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Electrophilic Metal Alkyl Chemistry in New Ligand Environments

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Final Project Report

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Electrophilic Metal Alkyl Chemistry in New Ligand Environments

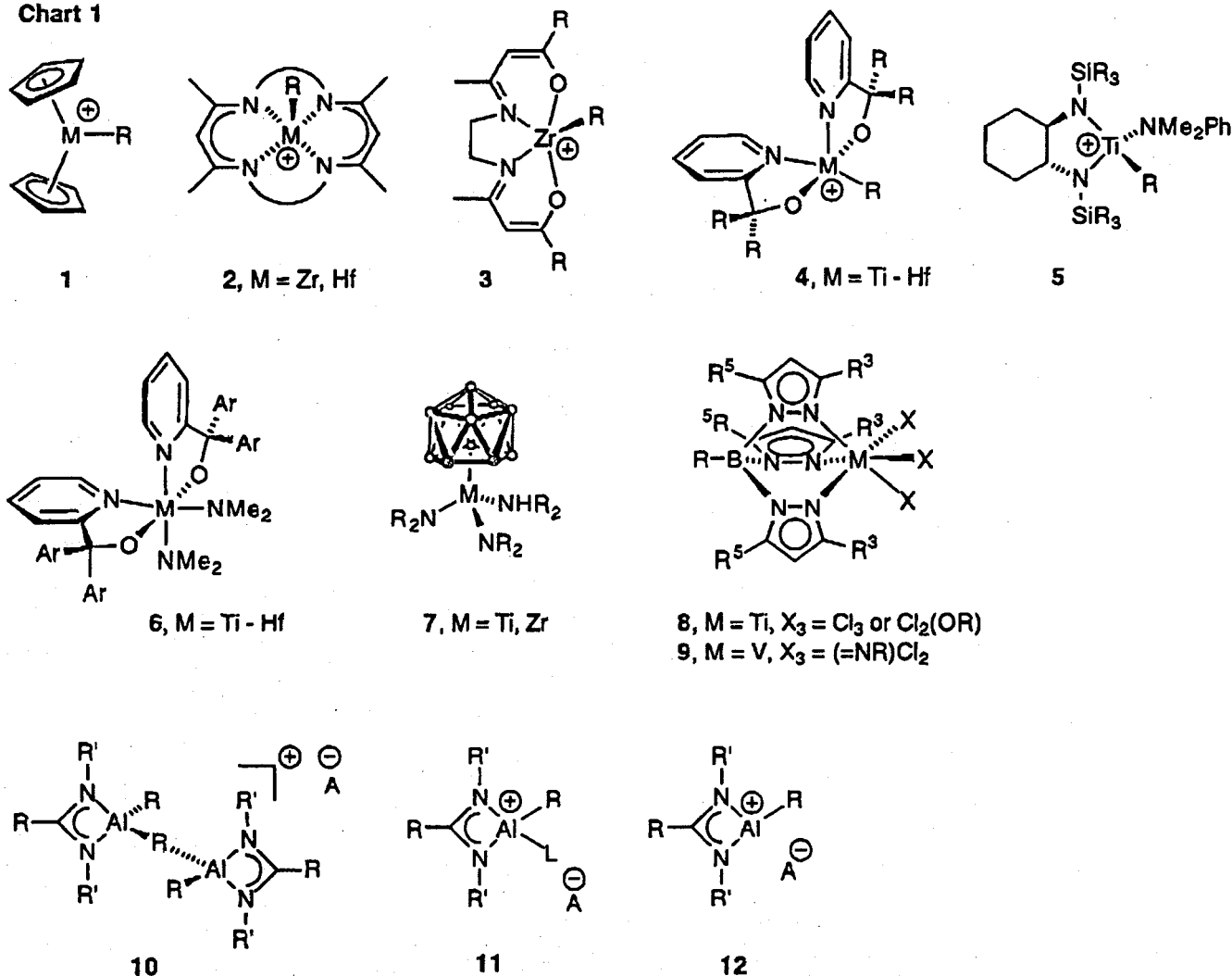### I. Results From Previous Project Period (1/1/95 - 8/31/98)

A. Introduction and Objectives. Cationic group 4 and actinide Cp_2MR^+ metallocenes (**1**, Chart 1), and isolobal neutral group 3 and lanthanide Cp_2MR 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*-Cp_2M 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 N_4-macrocycle (**2**, Chart 1), tetradentate 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-metallocene complexes containing bis-amide, pyridine-alkoxide, dicarbollide, or tris(pyrazolyl)borate (Tp^-) ligands (**5-9**), using AlR_3 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 activites 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 (10^3) more reactive with this substrate than are neutral AlR_3 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 d^0 $Cp_2M(R)^{n+}$ 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 d^0 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 $Cp_2M(R)^{n+}$ 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 L_nMR^+ 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 $B(C_6F_5)_4^-$ unless specified otherwise. Space limitations preclude discussion of experimental details, but it should be noted that $[L_nMR][B(C_6F_5)_4]$ salts normally separate

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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.
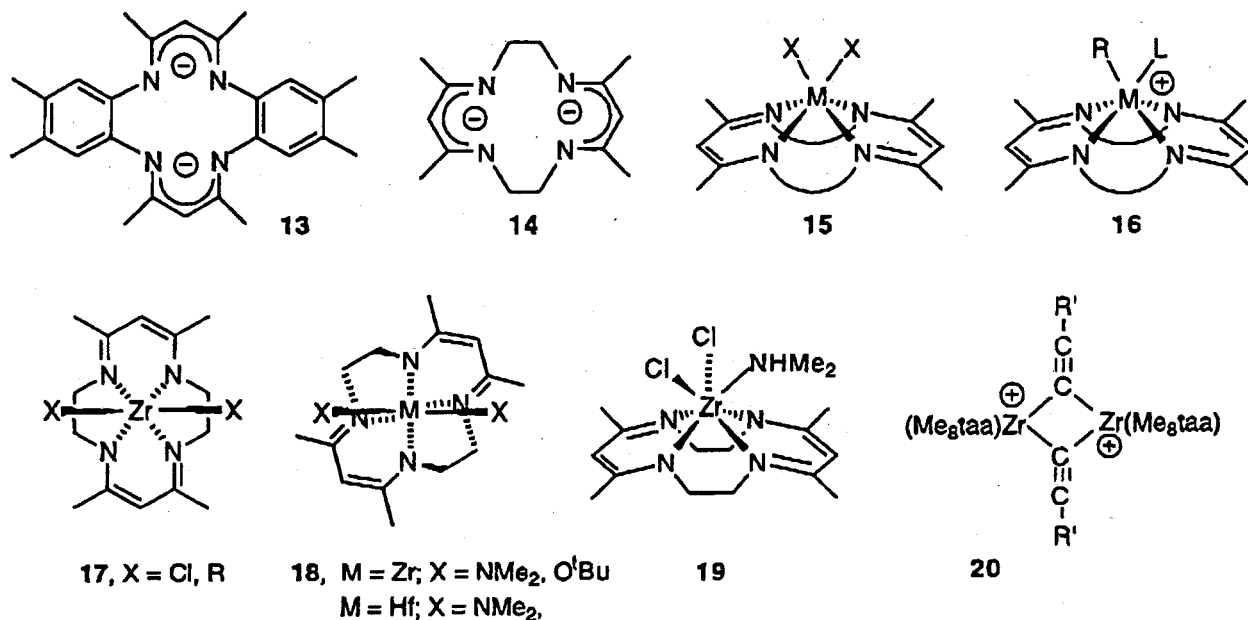
Chart 1

