CONFERENCE PROGRAM

4 - 7 DECEMBER 2023
CANBERRA, AUSTRALIA

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OZOM 14

14th Australasian Organometallic Chemistry Meeting

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Welcome Message

The Organising Committee warmly welcomes you to the 14th Australasian Organometallics Meeting (OZOM14) at the Australian National University in Canberra, ACT. Following the initial OZOM conference at the University of New England in Armidale in 1993, symposia were held in Adelaide (2004), Gippsland (2006), Canberra (2008), UNSW (2010), Hobart (2011), Wellington (2013), Magnetic Island (2014), Sydney (2015), Otago (2017), Perth (2018), Melbourne (2019) and Cairns (2022). OZOM14 sees the conference return to ANU for the first time in 15 years.

In maintaining the previous tradition of these successful meetings, OZOM14 will focus on presentations from students and early career researchers and be supported by a small number of invited distinguished national/international speakers. The conference will include all of the various aspects of fundamental and applied organometallic chemistry, including:

- Organometallic chemistry of main group, transition metal and lanthanoid elements
- Structure and reactivity
- Catalysis
- Asymmetric synthesis
- Theoretical chemistry
- Bio-organometallic chemistry
- Application of organometallic complexes in life science
- Application of organometallic complexes in materials science
- Synthetic chemistry
- Physical properties of organometallic complexes, including photophysical and electronic properties

We wish to acknowledge the generosity of the RACI and our sponsors, whose support has enabled this conference to take place: EzziVision, AXT, ANU Research School of Chemistry, MDPI (Photochem and Molecules) and the Royal Society of Chemistry (Dalton Transactions and Chemical Communications).

We hope you enjoy this opportunity for the Australasian organometallics community to meet and discuss the exciting chemistry going on in our community in a friendly and social setting.

Jamie Hicks and Annie Colebatch

OZOM14 Organising Committee

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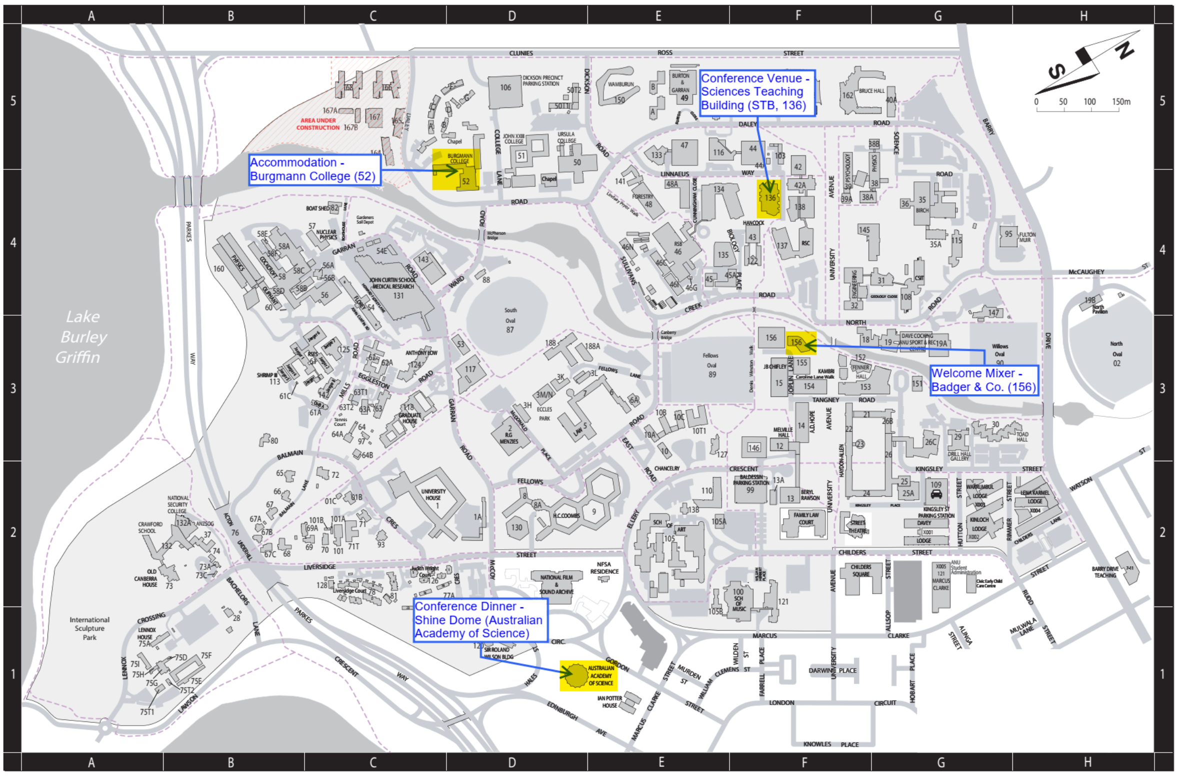
Program

	Monday 4 Dec	Tuesday 5 Dec	Wednesday 6 Dec	Thursday 7 Dec
		9:00 - 10:20 Chair: Fabian Kallmeier	**9:00 - 10:20 Chair: Rosemary Avery**	**9:00 - 10:20 Chair: Mahbod Morshedi**
9:00		Keynote lecture - Véronique Guerchais	Keynote lecture - George Britovsek	Keynote lecture - Franck Camerel
9:20				
9:40		Mahbod Morshedi	Zack Avery	Matthew Evans
10:00		Charles Soukup	Miracle Ekavhiare	Vuyelwa Ngwenya
10:20		**Break 10:20 - 10:50**	**Break 10:20 - 10:50**	**Break 10:20 - 10:50**
		10:50 - 12:30 Chair: Rebekah Duffin	**10:50 - 12:30 Chair: Matthew Evans**	**10:50 - 12:30 Chair: Peter Hall**
10:50		Nicholas Solomon	Sumiyyah Hameed	Tien Nguyen
11:10		Claudia Giarrusso	Andrea O'Reilly	Md Abdul Halim
11:30		Jingyun Wu	Guochen Bao	George Smith
11:50		Tylah Sweet	Fabian Kallmeier	Dejan Mizdrak
12:10		Tom Nicholls	Neelofur Jaunnoo	Huan Wang
12:30		**Lunch 12:30 - 2:00**	**Lunch 12:30 - 2:00**	Awards and closing remarks 12:30 - 1:00
		2:00 - 4:00 Chair: Ryan Kirk	**2:00 - 3:20 Chair: Thomas Nicholls**	
2:00		Loïc Lemiègre	Emma Gaschk	
2:20		Libing Fu	Ryan Kirk	
2:40	Registrations (STB) 2:30 - 3:50	Stephen Cameron	Jeremy Mullins	
3:00		Zhifang Guo	Vidushi Vithana	
3:20		Christopher Barnett	**Break 3:20 - 3:50**	
3:40	Opening remarks 3:50 - 4:00	Aidan Matthews	**MDPI Afternoon Tea**	
4:00	**4:00 - 5:00 Chair: Jamie Hicks**	Poster session (STB) 4:00 - 6:00	**3:50 - 4:50 Chair: Annie Colebatch**	
4:20	Plenary lecture - David Liptrot		Plenary lecture - Sinead Keaveney	
4:40				
5:00	Welcome mixer (Badger) 5:00 - 6:30			
			Conference dinner (AAS Shine Dome) 6:30 - 9:30	

Conference Venues



The conference will be held at the Australian National University in Canberra.

Conference registration and all talks and poster presentations will take place on the **third floor of the Sciences Teaching Building (STB), Building 136, Linneaus Way.**

The conference welcome mixer will take place at **Badger & Co., Building 156, Kambri, University Avenue.**

The conference dinner will be held at the **Australian Academy of Science Shine Dome, Gordon Street.**

The closest place to the conference venue to get food and drinks is **Kambri, University Avenue** (the same area as the welcome mixer venue Badger & Co.). Here you will find numerous food venues and cafes along University Avenue and Joplin Lane.

If you are staying in the conference accommodation, this is at **Burgmann College, Building 52, Daley Road.**

Detailed Program

Monday 4 December	
2:30 – 3:50	Registration (STB, third floor)
3:50 – 4:00	Opening remarks
4:00 – 5:00	**Plenary Lecture: David Liptrot, University of Bath** NHC-supported Copper(I) Main Group Complexes for Synthesis and Catalysis *Chair: Jamie Hicks*
5:00	Welcome Mixer: Badger & Co, Kambri, University Avenue

Tuesday 5 December	
9:00 – 10:20 Session Chair: Fabian Kallmeier	
9:00 – 9:40	**Keynote Lecture: Véronique Guerchais, Université de Rennes, CNRS** Luminescent cyclometalated complexes (Pt, Ir) and catalytic post-modification: C-H bond arylation and annulation
9:40 – 10:00	Mahbod Morshedi – *Bigger is Better!*
10:00 – 10:20	Charles Soukup – *The Synthesis, Characterisation, and Anti-leishmanial Activity of Tri-aryl Antimony(V) Hydroxamates*
10:20 – 10:50 Break	
10:50 – 12:30 Session Chair: Rebekah Duffin	
10:50 – 11:10	Claudia Giarrusso – *Lewis base alterations of Ag(I) complexes and their catalytic potential*
11:10 – 11:30	Nicholas Solomon – *Understanding and enhancing nickel catalysed cross-coupling reactions: insight from synthesis and a novel method of kinetic analysis*
11:30 – 11:50	Jingyun Wu – *Synthesis of bimetallic complexes of an unsymmetric PNNN expanded pincer ligand*
11:50 – 12:10	Tylah Sweet – *Synthesis and Reactivity of the Indyl Anion*
12:10 – 12:30	Tom Nicholls – *Electrochemical Synthesis of Gold-N-Heterocyclic Carbene Complexes*
12:30 – 2:00 Lunch	
2:00 – 4:00 Session Chair: Ryan Kirk	
2:00 – 2:20	Loïc Lemiègre – *How a boron atom impacts organogelation properties*
2:20 – 2:40	Libing Fu – *The controlled synthesis of lanthanide complexes and their biomedical applications*
2:40 – 3:00	Stephen Cameron – *Nitrogen Fixation by Highly Structured Phosphine Containing Transition Metal Complexes*
3:00 – 3:20	Zhifang Guo – *Exploring the reactivity of lanthanoid pseudo-Grignard reagents*
3:20 – 3:40	Christopher Barnett – *3D printed device to test electrochemical nitrogen fixation*
3:40 – 4:00	Aidan Matthews – *An Acyclic Aluminyl Anion: Breaking Bonds, Conflicting Chelation*
4:00 – 6:00	Poster Session

Wednesday 6 December	
9:00 – 10:20 Session Chair: Rosemary Avery	
9:00 – 9:40	**Keynote Lecture: George Britovsek, Imperial College London** Light-Driven Oxygen Insertion Reactions in Late Transition Metal Alkyl Complexes
9:40 – 10:00	Zack Avery – *Improving the Synthetic Accessibility of Platinum(II) Cages*
10:00 – 10:20	Miracle Ekavhiare – *C-F activation adventures with mono- and bi-metallic main group bases*
10:20 – 10:50 Break	
10:50 – 12:30 Session Chair: Matthew Evans	
10:50 – 11:10	Sumiyyah Hameed – *Dimethylgallium(III) complexes of indeno[1,2]quinoline derivatives as antibacterial agents.*
11:10 – 11:30	Andrea O'Reilly – *Pinacol Cross-Couplings Promoted by an Aluminyl Anion*
11:30 – 11:50	Guochen Bao – *Lanthanide complex for biomedical applications*
11:50 – 12:10	Fabian Kallmeier – *Increasing the Reactivity of Anionic Low-Valent Aluminium Compounds*
12:10 – 12:30	Neelofur Jaunnoo – *Aluminium-based Lewis Acid Catalysts for Enantioselective Organic Transformations*
12:30 – 2:00 Lunch	
2:00 – 4:00 Session Chair: Thomas Nicholls	
2:00 – 2:20	Emma Gaschk – *Multistate Switching of Some Ruthenium Alkynyl and Vinyl Spiropyran Complexes*
2:20 – 2:40	Ryan Kirk – *The Organometallic Potential of Arsoles*
2:40 – 3:00	Jeremy Mullins – *Reductive Metallation of Dendralenes and Myrcene using Dimagnesium(I) Compounds*
3:00 – 3:20	Vidushi Vithana – *RE(III) 3-Furoate Complexes: Synthesis, Structure, and Corrosion Inhibiting Properties*
3:20 – 3:50 Break – MDPI Afternoon Tea	
3:50 – 4:50	**Plenary Lecture: Sinead Keaveney, University of Wollongong** Development of new catalytic reactions using a combined experimental and computational approach
6:30	Conference Dinner, AAS Shine Dome

Thursday 7 December	
9:00 – 10:20 Session Chair: Mahbod Morshedi	
9:00 – 9:40	**Keynote Lecture: Franck Camerel, Université de Rennes 1** Metal-bis(dithiolene) complex as a Swiss Army knife for many applications
9:40 – 10:00	Matthew Evans – *Synergy in the s-Block: Alkali Metal Magnesiates for Small Molecule Activation*
10:00 – 10:20	Vuyelwa Ngwenya – *Ni(II) pincer complexes for the electrocatalytic production of* H_2
10:20 – 10:50 Break	
10:50 – 12:30 Session Chair: Peter Hall	
10:50 – 11:10	Dat Tien Nguyen – *Synthesis of terphenyl-based bis(anilido) alkaline-earth metal complexes: Investigation of arene-metal interactions*
11:10 – 11:30	Md Abdul Halim – *Exploring the reactivity of lanthanoid pseudo-Grignard reagents*
11:30 – 11:50	George Smith – *Synthesis and Reactivity of Novel Group 14 – Aluminium Heterobimetallic Complexes*
11:50 – 12:10	Dejan Mizdrak – *An NMR method to measure stretched C-H bond lengths*
12:10 – 12:30	Huan Wang – *Exceptional Hyperpolarizabilitie: Molecular Symmetry and Solution-Phase Structure of Ruthenium Alkynyl Porphyrin Triads/Pentads*
12:30 – 1:00	Awards and closing remarks

Poster Presentations

Poster Presentations		
Poster	**Presenter**	**Presentation Title**
1	Fredric Paul	Two-photon absorption properties of triarylamine-based multipolar 1,1,4,4-tetracyanobutadienes: the effect of ferrocenyl peripheral substituents
2	Fredric Paul	Electronic Absorption, Emission, and Two-Photon Absorption Properties of 2,4,6-Triphenyl-1,3,5-Triazines
3	Anna Bielawska	Metal (Au, Pd, Pt) nitroimidazole complexes as potential antitumor metallodrugs
4	Krzysztof Bielawski	Synthesis and cytotoxic activities of novel transition metal complexes with berenil and nitroimidazole
5	Ameen Eradiparampath	Novel and Convenient Synthesis of Copper Formamidinates
6	Pratima Sharma	Experimental and Theoretical Investigations on Cu and Ni Complexes of the Anti-diabetic Drug Metformin Hydrochloride
7	Pradnya Pratap Patil	Unlocking the Potential of Electrochemistry: Fabrication and Characterisation of Lanthanum Oxide Nanoflakes for Advanced Resistive Switching Applications.
8	Rebekah Duffin	Sb(V) aryl anthraquinone complexes: Enhanced stability and antileishmanial activity of a fluorescent anthracycline system
9	Rosemary Avery	Hydrazone based coordinatively unsaturated metallocages
10	David Shooto	Synthesis of metal organic frameworks of copper and cobalt and their application in removing lead ions from water
11	Peter Hall	Bimetallic 1,8-diazaanthracene complexes for CO_2 electroreduction
12	Caitlyn Whan	Synthesis and characterisation of organometallic gallium(III) compounds.
13	Zhan Yang Kenneth Lye	18F-labelling of difluoro- and trifluoromethyl groups via FLP-mediated selective C-F activation; towards the synthesis of new radiotracers from off-the-shelf drugs
14	Liam Pascoe	Reduction chemistry of group 13 dipyrromethene compounds
15	Michael Gardiner	(parenting) tools for your problem children (a.k.a. crystals)
16	Emily Nahon	Investigations into N-O-N Chelating Ligands in the Stabilisation of Boron(I) Anions

Poster Presentations		
Poster	**Presenter**	**Presentation Title**
17	Jessica Porter	Oxidative Addition of Alkyl Halides at a Group 14 Centre
18	Ryan Huo	Synthesis and Reactivity of the $[SiH_6]^{2-}$ Dianion Stabilised within a Supramolecular Assembly
19	Marcus Korb	Charge Transfer in Ferrocenyl-Functionalized Cyclobutene Macrocycles
20	Marcus Korb	Overcoming the Steric Limitations of the Alkyne/Vinylidene Rearrangement
21	Callum Inglis	Lowering the LUMO Energy of Aluminyl Anions
22	Mia Patroni	Flip the Switch
23	Li Feng Lim	Low-Valent Group 12 Chemistry: A Radical Approach
24	Hannah Nandan	Towards a mixed valence dicopper complex
25	Daniel Mazzucato	Quantum Interference in Mixed-Valence Complexes: Tuning Electronic Coupling Through Substituent Effects
26	Thokozani Xaba	Green synthesis of MS nanoparticles and the preparation of MS–chitosan nanocomposites for the removal of Cr(VI) ion from wastewater
27	Bandar Babgi	Enhancing Anticancer Properties and Biomolecule-Binding of Metal(II) (Pd/Pt) Complexes by Modifying Tridentate Ligands
28	Lloyd Kellermann	Palladium-catalysed cycloaddition reactions: Synthesis of 5,6-membered spirocycles and an exploration of a novel 1,4-silyl dipole precursor
29	Caitlin Lindsay	Resurrecting the Forgotten Kin: Coordination Chemistry of Stiboles
30	Marcus Sceney	C-H, Si-H, and C-F Abstraction with an Extremely Electron Poor I(III) Reagent
31	Jason Bennetts	Structural verification and new reactivity for Stang's reagent, [PhI(CN)][OTf]
32	Lachlan Barwise	Beating a dead horse (or how to resurrect a horse with sufficient beating)
33	Chi Canty	Synthesis, characterisation and reductions of bulky BODIPY analogues

Abstracts

1. Plenary Lecture Abstracts

2. Keynote Lecture Abstracts

3. Oral Presentation Abstracts

4. Poster Presentation Abstracts

NHC-supported Copper(I) Main Group Complexes for Synthesis and Catalysis

David J Liptrot[a,*]

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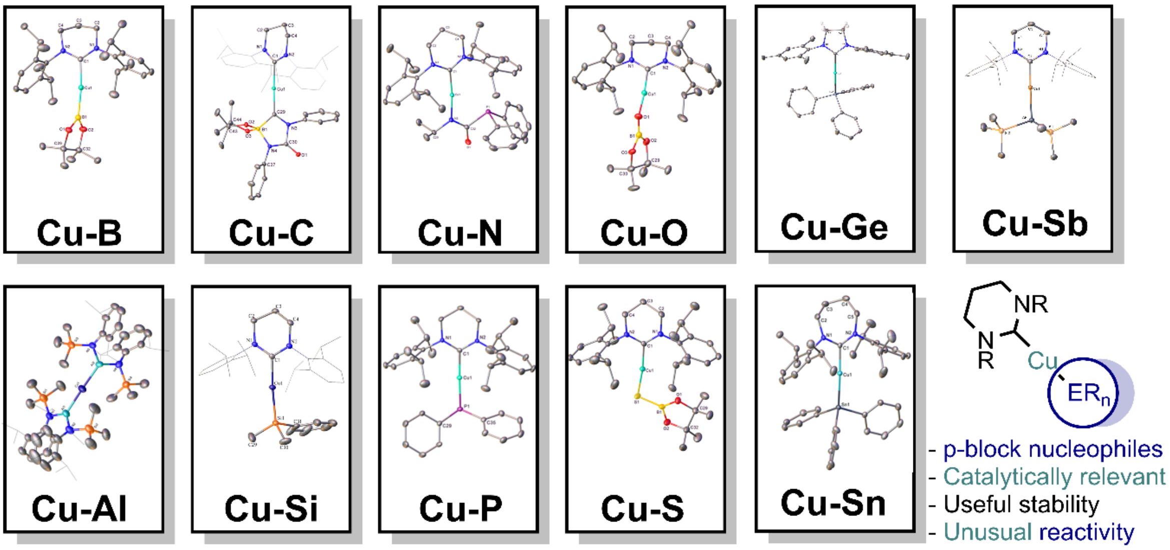
Inclusion of “inorganic” p-block elements in functional materials and molecules has profound potential to significantly influence their properties. Despite the promise presented by these inclusions, methods to synthesise main group centred molecules are underdeveloped relative to their more carbon-centric cousins. Copper(I) catalysis has an enduring pedigree in facilitating controlled organic transformations, but has found less application in the rational assemblage of main-group element-element bonds. In this talk, we will discuss our contributions to the completion of a “p-block” of catalytically relevant copper-element bonds and the applications of such moieties in catalytic and stoichiometric transformations.

Focussing on N-heterocyclic carbenes (NHCs), including ring-expanded NHCs, we have synthesised a range of ligand supported copper(I) boryls, silyls, germyls, stannyls, phosphides and sulfides. These compounds are generally generated via σ-bond metathesis reactions and, with few exceptions, form as linear, two-coordinate monomers. They consistently act as sources of p-block nucleophiles which attack electrophilic organic, and inorganic substrates to give rise to new element-element bonds. These bond forming steps can also be rendered catalytic giving access to p-block/p-block cross-coupling chemistry.

During this talk, we will discuss the reactivity of copper(I) hydrides, boryls, silyls, germyls, stannyls, phosphides and stibnides supported by NHCs towards organic and organometallic reagents. These species provide a platform for exquisite control in the introduction of main group fragments into molecules which can provide both novel structures and mechanistic insight.



- p-block nucleophiles
- Catalytically relevant
- Useful stability
- Unusual reactivity

Figure 1. A selection of NHC-supported copper(I) element bonds

Development of new catalytic reactions using a combined experimental and computational approach

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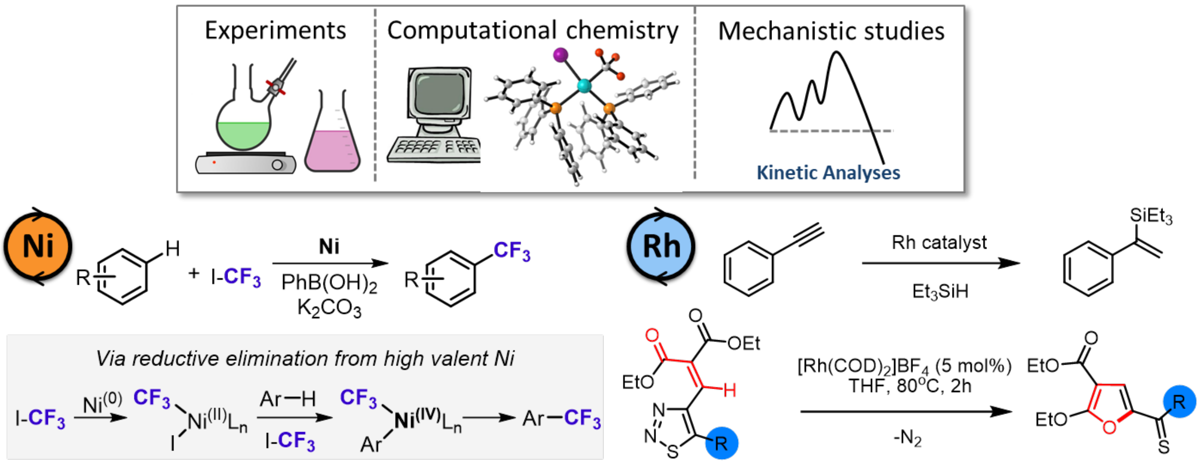
Complex organic compounds are ubiquitous in the pharmaceutical, agrochemical and materials chemistry industries, with these compounds often featuring a diverse range of functional groups. To meet the continuing demand for efficient, sustainable and selective strategies to access complex organic compounds, our toolbox of synthetic methods needs to continually expand. To address these challenges, my research focuses on applied organometallic catalysis and photocatalysis, to allow new synthetic methods to be developed. In particular, I am interested in rationally designing catalysts to facilitate challenging and high-value chemical transformations, with detailed mechanistic studies used to guide catalyst design, to understand trends in chemical reactivity and to direct the choice of experimental parameters. We use a range of different mechanistic tools to provide unique insight into reaction mechanisms, including kinetic analyses, computational studies and a suite of X-Ray based techniques. This presentation will focus on our recent work where combined experimental and computational studies have been used to develop new reactivity, such as C-H trifluoromethylation,[1] nickel-catalysed cross coupling reactions,[2] denitrogenation reactions of thiadiazoles[3,4] and photocatalysed oxidation reactions.[5-6]



References

[1] Solomon, N. S. D.; Bhadbhade, M.; Tian, R.; Keaveney, S. T,. *ChemCatChem* **2022**, *14*, e202200918.
[2] Jacobs, E.; Keaveney, S. T. *ChemCatChem* **2021**, *13*, 637
[3] Tokareva, M. A.; Pernik, I.; Lewis, W.; Messerle, B. A.; Glukhareva, T. V.; Keaveney, S. T., *ACS Catal.* **2022**, *12*, 5574
[4] Tokareva, M. A.; Pernik, I.; Messerle, B. A.; Glukhareva, T. V.; Keaveney, S. T., *Catal. Sci. Technol.* **2023**, *13*, 2772
[5] Wang, D.; Malmberg, R.; Pernik, I.; Prasad, S. K. K.; Roemer, M.; Venkatesan, K.; Schmidt, T. W.; Keaveney, S. T.; Messerle, B. A., *Chem. Sci*. **2020**, *11*, 6256
[6] Wang, D.; Pernik, I.; Keaveney, S. T.; Messerle, B. A., *ChemCatChem* **2020**, *12*, 5091

Luminescent cyclometalated complexes (Pt, Ir) and Catalytic post-modification: C-H bond arylation and annulation

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Over the last few decades, transition metal-catalyzed C-H bond functionalizations of (hetero)aromatics have emerged as powerful synthetic tools, obviating the need for laborious substrate pre-activation procedures. Nevertheless, a significant challenge still persists in this field: extending this approach to enable direct functionalization of metalated ligands within photo-active metal complexes,

Furthermore, the luminescence properties of cyclometalated Ir(III) complexes rely on strategic molecular design and therefore, readily access to novel functionalized C^N ligands is a crucial and defining step towards efficient luminescent complexes. Consequently, there is a strong demand for the development of synthetic methods aimed at modifying chelated C^N-ligands enhancing the brightness iridium(III) complexes and/or to fine-tuning their photophysical properties.[1,2]

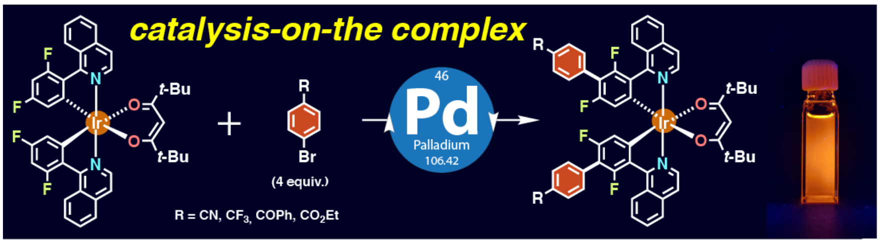

Figure 1. Post-modification via Pd-catalysed C-H bond arylation of Ir(III) complexes

Our "*catalysis-on-the-complex*" strategy[3] based on C-H bond arylation simplifies and, more importantly, provides a new tool for accessing Ir(III) complexes decorated with target functions that are essential for their applications in optoelectronics and bio-imaging.

