Divalent Transition Metal Centers: The Synthesis of New Chemical Vapor Deposition Precursors and Studies of Ethylene Polymerization and Oligomerization Catalysts

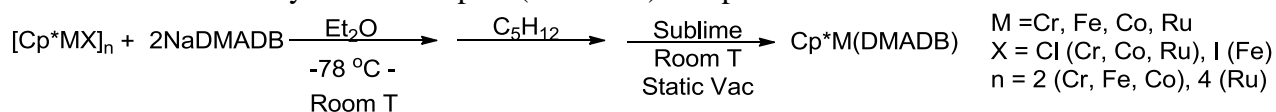Jennifer L. Steele   Final Seminar   October 18, 2013

Volatile transition metal complexes that contain boron hydride ligands are desirable for their potential as precursors for metal diboride films for microelectronics applications.[1] Recently our group has discovered a new class of potential precursors in the metal complexes of the chelating borohydride, *N,N*-dimethylaminodiboranate (DMADB).[2-3] To date, attempts to synthesize homoleptic complexes of the late transition metals have afforded intractable mixtures, likely the result of overreduction of the metal center.[3] This work has focused on the synthesis and characterization of heteroleptic complexes of the late transition metals that contain both DMADB and pentamethylcyclopentadienyl ligands.

Figure 1: Molecular structure of Cp*Cr(DMADB)

As shown in Scheme 1, the reaction of metal complexes of the form $[Cp*MX]_n$, where Cp* is 1,2,3,4,5,-pentamethylcyclopentadienyl, M = Cr, Fe, Co, or Ru, and X = Cl, or I with sodium dimethylaminodiboronate (NaDMADB) in diethyl ether affords the divalent complex [Cp*M(DMADB)]. Additionally, the analogous vanadium compound [Cp*V(DMADB)] can be synthesized from the reduction of $[Cp*VCl_2]_3$ with NaDMADB in diethyl ether. All of these compounds are volatile under static vacuum at room temperature, but are also thermally sensitive; the iron and ruthenium derivatives decompose at room temperature over a day.

Scheme 1: General synthesis of Cp*M(DMADB) complexes

$$[Cp*MX]_n + 2NaDMADB \xrightarrow[\text{-78 °C - Room T}]{Et_2O} \xrightarrow{C_5H_{12}} \xrightarrow[\substack{\text{Room T} \\ \text{Static Vac}}]{\text{Sublime}} Cp*M(DMADB)$$

M = Cr, Fe, Co, Ru
X = Cl (Cr, Co, Ru), I (Fe)
n = 2 (Cr, Fe, Co), 4 (Ru)

These complexes exhibit a fascinating variety of binding modes of the DMADB ligand driven by the electronic structure of the metal center. The green compound [Cp*V(DMADB)] exhibits a κ^2, κ^2 binding mode of the DMADB ligand; this is the binding mode normally seen for homoleptic early transition metal DMADB compounds. In the blue compound [Cp*Cr(DMADB)], which is shown in Figure 1, the DMADB ligand is bound in a κ^1, κ^1 fashion. This binding mode of the DMADB ligand can be rationalized on the basis of the number of orbitals available on the high-spin chromium(II) center. The iron and ruthenium complexes are isostructural with one another with the DMADB bound in an asymetric κ^1, κ^2 fashion, giving a pseudo-octahedral structure. Both of these complexes are diamagnetic and are low spin d^6. The red compound [Cp*Co(DMADB)] is also isostructural with the iron and ruthenium compounds.

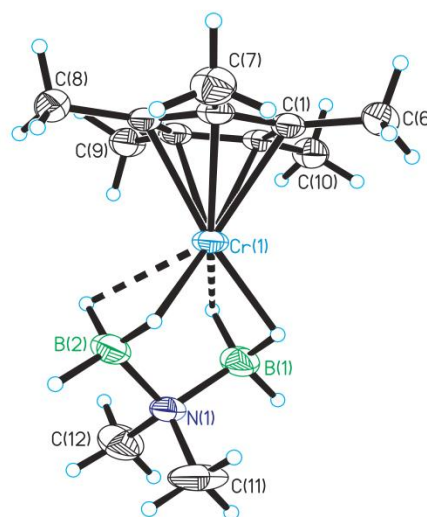This work also will explore the reaction of a series of titanium(II) species with ethylene in the presence of an aluminum alkyl catalyst. Since the discovery of the Ziegler-Natta catalysts in the mid-twentieth century, titanium compounds have been of interest as ethylene polymerization catalysts and more recently as selective oligomerization catalysts.[4] Previously, our group has shown that the titanium(II) complexes, $TiX_2(dmpe)_2$, where X = Cl, BH_4, or Me and dmpe = 1,2-bis(dimethylphosphino)ethane, dimerize ethylene to form 1-butene in NMR scale reactions at low pressures. Similarly, the cyclopentadienyl titanium(II) complexes, $CpTiX(dmpe)_2$, where X = Me, H, or Cl, are catalysts for the dimerization and trimerization of ethylene (the latter generating only branched products).[5] This work examines these systems at higher ethylene pressures and when activated with an aluminum alkyl co-catalyst.
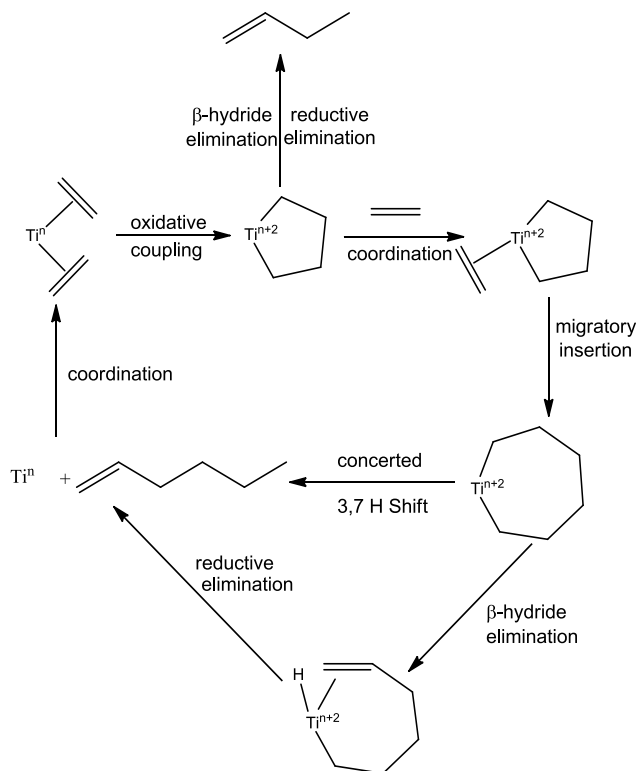