1   2, M = Zr, Hf   3   4, M = Ti - Hf   5

6, M = Ti - Hf   7, M = Ti, Zr   8, M = Ti, X_3 = Cl_3 or Cl_2(OR)
9, M = V, X_3 = (=NR)Cl_2

10   11   12

C. Key Results

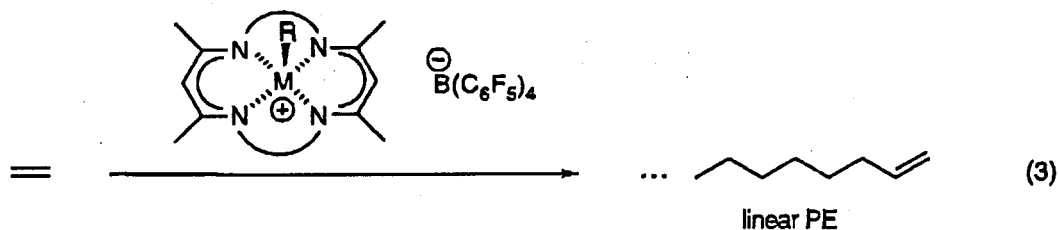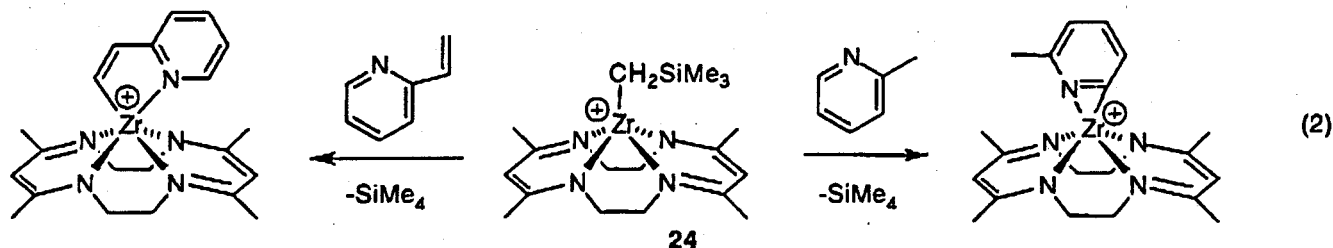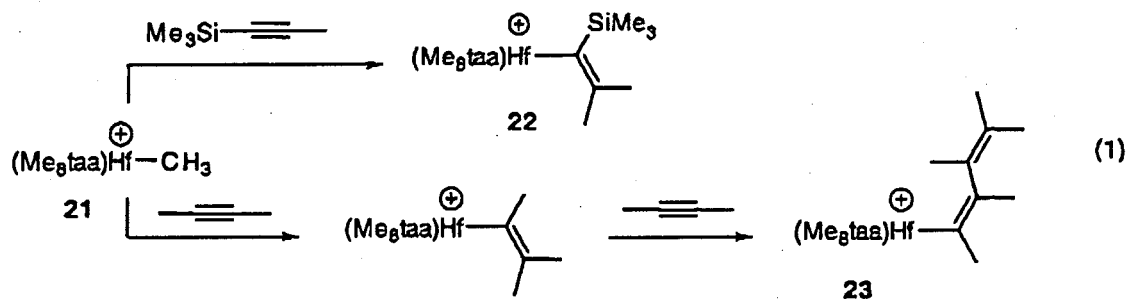### (i) Discrete Non-metallocene Cationic Group 4 Alkyls

(a) (N_4-macrocycle)MR^+ Complexes.[3] In our initial approach to non-metallocene cationic alkyls, we investigated (N_4-macrocycle)MR^+ species (2) which incorporate the tetraaza-macrocycles Me_8taa^{2-} (13) or Me_4aen^{2-} (14). The binding pockets of these macrocycles are too small to accommodate Zr^{4+} and Hf^{4+} ions and therefore (N_4-macrocycle)MX_2 compounds adopt "out-of-plane" cis structures 15. On this basis we anticipated that d^0 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) (Me_8taa)MX_2 compounds adopt trigonal prismatic (*tp*) structures with a "saddle" Me_8taa^{2-} conformation (15). The structures of (Me_4taen)MX_2 complexes are more variable due to the greater flexibility of Me_4taen^{2-} vs Me_8taa^{2-}, 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_h) structures (**18**). Seven-coordinate (Me$_4$-taen)ZrCl$_2$(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 Cp$_2$ML$_3$.
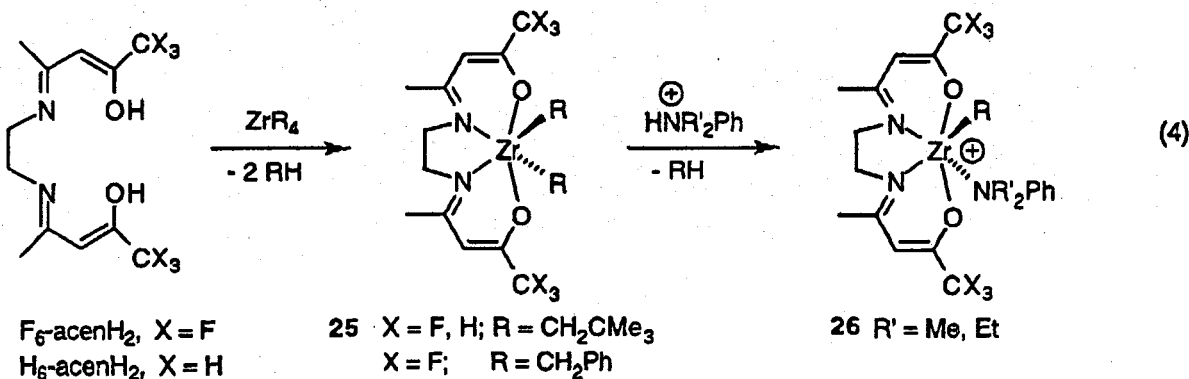

13   14   15   16

17, X = Cl, R   **18, M = Zr; X = NMe$_2$, O^{t}Bu**   **19**   **20**
                       M = Hf; X = NMe$_2$,

