Synthesis and Chemistry of Cationic d^0 Metal Alkyl Complexes

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Summary of Results for 1990. The long term goals of this project are to design and synthesize highly unsaturated, electrophilic metal complexes and to explore their use as catalysts, reagents, and/or model systems for olefin polymerization and C-H activation chemistry. During the 1990 budget year we have focused our attention on (i) the ligand C-H activation chemistry of $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})^+$ and related cationic, d^0 Zr alkyl complexes, and (ii) the synthesis of new classes of group 4 metal alkyl complexes with non- Cp_2M ligand environments.

We have discovered that the cationic methyl complex $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})^+$ reacts with a wide range of pyridine substrates to form thermally sensitive $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{py})^+$ adducts. These in turn undergo C-H activation/ CH_4 elimination to yield $\text{Cp}_2\text{Zr}(\text{pyridyl})^+$ complexes which contain three-membered Zr-C-N rings. The regioselectivity and mechanistic aspects of these reactions have been studied in detail. The cationic pyridyl complexes undergo insertion reactions with olefins, acetylenes, nitriles, and carbonyl compounds to yield expanded metallacycles. The functionalized pyridyl ligands can be removed from Zr by β -H elimination or Zr-C bond hydrogenolysis reactions. This combination of ligand C-H activation and insertion constitutes a general approach to productive C-H activation chemistry. We continue to explore stoichiometric and catalytic applications of this chemistry.

Two classes of electrophilic $\text{Cp}_2\text{M}(\text{R})^{n+}$ complexes are known: cationic group 4 and actinide systems of general form $\text{Cp}_2\text{M}(\text{R})^+$ or $\text{Cp}_2\text{M}(\text{R})(\text{L})^+$, and neutral group 3 and lanthanide systems $\text{Cp}^*\text{M}(\text{R})$. We have explored a novel approach to achieving new metal/charge combinations in these systems which involves replacement of a uninegative Cp^- ligand by the isolobal, dinegative dicarbollide ligand ($\text{C}_2\text{B}_9\text{H}_{11}^{2-}$). This formal substitution reduces the metal charge by one unit but does not change the gross features of the metal frontier orbitals. We have prepared the neutral pseudo bent-metallocene alkyls (dicarbollide)(Cp^*) $\text{M}(\text{CH}_3)$ ($\text{M} = \text{Zr}, \text{Hf}$) by reaction of $\text{Cp}^*\text{M}(\text{CH}_3)_3$ with $\text{C}_2\text{B}_9\text{H}_{13}$, the parent acid of the dicarbollide ion. These new complexes exhibit an extensive insertion and σ -bond metathesis chemistry and are active olefin polymerization catalysts. Thermolysis of (dicarbollide)(Cp^*) $\text{M}(\text{CH}_3)$ yields the methylene bridged dimers [(dicarbollide)(Cp^*) M] $2(\mu\text{-CH}_2)$ via M- CH_3 C-H activation. The observation that these species do not insert ethylene or 2-butyne suggests that this type of C-H activation/condensation may be an important catalyst deactivation process in some Ziegler-Natta systems. We have completed several X-ray structures of these systems which establish the η^5 bonding mode of the dicarbollide ligand and the bent-metallocene-like geometry at M.

Most model studies of Ziegler-Natta polymerization chemistry, and indeed most chemistry involving electrophilic early metal alkyl systems, has utilized compounds incorporating the Cp_2M ligand system. We are exploring the development of new classes of early metal alkyls which incorporate other ligand systems and allow greater variation of metal steric and electronic properties. We have prepared the first cationic mono- Cp group 4 complexes, $\text{Cp}^*\text{Zr}(\text{R})_2(\text{L})_n^+$, as the BPh_4^- salts. Structural and reactivity studies show that these compounds contain sterically uncrowded, highly electrophilic metal centers and exhibit a rich insertion chemistry.