Furthermore, we will show the impact of incorporating a polarizable, π-delocalized, and bulky substituent on the phosphorescent characteristics of *N^C^N*-(1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene)Pt(II) complexes.

[1] R. Boyaala, R. Touzani, T. Roisnel, V. Dorcet, E. Caytan, D. Jacquemin, J. Boixel, V. Guerchais, H. Doucet, J.-F. Soule, *ACS Catal.* **2019**, *9*, 1320.
[2] R. Boyaala, M. Peng, W.-S Tai, R. Touzani, T. Roisnel, V. Dorcet, Y. Chi, V. Guerchais, H. Doucet, J.-F Soulé,. *Inorg. Chem*. **2020**, *59*, 13898.
[3] M. Peng, J. Lin, W. Lu, T. Roisnel, V. Guerchais, H. Doucet, J.-F. Soule, *Chem. Eur. J.* **2021**, *27*, 12552.
[4] A. Colombo, G. De Soricellis, F. Fagnani, C. Dragonetti, M. Cocchi, B. Carboni, V. Guerchais, D. Marinotto, *Dalton Trans***. 2022,** *51***,** 12161.

Light-Driven Oxygen Insertion Reactions in Late Transition Metal Alkyl Complexes

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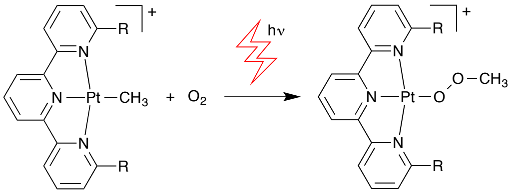
The use of O_2 as an oxidant of late transition metal alkyl complexes constitutes an important step in the Shilov reaction: the direct platinum-catalysed oxidation of methane to methanol. During our studies on this reaction, we discovered a light-driven insertion reaction of O_2 into platinum(II) and palladium(II) methyl bonds to give methyl peroxo complexes (Eq. 1).[2,3]



(1)

A combination of experimental and computational studies have shown that exposure to light results in the formation of excited state metal complexes, which are believed to react with dioxygen to form the methyl peroxo complexes. Spectroscopic studies using LED-NMR have enabled the monitoring of the progress of the reaction in great detail. These studies have shown that the addition of light not only affects the substrate, but also the product as well as the solvent. The methyl peroxo complexes can eliminate formaldehyde to form a hydroxo platinum(II) or palladium(II) complex. These novel reactions suggest the possibility for the selective light-driven oxidation of alkanes to aldehydes.

References

[1] L. A. Kushch, V. V. Lavrushko, Y. S. Misharin, A. P. Moravsky, A. E. Shilov, *Nouv. J. Chim.*, **1983**, *7*, 729.

[2] R.A. Taylor, D.J. Law, G.J. Sunley, A.J.P. White, G.J.P. Britovsek, *Angew. Chem. Int. Ed.* **2009**, *48,* 5900.

[3] K. A. Grice and K. I. Goldberg, *Organometallics*, **2009**, 28, 953–955.

[4] A. R. Petersen, R. A. Taylor, I. Vicente-Hernández, P. R. Mallender, H. Olley, A. J. P. White, G. J. P. Britovsek, *J. Am. Chem. Soc.*, **2014**, 136, 14089– 14099.

[5] V. Fernández-Alvarez, S.K.Y. Ho, G.J.P. Britovsek, F. Maseras, *Chem. Sci.*, **2018**, *9*, 5039-5046. doi:10.1039/c8sc01161c

[6] Ho, S. K. Y., Lam, F. Y. T., de Aguirre, A., Maseras, F., White, A. J. P., Britovsek, G. J. P. *Organometallics*, **2021**, *40*, 4077-4091. doi:10.1021/acs.organomet.1c00487

[7] Ho, S. K. Y., Ezeorah, C., Chari, S., Salehi-Reyhani, A., Britovsek, G. J. P. *ChemPhotoChem*, **2023**, *7*. doi:10.1002/cptc.202200290

Metal-bis(dithiolene) complex as a Swiss Army knife for many applications

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Transition metal-bis(dithiolene) complexes, with their original and exceptional electronic properties, find applications in many areas of materials science.[1,2] These complexes exhibit a wide variety of physical properties such as conductivity, magnetism and optics, making them attractive for new generations of devices. A quick overview showing how the structural and electronic properties of this class of coordination complexes can be exploited to develop conductive and magnetic materials, laser dyes, metallogens, metallogelators as well as photohermal agents for the development of therapeutic agents and photoresponsive materials will be presented.

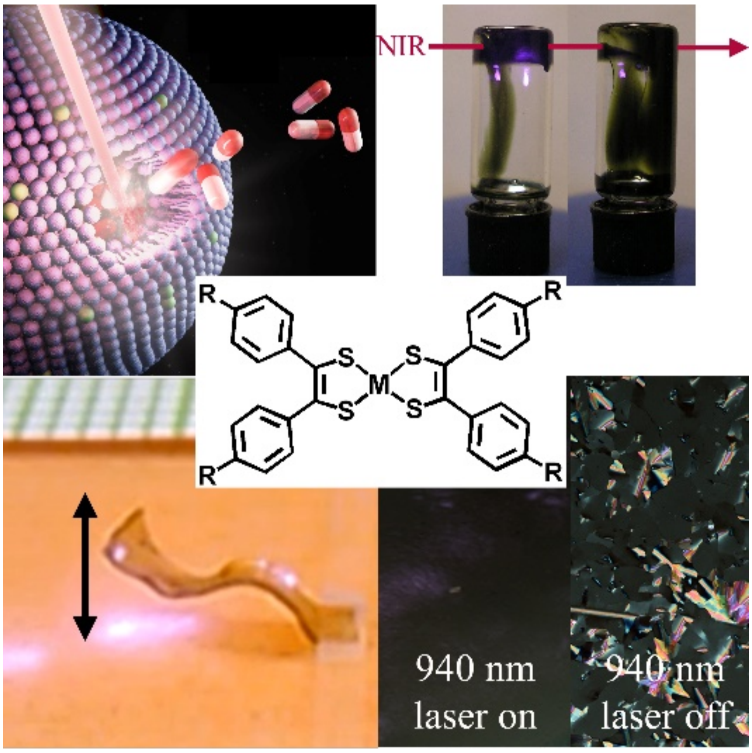

Figure 1. Overview of the photoresponsive systems presented.

References

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[2] Franck Camerel, Marc Fourmigué, *Eur. J. Inorg. Chem.* **2020**, 2020, 508-522.

Bigger is Better!

Mahbod Morshedi,[a] Ling Zhang,[a] Mark G. Humphrey,[a]

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Higher-order nonlinear optical (NLO) responses are sought after due to their potential to open new avenues of technology, such as telecommunications, bio-imaging, and other technologies that require greater precision and higher spatial resolution.

Although the NLO phenomena have been around for a long time, reports of higher-order responses with any non-negligible magnitude are sparse.[1-4] Here, we present the findings of the only 3rd generation ruthenium-based dendrimers with astonishing up to 6 photon absorption (6PA) response, along with a computational study of the two-photon absorption (2PA).

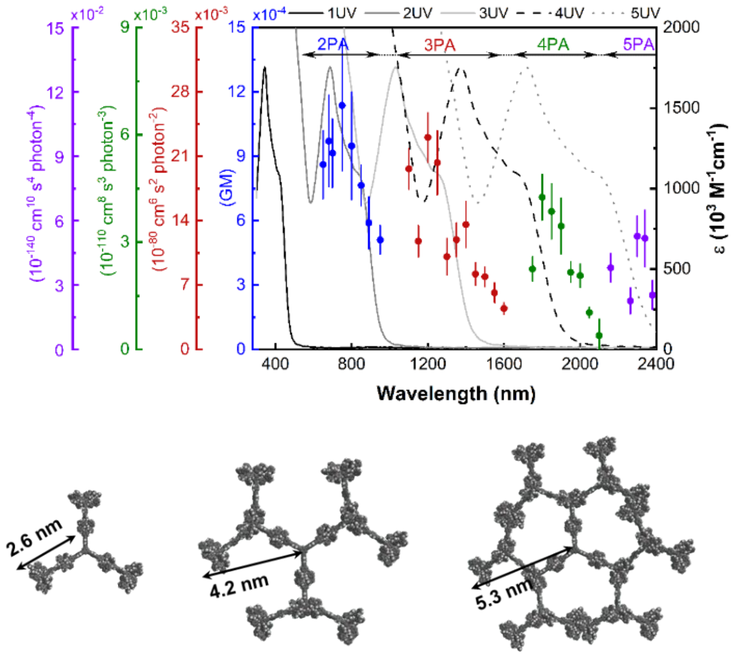

Figure 1. Presentation of 1st, 2nd and 3rd generation ruthenium-based dendrimers.

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The Synthesis, Characterisation, and Anti-leishmanial Activity of Tri-aryl Antimony(V) Hydroxamates

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Leishmania is a single-celled parasite responsible for the disease Leishmaniasis. Leishmaniasis is present in over 90 tropical and subtropical countries and results in one million infections per year worldwide.[1] Traditional pentavalent antimonials used to treat Leishmaniasis include meglumine antimoniate (MA) and sodium stibogluconate (SSG), which cannot be administered orally due to their high polarities and high hydrophilicities.[2] Instead, these antimonials must be administered daily via painful intramuscular or intravenous injections for a period of roughly 30 days, which has led to significant patient non-compliance.[2,3] Incorrect usage of these antimonials has led to drug pressure, resulting in drug tolerance and drug resistance.[4] Additionally, these traditional drugs cause a variety of undesirable side effects such as cardiotoxicity, nephrotoxicity, and pancreatitis.[2] Therefore, novel drug candidates are needed for the treatment of Leishmaniasis that are more selective, less susceptible to antimicrobial resistance, and can ideally be administered orally. A previous study by Andrews *et al*. successfully synthesised a series of tris-aryl antimony(V) a-hydroxy cyclometallate complexes, which identified trends in relation to changes in the aryl moiety.[5] In order to assess whether these trends continue with a similar doubly deprotonated class of organic molecules, we synthesised and characterised a series of novel triphenyl and tris-mesityl antimony(V) hydroxamates and assessed their potential antileishmanial activity (Figure 1).

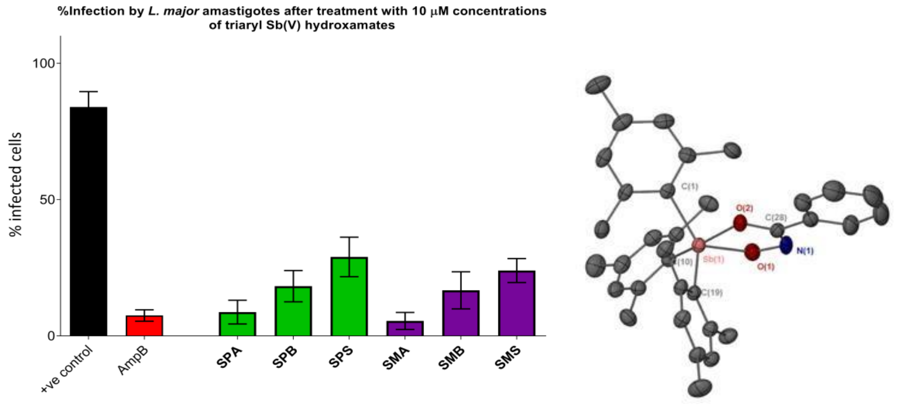

Figure 1. % of infected macrophages with L. major amastigotes after treatment with Sb(V) hydroxamates (left). Chosen x-ray crystal structure of a tri-aryl Sb(V) hydroxamate (right).

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Lewis base alterations of Ag(I) complexes and their catalytic potential

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Interest in the use of silver in catalysis has increased tremendously over the past few decades, owing to silvers low cost, selectivity, and low toxicity in comparison to other late transition metals. [1,2] The synthetic versatility and application of NHC and phosphine stabilised Ag(I) complexes has since been assessed against a wide range of catalytic and organic transformations including hydroboration, hydrosilylation, A^3 coupling, alkynylation, CO_2 insertions and cyclisation reactions.[3-7]

Previous studies by the Blair group highlighted the catalytic potential of NHC and phosphine stabilised Ag(I) amido complexes in both the hydroboration and hydrosilylation of carbonyls.[6,7] Encouraged by these studies and seeking to improve upon our previously reported pre-catalysts. We now report the synthesis and characterisation of three Ag(I) complexes with alternating Lewis bases (CH_2SiMe_3, PPh_2 and O^tBu), alongside substrate screenings of these potential pre-catalysts in hydrofunctionalisation reactions (Figure 1).

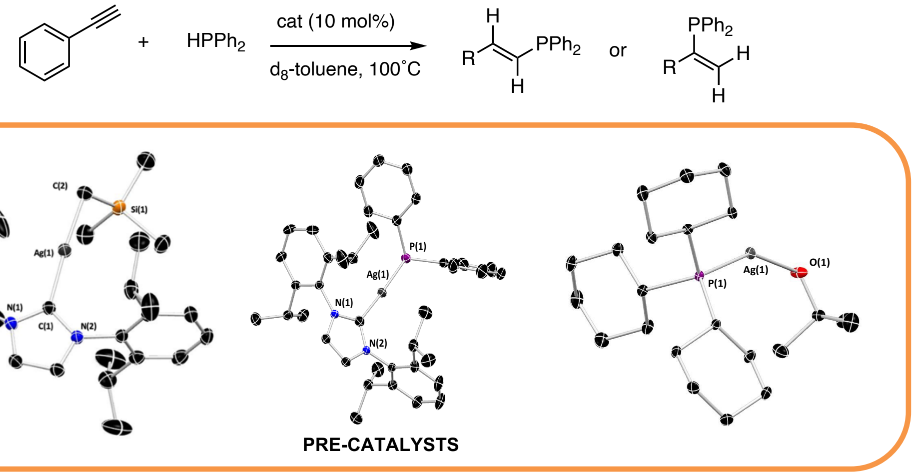

Figure 1. Hydrophosphination of alkynes using Ag(I) complexes with alternating Lewis bases (CH_2SiMe_3, PPh_2 and O^tBu),

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Understanding and enhancing nickel catalysed cross-coupling reactions: insight from synthesis and a novel method of kinetic analysis.

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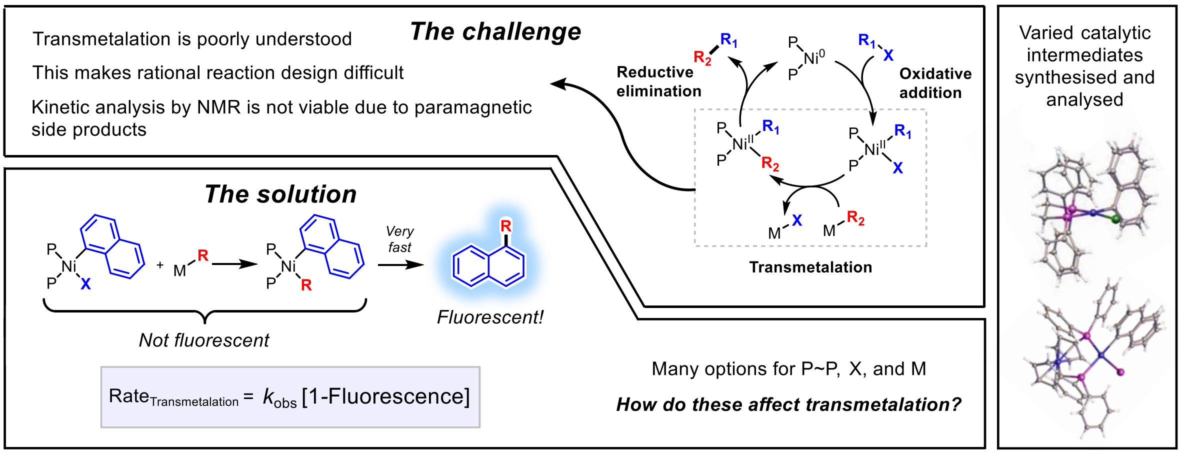
Cross-coupling chemistry is a central tool in the synthetic chemists' repertoire, and enjoys routine use in both research and industry.[1] Despite this widespread use, cross-coupling reactions often suffer from the need for expensive palladium catalysts. In contrast to this, nickel catalysts are cheaper, but are often less efficient with more side reactivity.[2]

This talk will focus on our recent efforts to study and understand the sources of unusual reactivity often encountered with nickel catalysts. In particular, we have examined the poorly characterised catalytic step of transmetalation; a process for which kinetic analysis is complicated by the proclivity of nickel species to decompose,[3] and comproportionate,[4] leading to paramagnetism, rendering ubiquitous NMR spectroscopic techniques unviable.

As a new approach, we have synthesised and isolated 25 (mostly new) nickel-based catalytic intermediates and subjected them to a variety of transmetalating agents. Importantly, by carefully designing the nickel species and tuning the transmetalating agents, we have found a regime in which non-fluorescent starting materials yield fluorescent products. This provides a convenient method for analysing the kinetics of transmetalation, enabling a deeper understanding of this process, and affording insight for rational reaction design.


The challenge

Transmetalation is poorly understood

This makes rational reaction design difficult

Kinetic analysis by NMR is not viable due to paramagnetic side products

The solution

$\text{Rate}_{\text{Transmetalation}} = k_{\text{obs}}\,[1\text{-Fluorescence}]$

Many options for P~P, X, and M

How do these affect transmetalation?

Varied catalytic intermediates synthesised and analysed

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Synthesis of bimetallic complexes of an unsymmetric PNNN expanded pincer ligand

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Development of cooperative catalysis is one of the current focuses in the field of homogeneous catalysis.[1] One of the most well-known examples of metal-ligand cooperativity (MLC) is Milstein's catalyst, which reacts via an aromatisation-dearomatisation MLC process with no formal change in the metal oxidation state.[2] Along with monometallic metal-ligand cooperativity, there is also increasing interest in metal-metal cooperativity (MMC) in bimetallic complexes. Combining the approaches of metal-ligand cooperativity and metal-metal cooperativity, led to a new idea of metal-metal-ligand cooperativity (MMLC), in which the catalyst contains both a non-innocent ligand and the potential for a metal-metal interaction. One of the most promising ligand architectures being explored in the literature is using a 1,8-naphthyridine backbone. This class of expanded pincer ligands has recently been investigated by a number of research groups and demonstrated to have powerful bond activation properties.[3-4]

This presentation will explore the chemistry of a new class of unsymmetric expanded pincer ligand, PNNN, with the aim of preparing Cu(I)Ru(II) heterobimetallic complexes and investigating their cooperativity. We have explored its complexation with both ruthenium and copper metal precursors, and demonstrate that the PNNN ligand can accommodate various coordination modes depending on the metal(s) and co-ligands. The dearomatisation and hydrogenation investigation of obtained monometallic Ru(II), homobimetallic Cu(I)Cu(I) and heterobimetallic Cu(I)Ru(II) complexes demonstrated this PNNN expanded pincer ligand is capable of metal-ligand and metal-metal cooperative reactivity, furthermore, such PNNN complexes are able to catalyse hydrogenation under mild conditions.

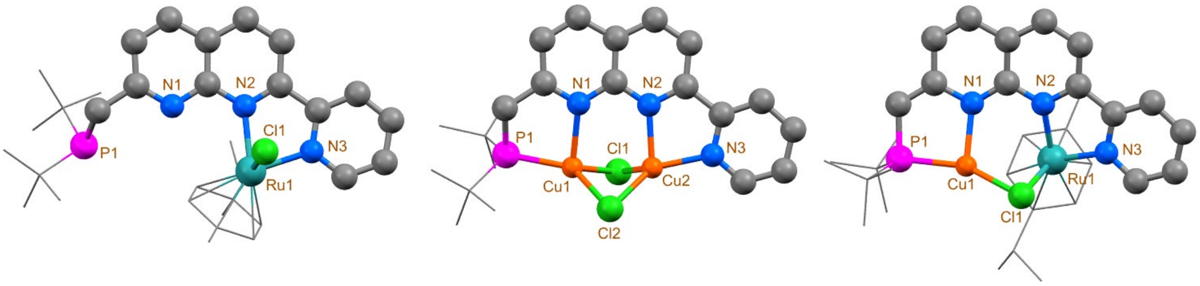

Figure 1. Solid state structure of (a) monometallic Ru(II) complex, (b) homobimetallic Cu(I)Cu(I) complex, (c) heterobimetallic Cu(I)Ru(II) complex.

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Synthesis and Reactivity of the Indyl Anion

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Over the last two decades main group elements have demonstrated the ability to activate and reduce small molecules, such as CO_2, CO and N_2O as well as participating in catalysis.[1],[2] More recently, anionic aluminium(I), termed aluminyl anions, have been developed and demonstrated a range of exotic reactivities, such as C-C activation, small molecule activation and M-M bond formation.[3],[4] However, the indium analogue, the indyl anion, is less developed with only one ligand framework reported to stabilise this compound.[5]-[7] The indyl anion has a vast amount of unexplored reactivity and has the potential to open a wide range of applications that are currently unexplored. Thus far, we have successfully synthesised four new indyl anions and exploration into their reactivities has begun (Figure 1). We have explored small molecule activation by reacting the indyl anions with CO_2. Additionally, we have explored the formation of new metal-metal bonds and have looked at reactivity of the indyl anion with group 2 metals supported by monoanionic ligand systems.

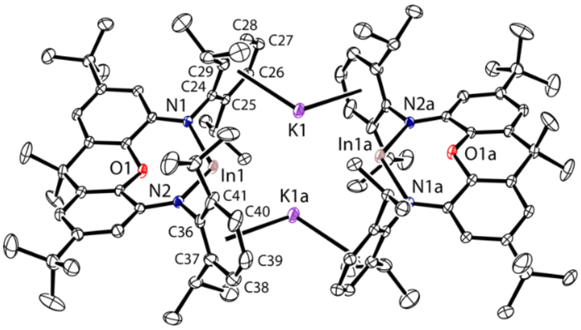

Figure 1. ORTEP representation (30% probability ellipsoids) Xanth^{Dipp} Indyl

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Electrochemical Synthesis of Gold-*N*-Heterocyclic Carbene Complexes

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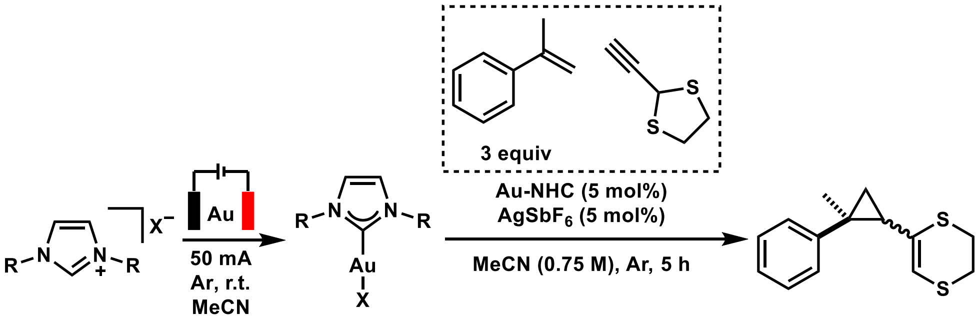
Gold-*N*-heterocyclic carbene (Au-NHC) complexes have been synthesised using an electrochemical methodology. The use of electrochemistry obviates the need for strong or weak base or Cu/Ag-based carbene transfer complexes. The Au-NHC complexes can be produced starting from just the imidazolium salt, Au metal electrodes, and electricity. There is no requirement for exogeneous redox agents or supporting electrolyte as the imidazolium salt itself is the electrolyte. The only by-product of the reaction is H_2 gas which is released to the atmosphere meaning that at the completion of the reaction the only species in solution is the Au-NHC complex.

