). The effect of ruthenium-ligated phenylalkynyl, 4-nitrophenylalkynyl and chloro substituents at the peripheral positions was studied. The linear absorption spectra of a few of these model compounds were rationalized using TD-DFT computations.

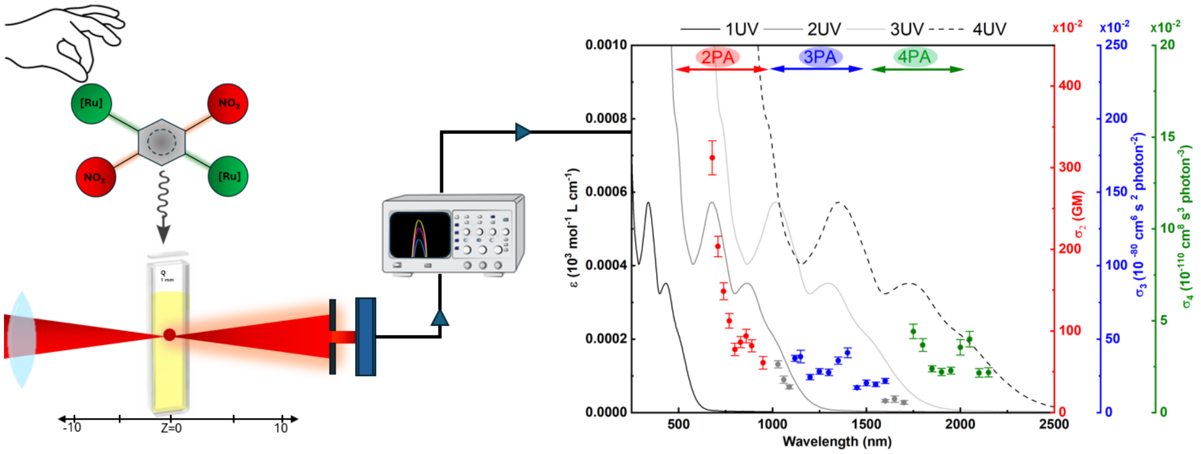

Figure 1. Multiphoton absorption studies of ruthenium alkynyl cruciform compounds using the Z-scan technique.

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Synthesis and Characterisation of Organogallium Complexes with Hydroxyanthraquinones

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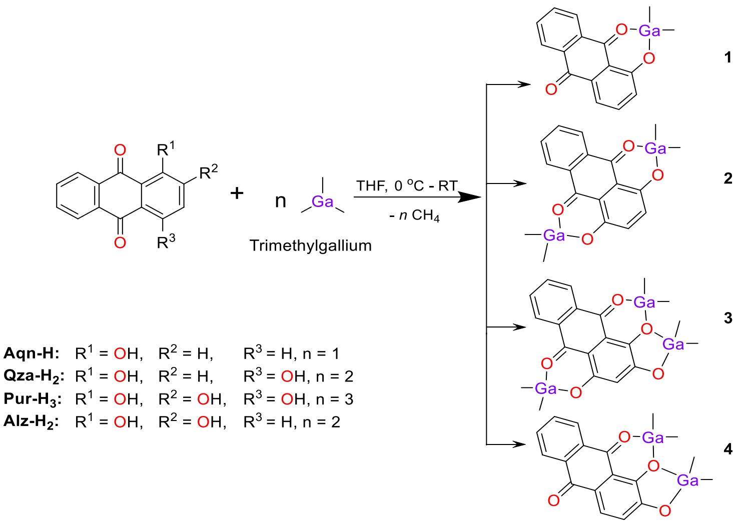
Hydroxyanthraquinones are a highly coloured class of natural compounds, with reported versatility across many applications, including medicine, food additives, textiles, dying and paint pigments, and photocatalysis.[1,2] Metal complexes with hydroxyanthraquinones as ligands have also been of particular interest in due to the impact of complexation on fluorescence, colour and medicinal properties.[3,4] Whilst examples of transition metal systems have been reported,[5] very little work has been done in the area of main group chemistry, and there are currently no reports, to the best of our knowledge, of isolable complexes with Group 13 metals.[4]

Thus, four novel dimethylgallium(III) compounds have been synthesised, isolated, and characterised. The aim was to explore the potential of this ligand class to support *mono*, *di*, and *tri* nuclear gallium compounds. It was found that gallium centres saturated potential binding sites, regardless of stoichiometric conditions. These discrete compounds have been characterised using NMR, FT-IR, elemental analysis and X-ray crystallography. Primary results of UV-vis and fluorescence spectroscopy have revealed interesting differences between free and complexed hydroxyanthraquinones, offering new insight into the photophysical behaviour of these ligands in well-defined organometallic compounds.



Scheme 1. General synthetic procedure for novel complexes ***1-4****.*

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The Use of the bpp Ligand in Synthesis and Catalysis

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Bimetallic complexes are of great interest to chemists because the presence of two metals in a single molecule can cause significant alterations to the properties and reactivities of each metal as well as the emergence of features not present in monometallic complexes. The unique electrochemical and photochemical properties can lead to metal-metal communication, which has potential applications in "molecular electronics" or photonics.[1] Bimetallic complexes also have the potential to enhance catalysis. Intramolecular photoinduced electron or energy transfer, a form of metal-metal communication, could allow for more efficient interaction between a photocatalyst and a transition-metal catalyst in systems using photocatalysis in tandem with transition-metal catalysis.[2] Bimetallic complexes can also exhibit metal-metal cooperativity, a powerful but underexplored catalytic strategy.[3] No matter the features of interest, the ligand that links the two metal centres needs to be carefully considered as it has significant influence on the properties of the resulting complex.

The ligand 3,5-bis(2-pyridyl)pyrazolyl (bpp) is an attractive scaffold for the synthesis of well-defined, catalytically-relevant bimetallic complexes as it is can be synthesised with ease, the pyrazole NH of the proligand prevents bimetallic synthesis until a base is added, allowing for controlled synthesis of heterobimetallic complexes, and the aromatic heterocycles yield N^N binding sites similar to those of common monometallic photocatalysts and catalysts for CO_2 reduction. This work investigates the use of bpp in synthesis with the intent to explore the applications of bimetallic complexes in cooperative CO_2 reduction and tethered tandem photocatalyst transition-metal catalysis (Figure 1).

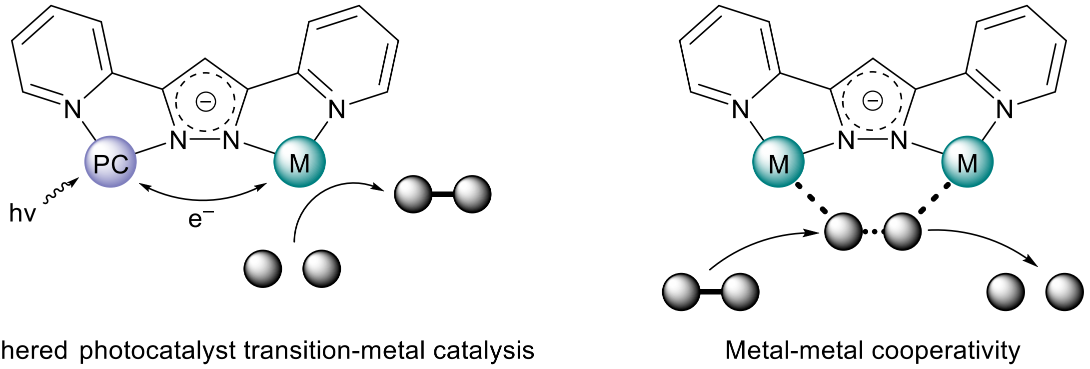

Figure 1. This work is interested in the synthesis of bimetallic complexes of bpp with potential applications in catalysis – both tethered tandem photocatalyst transition-metal catalysis and metal-metal cooperativity.

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Organo-gallium(III) and bismuth(III) Complexes of Indeno[1,2]quinoline Derivatives as Antibacterial AAgents

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The rapid increase of antimicrobial resistance (AMR) has become a life-threatening issue worldwide, with immediate intervention essential.[1] It has been predicted by the World Health Organisation (WHO) that if no action is taken, then there will be approximately 10 million deaths from AMR infections annually by 2050.[2] The urgent need for new antimicrobial agents has led to the synthesis and assessment of metal-derived compounds as therapeutics to combat resistant pathogens. Ga(III) is considered a competitor of Fe(III) because of their chemical similarity, and interferes with iron homeostasis in biological systems and can inhibit the growth of bacteria.[3] However, the therapeutic potential of organogallium(III) compounds remains relatively unexplored.

Research in our group has demonstrated that the introduction of the organogallium moiety significantly enhances the antibacterial efficacy against multidrug-resistant *Klebsiella Pneumoniae*.[4] Other main group metals, such as Bismuth(III) salts have been used for decades to treat infections. Bismuth(III) quinoline thiosemicarbazone complexes have been reported to restore the carbapenem drug sensitivity in *Klebsiella pneumoniae*.[5]

The quinoline scaffold (Figure 1-A) occurs widely in natural products and pharmaceutical compounds. Tetracyclic derivatives of quinolines, such as indenoquinoline, exhibit various biological properties.[6] This work, therefore, aims to investigate the use of the indenoquinoline carboxylic acids (Figure 1-B) for the preparation of novel organometallic bismuth(III) and gallium(III) indenoquinoline-carboxylates. Complexes will be assessed for their anti-bacterial potential.

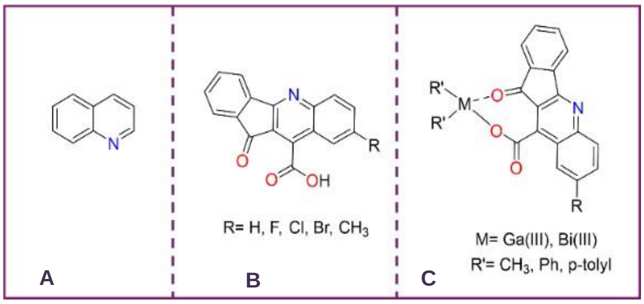

Figure 1. (A): Structure of quinoline; (B): basic structure of the indenoquinoline-carboxylic acid derivative; (C): targeted organometallic Bi(III) and Ga(III) carboxylate complexes.

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A Frustrated Lewis Pair Approach for the Synthesis of Monofluoroallenes

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The introduction of fluorine into organic molecules has led to great strides in fields such as medicinal chemistry, materials science and agrochemicals, where fluorinated moieties have been indispensable for modulating lipophilicity and stability. [1] Unfortunately, the stability of the C-F bond has resulted in compounds that are highly persistent in the environment and difficult to dispose of through traditional chemical waste streams. C-F bond activation provides an interesting solution to this problem, where low-value waste fluorocarbons can be converted to high-value fluorinated synthons, giving them second life in the chemical economy. [2]

Allenes are regarded as unique and privileged building blocks in chemical synthesis. While methods for the synthesis of allenes are well developed and widely applied, the same cannot be said for fluorinated derivatives. [3] Specifically, access to monofluoroallene skeletons is limited, with available methods being dependent on metal catalysed processes that utilize expensive and complicated ligands; these methods often have a narrow substrate scope. [4-5]

We report a Frustrated Lewis Pair (FLP) approach for the synthesis of trapped cationic monofluoroallenes through the C-F bond activation of difluoroalkyne substrates. This method is facile, operates under mild conditions, makes use of widely available reagents, demonstrates a good tolerance of different functionalities on the dilfluoroalkyne and operates with a variety of Lewis bases. Moreover, the resulting cationic fluoroallene species present unique reactivity, giving access to structures not possible through other approaches.

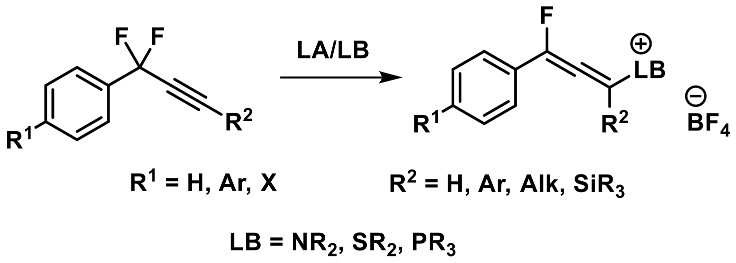

Figure 1. General Scheme for the FLP activation of difluoroalkyne substrates.

References

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NHC-Stabilized Inorganic Carbamic Acid, (Thio)Urethane and Urea from NHC-Stabilized Heavier Isocyanates

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Isocyanates (R-NCO) are fundamental building blocks in the chemical industry, primarily due to their crucial role in the production of polyurethanes. Their most significant reactivities involve nucleophilic additions of alcohols, amines, or thiols, leading to the formation of (thio)ureas and (thio)urethanes.[1] Given the diverse chemistry of these compounds, there is increasing interest in modifying their molecular scaffold. Recent advances in organophosphorus chemistry include the isolation of phosphorus-containing analogues of urea, urethane, and isocyanuric acid.[2-4] Notably, all these compounds feature carbon as their central atom. Herein, we describe the mild oxidation of our previously reported NHC-stabilized heavy isonitrile with elemental tellurium, affording an NHC-stabilized 'heavy isocyanate' with a central silicon atom.[5] Similar to classic organic isocyanates, this heavier congener exhibits selective addition reactions with water, alcohol, ammonia, and ethanethiol.