(ii) (N$_4$-macrocycle)MR$^+$ species coordinate Lewis bases (**16**) and exhibit agostic/distorted hydrocarbyl structures; e.g. (Me$_4$taen)Zr(CH$_2$SiMe$_3$)(THF)$^+$ has an α-agostic structure at low temperature. Dinuclear {(Me$_8$taa)M}$_2$(μ-X)$^{2+}$ *dications* form when X is a good bridging ligand (X = OR, CCR; e.g. **20**). (iii) Reactivity studies show that the M-R bonds of (Me$_8$taa)MR$_2$ compounds are more polar/ionic than the M-R bonds of Cp$_2$MR$_2$ species. (iv) Trends in ligand lability and the strengths of agostic and η^2-benzyl interactions in (Me$_8$taa)MR(L)$_n$$^+$ (n = 0,1) suggest that (Me$_8$taa)MR$^+$ cations are harder and weaker Lewis acids than Cp$_2$MR$^+$. In particular, while Cp$_2$Zr(OCMe$_2$CH$_2$CH$_2$CH=CH$_2$)$^+$ coordinates the pendant olefin, (Me$_8$taa)Zr(OCMe$_2$CH$_2$CH$_2$CH=CH$_2$)$^+$ does not, indicating that Cp$_2$Zr(OR)$^+$ is a stronger Lewis acid for unsaturated hydrocarbons than is (Me$_8$taa)Zr(OR)$^+$.[4] (v) (Me$_8$taa)MR$^+$ cations insert alkynes and undergo C-H activation reactions (e.g. eq 1,2). (vi) [(Me$_8$taa)Zr(CH$_2$Ph][B(C$_6$F$_5$)$_4$] polymerizes ethylene (M$_w$ = 100,000; M$_w$/M$_n$ = 2.6; 50 °C, 1.3 atm, toluene), but with low activity (300 g/(mol*h*atm); eq 3). (vii) In general (N$_4$-macrocycle)MR$^+$ cations are less reactive for insertion of unsaturated hydrocarbons than are Cp$_2$MR$^+$ cations. This difference largely reflects the difference in Lewis acid properties of the metal centers.
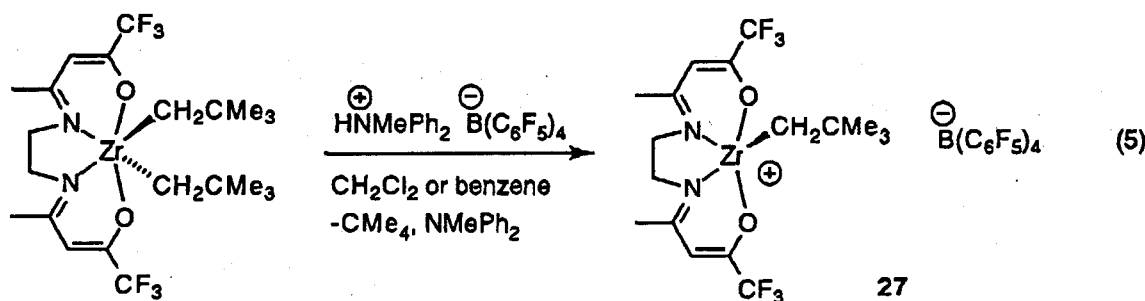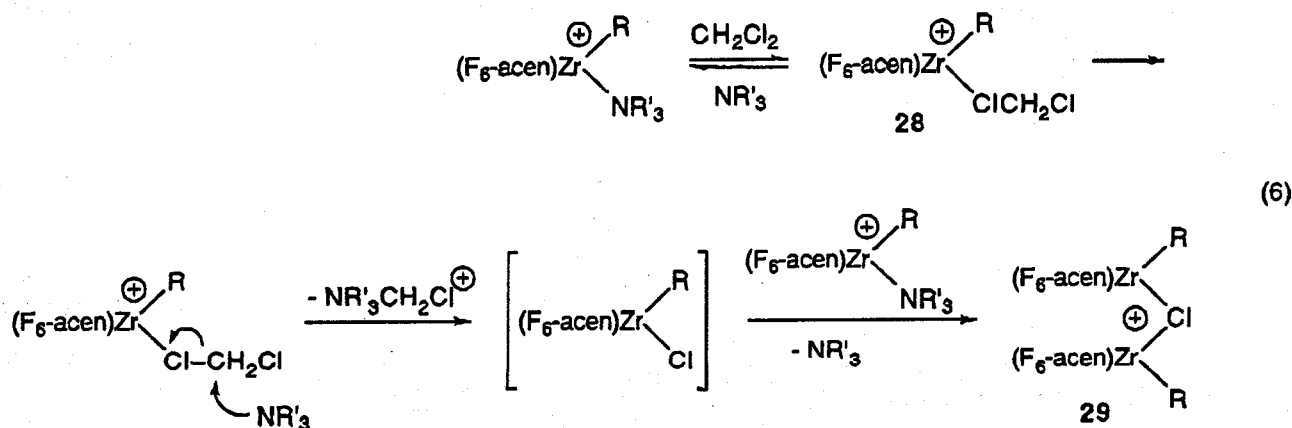
(1)

(2)

(3)

(b) $(N_2O_2$-chelate)MR$^+$ Complexes.[5] One approach to increasing the electrophilicity of $(N_4$-macrocycle)MR$^+$ species is to replace the N-donors with more electronegative O-donors. With this goal in mind, we investigated d^0 $(N_2O_2$-chelate)MX$_2$ and $(N_2O_2$-chelate)MR$^+$ complexes. Key results are as follows: (i) $(R_6$-acen)Zr(CH$_2$CMe$_3$)$_2$ species (**25**, R = H, F) were prepared by alkane elimination and protonolyzed to $(R_6$-acen)Zr(R)(NR'$_2$Ph)$^+$ (**26**) or base-free $(R_6$-acen)ZrR$^+$ (**27**) by [HNR'$_2$Ph][B(C$_6$F$_5$)$_4$] or [HNMePh$_2$][B(C$_6$F$_5$)$_4$] respectively (eq 4,5). The strong amine coordination in **26** implies that $(X_6$-acen)Zr(R)$^+$ species are effectively more electrophilic than $(N_4$-macrocycle)ZrR$^+$ cations, which do not coordinate NMe$_2$Ph, and comparable to sterically open Cp$_2$ZrR$^+$ cations which do coordinate this amine.
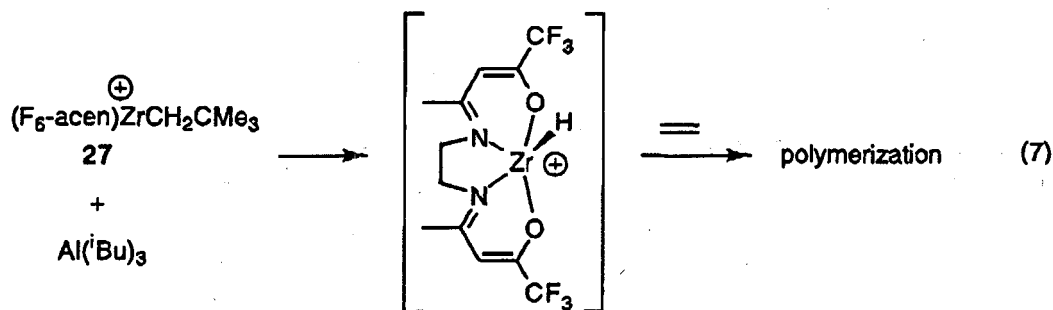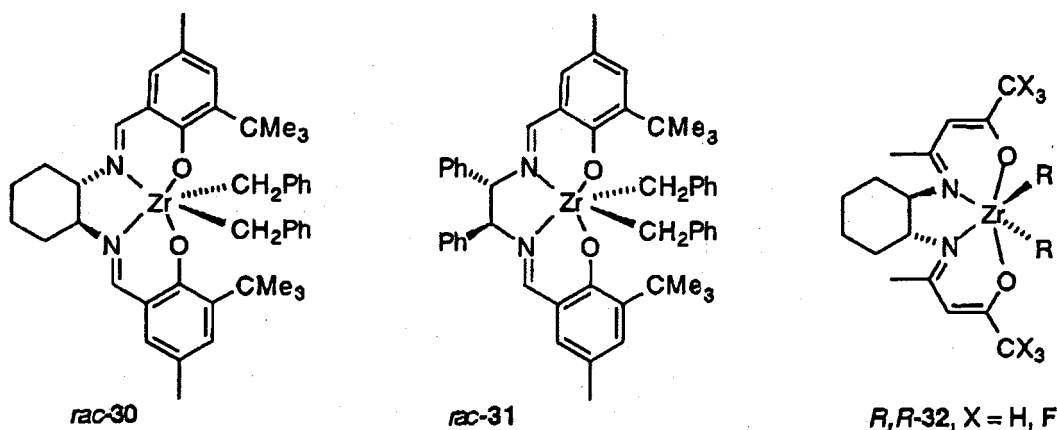

