

Royal Society of Chemistry

# Dalton 2025

University of Warwick, 1-3 Apr 2025

Book of abstracts

**CODG Oral Presentations**



ROYAL SOCIETY  
OF **CHEMISTRY**

DALTON  
COMMUNITY

We thank the following sponsors for their support:





**INORGANIC** CHEMISTRY  
FRONTIERS

## Design of a Janus-type Bis(abnormal N-heterocyclic carbene)

Kai Pfefferkorn, Tobias Rüffer, and Robert Kretschmer<sup>a</sup>

<sup>a</sup>Chemnitz University of Technology

email: kai.pfefferkorn@chemie.tu-chemnitz.de

The synthesis of Janus-type bis(N-heterocyclic carbene)s (NHCs) and abnormal N-heterocyclic carbenes (aNHCs) has gathered significant attention of the last years. They can serve as flexible precursors for (hetero)bimetallic complexes that act as highly active catalysts<sup>1</sup> and have also high value for the preparation of organometallic polymers.<sup>2</sup> However, sterically more demanding bis(carbene)s have been so far rather elusive compounds as the synthetic approaches are often limited to small, aliphatic, and linear substituents on the nitrogen atoms of the carbene.<sup>3</sup> In this work, the synthesis of a bulky bis(aNHC) from readily available starting materials is reported. The stronger nucleophilicity of aNHCs compared to NHCs makes them even more promising candidates for transition-metal and main-group metal catalysts and materials.<sup>4</sup> The spatial separation of the carbene centres in Janus-type ligands is beneficial in preventing side reactivity, for example the chelation of one metal atom.<sup>2</sup> Furthermore, the distinct orientation enforced by the ligand framework allows new motifs in supramolecular chemistry.

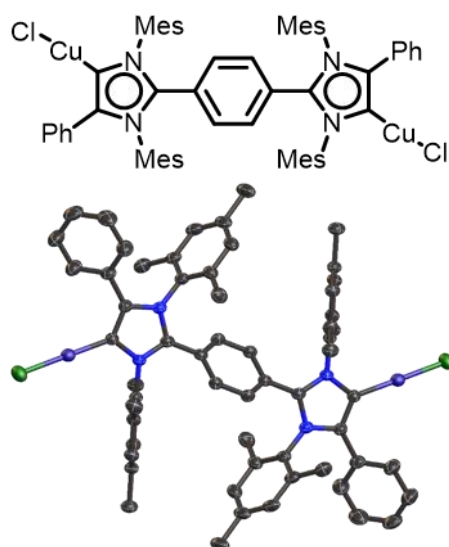


Figure 1. Chemical structure of the bimetallic bis(aNHC) copper(I) chloride complex.

### References

1. M. Poyatos and E. Peris, *Dalton Trans.*, 2021, **50**, 12748-12763.
2. A. J. Boydston, K. A. Williams and C. W. Bielawski, *J. Am. Chem. Soc.*, 2005, **127**, 36, 12496-12497.
3. S. Gonell, M. Poyatos and E. Peris, *Chem.-Eur. J.*, 2014, **20**, 31, 9716-9724.
4. S. C. Sau, P. K. Hota, S. K. Mandal, M. Soleilhavoup and G. Bertrand, *Chem. Soc. Rev.*, 2020, **49**, 1233-1252.

# Iron Complexes Supported by a Double Dearomatized PNP Ligand

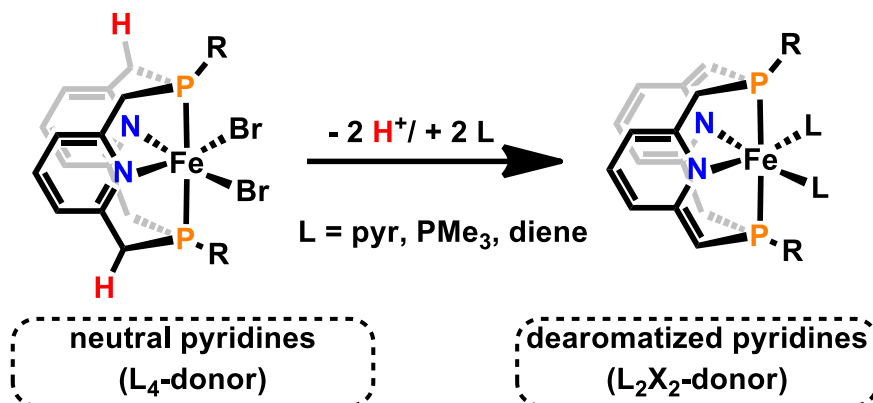
Stefan Weber<sup>a,b</sup>, Alex M. Pavelic<sup>b</sup>, Jonas C. Peters<sup>b</sup>

<sup>a</sup>TU Wien, Institute of Applied Synthetic Chemistry, Getreidemarkt 9, 1060, Vienna, Austria

<sup>b</sup>Caltech, 1200 E California Blvd., Pasadena 91125, Ca, United States

email: stefan.e163.weber@tuwien.ac.at

The activation of weakly (or non-) polarized bonds represents a challenging task in the field of modern organometallic chemistry. In order to facilitate such transformations, the metal center can be supported by ligands containing an acidic site which can be reversibly (de)protonated in order to achieve metal-ligand cooperativity (MLC). This process may lead to a dearomatized system which is capable of activating strong bonds.<sup>1</sup> Such mono dearomatized systems were intensively studied over the last decades for a broad variety of transition metals. However, reports of double dearomatized systems are thus limited to manganese<sup>2</sup> and ruthenium<sup>3</sup> supported by NSNS ligands.



Scheme 1: Synthesis of iron complexes supported by a double deprotonated PNP ligand.

This contribution will focus on iron(II) complexes supported by a macrocyclic PNP ligand containing two acidic sites. Deprotonation leads to double dearomatization in conjunction with uptake of  $\pi$ -acidic ligands. A library of iron complexes containing pyridines, phosphines and isonitrile was synthesized. Delightfully, the double dearomatized system could be stabilized upon coordination of norbornadiene. Iron(II) alkene complexes are rare and a diene complex has thus far not been reported. The structure of these systems was elucidated by e.g., multinuclear NMR- <sup>57</sup>Fe-Mössbauer spectroscopy and single crystal analysis. The reactivity of these complexes with small molecules e.g., H<sub>2</sub>, CO and ligand substitution reactions will be discussed.

## References

1. J. R. Khusnutdinova and D. Milstein, *Angew. Chem Int. Ed.*, 2015, **54**, 12236-12273.
2. A. Sarbanja, P. H. Patil, H. Hoan Dinh, O. Gladkovskaya, R. R. Fayzullin, S. Lapointe, E. Khaskin and J. R. Khusnutdinova *Chem. Commun.* 2019, **55**, 3282-3285.
3. H. Minh Dinh, T. Gridneva, A. Karimata, A. Garcia-Roca, J. Pruchyathamkorn, P. H. Patil, A. Petrov, A. Sarbajna, S. Lapointe, E. Khaskin, R. R. Fayzullin and J. R. Khusnutdinova *Dalton Trans.* 2022, **51**, 14734-14746.

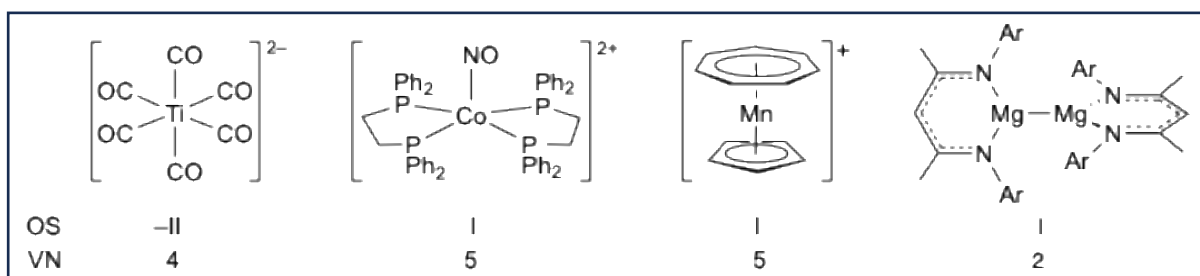
## Oxidation state or valence: which is the better descriptor for organometallic and coordination complexes?