The Au-NHC complexes produced electrochemically can be used directly in catalysis without any work-up or purification. A telescoped Au-NHC-catalysed vinylcyclopropanation reaction has been developed in which the Au-NHC complex is produced electrochemically and then transferred directly to the catalytic reaction mixture (Scheme 1).[1] Benchmarking experiments show that the telescoped procedure is equally as effective as using a pre-prepared Au-NHC complex despite the absence of work-up or purification.



Scheme 1. Telescoped synthesis of Au-NHC complexes and direct addition to a vinylcyclopropanation reaction.

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How a boron atom impacts organogelation properties

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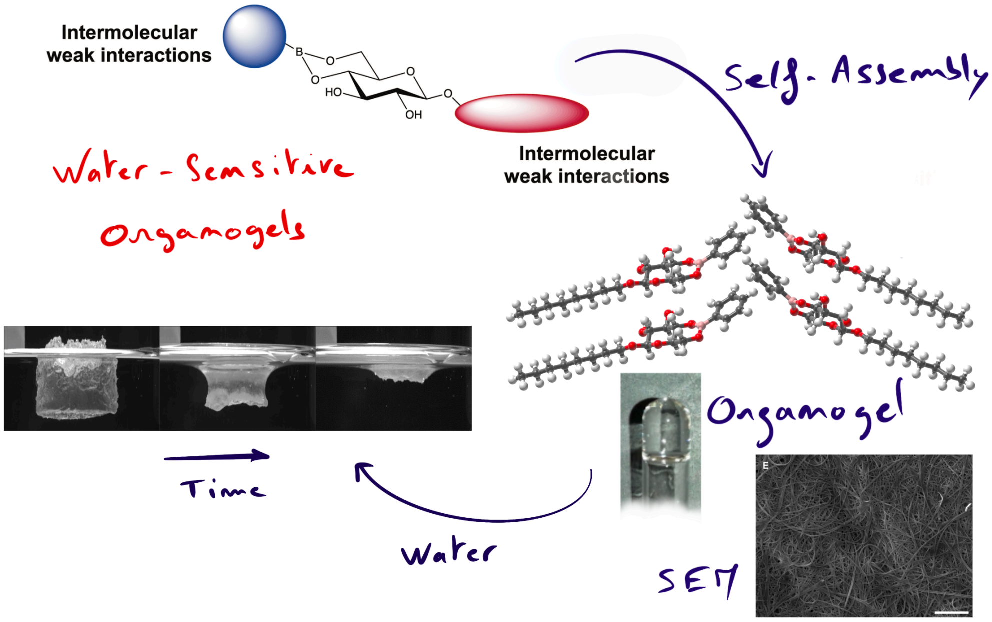
The preparation of gels with low-molecular-weight gelators is based on the formation of a 3D-network responsible for the immobilisation of a solvent. The corresponding fibers are obtained through the self-assembly of those gelators thanks to van der Waals interactions, π–π interactions, hydrogen bonding or electrostatic interactions.[1] It turns then aqueous or organic solutions into hydrogels or organogels, respectively. Sugar-based derivatives are already known for their potential as remarkable organogelators.[2] Recently, we described an easy synthesis of a new class of organogelators obtained by esterification of glucosides with aromatic or aliphatic boronic acids.[3] The additional boron atom dramatically changed the gelation properties. All organogels were fully characterized by rheometry, electron microscopy (SEM) and X-ray diffraction to understand as much as possible the type of self-assembly involved during the formation of the organogels. Thanks to the boronate chemistry, those organogels demonstrated a remarkable water-sensitivity which can be tuned through variations on the chemical structure of the gelators.



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The controlled synthesis of lanthanide complexes and their biomedical applications

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Lanthanide complexes involve the utilization of organic ligands to form chelates with individual lanthanide ions. Their many exceptional properties including large Stokes' Shift, long lifetimes, tuneable absorption and emission bands, and resistance to concentration quenching, allow widespread applications in therapy, early diagnosis, bioimaging, and drug delivery.[1-3] The key to achieving these properties is the coordination of inorganic lanthanide ions by organic ligands. In the past decades, researchers have pushed the lanthanide coordination chemistry boundary from a single atom level to a nanoscale, forming a lanthanide nanocomplex. There have been notable advancements in harnessing the hybrid configuration of inorganic nano-complex doped with lanthanides, all encapsulated within organic coatings. These nanocomplexes offer diverse characteristics including adjustable ratios, morphologies, sizes, and structures. This development marks a significant evolution in the field of lanthanide-based applications, offering novel opportunities and enhanced capabilities for application in the medical diagnosis and therapy of diseases.

In this presentation, I will present our works on lanthanide complex synthesis, modification, and biomedical applications. Firstly, I will introduce the properties and development principles of the lanthanide complex, including the chelation, sensitization, and energy transfer mediated by triplet states. Learning from these principles, I will introduce the development of lanthanide nanocomplexes, including their synthesis strategy, surface coordination, properties, and benefits of the coordination of multiple lanthanide atoms. Then, I will present our recent progress in applying these organometallics-based luminescent probes for broad biomedical applications in cell imaging, *in vivo* imaging of zebrafish, disease diagnostics, point-of-care tests, and drug delivery.

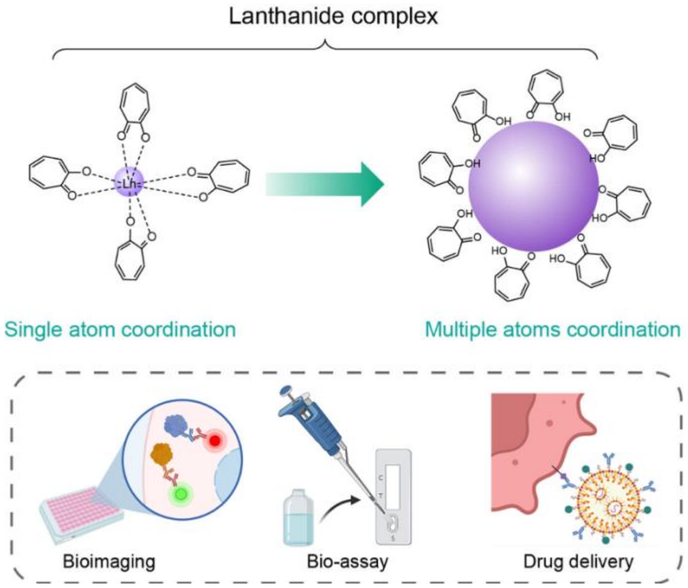

Figure 1. Schematic representation of lanthanide complexes and their applications.

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Nitrogen Fixation by Highly Structured Phosphine Containing Transition Metal Complexes

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Ammonia production is one of the largest industrial processes on the planet accounting for nearly 1% of global energy usage.[1] The current method, developed in the early 20th century, is quite inefficient requiring high temperature and pressure as well as producing several unwanted biproducts such as CO_2. As such, investigations into a more efficient and environmentally sustainable method for NH_3 production are of vital importance.

Plants and microorganisms are able to convert atmospheric nitrogen (N_2) into NH_3 at ambient temperature and pressure using the enzyme nitrogenase. The exact mechanism for this process is unknown but it is clear that N_2 binding to a metal centre is a key step.

Since the first dinitrogen complex was reported in 1965[2] there have been many complexes explored as potential catalysts for NH_3 production. Initially a major focus was placed on molybdenum containing complexes as this was believed to be the metal necessary for biological nitrogen fixation. However, when it was discovered that iron was actually the common metal in the different forms of nitrogenase interest was renewed in the group 8 metal complexes.

This project focusses on group 8 and 9 phosphine containing metal complexes that can bind dinitrogen and activate it towards NH_3 production. These complexes will be treated with acid in order to produce ammonia (and hyrdrazine). An example of the reaction with acid can be seen in figure 1.

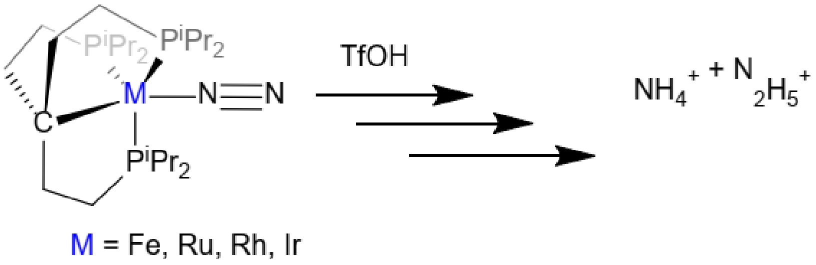

Figure 1. Reaction scheme for reduction of N_2 to NH_4^+ and $N_2H_5^+$

The amount NH_3 as well as N_2H_4 produced will be quantified using GCMS. Development of the GCMS method has also been a major step in this project as it allows hydrazine and ammonia to be quantified effectively using the same analytical technique.

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Selective Oxidation of Divalent Calix[4]pyrrolide Compounds $[Ln_2(N_4Et_8)(thf)_4]$, Giving Mixed Valent Lanthanoid(II/III) Complexes

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A number of remarkable heteronuclear mixed-valent samarium(II/III)/transition metal (TM = Mo, Cr, Co, Fe, Mn, W) complexes were prepared by reactions of the divalent samarium(II) complex $[Sm_2(N_4Et_8)(thf)_4]$ with corresponding transition metal carbonyls. Trivalent $[(thf)Sm^{III}(N_4Et_8)Sm^{III}(COT)]$ complex was obtained by the reaction of $[Sm^{II}{}_2(N_4Et_8)(thf)_4]$ and cyclooctatetraene (COT). Meanwhile, the mixed-valent europium(II/III) complexes $[(thf)_2Eu^{II}(N_4Et_8)Eu^{III}(\mu\text{-}X)]_2$ (X = F, Cl, Br) were prepared in good yields, the Eu^{II} complex $[Eu_2(N_4Et_8)(thf)_4]$ was oxidized by perfluorodecalin, hexachloroethane, and bromoethane respectively. The synthetic potential of these halogenidoeuropium complexes was illustrated by reaction of $[(thf)_2Eu^{II}(N_4Et_8)Eu^{III}(\mu\text{-}Br)]_2$ with sodium bis(trimethylsilyl)amide giving $[(thf)_2Eu^{II}(N_4Et_8)Eu^{III}(N(SiMe_3)_2)]$.[1-2] The polymeric samarium/ytterbium calix[4]pyrrolide complexes, $\{[Sm_2(N_4Et_8)(4,4´\text{-Dipyridyl})_2]_n{\cdot}(nPhMe)\}$ and $\{[Yb^{II}{}_2(N_4Et_8)(4,4´\text{-Dipyridyl})_2]_n{\cdot}(nPhMe)\}$ (Figure 1) were prepared by the reaction of $Ln_2(N_4Et_8)$ (Ln = Sm, Yb) and 4,4´-Dipyridyl.

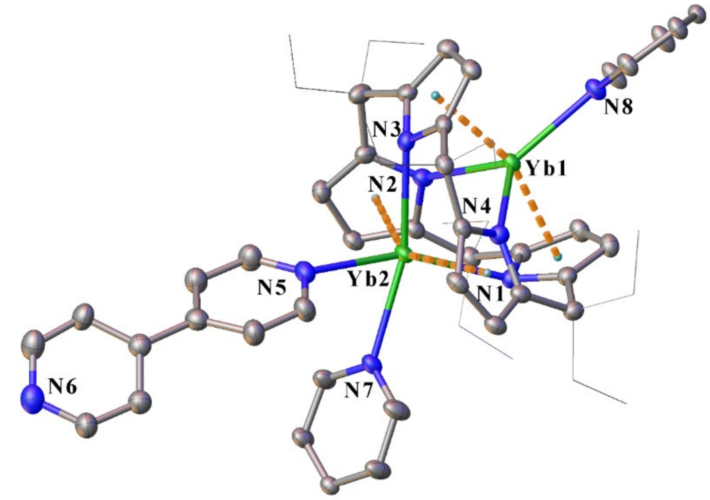

Figure 1. Molecular diagram of $\{[Yb_2(N_4Et_8)(4,4´\text{-Dipyridyl})_2]{\cdot}(PhMe)\}_n$

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3D printed device to test electrochemical nitrogen fixation

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The electrochemical fixation of dinitrogen to ammonia is a fraught field of false positives.[1] Efficient aqueous electrochemical fixation, at atmospheric temperature and pressure, would decarbonise the process, and be a key step towards being commercially competitive with the Haber-Bosch process. We are focussing on a suite of potential catalysts for this reaction.

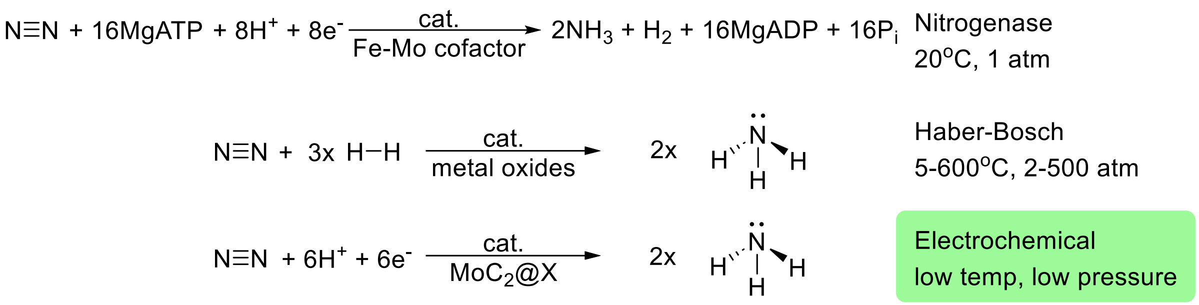

Figure 1. Comparison of the two well established methods of nitrogen fixation, that of nature – nitrogenase, and that of humanity – the Haber-Bosch process.[2] Electrochemical fixation, the target of this work, with a focus on molybdenum carbide supported on various substrates.

This presentation describes our recent studies to test the catalysts in gas-phase, commercial fuel cell devices. However, a modular, cheap, and easily 3D printable version is being iteratively designed and tested, allowing for parallel testing of multiple catalysts, and optimisation of process parameters.

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An Acyclic Aluminyl Anion: Breaking Bonds, Conflicting Chelation

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Nucleophilic aluminium(I) chemistry has seen accelerating advancement as novel umpolung systems of the traditionally Lewis acidic/electrophilic metal centre.[1] Since the first report of an aluminyl anion in 2018, these systems have shown unprecedented reactivity towards an array of small molecules (H_2, CO_2, N_2O), quickly becoming a 'hot topic' in main group chemistry.[2,3]

Earlier this year, we reported the first acyclic aluminyl anion, breaking the cycle of utilising bulky chelating ligands constricting the aluminium(I) centre within a metallocycle.[4] A sterically demanding bis-silyl(aryl)amido aluminium(III) iodide precursor complex $[\mathrm{Al(I)\{N(DIPP)SiMe_3\}_2}]$ was prepared and subsequent reduction yielded the first acyclic aluminyl anion. This highly reactive aluminium(I) centre has been isolated as both a potassium-bridged dimer and monomeric magnesium complex. The conformational flexibility of the acyclic ligands offers arrangements not before identified within previously reported aluminyl systems. Reactivity studies are ongoing and will be discussed.

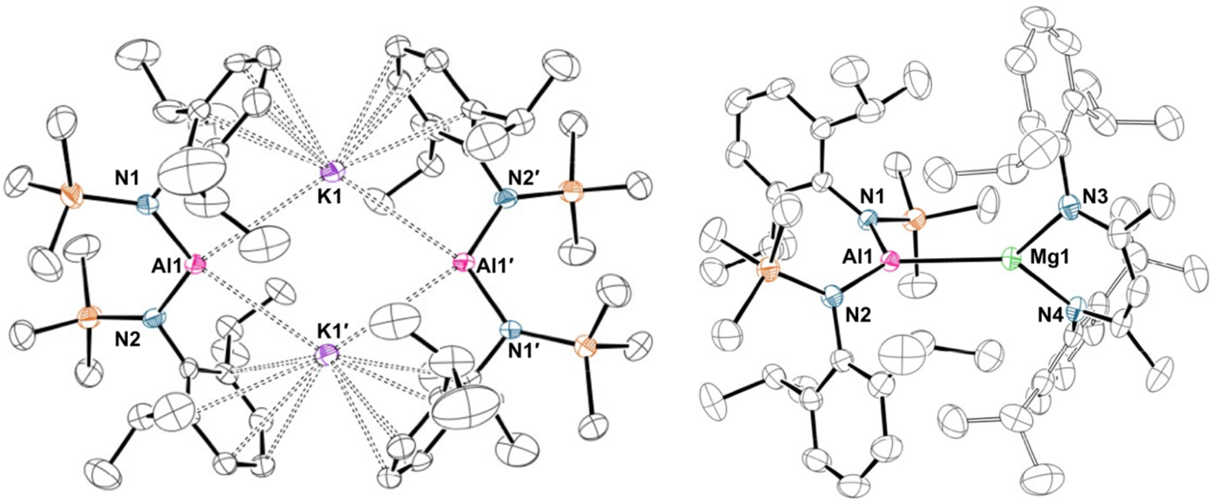

Figure 1. The first acyclic aluminyl anion stabilised by bulky monodentate silyl(aryl)amido ligands as both a dimeric both a potassium-bridged dimer (left) and monomeric magnesium complex (right).

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Improving the Synthetic Accessibility of Platinum (II) Cages

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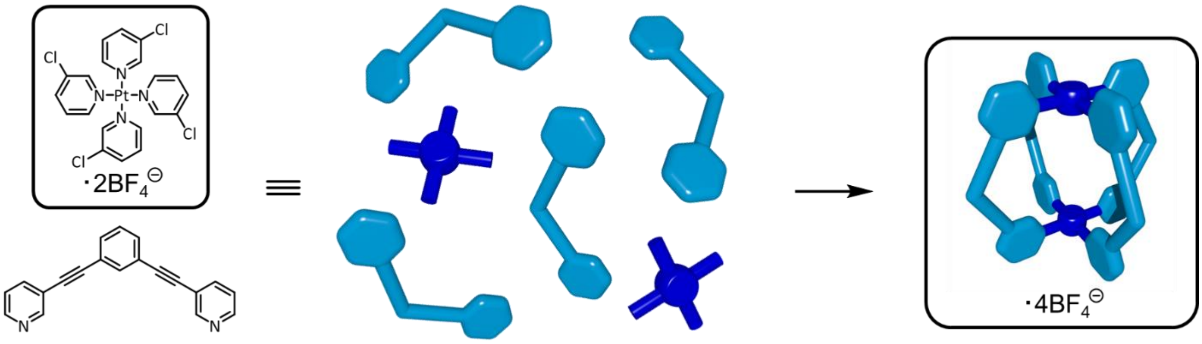
Metallo-supramolecular cages are discreet synthetic entities which can effectively act as host molecules. Potential applications for these structures include catalysis, drug delivery, binding pollutants, and use as sensors. While many metal ions and architectures can be used, palladium (II) systems have proven immensely popular due to their relative ease of synthesis and well understood properties.[1-3] Platinum (II) systems are expected to be analogous to their palladium counterparts, boasting improved stability at the cost of synthetic inaccessibility. This improved stability may enable their application in more demanding situations, where other cages may be unsuitable.

When comparing cages, such as the widely reported M_2L_4 'lantern' architecture (Figure, right), Pd (II) variants typically form readily with minimal heating, regardless of the presence of water and oxygen in the reaction, due to the hemi-lability of the metal ion. Following current literature standards, Pt (II) variants are expected to take days to form under high heat, using dry solvent and air-free conditions, or may not form cleanly at all.[4] Alternatively, subcomponent self-assembly can be used to generate heterometallic variants, though this limits the synthetic scope.[5] Our work seeks to amend these shortcomings, reducing the timeframe from days to hours, even in the presence of water and oxygen, allowing direct coordination rather than requiring condensation. We propose an alternative Pt (II) source (Figure, left) be used in an operationally simple method (Figure, middle) as a reliable way of forming Pt (II) cages directly, greatly enhancing the synthetic ease in construction.



Platinum precursor and ditopic ligands (left, middle) reacting to form M_2L_4 structure (right).

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C-F activation adventures with mono- and bi-metallic main group bases

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The chemistry of bimetallic compounds have received a lot of attention following the discovery of the Lochmann Schlosser "superbase".[1] Alkali metals are known to form metalate complexes with other metals or themselves.[2] These bimetallic systems are characterized by their ability to synergistically promote reactivities inaccessible to their parent moieties.[2]

C-F activation is one of the most widely studied areas in chemistry, fuelled by the negative impact of fluorinated substances on the ecosystem.[3] Thus, alternative ways of breaking down these substances as well as routes for formation of novel compounds are highly appreciated. A growing number of reports have shown that bimetallic compounds exhibit superior reactivity in facilitating this process.[2]

Herein, we present the synthesis of a series of 7-membered N-heterocyclic compounds of various fluorinated imines mediated by the sodium magnesiate bimetallic base. In contrast to their monometallic moieites which facilitate either C-F activation or 1,2-nucleophilic addition. The presence of sterics on certain positions of the phenyl ring is critical for the formation of these 7-membered N-heterocycles or a fluorinated magnesium cage.

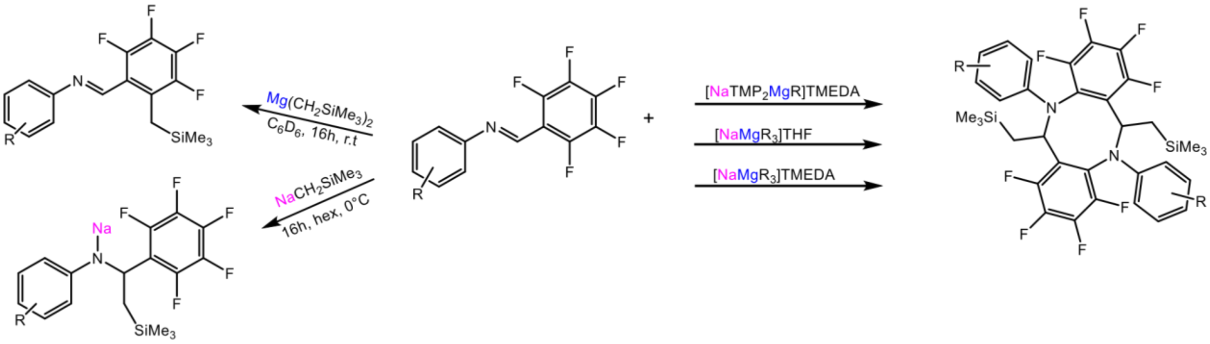

Figure 1. Reactivity of mono- and bi-metallic reagents with fluorinated imines.

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Dimethylgallium(III) complexes of indeno[1,2]quinoline derivatives as antibacterial agents

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Antimicrobial resistance (AMR) – the decreased susceptibility of pathogenic microorganisms to available antimicrobial treatments – has become a life-threatening issue throughout the world.[1] It has been predicted that if no action is taken then there will be approximately 10 million deaths from AMR infections globally each year 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 its chemical similarity, allowing interference with iron homeostasis in biological systems and inhibition of bacteria growth and virulence.[3] Indeed, gallium(III) nitrate is in clinical trials for the treatment of *Pseudomonas aeruginosa* infections in patients with chronic cystic fibrosis. However, the therapeutic potential of organogallium(III) compounds remains relatively unexplored.

We have recently shown that dimethylgallium(III) complexes of fluoroquinolone antibiotics display potent antibacterial activity towards fluoroquinolone-resistant *Klebsiella pneumoniae.*[4] In our efforts to further explore the relationship between the structure of the chelating ligand and the antibacterial activity of $[Ga(CH_3)_2(L)]$ compounds, a series of dimethylgallium(III) complexes bearing indeno[1,2]quinoline-carboxylate ligands have been prepared (see Figure 1). Tetracyclic derivatives of quinolines, such as indeno[1,2]quinolines, are pharmacologically interesting compounds that exhibit a wide variety of biological properties.[5] This presentation describes the synthesis, structural characterisation, and antibacterial activity of these novel organogallium(III) complexes.