(4)

F$_6$-acenH$_2$, X = F   **25** X = F, H; R = CH$_2$CMe$_3$ **26** R' = Me, Et
H$_6$-acenH$_2$, X = H   X = F;   R = CH$_2$Ph

6

(5)

(ii) (F_6-acen)Zr(CH$_2$CMe$_3$)$_2$ adopts an elongated *tp* structure (**25**) in which the R-Zr-R angle (129°) is larger than in (N$_4$-macrocycle)ZrR$_2$ (ca. 85°) or Cp$_2$ZrR$_2$ (ca. 95°). The (F_6-acen)Zr(CH$_2$CMe$_3$)(NMe$_2$Ph)$^+$ cation **26** exhibits a wide R-Zr-amine angle (144.7°). (iii) The reaction of (F_6-acen)Zr(CH$_2$CMe$_3$)(NEt$_2$Ph)$^+$ with CH$_2$Cl$_2$ proceeds by nucleophilic attack of NEt$_2$Ph on the CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$) is very stable in CH$_2$Cl$_2$ in the absence of nucleophilic species. We have since found that most of the L$_n$MR$^+$ species discussed in this proposal exhibit similar properties in chlorinated solvents.

(6)

(iv) Amine adducts **26** undergo ligand exchange reactions forming (F_6-acen)Zr(R)(L)$_n$$^+$ adducts (n = 1,2; L = PR$_3$, RCN, THF) and insert CO and ketones. (v) Surprisingly, base-free cation **27** does not react with ethylene. However, addition of *1 equiv* Al(^{i}Bu)$_3$ to **27** (cq 7) generates an active catalyst. Control experiments suggest that Al(^{i}Bu)$_3$ functions by generating a Zr hydride species which is more reactive with ethylene than neopentyl complex **27**. The (F_6-acen)ZrR$^+$ derived catalyst is much more reactive than the (H$_6$-acen)ZrR$^+$ derived catalyst, activities being 14,000 and 800 g/(mol*h*atm) respectively (3 atm, 50 °C, C$_6$H$_5$Cl/toluene).

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$$(F_6\text{-acen})ZrCH_2CMe_3 \overset{\oplus}{} \quad 27 \quad + \quad Al(^iBu)_3 \longrightarrow \left[\quad Zr \overset{\oplus}{} \quad \right] = \longrightarrow \text{polymerization} \quad (7)$$

(c) Chiral (N$_2$O$_2$-chelate)M(R)$^+$ Complexes. We have prepared several chiral d^0 (N$_2$O$_2$-chelate)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) Zr benzyl complexes 30-32 containing chiral salen or acen ligands were prepared by alkane elimination reactions of Zr(CH$_2$Ph)$_4$ and the neutral ligands. 30 adopts a C$_1$-symmetric structure in the solid state, with one η^2 and one η^1 benzyl ligand, but exhibits C$_2$ symmetry in solution on the NMR time scale.

rac-30   *rac*-31   *R,R*-32, X = H, F
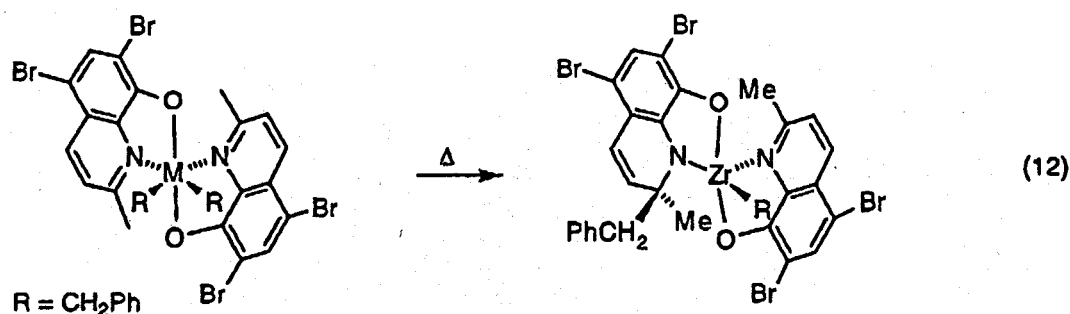
(ii) 31 (t$_{1/2}$ < 1 h, 23 °C) and 30 (t$_{1/2}$ < 12 h, 23 °C) rearrange by stereospecific benzyl migration to a salen* imine carbon (eq 8), while 32 is stable due to the increased crowding at the imine carbon.

rac-31 $\xrightarrow{23\ °C}$ (8)

(iii) *Rac*-**30** is converted to a single-site *isospecific* propylene polymerization catalyst by reaction with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] and 2 equiv of Al(^{i}Bu)$_3$ (M$_w$ = 17,200, M$_w$/M$_n$ = 2.48; 40 °C, liquid propylene, eq 9). The (salen*)Zr(R)$^+$/Al(^{i}Bu)$_3$ catalyst polymerizes propylene with high iso-selectivity (>95% mmmm) by an enantiomorphic site-control process (^{13}C NMR pentad analysis). Regioerrors (1,3 insertions; i.e. 2,1 insertion followed by β-H elimination and reinsertion) occur to a minor extent (^{13}C 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(^{i}Bu)$_3$ is believed to scavenge the NMe$_2$Ph and to generate a (salen*)ZrH$^+$ species (cf. 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.

$$\tag{9}$$

We have also studied the utility of chiral (N$_2$O$_2$-chelate)Zr(OTf)$_2$ and {(N$_2$O$_2$-chelate)Ti(OTf)$_2$}$_2$(μ-O) compounds as catalysts for stereoselective Diels-Alder reactions.

(d) **(N,O-chelate)$_2$MR$^+$ Complexes.**[7] To circumvent the undesired features of facile ligand alkylation in (N$_2$O$_2$-chelate)ZrR$_2$ compounds and wide R-Zr-L angles (non-optimum for insertion) in (N$_2$O$_2$-chelate)Zr(R)(L)$^+$ species, we investigated (N,O-chelate)$_2$MR$^+$ cations containing bidentate N,O-chelate$^-$ ligands. We first investigated the substituted 8-quinolinolato ligands MeOx$^-$ or MeBr$_2$Ox$^-$ (eq 10). Key results: (i) (MeOx)$_2$MX$_2$ and (MeBr$_2$Ox)$_2$MX$_2$ compounds adopt C$_2$-symmetric *trans*-O, *cis*-N, *cis*-X O$_h$ structures **33** and undergo racemization with barriers in the range ΔG$^{\neq}$ = 15-18 kcal/mol. (MeBr$_2$Ox)$_2$M(R)(L)$^+$ cations (L = NR$_3$, PR$_3$) adopt analogous O$_h$ structures (**34**, eq 10).