Paul G Pringle<sup>a</sup> and Nicholas C. Norman<sup>a</sup>

<sup>a</sup> School of Chemistry, University of Bristol, UK

paul.pringle@bristol.ac.uk

Oxidation state (OS) is a concept that is widely used by organometallic and coordination chemists because it provides a simple, practical framework for organising, categorising, and understanding the chemistry of the elements.<sup>1</sup> For example, it is useful to characterise, say,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$  and  $[\text{Fe}(\text{CO})_6]^{2+}$  as pseudo-octahedral,  $d^6$ , Fe(II) complexes because they have commonalities in their chemistry, and the differences there are, can be attributed to the overall (real) charge on the complex as well as the properties engendered by the ancillary ligands. OS is a model for MO theory based on the idea that the electrons are divided between the atoms according to their electronegativities in an ionic approximation; there is no suggestion, implication or assumption that the bonding in the compound in question is ionic: almost always, it is not. However, OS has been criticised as being fundamentally flawed, particularly for covalent compound where valence (or valence number, VN) should be used instead. The VN can be defined as, *the number of electrons involved in bonding*, which is an attractively simple definition that appears to be more in keeping with a description of covalent bonding in terms of molecular orbitals.



**Figure 1.** Examples of complexes where OS  $\neq$  VN

In the great majority of cases OS = VN, but in this talk we will discuss examples where OS  $\neq$  VN; in particular, metal carbonyl anions, nitrosyl complexes, complexes of cationic ligands, and metal-metal bonded binuclear complexes (an example of each is shown in Figure 1). In these instances, we will attempt to answer the question posed in the title.

### References

1. N. C. Norman, P. G. Pringle, *Dalton Trans.*, 2022, **51**, 400-410.
2. S. C. C. van der Lubbe, P. Vermeeren, C. Fonseca Guerra, F. M. Bickelhaupt, *Chem. Eur. J.*, 2020, **26**, 15690-15699.
3. J. Popp, T Riggermann, D. Schröder, T. Ampßler, P. Salvador, P. Klüfers, *Inorg. Chem.*, 2021, **60**, 15980-15996.
4. A. Pavun, Kopacka, H. Wurst, T. Müller, F. R. Neururer, S. Hohloch, B. A. Bildstein, *J. Organometallic Chem.*, 2023, 985, 122594.
5. J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 4810-4813.

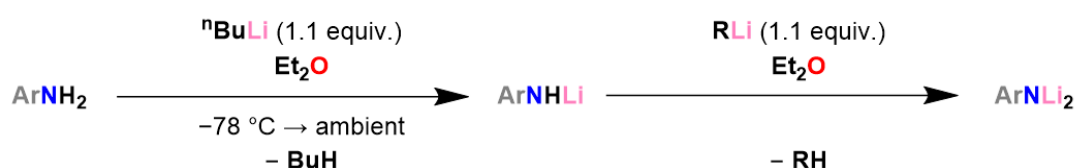
# Synthesis and Reactivity of Dilithiated Anilides facilitated by Digital Lab Tools

R. Drummond Turnbull, N. L. Bell

Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ

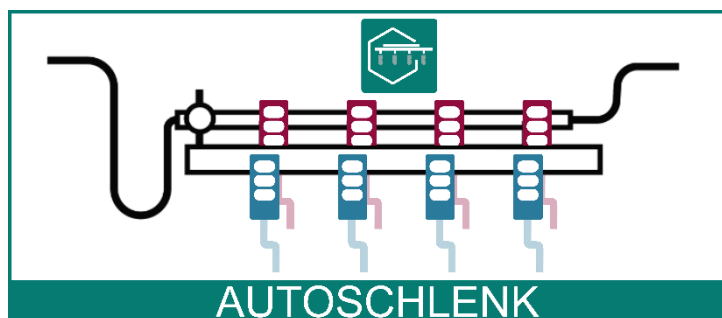
email: richard.drummondturnbull@glasgow.ac.uk

Whereas amides ( $\text{MNR}_2$ ) are commonly and straightforwardly prepared derivatives of the s-block elements, their dimetalated imide analogues ( $\text{M}_2\text{NR}$ ) remain an exceedingly rare motif in the published literature,<sup>1</sup> despite being common coordination motifs in other parts of the periodic table. That a wide array of these useful synthons have not been forthcoming is unsurprising: accessing strongly basic s-block imides generally require stabilizing electron withdrawing groups and bespoke synthetic conditions to mitigate their aggressive reactivity.<sup>2</sup>



We present a general route to a set of dilithiated arylimides with a range of electronic properties, including electron-donating groups, which may be prepared from commercially-available organolithium reagents.

Furthermore, supported by our novel, digital Autoschlenk line, we uncover the reactivity of these superbases towards gaseous reagents and demonstrate how digital lab equipment can upskill organometallic labs.<sup>3</sup>



## References

1. D. R. Armstrong, S. C. Ball, D. Barr, W. Clegg, D. J. Linton, L. C. Kerr, D. Moncrieff, P. R. Raithby, R. J. Singer, R. Snaith, D. Stalke, A. E. H. Wheatley and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, **2002**, 2502-2511.
2. A. Schulz, M. Thomas and A. Villinger, *Inorg. Chem.*, **2020**, 59, 3344-3352.
3. N. L. Bell, M. Gladkikh, C. Fraser, M. Elsayed, R. Drummond-Turnbull, *Chemrxiv*, 10.26434/chemrxiv-2024-t24pz

## Easily Accessible and Solution-Stable Ni(0) Precatalysts for High-Throughput Experimentation

Gilian T. Thomas,<sup>a,b</sup> Odhran D. Cruise,<sup>a,b</sup> Daelin Peel-Smith,<sup>b</sup> Nahiane Pipaón Fernández,<sup>b</sup> Charles Killeen,<sup>b</sup> David C. Leitch<sup>b</sup>

<sup>a</sup> *Current Affiliation: University of Leeds, Leeds, LS2 9JT UK*

<sup>b</sup> *University of Victoria, Victoria, BC V8P 5C2 Canada*

email: g.t.thomas@leeds.ac.uk

With High-Throughput Experimentation (HTE) investigations being at the forefront of efficient API synthesis, there is a significant need for the development of stable Ni(0) precursors. Currently, Ni(COD)<sub>2</sub> functions as a powerful precursor in cross-coupling reactions, however it is accompanied by a variety of known disadvantages in the context of HTE (e.g. not air-stable). Herein, we present an assortment of *N,N'*-dialkyl diazabutadiene (DAB)-equipped Ni(0) precursors which have proven to be more reactive, and practically manageable (HTE compatible) as compared to existing Ni(0) sources in a multitude of cross-coupling reactions.<sup>1</sup>

### References

1. G. T. Thomas, O. D. Cruise, D. Peel-Smith, N. Pipaón Fernández, C. Killeen, D C. Leitch. *Chem–Eur. J.*, 2025, **31**, e202403960.



# High-throughput Combinatorial Click Chemistry for the Exploration of Functional Metal Complex Space

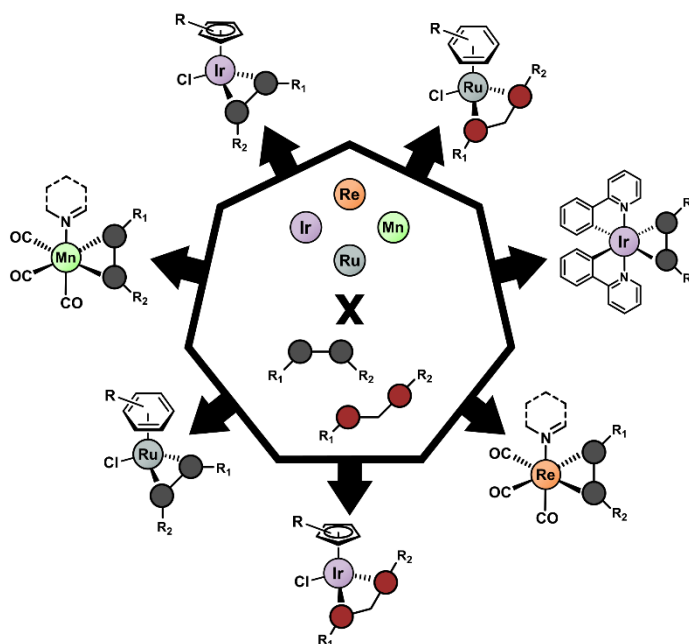
David Husbands<sup>a</sup>, Çağrı Özsan<sup>a,b</sup>, Athi Welsh<sup>a,b</sup>, Angelo Frei<sup>a,b</sup>

<sup>a</sup> Department of Chemistry, University of York, York YO10 5DD, U.K.