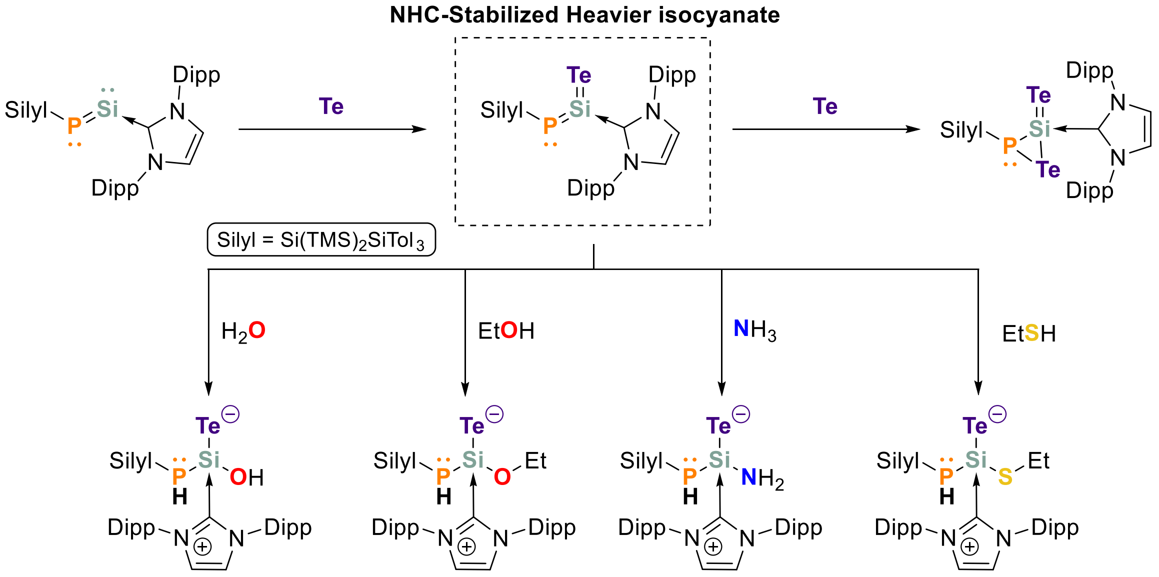

Figure 1. Oxidation of an NHC-stabilized heavy isonitrile with elemental tellurium and the addition of water, alcohols, ammonia, and ethanethiol.

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High-Resolution Photocrystallography of Transition Metal Complexes

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The field of crystallography has found broad interdisciplinary application, owing to the diverse range of techniques it encompasses. Two well-established techniques are high-resolution crystallography, and photo-crystallography. High-resolution crystallography allows for modelling the charge density around molecules, though its reliance on crystals with exceptional diffraction quality often confines its use to small molecules and materials science in analysing bond critical points.[1] Photo-crystallography involves molecular excitation within the crystal during X-ray exposure, which has enabled investigation of phenomena such as photoinduced linkage isomerism and reversible cyclisation reactions.[2,3]

Both techniques offer valuable insights into structure and function, however, there have been few investigations integrating both methods simultaneously. Preliminary work has been conducted by photoexciting several analogous transition metal complexes, allowing for a direct visualisation of excited-state charge densities that are typically limited to computational techniques.

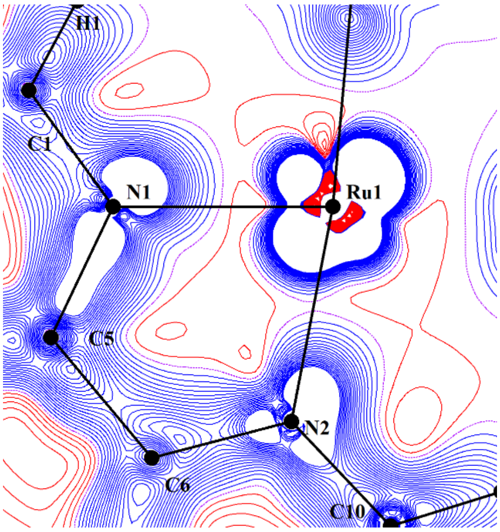

Figure 1. Static electron density map of ruthenium-nitrogen bonding in (2,2'-bipyridine)bis(1,10-phenanthroline)ruthenium(II) iodide. Contour: 0.05 e/Å^3, blue: positive electron density.

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Electrochemically-mediated Copper-catalyzed Atom Transfer Radical Addition Using Polyhaloacetamide Derivatives

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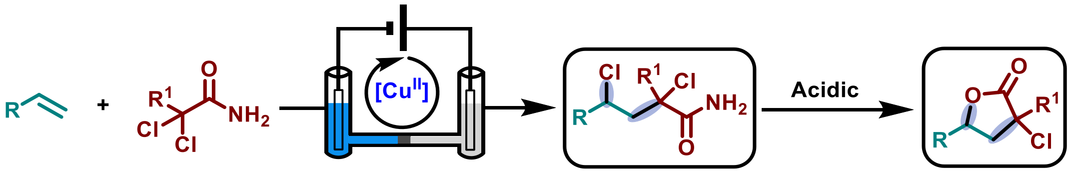
Electrochemically mediated atom transfer radical addition (*e*ATRA) catalyzed by copper(II) has recently emerged as a powerful and sustainable strategy for carbon–carbon (C–C) bond formation in organic synthesis. Building on earlier investigations into robust but active copper(II) complexes,[1][2] the recent study explores their catalytic role in the *e*ATRA of α-haloamides with a range of functionalized alkenes. The initial addition products undergo subsequent intramolecular cyclization to afford five-membered lactones. A key feature of this transformation is the electrochemical generation of an unusual and highly reactive O-bound copper(II) species, $[Cu^{II}(Me_6tren)(OR)]^+$, in the presence of polyhalogenated primary amides. This enolate intermediate serves as the active catalyst by modulating radical ($OR^{\bullet}$) concentrations to promote efficient *e*ATRA. Mechanistic insights supported by cyclic voltammetry and UV-vis spectroelectrochemical studies further clarify the role of copper intermediates in this process. This work demonstrates the versatility and efficiency of copper-catalyzed *e*ATRA under mild electrochemical conditions, offering a valuable pathway for the synthesis of five-membered structures from readily available starting materials.



Scheme 1. Electrochemical-mediated copper-catalysed atom transfer radical addition (eATRA) with α-chloroacetamides.

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Ligand Design for Modulating Mono- and Bimetallic Ni Complexation

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Cooperative bond activation continues to grow in relevance in the broader field of homogeneous catalysis.[1] Exploiting bespoke low-valent ligand systems can expand these horizons, growing on a strong base of carbene-transition metal chemistry. In our research, we focus on the development of chelating heavier tetrylene systems, due to their simultaneous Lewis basic and Lewis acidic properties, they can play an active role in the activation of small molecules in multicentre systems, i.e. when bound to a transition metal.[2] A key design feature in these ligands is a chelating phosphorous arm, which partially constrains formed complexes, delivers a low-valent tetrylene binding site, and entropically stabilises target compounds. Key examples from our previous work have demonstrated the reversible and cooperative activation of dihydrogen, the energetics of which can be directly tuned by modification of substituents at the germylene,[3] and even the discovery of previously unexplored mechanistic pathways in catalytic hydrogenation.[4]

In the scope of the presented work, the concept described above has been expanded through further ligand development, now utilising two phosphine arms. This allows for tripodal complex formation, comparable to other PEP type (E = Ge, Sn) pincer complexes,[5] all the while retaining a high degree of tunability and a low-coordination environment at the low-valent ligand binding centres.

The system presented in this work demonstrates an apparently rigid geometry in monometallic Ni^0 complexation, accessible through reductive routes. In contrast, the direct addition of Ni^0 (i.e. $Ni(cod)_2$) leads instead to unprecedented bimetallic Ni^0 complexes, demonstrating the coordinate fluxionality of this novel ligand class. Factors allowing for this new coordination mode, and further coordination chemistry of these species is discussed.

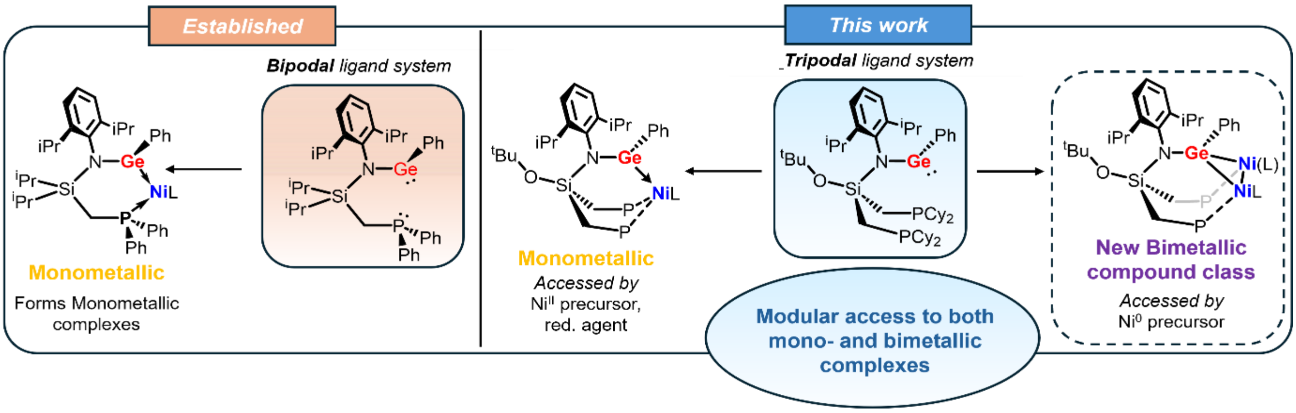

Figure 1. Tripodal ligand system allowing modular access to mono and bimetallic complexes.

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Counterion Effects in Photocatalysis: Insights from DFT

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Photocatalysis uses the energy of light to promote chemical transformations that are otherwise unaccessible. Thanks to their strong absorption in the visible region, rapid intersystem crossing, and long-lived triplet excited states, polypyridyl ruthenium (II) and cyclometalated iridium (III) complexes are the most widely explored classes of photoredox catalysts and photosensitizers. In the past decades, their properties have been tuned over a broad range by sophisticated modifications of the ligands, sometimes at high synthetic cost.

Working on the photocatalytic activity of the archetypal $[Ru(bpy)_3](X)_2$ complex in triplet-triplet energy-transfer (TTEnT)-activated cycloadditions, we came across interesting variations depending on the nature of the counterion, X. These variations were investigated further, both experimentally and theoretically (Figure 1).[1] If most complexes are usually modelled as bare cations, our calculations have focused on trimolecular systems composed of cation and explicit counterions. This study has revealed how they may, in a low polarity solvent, directly influence not only photophysical and photocatalytic properties, but also photostability, in line with our previous mechanistic hypotheses.[2,3]

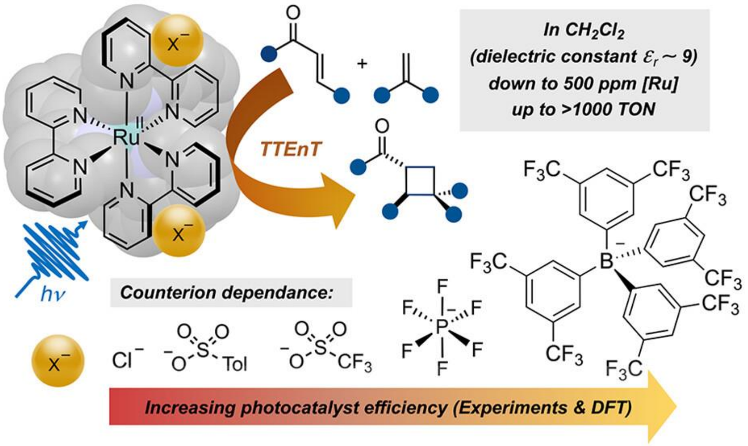

Figure 1. Counterion dependence on the photocatalytic properties of $[Ru(bpy)_3](X)_2$.

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A Revision of the Common Practice for Calculating CH Acidities (pK_a values) of Substituted Benzenes and Ferrocenes

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The computational determination of pK_a values receives increasing popularity. It replaces time consuming titration methods and allows for a prediction of values in target molecules and considers additional functional groups. The correlation of predicted *versus* experimental values improved significantly when solvent models, such as PCM and SMD were incorporated and benchmark studies for selecting the ideal functional/basis set combination let to further improvement.[1] Based on the large volume of available experimental data, acids and bases with pK_a values between 0 to 14, such as carboxylic acids (-COOH), phenols (-OH), and amines (-NR$_2$), were most investigated. However, it was found that the determination of pK_a values in aqueous media shows high systematic errors if 'naked' molecules and anions were investigated, whereas the incorporation of explicit molecules of water improved the correlation.[2]

The calculation of CH acidities in non-aqueous media remains a challenge. Compared to carboxylic acids with distinct reactive sites, CH-acidic (hetero)aromatic compounds contain several reactive sites of similar reactivity, which cannot be determined experimentally. Several studies report about a miss-match between functionalization at the 'most acidic site', determined by DFT, and experimental findings, which remained mostly unquestioned. During our studies of the anionic Fries rearrangement[3] we noticed a similar miss-match, which we revised by considering C–Li bonding and is presented herein.

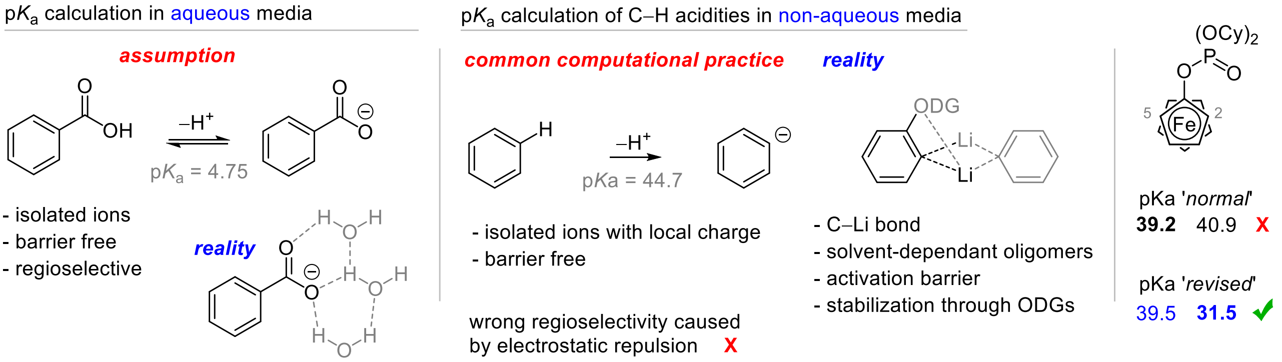

Figure 1. Internal alkyne/vinylidene rearrangement and unwanted decomposition.