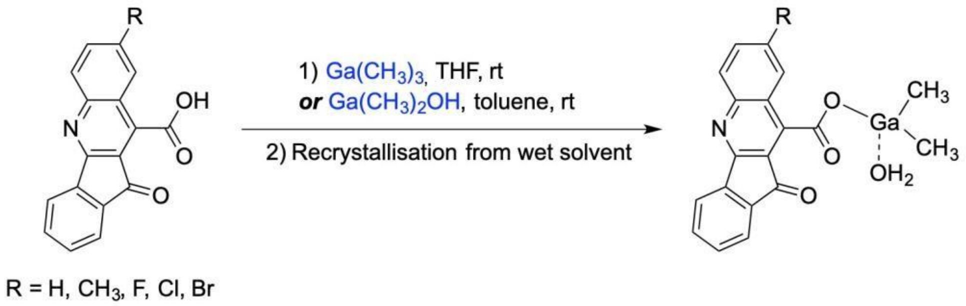

Figure 1. *Synthesis of dimethylgallium(III) indeno[1,2]quinoline carboxylate complexes.*

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Pinacol Cross-Couplings Promoted by an Aluminyl Anion

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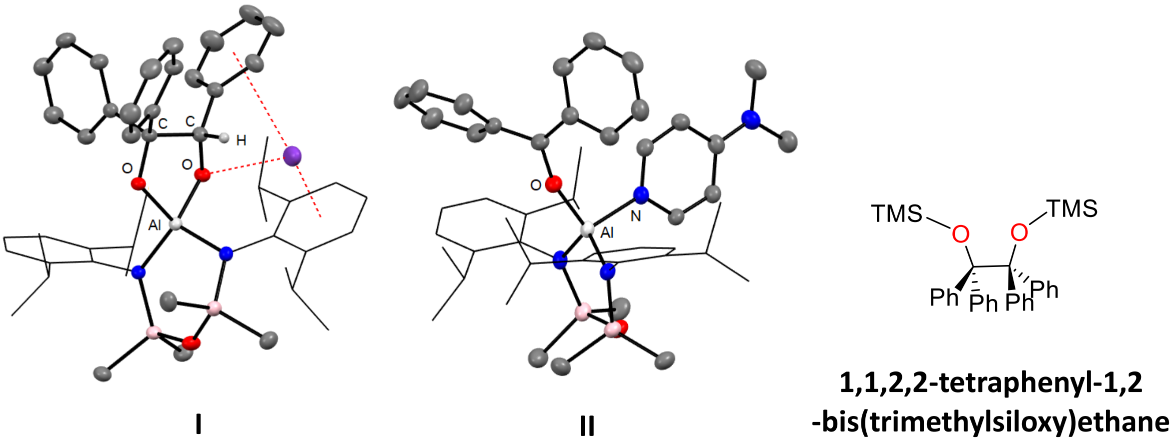
Non-selective, symmetric pinacol coupling reactions of aldehydes and ketones are established in literature.[1] This work demonstrates the facile unsymmetric coupling of ketones and aldehydes (**I**) targeting a series of mixed pinacolate products utilising the potassium aluminyl, $[K\{Al(NON^{Dipp})\}]_2$ ($[NON^{Dipp}]^{2-}$ = $[O\{SiMe_2NDipp\}_2]^{2-}$, Dipp = 2,6-$iPr_2C_6H_3$). Cleavage of the resulting pinacolate was achieved utilising iodotrimethylsilane, which also regenerates a suitable aluminyl precursor thereby demonstrating a closed synthetic cycle. Isolation of a rare example of *p*-block ketyl radical was also shown (**II**).[2]



I

II

1,1,2,2-tetraphenyl-1,2 -bis(trimethylsiloxy)ethane

*Figure 1. Pinacol coupled product of benzophenone and benzaldehyde (**I**), O-Al Ketyl radical (**II**) and cleaved 1,1,2,2-tetraphenyl-1,2-bis(trimethylsiloxy)ethane.*

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Lanthanide complex for biomedical applications

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Lanthanide complexes, where organic ligands are used to chelate individual lanthanide ions, are rising stars in biomedical fields.[1, 2, 3, 4] Thought the potential risk of gadolinium retention in the human body has raised concerns regarding certain chelator-based contrast agents, the success of gadolinium complex-based magnetic resonance contrast agents in clinical practice demonstrates the viability of lanthanide complexes for clinical translation. Furthermore, the significant separation between excitation and emission wavelengths minimizes background interference from biological samples and light sources. The long lifetime enables the enhancement of the signal-to-noise ratio through time-gated techniques. The heavy atom effect imparted by lanthanide ions enhances intersystem crossing for triplet generation, facilitating the production of radicals and/or reactive oxygen species, which makes lanthanide complexes as excellent candidates for photodynamic therapeutic agents.[5]

In this presentation, I will discuss our recent works on lanthanide complexes synthesis, luminescent properties and their biomedical applications. I will introduce a new strategy to realising the controlled synthesis of dinuclear lanthanide complex with different lanthanide ions in one molecule. I will discuss the principles for sensitisation of lanthanide ions and the energy transfer processes in the lanthanide complexes. I will also present our recent achievement in lanthanide complex probes development, their application in sensing, biological imaging and drug discovery, and prospective opportunities in clinical translation of the lanthanide complex.

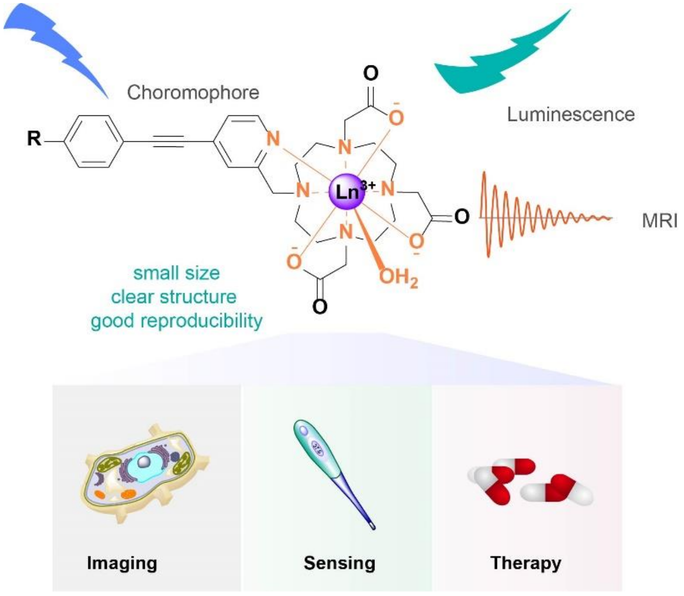

Figure 1. Illustration of lanthanide complexes and their applications.

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Increasing the Reactivity of Anionic Low-Valent Aluminium Compounds

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In recent years, low-valent main-group complexes have seen a renaissance in organometallic chemistry that came along with renewed interest owing to the relatively non-toxic, earth-abundant, and cheap nature of these elements. A major driving force of this trend lies in the interesting reactivity that these compounds offer. Group 13 compounds, especially those based on aluminium, have traditionally been used as Lewis acids with a wide array of industrial and academic applications. However low-valent group 13 complexes that act as nucleophiles have lagged behind in their development. Recently, Hicks *et al.* reported an anionic Al^{+I} compound [K{Al($^{\mathrm{Dipp}}$**NON**)}]$_2$ stabilised by the bulky xanthene based ligand [$^{\mathrm{Dipp}}$**NON**]$^{2-}$ (Dipp: 2,6-diisopropylphenyl).[1] The compound was found to react as the first nucleophilic source of aluminium, and its monomeric form is even able to activate a C-C bond of benzene.[2]

With our sights set on activating even more stable bonds, more reactive aluminyl anions are desirable. The diisopropylphenyl groups in [K{Al($^{\mathrm{Dipp}}$**NON**)}]$_2$ stabilize the dimeric form in both the liquid and solid states through potassium-arene interactions. Thus, we hypothesize that replacing the Dipp amide with bulky silyl amides should eliminate these interactions and therefore increase the reactivity of the corresponding anionic aluminyl. The increase in reactivity is further exacerbated by the more electron-rich nature of silyl amides compared to aryl amide donors. Accordingly, the triisopropylsilyl substituted ($^{\mathrm{TIPS}}$**NON**)Al-I was synthesized from the lithium or potassium salts of [$^{\mathrm{TIPS}}$**NON**]$^{2-}$ and aluminium iodide. Reduction of ($^{\mathrm{TIPS}}$**NON**)Al-I with potassium graphite in benzene yielded the compound K[**Al**(H)(Ph)($^{\mathrm{TIPS}}$**NON**)] shown in Figure 1, the product of the oxidative addition of the aluminyl into a C-H bond of benzene. Ongoing reactivity of this highly reactive aluminyl anion will be discussed.

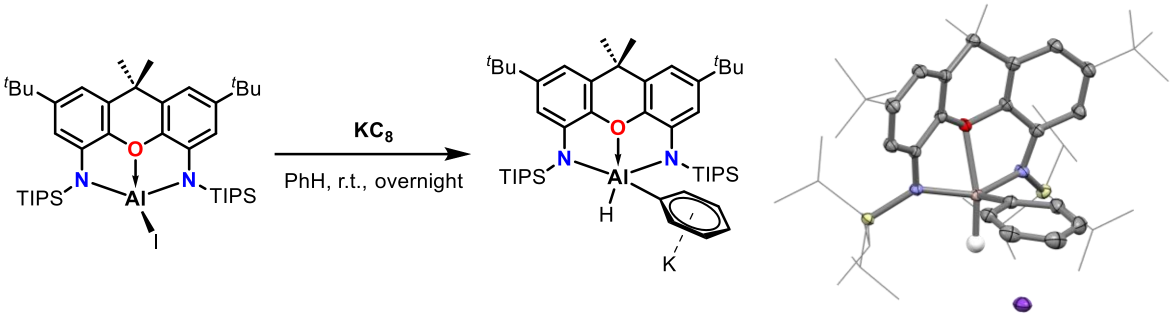

*Figure 1. Reduction of ($^{\mathrm{TIPS}}$**NON**)Al-I using potassium graphite yielding K[**Al**(H)(Ph)($^{\mathrm{TIPS}}$**NON**)] (TIPS: triisopropylsilyl).*

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Aluminium-based Lewis Acid Catalysts for Enantioselective Organic Transformations

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As aluminium is the most abundant metal in the Earth's crust, various applications involving this metal are considered sustainable, including catalysis. As such our perennial aims have been to establish new directions in the field of Lewis acid catalysis through the creation of a unique set of aluminium compounds. Our group previously demonstrated that a β-diketiminate supported aluminium bistriflate complex could act as an excellent Lewis acid catalyst for challenging Diels-Alder and Michael addition transformations in the presence of one equivalent of $Na[BAr^{Cl}_4]$ (Ar^{Cl} =3,5-$Cl_2C_6H_3$).[1], [2] Following this success, our next step was to extend the achiral catalytic system to enantioselective catalysis by structurally modifying either the β-diketiminate ligand or the sodium salt motif to induce chirality in the overall system. Our recent work in this direction entailed introducing chirality into the β-diketiminate ligand via an oxazoline unit. However, the best enantiomeric excess value isolated after having subjected the overall ligand to numerous structural variations at the "achiral end" (**Ar**) and "chiral end" **R** (Figure 1), was 68% for a difficult Diels-Alder reaction.[3] In the quest of achieving higher enantioselectivity levels, we herein present the findings of inducing chirality into the achiral catalytic system by means of BINOL-derived chiral sodium phosphates and chiral bis(oxazoline)-based ligands.

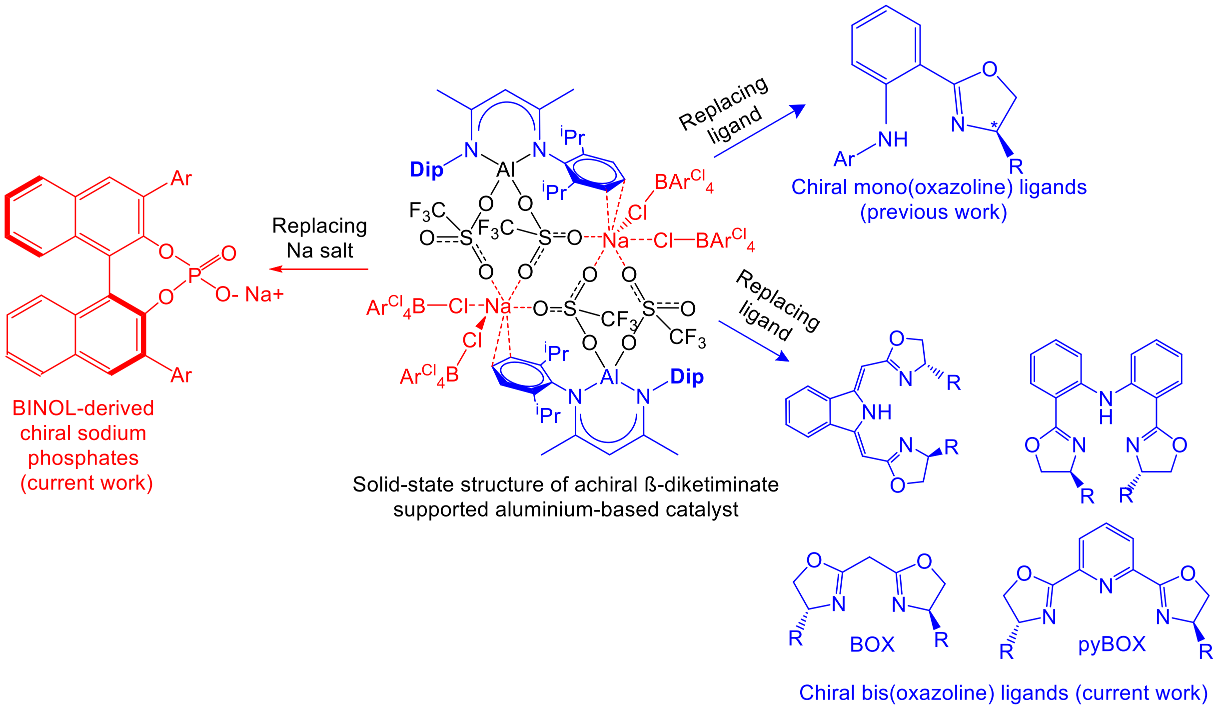

Fig. 1 Inducing chirality in the previously reported achiral β-diketiminate supported Al-based complex.

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Multistate Switching of Some Ruthenium Alkynyl and Vinyl Spiropyran Complexes

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To study the switching properties of photochromes, we undertook the synthesis and characterisation of several organometallic complexes of the type [Ru(Cp*)(dppe)(C≡C-SP)] or [Ru(CO)(dppe)(PPh_3)Cl(CH=CH-SP)], where SP = spiropyran. The spectroscopic and electrochemical properties of the complexes were determined by careful cyclic voltametric and spectroelectrochemical experiments. Whereas the mononuclear alkynyl ruthenium complexes undergo one-electron oxidations localised over the metal alkynyl moiety, the oxidation of the mononuclear vinyl ruthenium complexes is centred on the indoline moiety of the spiropyran. Through these studies, we demonstrate access to several stable redox states, in addition to switching states attained via acidochromism and/or photoisomerisation.[1]

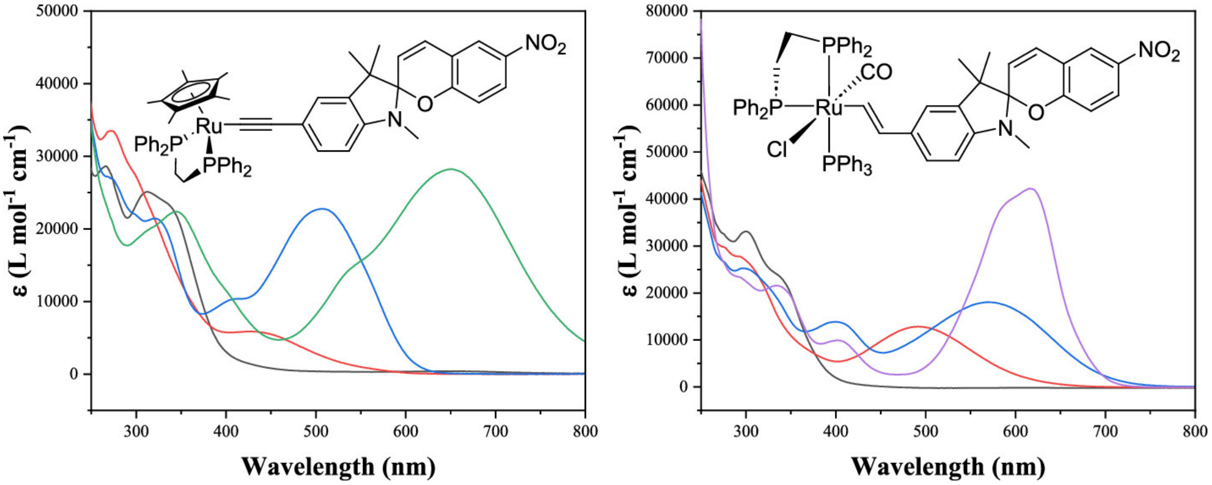

Figure 1. Representative UV-Vis spectra for the alkynyl-SP (left) and vinyl-SP (right) complexes.

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The Organometallic Potential of Arsoles

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Arsoles (1*H*-arsacyclopentadienes) are a neglected class of ligand within the theatre of transition metal coordination chemistry. Only weakly aromatic and of modest basicity, arsoles were first synthesised in the late 1950's[1] however their exploration has been sporadic and esoteric; it is only in recent years that their study has been revitalised as a result of appealing photophysical properties.[2] Transition metal complexes, however, remain few in number: this work focuses on the preparation of new arsole complexes featuring a range of coordination modes including σ-dative (neutral *arsole*), μ-covalent (anionic *arsolyl*), σ-covalent (*arsolyl*) and η^5 (*arsolyl*) ligands, and the derivative chemistry therein. This conversation at *OZOM-14* will introduce the provenance and properties of the arsole ligand and discuss synthetic strategies towards the first arsole/arsolyl complexes of cobalt (**Fig. 1, top**), which serve as a novel type of ditopic Lewis base toward Lewis acidic d^8 and d^{10} metal centres (**Fig. 1, bottom**).[3]

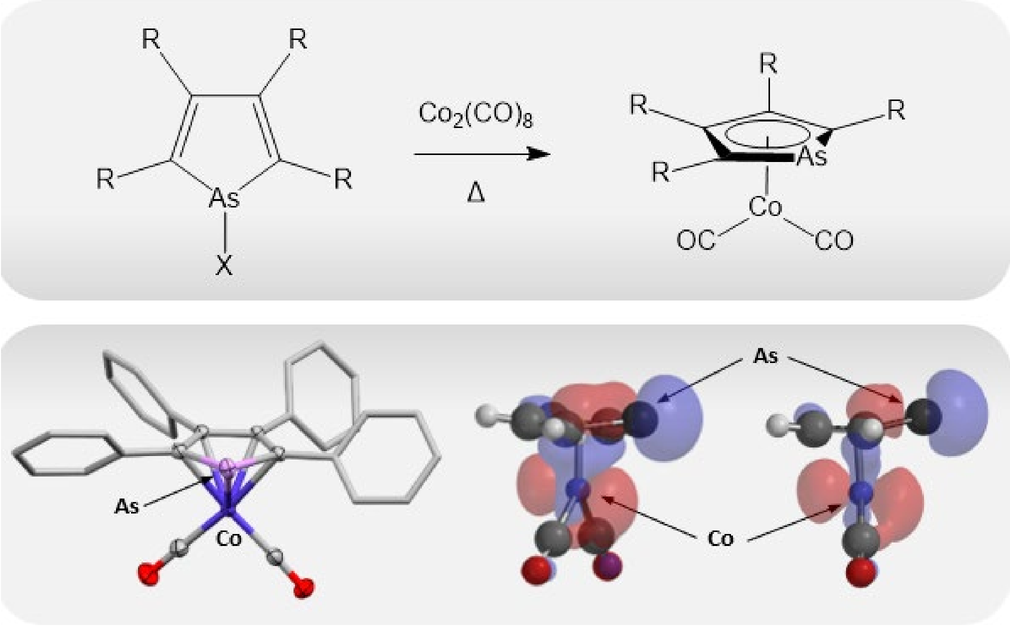

Figure 1, top: *Synthesis of η^5-arsolyl complexes of Co(I).* ***Bottom****: Crystal structure of [$Co(CO)_2(\eta^5\text{-}AsC_4Ph_4)$] and HOMO-1 of the model complex [$Co(CO)_2(\eta^5\text{-}AsC_4H_4)$].*

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Reductive Metallation of Dendralenes and Myrcene using Dimagnesium(I) Compounds

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Dendralenes are simple acyclic poly-olefins, that are typically used as building blocks in the synthesis of natural products and complex heterocyclic systems. Originally believed to be unstable at room temperature, and thus of limited synthetic utility, Sherburn and co-workers established straightforward multi-gram synthetic routes to an extensive family of parent and substituted dendralenes which are considerably more stable than previously thought.[1,2] Reduction of these dendralenes using conventional organometallic reducing agents has been poorly investigated. Since their development in 2007,[3] dimagnesium(I) compounds ([Mg]–[Mg], [Mg] = ^{Ar}Nacnac, $[HC(MeCNAr)_2]^-$, or ^{Ar}Priso = $[(DipN)_2CNPr^i{}_2]^-$, Ar = bulky aryl) have been widely used as soluble and easy to handle reagents, that are capable of selectively reducing a variety of small organic substrates, including alkenes.[4] For instance, the insertion of 1,1-diphenylethylene into the Mg-Mg bond of the dimagnesium(I) compound was found to be the first room-temperature reversible redox process for s-block metal complexes.[5] In the search of further expanding this chemistry, we have reduced the poly-olefins: 2,3-dimethyl-1,3-butadiene (DMB), [4]dendralene (4dend) and the related acyclic monoterpene, myrcene (Myr), to assess reactivity of the reduced products with H_2 and/or CO, to form value-added organic products.

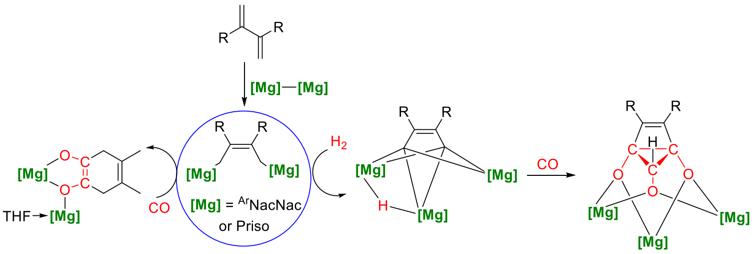

Figure 1. Reductive metallation of polyolefins and further reactivity with H_2 and/or CO.

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RE(III) 3-Furoate Complexes : Synthesis, Structure, and Corrosion Inhibiting Properties

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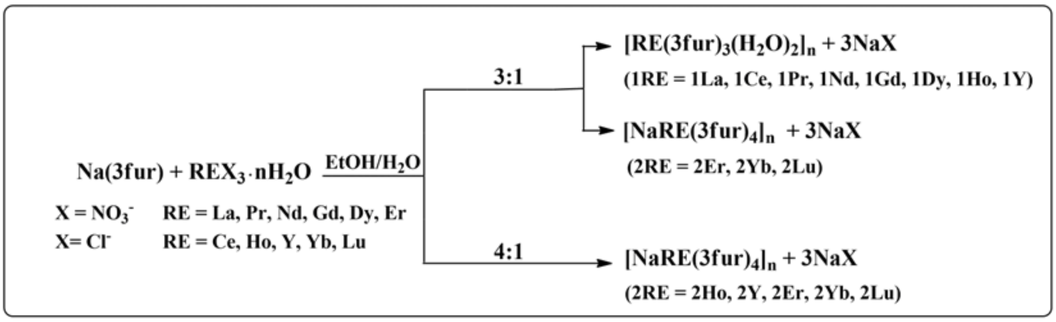
Corrosion is a widespread and extremely costly issue for engineering materials in diverses industries. It has been shown that a combination of rare earth metals with organic corrosion inhibitors can form new complexes with improved inhibitory effects.[1,2,3] In this study, two types of Rare Earth (RE) 3-furoate complexes were synthesized by metathesis reactions between RE chlorides or nitrates and preformed sodium 3-furoate. Two different structural motifs were identified as Type **1RE** and Type **2RE**. The Type **1RE** monometallic complexes form 2D polymeric networks with the composition $[RE(3fur)_3(H_2O)_2]_n$ (**1RE** = 1La, 1Ce, 1Pr, 1Nd, 1Gd, 1Dy, 1Ho, 1Y; 3furH = 3-furoic acid) while Type **2RE** bimetallic complexes form 3D polymeric systems $[NaRE(3fur)_4]_n$ (**2RE** = 2Ho, 2Y, 2Er, 2Yb, 2Lu). The stoichiometric mole ratio used (RE: Na(3fur) = 1:3 or 1:4) in the metathesis reaction determines whether **1RE** or **2RE** (RE = Ho or Y) is formed, but **2RE** (RE = Er, Yb, Lu) were obtained regardless of the ratio. The corrosion inhibition behaviour of the compounds has been examined using immersion studies and electrochemical measurements on AS1020 mild steel surfaces by a 0.01 M NaCl medium. Immersion test results revealed that $[Y(3fur)_3(H_2O)_2]_n$ has the highest corrosion inhibition capability with 90% resistance after 168 h of immersion. Potentiodynamic polarisation (PP) measurements also indicate the dominant behaviour of the **1Y** compound, and the PP curves show that these rare earth carboxylate compounds act predominantly as anodic inhibitors.