X = H, MeOxH,
X = Br, MeBr$_2$OxH

M = Zr, Hf
R = CH$_2$Ph, CH$_2$CMe$_3$

L = NMe$_2$Ph, PR$_3$, THF

33   **34**

$$\tag{10}$$

(ii) Base-free $(MeBr_2Ox)_2MR^+$ cations **35** are generated by protonolysis of **33** with $HNMePh_2^+$ (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** $(\Delta G_{racem}^{\neq} > 20$ 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 $(Ox)_2M(CH_2Ph)^+$ species show that the metal Lewis acidity varies in the order MeBr₂Ox⁻ > MeOx⁻, and Zr > Hf.

M = Zr, Hf
R = CH₂Ph, CH₂CMe₃
X = H,Br

35   **36**   (11)

(v) Thermolysis of $(MeBr_2Ox)_2Zr(CH_2Ph)_2$ results in rearrangement via benzyl migration to C2 of a MeBr₂Ox⁻ ligand (eq 12); however, $(McOx)_2MR_2$ and Hf analogues are resistant to this process.
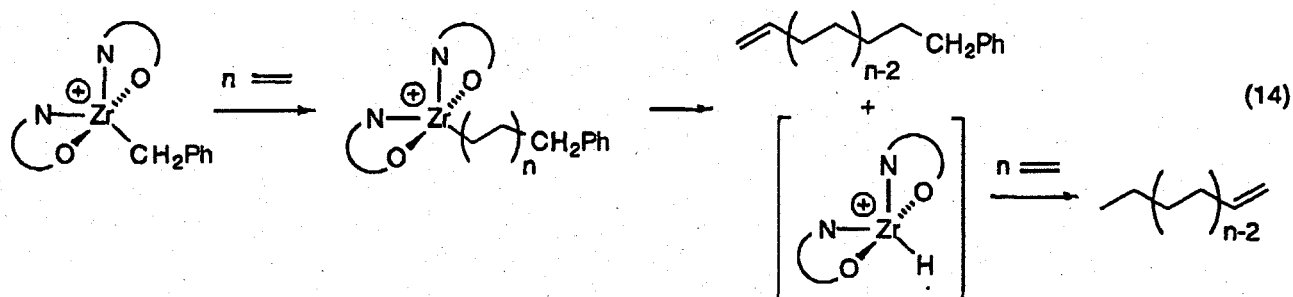

R = CH₂Ph   (12)

We also prepared a series of $(pyCR_2O)_2ZrR_2$ and $(pyCR_2O)_2ZrR^+$ complexes (**37**) incorporating bidentate pyridine-alkoxide ligands (eq 13). The structures (e.g. Fig. 1b) and reactivity of $(pyCR_2O)_2ZrR_2$ and $(pyCR_2O)_2ZrR^+$ species follow the general trends observed for $(Ox)_2MR^+$ systems. However, racemization of $(pyCR_2O)_2Zr(CH_2Ph)_2$ compounds is facile $(\Delta G^{\neq} = 8\text{-}10$ kcal/mol) due to the flexibility of the pyCR₂O⁻ ligands.

R$_2$ = (CF$_3$)$_2$, Me$_2$, (H)(CF$_3$)   37, A$^-$ = B(C$_6$F$_5$)$_4^-$ or PhCH$_2$B(C$_6$F$_5$)$_3^-$

(13)
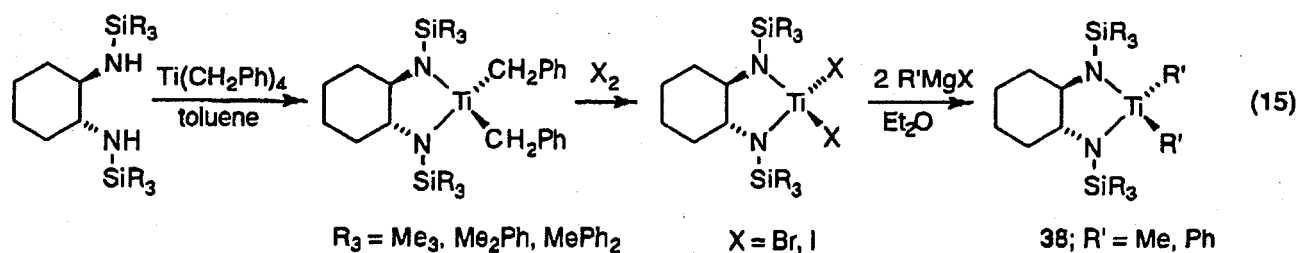
The ethylene polymerization behavior of representative (N,O-chelate)$_2$ZrR$^+$ cations was examined. Key results: (i) (N,O-chelate)$_2$MR$^+$ cations are single-site ethylene polymerization catalysts, and exhibit a reactivity order which parallels the Lewis acidity order; i.e. (MeBr$_2$Ox)$_2$Zr(CH$_2$Ph)$^+$ (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(η^2-CH$_2$Ph)$^+$ (32 kg/(mol*h*atm); 40 °C, 3 atm) > (pyCH(CF$_3$)O)$_2$Zr(η^2-CH$_2$Ph)$^+$ >> (pyCMe$_2$O)$_2$Zr(η^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(η^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(η^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(η^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 14).
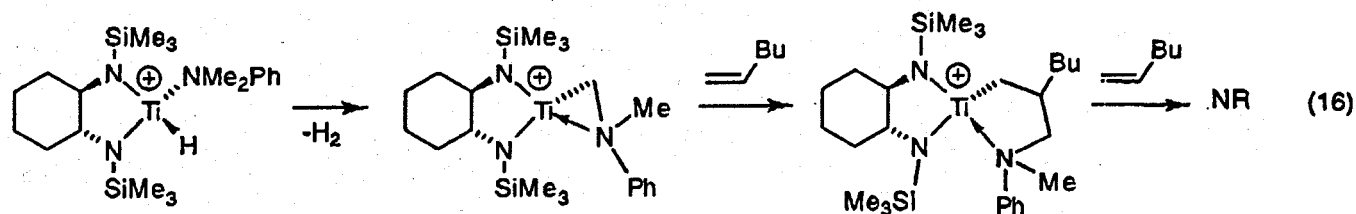

(14)

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 {trans-1,2-(NSiR$_3$)$_2$-Cy}TiR$_2$ compounds (38) based on an alkane elimination/halogenolysis/alkylation sequence was developed. {trans-1,2-(NSiR$_3$)$_2$-Cy}TiX$_2$ compounds have distorted T_d structures (e.g. Fig. 1c).
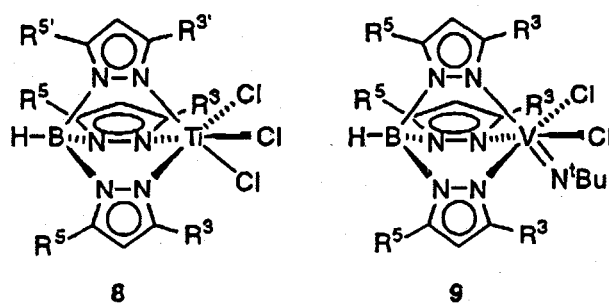

