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"Synthesis of the Low-Coordinate Bis(Alkoxide) Metal Complexes and Their Reactivity in N-N and C-N bond Formation Reactions"

We are designing low-coordinate metal complexes in bis(alkoxide) ligand environments for the activation of small molecules. Our current research focuses on bond activation and bond formation reactions involving azide precursors, with the goal to develop new catalysts for N-N and C-N bonds formation. We have recently reported synthesis of quasi-two-coordinate complexes $M(OR)_2(THF)_2$ ($OR = OC(tBu)_2Ph$, $M = Mn, Fe, Co$) that proceeds via unusual cluster intermediates featuring seesaw transition metal centers. Iron(II) complex $Fe(OR)_2(THF)_2$ undergoes facile reaction with aliphatic and aromatic azides. The reaction of the iron(II) precursor with aliphatic azides results in the reductive coupling of azides to form the iron(III) hexazene complex $(RO)_2Fe(\mu-\kappa^2:\kappa^2-RN_6R)Fe(OR)_2$. DFT studies propose formation of the Fe-azide dimer on the route to hexazene in which each azide is monoreduced, and the iron centers are oxidized to the 3+ oxidation state. The reaction of the iron(II) precursor with aromatic azides ArN_3 leads to the formation of azoarenes $ArNNAr$, with concomitant liberation of dinitrogen. The reaction is catalytic in coordinating solvents (THF), and is postulated to involve metal-nitrene intermediate. Mechanistic, spectroscopic, structural, and theoretical studies will be reported. We will also describe our most recent results on the coupling of nitrenes with isocyanides.

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4:00 pm

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