<sup>b</sup> Department of Chemistry, Biochemistry & Pharmaceutical Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

email: angelo.frei@york.ac.uk

In our efforts for an efficient exploration of the transition metal complex chemical space for compounds with promising properties<sup>1</sup> we have developed a novel combinatorial and high-throughput approach for the preparation of triazole-based bidentate ligands and their coordination to a suite of metal scaffolds. We demonstrate that this approach can be applied to easily prepare hundreds of diverse metal complexes with excellent conversion efficiencies at once. We further show that these libraries can be used to efficiently identify novel metal complexes with interesting fluorescent, catalytic and antibacterial properties.



**Figure 1.** Overview of metal complex libraries prepared in this work.

## References

1. A. Welsh, D. Husbands, A. Frei, *Angew. Chem. Int. Ed.* 2025, 64, e202420204.

# Synthesis and spectroscopy of radical-bridged lanthanide heterobimetallic complexes

Samuel J. Horsewill,<sup>a</sup> Tajrian Chowdhury,<sup>b</sup> Anna G. Bailey,<sup>c</sup> William J. Peveler,<sup>c</sup> Gordon J. Hedley,<sup>c</sup> Claire Wilson,<sup>c</sup> and Joy H. Farnaby<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Bath, BA2 7AY, UK

<sup>b</sup> Department of Chemistry, Indiana University, Bloomington, USA

<sup>c</sup> School of Chemistry, University of Glasgow, G12 8QQ, UK

email: joy.farnaby@glasgow.ac.uk

Heteromultimetallic molecules, which selectively combine the luminescent and magnetic properties of the lanthanides (Ln) have significant application potential in magneto-optical technologies and quantum information science.<sup>1,2</sup> However, the directed synthesis of Ln,Ln' complexes is very challenging because of the similar chemistry of Ln(III) ions across the series. Redox chemistry and the distinct *N,N'* and *O,O'* binding sites of the 1,10-phenanthroline-5,6-dione (pd) ligand have enabled the synthesis of radical-bridged heterobimetallic complexes [Ln(Tp)<sub>2</sub>(*O,O'*-*N,N'*-pd<sup>•-</sup>)Ln'(hfac)<sub>3</sub>] (Ln,Ln' = Yb,Eu or Dy,Yb; Tp = tris(pyrazolyl)borate; hfac = hexafluoroacetylacetonate) (Figure 1a).<sup>3-5</sup> This presentation will detail the two modular synthetic routes, and discuss the utilisation of SCXRD, NMR, UV-vis, and photoluminescence (PL) spectroscopies to characterise the selectivity of Ln,Ln' to ligand binding (*N,N'* and *O,O'*). Individual Ln PL can be selectively sensitised: classically using UV excitation of the hfac ligand, or unusually by visible excitation of the semiquinone radical (*O,O'*-pd<sup>•-</sup>). Multiple energy transfer pathways (example shown in Figure 1b) are observed in Ln,Ln', highlighting their potential for complex input/output, and providing a guide for future work.

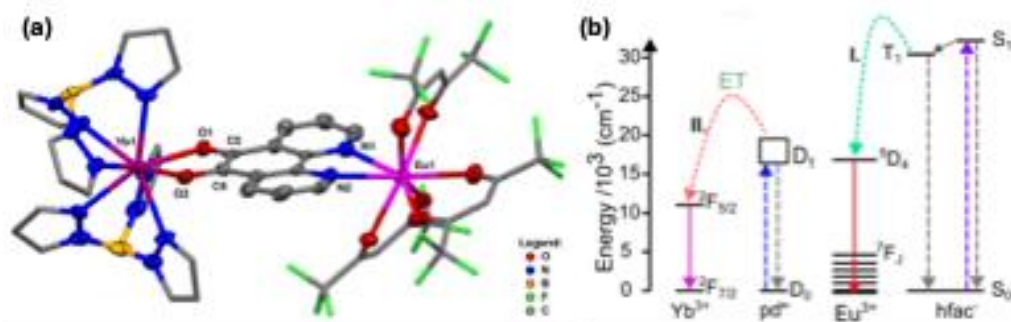


Figure 1. **(a)** Crystal structure of the Yb,Eu heterobimetallic radical-bridged complex; **(b)** Energy level diagram depicting either hfac (I) or radical (II) sensitization of lanthanide photoluminescence.

## References

- (a) J.-C. G. Bünzli, *Eur. J. Inorg. Chem.*, 2017, **44**, 5058. (b) M. A. Hay and C. Boskovic, *Chem. Eur. J.*, 2021, **27**, 3608. (c) T. Cheisson and E. J. Schelter, *Science*, 2019, **363**, 489.
- (a) N. Mahieu *et al.*, *Chem. Sci.*, 2023,**14**, 443. (b) *Advancing Chemistry and Quantum Information Science*, The National Academies Press: Washington, D.C., 2023. DOI: doi:10.17226/26850.
- J. R. Hickson *et al.*, *Dalton Transactions*, 2018, **47**, 10692.
- T. Chowdhury *et al.*, *Chem. Commun.* 2023, **59**, 2134.
- S. J. Horsewill *et al.*, 2025, *submitted*.

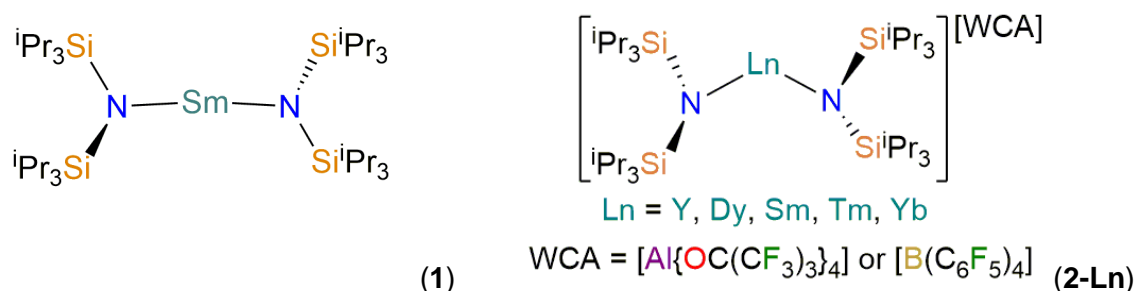
## Towards linear lanthanide single-molecule magnets

Jack Emerson-King,<sup>a</sup> Gemma K. Gransbury,<sup>a</sup> Benjamin E. Atkinson,<sup>a,b</sup> William J. A. Blackmore,<sup>a</sup> George F. S. Whitehead,<sup>a</sup> Nicholas F. Chilton,<sup>a,b,\*</sup> David P. Mills<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.; <sup>b</sup>Research School of Chemistry, The Australian National University, Sullivans Creek Road, Canberra, ACT, 2601, Australia.

email: david.mills@manchester.ac.uk

Linear dysprosium and terbium single-molecule magnets (SMMs) should provide the largest energy barriers to magnetic reversal ( $U_{\text{eff}}$ ) and the highest hysteresis temperatures ( $T_{\text{H}}$ ).<sup>1</sup> In 2015 we reported the first near-linear lanthanide (Ln) complex  $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2]$  (**1**), and predicted that a linear Dy(III) analogue could exhibit a record  $U_{\text{eff}}$  of ca. 2600 K.<sup>2</sup> In the interim we have reported the bent Ln(III) complexes  $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_2][\text{WCA}]$  (**2-Ln**; Ln = Sm, Tm, Yb, WCA =  $[\text{B}(\text{C}_6\text{F}_5)_4]$ ; Ln = Y, Dy, WCA =  $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ),<sup>3,4</sup> the Dy(III) analogue showed a lower than predicted  $U_{\text{eff}} = 950 \pm 30$  K, due to a combination of the bent N–Dy–N angle ( $128.7(2)^\circ$ ) and the flexible Dy coordination sphere facilitating magnetic relaxation. Here we report efforts to synthesise Dy bis-amide complexes with N–Dy–N angles closer to linearity, in order to provide two-coordinate Ln SMMs with  $U_{\text{eff}}$  and  $T_{\text{H}}$  values that rival those containing isolated dysprosocenium cations.<sup>5,6</sup>



**Figure 1.** Lanthanide complexes **1** and **2-Ln**.

**Acknowledgments:** We thank the European Research Council (StG-851504 and CoG-816268), the EPSRC (EP/R002605X/1, EP/P001386/1, EP/S033181/1 and EP/T011289/1), the Royal Society (URF191320), the EPSRC UK National Electron Paramagnetic Resonance Service, and the University of Manchester Computational Shared Facility.

