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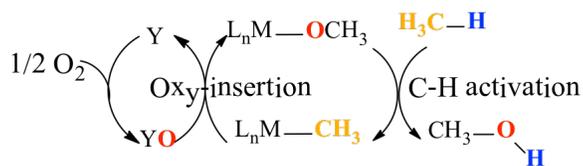
DEPARTMENT OF PHYSICS
Texas Southern University

August 9th, 2013, 3:00 p.m.
Science Building – Room 113

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Platinum Mediated C-H and C-O Bond Formation

The design of catalysts for the partial oxidation of alkanes could provide efficient pathways for the production of valuable chemicals and fuels. In particular, the conversion of methane (the primary component of natural gas, ~ 78% by volume) into a more functionalized product such as methanol would have many benefits for our economy. Catalysts for hydrocarbon oxidation must perform three key steps: carbon-hydrogen bond scission, transfer and insertion of oxygen into the metal-hydrocarbyl (M-C) bond, and, also utilize dioxygen (O₂) as oxidant, directly or indirectly. The goal of the CCHF is to combine these three fundamental steps into a single catalytic cycle via carbon-hydrogen activation across a metal alkoxide bond [M-OR + R'-H → M(ROH)(R')], followed by dissociation of ROH (alcohol) and oxygen atom insertion into the newly formed metal-carbon (M-R') bond, **Scheme 1**. However, while C-H bond activation has been well studied, oxy-insertion is less studied, which is thus the main focus of our potential energy surface (PES) studies. This portion of the seminar provides initial results for oxidant (YO), ligand (L_n) and metal (M) effects upon the PES of the aforementioned catalytic cycle, with special emphasis on making appropriate predictions for experimental collaborators.



L_n = Supporting Ligand, YO = Oxidant

Scheme 1

Functionalization of unactivated α -olefins and arenes into alkyl arenes represents an important industrial process that suffers from drawbacks that generate significant environmental waste via traditional Friedel-Crafts chemistry. Our research seeks to avoid the use of strong acids, and focuses on homogenous catalysis by late transition metals for the production of alkyl arenes by pathways that involve oxidative hydrogen migration (OHM) or oxidative addition/reductive elimination (OA/RE). The energetics of propylene binding – C₃H₆ + [xbpyPtII(Ph)]⁺ → [xbpyPtII(Ph)(η^2 -C₃H₆)]⁺ are studied at the B3LYP/CEP-31G(d) level of theory to assess the factors that yield the preferred propylene adduct. For simplicity, x represents tBu, NO₂, and CH₃ group for the 4,4'-substituents and 6,6'-substituents on the bpy complex, respectively. This portion of the presentation will discuss initial results for the preferred binding mode of η^2 -olefin to a cationic xbpypPtII-Ph complex, and its implications for linear versus branched selectivity.

Refreshments will be served