MISSOURI S&T Chemistry Seminar

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Reactivity of Coinage Metal Complexes Supported by Tetramethylguanidinyl Triphenyl Stibine and Bismuthine Ligands towards Nitrene Transfer Chemistry

Abstract: Carbon Nitrogen (C-N) bonds are ubiquitous in pharmaceuticals, agrochemicals, natural products, and ligands for transition metal catalysts. Transition-metal catalysts introduce new C-N bond into the desired molecules by C-H bond activation or by addition of nitrene across a C=C bond to form aziridines, which can easily be converted into an amine by various chemical transformations.

Transition-metal catalyst frameworks supported by tripodal [TMG_3trphen] ligands mediate nitrene transfer from nitrogen sources such as PhI=NR (PhI=NTs or PhINTces) to a diverse group of aliphatic and aromatic hydrocarbons and olefins. These reactions are categorized as amination and aziridination reactions. Novel tripodal ligands and their complexes with coinage transition metals (Cu, Ag, Au) with different axial atoms such as CH, Sb and Bi and benzene platform have been designed to impart weaker axial ligand field, which, in turn, enhances the electrophilicity of nitrene, potentially affording more reactive and site-selective aminated products. The trinuclear copper catalysts [TMG_3trphen$SbCu_3(\mu_2\text{-}Cl)_3$] and [$TMG_3$trphen$BiCu_3(\mu_2\text{-}Cl)_3$] have shown promising results towards aziridination of styrenes with excellent yields though the reactivity of the silver catalyst [TMG_3trphen$SbAg_3(\mu_2\text{-}Cl)_3$] needs to be explored more for comparative studies. The copper complexes are also reactive for the selective amination of various hydrocarbons at benzylic and tertiary C–H sites.