Scheme 1 : The synthesis of RE 3-furoate complexes. The ratios shown in the Scheme refer to the Na(3fur) : REX_3 ratios of reactants.

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Synergy in the s-Block: Alkali Metal Magnesiates for Small Molecule Activation

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Organoalkali reagents provide access to an array of reactive nucleophiles and are used extensively in academic chemical research and in industry.[1] Accessing heavier derivatives of these species by pairing an alkali metal with an alkaline earth or p-block element has become a core facet of main-group chemistry.[2] In this regard, alkali metal magnesiates have attracted considerable interest within the realm of small-molecule activation.[3] These synergistic combinations can be used to enable reactivity not previously accessible by related monometallic magnesium systems.[4] We recently reported that a potassium/magnesium bimetallic could promote the reductive capture of dinitrogen through a transient *'anionic'* magnesium(I) radical intermediate – the first example of nitrogen activation facilitated by a molecular magnesium complex.[4] We have also investigated the role of alkali metals in the chemistry of magnesium(II) hydride complexes through simple coordination processes.[5] This presentation will discuss our recent breakthroughs in the convenient synthesis of these mixed magnesium/s-block systems and their role in the activation of small molecule substrates (*i.e.* CO and N_2).

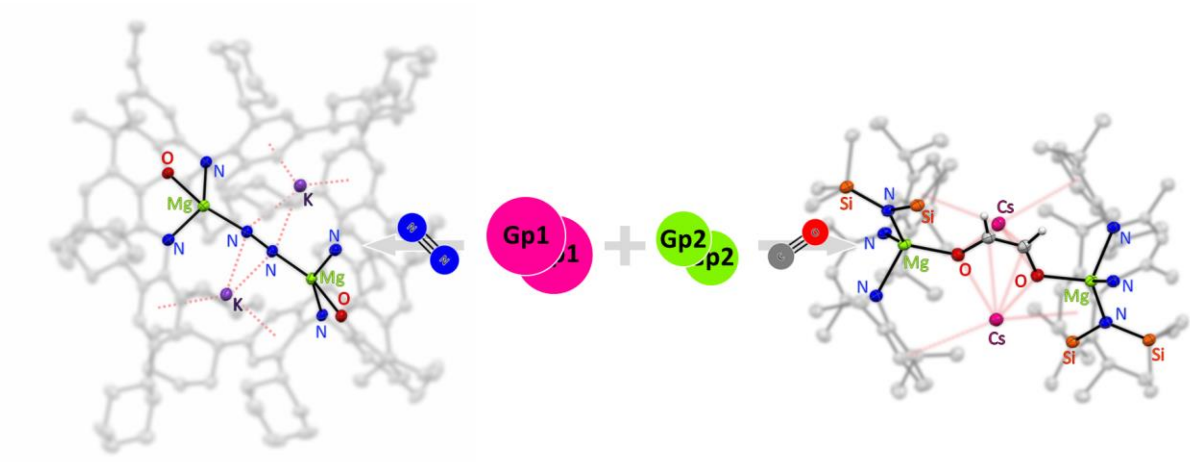

Figure 1. Synergistic small molecule activation by mixed s-block magnesium bimetallics.

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Ni(II) pincer complexes for the electrocatalytic production of H_2

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Hydrogen gas has been proposed as an alternative green fuel in place of fossil fuels and as such significant research is being done to develop catalysts that can efficiently reduce protons into molecular hydrogen.[1,2] [Fe-Fe] and [Fe-Ni] hydrogenases that exist in certain bacteria and organisms have been found to carry out proton reduction with low activation barriers and high turnover rates.[3] Their efficiency stems from the bimetallic cooperativity between the two metals, a phenomenon in which both metals are involved in reactivity.[4] This discovery has inspired organometallic chemists to design and synthesize complexes that mimic the active sites of these hydrogenase enzymes. Numerous nickel pincer complexes have been reported in literature that have the potential to act as proton reduction catalysts in various media.[5-7] In this work we report Ni(II) complexes of an unsymmetrical pincer ligand (**Fig. 1A**), their redox properties (**Fig 1B**) and their potential use in the electrocatalytic production of H_2.

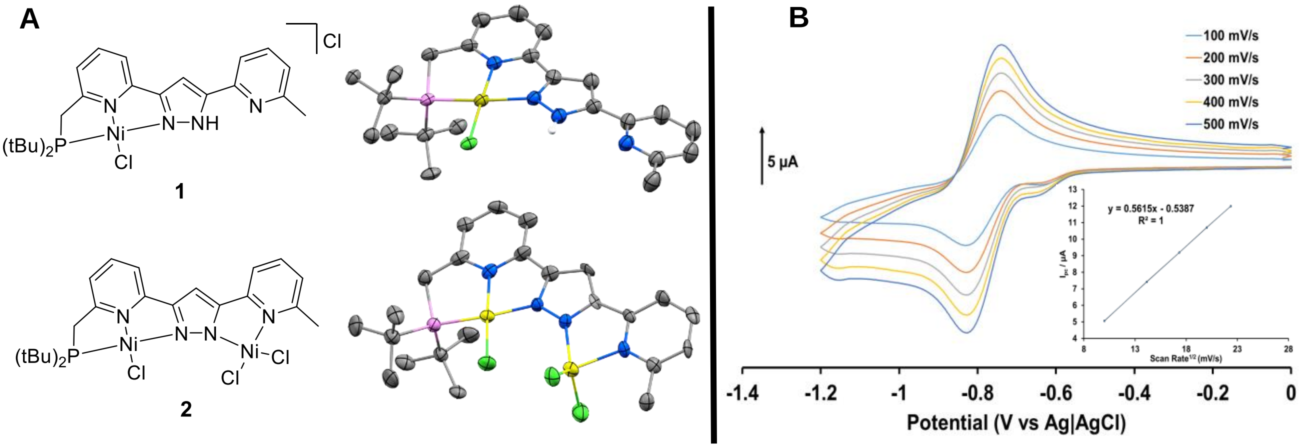

*Figure 1: (**A**) Mono and dinickel complexes used in this study. (**B**) Overlay CVs of **1** at incrementing scan rates. Insert: Plot of I_{pc} against square root of scan rate showing diffusion-controlled behaviour.*

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Synthesis of terphenyl-based bis(anilido) alkaline-earth metal complexes: Investigation of arene-metal interactions

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Metal-arene interactions have recently attracted considerable attention, due to their relevance in biological systems[1] and arene functionalisation.[2] In contrast to transition metals and *f*-block metals[3], where the covalent π-arene bonding relies on the interaction between *d*-orbitals of the metal and the π system of arene ligands, metal–arene bonding between hard Lewis acidic group 2 metals and soft π-ligands are less investigated. To study these interactions, hard donor atoms are introduced as an "anchor point" to impose the metal-arene contacts through spatial proximity. Using this tethered arene strategy, *p*-terphenyl bis(anilide) ligands were prepared and converted to the corresponding alkaline-earth metal bis(anilido) complexes. The monometallic complexes feature metal-η^6-arene interactions with relatively short metal-centroid distances. In this contribution, the synthesis and solid-state structures of the bis(anilido) group 2 metal species are presented and the metal-arene interactions are discussed. Moreover, bimetallic systems using these ligands are presented.

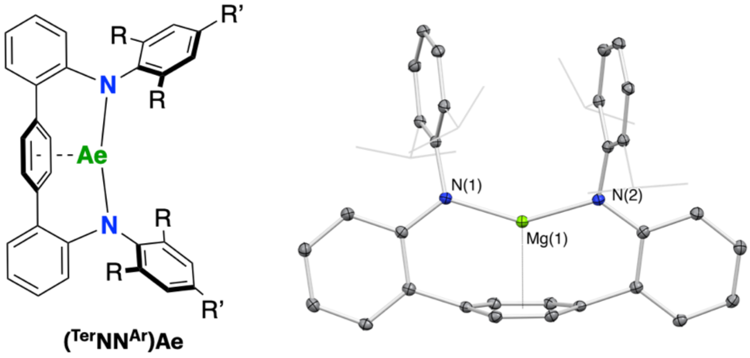

Figure 1. *Terphenyl-based bis(anilido) alkaline-earth metal complexes.*

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Exploring the reactivity of lanthanoid pseudo-Grignard reagents

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Rare earths (Sc, Y, and La-Lu) and their compounds have a wide variety of applications. Different synthetic approaches can be applied for the synthesis of these compounds. Approaches to RLnX (lanthanoid pseudo-Grignard reagents) have shown their potential for divalent complexes (Yb, Eu)[1,2] but are much less explored for Sm, Nd, La and Y. RLnX reacts with bulky *N,N*-bis(2,6-di-*iso*propylphenyl) formamidine (DippFormH) to generate different Ln^{II} complexes (for PhBr), namely $[Ln(DippForm)Br(thf)_3]_2$·6thf (**1; Sm, 2; Eu**) and Ln^{III} complexes (for PhI) $[Sm(DippForm)I_2(thf)_3]$·thf (**3**). Complexes (**1** and **2**) are seven coordinates, all are bromine-bridged dimers and complex (**3**) is seven coordinates monomer. Diverse divalent $[Ln(L)X(thf)_n]$ and trivalent $[Ln(L)X_2(thf)_n]$ complexes also synthesised by the reported methods[1,2] and the representative structure of complex (**1**, **2** and **3**) is shown in Figure 1. This work aims to explore the trapping method for divalent lanthanoids with different ligands.

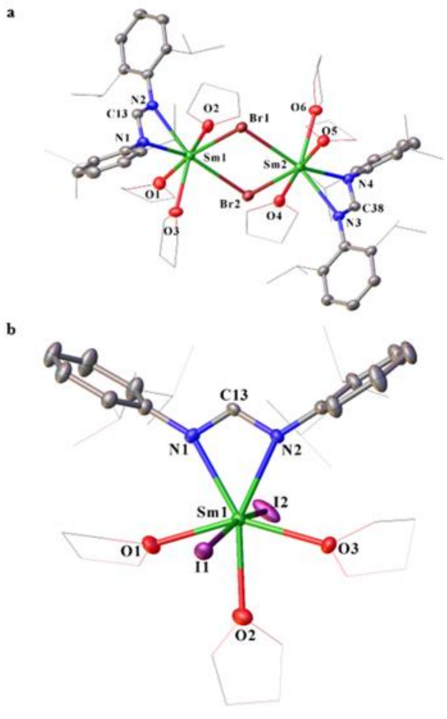

Figure 1. Molecular diagram of a) $[Sm(DippForm)Br(thf)_3]_2$·6thf (representative of Sm, 1, Eu, 2); b) $[Sm(DippForm)I_2(thf)_3]$·thf (3). Hydrogen atoms and lattice thf molecules are omitted and coordinated thf molecules and iPr groups are drawn as wireframe for clarity.

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Synthesis and Reactivity of Novel Group 14 – Aluminium Heterobimetallic Complexes

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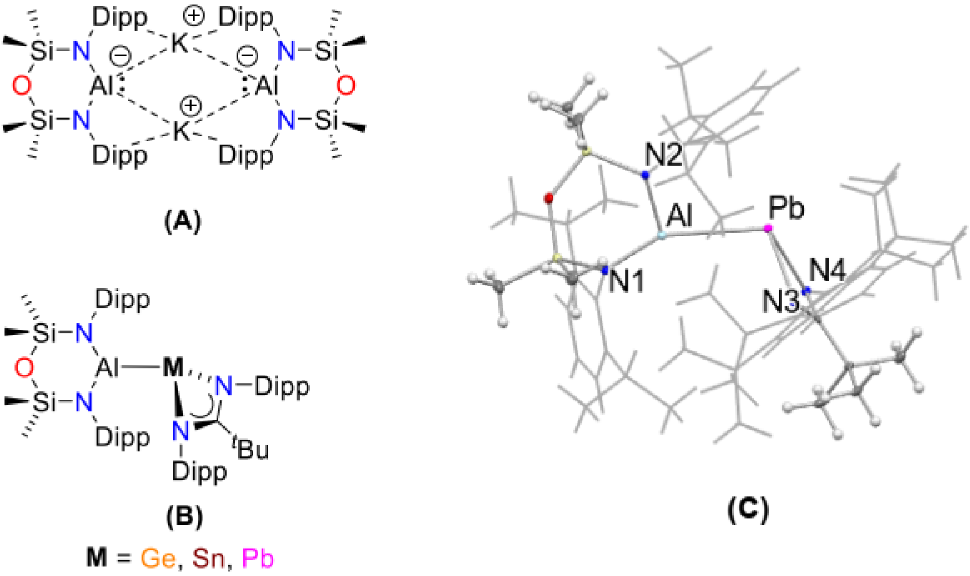
We have developed a new series of aluminium-containing Group 14 heterobimetallic complexes using the low valent aluminyl compound (**A**)[1], including the first example of an AlPb bond. This presentation will discuss the synthesis and physical characteristics of these novel heterobimetallic systems [(NON$^{\mathrm{Dipp}}$)Al-**M**(AMI$^{\mathrm{Dipp}}$)] (**B**) (NON$^{\mathrm{Dipp}}$ = $[\mathrm{O(SiMe_2NDipp)_2}]^{2-}$, AMI$^{\mathrm{Dipp}}$ = $[\mathrm{C(tBu)(NDipp)_2}]^{-}$. Dipp = 2,6-$\mathrm{iPr_2C_6H_3}$, **M** = Ge, Sn, Pb). Reactivity with organic molecules and functional groups will also be examined, including the addition of Group 16 elements into the heterobimetallic Al-**M** bond; furthermore, further functionalization of these reaction products will be discussed.[2],[3]



(A)

(B)

M = Ge, Sn, Pb

(C)

*Figure 1. Aluminyl compound **A**, heterobimetallic system **B** (M = Ge, Sn, Pb) and aluminium-lead complex **C**.*

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An NMR method to measure stretched C-H bond lengths

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One application of solution NMR relaxation is the determination of inter- and intra-nuclear distances between a pair of isotopically abundant spin-active nuclei with high gyromagnetic ratios; most, if not all the time, at least one ^{1}H nucleus is involved (*Figure 1*). The underlying principle of solution NMR relaxation is that the T_1 relaxation rate contribution from one nucleus to another is inversely proportional to the sixth power of the internuclear distance between the nuclei.

This work aims to expand upon the repertoire of solution NMR relaxation studies to include the measurement of stretched C-H bonds, which is a difficult task for x-ray diffraction, and the amount of neutron diffraction data is scarce. Stretched C-H bonds are present in agostic complexes, where a C-H bond is participating in a 3-centre-2-electron interaction with the metal centre. The $^1J_{CH}$ of said C-H bond is smaller than an unperturbed C-H bond – implying that the agostic C-H bond is stretched.

Modified inversion recovery experiments were employed to obtain T_1 relaxation rates from the centre line and ^{13}C satellites of ^{1}H resonances. The T_1 relaxation rate of a ^{13}C satellite includes the sum of all relaxation sources, while the T_1 relaxation rate of the centre line lacks the T_1 relaxation contribution from the ^{13}C-H bond. The difference between the two T_1 relaxation rates, and subsequent calculations, reveal that the agostic C-H bond length is 7.5(1.0)% longer than the unperturbed geminal C-H bond in $[(\eta^5\text{-Cp*})Rh(C_{10}H_{13})][PF_6]$ (**4**). Additionally, DFT calculations report a 7.4% longer C-H bond.

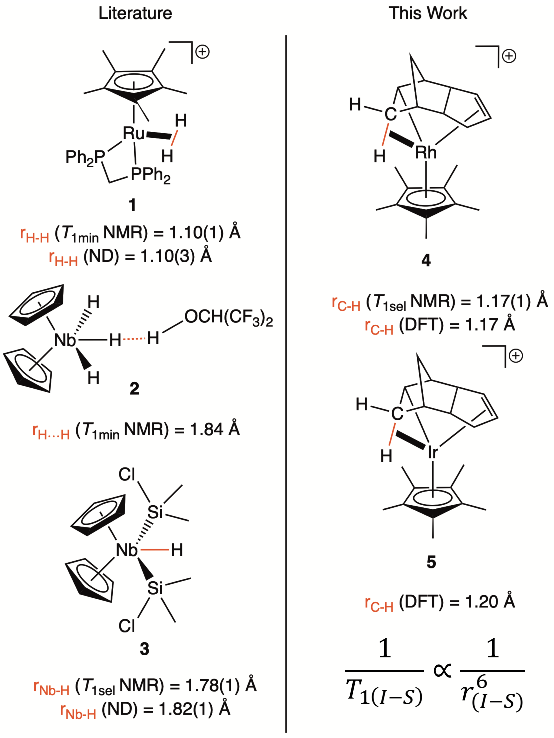

Figure 1. Bond length comparisons between NMR, DFT, and neutron diffraction (ND) studies on dihydrogen, dihydrogen bonded, hydride, and agostic complexes; **1**[1], **2**[2], **3**[3], **4**, and **5**, respectively.

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Exceptional Hyperpolarizabilitie: Molecular Symmetry and Solution-Phase Structure of Ruthenium Alkynyl Porphyrin Triads/Pentads

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In a continuation of studies exploring the nonlinear optical (NLO) properties of new metal-containing molecules, several new octupolar D_2-symmetric porphyrin-bridged ruthenium alkynyl triads/pentads have been synthesized, with a systematic variation in bridge length, co-ligand, ene/yne linkage, and the presence/absence of porphyrin-core metal. By undertaking femtosecond Z-scan measurements at incident irradiation wavelengths spanning the 800–2150 nm spectral range. we have noted that specific examples exhibit exceptional two-photon absorption and outstanding three-photon absorption, and we have found the first porphyrins to exhibit five-photon absorption.

We have also measured the quadratic hyperpolarizability (β) values of the new porphyrins, using hyper-Rayleigh light scattering (HRS) measurements at an incident irradiation wavelength of 1064 nm. The HRS results for these triads/pentads reveal very large hyperpolarizabilities (510 - 3050 × 10^{-30} esu) that derive predominantly from conformers in which there are significant torsional angles between the alkynyl ruthenium units and the porphyrin plane, consistent with this solution-phase structural subpopulation exhibiting exceptional hyperpolarizabilities. These ruthenium alkynyl porphyrin triads/pentads have potential as building blocks for new classes of nonpolar electrooptic materials as well as outstanding multiphoton absorbers.

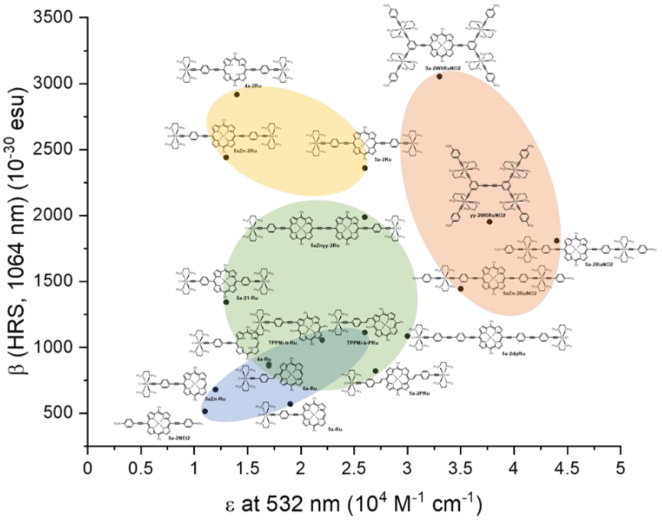

Figure 1. Hyperpolarizability of Ruthenium Alkynyl Porphyrin Hybrids

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Two-photon absorption properties of triarylamine-based multipolar 1,1,4,4-tetracyanobutadienes: the effect of ferrocenyl peripheral substituents

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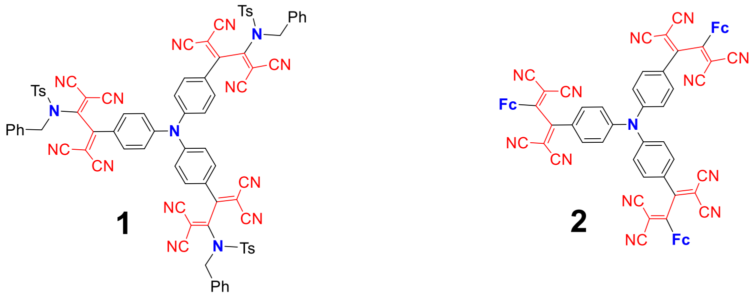
The synthesis and characterization of several new tetracyanobutadiene (TCBD) derivatives incorporating toslylamido, 4-triphenylamino and ferrocenyl moieties will be reported.[1] Their linear and (third-order) nonlinear optical (NLO) properties investigated by electronic absorption spectroscopy and Z-scan measurements will then be reported. Among these compounds, the tri-branched compounds **1** and **2** (scheme) turned out to be the most active two-photon absorbers. These properties will be discussed with the help of DFT calculations,[2] focussing on structural and electronic factors and contextualized with the few two-photon absorption results previously published for related TCBD compounds.[3-6]



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2

Figure 1. Some trigonal multipolar TCBD derivatives discussed in this contribution

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Electronic Absorption, Emission, and Two-Photon Absorption Properties of 2,4,6-Triphenyl-1,3,5-Triazines

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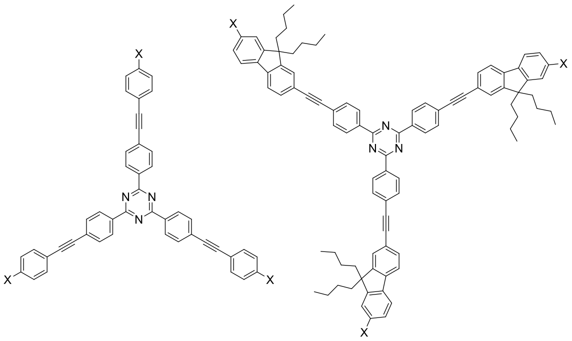
The linear optical properties of some extended 2,4,6-triphenyl-s-triazines of formula 2,4,6-$[(1,4\text{-}C_6H_4)C{\equiv}C(4\text{-}C_6H_4X)]_3\text{-}1,3,5\text{-}(C_3H_3N_3)$ (**1-X**; X = NO_2, CN, OMe, NMe_2, NPh_2) and related analogues **2-X** (X = H, NPh_2) are reported, followed by their two-photon absorption (2PA) properties. When compared to corresponding isocyanurates[1-2] or 1,3,5-triphenylbenzene derivatives,[3] their 2PA performance turns out to be quite good for molecules of that size in the near-IR range, especially when functionalised by electron-releasing substituents at their periphery. However, they present a decreased transparency window in the visible range due to their first 1PA peak. Furthermore, due to their significantly large two-photon brilliancy, 2,4,6-triphenyl-s-triazines appear also promising for two-photon fluorescence bio-imaging purposes.[4]



1-X **2-X**

*Figure 1. Chemical structures of compounds **1-X** and **2-X***

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Metal (Au, Pd, Pt) nitroimidazole complexes as potential antitumor metallodrugs

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Today, platinum-based cytostatics are much more common, but they have low solubility in water, significant toxicity, and studies have documented the development of cancer cell resistance. The problematic nature of platinum-based drugs has stimulated the search for alternatives, which may be palladium and gold complexes. In recent years, there have been more and more scientific reports about imidazole and the related azole moiety. The imidazole ring is an important five-membered aromatic heterocycle widely present in natural products and synthetic molecules. We therefore designed a series of novel transition metal complexes (Au, Pd, Pt) with berenil and nitroimidazole. Imidazole moiety allowed us to increase molecular stability that may improve the physicochemical property and anchor an electron-rich aromatic ring on the N-moiety that helps to enhance antitumor activity. We observed that these complexes selectively concentrate in tumor cell mitochondria due to the characteristic for these cells increased membrane potential that may explain their increased proapoptotic activity. 24-h incubation with the tested complexes (concentration of 50 μM) caused an increase in the proportion of breast cancer cells MCF-7 and MDA-MB-231 with depolarized mitochondria. The highest mitochondrial membrane potential (MMP) decrease was observed in the palladium complex and it was 67.1 ± 3.5% in MCF-7 cells and 63.8 ± 2.7% in MDA-MB-231 cells. The MMP decrease induced by the remaining complexes was higher than the reference compound – cisplatin. It was proved that the palladium and gold complexes had a greater effect on programmed cell death measured by annexin V binding and an MMP decrease than cisplatin. The mitochondrial membrane potential results are consistent with those obtained in the annexin V/iodium propidium test and show that programmed cell death induced by the novel series of transition metal complexes may go through the mitochondrial pathway. The activity of the synthesized compounds against topoisomerase type II and their increased impact on DNA defragmentation also were documented. The novel complexes also induced autophagosome changes and inhibited tumor growth in xenograft models.