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The Influence of Structurally Modified Cyclopentadienyl Ligands in Group-9 Metal Catalysed C-H Functionalisation

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The site selective C-H functionalisation of arenes, alkenes and alkanes via transition-metal catalysis is an increasingly useful strategy in chemical synthesis with wide ranging applications across natural product synthesis, material sciences, and drug discovery.[1] Many of these C-H functionalisation processes are catalysed by pentamethylcyclopentadienyl-derived Group-9 metal complexes (i.e. Cp*M^{III} where M = Co, Rh, Ir). The relatively electron-rich pentamethylcyclopentadienyl ligand affords stable catalytic complexes that drive both directed and non-directed C-H functionalisation reactions for the formation of new carbon-carbon and carbon-heteroatom (i.e. C-N, C-O, C-S) bonds.

The use of structurally modified cyclopentadienyl ligands in Group-9 metal complexes has recently been explored as a means to influence both the reactivity and selectivity of C-H functionalisation processes. For example, the incorporation of electron-withdrawing substituents (e.g. -CO_2Et or -CF_3) alters the electronic nature of the metal complex which can lead to accelerated catalytic activity, while the inclusion of bulky substituents (e.g. -^{t}Bu or -Cy) can dramatically influence both chemo- and regio-selectivity.[3] Chiral cyclopentadienyl ligands have also been employed to influence enantioselectivity in asymmetric C-H functionalisation.[4]

The outcomes of our recent studies into the impact of electronic and steric variations within cyclopentadienyl ligands on catalytic activity in Group-9 metal catalysed C-H functionalisation reactions will be discussed. This includes the discovery of new Group-9 metal catalysed site selective C(sp^3)-C bond forming processes in addition to novel catalytic strategies for the amination of C(sp^3)-H bonds via both inner-sphere and outer-sphere nitrene transfer mechanisms.[4]

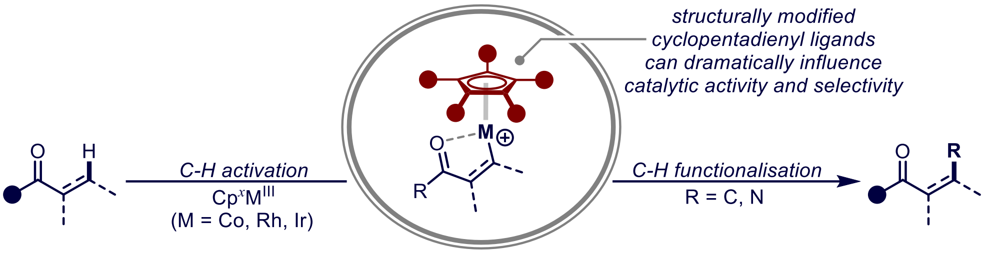
structurally modified cyclopentadienyl ligands can dramatically influence catalytic activity and selectivity

Figure 1. The influence of structurally modified cyclopentadienyl ligands in Group-9 metal catalysed C-H functionalisation has been explored to enhance catalytic activity and selectivity.

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Synthesis and Reactivity of Organolanthanide(II) Hydrides

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Since the first report on the synthesis of an organolanthanide(III) hydride over 40 years ago, the field has witnessed enormous growth with hundreds of examples of organolanthanide(III) hydride based on every element in the lanthanide series. These complexes have now found applications in a range of industrially and academically important catalytic transformations, such as hydroboration, hydroamination and olefin polymerisation. In contrast, the synthesis and reactivity of lanthanide(II) hydrides is underdeveloped, with only a handful of examples in the literature.

The reactivity of these organolanthanide(II) hydrides is already beginning to diverge from that reported for the well-established organolanthanide(III) hydrides. For example, we have recently demonstrated that a low-coordinate organoytterbium(II) hydride could facilitate the first example of catalytic nucleophilic alkylation of benzene. This presentation will cover the new reactivity we have uncovered on our journey to extend the range of organolanthanide(II) hydrides beyond ytterbium to europium and samarium.

Synthesis, Structure and Properties of 4-Nitrophenylaceto-Rare-Earth (III) Complexes for the Application of Corrosion Inhibition.

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Three structural types of rare-earth (RE) aqua 4-nitrophenylacetate (4NPhAc) complexes $\{[Ce(L)_3(H_2O)_2]\}_n$ (**a**), $\{[RE(L)_3(H_2O)_2]\cdot 2H_2O\}_n$ (RE = La (**b**), Nd (**c**)), $\{[RE_2(L)_6(H_2O)]\cdot 2H_2O\}_n$ (RE = Y (**d**), Gd (**e**), Dy (**f**), Er (**g**), Yb (**h**)), (L = 4-nitrophenylacetate) were synthesised by salt metathesis reaction of RE^{III} chlorides or nitrates with the sodium salt of 4-nitrophenylacetate Na(L) in a water/ethanol solvent system. Traditional corrosion-inhibiting methods have employed toxic compounds such as chromates, prompting the search for safer alternatives. Compounds such as benzoates, nitrites, and oxalates have been used effectively in preventing corrosion, and more recently, lanthanoid metal complexes have had proven success with the exploration of hydroxyphenylacetates as coordinating ligands, prompting the exploration of the corrosion inhibition properties of similarly substituted phenylacetate complexes. Single-crystal X-ray diffraction (SCXRD) was used to determine the structures of all complexes except Gd (**e**), which was determined to be isomorphous with the Er complex (**g**) by X-ray powder diffraction (XRPD). All isolated complexes crystallise as one-dimensional polymers, where complexes **a-c** have mononuclear repeating units with two coordinated waters, and complexes **d-h** have binuclear repeating units with a single coordinated water. Weight loss tests reveal $\{[Dy_2(4NPhAc)_6(H_2O)]\cdot 2H_2O\}_n$ showed the greatest inhibition efficiency of 89% out of the tested the rare-earth complexes (**a, b, c, d, e, g, h**).

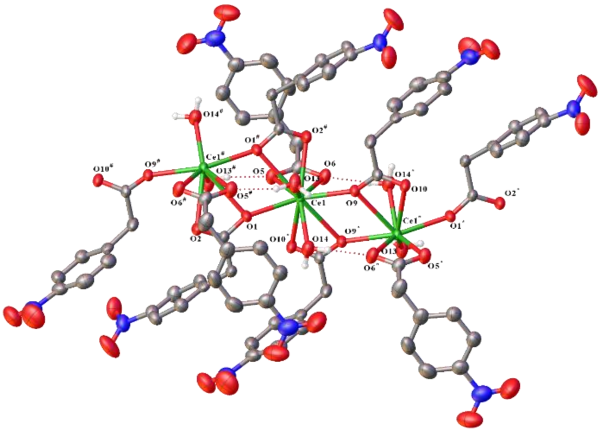

*Figure 1. A section of the polymer of $\{[Ce(4NPhAc)_3(H_2O)_2]\}_n$ with 50% thermal ellipsoids. Dotted lines indicate the intra-molecular hydrogen bonds. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **(a)**: Ce1-O1$^{\#}$ 2.757(2), Ce1-O2$^{\#}$ 2.565(2), Ce1-O5 2.573(3), Ce1-O6 2.563(3), Ce1-O9 2.452(2), Ce1-O9* 2.692(2), Ce1-O10* 2.570(2), Ce1-O13 2.628(3), Ce1-O14 2.638(3). Symmetry Code: #1-X,1-Y,1-Z; *2-X,1-Y,1-Z.*

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“Interpreting” Quantum Chemistry with tools of Spectroscopic Analysis

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Understanding the fine energy structure of lanthanoid ions is crucial for harnessing their unique properties in various applications. Traditionally, Ligand Field Theory and "Crystal Field" calculations have provided insights into this electronic fine structure; however, their effectiveness diminishes under low symmetry conditions, complicating the modeling process due to numerous constraints. In contrast, modern ab initio quantum chemistry methods allow for an alternative analysis based solely on structural coordinates.

We systematically compare these two approaches by examining a series of lanthanoid systems with progressively lower symmetry. By integrating experimental data, we will elucidate the similarities and differences between traditional ligand field models and contemporary computational methods. Finally we emphasize that a combination of both approaches provides a unique viewpoint whichmay aid future synthetic efforts towards designing molecules with desired properties.

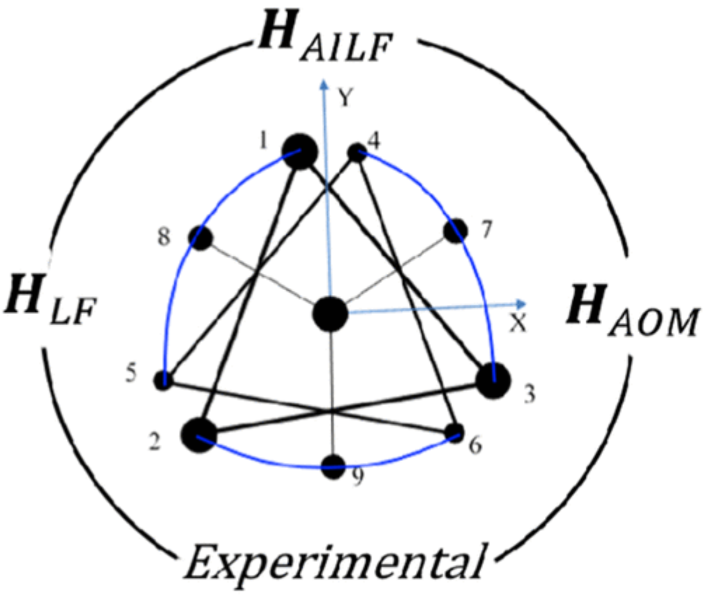

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Figure 1. Relationship between ab initio, Ligand Field, experimental, and the Angular Overlap Model.

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Synthesis, and Structural Characterization of Rare-Earth Hydroxyphenylacetate Complexes and Their Corrosion Inhibition Properties

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The corrosion process involves the deterioration of metallic structures resulting in structural failures of their applications. It leads to a massive global issue where an effective solution is yet to be established.[1] Corrosion inhibitors play a significant role as an effective, simple, and comparatively economical solution to reduce this massive damage.[2] Despite chromium (VI) compounds have been exceptional corrosion inhibitors for over a century, their extreme toxicity and carcinogenic nature led to legal restrictions on their usage.[3] During the past two decades, rare-earth (RE) carboxylates with different structural motifs have been synthesized to study their anticorrosion properties and have become a promising alternative for chromate corrosion inhibitors for steel and aluminium alloys.[4] In our recent study on RE-phenylacetate complexes, we studied the performance of these simple carboxylates having no extra functional groups, but frustratingly, all those complexes had poor inhibition properties on mild steel.[5] Our current study attempts to improve the anti-corrosion properties of RE-phenylacetate compounds on mild steel and study the impact of the presence of hydroxyl functional groups on the benzene ring in addition to the carboxylate group, thereby studying their structure-function relationship. As a result, two series of rare earth one-dimensional (1-D) coordination polymers with 4-hydroxyphenylacetate (4hpa) or 2-hydroxyphenylacetate (2hpa) were synthesized via the salt metathesis reaction in an aqueous ethanol medium and four different structures of series 1;$\{[Ce(4hpa)_3(H_2O)_2]\cdot H_2O\}_n$ (**1a**), $\{[RE_2(4hpa)_6(H_2O)]\cdot 4H_2O]\}_n$ (RE = Nd (**1b**), Gd (**1c**)), $\{[RE_2(4hpa)_6(H_2O)]\cdot 3H_2O]\}_n$ (RE = Dy (**1d**), Y (**1e**)), and $\{[RE_2(4hpa)_6(H_2O)]\cdot 5H_2O]\}_n$ (RE = Er (**1f**), Yb (**1g**)), and three different structures of series 2;$[La(2hpa)_3(H_2O)_2]_n$ (**2a**), $\{[RE_2(2hpa)_6(H_2O)_4]\cdot 3.5H_2O\}_n$ (RE = Ce (**2b**), Nd (**2c**)), and $\{[RE_2(2hpa)_6(H_2O)_2]\cdot 3H_2O\}_n$ (RE = Gd (**2d**), Dy (**2e**), Y (**2f**), Er (**2g**), Yb (**2h**)) complexes were determined. In the weight loss anti-corrosion tests for mild steel in 0.01 M NaCl, compound **1c** from series 1, and compound **2d** from series 2 demonstrated the highest inhibition efficiency of 88% and 57% respectively. None of the RE 2-hydroxyphenylacetate compounds outperformed the anti-corrosion properties of RE 4-hydroxyphenylacetates indicating the positive effect of the *p*-OH group on the benzene ring on anti-corrosion properties for mild steel in a mild corrosive environment.