### References

1. J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078-2085.
2. N. F. Chilton, C. A. P. Goodwin, D. P. Mills and R. E. P. Winpenny, *Chem. Commun.*, 2015, **51**, 101-103.
3. H. M. Nicholas, M. Vonci, C. A. P. Goodwin, S.-W. Loo, S. R. Murphy, D. Cassim, R. E. P. Winpenny, E. J. L. McInnes, N. F. Chilton and D. P. Mills, *Chem. Sci.*, 2019, **10**, 10493-10502.
4. J. Emerson-King, G. K. Gransbury, G. F. S. Whitehead, I. J. Vitorica-Yrezabal, M. Rouzières, R. Clérac, N. F. Chilton and D. P. Mills, *J. Am. Chem. Soc.*, 2024, **146**, 3331-3342.
5. C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439-442.
6. J. Emerson-King, G. K. Gransbury, B. E. Atkinson, W. J. A. Blackmore, G. F. S. Whitehead, N. F. Chilton and D. P. Mills, *ChemRxiv* **2024**, DOI:10.26434/chemrxiv-2024-36vjp.

# Solvent Controlled Self-Assembly of Lanthanide-Foldamer Metallosupramolecular Architectures

Sarah J. Pike<sup>a</sup>

<sup>a</sup> School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK.

email: s.j.pike@bham.ac.uk

Lanthanide complexes have excited great interest due to their luminescent and magnetic properties which have led them to find important applications in sensing, biomedical imaging and materials chemistry.<sup>1</sup> Metallofoldamers which contain both organic foldamer ligands and metals, are emerging as an important area within the field,<sup>2,3</sup> due to their inherent flexibility of the foldamer ligand which, when combined with predictable nature of the metal coordination geometry, enables access to more complex self-assembled foldamer architectures.<sup>4</sup> However, to date, there are no reported examples of lanthanide-foldamer architectures and this absence of data severely hinders the advancement of this emerging area.

Herein, we report on the first examples of lanthanide-foldamer complexes and detail our systematic solid state studies into the effect of solvent on controlling their self-assembly. We report that these novel metallofoldamers assemble into a diverse array of higher-order architectures including 1D-coordination polymer chains, dimers, tetramers and decorated macrocycles (Figure 1). Whilst, in general, the influence of solvent effects on the self-assembly of supramolecular architectures is generally poorly understood, this work offers insights into the role of the solvent in facilitating the formation of these higher-order structures by probing the effect of the solvent on the self-assembly process. We anticipate that this work will enable the future design of foldamer metallosupramolecular architectures of increasing structural complexity and diversity with potential applications in sensing and imaging.

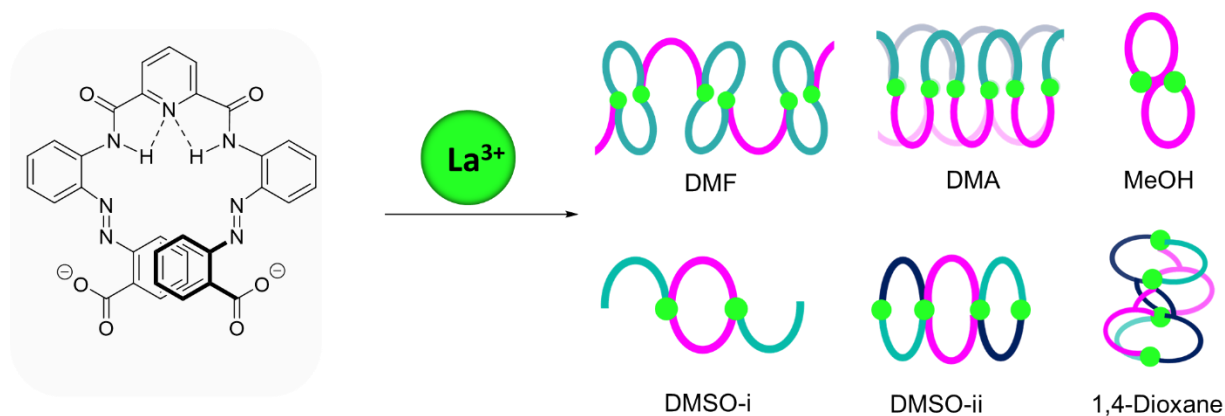


Figure 1. The solvent controlled self-assembly of a diverse array of lanthanide-foldamer metallosupramolecular architectures including dimers (from methanol), tetramers and hexamers (from dimethylsulfoxide (DMSO)), decorated macrocycles (from 1,4-dioxane) and 1D-coordination polymers (from dimethylformamide (DMF) and dimethylacetamide (DMA)).

## References

1. N. C. Martinez-Gomez, H. N. Vu and E. Skovran, *Inorg. Chem.*, 2016, **55**, 10083-10089.
2. I. Huc, S. Kwon and H. -S. Lee, *ChemPlusChem*. 2021, **86**, 1042-1043.
3. J. L. Algar, J. A. Findlay and D. Preston, *ACS Org. Inorg. Au.*, 2022, **2**, 464-476.
4. B. B. Barber, M. G. Jamieson, L. E. M. White and C. T. McTernan, *Chem.*, advance article, DOI: doi.org/10.1016/j.chempr.2024.05.002.

# Metal-ligand coordination-driven self-assembly of topologically rare $\text{Pd}_n\text{L}_{2n}$ cages

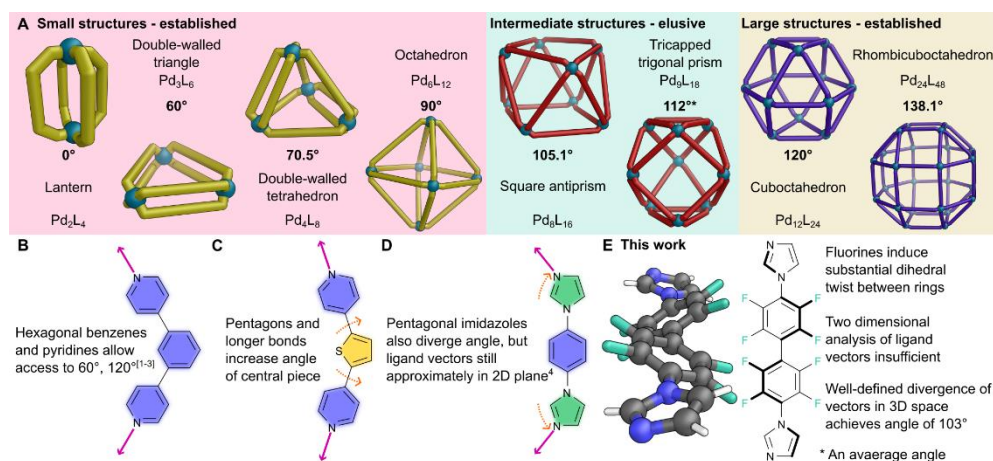
Soumalya Bhattacharyya, Stephen P. Argent, Ben S. Pilgrim\*

*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

email: soumalya.bhattacharyya@nottingham.ac.uk

The assembly of metal-organic cages<sup>1</sup> follows rules based on the coordination preferences of metal ions and the geometries of their typically rigid and planar precursor ligands.  $\text{Pd}_n\text{L}_{2n}$  metal-organic cages are amongst the most structurally diverse with subtle differences in the metal-ligand coordination vectors giving rise to drastically different assemblies<sup>2</sup>, however almost all rely on the rigidity of aromatic linker groups to avoid the formation of intractable mixtures of structures. The metal-ligand coordination vectors ( $\Theta_{av}$ ) are responsible for dictating the final geometry and nuclearity of the cages, and, by using the appropriate  $\Theta_{av}$ , starting from a small  $\text{Pd}_2\text{L}_4$  lantern to a giant  $\text{Pd}_{48}\text{L}_{96}$  spherical polyhedra are accessible. Within this family there are metastable and elusive structures like  $\text{Pd}_8\text{L}_{16}$  which is challenging to access due to an unusual  $\Theta_{av}$  of  $105.1^\circ$ .

This talk will focus on unpublished work on how we have addressed this challenge by using perfluorinated ligands with imidazole donors. Whilst most ligands are constructed via metal-catalysed coupling reactions, we have shown facile approaches to perfluorinated ligands through  $\text{S}_{\text{N}}\text{Ar}$  reactions. Whilst a C–F bond is not substantially larger than a C–H bond sterically, we have observed profound differences in cage assemblies when switching from an aryl to a perfluoroaryl ligand scaffold. This has led to the switching from a more well-established  $\text{Pd}_6\text{L}_{12}$  octahedron to more a more unusual  $\text{Pd}_8\text{L}_{16}$  square antiprism assembly – we believe the first such reported example with  $\text{Pd}(\text{II})$ .<sup>3</sup>



Different possible strategies to access  $\text{Pd}_n\text{L}_{2n}$  structures of various shapes and nuclearity.

