

Highly Selective Catalytic Syntheses of Heterocyclic Compounds

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Chiral dirhodium catalysts are highly effective as Lewis acids and in metal carbene syntheses. As Lewis acids they are highly selective single-point binding catalysts that exhibit high levels of enantiocontrol. In metal carbene transformations dirhodium catalysts are exceptionally versatile, and focus in this presentation will be on catalytic processes with easily prepared enoldiazoacetates that include cycloaddition reactions that operate through metal carbene intermediates. Metal enolcarbenes are susceptible to both [3 + 3]- and [2 + 3]-cycloaddition reactions^{1,2} with hydrazones, nitrones, and azomethine ylides, to form oxazines, pyrazolidinones, quinolizidines, tetrahydropyridazines, tetrahydroquinolines and other heterocycles in vinylogous processes that include dearomatization. Stereocontrol generally exceeds 90% ee and 95% de. The divergent activities of copper and dirhodium catalysts are evident in these reactions, with copper directing reactant enoldiazoacetates along an acid-catalyzed pathway, and dirhodium taking the reactants through a metal carbene pathway. A more precise understanding of catalysis in these reactions allows predictability in their applications for synthesis.

¹ Xu, X.; Zavalij, P. Y.; Doyle, M. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 9829-9833.

² Xu, X.; Qian, Y.; Zavalij, P. Y.; Doyle, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 1244-1247.