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Accessing Lanthanoid Metal Complexes Using Copper (I) Reagents

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Lanthanoid metals and their complexes are becoming an essential topic given their modern day applications.[1] Free lanthanoid metals are an essential source for synthesising the lanthanoid metal complexes due to their ability to be easily oxidised.[2] Redox transmetallation protolysis (RTP) and redox transmetallation (RT) are the reaction pathways used to synthesise the lanthanoid metal complexes from their zero-oxidation state.[3] RTP reactions are established by using mercuric reagents as the redox transmetallating agent followed by the protolysis with a protic ligand.[4] Because of the toxicity of mercury, an alternative less toxic transmetalating reagent is preferred.[5] Silver and bismuth reagents have been established as an alternative to the mercuric reagents.[6] In this work we are exploring pentafluorophenyl copper (CuC_6F_5) as a redox transmetallating reagent for the synthesis of divalent and trivalent lanthanoid complexes. The ^{19}F NMR monitoring of the reaction suggests that instead of RTP, the reaction follows PRT (protolysis followed by redox transmetallation) in one-pot syntheses. Complexes of europium (Eu), ytterbium (Yb) and samarium (Sm) with proligands formamidines (FormH), pyrazoles (PzH) and phenols (ArOH) were synthesised in pyridine. Ytterbium complexes were formed in the presence of a catalytic amount of iodine, whereas the samarium complexes were formed when activated Sm with iodine prior to the reactions. The complexes formed were characterised by X-ray crystallography, multinuclear NMR and IR spectroscopy.

$$2\ \mathrm{Eu\ (s)} + 2\ \mathrm{CuC_6F_5} + 2\ \mathrm{LH} \xrightarrow[\mathrm{py}]{} [\mathrm{Eu(L)_2(py)_2}] + 2\ \mathrm{C_6F_5H} + 2\ \mathrm{Cu} \qquad (1)$$

$$n\ \mathrm{Yb\ (s)} + n\ \mathrm{CuC_6F_5} + n\ \mathrm{LH} \xrightarrow[\mathrm{py}]{\mathrm{cat.\ I_2}} [\mathrm{Yb(L)}_n\mathrm{(py)_2}] + n\ \mathrm{C_6F_5H} + n\ \mathrm{Cu} \qquad (2)$$

$$n = 3 \text{ or } 2$$

$$\mathrm{Sm\ (s)} + 3\ \mathrm{CuC_6F_5} + 3\ \mathrm{LH} \xrightarrow[\mathrm{py}]{\mathrm{cat.\ I_2}} [\mathrm{Sm(L)_3(py)_2}] + 3\ \mathrm{C_6F_5H} + 3\ \mathrm{Cu} \qquad (3)$$

$$\mathrm{LH = FormH,\ PzH,\ ArOH}$$

Scheme 2: Syntheses of Eu, Yb and Sm complexes using CuC_6F_5

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Sensitised Lanthanoid Luminescence using Bimetallic Cu(I) – Ln(III) Complexes

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The photophysical properties of Cu(I) phenanthroline complexes make them promising candidates as a more sustainable replacement of precious metal lumiphores such as Ru(II) and Ir(III) complexes for photophysical applications. One such application is the use as a photosensitiser for Ln(III) emission.
Ln(III) ions have sharp emission bands and long excited state lifetimes with applications in sensing, imaging, and telecommunications.[1] Unfortunately, direct photoexcitation of these states is inefficient. A strategy to circumvent this is the antenna effect, whereby a light absorbing ligand is bound to the Ln(III). Absorbance of the chromophore leads to an excited state, then, through an energy transfer process, a Ln(III) excited state can be generated.

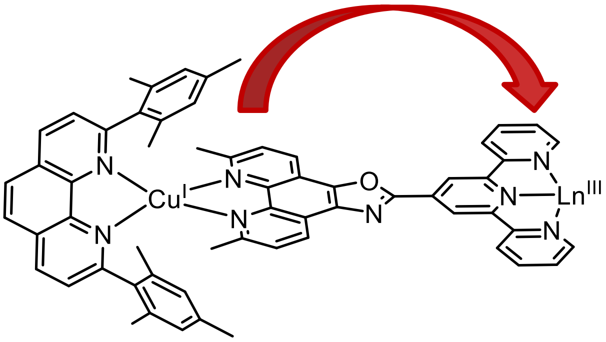

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Figure 1. Relationship between ab initio, Ligand Field, experimental, and the Angular Overlap Model.

Cu(I) contains a $3d^{10}$ electronic configuration, and upon MLCT excitation, the Cu(I) centre is oxidised to Cu(II), which is accompanied by a distortion of the ligands towards a square planar geometry. This distortion is correlated with non-radiative deactivation pathways, but the use of sterically demanding ligands has been shown to limit this pathway.[2]

Herein we report the synthesis and photophysical characterisation of two hetero-bimetallic *d-f* complexes with Cu(I) and Ru(II) chromophores using steady state and time resolved spectroscopy. Excitation of the MLCT band of each transition metal chromophore leads to characteristic emission from NIR emitting lanthanoids. This represents the first example of sensitised lanthanoid luminescence by a Cu(I) chromophore, and comparison to the analogous Ru(II) complex provides and insight into the energy transfer processes involved.

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3. Poster Presentation Abstracts

Structure-Property Relationships: Metal Complexes in Molecular Junctions

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The field of Molecular Electronics can be broadly defined as being concerned with the scientific, engineering and technological challenges and opportunities associated with the study of electron transfer through one or more molecules between two electrodes in structure known as *molecular junctions*. [1], [2] Whilst initially envisioned as a route to overcoming the lithographic and nanoscale materials challenges associated with the pursuit of Moore's Law, Molecular Electronics has emerged as broader discipline concerned with electronic, chemical and materials properties on the molecular scale and of molecular assemblies. [1] To date, the vast majority of compounds studied in molecular junctions have been based on conjugated organic backbones.[3] However, in more recent times the role that metal complexes may play in fine tuning the electrical response of the junction, by more readily changing frontier orbital energies, introducing redox properties or multiple unpaired spins, and controlling their distribution in space through simple changes in the coordination geometry have attracted attention. [4]

This presentation highlights the synthesis and electrical characterization of metal complexes designed for molecular junction studies. We introduce a novel series of symmetrical complexes, *trans*- [M(C≡CR)$_2$L$_2$] species featuring Ni or Pt centres with ancillary phosphine ligands, L, and demonstrate the role of the metal centre and nature of the nd orbitals and supporting ligand on the junction conductance behaviour. Additionally, we report the synthesis of Ni- and Mn-salen complexes and *trans*-[M(C≡CR)$_2$(cyclam)]OTf (M = Cr(III) or Co(III)) with a view to exploring links between molecular structure and redox state with electronic transport properties.

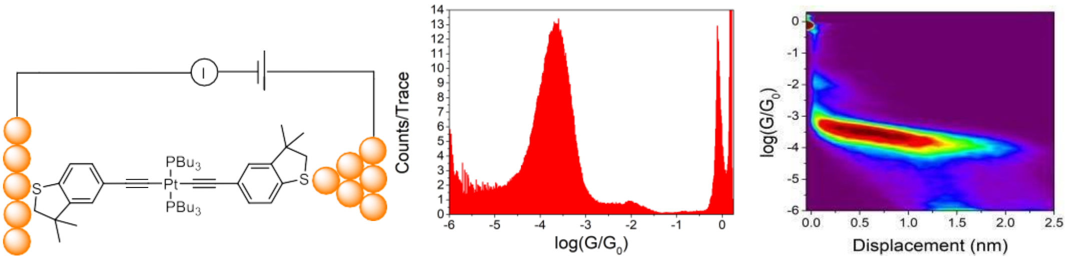

Figure 1. (a) A molecular junction of the metal complex molecular wire trans-Pt(C≡CR)$_2$(PBu$_3$)$_2$ (R = 3,3-dimethyl- 2,3-dihydrobenzo[b]thiophene (DMBT)) and plots of the (b) one-dimensional conductance histogram and (c) two-dimensional histogram (heat map) of this complex.

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Synthesis of Hemilabile Iron Half-Sandwich Complexes

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Throughout history, chemists have developed new types of reactions to formulate new molecules. One of the most important types of reactions are C,C cross-coupling reactions, which are crucial for the synthesis of molecular building blocks, drugs and pesticides.[1] Air and moisture stable palladium pre catalysts are commonly used, due to their high selectivity and tolerance towards functional groups. However, increasing demand and prices of noble metals require alternative metal sources to be explored.[2] Iron is the second most abundant metal in the world, with several advantages for catalysis, is cheaper, widely available, and has a low environmental and biological toxicity.[3] Especially the half-sandwich motif has been demonstrated to be of superior stability.[4] However, they only allow for a single coordination site to be generated. We focus on a modular design that includes a hemilabile bonding site, which can reversibly bind to the metal centre. Thus, an additional coordination site can be generated during the catalytic cycle and a 'classic' oxidative addition/reductive elimination mechanism, similar to palladium, can be achieved. The synthesis and stability of the first examples of that type of complexes will be presented, including computational studies to compare the stability of individual steps during the process.

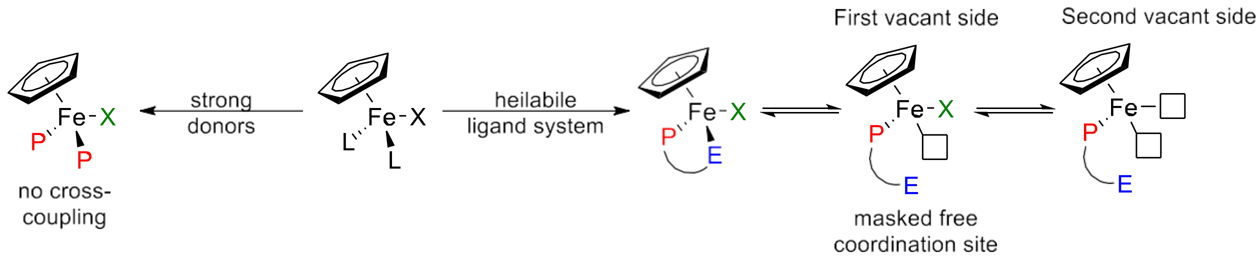

Figure 1. Possible mechanism to obtain two vacant side in iron half-sandwich complexes.

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Copper(II)-Mediated Electrocatalytic Activation of C–X Bonds in Polyhalogenated Compound Synthesis

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Electrochemically mediated atom transfer radical addition (*e*ATRA) is a new and versatile method of carbon bond formation.[1] This method uses a controlled potential electrolysis to generate an active Cu(I) complex capable of cleaving alkyl halide bonds. The key advantage of this protocol is the generation of a rare organometallic Cu(II) complex $[Cu(Me_6tren)(R)]^+$ (Me_6tren = tris(2- (dimethylamino)ethyl)amine) under electrochemical condition which acts as a controlled source of organic radicals via reversible homolysis of the Cu^{II}-C bond.[2]

These reactions remain largely unexplored. This work investigates a series of simple alkyl halides like $CHCl_3$, CH_2Cl_2, tetrachloroethane and tetrabromoethane in generating complex long chain alkyl halides. Cyclic voltammetry and spectroelectrochemistry have been used to determine the suitability of the polyhalogenated alkanes, and NMR spectroscopy as well as a series of mass spectrometry experiments, have been used to analyse reaction products. Preliminary data suggest the formation of relatively high order oligomers as well as the observation of interesting processes such as hydrogen abstraction and aldehyde functionalization.

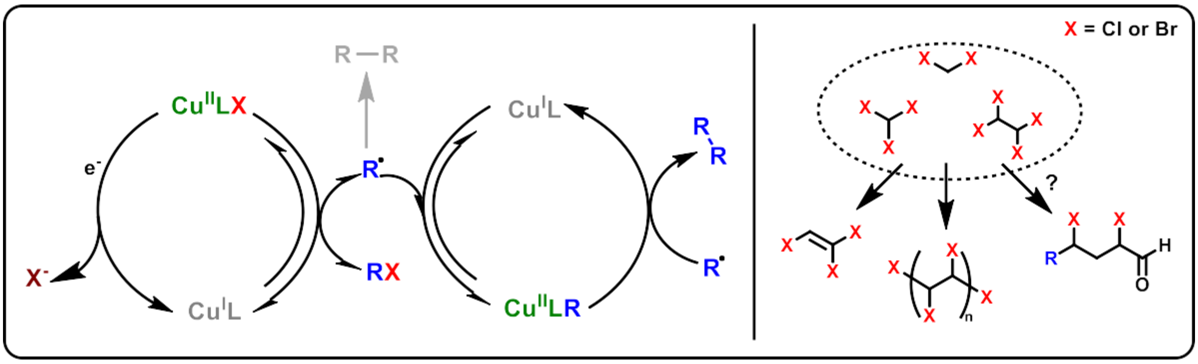

Figure 1. Schematic representation of Cu(II)-mediated electrocatalytic generation of organic radicals from alkyl halides and the resulting oligomeric products.

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Sb(V) Aryl Anthraquinone Complexes: Enhanced Stability and Antileishmanial Activity of a Fluorescent Anthracycline System

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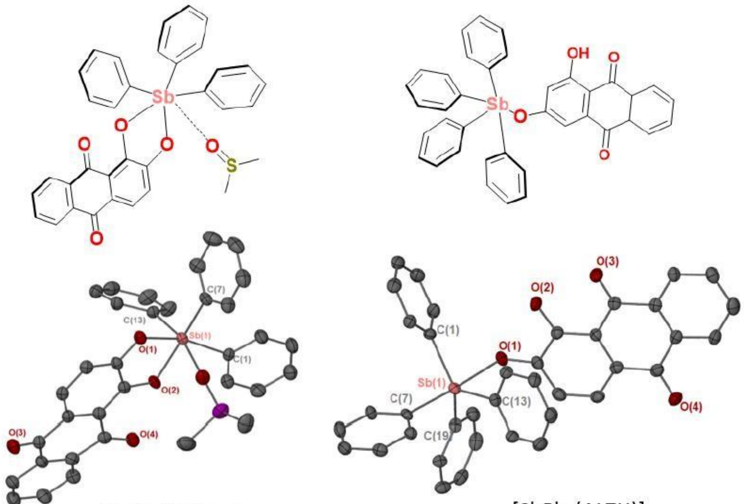
Hydroxyanthraquinones are naturally derived cyclic compounds with a variety of biological functions. Their delocalised nature gives rise to a number of spectacular colours through resonance stabilisation at the different functional groups around the ring. The downside to their high resonance capability is the stability of potential metal chelates.[1] Facile hydrolysis of the *O,O* di-ketonate binding mode has been observed by the Andrews group to occur with organometallic based complexes of group 13, rendering them unable to undergo biological assessment. Therefore, we turned our attention to larger group 15 organometallics, tris/tetra-phenyl Sb(V), as the metal template for stabilisation.