## References

1. B. S. Pilgrim and N. R. Champness, *ChemPlusChem*, 2020, 85, 1842-1856.
2. M. R. Black, S. Bhattacharyya, S. P. Argent and B. S. Pilgrim *J. Am. Chem. Soc.*, 2024, 146, 28233-28241.
3. S. Bhattacharyya, S. P. Argent and B. S. Pilgrim manuscript under preparation.



# The First Non-Pyrophoric Precursor for the Low Temperature Deposition of Metallic Aluminium

Caroline E. Knapp\*

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ.

e-mail: caroline.knapp@ucl.ac.uk

The advancement of microelectronics on flexible plastic substrates has sparked a search for precursors capable of depositing conductive features at low temperatures.[1,2] However, there is limited research on aluminum (Al), as it is typically deposited using pyrophoric and highly air- and moisture-sensitive  $\text{AlH}_3$  etherates or aminates.[3] By carefully selecting ligands, it is possible to enhance stability while still enabling the deposition of the desired materials. In this work, we have developed an aluminum complex that can be converted to  $\text{Al}(0)$  without a reductant at  $100^\circ\text{C}$ .

Our approach employed a multi-step synthetic strategy utilizing  $\beta$ -ketoiminate (acnac) bidentate ligands,  $[\text{Al}(\text{R-acnac})_2\text{Cl}]$  (where  $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Ph}, \text{or Mes}$ , **1-5**), which served as precursors to create aluminum hydride complexes: the polymeric amidoalane  $\text{Li}[\text{AlH}_2(\text{Pr-Hacnac})\text{AlH}_3]_n$  (**6**) and the imidoalane cluster  $[\text{AlH}_2\text{AlH}_2(\text{N-Mes})_3(\text{AlH}_2\text{-Li}(\text{Et}_2\text{O})_2)_2]$  (**8**). When heated under vacuum at  $100^\circ\text{C}$ , complex **8** decomposes into aluminum metal, as confirmed by XRD, TEM, and XPS. This represents the first example of a low-temperature route to metallic aluminum using non-pyrophoric precursors.[4]

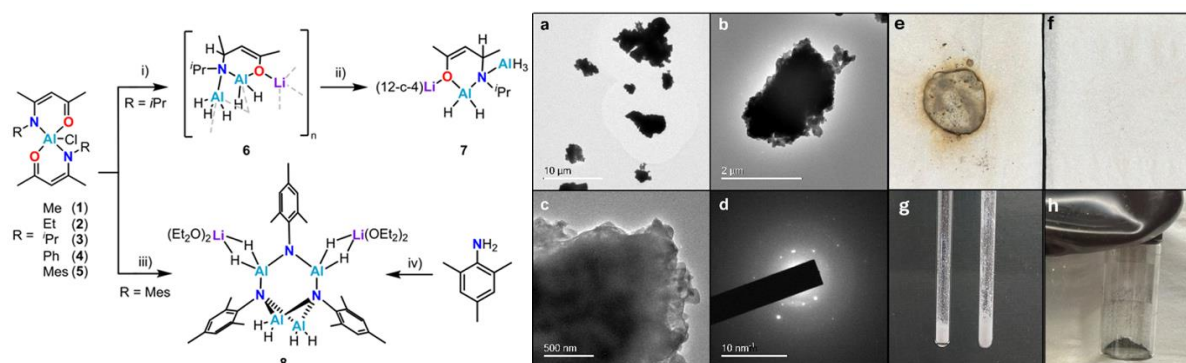


Fig. 1. Left: Synthesis of complexes **1-8**. Right: a-c TEM micrographs of dispersed Al powder from **8** heated under vacuum; d) selected area electron diffraction (SAED) of dispersed Al powder from **8** heated under vacuum; e) tissue after addition of hexane solution of DMEAA; f) and tissue after addition of a toluene solution of cluster **8**; g) precursor **8** before heating and h) grey powder containing metallic aluminium.

## References

1. S. P. Douglas, S. Mrig, and C. E. Knapp, *Chemistry—A European Journal*, 2021, **27**, 8062-8081.
2. S. Mrig, M. A. Bhide, Y. Zhou, N. Staton, J. Wang, S.P. Douglas, H. R. Tinker, K.L. Mears, C. M. Bakewell and C. E. Knapp, *Small Methods*, 2023, **7**, 2300038.
3. C. Knapp, E. N. de Faria, S. Douglas, S. Mrig, L. Santoni, D. Wilson, Preprint on Research Square, Nature Portfolio, 2025, <https://doi.org/10.21203/rs.3.rs-5544055/v1>
4. S. P. Douglas, and C. E. Knapp, *ACS Appl. Mater. Interfaces*, 2020, **12**, 26193.

# A Platinum Butterfly Effect: Small Changes Turn a Chemotherapeutic into a Non-toxic Metalloantibiotic with *In Vivo* Efficacy

Cagri Ozsan<sup>†1,2</sup>, Ann-Britt Schäfer<sup>†3,4</sup>, Sidharth Chopra<sup>5,6</sup>, Michaela Wenzel<sup>\*3,4</sup>, Angelo Frei<sup>\*1,2</sup>

<sup>1</sup> Department of Chemistry, Biochemistry & Pharmaceutical Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

<sup>2</sup> Department of Chemistry, University of York, York YO10 5DD, U.K.

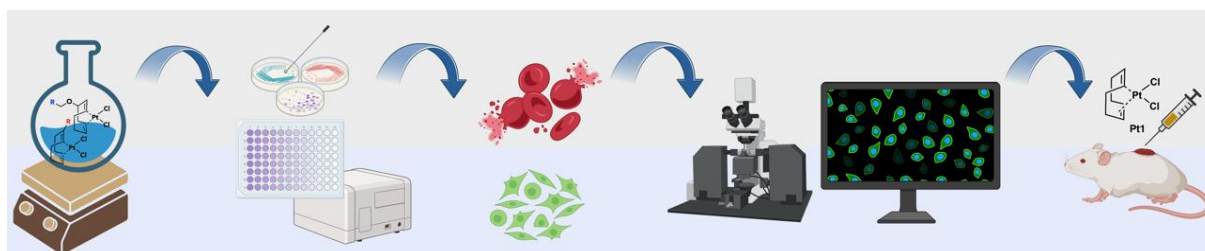
<sup>3</sup> Division of Chemical Biology, Department of Life Sciences, Chalmers University of Technology, Kemigården 4, 412 96 Gothenburg, Sweden

<sup>4</sup> Center for Antibiotic Resistance Research in Gothenburg (CARE), Guldhedsgatan 10, 413 46 Gothenburg, Sweden

<sup>5</sup> Department of Molecular Microbiology and Immunology, CSIR-Central Drug Research Institute, Lucknow-226031, India

<sup>6</sup> Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

Antimicrobial resistance (AMR) is a major global health threat, linked to 4.95 million deaths in 2019, including 1.27 million directly caused by resistant infections. Projections indicate that by 2050, AMR could become the leading cause of mortality, with an estimated 10 million deaths annually.<sup>1,2</sup> These statistics highlight the pressing need for innovative strategies to address this growing threat to public health. While the conventional drug pipeline of antibiotics, based on organic chemistry, has shown insufficient development, exploring novel chemical spaces and unconventional approaches in antibacterial drug discovery is emphasized as an urgent need.<sup>3</sup> Although metals have been used for medical purposes stretching back thousands of years, cisplatin marked a paradigm shift in modern medicine as one of the first metal-containing anticancer drugs.<sup>4</sup> Recently, our group conducted a study on 1,5-cyclooctadiene (COD) complexes of platinum(II), which led to the discovery that PtCODCl<sub>2</sub> exhibits broad activity against Gram-positive bacteria and low *in vivo* toxicity.<sup>5</sup> To investigate the structure-activity relationship (SAR) of this compound class, the COD ring was modified, and the corresponding Pt(II) complexes were synthesized. In-depth mechanistic studies revealed their mode of action, comparing the effects of cisplatin and lead compounds through cellular uptake and activity assays. Despite structural similarities to cisplatin, PtCOD complexes displayed distinct antibacterial properties against Gram-positive bacteria. Furthermore, *in vivo* studies showed that **Pt1** effectively reduced bacterial load in a Gram-positive mouse skin infection model.



