Electrophilic Metal Alkyl Chemistry in New Ligand Environments

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I. Results From Previous Project Period (1/1/95 - 8/31/98)

A. Introduction and Objectives. Cationic group 4 and actinide Cp₂MR⁺ metalloccenes (1, Chart 1), and isolobal neutral group 3 and lanthanide Cp₂MR analogues, are exceptionally reactive in insertion and σ-bond metathesis processes, and have been exploited extensively in catalysis and synthesis, most notably single-site olefin polymerization.¹ The objectives of this project during the 1995-98 period were to design new electrophilic metal alkyls based on non-Cp₂M structures, and to exploit these systems in fundamental and applied studies related to olefin polymerization and other catalytic reactions. We have made significant progress in three areas: (i) We investigated new cationic group 4 metal alkyls based on N₄-macrocycle (2, Chart 1), tetradoentate Schiff base (3), bidentate pyridine-alkoxide (4), and bidentate bis-amide ligands (5). Cations 2-5 exhibit tunable electrophilic reactivity, including alkyne insertion, catalytic olefin polymerization, pyridine C-H activation, chlorocarbon activation and other reactions. (ii) We investigated the olefin polymerization reactivity of non-metalloocene complexes containing bis-amide, pyridine-alkoxide, dicarbollide, or tris(pyrazolyl)borate (Tp⁻) ligands (5-9), using AlR₃ and/or methylalumoxane (MAO) activation approaches. MAO activation of Ti and V complexes 8 and 9 incorporating aryl-substituted Tp⁻ ligands produces single-site catalysts with activities approaching those of metallocene catalysts. (iii) In a major new thrust, we synthesized novel cationic aluminum alkyls 10-12 which contain bulky amidinate (or related) ancillary ligands. These main-group cations are single-site ethylene polymerization catalysts and are significantly (10³) more reactive with this substrate than are neutral AlR₃ compounds. This work opens the door to the development of transition-metal-free catalysts. The results of (i) - (iii) are discussed in Section I-C.

B. Key Working Hypothesis. The insertion and σ-bond metathesis reactivity of d⁰ Cp₂M(R)ⁿ⁺ species results from the combination of (i) the inherent reactivity of the polar M-R bond, (ii) the Lewis acidity and poor backbonding properties of the unsaturated d⁰ metal center, and (iii) the bent-metallocene structure which forces substrates to coordinate cis to the M-R bond. Additionally, (iv) the steric, electronic and chirality properties of Cp₂M(R)ⁿ⁺ species can be tuned by modification of the Cp⁻ ligands, which facilitates fundamental studies and greatly expands the scope of catalytic applications (e.g. stereoselective α-olefin polymerization).² The key working hypothesis of this project is that new electrophilic metal alkyls can be constructed by choosing ligand/metal combinations which allow incorporation of these key structural and electronic features into LnMR⁺ species. We have utilized chelating ancillary ligands in 2-12 to minimize ligand redistribution reactions, and to avoid ligand dissociation complications when weak donor ligands are used to enhance the metal electrophilicity. Additionally, the ancillary ligands in 2-12 can be modified easily by variation of the substituents.

In this proposal the counterion is B(C₅F₅)₄⁻ unless specified otherwise. Space limitations preclude discussion of experimental details, but it should be noted that [LnMR][B(C₅F₅)₄] salts normally separate
from aromatic solvents as liquid clathrate phases which can be directly characterized by NMR, and are normally soluble but may decompose in chlorinated solvents. In some cases these salts may be crystallized and characterized by X-ray diffraction.