The resultant complexes were observed to be stable to hydrolysis under ambient conditions giving rise to six distinctive Sb(V) complexes. These highly coloured complexes were analysed via single-x- ray crystallography to ascertain the binding mode of the anthraquinone. Interestingly, the triphenyl complexes exhibited bidentate binding mode of the anthraquinone through a double deprotonation of both hydroxyls, with the sixth position occupied by a solvent molecule. For the tetra-aryls, a monodentate binding of the most acidic 2nd position was noted. With a high degree of aqueous stability, the complexes underwent biological assessment toward *Leishmania* parasites, the causative agent of the neglected disease which unfortunately incorporates detrimental antimonials as the frontline treatment.[2] The activity of these Sb(V) complexes was obtained, highlighting a good degree of selective activity. Preliminary fluorescence on the complexes has alluded to potential use in identifying the localisation intracellularly through microscopy. These studies are currently underway.



$[SbPh_3(ALZ)]$.dmso $[SbPh_4(ALZH)]$

Figure 1. Structural comparison of triphenyl and tetra phenyl antimony alizarin complexes

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Stabilisation of Hypervalent Aluminium Hydride Anions in Solution

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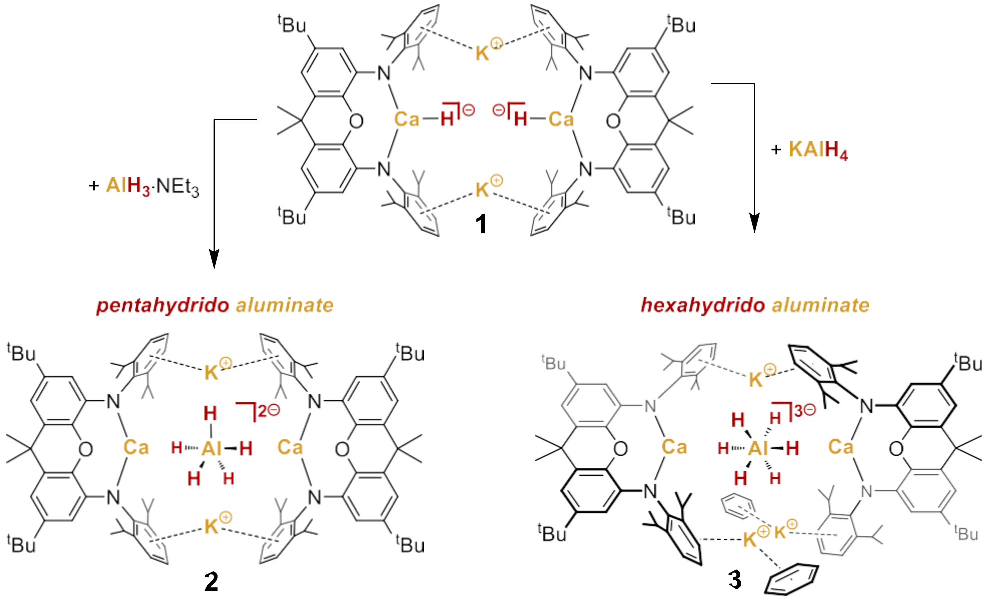
$LiAlH_4$ is a common reagent for various organic and inorganic syntheses.[1] Including additional hydride ions in the coordination sphere of the aluminium centre should further increase its reactivity. Hypervalent aluminium hydride anions of the form AlH_5^{2-} and AlH_6^{3-} have been thoroughly studied with regard to their applicability as solid-state hydrogen storage materials.[2,3] However, to our knowledge, they have never been observed in solution.

Recently, our group stabilised the hypervalent silicon dianion SiH_6^{2-} in a supramolecular assembly, gaining high temperature tolerance in solution.[4] We now expand this work to group 13 hydrides. By reaction between the anionic calcium hydride **1** and alane ($AlH_3 \cdot NEt_3$), we are able to isolate a complex of the hypervalent pentahydrido aluminate dianion (AlH_5^{2-}, **2**, Scheme 1). Introducing one more hydride anion by using $KAlH_4$ as a precursor allows us to stabilise the hexahydrido aluminate trianion AlH_6^{3-} with the same ligand system (**3**, Scheme 1). Besides the synthesis and structure of these two compounds, we will also present the first reactivity studies.



*Scheme 1. Synthesis of solution-stable AlH_5^{2-}(**2**) and AlH_6^{3-}(**3**) complexes.*

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Enzymes and Electrochemistry: A Dynamic Connection

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Oxidoreductase enzymes catalyse redox reactions including biologically essential ones including biosynthesis, respiration and metabolism. Formate dehydrogenase (FdsDABG) from *Cupriavidus necator* is an interesting enzyme that is capable of catalysing formate oxidation to CO_2, utilising NAD^+ as an electron sink and ultimately regenerating the economically valuable NADH. Additionally, FdsDABG also catalyses the reverse reaction, namely CO_2 reduction to formate utilising NADH. Typical steady-state studies and efforts to examine the kinetics of the oxidation half reaction have been unsuccessful with chemically reduced FdsDABG showing no activity with NAD^+. In this work, electrochemistry is utilised to both oxidise and reduce formate dehydrogenase and analyse the rate of catalysis as a product of change in observed current.

All oxidoreductases require redox partner proteins such as electron transfer proteins. In enzyme electrochemistry, electron transfer can occur directly between a working electrode and the enzyme. Furthermore, the rate of catalysis (the observed electrochemical current) is measured as a function of applied potential through cyclic voltammetry. However, electron transfer between an electrode and enzyme are typically slow to reach an electrochemical equilibrium. To overcome this, small molecules called mediators are included in solution. These mediators are capable of rapidly transferring electrons between an electrode and an enzyme typically through an outer-sphere cross-reaction. Furthermore, they have a well-defined cyclic voltammogram, allowing for a more suitable platform to analyse catalytic activity.

FdsDABG is a large protein (~180 kDa) that contains 9 cofactors scattered throughout 3 of the 4 subunits. In this work, the structurally simpler subcomplex FdsBG is used which only contains 3 cofactors and the all-important NAD(H) binding site and previous research has shown FdsBG still displays its redox activity towards NAD(H).[1] In this work, I have used mediated electrochemistry to determine the Michaelis-constant (K_m) of FdsBG for both NADH (174 µM) and NAD^+ (950 µM) which both agree with previously performed stead-state studies of other formate dehydrogenases.

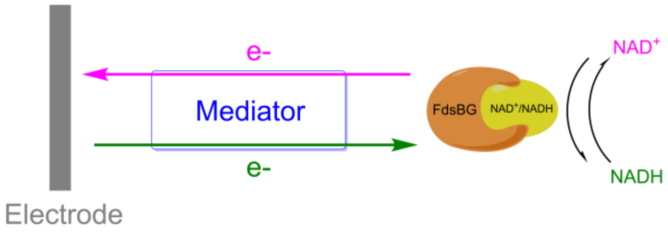

Figure 1. Cartoon scheme of mediated enzyme electrochemical turnover of NADH/NAD^+ by FdsBG.

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New investigations on Asymmetric eATRA, Ligand Design and Copper Complex Characterisation

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Copper-catalyzed electrochemical atom transfer radical addition (*e*ATRA) is a newly developed method for the creation of new C–C bonds under mild conditions. In the present study, we describe the synthesis of new chiral ligand inspired from the work of Clarosó et al.[1] based on a octahydro-biisoquinoline scaffold, an instance of underexplored C_2 symmetric diamine platform, for copper (II) catalysis. The synthetic route to this ligand has been improved and full characterisations have been conducted for the new species. We also report the synthesis of parent copper (II) complexes, new X-ray structures and electrochemical evaluations of activity in the *e*ATRA reaction using methodologies previously tailored in our group[2][3]. Although modest yields and a staggering absence of enantioenrichment has been observed, comparisons with other tetradentate N-donor ligand-based copper (II) complex have been established. Overall, these results highlighted the need for further investigations on the *e*ATRA mechanism and the overall viability of the reaction asymmetrisation.

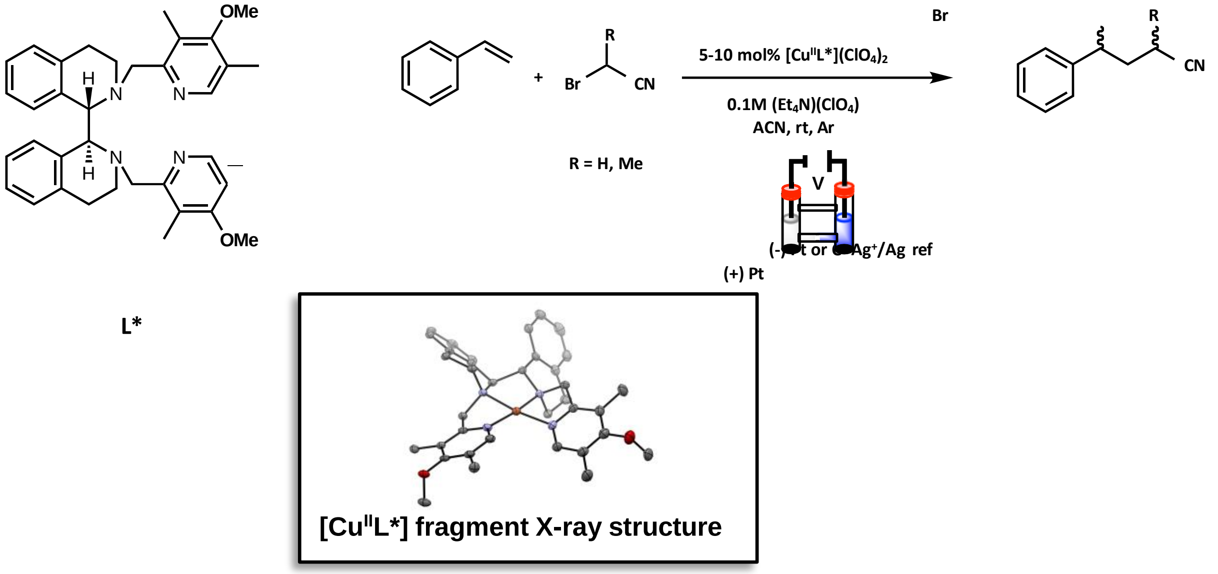

Figure 1. eATRA reaction using the designed chiral Cu (II) complex.

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Synthesis and Characterisation of New Divalent or Trivalent Lanthanoid Complexes from Free Metals and Pyrazolato Ligands

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Synthesis of lanthanoid complexes have been known for years, but very limited data is available for the synthesis of lanthanoid complexes from free metals due to their high sensitivity towards air and water[1]. Apart from this, lanthanoid metals also have the ability to form strong metal-ligand covalent bonds with various ligands with coordination number greater than six[2]. Pyrazoles, heterocyclic aromatic ligands having donor atom and substituents, are very good ligands that can also increase the number of potential metal binding sites to form polynuclear types of compounds[3]. These ligands are also known for their notable applications in diverse fields and also the combination of pyrazole with lanthanoid metal and iodine enhances their complexing tendency[4]. The reaction of lanthanoid metal with I_2 and 3,5-disubstituted pyrazoles in the presence of a suitable solvent yield either $[LnL_2I(solv)_n]$ or $[LnLI_2(solv)_n]$ products. For the synthesis of the organolanthanum iodide complex, conventional Schlenk line and glove box techniques were utilized[5]. La, Nd, and Ce metals produce crystals of the type $[LnLI_2(thf)_4]$ when they react directly with the ligands tBu_2pzH (3,5-ditertbutyl pyrazole) and PhMepzH (phenylmethyl pyrazole) in the presence of a solvent and iodine. Then, Lu and Er react with tBu_2pzH to form a product of the type $[LnL_2I(thf)_4]$, while Lu and Tb metals with PhMepzH produce $[LnLI_2(thf)_3]$ and $[LnLI_2(thf)_3]$.thf type products, respectively.

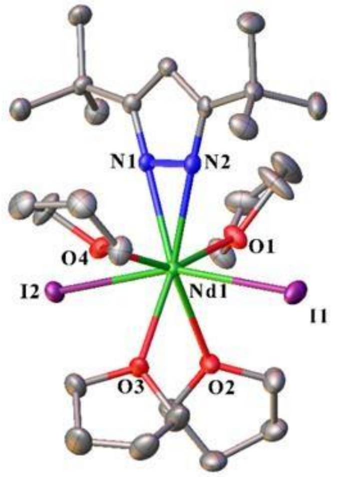

Figure 1. Molecular structure of $[Nd(tBu_2pzH)I_2(thf)_4]$ crysta.

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Finetuning Ligand Sterics and Electronics for Stabilising Low-Valent Aluminium Species

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Group 13 compounds, especially those based on aluminium in the +3 oxidation state, are archetypical Lewis acids and have various industrial and academic uses.[1] However, the chemistry of low-valent aluminium complexes, aimed at flipping this reactivity on its head, has experienced a surge of interest since the seminal report of a nucleophilic aluminyl anion in 2018.[2] Additionally, an aluminium(II) radical has recently been observed *in situ* and trapped with benzene as a bisaluminated 1,4- cyclohexadiene.[3] At the core of these developments lie thoughtfully designed, tailor-made ligands that allow fine-tuning of the electronic structure at the metal centre, whilst kinetically stabilising reactive compounds by strategically introducing steric bulk.