Synthesis and cytotoxic activities of novel transition metal complexes with berenil and nitroimidazole

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Novel transition metal complexes (Au, Pd, Pt) with berenil and 2-(1-methyl-5-nitroimidazol-2-yl)ethanol were obtained through two-step synthesis. In the first stage of the synthesis, inorganic metal salts of gold, palladium and platinum were treated with 2-(1-methyl-5-nitroimidazol-2-yl)ethanol to give stable intermediates. After isolation and purification, the obtained intermediates were used for the second stage. For this purpose, the previously obtained compounds were treated with an aqueous solution of $AgNO_3$ followed by berenil in a 10% NaCl. The cytotoxicity assay against MCF-7 and MDA-MB-231 breast cancer cells revealed that novel platinum, gold and palladium complexes cause a reduction on the viability of MCF-7 and MDA-MB-231 breast cancer cells to a greater extent than cisplatin. The complexes showed lower cytotoxicity on normal MCF-10A human breast epithelial cells than on tumor cells. Following 24 h of incubation with the tested compounds (concentration of 50 μM), we observed that all of them significantly induced apoptosis in MCF-7 and MDA-MB-231 cells compared with the control. The strongest proapoptopic properties on both cell lines after 24 h of incubation were exhibited by the palladium complex, where we observed 58.4 ± 2.8% viable cells and 39.7 ± 4.5% apoptotic cells in MCF-7 cells and 58.3 ± 2.9% viable cells and 40.2 ± 4.2% apoptotic cells in MDA-MB-231 cells. The weakest proapoptopic properties in both cell populations were exhibited by the gold complex, where we observed 72.2 ± 2.9 (MCF-7) and 70.6 ± 2.4% (MDA-MB-231) viable cells; 29.0 ± 4.5 (MCF-7) and 29.1 ± 4.7% (MDA-MB-231) apoptotic cells, respectively. At the same time, it's worth emphasizing that in the case of cisplatin, the percentage of apoptopic cells was only 20.4 ± 0.8% (MCF-7) and 20.6 ± 3.6% (MDA-MB-231). Based on the obtained results, we concluded that the cytotoxic activity of the novel series of transition metal (AuMet-1, PdMet-1, PtMet-1) compounds with nitroimidazole and berenil moiety against both breast cancer cells may dependent on the induction of programmed cell death.

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Novel and Convenient Synthesis of Copper Formamidinates

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Copper formamidinates were successfully synthesized by using cuprous oxide and formamidines with pyridine (Py) as a solvent by stirring at room temperature which is more convenient method than the reported methods.[1–4] The reaction of copper(I)oxide in organic solvents is difficult due to its low solubility and the high bond dissociation energy of the Cu-O bond. [Cu_2(DippForm)$_2$], [Cu_2(EtForm)$_2$Py], and [Cu_2(XylForm)$_2$Py] have been obtained as crystals by the reaction of Cu_2O with N,N′-bis(2,6-di-isopropylphenyl)formamidine (DippFormH), N,N'-bis(2,6-diethylphenyl)formamidine (EtFormH), and N,N'-bis(2,6-dimethylphenyl)formamidine (XylFormH), respectively. The formation of the product was confirmed by Single Crystal X-Ray Diffraction and Multinuclear NMR spectroscopy. All the crystals show luminescence and act as an active reagent for the redox transmetallation reaction with Rare Earth Metals.

$$\mathrm{Cu_2O + 2\ FormH \xrightarrow[\text{7 days}]{\text{Pyridine}} Cu_2(Form)_2 + H_2O}$$

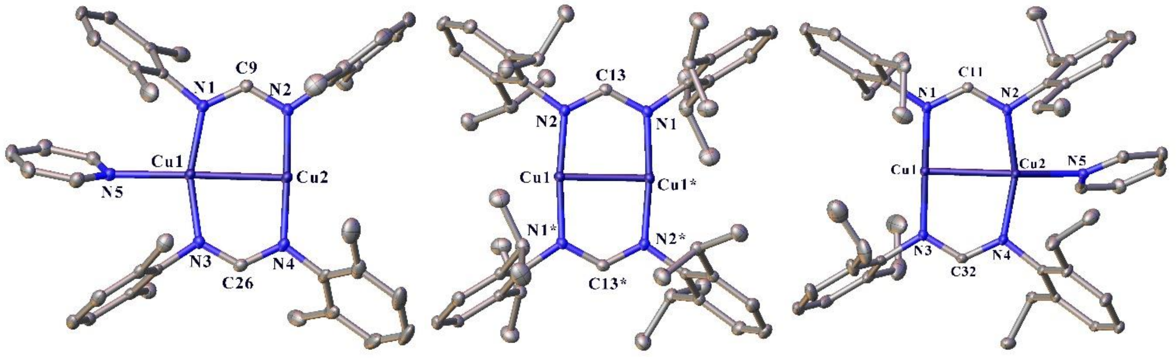

Figure 1. Molecular diagrams of [Cu_2(XylForm)$_2$Py], [Cu_2(DippForm)$_2$] and [Cu_2(EtForm)$_2$Py] (left to right)

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Experimental and Theoretical Investigations on Cu and Ni Complexes of the Anti-diabetic Drug Metformin Hydrochloride

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The anti-diabetic drug Metformin is one of the most common drug therapies worldwide for the treatment of diabetes mellitus. Due to its low absorption, a large portion of the drug is excreted from the body unchanged. The present work is concerned with detecting Metformin in wastewater by metal complexation, and more broadly on drug interaction with biologically active metals. The presence of primary amine and imine groups imparts remarkable complexing ability to Metformin, which acts as a bidentate ligand. At pH 7, the interaction of Metformin with Cu^{2+} ions shifts the UV-visible absorption maximum of copper sulphate from 635 nm to 647 nm. Optimization of the concentration of Cu^{2+}, the concentration of Metformin, the amount of ammonia, and the reaction time afforded the maximum response factor of the drug. The Beer-Lambert law is followed in the linear dynamic range 5 -25 μg/ml. Complexes of Metformin-Cu^{2+} and Metformin-Ni^{2+} were prepared and characterized by elemental analysis and spectroscopic technique. Proposed structures of Metformin-Cu^{2+} and Metformin-Ni^{2+} were optimized by theoretical calculations using semi-empirical and DFT methods, and the experimental results were compared with the theoretical data.

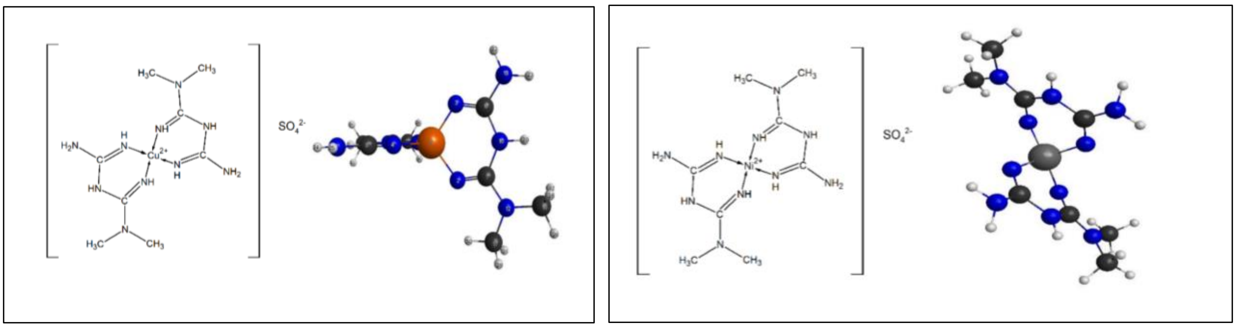

Figure 1. Proposed structure and DFT optimized structure of Metformin-Cu^{2+} (left) and Metformin-Ni^{2+} (right).

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Unlocking the Potential of Electrochemistry: Fabrication and Characterisation of Lanthanum Oxide Nanoflakes for Advanced Resistive Switching Applications

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In this study, we harnessed electrochemistry as a powerful tool for synthesizing and exploring the electrochemical properties of self-assembled lanthanum oxide (La_2O_3) nanoflakes, focusing on their potential for resistive switching applications. The deposition of La_2O_3 nanoflakes was achieved through chronoamperometry, following a thorough analysis of cyclic voltammetric and linear sweep voltammetric graphs [1]. Subsequently, we conducted comprehensive electrochemical investigations on a thin film of the deposited nanoflakes, including *in-situ* electrochemical impedance spectroscopy (EIS), Mott-Schottky analysis, two-terminal EIS, and frequency-dependent and scan rate-dependent cyclic voltammetric techniques.

Our findings revealed several significant outcomes. Firstly, La_2O_3 thin films can be rapidly deposited at low voltages within seconds, showcasing their potential for efficient and scalable fabrication. These films exhibited n-type resistive behavior with an appreciable carrier density. Moreover, solid-state electrochemical measurements displayed substantial current levels, with the hysteresis area of the IV curves diminishing as the frequency increased. The scan rate-dependent studies confirmed that the migration of charged species within this device follows a surface-mediated drift process. Furthermore, two-terminal EIS analysis demonstrated a decrease in impedance in the low-resistance state (LRS) compared to the high-resistance state (HRS), indicating that the formation of conduction filaments is a key contributor to the resistive switching phenomenon.

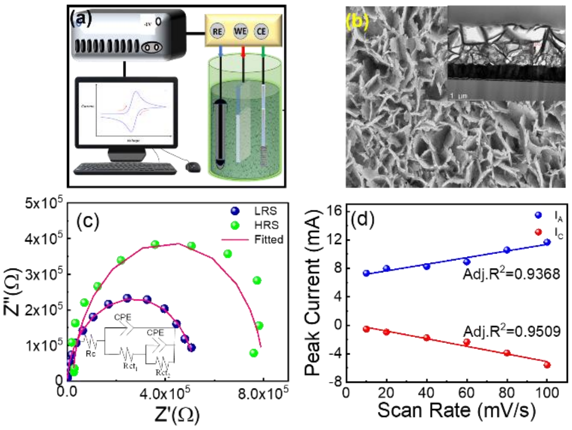

Figure 1. *(a) Schematic illustration of a three-electrode system used for electrodeposition. (b) SEM micrograph (inset: TEM micrograph). (c) Two-terminal EIS studies and (d) plot of anodic and cathodic peak current versus scan rate of the* La_2O_3 *nanoflakes-based RS device.*

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Sb(V) aryl anthraquinone complexes: Enhanced stability and antileishmanial activity of a fluorescent anthracycline system

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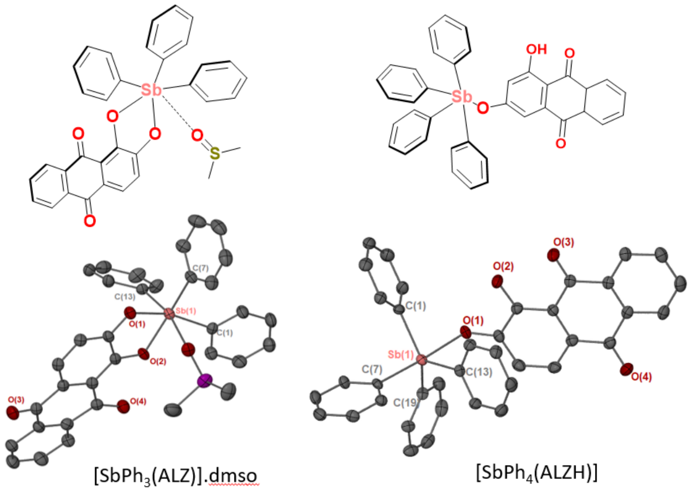
Hydroxyanthraquinones are naturally derived cyclic compounds with a variety of biological functions. Their delocalised nature gives rise to a number of spectacular colours through resonance stabilisation at the different functional groups around the ring. The downside to their high resonance capability 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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Hydrazone based coordinatively unsaturated metallocages

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The use of transition metal ions to form self-assembled metallocages has been used to great effect throughout supramolecular chemistry, especially in host-guest recognition[1] and as containers for catalysis.[2] The majority of these structures are constructed through the coordination of metal ions to organic ligands, with only a few cage architectures being composed of an organic cage containing metal ions with available coordination sites.[3] By incorporating these coordinatively unsaturated metal ions into an organic capsule the remaining available coordination sites can be investigated for guest binding and potential catalytic reactivity and selectivity.

In this work, the use of hydrazone motifs to facilitate the self-assembly of tripodal cages will be reported, as well as the potential for these cages to complex coordinatively unsaturated transition metal ions (Figure 1).

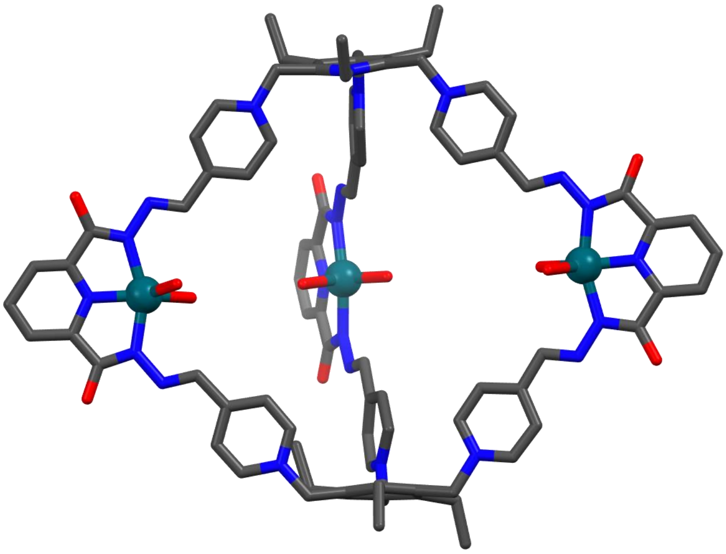

Figure 1. Crystal structure of hydrazone cage with coordinatively unsaturated transition metal ions (M_3L).

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Synthesis of metal organic frameworks of copper and cobalt and their application in removing lead ions from water

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The presence of pharmaceutical products, dyes, and toxic metal ions in water is a major problem worldwide. This work developed metal organic frameworks based on Copper- and cobalt-1,2,4,5-tetrabenzenecarboxylates. Cu- and Co-MOFs were synthesized, characterized and employed in metal adsorption studies. Characterization results were obtained from scanning electron microscopy, energy dispersive x-ray, thermogravimetric analysis and x-ray diffraction spectroscopy. The morphological features of Copper- and Cobalt-MOFs showed highly crystalline material as confirmed by the SEM micrographs. EDX spectra of both Metal organic frameworks also showed the presence of C, O and OH which may facilitate in creating charges and functionalities on the surface of the Metal organic frameworks for adsorption. Thermodynamic, equilibrium and isotherm batch adsorption experiments were carried out to determine concentration, time and temperature effects. The results obtained showed that Cu-MOFs were more effective adsorbent than Co-MOFs. The adsorption of Pb^{2+} was observed to be enhanced by the increase in temperature. This improvement could be due to increased kinetic energy of adsorbate and formation of new binding sites on the surface of Copper-MOF. The values of ΔG^o indicates that the sorption process was spontaneous. A positive ΔH^o suggests that sorption proceeded favourably at a higher temperature and the sorption mechanism was endothermic. A positive ΔS^o suggests that the freedom of the adsorbed Pb^{2+} was not restricted in the MOFs, indicating that physic-sorption mechanism occurred. Copper-MOF plot showed a maximum of 80.91% removal of Pb2+ was observed in 30 minutes and Cobalt-MOF 72.18% in 20 minutes.

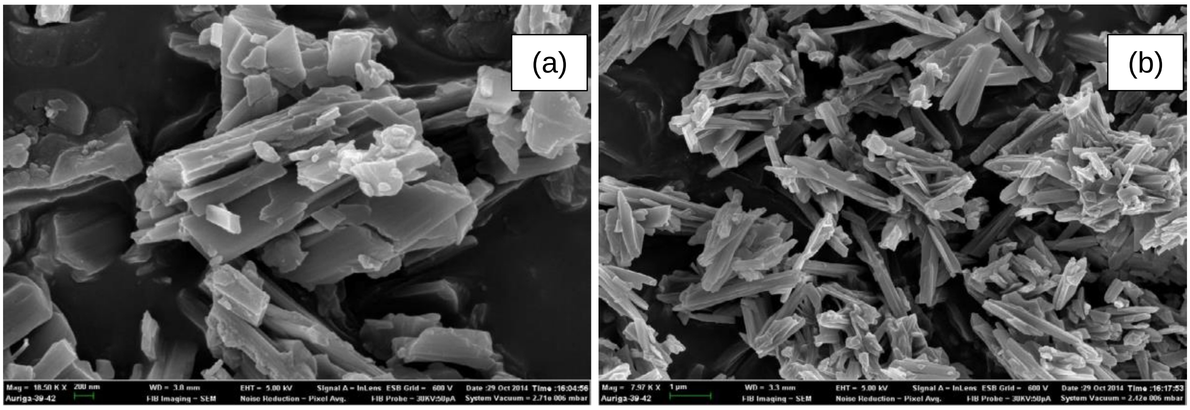

Figure 1. SEM images for (a) Cu-MOF and (b) Co-MOF

Bimetallic 1,8-diazaanthracene complexes for CO_2 electroreduction

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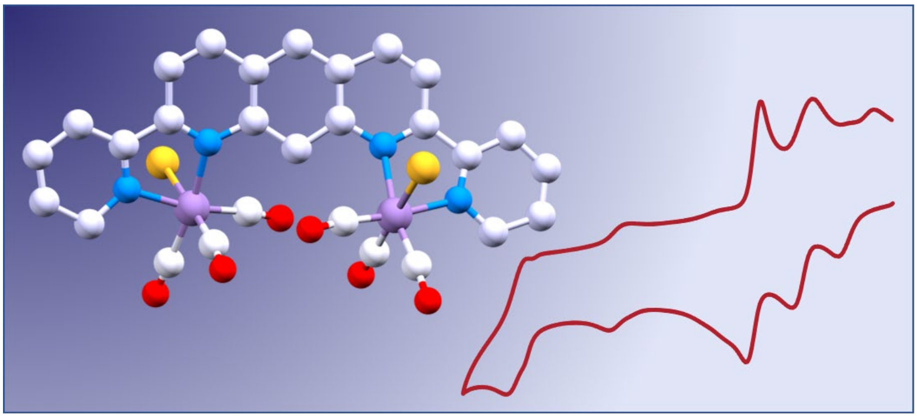
Group 7 metal complexes of the form $[M(bpy)(CO)_3X]$ (M = Mn, Re; bpy = 2,2′-bipyridine; X = Br, Cl) are prototypical catalysts for electroreduction of CO_2 to CO.[1,2] Interest in metal-metal cooperative reactivity in this context has led to the design of ligands which incorporate two metal-binding sites favouring the positioning of metals in close spatial arrangements which enable bimetallic modes of reactivity.[3,4] In particular, metal-metal cooperative modes of reactivity in the CO_2 reduction reaction are envisaged to offer access to different product profiles and selectivity when compared to monometallic systems.[5]

In this work, we explore the usage of the 2,7-bis(2-pyridyl)-1,8-diazaanthracene ligand (**L**)[6] and derivatives in the synthesis of bimetallic manganese and rhenium complexes for use in studies of CO_2 electroreduction chemistry, and compare the reactivity of bimetallic complexes to their monometallic counterparts. This ligand is designed to promote side-by-side metal binding through the two *'bpy-like'* moieties, which position two metal sites at distances of approximately 5 Å. **L** also allows strong electronic communication between metal centres through the polyaromatic core. The bimetallic coordination potential of the ligand is demonstrated by the complex $[Mn_2(\mathbf{L})(CO)_6(Br)_2]$ (**1**), accessible via heating of $[Mn(CO)_5Br]$ with **L**.

Ongoing work explores the nature of observed electrochemical reduction events and the reactivity of **1** and related complexes with respect to CO_2 electroreduction.



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Synthesis and characterisation of organometallic gallium(III) complexes

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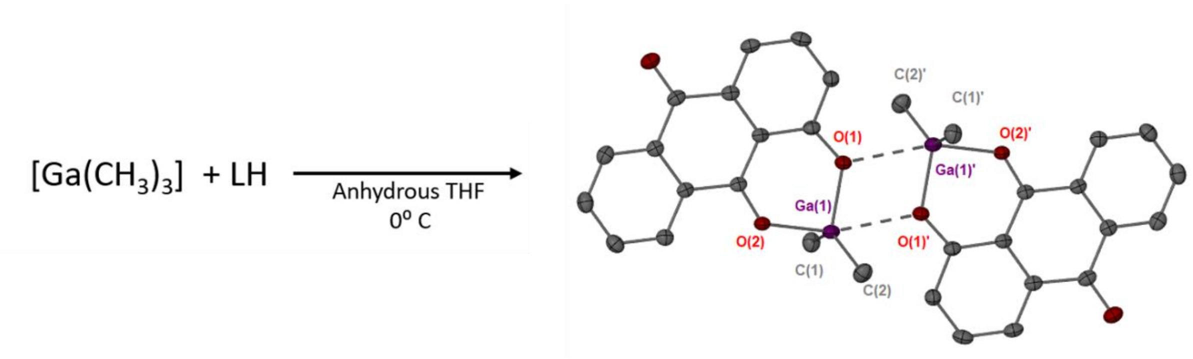
With the rise in antimicrobial resistance (AMR) leading to preventable infections and deaths worldwide, the need for new treatments has become apparent.[1] The use of metals to combat AMR has become an area of interest due to the unique chemistry and potential synergistic relationships between metals and bioactive organic compounds.[2]

Previous studies by Andrews *et al* found organometallic gallium complexes of halido-quinolinol to be effective anti-leishmanials.[3] Therefore, we aimed to expand on the library of organometallic gallium compounds to address a range of microbes, including resistant bacteria.

A series of novel organometallic gallium(III) compounds have been synthesised with the aim of assessing their suitability for biological use. Interesting observations regarding solution and solid state chemistries were made for organometallic hydroxyanthraquinone and alpha-hydroxy acid complexes. Solid state data, including FT-IR, elemental analysis and XRD were collected and analysed, and solution state and stability studies were conducted using NMR techniques. Herein, this poster presents the synthesis and characterisation of these novel compounds.



$$[Ga(CH_3)_3] + LH \xrightarrow[0^{o}\,C]{\text{Anhydrous THF}}$$

Figure 1. General synthetic conditions for the synthesis of dimethylgallium(III) organometallic compounds. Crystal structure shown is a dimer of the product 1-hydroxyanthraquinone dimethylgallium(III). Hydrogen atoms have been omitted for clarity.

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^{18}F-LABELLING OF DIFLUORO- AND TRIFLUOROMETHYL GROUPS VIA FLP-MEDIATED SELECTIVE C-F ACTIVATION; TOWARDS THE SYNTHESIS OF NEW RADIOTRACERS FROM OFF-THE-SHELF DRUGS

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Fluorocarbons have found increased applications in many fields: pharmaceutical, material, agrochemical etc. Although ^{18}F-labelling of monofluorides have been widely studied, the efficient labelling of difluoro- and trifluoromethyl groups continues to be challenging. Previous literatures have reported protocols but with a range of shortcomings (multistep synthesis of target compounds). Herein, we report a general method for labelling both -CF_2H and -CF_3 groups with good functional group tolerance, radiochemical yields and molar activities. The method employs selective C-F activation via a Frustrated Lewis pairs (FLP) approach [1] which allows ^{19}F-^{18}F substitution, using an isolable and bench-stable intermediate. This method has proved to also be applicable to biologically relevant molecules. The potential of synthesizing ^{18}F-labelled radiotracers using off-the-shelf target biomolecules as starting materials, coupled with the increasing use of -CF_2H and -CF_3 groups in pharmaceuticals makes this an attractive method for the development of radiotracers.

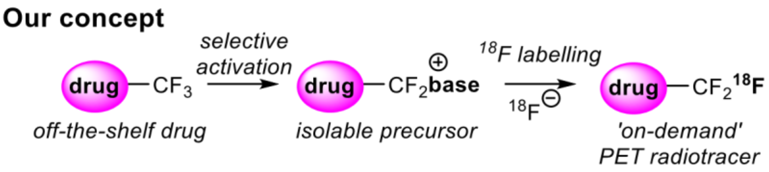

Figure 1. Our proposed concept of applying this protocol using off-the-shelf drugs as starting materials, enabling late-stage ^{18}F-labelling and their subsequent use as PET radiotracers.

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Reduction chemistry of group 13 dipyrromethene compounds

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The boron-dipyrromethenes (BODIPYs) represent a fascinating family of compounds that have attracted much interest as fluorescent dyes and markers in biological research.[1] To a main group chemist however, bulky dipyrromethene ligands are an attractive target for the stabilisation of low valent group 13 compounds.