C. Key Results

(i) Discrete Non-metallocene Cationic Group 4 Alkyls

(a) (N₄-macrocycle)MR⁺ Complexes. In our initial approach to non-metallocene cationic alkyls, we investigated (N₄-macrocycle)MR⁺ species (2) which incorporate the tetraaza-macrocycles Megtaa²⁻ (13) or Me₄taen²⁻ (14). The binding pockets of these macrocycles are too small to accommodate Zr⁴⁺ and Hf⁴⁺ ions and therefore (N₄-macrocycle)MX₂ compounds adopt "out-of-plane" cis structures 15. On this basis we anticipated that d⁰ cations 2 would coordinate substrates cis to the M-R group (e.g. 16), and would be highly reactive. Key results are as follows: (i) (Megtaa)MX₂ compounds adopt trigonal prismatic (tp) structures with a "saddle" Megtaa²⁻ conformation (15). The structures of (Me₄taen)MX₂ complexes are more variable due to the greater flexibility of Me₄taen²⁻ vs Megtaa²⁻, and are determined by the electronic properties of the X ligands. Sigma-donor ligands favor tp structures (17) and
σ,π-donors favor octahedral \((O_6)\) structures (18). Seven-coordinate \((\text{Me}_4\text{taen})\text{ZrCl}_2(\text{NHMe}_2)\) (19) adopts a face-capped \(tp\) structure with a triangular placement of chloride and amine ligands; this differs from the planar \(L_3\) arrangement in \(\text{Cp}_2\text{ML}_3\).

(ii) \((\text{N}_4\text{-macrocycle})\text{MR}^+\) species coordinate Lewis bases (16) and exhibit agostic/distorted hydrocarbyl structures; e.g. \((\text{Me}_4\text{taen})\text{Zr}(\text{CH}_2\text{SiMe}_3)(\text{THF})^+\) has an \(\alpha\)-agostic structure at low temperature. Dinuclear \{(\text{Me}_8\text{taa})\text{M}_2(\mu-X)^{2+}\} dications form when \(X\) is a good bridging ligand (\(X = \text{OR}, \text{CCR}\); e.g. 20). (iii) Reactivity studies show that the M-R bonds of \((\text{Me}_8\text{taa})\text{MR}_2\) compounds are more polar/ionic than the M-R bonds of \(\text{Cp}_2\text{MR}_2\) species. (iv) Trends in ligand lability and the strengths of agostic and \(\eta^2\)-benzyl interactions in \((\text{Me}_8\text{taa})\text{MR}(\text{L})_n^+\) (\(n = 0, 1\)) suggest that \((\text{Me}_8\text{taa})\text{MR}^+\) cations are harder and weaker Lewis acids than \(\text{Cp}_2\text{MR}^+\). In particular, while \(\text{Cp}_2\text{Zr}(\text{OCMe}_2\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2)^+\) coordinates the pendant olefin, \((\text{Me}_8\text{taa})\text{Zr}(\text{OCMe}_2\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2)^+\) does not, indicating that \(\text{Cp}_2\text{Zr}(\text{OR})^+\) is a stronger Lewis acid for unsaturated hydrocarbons than is \((\text{Me}_8\text{taa})\text{Zr}(\text{OR})^+\). (v) \((\text{Me}_8\text{taa})\text{MR}^+\) cations insert alkynes and undergo C-H activation reactions (e.g. eq 1,2). (vi) \[^{(\text{Me}_8\text{taa})\text{Zr}(\text{CH}_2\text{Ph})[\text{B}(\text{C}_6\text{F}_3)_4]}\] polymerizes ethylene \((M_w = 100,000, M_w/M_n = 2.6; 50 \degree\text{C}, 1.3 \text{atm}, \text{toluene})\), but with low activity \((300 \text{g}/(\text{mol}^*\text{h}^*\text{atm}); \text{eq 3})\). (vii) In general \((\text{N}_4\text{-macrocycle})\text{MR}^+\) cations are less reactive for insertion of unsaturated hydrocarbons than are \(\text{Cp}_2\text{MR}^+\) cations. This difference largely reflects the difference in Lewis acid properties of the metal centers.
(b) \((\text{N}_2\text{O}_2\text{-chelate})\text{MR}^+\) Complexes.\(^5\) One approach to increasing the electrophilicity of \((\text{N}_4\text{-macrocycle})\text{MR}^+\) species is to replace the N-donors with more electronegative O-donors. With this goal in mind, we investigated \(d^0\) \((\text{N}_2\text{O}_2\text{-chelate})\text{MX}_2\) and \((\text{N}_2\text{O}_2\text{-chelate})\text{MR}^+\) complexes. Key results are as follows: (i) \((\text{R}_6\text{-acen})\text{Zr(CH}_2\text{CMc}_3\text{)}_2\) species (25, \(R = H, F\)) were prepared by alkane elimination and protonolyzed to \((\text{R}_6\text{-acen})\text{Zr}(\text{NR}_2\text{Ph})_\text{R}\) (26) or base-free \((\text{R}_6\text{-acen})\text{ZrR}^+\) (27) by \([\text{HNR}_2\text{Ph}][\text{B(C}_6\text{F}_5\text{)}_4]\) or \([\text{HNMePh}_2][\text{B(C}_6\text{F}_5\text{)}_4]\) respectively (eq 4.5). The strong amine coordination in 26 implies that \((\text{X}_6\text{-acen})\text{Zr}(\text{R})^+\) species are effectively more electrophilic than \((\text{N}_4\text{-macrocycle})\text{ZrR}^+\) cations, which do not coordinate NMe\(_2\)Ph, and comparable to sterically open \(\text{Cp}_2\text{ZrR}^+\) cations which do coordinate this amine.
(ii) (F₆-acen)Zr(CH₂CMe₃)₂ adopts an elongated μₚ structure (25) in which the R-Zr-R angle (129°) is larger than in (N₄-macrocycle)ZrR₂ (ca. 85°) or Cp₂ZrR₂ (ca. 95°). The (F₆-acen)Zr(CH₂CMe₃)(NMe₂Ph)⁺ cation 26 exhibits a wide R-Zr-amine angle (144.7°). (iii) The reaction of (F₆-acen)Zr(CH₂CMe₃)(NMe₂Ph)⁺ with CH₂Cl₂ proceeds by nucleophilic attack of NMe₂Ph on the CH₂Cl₂ ligand of the transient solvent adduct 28 (cq 6), ultimately yielding dinuclear μ-Cl cation 29. Direct chloride abstraction is not observed, and in fact base-free cation 27 (which likely exists as 28 in CH₂Cl₂) is very stable in CH₂Cl₂ in the absence of nucleophilic species. We have since found that most of the LnMR⁺ species discussed in this proposal exhibit similar properties in chlorinated solvents.