R$_3$ = Me$_3$, Me$_2$Ph, MePh$_2$ X = Br, I   38; R' = Me, Ph

(15)

(ii) Protonolysis of 38 with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] yields {trans-1,2-(NSiR$_3$)$_2$-Cy}Ti(R)(NMe$_2$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 β-H elimination. (iii) Activation of {trans-1,2-(NSiR$_3$)$_2$-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 {trans-1,2-(NSiMe$_3$)$_2$-Cy}Ti(Ph)(NMe$_2$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 β-H elimination is sufficiently long-lived to initiate a new chain. Deactivation occurs by metallation of NMe$_2$Ph following β-H elimination (eq 16). These results contrast with the living hexene polymerization observed by McConville for {ArN(CH$_2$)$_3$NAr}TiR$_2$/B(C$_6$F$_5$)$_3$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$).[9] Currently we are investigating the generation and olefin reactivity of base-free {trans-1,2-(NSiMe$_3$)$_2$-Cy}TiR$^+$ species using B(C$_6$F$_5$)$_3$ and [CPh$_3$][B(C$_6$F$_5$)$_4$] activators to probe if the amine plays a role in chain transfer. (v) The {trans-1,2-(NSiR$_3$)$_2$-Cy}Ti(R)(NMe$_2$Ph)$^+$ cations are resistant to reduction to Ti^{III} species, which is in direct contrast to Cp$_2$TiR$^+$ or CpTiR$_2^+$ species which reduce readily.

(16)

(ii) **Activation of Non-Metallocene Compounds with MAO.**[10,11] Section I-C-i above summarizes our studies of discrete, d^0, non-metallocene L$_n$MR$^+$ cations. In addition to these fundamental studies we have investigated the ethylene polymerization performance of a wide range of non-metallocene complexes containing macrocycle, pyridine-alkoxide, dicarbollide, bis-amide or Tp$^-$ ligands, using AlR$_3$ 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 metallocene catalysts, under conditions designed to minimize mass transport limitations. Analogous compounds lacking the R^3 = 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.

Chart 2

Catalyst	Activity[a,b] 10^6 g/(mol·h·atm)[a]
C p_2ZrCl_2	15
{Tp^{Mes*}}$TiCl_3$	9.1
{Tp^{Mes}}$TiCl_3$	1.7
{Tp^{Me2}}$TiCl_3$	0.04
{Tp}$TiCl_3$	0.03
{^{nBu}Tp}$TiCl_3$	0.03
{Tp^{Mes*}}$V(N^tBu)Cl_2$	2.2[c]
{^{nBu}Tp}$V(N^tBu)Cl_2$	0.07[c]

Tp^{Mes*} $R^3 = R^{5'} = $ Mes; $R^{3'} = R^5 = $ H
Tp^{Mes} $R^3 = R^{3'} = $ Mes; $R^5 = R^{5'} = $ H
Tp^{Me2} $R^3 = R^{3'} = R^5 = R^{5'} = $ Me
Tp $R^3 = R^{3'} = R^5 = R^{5'} = $ H
Mes = $2,4,6\text{-}Me_3\text{-}C_6H_2$
$^{nBu}Tp = {}^nBuB(pz)_3$

[a] Average of 3 runs, reproducibility ±10%
[b] 70 mL toluene, 1 μmol catalyst, Al/M = 900,
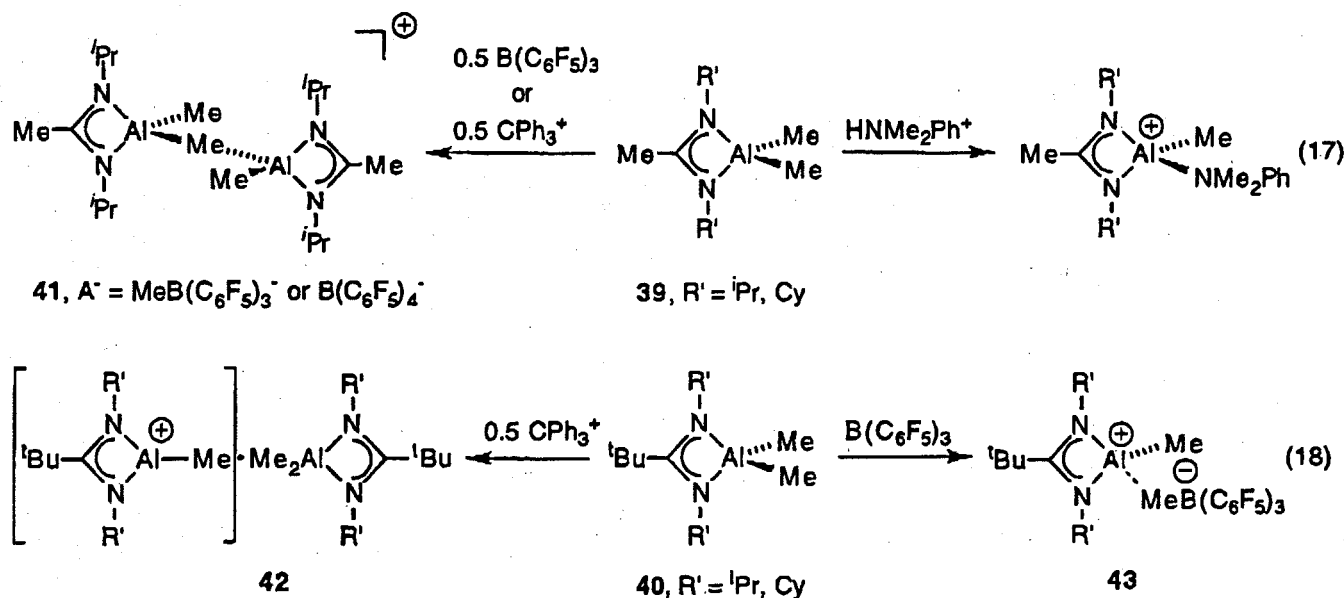   T = 60 °C, 4.4 atm ethylene,
[c] 0.5 μmol catalyst, 25 °C