In previous work, we reported the one- and two-electron reductions of a bulky BODIPY compound.[2] These reactions did not yield low valent boron compounds, but led to the reduction of the dipyrromethene core. In this work, we explore the reduction chemistry of the heavier dipyrromethene analogues, aluminium and gallium. Synthesis, spectroscopic, and DFT analysis (Figure 1) of the reduction products will be discussed.

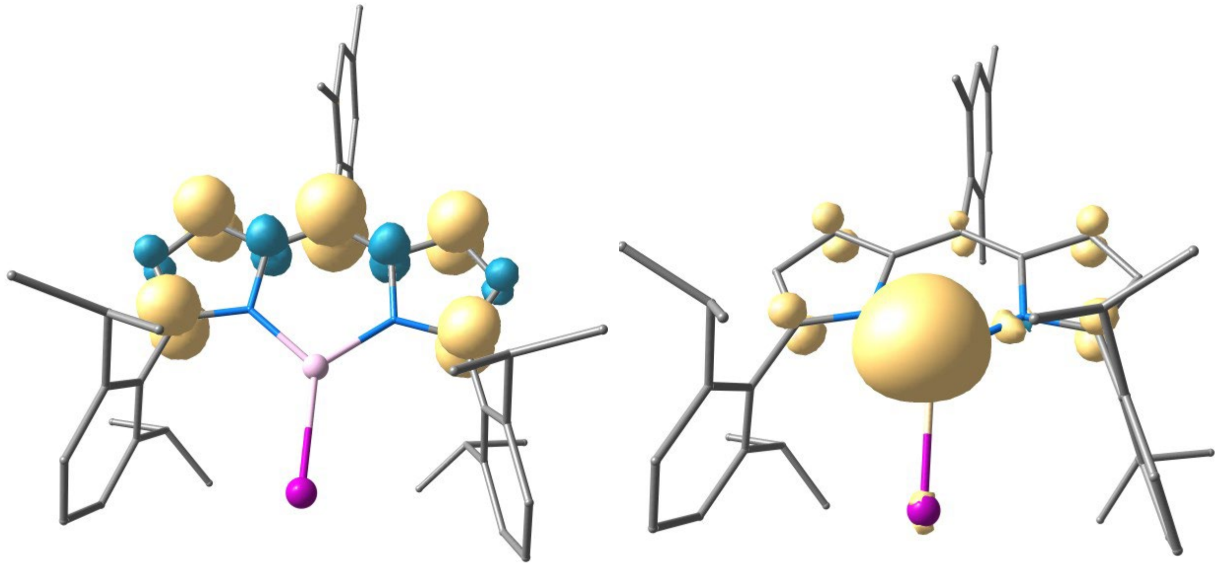

Figure 1. Spin density of the dipyrromethene aluminium iodide (left) and dipyrromethene gallium iodide (right) radical complexes, synthesised by the one-electron reduction of the heavy BODIPY analogues.

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Investigations into N-O-N Chelating Ligands in the Stabilisation of Boron(I) Anions

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The stabilisation of highly reactive low-oxidation state compounds is an area of considerable interest in current main group chemistry.[1] Boryl anions are a class of low-oxidation state boron compounds where the boron centre occupies the formal +I oxidation state, contains a lone pair of electrons, and consequently react as nucleophilic sources of boron. To date, eight structurally different boryl anions with *s*-block metal cations have been reported.[2-5] In each of these boryl anions, the boron(I) centre is constrained within a 5-membered heterocycle.[2-5] As a result, there has been little investigation into how a change in geometry about the boron(I) centre effects a boryl's reactivity.

To this end, the synthesis of a boryl anion with a wider coordination angle is being investigated, through the use of two diamido ligands, **NON** and **^{F}NON** (Figure 1). Upon coordination to boron, both ligands form an eight-membered heterocycle allowing for a wider coordination angle, and therefore a potentially more reactive boryl anion. Preliminary reduction studies have been carried out, with the formation of unprecedented ligand activation products seen. Results and proposed mechanisms will be discussed.

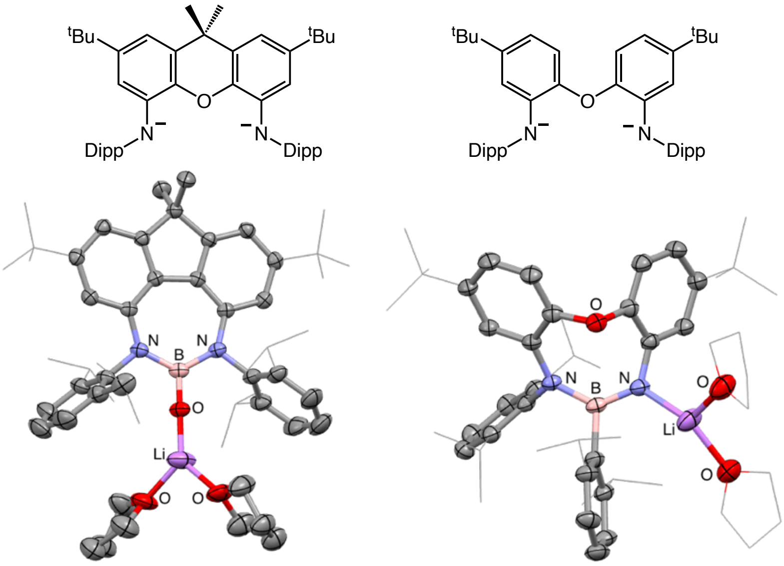

*Figure 1. The **NON** ligand (top left) and **NON** boron(III) ligand activation product (bottom left). The **^{F}NON** ligand (top right) and **^{F}NON** boron(III) ligand activation product (bottom right).*

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Oxidative Addition of Alkyl Halides at a Group 14 Centre

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Main group elements as replacements for transition metals in redox process catalysis has become an area of significant interest within chemistry. A promising alternative to transition metals are the Group 14 tetrylenes, which are able to partake in redox processes due to their amphiphilicity.[1] Specifically, germylenes have shown great potential in redox catalysis. However, little research has examined germylenes in the context of alkyl halide oxidative addition, which is a vital first step in many redox catalytic processes.

In this work, three novel compounds have been synthesised through the oxidative addition of alkyl halides across a germylene centre: (**NON**)Ge(Me)(I), (**NON**)Ge(^{s}Bu)(Br), and (**NON**)Ge(^{n}Bu)(I), (**NON** = 4,5-bis(2,6-diisopropylanilido)-2,7- di-tert-butyl-9,9-dimethylxanthene). These compounds have been found to exist as two structural isomers in equilibrium (Figure 1). Spectroscopic data, a mechanism for interconversion of these isomers, and the effects of steric bulk on the equilibrium will be discussed.

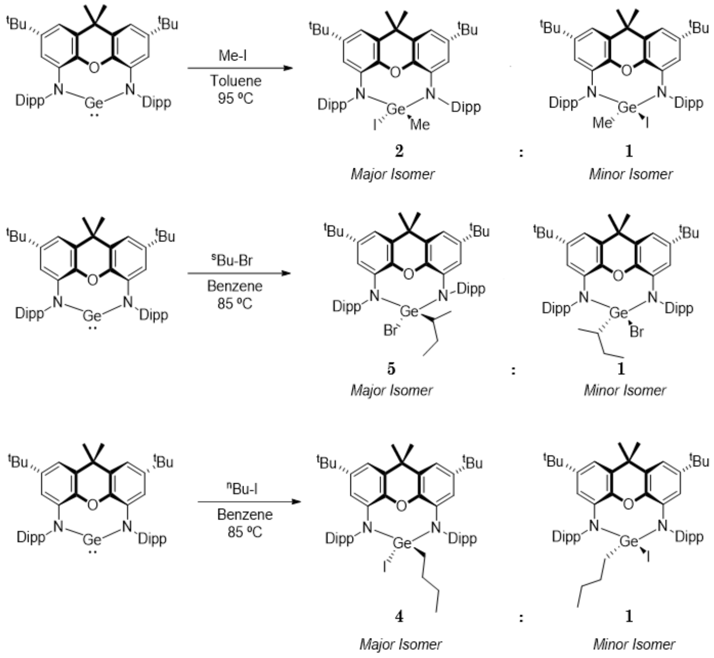

Figure 1. Synthesis of major and minor isomers of (NON)Ge(Me)(I), (NON)Ge(^{s}Bu)(Br), and (NON)Ge(^{n}Bu)(I)

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Synthesis and Reactivity of the $[SiH_6]^{2-}$ Dianion Stabilised within a Supramolecular Assembly

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A hypervalent silicate is a silicon-containing anion where the silicon atom bears more than the typical eight valence electrons.[1] Hypervalent silicates typically involve ligands that are highly electronegative, such as fluorine. Examples include the first of its kind, $SiF_4{\cdot}2NH_3$ (reported by Gay-Lussac in 1809) and the common counter anion hexafluorosilicate, $[SiF_6]^{2-}$.[2] In contrast, the electronegativity of hydrogen is comparable to that of silicon, making hydride coordination in hypervalent silicates uncommon. Hypervalent all-hydrido silicates (e.g. $[SiH_5]^-$ and $[SiH_6]^{2-}$) can be synthesised under high pressure or in the gas phase, however, these species are typically unstable under ambient conditions or in solution.[3-7]

Here, we report the first soluble, room temperature stable hexahydridosilicate complex $[\{KCa(NON)(OEt_2)\}_2][SiH_6]$. The $[SiH_6]^{2-}$ dianion is stabilised within a supramolecular assembly, which is decorated with four Lewis acidic metal centres (two Ca^{2+} and two K^+ cations). The synthesis, characterisation, along with ongoing reactivity studies of the complex will be discussed.

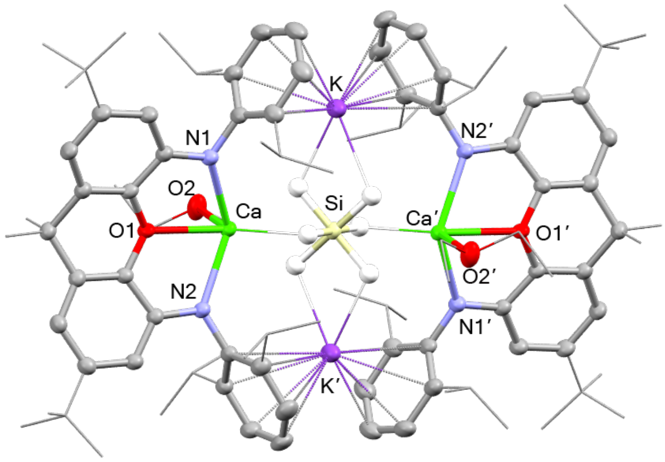

Figure 1. The hexahydridosilicate $[\{KCa(NON)(OEt_2)\}_2][SiH_6]$ as determined by X-ray crystallography.

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Charge Transfer in Ferrocenyl-Functionalized Cyclobutene Macrocycles

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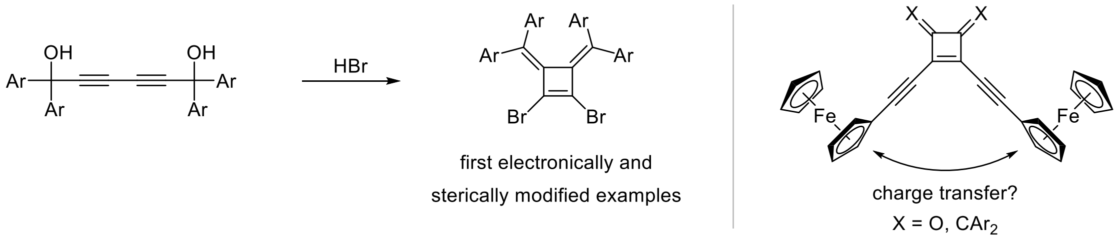
Redox active macrocycles, such as porphyrins, are of unbroken interest due to their facile generation of aromatic and antiaromatic states by redox processes. A major proportion of research, thus, focused on their inherent aromaticity, conductance, and charge-transfer properties through the building block.[1] This led to the development of three-dimensional objects, such as gigantic porphyrin$_{12}$ nano rings where computational and experimental results verified aromatic and anti-aromatic ring currents in addition to the porphyrin's local aromatic π-system on a global scale.[2]

In addition to such well-studied systems based on pyrrole precursors, other building blocks are similarly suited to generate large conjugated cycles. One of the most prominent examples are di-oxo-cyclobutenes as they are key elements during the synthesis of the carbon allotrope C_{18}, an cyclic all-carbon polyyne.[3] However, the so far used di-oxo derivative does not allow for functionalization, including the steric and electronic modification. Furthermore, little is known about the electronic communication through the cyclobutene entity itself. Thus, a variety of novel sterically and electronically-modified cyclobutene derivatives were synthesized and investigated towards their electrochemical properties. Selected examples were functionalized with ferrocenyl-entities allowing for the quantification of charge-transfer properties in the mixed-valent state to ultimately describe macromolecular systems.



first electronically and sterically modified examples

charge transfer?
X = O, CAr_2

Figure 1. Synthesis and structure of novel electronically and sterically modified dibromo cyclobutenes and diferrocenyl derivatives thereof.

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Overcoming the Steric Limitations of the Alkyne/Vinylidene Rearrangement

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16 Valence electron half-sandwich complexes of type [M(dppe)Cp]$^+$ (M = Fe, Ru) are known for their ability to coordinate and activate functional groups, including nitro (NO_2)[1] and internal alkyne functionalities (Ar-C≡C-Ar, **2**).[2] Those reactive intermediates can be prepared in situ from their parent chloride complexes **1** upon halide abstraction (Figure 1). Their reaction with, for example, internal alkynes results in germinal vinylidene complexes of type [M{=C=C(Ar)(Ar')}(dppe)Cp]$^+$ (**3**) for which a migration of one of the substituents Ar/Ar' along the unsaturated bond is required.

The kinetics of this process and the impact of either electron donating or withdrawing groups in case of Ar = Ph are well investigated,[2] and additional donor functionalities, such as amines, allow for the synthesis of indole derivatives in a catalytic manner.[3] However, those examples are limited to substituents in which steric effects of additional groups are minimized. Furthermore, rearrangement processes at bisalkynes were not investigated until recently by our group.[4] Herein, the scope of the alkyne/vinylidene rearrangement is extended to sterically hindered alkynes, as well as bisalkynes of various substitution pattern, resulting in homo¬-bi- and hetero-tetra-metallic organometallic vinylidene complexes. Their properties, solid-state structures and redox properties (Ar/Ar' = ferrocenyl) will be discussed. For M = Fe, the competition between the vinylidene rearrangement and an iron-mediated nitro/nitroso reduction will be discussed for appropriate bifunctional substrates. Those improvements extend the applicability for catalytic processes.

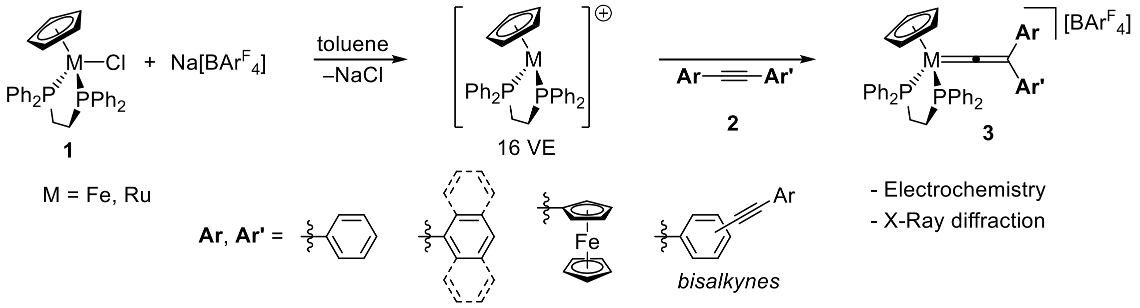

Figure 1. *Formation of 16 Valence Electron complexes from half-sandwich chlorides **1** and their activation of internal alkynes **2** into bisarylvinylidene complexes **3**.*

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Lowering the LUMO Energy of Aluminyl Anions

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With the synthesis of the first aluminyl anion reported in 2018, the topic of aluminyl anions is rapidly emerging.[1] Typical aluminium compounds are electrophilic, however aluminyl anions place the aluminium in the +1 formal oxidation state with a metal-centred lone pair, resulting in an aluminium centred nucleophile, inverting the classical reactivity of aluminium. This property, coupled with the inherently small HOMO-LUMO gap, has permitted aluminyl anions new and fascinating reactivity, such as nucleophilic substitution, cycloaddition and oxidative addition including C-H activation.[2]

In this work, we are interested in further shrinking the HOMO-LUMO gap to afford an even more reactive aluminyl anion. We aim to achieve this by lowering the amount of π-electron donation from the ligand into the empty p_z-orbital on the aluminium centre. For this purpose, the novel diamido ligand ^{s}NON (Figure 1 – right) has been developed. Compared to the NON aluminyl anion reported in 2018 (Figure 1 – centre), the ligand has an expended 7-membered central ring. This has the effect of bringing the two amido donors closer together, forcing the aluminium centre out of the plane and therefore decreasing the π-electron donation from the ligand to the metal centre. Synthesis of the aluminyl anion, DFT analysis and preliminary reactivity will be discussed.

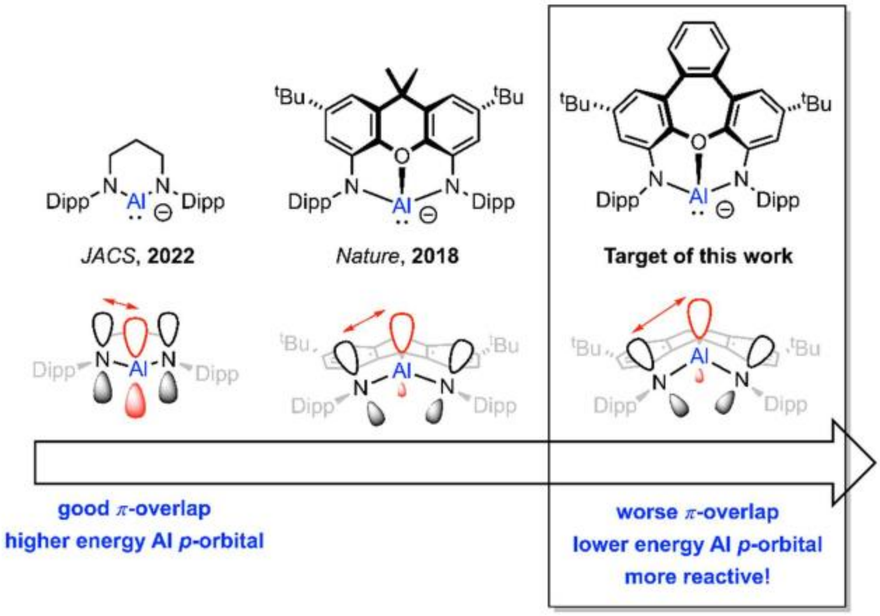

Figure 1. Two recently reported aluminyl anions[2,3] along with the target of this work, showing decreasing π-donation into the Al empty p-orbital.

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Flip the Switch

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Molecular switches promise applications in computing, communications, and data storage because they may afford access to two or more forms of a compound exhibiting different properties[1].

Homonuclear bi- and tri-metallic complexes and heteronuclear bimetallic complexes that incorporate group 8 metals have been synthesised,[2-4] with the goal of increasing the switching capabilities by increasing the available oxidation states; however, this approach has faced challenges due to a lack of electrochemical reversibility, and problems in fully resolving the redox states due to insufficient differences in potentials of the redox processes.

Presented here are our efforts to synthesise a Ru/Fe/Os heterotrimetallic switch[1], with the goal of accessing four distinct redox states, as well as studies of its spectroelectrochemical properties, and computational studies on model complexes that shed light on the optical properties.

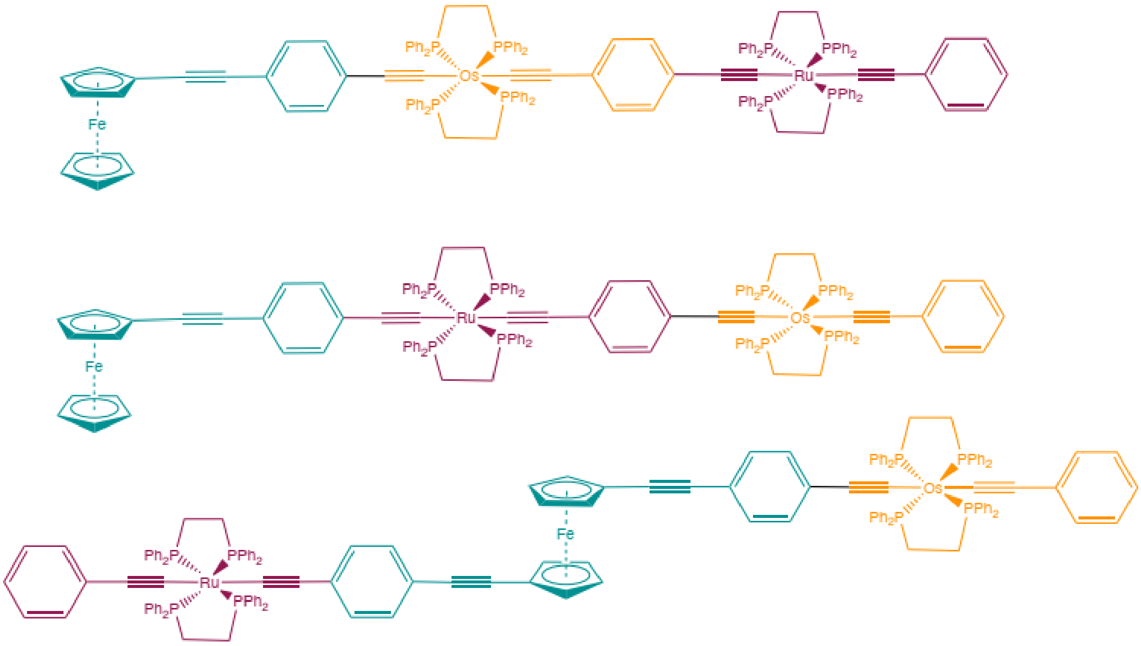

Figure 1. Ru/Fe/Os heterotrimetallic switches.

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Low-Valent Group 12 Chemistry: A Radical Approach

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Low-valent group 12 chemistry is a field that is well-furnished with examples featuring metal-metal bonds, ranging from simple inorganic salts such as mercur*ous* chloride (Cl-Hg-Hg-Cl) to more molecular examples like decamethyldizincocene, featuring steric protection of the Zn^I-Zn^I bond *via* the pendant pentamethylcyclopentadienyl (Cp*) ligands.[1] Much more elusive, however, are the monomeric E^I compounds – these retain an s^1 valency, and the only reported examples to date were generated using exotic gas-phase techniques.[2] In the solution phase, these open-shell compounds frequently dimerise to form the corresponding diamagnetic, metal-metal bonded dimers.[3] This work seeks to address the paucity in low valent group 12 radicals, and describes various targeted syntheses of anionic group 12 radicals with particular attention paid to zinc (Figure 1). Consideration of possible electronic structures will be discussed, alongside downstream reactivity studies.

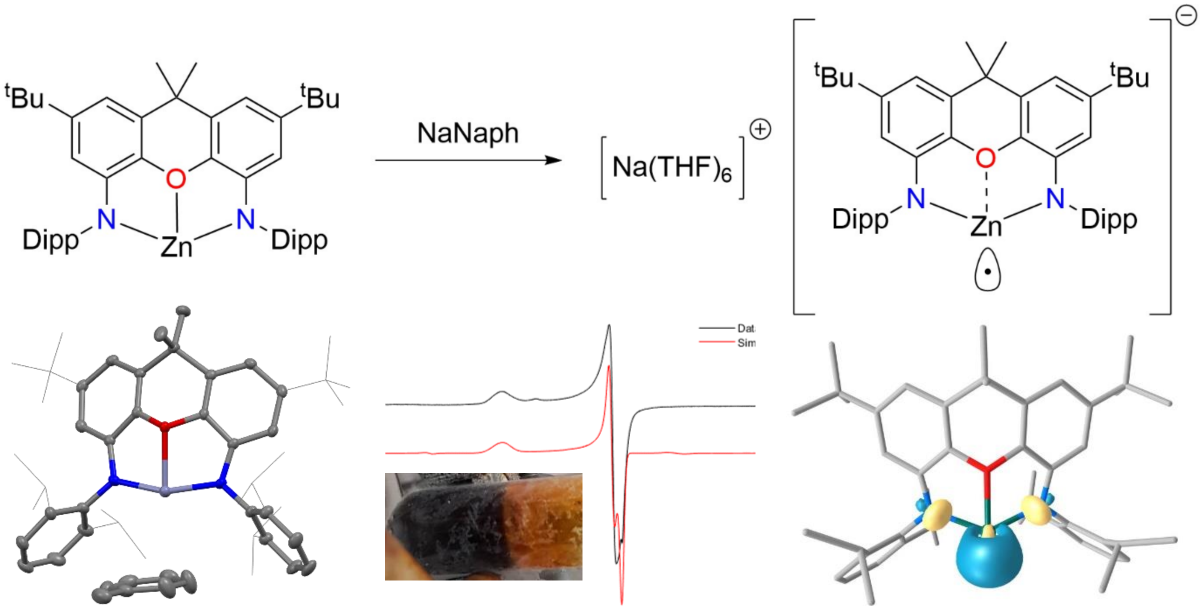

Figure 1: The one electron reduction of a Zn(II) complex (left) to the first anionic Zn(I) radical (top right). CW X-band EPR spectrum of the dark orange solution (bottom centre), alongside the computed spin density (bottom right) suggesting a degree of orbital hybridisation.