(iv) Amino adducts 26 undergo ligand exchange reactions forming (F₆-acen)Zr(R)(L)ₑ⁺ adducts (n = 1,2; L = PR₃, RCN, THF) and insert CO and ketones. (v) Surprisingly, base-free cation 27 does not react with ethylene. However, addition of 1 equiv Al(iBu)₃ to 27 (cq 7) generates an active catalyst. Control experiments suggest that Al(iBu)₃ functions by generating a Zr hydride species which is more reactive with ethylene than neopentyl complex 27. The (F₆-acen)ZrR⁺ derived catalyst is much more reactive than the (H₆-acen)ZrR⁺ derived catalyst, activities being 14,000 and 800 g/(mol·h·atm) respectively (3 atm, 50 °C, C₆H₅Cl/toluene).
(c) Chiral \( (\text{N}_2\text{O}_2\text{-chelate})\text{M}(\text{R})^+ \) Complexes. We have prepared several chiral \( \text{d}^0 \) \( (\text{N}_2\text{O}_2\text{-chelate})\text{MX}^+ \) species and demonstrated their utility in stereoselective catalysis. Key results of these studies, which are as yet only published in thesis form, are as follows.\(^6\) (i) \( \text{Zr} \) benzyl complexes 30-32 containing chiral salen or acen ligands were prepared by alkane elimination reactions of \( \text{Zr}(\text{CH}_2\text{Ph})_4 \) and the neutral ligands. 30 adopts a \( \text{C}_1 \)-symmetric structure in the solid state, with one \( \eta^2 \) and one \( \eta^1 \) benzyl ligand, but exhibits \( \text{C}_2 \) symmetry in solution on the NMR time scale.