## References

1. Tang, K. W. K.; Millar, B. C.; Moore, J. E. *Br. J. Biomed. Sci.* 2023, **80**, 11387.
2. Murray, C. J. L. *et al. The Lancet* 2022, **399**, 629–655. 6736(21)02724-0.
3. Butler, M. S.; Henderson, I. R.; Capon, R. J.; Blaskovich, M. A. T. *J. Antibiot.* 2023, **76**, 431–473.
4. Chattaraj, A.; Syed, M. P.; Low, C. A.; Owonikoko, T. K. *JCO Oncol. Pract.* 2023, **19**, 278–283.
5. Frei, A.; Ramu, S.; Lowe, G. J.; Dinh, H.; Semeneć, L.; Elliott, A. G.; Zuegg, J.; Deckers, A.; Jung, N.; Bräse, S.; Cain, A. K.; Blaskovich, M. A. T. *ChemMedChem* 2021, **16**, 3165–3171.

## Mixed valence $\{\text{Ni}^{2+}\text{Ni}^{1+}\}$ complexes as models of Acetyl Coenzyme A Synthase intermediates

Nadia T. Stephaniuk, Daniel W. N. Wilson, Benedict C. Thompson, Alberto Collauto, Maxie M. Roessler and Rebecca A. Musgrave

Department of Chemistry, King's College London, 7 Trinity Street, London, SE1 1DB, UK

email: nadia.stephaniuk@kcl.ac.uk

Bacterial enzymes are known to utilize the Wood-Ljungdahl Pathway (WLP), which outlines the conversion of carbon dioxide into acetyl coenzyme A (acetyl-CoA), a key biological metabolite.<sup>1,2</sup> Central to the WLP is acetyl-CoA synthase (ACS), one of the few nickel-containing enzymes, which catalyzes the synthesis of acetyl-CoA from CO. The active site of ACS is known as the A-cluster, which consists of a  $\{\text{NiNi}\}$  cluster bridged to a  $[\text{Fe}_4\text{S}_4]^{n+}$  cluster (Figure 1, left).

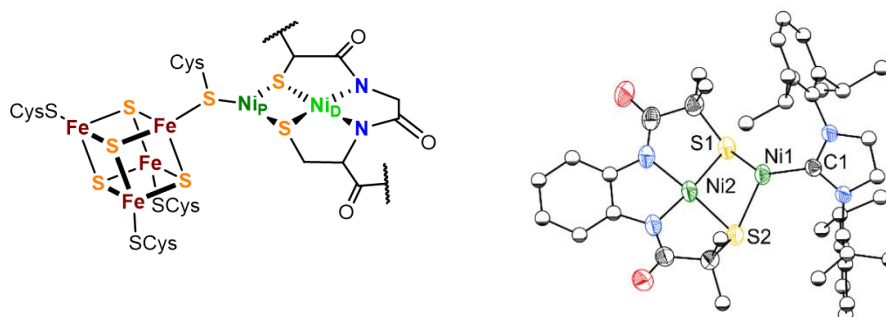


Figure 1: (left) The A-cluster of the ACS cofactor, highlighting the coordination environments of the two nickel centers, namely  $\text{Ni}_\text{P}$  (proximal) and  $\text{Ni}_\text{D}$  (distal); (right) Solid-state structure of the isolated mixed valent bimetallic anion,  $[\mathbf{1}]^-$ .

Many mechanisms have been proposed to describe the activity of ACS, including divergent diamagnetic (nickel (0/II)) and paramagnetic (nickel (I/III)) mechanisms, with extensive research conducted to understand, isolate, and quantify intermediates along both proposed pathways.<sup>2,3</sup> In an effort to probe the role of the two nickel centers (with varying oxidation states) of significance to the A-cluster, we report bimetallic models of two hypothesized intermediates on the paramagnetic pathway of ACS function, namely an anionic  $\{\text{Ni}^{2+}\text{Ni}^{1+}\}$  complex  $[\mathbf{1}]^-$  featuring a three-coordinate Ni-center with similarity to the A-cluster, which reacts with carbon monoxide to yield a  $\{\text{Ni}^{2+}\text{Ni}^{1+}\text{-CO}\}$  complex  $[\mathbf{2}]$  analogous to the enzymatic CO-bound A-cluster. Synthesis of these bimetallic complexes, along with characterization by X-ray diffraction, NMR, UV-Vis, and electron paramagnetic resonance spectroscopies, will be discussed.<sup>4</sup>

### References

1. S. Ragsdale. *Comp. Coord. Chem. III.*, **2021**, 1-9, 611-633.
2. S. Ragsdale and M. Kumar. *Chem. Rev.*, **1996**, 96, 2515-2539.
3. M. Can, F. A. Armstrong, and S. W. Ragsdale. *Chem. Rev.*, **2014**, 114, 4149-4174.
4. D. W. N. Wilson, B. C. Thompson, A. Collauto, R. X. Hooper, C. Knapp, M. M. Roessler, and R. A. Musgrave. *J. Am. Chem. Soc.*, **2024**, 146, 21034-21043.



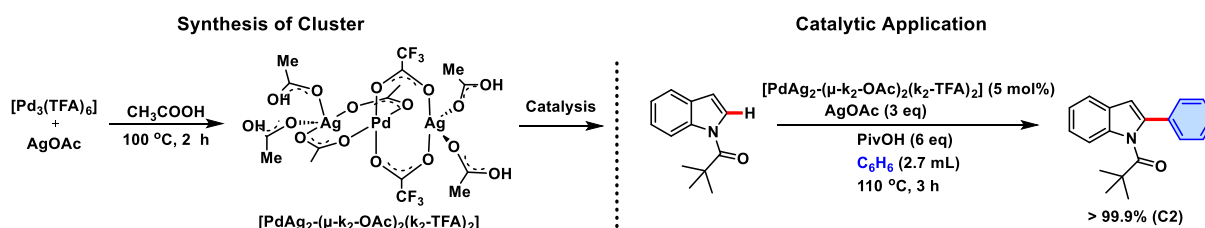
# Investigating the Roles of Bimetallic Species in Oxidative Cross-Coupling Reactions

Mandalena Mendy, William Evans, Neil W. J. Scott, Adrian C. Whitwood and Ian Fairlamb\*

Department of Chemistry, University of York, York, YO10 5DD, UK

email: mm2519@york.ac.uk

Cross-coupling reactions, particularly those involving indoles, serves as synthetically useful substrates for pharmaceuticals and agrochemical agents. Indoles are further abundant in nature and exhibit a range of biological activities.<sup>1</sup> Indoles possess intrinsic chemical reactivity, which can be exploited in C-H bond activation chemistry. Oxidative cross-couplings involving indoles has been of interest, particularly controlling the regioselectivity – the position of chemical functionalisation.<sup>2, 3</sup> In this study, we have investigated the role of bimetallic species in oxidative cross-coupling reactions of indoles through traditional studies in organometallic chemistry complemented by kinetic analysis. We have found that the bimetallic cluster ( $[\text{PdAg}_2-(\mu\text{-}\kappa_2\text{-OAc})_2(\kappa_2\text{-TFA})_2]$ ) can influence the reaction, with product conversions and reaction times varying depending on the catalyst loading. Rapid reactions are observed (between 1-5 hours depending on the catalyst loading). Using 10 mol% bimetallic cluster, only the major isomer ( $\text{C}_2$ ) was observed spectroscopically (quantitatively). This study highlights the potential and performance of preformed bimetallic species for improving catalysis. Future work will expand on understanding the mechanistic role of these bimetallic species for wider application in catalytic chemistries.



## References

1. D. Wang, C. A. Salazar and S. S. Stahl, *J. Organomet.*, 2021, **40**, 2198-2203.
2. D. R. Stuart and K. Fagnou, *J. Sci.*, 2007, **316**, 1172-1175.
3. D. R. Stuart, E. Villemure and K. Fagnou, *J. Am. Chem. Soc.*, 2007, **129**, 12072-12073.

## Platinum Group Metal catalysis for fine chemicals

Antonio Zanotti Gerosa,<sup>a</sup> Jane Patrick,<sup>a</sup> Sarah Facchetti<sup>a</sup>

<sup>a</sup> *Johnson Matthey, Life Science Technologies, 28 Cambridge Science Park, CB4 0FP, UK*

email: antonio.zanotti-gerosa@matthey.com

Platinum Group Metal (PGM) catalysts are essential tools in the chemical industry, impacting any area of modern life, from transport to food and drugs productions. However, PGMs are under scrutiny for their cost and scarcity, fuelling interest in alternative catalysts based on earth-abundant metals. Yet, a simple like-for-like replacement can be a misleading option. Whichever the catalyst, process optimization is the key!