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Towards a mixed valence dicopper complex

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Mixed valence dicopper complexes are encountered in biological systems, such as the CuA sites of cytochrome c oxidase and nitrous oxide reductase which catalyses electron transfer.[1] This catalytic feature has inspired researchers to investigate synthetic dicopper mixed valence complexes, both for potential catalytic activity as well as from a fundamental perspective to understand the mixed valence behaviour.[2,3]

The dicopper(I) complex $[Cu_2(^{Me}BPNP)_2]^{2+}$ is the subject of investigation as a part of broader work relating to metal-metal cooperativity.[4] This presentation investigates the single electron oxidation of $[Cu_2(^{Me}BPNP)_2]^{2+}$ to $[Cu_2(^{Me}BPNP)_2]^{3+}$ to access the mixed valence state. Computational calculations and in situ spectroelectrochemical analysis of the oxidised species predicted a fully delocalised system and partially delocalised system, respectively.[4] The aims of this work were to synthesise the complex on a bulk scale to allow further higher resolution EPR analysis to confirm the computational and spectroelectrochemical results.

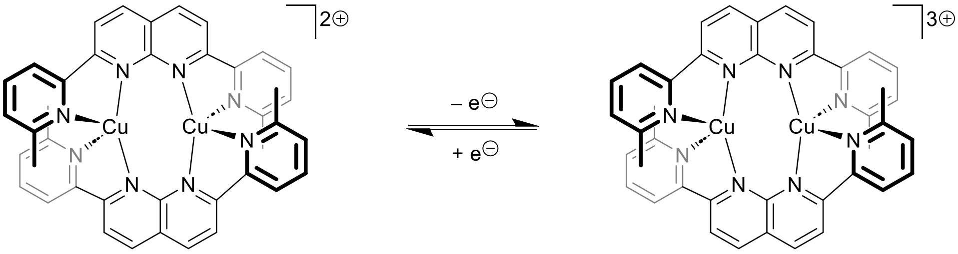

Figure 1. $[Cu_2(^{Me}BPNP)_2]^{n+}$ *in the* Cu_2^{2+} *and* Cu_2^{3+} *oxidation states.*

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Quantum Interference in Mixed-Valence Complexes: Tuning Electronic Coupling Through Substituent Effects

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The manipulation of electronic structure and transfer, through molecular design, has become a prevalent topic of study, especially with regards to quantum interference (QI) effects. Computational calculations, and experimental studies have shown that site connectivity and substituent groups influence the capacity of a phenylene molecular bridge to transmit electrons.[1] This has been demonstrated in both the through-molecule electron transfer process in molecular junctions,[2] and the charge transfer process within molecules in mixed-valence systems,[3] prompting discussions into the significance of correlations between the electron transfer processes.[4] This research (Figure 1) shows that while 2- or 5-position substituent groups on the bridging phenylene in $[\{Cp^*(dppe)RuC{\equiv}C\}_2(\mu\text{-}1,3\text{-}C_6H_4)]^+$ have insignificant influence on the weakly coupled mixed-valence complex, a 4-position substituent enhances the electron delocalisation and increases the intensity of the intervalence charge transfer (IVCT) transition.[3] These IVCT manipulations by molecular design are in agreement with conductance manipulation in molecular junction studies.[2] Thus, intramolecular coupling between metal centres of the mixed-valence complex demonstrate the potential to be used as predictive models for QI effects in molecular junctions.

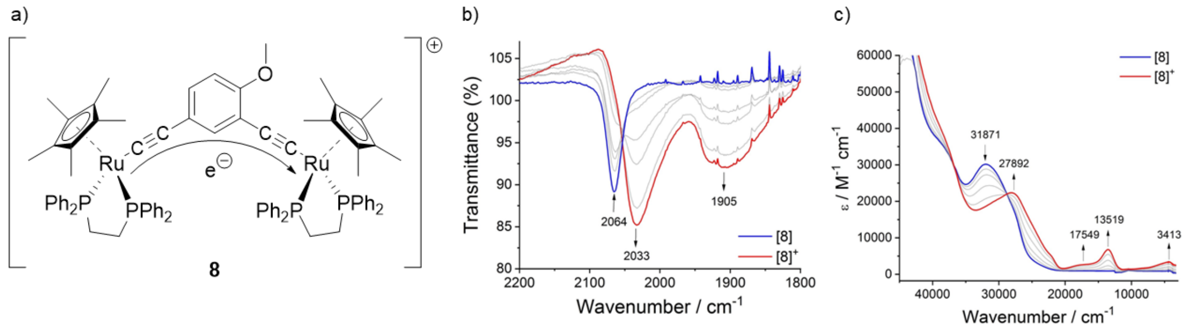

Figure 1. a) Mixed-valence complex $[\{Cp^*(dppe)RuC{\equiv}C\}_2(\mu\text{-}1,3\text{-}C_6H_4\text{-}4\text{-}OMe)]^+$ b) Neutral (blue) to singly oxidised (red) IR spectra showing the formation of the oxidised acetylide stretch of the 4-methoxy benzene species. c) Neutral (blue) to singly oxidised (red) UV spectra illustrating electronic changes upon single oxidation of the 4-methoxy benzene species.

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Green synthesis of MS nanoparticles and the preparation of MS–chitosan nanocomposites for the removal of Cr(VI) ion from wastewater

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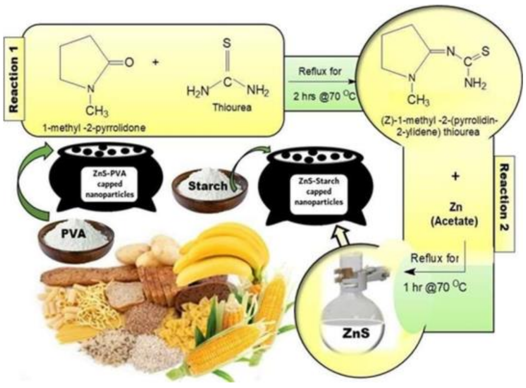
The extreme discharge of heavy metals into the environment due to industrialization and urbanization has created difficult challenges worldwide. The existence of heavy metal ions in the water systems is a major concern due to their toxicity and non-biodegradability which can cause problems to the environment [1]. Among these heavy metals, chromium is graded as one of the top sixteen toxic pollutants that have harmful effects on human well-being [2]. A high concentration of chromium can cause a bad effect on human kidneys and livers [3]. Most of the technologies that have been used in water treatment together with their starting materials are generally expensive, complicated, and time-consuming. Adsorption process has been proven to be a highly effective method that has been used lately for the removal of heavy metals from waste streams. It has been proven to be cost-effective, long-lasting, renewal adsorbent, and an easy method to operate when compared with the other techniques. Here, we report a modified homogeneous precipitation method has been used to synthesize metal sulphides. Starch and polyvinyl alcohol (PVA) were utilized as capping molecules (Scheme 1), and later, the MS–PVA-capped nanoparticles were then incorporated with chitosan to form MS–chitosan nanocomposites for the removal of Cr(VI) ion from wastewater. The removal of Cr(VI) ion from wastewater was studied through the adsorption process. Atomic Adsorption Spectroscopy was used to measure the concentrations of the solutions. The effect of pH, dosage, and contact time was investigated. More than 95% of the metal ion recovery was achieved through using MS–chitosan nanocomposites.



Scheme 1. Preparation of the ligand capped nanoparticles.

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Enhancing Anticancer Properties and Biomolecule-Binding of Metal(II) (Pd/Pt) Complexes by Modifying Tridentate Ligands

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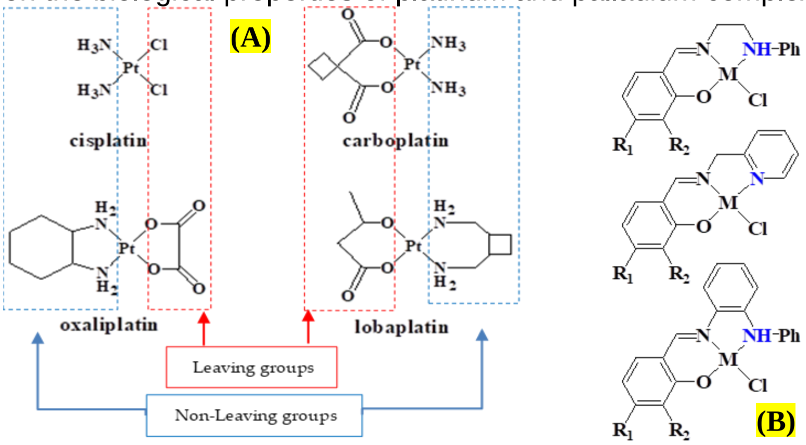
Cisplatin is an approved chemotherapeutic drug that is known to bind DNA covalently. It is activated for binding by the hydrolysis of its labile chlorido ligands. Inside the cell, the aqua ligands are exchanged with N7-guanine (or other nucleobases on the DNA), forming a cross-linked DNA (either intra-strand or inter-strand) [1]. The drug-DNA binding causes conformational changes to DNA, promoting apoptotic cell death [2,3]. Although cisplatin is used to treat a range of cancer types, it has several drawbacks, including lack of selectivity toward cancer cells, acquired resistance, and severe side effects [4]. Cisplatin analogues have been developed either by structurally replacing the leaving ligands and/or the non-leaving ligands. These modifications have resulted in a few clinically approved Pt(II)-based drugs (Figure 1a). In our work, we focus on synthesizing complexes with one leaving group (a single chlorido ligand) rather than two (Figure 1b). A set of tridentate Schiff base ligands of the type (N^N^OH) were synthesized from reactions of the amines {2-picolylamine (Py), *N*-phenyl-1,2-diaminobenzene (PhN), and *N*-phenyl-1,2-diaminoethane(EN)} with the salicylaldehyde derivatives; these ligands were employed to synthesize Pt(II) and Pd(II) complexes. The DNA-binding behaviours of the metal complexes were investigated by two techniques, indicating good binding affinities and a two-stage binding process for the majority of the Pt(II) complexes: intercalation followed by switching to a covalent binding mode over time. The Pd(II) complexes covalently bind to ct-DNA without observable intercalation. The binding of the complexes with bovine serum albumin (BSA) indicated a static interaction (adduct formation) with higher binding affinities for the ethoxy-containing complexes. The half maximal inhibitory concentrations (IC_{50}) values against MCF-7 and HepG2 cell lines suggest that Pt-Py-OEt and Pt-PhN-OEt are good chemotherapeutic candidates with IC_{50} values less than that for cisplatin. On the other hand, the IC_{50} values of Pd-Py-OEt and Pd-Py-NEt were comparable to that of cisplatin. The cell cycle accumulation pattern of HepG2 treated with selected complexes suggests apoptotic cell death. The current work highlights the impact of the tridentate ligand on the biological properties of platinum and palladium complexes.



Code	R_1	R_2	M
Pt-Py-OEt	H	OEt	Pt
Pt-PhN-OEt	H	OEt	Pt
Pt-EN-OEt	H	OEt	Pt
Pt-Py-NEt	NEt_2	H	Pt
Pt-PhN-NEt	NEt_2	H	Pt
Pt-EN-NEt	NEt_2	H	Pt
Pd-Py-OEt	H	OEt	Pd
Pd-Py-NEt	H	OEt	Pd
Pd-EN-OEt	NEt_2	H	Pd
Pd-EN-NEt	NEt_2	H	Pd

Figure 1. (a) Clinically approved Pt-based anticancer drugs. (b) Metal complexes investigated.

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Palladium-catalysed cycloaddition reactions: Synthesis of 5,6-membered spirocycles and an exploration of a novel 1,4-silyl dipole precursor

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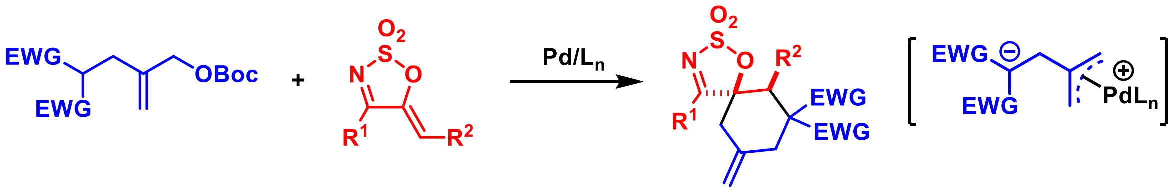
Abstract: Palladium-catalysed cycloaddition reactions represent a powerful tool for the synthesis of sp^3-rich, stereo-defined carbo and heterocyclic compounds.[1]

Previously, our group has developed a diastereo and enantioselective (3 + 2) cycloaddition reaction of vinyl cyclopropanes with cyclic sulfamidate imine-derived 1-azadienes to access 5,5-membered spirocycles.[2]

This presentation continues to explore on the use of zwitterionic palladium-catalysed cycloaddition reactions and 1-azadienes, for the regio- and diastereoselective synthesis of a 5,6-membered spirocyclic functionalised cyclohexanes using acyclic allylic carbamates.

Additionally, our progress towards the design and development of a novel silicon-based 1,4-zwiterionic dipole precursor for the synthesis of silicon-heterocycles will be discussed.



Synthesis of 5,6-Membered Spirocycles

Figure 1: Palladium-catalysed cycloaddition reactions of 1-azadienes with acyclic allylic carbamates.

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Resurrecting the Forgotten Kin: Coordination Chemistry of Stiboles

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The five-membered heterocycles of the lighter main group elements (Si, N, P, O, S *etc.*) are proliferous ligands throughout the field of coordination chemistry. However, little attention has been paid to the heavier element analogues, such as 1*H*-stibacyclopentadiene ("stibole"), which only appears sporadically within the literature despite being first prepared some 60 years ago[1]. This poster highlights synthetic strategies towards 1-chlorostibole and 1-ethynylstibole, in addition to a preliminary exploration of their coordination chemistry.

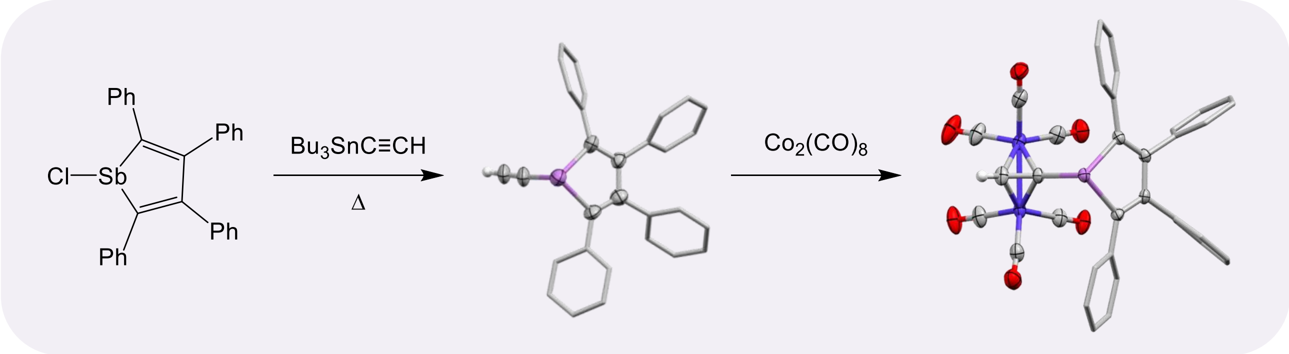

Figure 1. *Synthesis of dicobalt hexacarbonyl 1-ethynyl-2,3,4,5-tetraphenyl stibole adduct*

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C-H, Si-H, and C-F Abstraction with an Extremely Electron Poor I(III) Reagent

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An aryl iodine(III) bistriflate, *p*-NO_2-C_6H_4-I$(OTf)_2$, was recently isolated and characterized, becoming the first R-I$(OTf)_2$ confirmed to exist.[1] Preceding works involving activation of bisacetoxy iodoarenes, Ar-I$(OAc)_2$, have implicated generation of Ar-I$(OTf)_2$ *in situ* as a facilitator of oxidative transformations. However, these claims have proven incorrect, and the active species was instead found to be the asymmetric product of a single ligand substitution; Ar-I(OAc)(OTf), a compound of considerably lower oxidizing potential than Ar-I$(OTf)_2$.[2]

In this work, an initial NMR-based probe into the reactivity of EWG-C_6H_4-I$(OTf)_2$ (EWG = *p*-NO_2, *m*-CF_3) is carried out by evaluation of its ability to abstract hydride from sites of successively reducing reactivity. Conversion of relatively hydridic substrates such as triethylsilane and cycloheptatriene to their -OTf analogues is found to occur rapidly and completely at room temperature, as well as abstraction from the more robust adamantane to form adamantyl triflate. Aromatisation of cyclic alkenes (cyclohexene, α-pinene, limonene) by up to two hydride abstractions was also shown to occur quickly, though incompletely, even at temperatures as low as -90 °C.[3]

In addition, an exciting example of fluoride abstraction is provided in the reaction of fluoroadamantane with NO_2-C_6H_4-I$(OTf)_2$ to form adamantyl triflate and the asymmetric aryliodane *p*-NO_2-C_6H_4-I(F)(OTf). This direct metathesis evidences a mechanism of hydride abstraction involving an analogous, yet transient Ar-I-(H)(OTf).[3]

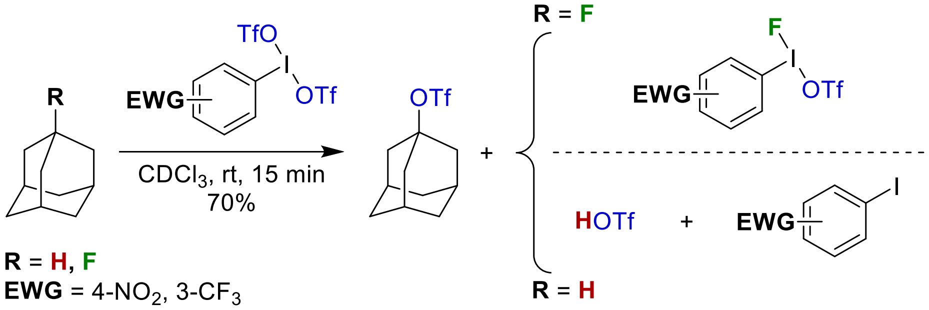

Figure 1. C-H and C-F abstraction using novel, extremely electron poor I(III) bistriflate reagents.

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Structural verification and new reactivity for Stang's reagent, [PhI(CN)][OTf]

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In recent years, there have been several misidentified iodine(III) complexes which turned out to be something else. The most famous of these is the purported $PhI(OTf)_2$.[1] In fact, the actual reactive species was PhI(OAc)(OTf). In chemical reactions, there is a very real need to be certain that the reactive species is indeed what it is claimed to be. Because of this, we investigated Stang's reagent, an iodine(III) complex with -CN bound to Lewis acidic iodine because there was no structural confirmation.[2] We were also uncertain that Stang's reagent existed as an ion pair in solution. To investigate, we conducted A/C electrochemical impedance spectroscopy. Our results confirmed that Stang's reagent is an ion pair in solution. This finding implies that trans to the iodine would be a vacant coordination site that could be occupied by a nucleophile. Therefore, we investigated the possibility of developing a mixed CN / pyridyl iodine(III) analogue. Our results found that rather than occupying the vacant coordination site, the pyridine underwent oxidative coupling with cyanide.

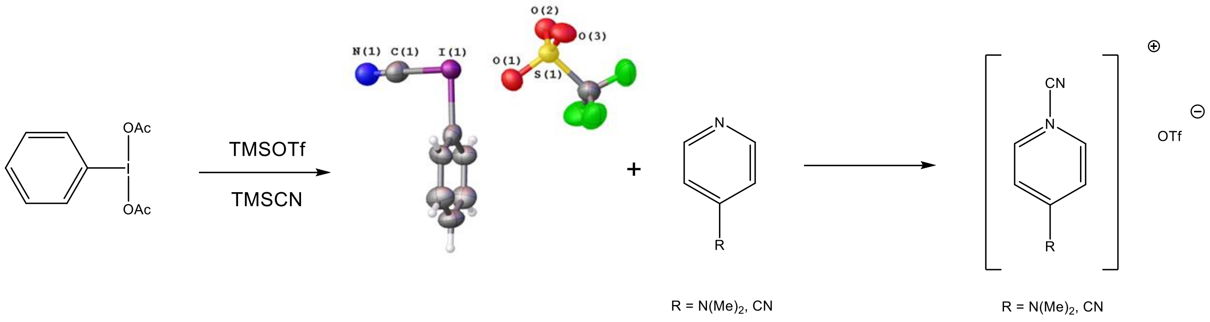

Figure 1. Structural verification and subsequent reactivity of Stang's reagent with pyridyl bases

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Beating a dead horse (or how to resurrect a horse with sufficient beating)

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Historically high oxidation state gold chemistry has been an unexplored avenue in organometallics. Recently our group presented a straightforward method for achieving Au^{III} difluorides that are uncharacteristically stable compared to previously reported $Au\text{-}F_2$ complexes.[1] These complexes undergo a variety of simplistic reactions such as metathesis with TMS bound reagents by utilising formation of Si-F as a thermodynamic driving force.[2]

Whilst exploring the possible reactivity of these $Au\text{-}F_2$, we noticed that upon reaction with TMSOTf, the $Au\text{-}F_2$ produced a rather unusually stable complex. While still participating in reactions of the same vein, such as N(Ar)-C(Ar) coupling, C-H activation of acetylene, and halogenation, the complex eluded isolation and direct characterisation.

In quest of understanding this reactive and elusive species as well as optimisation of the reaction pathway to remove dangerous and/or obnoxious chemicals (i.e F_2, XeF_2, etc), we decided to bypass the use of F based oxidants and modify I^{III} oxidants inspired by recent successes in our lab.[3] This method of direct Au^{I} to Au^{III} oxidation, and the use of BF_3-etherate, allowed isolation of an 'effectively' naked Au^{III} species primed for modification, bound by two *trans* acetonitrile ligands aside from the initial imidazole 'scaffold'. This has since allowed us to isolate a monoarylated Au^{III} complex showing Au's place as a possible metal catalyst.

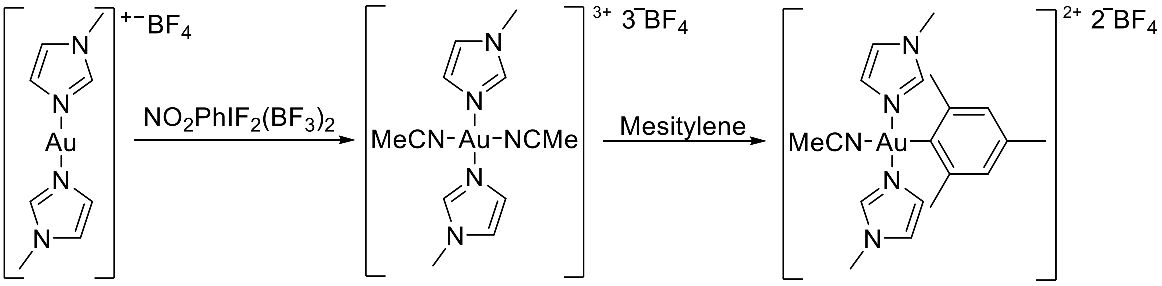

Figure 1. General reaction scheme for synthesis of monoarylated Au^{III}

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Synthesis, characterisation and reductions of bulky BODIPY analogues

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4,4-Difluoro-4-bora-3a,4a-diaza-s-indacenes, more commonly known as BODIPYs, are typically small molecules that fluoresce at visible wavelengths with high quantum yields.[1] Due to these excellent photophysical properties along with their easy synthesis, low toxicity, and high stability, BODIPYs have found wide applications in biological imaging,[2] optoelectronics[3] and sensing.[4] The redox chemistry of BODIPYs has recently attracted interest, with several studies showing that BODIPY compounds can undergo reversible redox processes.[4]

In this work, bulky BODIPY analogues where the boron is replaced with aluminium (ALDIPY) and gallium (GADIPY) are reported (Figure 1). Moreover, the reduction chemistry of these heavy analogues is investigated and compared to BODIPY.[5]

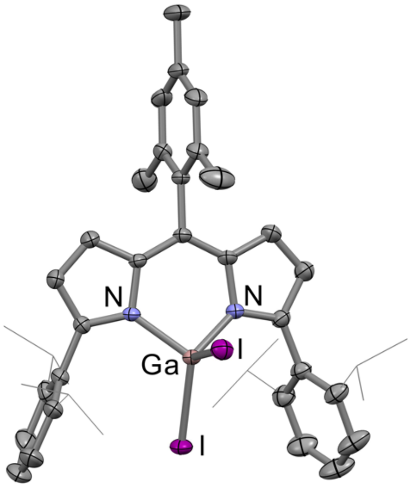

Figure 1. Solid state structure of the bulky GADIPY compound

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