\[
\text{(F}_6\text{-acen})\text{ZrCH}_2\text{CMe}_3 \\
\overset{27}{\text{+}} \text{Al('Bu)}_3
\Rightarrow \quad \text{polymerization} \quad (7)
\]

(ii) 31 (\( t_{1/2} < 1 \text{ h, } 23 \text{ °C} \)) and 30 (\( t_{1/2} < 12 \text{ h, } 23 \text{ °C} \)) rearrange by stereospecific benzyl migration to a salen* imine carbon (eq 8), while 32 is stable due to the increased crowding at the imine carbon.

\[
\begin{array}{c}
\text{rac-30} \\
\text{rac-31} \\
\text{R,R-32, } X = \text{H, F}
\end{array}
\]

\[
\begin{array}{c}
\text{rac-31} \\
\text{23 °C}
\end{array}
\]

\[
\begin{array}{c}
\text{eq 8}
\end{array}
\]
(iii) Rac-30 is converted to a single-site isospecific propylene polymerization catalyst by reaction with [HNMe2Ph][B(C6F5)4] and 2 equiv of Al(iBu)3 (Mw = 17,200, Mw/Mn = 2.48; 40 °C, liquid propylene, eq 9). The (salen*)Zr(R)+/Al(iBu)3 catalyst polymerizes propylene with high iso-selectivity (>95% mmmm) by an enantioselective site-control process (13C NMR pentad analysis). Regioerrors (1,3 insertions; i.e. 2,1 insertion followed by β-H elimination and reinsertion) occur to a minor extent (13C NMR) and are reflected in the DSC mp (134.7 °C). The activity is moderate (e.g. 9 g PP produced by 0.15 g catalyst at 40 °C, 45 min, liquid propylene). Based on the chemistry discussed above, our working hypothesis is that this polymerization proceeds by repetitive insertion into (salen*)ZrR+ species (R = growing chain). The Al(iBu)3 is believed to scavenge the NMe2Ph and to generate a (salen*)ZrH+ species (eq 7). The main drawback of this approach to stereoselective olefin polymerization is that the chemistry is complicated by (and indeed catalyst deactivation may occur by) ligand alkylation reactions similar to that in eq 8.

\[
\text{(salen*)Zr(CH2Ph)2} + \text{HNMe2Ph B(C6F5)4} + 2 \text{Al(iBu)3} \rightarrow \text{isotactic PP}
\]

We have also studied the utility of chiral (N2O2-chelate)Zr(OTf)2 and [(N2O2-chelate)Ti(OTf)2]2(μ-O) compounds as catalysts for stereoselective Diels-Alder reactions.

(d) (N,O-chelate)2MR+ Complexes.7 To circumvent the undesired features of facile ligand alkylation in (N2O2-chelate)ZrR2 compounds and wide R-Zr-L angles (non-optimum for insertion) in (N2O2-chelate)Zr(R)(L)+ species, we investigated (N,O-chelate)2MR+ cations containing bidentate N,O-chelate ligands. We first investigated the substituted 8-quinolinolato ligands MeOx- or MeBr2Ox- (eq 10). Key results: (i) (MeOx)2MX2 and (MeBr2Ox)2MX2 compounds adopt C2-symmetric trans-O, cis-N, cis-X O₈ structures 33 and undergo racemization with barriers in the range ΔG° = 15-18 kcal/mol. (MeBr2Ox)2M(R)(L)+ cations (L = NR3, PR3) adopt analogous O₈ structures (34, eq 10).
(ii) Base-free (MeBr₂Ox)₂MR⁺ cations 35 are generated by protonolysis of 33 with HNMePh₂⁺ (eq 11). Cations 35 adopt square pyramidal (sp) structures with agostic hydrocarbyl ligands in the apical site and a trans-O, trans-N ligand arrangement in the basal sites (eq 11; Fig. 1a, p15). In contrast, (MeOx)₂MR⁺ cations 36 adopt sp structures with apical-O, cis-N ligand arrangements (eq 11). Structure 36 is favored for the electron-donating MeOx⁻ ligand because it allows maximum O-M π-donation. Thus substantial structural differences may exist between (Ox)₂MR⁺ and (Ox)₂M(R)(L)⁺ species. (iii) Interestingly, 5-coordinate cations 35 and 36 (∆Gracem⁻ > 20 kcal/mol) are more stereochemically rigid than 6-coordinate species 33 or 34, probably because racemization requires ligand dissociation. (iv) Ligand binding studies and analysis of benzyl distortions in (Ox)₂M(CH₂Ph)⁺ species show that the metal Lewis acidity varies in the order MeBr₂Ox⁻ > MeOx⁻, and Zr > Hf.

