Demyan Prokopchuk Laboratory

Understanding C-H Bond Activation with Organometallic Molecules: The controlled delivery of protons (H^+), hydrides (H^-), and hydrogen atoms ($H\bullet$) is essential for synthesizing fuels, medicines, and chemical feedstocks. Sustainable synthetic methodologies for delivering these parcels should use Earth-abundant metals, ideally in catalytic quantities, coupled with electrochemical workflows that are seamlessly integrated with renewable energy grid systems. To accomplish this, the Prokopchuk lab aims to understand how C-H and N-H bonds can be weakened for delivering H^+, H^- or $H\bullet$ atoms in a sustainable and catalytic manner.

More specifically, the replacement of palladium catalysts for nickel is preferable for sustainability and economic reasons, however Pd and other precious metals are still routinely used in industry for the activation of strong C-H bonds. Thus, is it possible to compare the performance of precious and non-precious metal catalysts to gain a deeper understanding of why precious metals are better at C-H bond activation? Under which conditions can non-precious metals outperform precious metals in C-H bond activation catalysis? To begin answering these important questions, we have pioneered a new method to measure the degree of C-H bond weakening in the presence of nickel and palladium compounds by independently measuring C-H acidity (pKa) and bond dissociation free energy (BDFE).

These results have broad implications for the understanding of C-H activation for organic synthesis and drug discovery (Journal of the American Chemical Society, 2022; Chemical Communications, 2024).1,2 To further develop this areaof exciting research, the Beckman Scholar will synthesize bespoke transition metal compounds using Ni, Pd, Co, or Rh and study their C-H bond strength properties using techniques such as electrochemistry, X-ray crystallography, NMR spectroscopy, and mass spectrometry. Reaction kinetics will be monitored using time-resolved methods such as cyclic voltammetry and UV-vis spectroscopy. State-of-the-art Density Functional Theory (DFT) calculations will be employed to understand thermochemical and kinetic free energy landscapes with high levels of accuracy. To promote intellectual growth, the Scholar will be given unlimited access to all pertinent equipment and will independently analyze results under the mentorship of Prof. Prokopchuk and a senior PhD student.

(1) Lin, L.; Spasyuk, D. M.; Lalancette, R. A.; **Prokopchuk, D. E.** Coordination-Induced Weakening of a C(sp^3)-H Bond: Homolytic and Heterolytic Bond Strength of a CH-Ni Agostic Interaction. *Journal of the American Chemical Society* **2022,** *144*, 12632. 10.1021/jacs.2c05667

(2) Lin, L.; Tresp, D. S.; Spasyuk, D. M.; Lalancette, R. A.; **Prokopchuk, D. E.** Accessing Ni(0) to Ni(IV) via nickel–carbon–phosphorus bond reorganization. *Chem. Commun.* **2024,** *60*, 674. 10.1039/D3CC04687G