We will clarify the Global Warming Potential (carbon footprint) of PGMs, including the refining option, and how they influence the environmental impact of catalytic steps in fine chemicals applications with consideration for both heterogeneous and homogeneous catalysis.

We will also introduce the Johnson Matthey PGM Award Scheme to support academic research into new applications of PGMs.<sup>1</sup>

### References

1. <https://matthey.com/science-and-innovation/collaboration/jm-platinum-group-metal-award-scheme>.

# Organometallic complexes of tetraphenylpentalenide

Hugh Sanderson, Mandeep Kaur, Ulrich Hintermair\*

Department of Chemistry, University of Bath, BA2 7AY UK.

email: u.hintermair@bath.ac.uk

The rich organometallic chemistry of pentalenide, an intriguing bicyclic  $10\pi$  ligand with unique binding modes, has long been held back by the synthetic difficulties of accessing the precursor.<sup>1</sup> We have developed a straightforward, high-yielding and versatile synthesis of 1,3,5,6-tetrasubstituted dihydropentalenes which are bench-stable precursors to hydropentalenides and pentalenides with tuneable electronic properties.<sup>2,3,4</sup>

In this talk we will be presenting recent work in our group that has explored the organometallic chemistry of tetraphenylpentalenide with a range of s-, d- and f-block metals (Fig.1),<sup>5,6,7</sup> including examples of catalytic reactivity featuring bimetallic cooperativity.

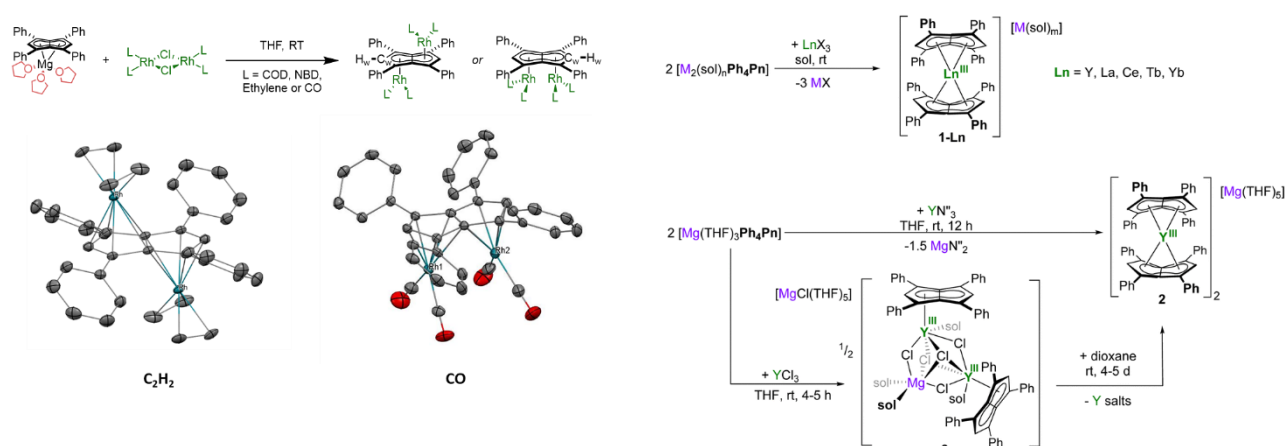


Figure 1:  $Ph_4Pn^{2-}$  complexes of s-, d-, and f-block metals.

## References

1. S. Boyt, N. Jenek, U. Hintermair, *Dalton Trans.* 2019, **48**, 5107-5124.
2. S. Boyt, N. Jenek, H. Sanderson, G. Kociok-Köhn, U. Hintermair, *Organomet.* 2022, **41**, 211-225.
3. N. Jenek, M. Balschun, S. Boyt, U. Hintermair, *J. Org. Chem.* 2022, **87**, 13790-13802.
4. N. Jenek, A. Helbig, S. Boyt, M. Kaur, H. Sanderson, S. Reeksting, G. Kociok-Köhn, H. Helten, U. Hintermair, *Chem. Sci.* 2024, **15**, 12765-12779.
5. H. Sanderson, G. Kociok-Köhn, U. Hintermair, *Inorg. Chem.* 2023, **62**, 15983-15991.
6. H. Sanderson, G. Kociok-Köhn, C. McMullin, U. Hintermair, *Dalton Trans.* 2024, **53**, 5881-5899.
7. N. Katzer, M. Kaur, A. Sen, R. Nimaiyar, J. Autschbach, P. Arnold, U. Hintermair, *Chem. Commun.* 2024, **60**, 9749-9752.

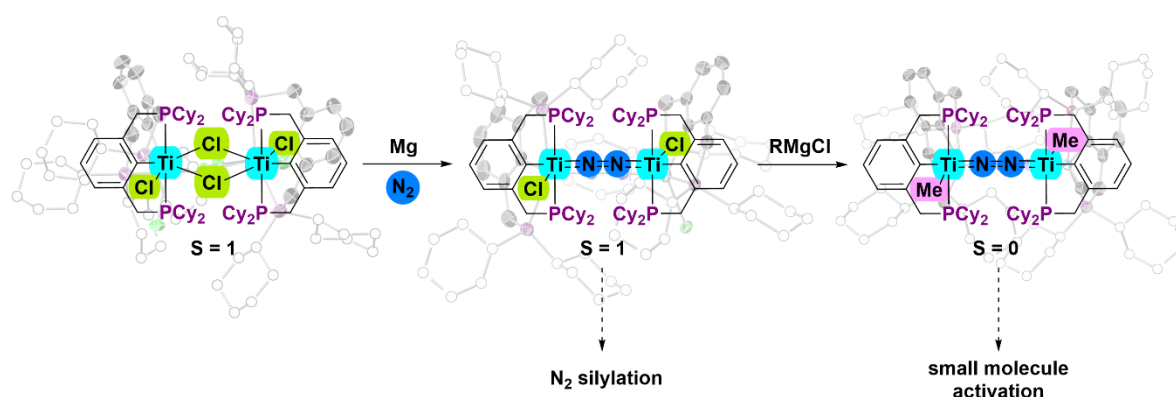
# Cyclohexyl-PCP Supported Titanium Dinitrogen Complexes for Nitrogen Silylation and Small Molecule Activation

Sara Belazregue<sup>a</sup>, F. Mark Chadwick<sup>\*a</sup>

<sup>a</sup> Molecular Sciences Research Hub, Imperial College London, London, W12 0BZ, UK

Email: s.belazregue19@ic.ac.uk

The activation and sustainable upgrading of typically inert small molecules like CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, is a field of growing interest and increasing importance.<sup>1</sup> Pincer complexes have gained traction in this field due to fine-tuning of their ligand architecture allowing for their excellent catalytic activity. There is, however, a distinct disparity in research employing pincer ligands, specifically the PCP moiety, with early transition metals, like earth abundant and non-toxic Ti.<sup>2</sup> This disparity is deemed to be largely due to a research deficiency rather than a lack of their utility.<sup>1</sup>



**Scheme 1.** Simplified scheme for the generation of CyPCP Ti(III) dinitrogen complexes, that are capable of nitrogen silylation (chloro-dinitrogen) and small molecule activation (methyl dinitrogen).

This work presents the synthesis of novel paramagnetic cyclohexyl-PCP Ti complexes. The parent compound [(CyPCP)TiCl(μ-Cl)]<sub>2</sub> is thermochromic and displays the elusive half-field signal in EPR due to its ferromagnetically coupled (S=1) Ti centres. The reduction of the dichloride under an atmosphere of nitrogen delivers [{(CyPCP)TiCl}<sub>2</sub>(μ-N<sub>2</sub>)] in excellent yield. The reduction of our previously published *tert*-butyl analogue (<sup>t</sup>BuPCP)TiCl<sub>2</sub> leads to the isolation of [{(<sup>t</sup>BuPCP)TiCl}<sub>2</sub>(μ-N<sub>2</sub>)]; interestingly these complexes show contrasting electronic properties.<sup>3</sup> Complexes have been characterised by XRD, EPR, and NMR. Both the cyclohexyl and *tert*-butyl dinitrogen compounds have been found to facilitate nitrogen silylation and can be derivatised to give alkyl and aryl dinitrogen compounds. The reactivity of these compounds, [{(R<sup>1</sup>PCP)TiMe}<sub>2</sub>(μ-N<sub>2</sub>)] (R<sup>1</sup> = Cy, <sup>t</sup>Bu), with small molecules like H<sub>2</sub> and CO is also explored.

