Title: Bimetallic Main-Group Catalysts for the Synthesis of Advanced Biodegradable Polymers

Abstract: Aliphatic polyesters represent biodegradable and biocompatible materials that could replace polyolefins in many applications. However, their synthesis with fine structural control remains challenging, limiting the ability to tailor these materials for specialty and advanced applications. Our laboratory has developed a class of bimetallic main group catalysts for lactone and lactide polymerization distinguished by their electronic and steric tunability. The catalysts are constructed from binucleating *bis*(pyrazolyl)alkane ligands, which we have prepared by a novel method. Targeting monomer selectivity, stereocontrol, and sequence control we have developed homobimetallic, heterobimetallic, and chiral analogues of these complexes. We show promising evidence for metal-metal cooperativity from significant enhancements in rate compared to monometallic analogues. Through systematic comparison of metal composition and ligand sterics, we have identified a highly selective catalyst for lactone incorporation into polylactide, providing copolymers with a highly alternating structure. We describe an unusual dilithium complex that polymerizes aldehydes with exceptional activity and selectivity, raising opportunities for more sophisticated and adaptable oxygenated polymers.

Biography. Robert completed his PhD in 2014 at Princeton with David MacMillan, studying asymmetric organocatalysis and total synthesis. Robert then pursued postdoctoral studies at MIT under Mircea Dinca, where he studied olefin upgrading and polymer synthesis with metal-organic frameworks. In 2018, Robert started his independent career at the University of Houston. His research is supported by the ACS Petroleum Research Fund and the Welch Foundation. Robert currently leads a team of 10 graduate students and three undergraduates, studying new reactions and catalysts for small molecule and polymer synthesis.

Recent Publications.

6. Ethylene polymerization with thermally robust vanadium(III) tris(2-pyridyl)borate complexes. Qian, J.; Comito, R. J.* *Organometallics* **2023**, *in press*.

5. Binucleating *Bis*(pyrazolyl)alkane Ligands and Their Cationic Dizinc Complexes: Modular, Bimetallic Catalysts for Ring-Opening Polymerization. Gu, Z.; Comito, R. J.* *Organometallics* **2022**, *41*, 1911-1916.

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3. One-Pot Synthesis of Primary and Secondary Aliphatic Amines via Mild and Selective sp^3 C-H Imination. Ghosh, S. K.; Hu, M.; Comito, R. J.* *Chem.-Eur. J.* **2021**, *27*, 17601-17608.

2. A Robust Vanadium(V) *Tris*(2-pyridyl)borate Catalyst for Long-Lived High-Temperature Ethylene Polymerization. Qian, J.; Comito, R. J.* *Organometallics 2021, 40, 1817-1821.*

1. Metal-Free, Mild, and Selective Synthesis of *Bis*(pyrazolyl)alkanes by Nucleophile-Catalyzed Condensation. Tansky, M; Gu, Z.; Comito, R. J.* *J. Org. Chem.* **2021**, *86*, 1601-1611.