INTRODUCTION

Ligands play a crucial role in transition metal catalyzed organic reactions, as they allow chemists to tune both the steric and electronic environment of a reactive metal center. While traditional ligands merely play a spectator role, redox non-innocent ligands can actively participate by modulating the Lewis acidity of a metal, serving as an electron reservoir, directly making or breaking bonds to a substrate, and stabilizing substrate centered radicals. Central to the goal of establishing ever increasingly selective and efficient catalytic processes is a firm understanding of mechanism. To utilize redox non-innocent ligands at their full potential, one must understand their structure and reactivity. In recent years, these ligands have begun to transition from the labs of inorganic chemists interested in their redox properties to synthetic organic labs hoping to develop novel transformations by harnessing their dynamic behavior. In particular, the development of unique cyclizations and cycloadditions to create carbocycles has been enabled by the application of redox non-innocent ligands in catalysis.

INTRAMOLECULAR (2+2) CYCLOADDITIONS AND REDUCTIVE CYCLIZATIONS

Chirik and coworkers disclosed an early report of intramolecular (2+2) cycloaddition using an iron bound pyridine diimine (PDI) complex (Scheme 1) and performed preliminary mechanistic study to support a proposed Fe(II) cycle, with the PDI ligand serving as an electron reservoir to avoid high energy oxidation states of iron. This complex was also discovered to catalyze the reductive cyclization of enynes and diynes under hydrogen atmosphere. In an effort to gain deeper mechanistic insight into these processes, a new catalyst design that allowed the isolation and characterization of metallocycle intermediates was applied. Based on a combination of spectroscopic, crystallographic, and computational observations, a revised Fe(I)-Fe(III) cycle was proposed for the intramolecular (2+2) cycloaddition, with a Fe(II)-Fe(III) cycle for the reductive cyclizations.

INTERMOLECULAR [2+2] CYCLOADDITIONS

The first example of an intermolecular (2+2) cycloaddition using the (PDI)Fe system was between ethylene and 1,3-butadiene, whereas other substrates gave 1,4-hydrovinylation or displayed no
reactivity.\textsuperscript{3a} Informed by mechanistic studies previously conducted on intramolecular cyclizations and knowledge of deleterious side reaction pathways, more efficient catalysts were applied that facilitated intermolecular (2+2) dimerizations of terminal olefins and impressive cross olefin-diene (2+2) cycloadditions on a variety of readily available, unactivated substrates (Scheme 2).\textsuperscript{3b} Recently, a more thorough mechanistic understanding of these reactions was established through kinetic, spectroscopic, crystallographic, and computational studies.\textsuperscript{3c}

**VINYLIDENE TRANSFER [2+1] AND [4+1] CYCLOADDITIONS**

The Uyeda group has developed a catalytic platform to allow the transfer of the reactive vinylidene group in reductive cycloadditions using a bimetallic nickel complex, ligated by a redox non-innocent naphthyridine diimine (NDI).\textsuperscript{4} The dynamic redox behavior of this complex was studied through chemical modification, CV, and DFT studies, and was found to support five different oxidation states.\textsuperscript{4a} This was applied in both (2+1)\textsuperscript{4b} and (4+1)\textsuperscript{4c} cycloadditions to form methylenecyclopropanes and 4-methylenecyclopentenes, respectively (Scheme 3). These functional group tolerant strategies for an uncommon bond disconnection are synthetically valuable, and their development has been shepherded by mechanistic insight.

**REFERENCES**


