PINDU October 30th, 2010

Low-Valent Uranium for Oraganometallic Processes: Functionalization of Carbon Dioxide and Carbon Disulfide

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Uranium is an ideal alternative to expensive precious metals for organic transformations due to its low cost, high availability, and unique reactivity. Although uranium(III) is especially attractive for it's electron rich nature, it's organometallic chemistry is not well explored. Recently, our lab has demonstrated the bis(hydrotris(3,5-dimethylpyrazolyl)borate ligand framework is particularly effective for stabilizing low valent uranium (III) compounds. These ligands are sterically bulky, protecting the reactive uranium(III) center from unwanted side reactions. Using this ligand scaffold, organouranium(III) alkyl species have been synthesized, allowing the exploration of the insertion chemistry of carbon dioxide and carbon disulfide into uranium-carbon bonds. Addition of carbon dioxide or carbon disulfide to these compounds resulted in the insertion of CO₂ or CS₂ into the uranium-carbon bond producing the respective carboxylate/thiocarboxylate derivatives. All compounds are fully characterized by ¹H NMR and infrared spectroscopies as well as X-ray crystallography. In some cases further reaction of these compounds with silylhalides regenerates the uranium-monohalide starting material, and releasing a silvl ester, closing a stoichiometric pathway for the functionalization of CO₂.