From the Molecular d- and f-Block to Nanomaterials: Synthetic Inorganic and Organometallic Chemistry

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Abstract:

This seminar will provide an overview of my research experiences as a PhD student at McMaster University, and as a Post-Doctoral Research Associate (PDRA) in the UK at the Universities of Edinburgh and Oxford. First, an ambiphilic ligand is one that contains both Lewis basic and Lewis acidic moieties, and my PhD research focussed on the synthesis of late transition metal complexes bearing Group 13 Lewis acid-containing ambiphilic ligands for small molecule activation and functionalization. Three different borane- (i.e. BR_3) and alane-containing (i.e. AIR_3) ambiphilic ligands were developed and investigated during my PhD, and results highlighting the potential advantages of utilizing ambiphilic ligands for metal-based small molecule activation will be presented.¹ Next, my Post-Doctoral research at the University of Edinburgh was focussed on discovering new avenues for the reductive functionalization of the uranyl ion, $[U^{VI}O_2]^{2+}$, which is the most prevalent form of molecular uranium in the environment. Reductive functionalization of uranyl is a reaction pathway that entails one or two electron reduction of the U^{VI} centre in uranyl to U^V or U^{IV}, respectively, with simultaneous conversion of the oxo ligands into new oxygen-containing ligands, such as boroxy or siloxy ligands, and represents a potentially vital transformation for uranium waste remediation within the environment. By deploying a macrocyclic Schiff base ligand (i.e. a Pacman ligand), two co-linear $[U^{VI}O_2]^{2+}$ ions have been installed within a single ligand framework, and reactions resulting in the reductive functionalization of uranyl, and subsequent reactivity with electrophilic reagents and small molecules, will be presented.² Finally, as a PDRA at the University of Oxford my research interests were focussed on the synthesis of copper-containing nanoparticles (NPs) for catalytic CO₂ reduction. Our organometallic strategy for synthesizing ultra-small (1-6 nm) colloidal nanoparticles of copper (Cu) and cuprous oxide (Cu_2O), a novel strategy for decorating the surface of Cu_2O colloids with potentially reactive organometallic fragments, such as $-OZn(C_6F_5)$ and $-OCo(C_6F_5)$, including subsequent functionalization of the surface organometallic fragment in the case of zinc, and characterization of the newly synthesized materials will be presented.^{3,4} The contents of this seminar will span synthetic inorganic and organometallic chemistry from ligand design and deploying molecular d- and f-block complexes for small molecule activation and fundamentally interesting reactivity, to the use of organometallic reactivity to synthesise novel nano-materials, and will be of relevance to a broad array of disciplines in inorganic chemistry.

- 1. Paskaruk, K. M.; Cowie, B. E.; Emslie, D. J. H. Coordination Chemistry of Lewis Acidic Ligands, *Comprehensive Coordination Chemistry III, Eds.* E. C. Constable, G. Parkin, L. Que Jr., Vol. 1, Elsevier, **2021**; pp. 717-805.
- 2. Cowie, B. E.; Purkis, J. M.; Austin, J.; Love, J. B.; Arnold, P. L. Chem. Rev. 2019, 119, 10595.
- 3. Cowie, B. E.; Häfele, L.; Phanopoulos, A.; Said, S. A.; Lee, J. K.; Regoutz, A.; Shaffer, M. S. P.; Williams, C. K. *Chem. Eur. J.* **2023**, *29*, e202300228.
- 4. Cowie, B. E.; S'ari, M.; Lee, J. K.; de Gutierrez, M. B.; Kalha, C.; Regoutz, A.; Shaffer, M. S. P.; Williams, C. K. Submitted to *J. Am. Chem. Soc.* **Submission ID:** ja-2023-10892q