## References

1. A.L. Odom and T. J. McDaniel, *Acc. Chem. Res.*, 2015, **48**, 2822 – 2833.
2. P. W. Roesky and A. R. Fout, *Inorg. Chem.*, 2021, **60**, 13757 – 13758.
3. B. Stadler et al., *Organomet.*, 2023, **42**, 1278 – 1285.

# The development of optically transparent porous thin films for *in situ* characterization of post synthetic metalation and active site reactivity

Joe D. Simmons,<sup>a</sup> Subham Sarkar,<sup>b</sup> Aishanee Sur,<sup>b</sup> David C. Powers,<sup>b</sup> Eric D. Bloch<sup>a</sup>

<sup>a</sup>Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

<sup>b</sup>Department of Chemistry, Texas A&M University, College Station, Texas, 77843, United States

email: jodasimm@iu.edu

Reactive metal complexes are often plagued by competing inter-complex reactions in solution chemistry. Active site isolation in porous solids eliminates the competing reactions but often suffers from low active site tunability and limited mechanistic insight. By isolating charged molecular complexes in porous salts, active site accessibility and tunability afforded to these complexes is retained, while the site isolation afforded by the solid-state minimizes inter-complex reactivity. Using a layer-by-layer assembly approach, optically transparent films of these reactive porous salts can be grown on a variety of surfaces allowing for *in situ* characterization of the reactive complex.<sup>1</sup> In operando kinetics studies of porphyrin-based complexes reveal insight into solid-state metalation of free-base porphyrins as well as subsequent substrate binding at metalloporphyrin sites.<sup>2</sup> This work highlights the utility of porous salts and their accompanying transparent porous films toward solid-state organometallic chemistry with highly tuneable reactivity while simultaneously facilitating the characterization of said reactivity.

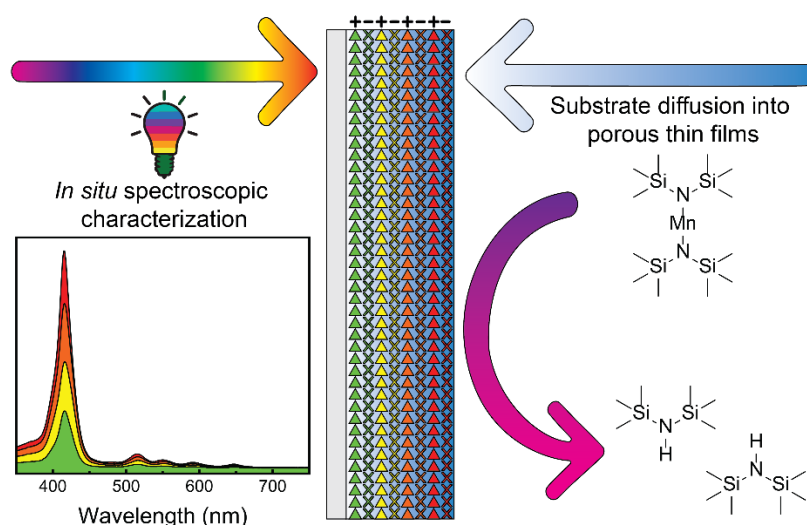


Figure 1: Optically transparent thin films enable *in situ* spectroscopic characterization of post synthetic metalation reactions and reveal a substrate diffusion limited depth dependence.

## References

1. J. D. Simmons, A. Sur, A. A. Ezazi, K. J. Korman, S. Sarkar, E. T. Iverson, E. D. Bloch, *J. Am. Chem. Soc.*, 2023, **145**, 25068-25073
2. J. D. Simmons, S. Sarkar, A. A. Ezazi, A. Sur, E. T. Iverson, M. N. Morey, A. D. Chivington, J. C. Grunlan, D. C. Powers, E. D. Bloch, *ChemRxiv*, 2024, DOI: 10.26434/chemrxiv-2024-8jxvh

# Role-reversal in hybrid polyoxometalate Donor- $\pi$ -Acceptor non-linear optical chromophores

Claire Jones<sup>1</sup>, John Fielden<sup>2</sup>, Koen Clays<sup>3</sup>, Benoit Champagne<sup>4</sup>

<sup>1</sup> University of East Anglia, Norwich, United Kingdom, <sup>2</sup> Lancaster University, Lancaster, United Kingdom, <sup>3</sup> KU Leuven, Leuven, Belgium, <sup>4</sup> Université de Namur, Namur, Belgium.

email: claire.jones@uea.ac.uk

The frequency doubling or second harmonic generation (SHG) properties of non-linear optical (NLO) materials are widely applicable in laser technology, from specialist applications in frequency conversion for spectroscopy, wider societal use in optical telecommunications and phototherapy treatments to handheld green laser pointers. Most commercially utilised NLO materials are crystalline inorganic salts e.g. potassium titanyl phosphate (KTP), except for 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST), which is a molecular donor- $\pi$ -acceptor (D- $\pi$ -A) NLO chromophore. Imido-functionalised polyoxometalates (POMs) are molecular NLO chromophores that feature Lindqvist POMs as highly transparent acceptors. We have demonstrated their design versatility and efficiency at SHG compared to inorganic salts improving the NLO performance of polyoxometalate chromophores (POMophores) by altering the conjugative bridge, the donor and the geometry.<sup>1,2</sup>

The redox chemistry of POMophores can be exploited to reversibly switch the NLO response on/off; this was studied by conducting chronoamperometry in-situ while simultaneously conducting HyperRayleigh Scattering (HRS) experiments [Fig. 1].<sup>3</sup> Here we present an alkyne-substituted aryl-imido POM post-functionalised by reaction with a Ru (II) complex forming a Ru-C bond. Our hypothesis was that these truly organometallic NLO POMophores could be switched on/off in two ways; either by oxidising the ruthenium metal centre (donor) or reducing the POM (acceptor). However, unexpectedly oxidation of the ruthenium centre instead reversed the donor and acceptor roles. The post-functionalisation chemistry employed has potential for binding POMophores onto silicon wafers to achieve a non-centrosymmetric NLO material.<sup>4</sup>

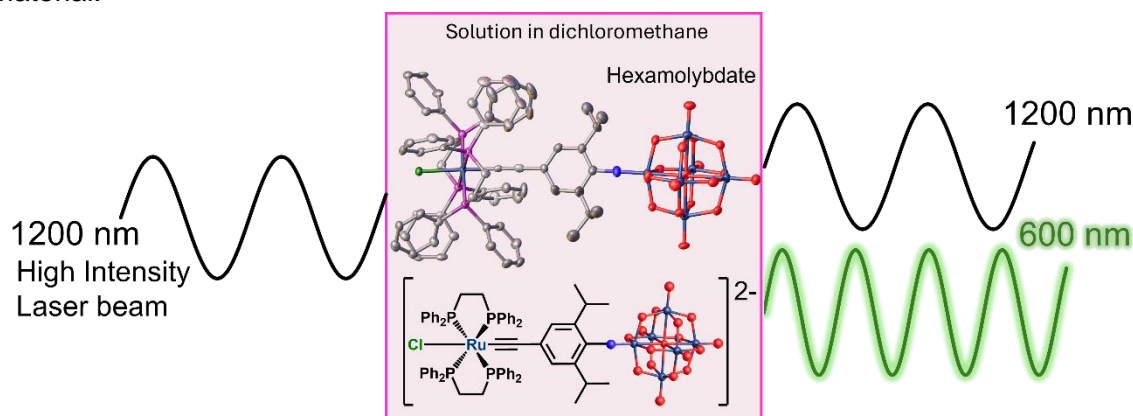


Fig.1: Schematic of the HRS experiment to measure the NLO activity of an organometallic POMophore

## References

1. C. F. Jones, B. R. Hood, Y. de Coene, I. Lopez-Poves, B. Champagne, K. Clays, J. Fielden, *Chem. Commun.*, 2024, 60, 1731-1734.
2. B. R. Hood, Y. de Coene, C. F. Jones, I. Lopez-Poves, N. Deveau, N. R. Halcovitch, B. Champagne, K. Clays, J. Fielden, *Inorg. Chem.*, 2024, **63**, 24250-24261
3. B. R. Hood, Y. de Coene, A. Froes, C. Jones, et al., *Angew. Chem. Int. Ed.*, 2023, **62**, e202215537
4. J. M. Buriak, *Chem. Commun.* 1999, 1051-1060