(v) Thermolysis of (MeBr₂Ox)₂Zr(CH₂Ph)₂ results in rearrangement via benzyl migration to C2 of a MeBr₂Ox⁻ ligand (eq 12); however, (MeOx)₂MR₂ and Hf analogues are resistant to this process.

We also prepared a series of (pyCR₂O)₂ZrR₂ and (pyCR₂O)₂ZrR⁺ complexes (37) incorporating bidentate pyridine-alkoxide ligands (eq 13). The structures (e.g. Fig. 1b) and reactivity of (pyCR₂O)₂ZrR₂ and (pyCR₂O)₂ZrR⁺ species follow the general trends observed for (Ox)₂MR⁺ systems. However, racemization of (pyCR₂O)₂Zr(CH₂Ph)₂ compounds is facile (∆G⁺ = 8-10 kcal/mol) due to the flexibility of the pyCR₂O⁻ ligands.
The ethylene polymerization behavior of representative (N,O-chelate)\(2\)ZrR\(+\) cations was examined. Key results: (i) (N,O-chelate)\(2\)MR\(+\) cations are single-site ethylene polymerization catalysts, and exhibit a reactivity order which parallels the Lewis acidity order; i.e. (MeBr\(2\)Ox)\(2\)Zr(CH\(2\)Ph)\(+\) (30 kg/(mol*h*atm); 23 °C, 3 atm) > (MeBr\(2\)Ox)\(2\)Hf(CH\(2\)Ph)\(+\) >> (MeOx)\(2\)M(CH\(2\)Ph)\(+\), and (pyC(CF\(3\))\(2\)O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\) (32 kg/(mol*h*atm); 40 °C, 3 atm) > (pyCH(CF\(3\))O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\) >> (pyCMe\(2\)O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\). Thus the more electron deficient catalysts are more active, which is opposite to what is observed for Cp\(2\)MR\(+\) catalysts.\(^1\) (ii) Polymer analyses reveal very low molecular weights (M\(n\) ca. 580 for (MeBr\(2\)Ox)\(2\)Zr(CH\(2\)Ph)\(+\); 6,000 for (pyC(CF\(3\))\(2\)O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\)), narrow dispersities (M\(w\)/M\(n\) ca. 2), and ca. 50% vinyl end groups, consistent with single-site behavior and rapid chain transfer by β-H elimination. Assuming that all cations are active, the activity and M\(n\) values imply that (MeBr\(2\)Ox)\(2\)Zr(CH\(2\)Ph)\(+\) and (pyC(CF\(3\))\(2\)O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\) generate 44 and 6 chains per site respectively, under the conditions studied. (iii) \(^{13}\)C NMR analysis of the polyethylene produced by (pyC(CF\(3\))\(2\)O)\(2\)Zr(\(\eta^2\)-CH\(2\)Ph)\(+\) reveals the presence of benzyl end groups and significant long chain branching (ca. one >C\(5\) branch per chain), indicating that ethylene insertion into the Zr-CH\(2\)Ph bond occurs and that insertion of α-olefins released by β-H elimination competes with ethylene insertion. These results are consistent with repetitive insertion by intact (N,O-chelate)\(2\)MR\(+\) species (eq (4)).