In many other cases we have found that AlR_3/MAO activation produces multi-site catalysts, presumably by abstraction of the N- or O-based ancillary ligand. For example, while treatment of chiral *ansa*-$Cp_2Zr(NMe_2)_2$ compounds (easily accessible in *rac* form by amine elimination) with AlR_3/MAO cleanly generates *ansa*-Cp_2ZrR^+ catalysts via alkylation by AlR_3 and subsequent alkyl abstraction by MAO,[13] analogous activation of {$pyCAr_2O$}$_2M(NMe_2)_2$ yields multi-site catalysts.
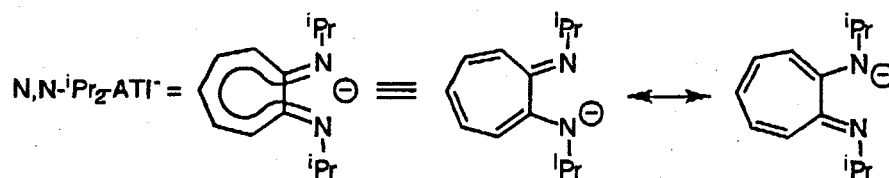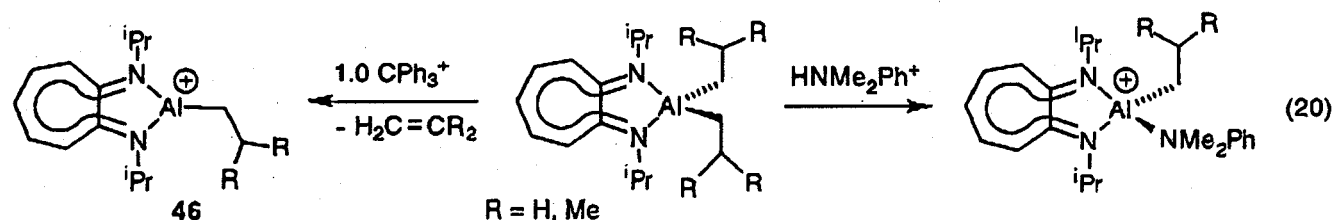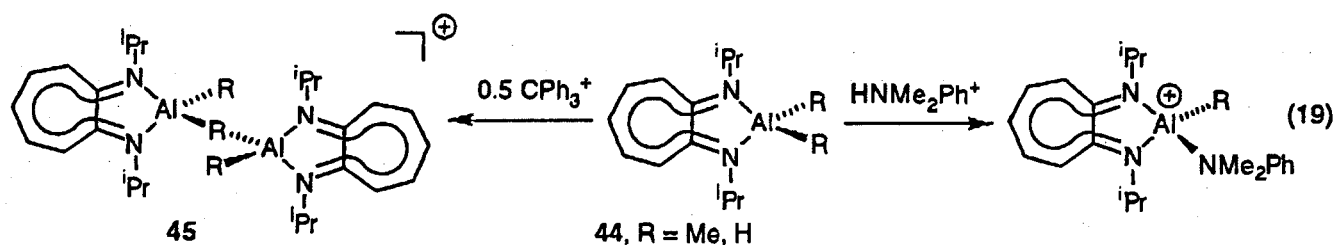
(iii) Cationic Aluminum Alkyl Compounds.[14] Our work on cationic non-metallocene d^0 metal alkyls shows that the key active site "design requirements" which have been identified for metallocene catalysts may be generalized to a wide variety of transition metal systems. Do these concepts apply to main group systems? To probe this possibility we investigated the chemistry of 3-coordinate {L-X}AlR^+ 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 {$RC(NR')_2$}AlR''_2 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 {$RC(NR')_2$}$AlMe_2$ compounds containing moderately bulky amidinates with cationic activators yields {$RC(NR')_2$}$Al(Me)(L')^+$ cations by methyl abstraction (eq 17,18). In these species, the

{RC(NR')$_2$}AlMe$^+$ cation is stabilized by an additional donor group (L' = {RC(NR')$_2$}AlMe$_2$ (41,42), NMe$_2$Ph, PMe$_3$ or MeB(C$_6$F$_5$)$_3^-$) (43), the precise product depending on the coordinating ability of potential ligands. Low temperature NMR studies establish that acetamidinate complex 41 has a dinuclear µ-Me structure. Pivamidinate cation 42 is more labile due to the increased steric crowding of the {^{t}BuC(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 McB(C$_6$F$_5$)$_3^-$ adducts (e.g. 43) decompose rapidly to {RC(NR')$_2$}Al(Me)(C$_6$F$_5$).

(iii) To disfavor the formation of dinuclear species by coordination of {L-X}AlR$_2$ 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-^{i}Pr$_2$-aminotroponiminate complexes {^{i}Pr$_2$-ATI}AlR$_2$ (44, R = H, Me)[17] with [Ph$_3$C][B(C$_6$F$_5$)$_4$] yields dinuclear [{^{i}Pr$_2$-ATI}Al(R)]$_2$(µ-R)$^+$ cations 45 (eq 19). An X-ray crystallographic analysis of [{^{i}Pr$_2$-ATI}AlMe]$_2$(µ-Me)][B(C$_6$F$_5$)$_4$] (Fig. 1f) confirmed the structure shown in eq 19 (< Al-Me-Al = 167.8°) and established that the anion is non-coordinating. In contrast, the reaction of {^{i}Pr$_2$-ATI}AlEt$_2$ and {^{i}Pr$_2$-ATI}Al^{i}Bu$_2$ yields isolable base-free, non-agostic {^{i}Pr$_2$-ATI}AlR$^+$ species 46 by β-hydride abstraction (eq 20)!

(19)

(20)

(iv) 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 $1\text{-}5 \times 10^3$ 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 $C_8\text{-}C_{20}$ α-olefins at high ethylene pressures and temperatures above 120 °C.[18] 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.[19] 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 β-H elimination by selectively strengthening the Al-R bond.[20] 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.
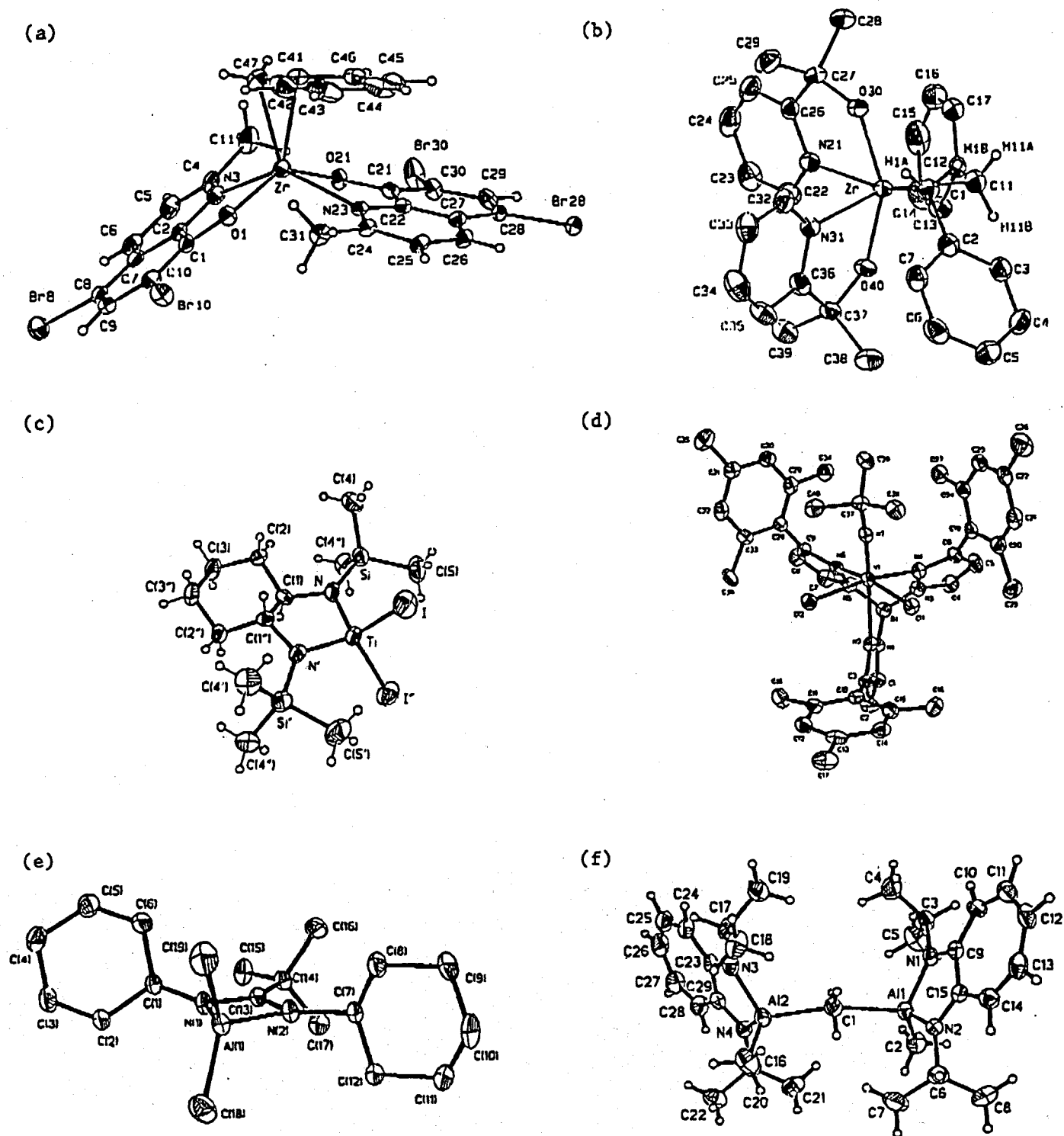
(a)

