Electrophilic Metal Alkyl Chemistry in New Ligand Environments.

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1992 Annual Report and 1993 Research Plan

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Introduction and Objectives. This report covers research performed during the period 1/1/92 - 9/15/92. The principal objective of this project is to develop new types of electrophilic metal alkyl complexes for fundamental studies in olefin polymerization and C-H activation catalysis. Most of our work during the current year has focused on the synthesis and chemistry of d^0 , group 4 metal alkyls of general type $(N_4)M(R)^+$ (1) and $(N_4)M(R)(L)^+$ (L = labile ligand, 2) which incorporate dianionic, 12-electron donor, tetradentate, N_4 macrocyclic ligands (abbreviated N_4^{2-}). We are interested to know how the chemistry of such complexes compares with that which we developed earlier for $Cp_2M(R)^+$ complexes (3), in order to understand ligand effects on reactivity and to develop new reaction chemistry.

1

2

3

Results. We have prepared a series of N_4^{2-} ligands via modified literature methods. The (Megg-dibenzo-taa) $^{2-}$ ligand (4) is similar to ligands used in the past, but is more highly methylated for increased solubility and NMR spectra simplification. The $(R_4-(CH_2CH_2)_2-taa)^{2-}$ ligands (5) are prototypes for chiral ligands (6) which we intend to develop later.

4, $R_1 = R_2 = Me$ 5, $R = Me, Et$

6

Two general routes to $N_4M(R)_2$ complexes have been developed. These are (i) generation of $(N_4)MX_2$ followed by alkylation (eq 1), and (ii) direct synthesis via RH elimination from MR_4 and $(N_4)H_2$ (eq 2).

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The X-ray structure of a representative (N₄)MR₂ complex, (Me₄-(CH₂CH₂)₂-taa)Zr(CH₂Ph)₂, confirms the cis, saddle-type structure, which is imposed by the fact that Zr⁴⁺ is too large to fit in the N₄ plane.

In initial work we have discovered that cationic complexes of types 1 and 2 can be generated in several ways. The reaction of (Meg-dibenzo-taa)ZrMe₂ with the strong Lewis acid B(C₆F₅)₃ results in formation of an adduct which catalyzes ethylene polymerization. It is believed that the active species is the ion-pair (Meg-dibenzo-taa)ZrMe⁺ MeB(C₆F₅)₃⁻ formed by full Me⁻ abstraction. This is an important result as it supports our major working hypothesis that cationic complexes of type will be highly electrophilic like the Cp₂M(R)⁺ analogues. Several base-stabilized cations (N₄)M(R)(L)⁺ BPh₄⁻ have been prepared by oxidation or protolysis of (N₄)MR₂ complexes and characterized. These first

generation, base-stabilized complexes are not very reactive however, most likely because the ligands are not very labile, and we have therefore turned our attention to the preparation of base-free systems. One such cation, $(R_4-(CH_2CH_2)_2-taa)Zr(CH_2SiMe_3)^+$ (dicarbollide) $_2Co^{2-}$ has been prepared and is under study presently.

Summary. We have worked out methods for the efficient synthesis of various N_4^{2-} macrocyclic ligands, neutral group 4 metal $(N_4)MR_2$ complexes, and cationic mono-alkyl $(N_4)M(R)^+$ species. Initial indications are that the latter will be highly reactive in base-free form.

Publications, 1992

(42) "Reaction of Cationic Zr Alkyl Complexes with CH_3CN , II. Competition Between Insertion and β -H Elimination." Y. W. Alelyunas, Z. Guo, R. E. LaPointe, and R. F. Jordan, *Organometallics* submitted.

(39) "Chemistry of New Electrophilic Metal Alkyl Compounds", R. F. Jordan, *Makromol. Chem., Macromol. Symp.* 1992, IN PRESS.

(36) "Structural Characterization of $Cp^*Hf(CH_2Ph)_3$. Evidence for an α -Agostic Interaction." Z. Guo, D. J. Crowther, N. C. Baenziger, R. F. Jordan, *Organometallics*, submitted.

(34) "THF Ring-Opening and H/D Exchange Reactions of $(C_5H_4Me)_2Zr(H)(THF)^+$. Evidence for Hydrogenolysis of Zr-Cp Bonds." Z. Guo, P. K. Bradley, and R. F. Jordan, *Organometallics*, 1992, 11, 2690.

Research Plan for 1993

In the upcoming year we will focus our attention on developing the chemistry of base-free, group 4 metal $(N_4)MR^+$ complexes. We will also investigate the synthesis and chemistry of neutral group 3 and lanthanide metal analogues. In parallel work we will investigate related $(N_4)M=CR_2$ and $(N_4)M=O$ alkylidene and oxo systems. When metal/ligand combinations which promote high reactivity are discovered, we will turn our attention to chiral systems, probably derived from 6 above, for asymmetric catalysis. Additionally we will begin studies of mono-Cp cations, $CpMR_2^+$ which we expect to be highly electrophilic due to the 10-electron configuration.

Statement of Expected Expenditures

It is anticipated that all remaining funds for the current budget year will be expended before 12/31/92.

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