Alkyne Functionalization via Metal Vinylidene-Mediated Catalysis

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Transition metals engage alkynes to generate σ-alkynyl, π-alkyne, and vinylidene complexes that often coexist in dynamic equilibrium and serve as key intermediates in catalytic transformations. Our laboratory has been developing new alkyne functionalization strategies for organic synthesis by exploiting catalytic cycles that proceed through transition-metal vinylidene intermediates. These efforts have produced a range of ring-forming reactions using terminal alkynes, including hydrative, alkylative, and carboxylative cyclizations as well as enyne cycloisomerizations. More recently, we have turned to oxygen transfer to metal-bound unsaturated carbene intermediates. This pursuit led to the discovery of an oxidative alkyne functionalization pathway mediated by metalloketene species, formed via catalytic oxygenation of metal vinylidenes. Extending this reactivity, we established an alkyne-to-acyl transformation that enables catalytic amidation of terminal alkynes, providing streamlined access to β-peptide building blocks. In parallel, we have explored a tandem addition–cyclization–rearrangement cascade, wherein alkynyl hydrazones react with organoboronic acids to yield cycloalkene products with high enantioselectivity in a traceless fashion. This transformation highlights the merger of pericyclic rearrangements with transition-metal catalysis via π-alkyne complexes. In this presentation, I will discuss the design, development, and mechanisms underlying these alkyne transformations, and their potential as versatile tools in synthetic organic chemistry.