Addition of aluminum cocatalysts to the (N,O-chelate)\(2\)MR\(+\) catalysts or use of MAO as an activator produces multi-site catalysts. Studies with AlMe\(3\) reveal that the N,O-chelate ligands are transferred to Al via attack of Al at the exposed oxygen centers.

(e) (N,N-chelate)TiR\(+\) Complexes.\(^8\) We have studied new cationic Ti alkyls containing chiral bidentate bis-amide ligands derived from trans-1,2-diaminocyclohexane (eq 15). Key
results: (i) An efficient synthesis of \( \text{trans-1,2-}(\text{NSiR}_3)_2\text{Cy} \)TiR\(_2\) compounds (38) based on an alkane elimination/halogenolysis/alkylation sequence was developed. \( \text{trans-1,2-}(\text{NSiR}_3)_2\text{Cy} \)TiX\(_2\) compounds have distorted \( T_d \) structures (e.g. Fig. 1c).

(ii) Protonolysis of 38 with \([\text{HNMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]\) yields \( \text{trans-1,2-}(\text{NSiR}_3)_2\text{Cy} \)Ti(R)(\text{NMMe}_2\text{Ph})\(^+\) cations which have been characterized by multinuclear NMR and are single-site ethylene and ethylene/hexene polymerization catalysts. Activities are moderate and molecular weights are low due to rapid \( \beta\)-H elimination. (iii) Activation of \( \text{trans-1,2-}(\text{NSiR}_3)_2\text{Cy} \)TiX\(_2\) compounds with MAO produces active multi-site catalysts. GPC analyses suggest that the sites produced using cationic activators and MAO are different. (iv) The oligomerization of 1-hexene by \( \{\text{trans-1,2-}(\text{NSiMe}_3)_2\text{Cy}\}\)Ti(Ph)(\text{NMMe}_2\text{Ph})\(^+\) was studied in detail by GC-MS analysis of the oligohexenes. This work shows that repetitive 1,2 insertions and repetitive 2,1 insertions into Ti-Ph, Ti-R and Ti-H bonds occur, but 1-2/2-1 and 2-1/1-2 insertion sequences do not occur. The hydride resulting from \( \beta\)-H elimination is sufficiently long-lived to initiate a new chain. Deactivation occurs by metallation of \( \text{NMMe}_2\text{Ph} \) following \( \beta\)-H elimination (eq 16). These results contrast with the living hexene polymerization observed by McConville for \( \{\text{ArN(CH}_2)_3\text{NAr}\}\)TiR\(_2\)/B(\text{C}_6\text{F}_5)_3 (\text{Ar} = 2,6-\text{Pr}_2-\text{C}_6\text{H}_3).9 \) Currently we are investigating the generation and olefin reactivity of base-free \( \{\text{trans-1,2-}(\text{NSiMe}_3)_2\text{Cy}\}\)Ti\(^+\) species using \( \text{B(C}_6\text{F}_5)_3 \) and \([\text{CPh}_3][\text{B(C}_6\text{F}_5)_4]\) activators to probe if the amine plays a role in chain transfer. (v) The \( \{\text{trans-1,2-}(\text{NSiR}_3)_2\text{Cy}\}\)Ti(R)(\text{NMMe}_2\text{Ph})\(^+\) cations are resistant to reduction to Ti\(^{\text{III}}\) species, which is in direct contrast to \( \text{Cp}_2\text{Ti}^+ \) or \( \text{CpTiR}_2^+ \) species which reduce readily.