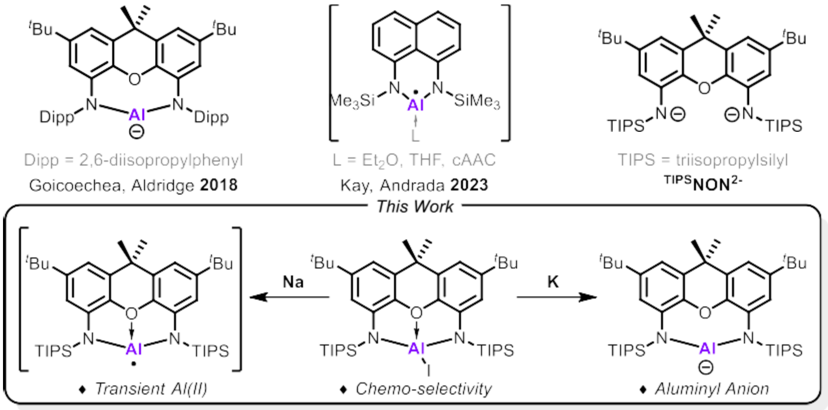

Figure 1. The first reported aluminyl anion and a transiently observed aluminium(II) radical. ***^{TIPS}NON^{2-}*** *used in this work to stabilise both aluminium(I) and aluminium(II) complexes.*

A possible drawback of custom-designed ligands for stabilising a single aluminium oxidation state is that other oxidation states may become inadequately stabilised, necessitating the costly and time-consuming development of a new ligand. In this work, we introduce **^{TIPS}NON**$^{2-}$ as a ligand platform on aluminium, enabling us to address both Al(II) and Al(I) oxidation states chemo-selectively.[4] By reduction of the precursor complex, **^{TIPS}NON**Al-I, with sodium-based reductants, we observed the formation of bisaluminated 1,4-cyclohexadiene. This is consistent with a transiently produced Al(II) radical, which subsequently adds to benzene. On the other hand, employing potassium-based reductants results in a potassium aluminyl complex, which is shown to spontaneously activate C-H and C-F bonds at room temperature, with drastically improved selectivity over its congener.[5]

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Group 13 Artificial Sweetener Complexes as Antimicrobials

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Contemporary overuse of antibiotics in the agriculture and healthcare sectors has led to a surge in infections and deaths caused by antimicrobial resistant (AMR) bacteria.[1] With the impact of AMR growing by the year, there is an urgency to investigate the development of new therapeutics.[2] Metal-based drugs have an advantage in this regard, as the evolution of bacterial resistance is less facile than for purely organic drugs, as many toxic metals share properties with essential ions bacteria need to survive.[3] Specifically, gallium is well known as a mimic for iron that interferes with bacterial redox metabolism.[4] Indium is another group 13 metal that has shown promising antibacterial properties.[5] Previous studies have demonstrated that group 13 metal complexes have significant antimicrobial activity.[6,7] In particular, gallium has proved to be a potent antimicrobial when complexed to artificial sweeteners, evidenced by the success of gallium(III) maltolate.[7]

Thus, in an effort to generate novel antimicrobial agents, attempts were made to synthesise and characterise a range of homoleptic [ML_3] and heteroleptic [MMe_2L] gallium(III) and indium(III) complexes of the artificial sweeteners saccharin, acesulfame and cyclamic acid, shown in Figure 1. Synthesis of heteroleptic and homoleptic gallium-sweetener complexes resulted in the acquisition of gallium(III) tris-saccharinate and dimethyl gallium(III) saccharinate. Additionally, the dimethyl analogue was further characterised by single crystal X-ray diffraction.

Three analogous homoleptic indium(III) complexes were obtained. Stability and suitability studies of these complexes for use in antimicrobials has revealed hydrolysis into a bis-sweetener mono-hydroxy motif as a potential decomposition pathway. Further analysis to determine the extent of hydrolysis and whether these are the stable configuration [ML_2OH] is underway.

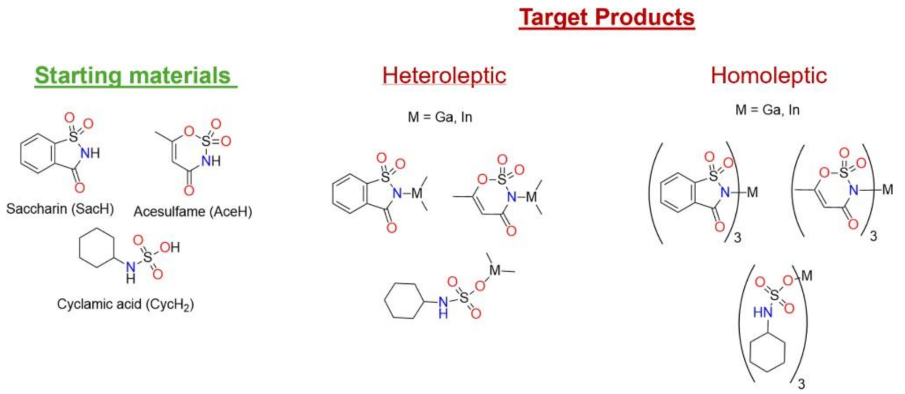

Figure 1. Structures of artificial sweeteners and target complexes relevant to this project

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Heavy Metal Molecular Qubits

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Quantum information science is poised to transform our world in the next few years. Practical realisation of this new era in computing relies on the design and implementation of quantum bits or 'qubits' — two-level quantum systems analogous to bits in classical computing. Qubits take advantage of quantum properties such as superposition and entanglement to perform logic operations that can be significantly faster and more efficient than classical computers.[1]

Recently the Hicks Group synthesised the first anionic Pb(I) radical (**1Dipp**) which was found to have an exceptionally large isotropic hyperfine interaction (nuclear-electron spin coupling) of 4929 MHz (Figure 1).[2] Therefore, this system has potentially interesting properties for qubit applications (where the two states are the unpaired electrons' spin).[3] However, **1Dipp** is extremely labile and decomposes rapidly in solution, even at −80 °C. Herein, we have synthesised an anionic Pb(I) radical with a modified ligand system including the sterically demanding EMind substituent (**1EMind**), drastically improving stability. We intend to take advantage of this by extensively characterising **1EMind** using continuous wave EPR (Figure 1), pulsed EPR and X-ray crystallography — all of which were not possible with **1DIPP**.

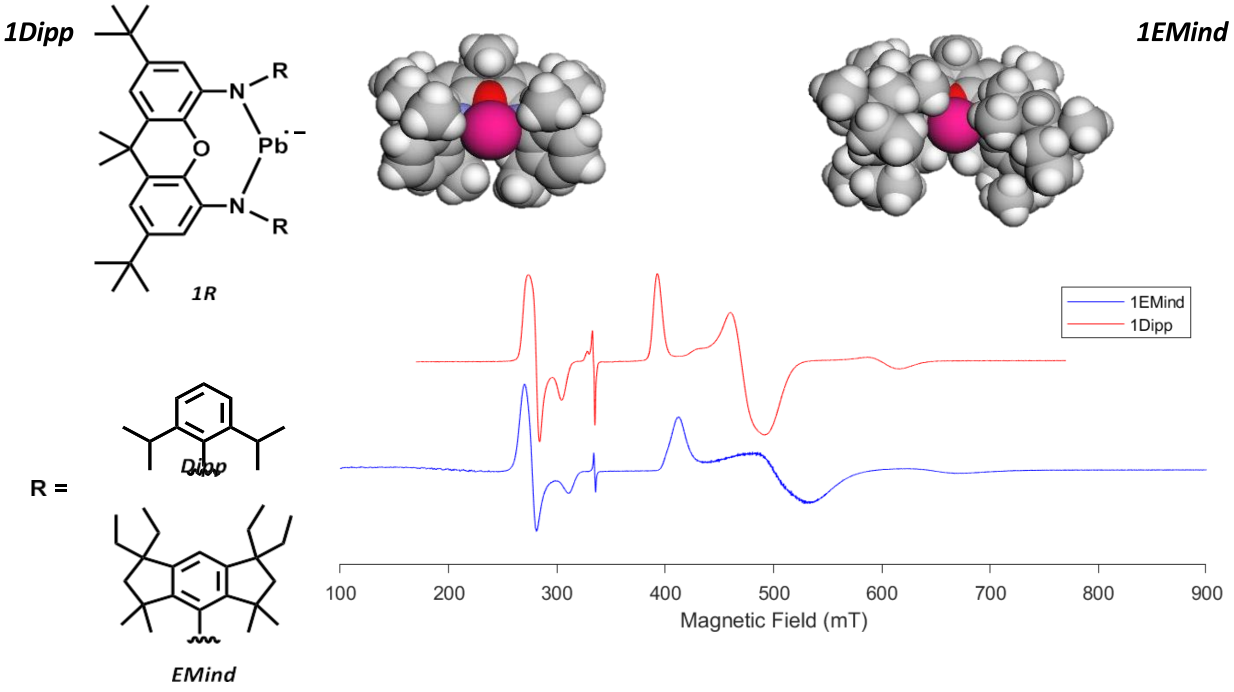

*Figure 1. Space-fill models showing the steric bulk of **1Emind** compared to **1Dipp** (top). Continuous wave EPR spectrum of **1Dipp** (red) and **1EMind** (blue) (bottom).*

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Superbasic Calcium Alkyl Complexes: Templated Two-Fold Deprotonation of Benzene

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The development of organocalcium chemistry has been hindered by an assortment of preparative difficulties – the relative inertness of calcium metal, poor stability in ethereal solvents and a high tendency to undergo Wurtz-type coupling.[1] One possible way to circumvent these issues involves the coordination of a sterically demanding, *mono*-anionic ligand to the calcium centre, which acts as a kinetic trap to shield the highly polar $^{\delta+}$Ca—C$^{\delta-}$ bond. These molecular calcium alkyl complexes are often more hydrocarbon soluble than their homoleptic counterparts, and can exhibit significantly enhanced reactivity. Figure 1(a) shows the β-diketiminato-coordinated calcium alkyl dimer, which was shown to be an incredibly potent nucleophile, capable of mediating the nucleophilic alkylation of benzene.[2] The work described here sought to enhance the reactivity of these calcium alkyls *via* the use of a bulky *di*-anionic ligand, which is believed to polarise the Ca—C bond further.[3] This results in the formation of a super-basic calcium alkyl complex, which templates the two-fold deprotonation of benzene to give an inverse crown areneide (Figure 1(b)).[4] Systematic control studies show that this proceeds *via* a stepwise deprotonation (Figure 1(c)), with the generation of phenylpotassium as an intermediate.

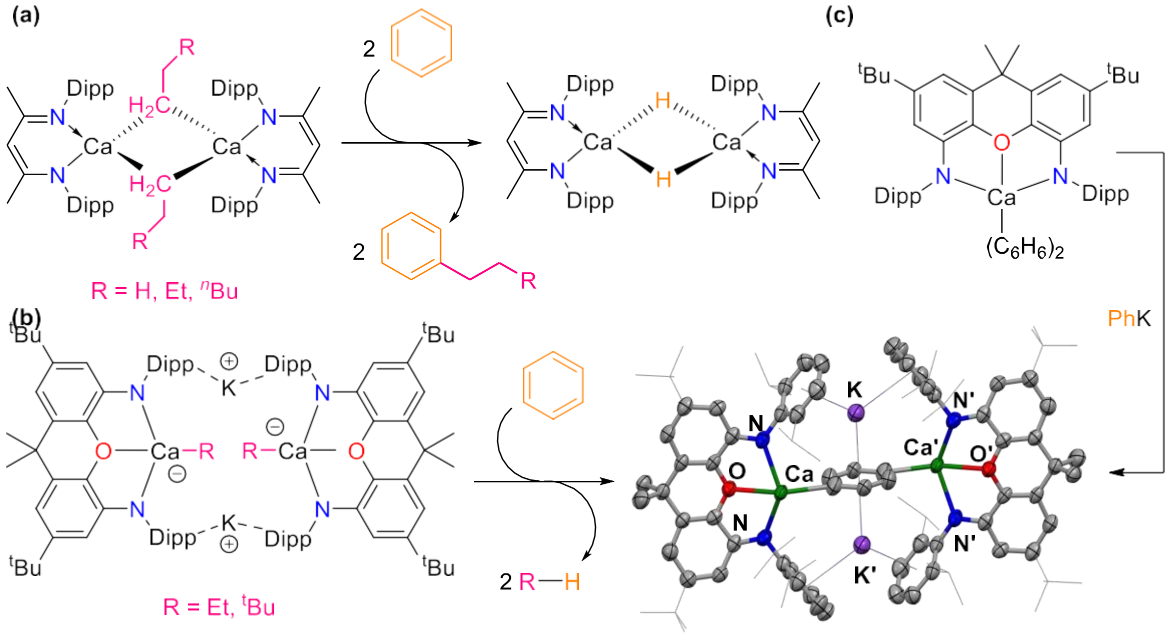

Figure 1. (a) the nucleophilic alkylation of benzene by neutral calcium alkyl complexes;[2] (b) this work – the templated two-fold deprotonation of benzene by anionic calcium alkyl complexes. Dipp = 2,4-diisopropylphenyl.

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Gotta Trap 'Em All: Capturing Anions for Hydrogen Storage

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Main group hydrides are a promising class of hydrogen storage materials, but many require high temperatures and suffer from poor reversibility.[1,2] Recent work in our group has demonstrated reversible H_2 capture and release by stabilising the hypervalent $[SiH_6]^{2-}$ anion within a supramolecular assembly containing four Lewis-acidic metal centres.[3] This lattice- like framework prevents decomposition and enables hydrogen release upon gentle heating (*ca.* 65 °C), forming $[SiH_2]^{2-}$ *via* a rare, thermally induced, four-electron reduction at silicon. Building on this foundation, this work targets the stabilisation of related all-hydrido main group anions ($[EH_n]^{m-}$, where E = Al, Ga, Ge; n/m = 0–6), which are of fundamental interest due to their novel structural and electronic properties. Concurrently, a covalently linked macrocyclic variant is being developed to enhance structural integrity in polar solvents.

