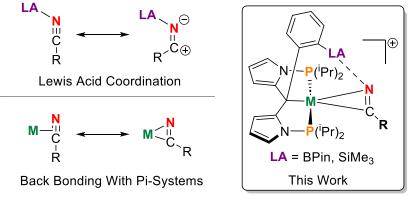
Green Chemistry Approaches to Base Metal Catalyst Design: Leveraging a Lewis Acidic Secondary Coordination Sphere for Small Molecule Activation

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Chemistry is experiencing a call to action concerning the development and implementation of sustainable chemical processes and transformations.¹ The development of base metal catalysts, in place of their precious metal counterparts, is one method to reduce both cost and toxicity while opening avenues for novel reactivity.² In recent years, pincer complexes have shown remarkable catalytic activity.³ Milstein *et al.* provide excellent examples of metal ligand cooperation utilizing the secondary coordination sphere utilizing pyridine and acridine-based ligands which undergo an aromatization/de-aromatization sequence during bond activation.⁴ Looking to further take advantage of the secondary coordination sphere, recent research has focused on the inclusion of Lewis basic and acid moieties into the ligand periphery as a means to tailor reactivity.⁵ Herein, we describe preliminary results in the synthesis of a series of PCP pincer ligands featuring Lewis acidic moieties (silyl or boryl) in the secondary coordination sphere. The formation of strong Si-O and B-O/N bonding interactions are leveraged to activate Lewis basic substrates, such as nitriles, utilizing base metals. Insights into the sustainability of the resulting complexes are provided through a truncated life cycle analysis.



Step to ligand
Abundant metals
Metal ligand cooperation

References

- (1) Matlin, S. A.; Cornell, S. E.; Krief, A.; Hopf, H.; Mehta, G. Chemistry Must Respond to the Crisis of Transgression of Planetary Boundaries. *Chem. Sci.* **2022**, *13* (40), 11710–11720. https://doi.org/10.1039/D2SC03603G.
- (2) Clapson, M. L.; Durfy, C. S.; Facchinato, D.; Drover, M. W. Base Metal Chemistry and Catalysis. *Cell Reports Phys. Sci.* **2023**, *4* (9), 101548. https://doi.org/10.1016/J.XCRP.2023.101548.
- (3) van Koten, G.; Hollis, T. K.; Morales-Morales, D. Pincer Chemistry and Catalysis. *Eur. J. Inorg. Chem.* 2020, 2020 (47), 4416–4417. https://doi.org/10.1002/ejic.202000858.
- Gunanathan, C.; Milstein, D. Metal–Ligand Cooperation by Aromatization–Dearomatization: A New Paradigm in Bond Activation and "Green" Catalysis. Acc. Chem. Res. 2011, 44 (8), 588–602. https://doi.org/10.1021/ar2000265.
- (5) Zurakowski, J. A.; Austen, B. J. H.; Drover, M. W. Exterior Decorating: Lewis Acid Secondary Coordination Spheres for Cooperative Reactivity. *Trends Chem.* 2022, *4* (4), 331–346. https://doi.org/10.1016/j.trechm.2022.01.007.

Dr. Marissa Clapson Biography

Dr. Marissa Clapson is a newly appointed assistant professor at the University of Prince Edward Island. She also currently holds the positions of Chair in the Canadian Institute of Chemistry (CIC) Green Division as well as Vice Chair of the CIC Pride Resource Group. Dr. Clapson is deeply passionate about sustainability in chemistry and the workplace. She believes that sustainability, equity, diversity, inclusivity, accessibility, and reconciliation (EDI-AR), and green chemistry go hand-in hand and allow us to create a better global future.

Dr. Clapson completed her PhD thesis at the University of Calgary, working with Dr. Warren Piers [Thesis Title: Organocobalt PCP Carbene Complexes for Small Molecule Activation & SoTL Explorations in the Gamification of Learning in General, Organic, and Polymer Chemistry]. Extending from that work, she stablished her company ChemEscape Consulting Inc. focused on developing gamified learning materials for applications in STEM classrooms. She completed her postdoctoral work with Dr. Marcus Drover at the University of Windsor focusing on the application of boranes in the secondary coordination sphere of nickel complexes for small molecule activation.

Throughout her research career Dr. Clapson has been awarded a series of research and teaching awards including a CNC-IUPAC Research Travel Grant to attend the Net Zero conference in Scotland, an RCS Travel award, the Science Atlantic Speaker Tour Fund, a UPEI internal research grant, NSERC (CGS-D) Scholarship, the Students' Union Teaching Excellence Award (Teaching Assistant), and the University of Calgary Teaching Award for Graduate Assistants (Teaching).

Her current research is focused on the development of sustainable catalysts for small molecule transformation including CO_2 and nitrate reduction, C-C cross coupling reactions, and the development of recyclable catalysts using waste textiles as supports. Similarly, Dr. Clapson works with her team to develop interactive, gamified activities to teach Inorganic and Green Chemistry in undergraduate classrooms and at chemistry conferences (the professional's classroom).