(ii) Activation of Non-Metallocene Compounds with MAO.\(^{10,11}\) Section I-C-i above summarizes our studies of discrete, \( d^0 \), non-metallocene \( \text{L}_n\text{MR}^+ \) cations. In addition to these fundamental studies we have investigated the ethylene polymerization performance of a wide range of non-metallocene complexes containing macrocyclic, pyridine-alkoxide, dicarbollide, bis-amide or \( \text{Tp}^- \) ligands, using \( \text{AIR}_3 \) and/or methylalumoxane (MAO) activation approaches. The objective of these exploratory studies was to
identify highly active catalysts from which new classes of reactive discrete \( L_nMR^+ \) cations might be developed. Our most interesting discovery in this area is that MAO activation of Ti and V complexes 8 and 9 which incorporate aryl-substituted tris(pyrazolyl)borate ligands (Chart 2 and Fig. 1d), produces single-site catalysts whose activities approach those of metalloccene catalysts, under conditions designed to minimize mass transport limitations. Analogous compounds lacking the \( R^3 = \text{aryl} \) substituents are \( >100 \) times less active.\(^{12} \) One of our goals in the next project period is to identify the active species in these systems and to generate these species using simpler activators.

In many other cases we have found that \( \text{AlR}_3/\text{MAO} \) activation produces multi-site catalysts, presumably by abstraction of the N- or O-based ancillary ligand. For example, while treatment of chiral \( \text{ansa-Cp}_2\text{Zr(NMe}_2)_2 \) compounds (easily accessible in \( \text{rac} \) form by amine elimination) with \( \text{AlR}_3/\text{MAO} \) cleanly generates \( \text{ansa-Cp}_2\text{ZrR}^+ \) catalysts via alkylation by \( \text{AlR}_3 \) and subsequent alkyl abstraction by MAO,\(^{13} \) analogous activation of \( \{\text{pyCAr}_2O\}_2\text{M(NMe}_2)_2 \) yields multi-site catalysts.

(iii) Cationic Aluminum Alkyl Compounds.\(^{14} \) Our work on cationic non-metalloocene \( d^0 \) metal alkyls shows that the key active site "design requirements" which have been identified for metalloccene catalysts may be generalized to a wide variety of transition metal systems. Do these concepts apply to main group systems? To probe this possibility we investigated the chemistry of 3-coordinate \( \{L-X\}\text{AIR}^+ \) species containing bidentate mono-anionic ancillary \( L-X^- \) ligands.\(^{15,16} \) Key results from our initial studies with nitrogen-based ligands are as follows: (i) General syntheses of \( \{\text{RC(NR}''_2\}_2\text{AIR}''^+ \) amidinate compounds have been developed (e.g. 39, 40; eq 17, 18). Bulky \( R \) and \( R'' \) substituents enforce mononuclear structures in these systems (e.g. Fig. 1e). (ii) The reaction of \( \{\text{RC(NR}''_2\}_2\text{AlMe}_2 \) compounds containing moderately bulky amidinates with cationic activators yields \( \{\text{RC(NR}''_2\}_2\text{Al(Me)(L'}^+ \) cations by methyl abstraction (eq 17,18). In these species, the...
(ii) The {RC(NR')2}AlMe+ cation is stabilized by an additional donor group \((L' = \{RC(NR')2\}AlMe2)\) \((41,42)\), NMc2Ph, PMe3, or MeB(C6F5)3 \((43)\), the precise product depending on the coordinating ability of potential ligands. Low temperature NMR studies establish that acetamidinate complex 41 has a dinuclear \(\mu\)-Me structure. Pivamidinate cation 42 is more labile due to the increased steric crowding of the \(\{cBuC(NR')2\}Al\) unit and a low temperature structure could not be frozen out in this case. Neither 41 nor 42 do not react with excess activator under mild conditions. The MeB(C6F5)3 adducts \((e.g. 43)\) decompose rapidly to \(\{RC(NR')2\}Al(Me)(C6F5)\).

\[
\text{41, } A' = \text{MeB(C6F5)3 or B(C6F5)4}
\]

\[
\text{42}
\]