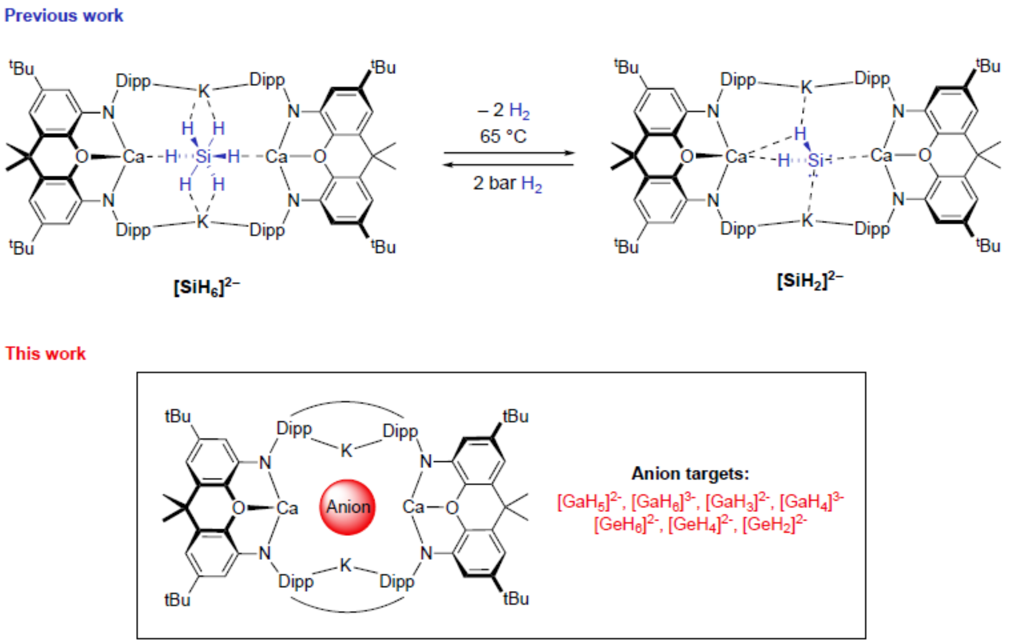

Figure 1. (top) Reversible uptake and release of H_2 by silicon anions 'trapped' within a supramolecular assembly. (bottom) Anion targets for 'trapping' within a proposed macrocycle analogue

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Binuclear Boron Compounds Supported by a Xanthene-Based Scaffold

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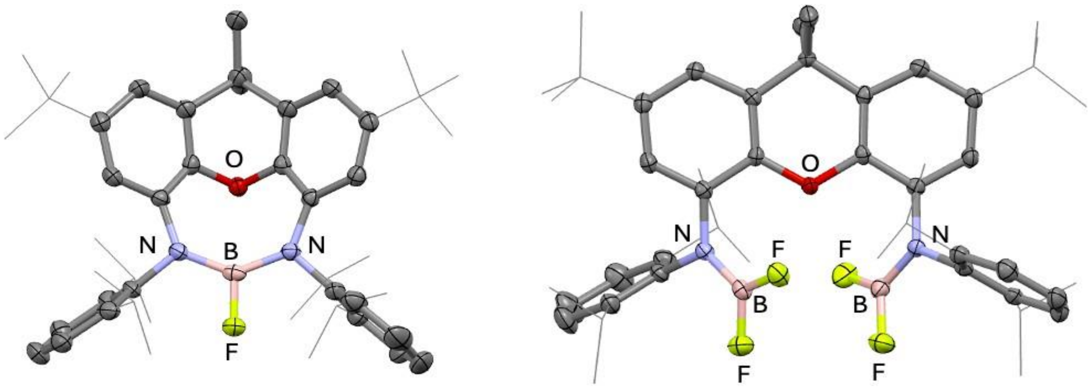
Main group compounds have shown potential as green catalysts in the activation of inert, abundant small molecules to produce value-added starting materials.[1] However, many of these compounds are highly reactive species and often require stabilisation by sterically bulky and electron-donating ligands.[2] One such example is the **NON**-ligand, known for its **N**itrogen-**O**xygen-**N**itrogen binding motif (Figure 1). This bulky, dianionic ligand has previously shown to be effective at stabilising low valent main group species, such as the first aluminium nucleophile.[3] Given the prior success within group 13, boron is a promising candidate for further investigations with the **NON** ligand.

To date, **NON** has only been reported as a dianionic, chelating ligand, such as in (**NON**)BF (Figure 1 - **1**). However, coordinating the ligand to one boron centre causes significant strain within the ligand scaffold due to the small atomic radius of boron. In recent work, we have found this strain is no longer observed when two boron centres are coordinated to the ligand (Figure 1 - **2**). In this instance, **NON** acts as a bridging ligand, a binding mode previously unseen. This binuclear system stabilises two Lewis acidic boron centres in proximity, presenting unique possibilities for further reactivity, such as small molecule activation. Further, the reduction of this compound also has the potential to yield multiply- bonded boron species.[4] Our most recent results will be presented.



1 **2**

*Figure 1. Molecular structures of mono- (**1**) and diboron (**2**) compounds using the **NON** ligand.*

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C-C Coupling in Late-Stage Ligand Functionalisation Through Low-Oxidation State Group 13 Radicals

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Ligand design is a vital part of inorganic chemistry, with the reactivity of many organometallic compounds dependent on the ligands in their coordination sphere.[1,2] However, the synthesis of the organic ligand species can often be a lengthy, multi-step process.[1,2] Late-stage functionalisation of pre-coordinated ligands can decrease the complexity of their synthesis and even allow for the formation of otherwise inaccessible species.[1,2] Low-oxidation state group 13 species provide highly reactive species through which intricate late-stage ligand functionalisation can be achieved.[3]

This work describes the use of transiently generated boron(II) and aluminium(II) radicals in the functionalisation of diamido aryl ether ligands.[4] Both have been shown to completely remove the oxygen from the ether linkage, resulting in the formation of a terminal B/Al-O bond and a new carbon-carbon bond (Figure 1). One powerful example of this is when using xanthene-based ligands, which results in the late-stage formation of 4,5-substituted fluorene units; challenging moieties to synthesise via current chemical routes. Further reaction scope and mechanistic studies will be discussed.

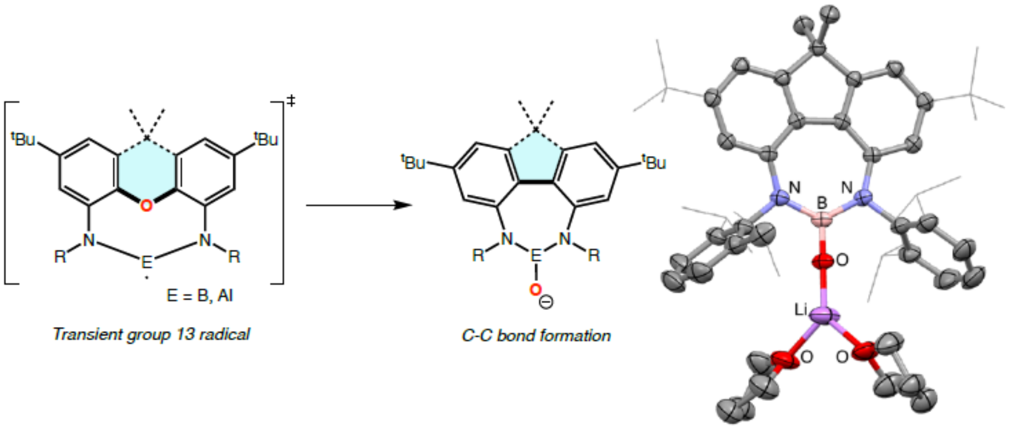

Figure 1. C-C bond formation from diaryl ethers mediated by low-oxidation state group 13 complexes (left) and the solid-state structure of the 4,5-diamido-substituted fluorene-based boryloxy product (right).

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Structure and Formation of the Parent Silylone Dianion

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Silylones are rare, divalent, formally silicon(0) compounds, the heavy analogues of carbones.[1] Recent work within the group has reported a molecular hexahydridosilicate dianion within a supramolecular framework.[2] Heating a solution of the $[SiH_6]^{2-}$ complex eliminates two equivalents of hydrogen gas, affording the remarkable $[SiH_2]^{2-}$ silylone dianion stabilised within the supramolecular assembly. Through computational and experimental methods, this dianion is shown to be two hydrido moieties ligating a Si(0) atom with two lone pairs, isoelectronic to traditional, neutral silylones (and perhaps even water).[3],[4] The mechanism of formation is modelled using density functional theory (DFT) and compared with experimental kinetics data, showing unprecedented autocatalysis, and comparative methods are used to investigate its unique electronic structure.

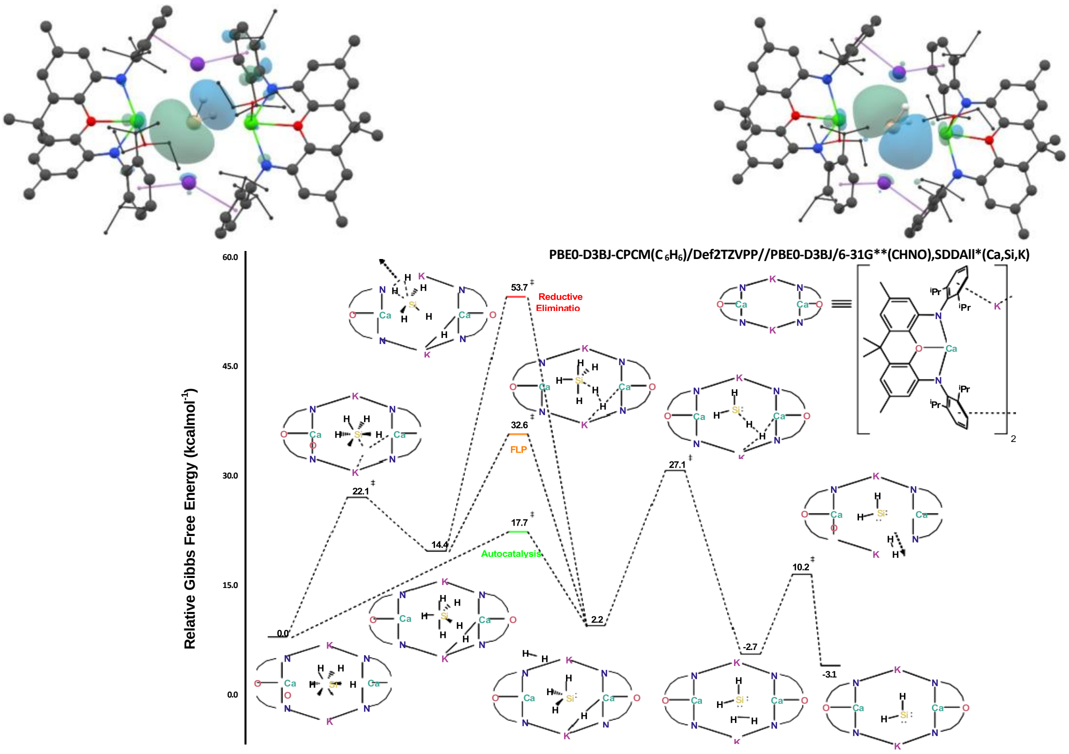

Figure 1. Top (left to right): Natural Molecular Orbital (NLMO) of the sp^2-like lone pair of $[SiH_2]^{2-}$; NLMO of the p-like lone pair of $[SiH_2]^{2-}$; Bottom: DFT calculated reaction mechanism for $[SiH_6]^{2-}$ to $[SiH_2]^{2-}$.

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Reactivity Study of Silyl-substituted Alanes with Isocyanides

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Organoaluminium compounds have garnered significant attention due to their high reactivity toward small molecules, contributing to the advancement of commercially relevant aluminum-based catalysts.[1] In contrast to the well-studied trialkylalanes, the reactivity of trisilylalanes remains largely unexplored.[2,3] In this presentation, we report the investigations into the reactivity of $Al(SitBu_2Me)_3$.[4] A series of isocyanides were examined, leading to the isolation of three isocyanide–trisilylalane complexes, $RNC{\rightarrow}Al(Si^tBu_2Me)_3$ (R = *tert*-butyl, xylyl, adamantyl). Additionally, we explored the reactions of the corresponding radical anion with various isocyanides. In each case, cleavage of the isocyanide fragment was observed, yielding the compound (18-crown-6)$KNC{\rightarrow}Al(Si^tBu_2Me)_3$.

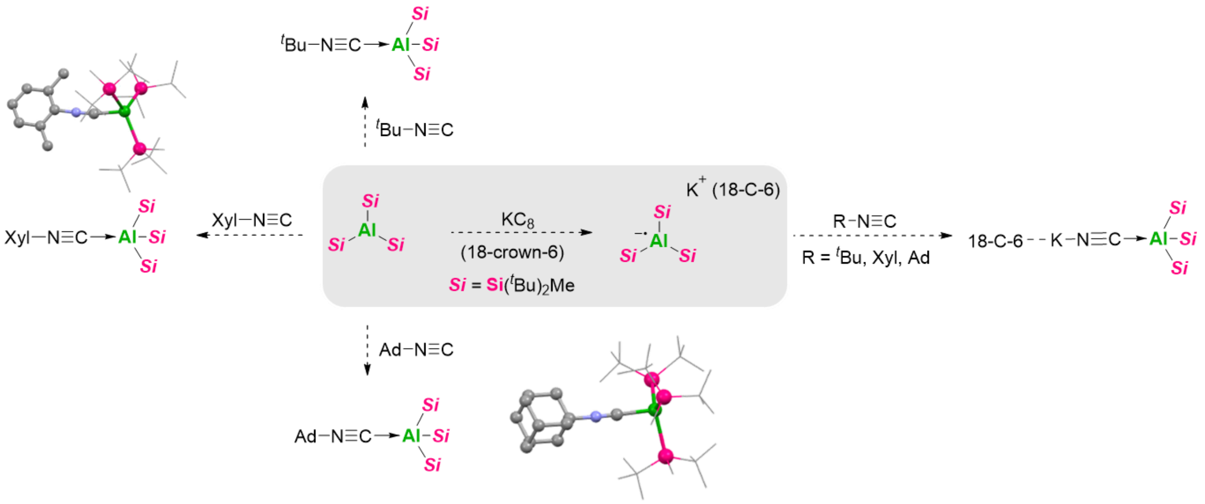

Figure 1. Reactions of silyl-substituted aluminium compounds with various isocyanides.

