

FRIDAY, February 6, 2026 - 12:00 Noon
MC H313

Harnessing Ligand Dynamics for Sustainable Catalysis



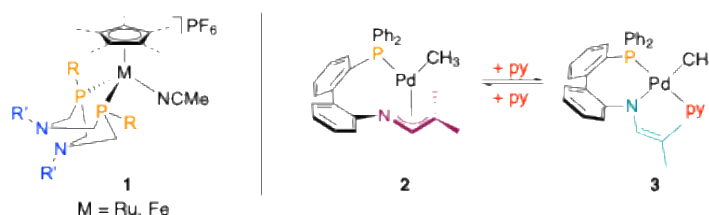
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Factors that promote sustainable catalysis include catalysts that can be used at very low catalyst loadings, and those that promote enabling transformations with minimal waste generation. These goals can be achieved with specially designed catalyst and ligand structures. We have pursued the development of catalysts with cooperative ligands that can assist catalytic turnover through reversible changes, such as proton shuttling,^[1] and changes to ligand coordination mode.^[2] Both of these ligand types will be covered in this presentation. First, we have demonstrated that $[\text{Ru}(\text{Cp})(\text{P}^{\text{R}_2}\text{N}^{\text{R}'_2})(\text{MeCN})]\text{PF}_6$ catalysts (**1**) are active catalysts for alkyne functionalization, which depends on proton shuttling by the pendant tertiary amine groups of the $\text{P}^{\text{R}_2}\text{N}^{\text{R}'_2}$ ligand.^[3] Mechanistic insight has guided catalyst redesign strategies, as well as redeployment toward intermolecular C-O bond formation. The second portion of the presentation will cover phosphine 1-azaallyl (P^{Aza}) complexes, which we designed to exploit dynamic changes in coordination mode. The P^{Aza} ligand effectively stabilizes operationally unsaturated metals via $\eta^3\text{-NCC}$ coordination of the 1-azaallyl moiety (e.g., **2**).^[4] Yet, it can permit ligand (or substrate) binding through a change in coordination to $\kappa^1\text{-N}$ (e.g., **3**). This, and other reactivity of **2**, will be discussed.



- [1] E. S. Wiedner, A. M. Appel, S. Rauegi, W. J. Shaw, R. M. Bullock, *Chem. Rev.* **2022**, *122*, 12427-12474.
[2] J. M. Blacquiere, *ACS Catal.* **2021**, *11*, 5416-5437.
[3] D. E. Chapple, M. A. Hoffer, P. D. Boyle, J. M. Blacquiere, *Organometallics* **2022**, *41*, 1532-1542.
[4] P. A. Fortuna, L. S. G. Kelley, Y. Sun, J. Xu, Z. Wang, P. D. Boyle, T. K. Sham V. N. Staroverov, J. M. Blacquiere, *Dalton Trans.* **2026**, *accepted*