(iii) To disfavor the formation of dinuclear species by coordination of \([L-X]AlR2\) to \([L-X]AlR^+\), we investigated the use of \(L-X^*\) ligands with larger bite angles \(vs\) amidinates and the use of higher alkyl groups which are less likely to bridge \(vs\) Me. The reaction of \(N,N-\text{iPr2-aminotroponinate complexes} \{\text{iPr2-ATI}\}AlR2 \,(44, R = H, Me)\,17\) with \([\text{Ph3C}]\text{B(C6F5)}4\] yields dinuclear \([\{\text{iPr2-ATI}\}Al(R)]_2(\mu-R)^+\) cations 45 \((eq 19)\). An X-ray crystallographic analysis of \([\{\text{iPr2-ATI}\}AlMe2(\mu-Me)]\text{B(C6F5)}4\] \(Fig. 1f)\) confirmed the structure shown in eq 19 \(\langle Al-\text{Me-Al} = 167.8^\circ\rangle\) and established that the anion is non-coordinating. In contrast, the reaction of \(\{\text{iPr2-ATI}\}AlEt2\) and \(\{\text{iPr2-ATI}\}Al^iBu2\) yields isolable base-free, non-agostic \(\{\text{iPr2-ATI}\}AlR^+\) species 46 by \(\beta\)-hydride abstraction \((eq 20)\).
These novel cationic Al alkyls are ethylene polymerization catalysts, producing high molecular weight linear polyethylene under mild conditions. Activities for 42 and 46 are in the 1-5 x 10^3 g/(mol*h*atm) range at 85 °C (1-3 atm) while 41, 43 and 45 are less active. For comparison, neutral aluminum alkyls oligomerize ethylene to C_8-C_{10} α-olefins at high ethylene pressures and temperatures above 120 °C. However this process is quite slow; for example AlEt_3 is reported to oligomerize ethylene with an activity of <10 g/(mol Al*h*atm) at >36 atm and 140 °C. Our working hypothesis is that \{L-X\}AlR^+ cations are the active species in these polymerizations and that activity is influenced by cation stability, anion degradation and competitive ligand/ethylene binding. The cationic charge promotes ethylene insertion by disfavoring dimerization and by increasing the electrophilic character of the Al center, which favors ethylene coordination and alkyl migration. The charge may also disfavor B-H elimination by selectively strengthening the Al-R bond. These results suggest that it may be possible to develop novel catalysts for olefin polymerization and other reactions by proper choice of ligand/metal combinations in cationic main group alkyls. A major objective of this program during the next project period will test these ideas.
Figure 1. Molecular structures of (a) (MeBr₂Ox)₂Zr(η²-CH₂Ph)⁺ (the B(C₆F₅)₄⁻ anion is not shown), (b) (pyCMe₂O)₂Zr(CH₂Ph)₂, (c) [trans-1,2-(NSiMe₃)₂-Cy]TiI₂, (d) [TpMes]V(N'Bu)Cl₂, (e) [tBuC(NCy)₂]AlMe₂ and (f) [[iPr₂-ATI]AlMe₂(μ-Me)⁺ (the B(C₆F₅)₄⁻ anion is not shown).
D. Publications From Previous Project Period (1/1/95 - 8/31/98)


(3) "Tetraaza Macrocycles as Ancillary Ligands in Early Metal Alkyl Chemistry. Synthesis and Characterization of Out-of-Plane (Me₄taen)ZrX₂ (X = alkyl, bcnzyl, NMe₂, Cl) and (Me₄taen)ZrX₂(NHMe₂) (X = Cl, CPh₂) Complexes." Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* 1995, 14, 3539-3550.


(1) "Synthesis, Structures, and Reactivity of (R₆-acen)ZrR₂ and (R₆-acen)Zr(R')⁺ Complexes (R = H, F; R' = CH₂CMe₃, CH₂Ph)." Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* 1995, 14, 371-386.

**E. Estimate of Unobligated Balance.** All remaining funds will be spent by the end of the current project period.