(b)

(c)

(d)

(e)

(f)

Figure 1. Molecular structures of (a) $(MeBr_2Ox)_2Zr(\eta^2\text{-}CH_2Ph)^+$ (the $B(C_6F_5)_4^-$ anion is not shown), (b) $\{pyCMe_2O\}_2Zr(CH_2Ph)_2$, (c) $\{trans\text{-}1,2\text{-}(NSiMe_3)_2\text{-}Cy\}TiI_2$, (d) $\{Tp^{Mes}\}V(N^tBu)Cl_2$, (e) $\{^tBuC(NCy)_2\}AlMe_2$ and (f) $[\{^iPr_2\text{-}ATI\}AlMe]_2(\mu\text{-}Me)^+$ (the $B(C_6F_5)_4^-$ anion is not shown).

D. Publications From Previous Project Period (1/1/95 - 8/31/98)

(18) "Cationic Aluminum Alkyl Complexes Incorporating Aminotroponiminate Ligands." Ihara, E.; Young, V. G. Jr.; Jordan, R. F. *J. Am. Chem. Soc.*, submitted.

(17) "Tris(pyrazolyl)borate Complexes of Titanium(IV). Synthesis, Structures and Ethylene Polymerization Activity. Casagrande, O. L.; Jordan, R. F.; Young, V. G., Jr. (manuscript complete; submission pending submission of patent application).

(16) "Tris(pyrazolyl)borate Imido Complexes of Vanadium(V). Synthesis, Structures and Ethylene Polymerization Activity." Casagrande, O. L.; Aiub, A. C.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. (manuscript complete; submission pending submission of patent application).

(15) "Aluminum Complexes Incorporating Bulky Nitrogen and Sulfur Donor Ligands." Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. *Organometallics*, submitted.

(14) "Aluminum Alkyl Complexes Containing Guanidinate Ligands." Aeilts, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. *Organometallics*, in press.

(13) "Neutral and Cationic Group 4 Metal Compounds Containing Octamethyl-dibenzo-tetraaza-annulene Ligands. Synthesis and Reactivity of (Me$_8$taa)MX$_2$ and (Me$_8$taa)MX$^+$ Complexes (M = Zr, Hf; X = Cl, hydrocarbyl, NR$_2$, OR)." Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* 1998, *17*, 382-397.

(12) "Olefin Polymerization Promoted by Monodicarbollide Complexes of Group 4 Metals." Saccheo, S.; Gioia, G.; Grassi, A.; Bowen, D. E.; Jordan, R. F. *J. Mol. Catal. A* 1998, *128*, 111-118.

(11) "Synthesis and Structures of Mono- and Bis-Amidinate Complexes of Aluminum." Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. *Organometallics* 1997, *16*, 5183-5194.

(10) "Cationic Aluminum Alkyl Complexes Incorporating Amidinate Ligands. Transition-Metal-Free Ethylene Polymerization Catalysts." Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* 1997, *119*, 8125-8126.

(9) "New Chiral Amide Ligands Derived from (±)-*trans*-1,2-Diaminocyclohexane. Applications in Ti(IV) Chemistry." Tsuie, B.; Swenson, D. C.; Jordan, R. F. *Organometallics* 1997, *16*, 1392-1400.

(8) "Synthesis, Structures, Bonding and Ethylene Reactivity of Group 4 Metal Alkyl Complexes Incorporating 8-Quinolinolato Ligands." Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* 1997, *16*, 3282-3302.

(7) "Synthesis, Structures, Dynamics and Olefin Polymerization Behavior of Group 4 Metal (pyCR$_2$O)$_2$M(NR$_2$)$_2$ Complexes Containing Bidentate Pyridine-Alkoxide Ancillary Ligands." Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G.P.A. *Organometallics* 1997, *16*, 3314-3323.

(6) "Neutral and Cationic Zirconium Benzyl Complexes Containing Bidentate Pyridine-Alkoxide Ligands. Synthesis and Olefin Polymerization Chemistry of {pyCR$_2$O}$_2$Zr(CH$_2$Ph)$_2$ and {pyCR$_2$O}$_2$Zr(CH$_2$Ph)$^+$ Complexes." Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* 1997, *16*, 3303-3313.

(5) "Structural Trends in Group 4 Metal Tetraaza Macrocycle Complexes. Molecular Structures of (Me$_4$taen)Zr(O^{t}Bu)$_2$ and (Me$_4$taen)Hf(NMe$_2$)$_2$." Black, D. G.; Jordan, R. F.; Rogers, R. D. *Inorg. Chem.* **1997**, *36*, 103-108.

(4) "Group 4 Metal Mono-Dicarbollide Piano Stool Complexes. Synthesis, Structure, and Reactivity of (η^5-C$_2$B$_9$H$_{11}$)M(NR$_2$)$_2$(NHR$_2$) (M = Zr; R = Et; M = Ti, R = Me, Et)." Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630-3635.

(3) "Tetraaza Macrocycles as Ancillary Ligands in Early Metal Alkyl Chemistry. Synthesis and Characterization of Out-of-Plane (Me$_4$taen)ZrX$_2$ (X = alkyl, benzyl, NMe$_2$, Cl) and (Me$_4$taen)ZrX$_2$(NHMe$_2$) (X = Cl, CCPh) Complexes." Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539-3550.

(2) "New Cationic Group 4 Metal Alkyl Complexes." Tjaden, E. B.; Jordan, R. F. *Makromol. Chem., Macromol. Symp.* **1995**, *89*, 231-235.

(1) "Synthesis, Structures, and Reactivity of (R$_6$-acen)ZrR'$_2$ and (R$_6$-acen)Zr(R')$^+$ Complexes (R = H, F; R' = CH$_2$CMe$_3$, CH$_2$Ph)." 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.