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Carbon-Carbon Bond Activation and Functionalisation by Mg Complexes

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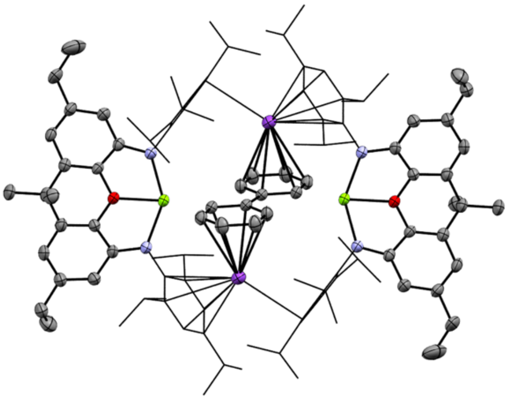
Carbon-carbon (C–C) bonds are ubiquitous, making up the internal scaffold of most organic molecules. Selective cleavage of C–C bonds is of fundamental importance in organic chemistry and the repurposing of hydrocarbon feedstocks.[1] Owing to the strong, non-polar nature of the C–C bond, efforts to activate and functionalise C–C bonds are often dependent on late transition metal complexes.[2] The use of earth abundant, main-group metal complexes as reagents and, in some cases, catalysts for C–C bond activation is an emerging field in organometallic chemistry.[3] This talk will highlight some of the key challenges and opportunities for chemists targeting C–C bond activation, then discuss our research efforts using soluble magnesium reagents to activate and functionalise C–C bonds in strained ring systems.[4-5]



- **Catalytic C–C Functionalisation**
- **DFT Calculations**
- **X-ray Crystallography**

Figure 1. C–C bond activation of biphenylene by a magnesium(I) complex.

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Synthesis and Reactivity of Lanthanide (II) Hydrides

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The synthesis of well-defined, discrete lanthanide (II) hydrides remain uncommon in the literature, with most examples involving ytterbium.[1] Recently, successful synthesis of samarium and europium hydride species have been reported, the latter including a range of bulky *β*-diketiminate (BDI) ligand frameworks.[2] Utilising a similar BDI framework, we have synthesised a novel ytterbium (II) hydride complex. Preliminary stoichiometric reactivity of this species have provided structures analogous to literature examples. Application of this ligand to a Sm (II) ion poses a greater challenge, due to the highly negative Sm^{3+}/Sm^{2+} reduction potential.[3] Despite this, we have successfully synthesised and fully characterised a BDI samarium (II) alkyl species. Utilising this reagent to generate the corresponding samarium (II) hydride has been accompanied by the four-electron reduction of aromatic solvents. Nevertheless, this remarkably strong reducing power provides scope for future reactivity studies, particularly involving its application as a reducing agent.

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Generation of Novel Tellurium Carbyne complexes.

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Carbonyl ligands ([M]CO) exist throughout organometallics and are often employed due to their potent pi donor character. The use of the heavier chalcogens in place of the oxygen atom has been an area of significant interest in recent history, in particular the use of sulfur to form thiocarbonyls.

The use of these heavier chalcogens allow for significant modifications that often cannot be performed on traditional carbonyls. While this interest has been partially extended to selenium, tellurium carbonyls have remained underexplore, largely due to the difficulties associated with their synthesis. despite these difficulties, there exist numerous avenues through which tellurocarbynes can be produced often resulting in connectivity unseen in the lighter chalcocarbynes.

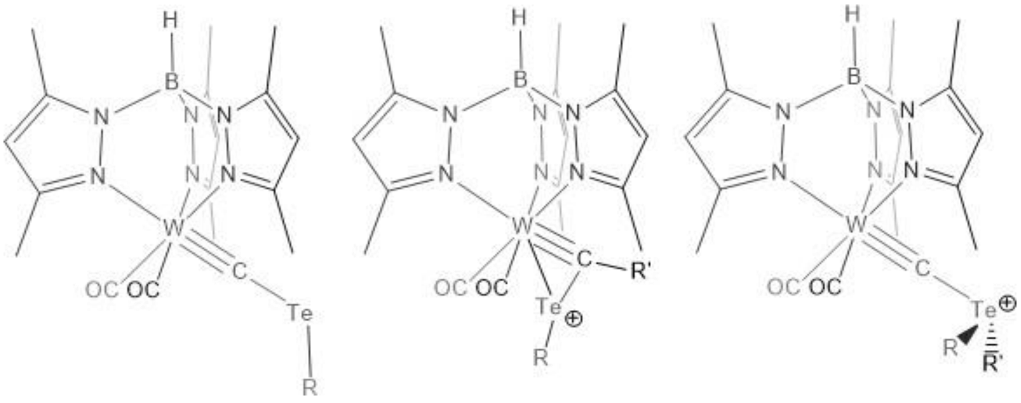

Figure 1. the 3 main forms of tellurocarbynes observed, the tellurireniocarbyne, the tellureniocarbyne and the telluroniocarbyne

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Antibiotics Revitalised: Therapeutic Potential of Organogallium (III) and Organoindium (III) Quinolonate Complexes

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Antimicrobial resistance (AMR) is an evolutionary phenomenon in which microorganisms stop responding to prescribed medicine. The nosocomial ESKAPE pathogens (*E. faecium, S. aureus, K. pneumoniae, S. pneumonia, A. baumannii, P. aeruginosa, E. spp*.) comprise most AMR associated deaths, accounting for 900,000 of those reported in 2019.[1] Among the ESKAPE pathogens, gram- negative *A. baumannii* and *K. pneumoniae* demonstrate some of the highest levels of resistance. [2,3] Their burden on public health is significant. Between 40 and 95% of hospital-acquired and ventilator- associated pneumonia is linked to *A. baumannii*, with mortality rates of approximately 40%.[4] *K. pneumoniae* accounts for 6-17% of hospital-acquired infections globally, undermining clinical management plans and prolonging hospital stays.[5]

Gallium and indium are group 13 metals which preferentially exist in the +3-oxidation state.[6] Being redox inert under physiological conditions and chemically alike iron, they may hijack bacterial iron uptake mechanisms.[6] While gallium salts already demonstrate antimicrobial potency, they are prone to hydrolysis.[7] Alternative ligand classes require exploration. Quinolones are broad-spectrum antibiotics for which *A. baumannii* and *K. pneumoniae* have demonstrated resistance. [8,9]

Previously, we identified that complexation of inactive quinolones with organogallium motifs lead to antibiotic revitalisation toward MDR *K. pneumoniae*.[10] Herein, we have expanded the scope to a larger range of quinolone antibiotics to identify structure activity relationships involved with small atomic changes. Additionally, the use of organoindium will be explored. Suitable complexes will undergo biological analysis against *A. baumannii* and *K. pneumoniae*.

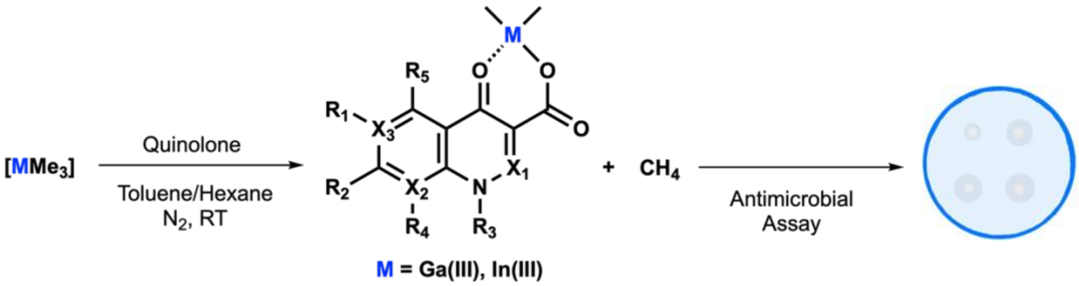

Figure 1. Synthetic method for organogallium (III) and organoindium (III) quinolonate complexes.

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Selective C-F Activation and Functionalisation of Polyfluorinated 2-Phenylpyridines

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Due to its small size and unique properties, the fluorine atom has been described as "a small atom with a big ego".[1] Despite its presence in 20% of active pharmaceuticals, 30% of agrochemicals, and commonly used materials like non-stick Teflon pans, few naturally occurring fluorinated species are known.[2] Moreover, the strength of the carbon–fluorine (C–F) bond presents significant challenges for both synthetic modification and environmental degradation.[2-3] Traditionally, the functionalisation of fluorinated compounds via C-F activation has been achieved using precious transition metals. However, the inherent toxicity and high cost of these materials necessitate the development of alternative methods.[4] Strategies involving main group metals in C-F activation are an emerging area of chemistry, showcasing promising activity with earth-abundant group 1 and 2 metals.[3, 5]

Recently, the Blair Group has explored the functionalisation of fluorinated imine-based substrates. Their research investigated the differences in reactivity of these substrates when using monometallic sodium and magnesium bases, as well as the synergistic effects of heterobimetallic sodium magnesiates.[6] Building on this research, we have expanded our investigation to include polyfluorinated 2-phenylpyridines. In this study, we report successful regioselective *ortho* C-F activation using magnesium alkyl and amido bases. Notably, we observed unexpected reactivity from magnesium bis((trimethylsilyl)methyl), which resulted in a homocoupled product (*Figure 1*).

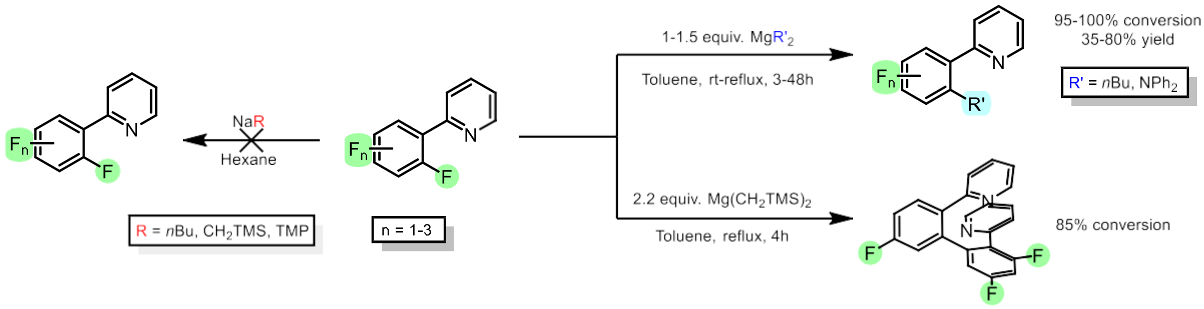

Figure 1. Reactivity of 2-phenylpyridines by Na and Mg alkyls and amides and C-F activation.

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Synthesis and Reactivity of a Mg(0) Compound

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Low oxidation state magnesium(I) compounds have been shown to act as homogeneous reducing agents since their discovery in 2007.[1] It wasn't until 2021 that the first, and to date only, magnesium(0) compound was reported by Harder and co-workers.[2] Studies into the onward reactivity of this Mg(0) complex remain underexplored.[3][4] This gap in the literature presents an opportunity for a new Mg(0) system that may provide differing reactivity and applications. In this poster, we report the synthesis of a Mg(0) complex stabilised by a new super bulky β-diketiminate ligand (Figure 1.). Onward reactivity with metal carbonyl complexes and SF_6 is highlighted. This work aims to expand the understanding and applicability of a Mg(0) compound.

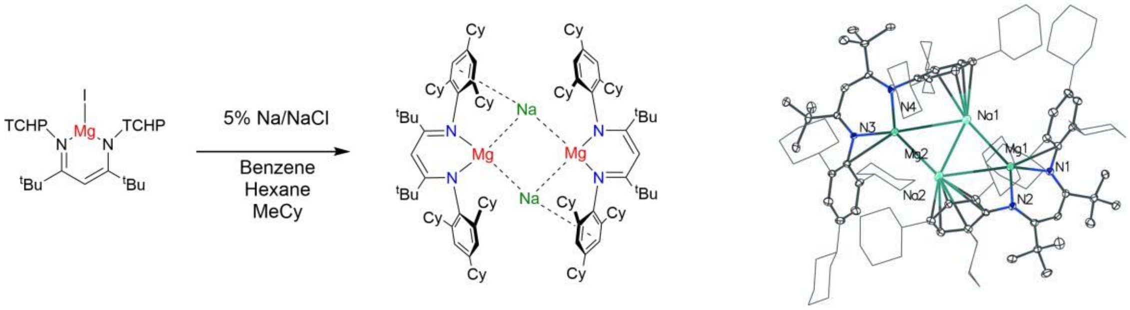

Figure 1. Reduction of $^{TCHP}BDI^{*}MgI$ to a magnesium zero compound ($\{[^{TCHP}BDI^{*}Mg^{-}][Na^{+}]\}_2$). Molecular structure of ($\{[^{TCHP}BDI^{*}Mg^{-}][Na^{+}]\}_2$, thermal ellipsoids shown at 30% probability; hydrogen atoms omitted for clarity.

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