Objectives for 1991. During the 1991 budget year we will concentrate our efforts on the development of new non- Cp_2M early metal systems. We will focus our studies of (dicarbollide)(Cp^*) $\text{M}(\text{R})$ complexes on experiments which allow comparisons with neutral and cationic $\text{Cp}_2\text{M}(\text{R})^{n+}$ systems to assess the influence of charge on reactivity. We will also study the mechanisms of olefin insertion reactions of these compounds and explore the development of productive C-H activation reactions. Our

studies of mono-Cp complexes $\text{Cp}^*\text{Zr(R)}_2(\text{L})_n^+$ have been hampered by the extreme sensitivity of these systems and by facile decomposition processes involving the BPh_4^- counterion. We will explore the utility of new non- and weakly-coordinating counterions in this system. We have prepared $[\text{Cp}^*\text{Zr}(\text{CH}_3)_2][\text{CB}_{11}\text{H}_{12}]$ which is soluble and stable in hydrocarbon solvents and is highly reactive with olefins. The $\text{CB}_{11}\text{H}_{12}^-$ anion coordinates via a weak B-H-Zr bridge and apparently is easily displaced. The use of $\text{CB}_{11}\text{H}_{12}^-$ should allow full exploration of the chemistry of $\text{Cp}^*\text{M(R)}_2^+$ and $\text{Cp}^*\text{Zr(R)}_2(\text{L})_n^+$ and comparison to related $\text{Cp}_2\text{Zr(R)(L)}^+$ complexes. Our major new initiative will be to develop the chemistry of new early metal alkyl complexes incorporating macrocyclic ligands, especially non-porphyrin, dinegative N_4 macrocycles such as Me_4 -tetraaza[14]annulene (TMTAA). This area of chemistry is virtually unexplored. Macrocyclic ligands are attractive because they are easily prepared and modified, are bulky and chelating so that oligomerization and ligand exchange problems are minimized, and contain hard N donor functions. Our initial efforts will be focused on cationic complexes of general type $(\text{TMTAA})\text{Zr(R)(L)}^+$.

Publications in 1990

- (1) "Synthesis and Structural Characterization of $(\text{C}_5\text{Me}_5)\text{Zr(R)}_2(\text{L})_n^+$ Complexes." D. J. Crowther, R. F. Jordan, and N. C. Baenziger, *Organometallics* **1990**, *9*, 2574-2580.
- (2) "Electronic Control of Regioselectivity in Coupling Reactions of SiMe_3 -Substituted Alkenes with $\text{Cp}_2\text{Zr}(\eta^2(\text{N,C})\text{-6-phenylpyridyl})(\text{THF})^+$." A. S. Guram and R. F. Jordan, *Organometallics* **1990**, *9*, 2190-2192.
- (3) "Scope and Regiochemistry of Ligand C-H Activation Reactions of $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})^+$." R. F. Jordan and A. S. Guram, *Organometallics* **1990**, *9*, 2116-2123.
- (4) "Synthesis and Insertion Chemistry of Cationic Zr(IV) Pyridyl Complexes. Productive Sigma-Bond Metathesis." R. F. Jordan, D. F. Taylor, and N. C. Baenziger, *Organometallics* **1990**, *9*, 1546-1557.
- (5) "Cationic Zirconium Catalysts for C-C Bond Forming Chemistry." R. F. Jordan, P. K. Bradley, R. E. LaPointe, and D. F. Taylor. Invited review, *New. J. Chem.*, **1990**, *14*, 505-511.
- (6) "Synthesis and Chemistry of $\text{Cp}_2\text{Zr(Ph)}(\text{THF})^+$. Selectivity of Protolytic and Oxidative Zr-R Bond Cleavage Reactions." S. L. Borkowsky, R. F. Jordan, and G. D. Hinch, *Organometallics*, submitted.
- (7) " CH_3CN Insertion Reactions of $(\text{C}_5\text{H}_4\text{R})_2\text{Zr(R)(L)}^+$ Complexes." Y. Wang, R. F. Jordan, S. F. Echols, S. L. Borkowsky, and P. K. Bradley, *Organometallics*, submitted.
- (8) "Insertion Chemistry of $\text{Cp}_2\text{Zr}(\eta^2(\text{C,N})\text{-CH}_2(6\text{-Me-pyrid-2-yl}))^+$. Zirconium Mediated Functionalization of Methyl C-H Bonds of 2,6-Lutidine." A. S. Guram, R. F. Jordan, D. F. Taylor, *J. Am. Chem. Soc.*, submitted.

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