Thursday, August 27, 2020 at 1:00pm
Register here for zoom link:
https://columbiauniversity.zoom.us/meeting/register/tJEtdO6pqDojH9b-a41I3lDDJZkPm04W-Pk

Rhodium(III)-catalyzed Difunctionalization of Alkenes Initiated by C–H Bond Activation
Presented by Erik Phipps, Rovis Group

The direct conversion of C–H bonds into valuable C–C and C-heteroatom bonds remains a significant challenge to synthetic organic chemists. In order to convert these inert C–H bonds, Rh(III)-catalysts bearing cyclopentadienyl (Cp) ligands have been employed with increasing popularity in recent years. Furthermore, manipulating the sterics and electronics of the Cp ligand display profound impacts on catalytic transformations.

We have previously reported that N-enoxyphtalimides are a unique one-carbon component for the cyclopropanation of activated alkenes. In an effort to expand the scope to accessible alkenes, we have found a number of symmetrical unactivated alkenes undergo [2+1] annulation to afford intriguing spirocyclic cyclopropanes.

Additionally, we have developed a Rh(III)-catalyzed diastereoselective [2+1] annulation onto allylic alcohols to furnish substituted cyclopropyl ketones. Notably, the traceless oxyphthalimide handle serves three functions: directing C–H activation, oxidation of Rh(III), and, collectively with the allylic alcohol, in directing cyclopropanation to control diastereoselectivity. Allylic alcohols are shown to be highly reactive olefin coupling partners leading to a directed diastereoselective cyclopropanation reaction, providing products not accessible by other routes.

Next, an artifact of previous cyclopropanation reactions leads to the formation of a Rh-π-allyl complex. Attempts at 1,1-carboamination of N-enoxyphtalimides are made using alkenes and nitrenoid precursors toward the 3-component synthesis of allylic amines.

Lastly, efforts toward 1,2-carboamination of alkenes initiated by sp3 C–H bond activation are made with employing synthetically viable starting materials.