Figure 2: Metallacycle mechanism proposed
for selective oligomerzation

These titanium(II) compounds are active as as polymerization catalysts and generate only small amounts of oligomeric side products. The compounds $TiX_2(dmpe)_2$ and $CpTiX(dmpe)_2$, when activated with MAO (methylaluminoxane), produce large amounts of a high molecular weight polyethylene, with the largest turnover number being 24,000 for $TiMe_2(dmpe)_2$. Reactions performed in the presence of $AlEt_3$ produced smaller quantities of polyethylene, and in some cases also produced small amounts of oligomers (Figure 2). There is some evidence for the oxidation of the titanium(II) species to a higher valent species that acts as the active catalyst, and the new compound $[TiCl_2(dmpe)_2][B(C_6H_3(CF_3)_2)_4]$ produced similar catalytic results as the titanium(II) analog with MAO and $AlEt_3$.

Finally, this work also explores the reactivity of transition metal DMADB species, focusing on the homoleptic titanium(II) and chromium(II) species, $Ti(DMADB)_2$ and $Cr(DMADB)_2$,[3] as

well as, the heteroleptic Cp*Cr(DMADB) species discussed above. The reactivity of these complexes with ethylene when activated with an aluminum alkyl co-catalyst will be of primary focus of this section.   The N,N-dimethylaminodiboranate compounds Ti(DMADB)$_2$, Cr(DMADB)$_2$, and Cp*Cr(DMADB) are active ethylene polymerization catalysts in the presence of an aluminum co-catalyst.   These complexes also produce variable amounts of ethylene oligomers.   Cp*Cr(DMADB) produces the largest amount of polyethylene, giving 35,000 turnovers when activated with AlEt$_3$.   Melting point data suggests that the product is a high density polyethylene.   The reaction of ethylene with Ti(DMADB)$_2$ in the presence of AlEt$_3$ produces 107 moles of 1-butene per mole of catalyst.

References:

1. (a) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643-1644. (b) Sung, J. W.; Goedde, D. M.; Girolami, G. S.; Abelson, J. R. *J. Appl. Phys.* **2002**, *91*, 3904-3911. (c) Jayaraman, S.; Yang, Y.; Kim, D. Y.; Girolami, G. S.; Abelson, J. R. *J. Vac. Sci. Technol., A* **2005**, *23*, 1619-1625. (d) Jayaraman, S.; Gerbi, J. E.; Yang, Y.; Kim, D. Y.; Chatterjee, A.; Bellon, P.; Girolami, G. S.; Chevalier, J.-P.; Abelson, J. R. *Surf. Coat.Technol.* **2006**, *200*, 6629-6633. (e) Yang, Y.; Jayaraman, S.; Kim, D. Y.; Girolami, G. S.; Abelson, J. R. *Chem. Mater.* **2006**, *18*, 5088-5096. (f) Kumar, N.; Yang, Y.; Noh, W.; Girolami, G. S.; Abelson, J. R. *Chem. Mater.* **2007,** *19,* 3802-3807

2. (a) Kim, D. Y.; Girolami, G. S. *Inorg. Chem.* **2010**, *49*, 4942-4948. (b) Daly, S. R.; Kim, D. Y.; Yang, Y.; Abelson, J. R.; Girolami, G. S. *J. Am. Chem. Soc.* **2010**, *132*, 2106-2107.

3. Kim, D. Y. Ph. D. Thesis. University of Illinois, Urbana-Champaign, 2007.

4. (a) Boor, J. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (b) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641. (c) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 1. (d) Al-Sa'doun, A. W. *Appl. Catal. A* **1993**, *105*, 1. (e) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321.

5. (a) Spencer, M. D. University of Illinois, Urbana-Champaign, 1993. (b) You, Y.; Girolami, G. S., *Organometallics* **2008,** *27*, 3172-3180.