

Diruthenium Amidates As A New Class of Oxygenation Catalysts

Leslie Villalobos and Tong Ren

Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907

Abstract:

Catalytic oxygenation of organic sulfides has been proved to be a convenient and effective method to remove sulfur compounds from fossil fuels and to detoxify V type agents and musters gas. Ruthenium catalysts such as $\text{Ru}_2(\text{OAc})_4\text{Cl}$ (**A**) and $\text{Ru}_2(\text{esp})_2\text{Cl}$ (**B**) have been successfully used to promote sulfide oxygenation by tert-butyl hydroperoxide (TBHP) in either an acetonitrile solution or neat (solvent-free) conditions. Recently, two novel diruthenium (II, III) tetraamidate compounds, $\text{Ru}_2(\text{NHOC}(\text{CH}_3)_2)_4\text{Cl}$ (**C**) and $\text{Ru}_2(\text{NHOCCH}_2\text{CH}_3)_4\text{Cl}$ (**D**) have been prepared and structurally characterized by X-ray crystallography. Molecular orbital diagram for complex **C** was obtained from DFT calculations. The activities in promoting sulfide oxygenation using simple oxidants like hydrogen peroxide and tert-butyl hydroperoxide were studied and sample analysis was performed using gas chromatography. Using excess oxidant and CH_3CN as the solvent, organic sulfides such as methyl phenyl sulfide (MPS) and diphenyl sulfide (PPS) were oxidized using 1 mol % of the catalytic species. Catalyst **C** was more effective than **D** in converting sulfides to sulfoxide under the same studied conditions. The enhanced reaction rate was achieved under solvent free conditions with the major oxidation product being the sulfoxide.