



2014 - 2015 Solvay Chair in Chemistry **Professor Richard Royce Schrock (MIT, USA)**

Lecture on Thursday 30 April 2015

4:00 p.m. (Forum OF2070)

Recent Advances in Olefin Metathesis by Molybdenum and Tungsten Catalysts

One of the most important developments in the last five years in olefin metathesis chemistry employing Mo or W catalysts has been the synthesis and application of $M(NR)(CHCMe_2R')(OR)(\text{Pyrrolide})$ (MonoAlkoxidePyrrolide or MAP) complexes, especially those in which OR is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT). MAP species under the right circumstances have proven to be Z-selective in a variety of olefin metathesis reactions, among them enantioselective ring-opening/cross-metatheses, ROMP to give highly stereoregular polymers, ethenolysis of internal olefins such as oleates, coupling of terminal olefins, cross coupling of terminal olefins, and synthesis of macrocyclic natural products. An important second recent development has been the synthesis of a variety of tungsten oxo alkylidene complexes. Oxo complexes can be "activated" by binding $B(C_6F_5)_3$ to the oxo ligand and are likely to be analogs of metathesis catalysts found in classical metathesis catalyst systems. Recent applications of metathesis includes stereoregular ring-opening metathesis polymerization to give *cis, isotactic* or *cis, syndiotactic* polymers as well as alternating AB copolymers. These and other subjects will be explored as time allows.

Lecture on Tuesday 5 May 2015

4:00 p.m. (Solvay Room)

Reduction of Dinitrogen Catalytically to Ammonia with Protons and Electrons

In 2003 we reported the first catalytic reduction of dinitrogen with protons and electrons. The process employs a molybdenum complex that contains a hexaisopropylterphenyl-substituted triamidoamine ligand ([HIPTN₃N]Mo, Figure 1). Dinitrogen is bound end-on in the trigonal coordination pocket and is reduced through a stepwise addition of protons ([2,6-lutidinium]BAr'₄ (Ar' = 3,5-(CF₃)₂C₆H₃)) and electrons (decamethylchromocene). Dinitrogen is reduced in heptane to yield 7-8 equivalents of NH₃ with the remaining electrons being used to make dihydrogen. Eight of the proposed intermediates in the Chatt-like reduction sequence have been isolated and characterized crystallographically and extensive calculations of the mechanism of reduction in the [HIPTN₃N]Mo system support the proposed mechanism. A second example of the catalytic reduction of dinitrogen employs a Mo(0) complex, [Mo(L)(N₂)₂]₂(m-N₂)₂ (where L is a "PNP pincer" ligand). Protons are added in the form of 2,6-lutidinium triflate, and electrons are added employing cobaltocene. No mechanistic details for this system have been elucidated. Both systems employ Mo catalysts, an acid that is readily reduced, and an organometallic reducing agent. Both are limited by loss of ligand from the metal. Both produce hydrogen as a byproduct (~1 equivalent or more). Recent synthesis of a TREN ligand that could lead to a more robust catalyst and higher turnovers will be described.

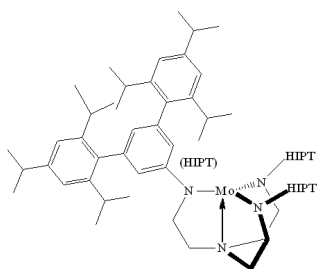


Figure 1. The Mo(III) core of [HIPTN₃N]Mo complexes.