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Assembling Heterometals through Oxygen: An Efficient Way To Design Homogeneous Catalysts

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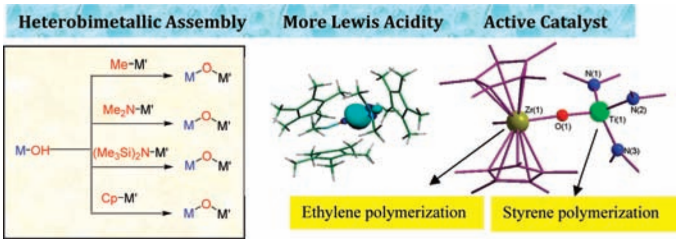
CONSPECTUS



Assembling a molecule containing two metal centers with entirely different chemical properties remains a synthetic challenge. One of the major motivations for this chemistry is its ability to catalyze various organic transformations. The proximity between two different metals in a heterometallic complex allows more pronounced chemical communication between the metals and often leads to the modification of the fundamental properties of the individual metal atoms through the well-known *cooperative interaction*. Although various types of heterometallic systems are known, the M—O—M′ framework is particularly important because it brings the metals into close proximity with each other.

In this Account, we describe several suitable synthetic routes for the assembly of heterometals of entirely different chemical properties through an oxygen atom. The new synthetic strategies for the construction of heterobimetallic complexes take advantage of unprecedented syntheses of a number of hydroxide precursors of the type LMR(OH) [$L = CH\{N(Ar)(CMe)\}_2$, $Ar = 2,6\text{-}i Pr_2C_6H_3$; M = Al, Ga, or Ge; R = alkyl, aryl, or lone pair of electrons], $[LSr(\mu\text{-}OH)]_2\cdot(THF)_3$, and $Cp^*_2ZrMe(OH)$. We used the Brønsted acidic character of the proton in the M(O—H), Sr(O—H), or Zr(O—H) moiety, to build a new class of heterobimetallic complexes based on M—O—M′ motif. This synthetic strategy assembles a main group element with another main group element, a transition metal, or a lanthanide metal.

This synthetic development provides access to a new class of heterobimetallic complexes through oxygen bridging. In many cases these complexes prove to be excellent candidates for polymerization of monomers including ε-caprolactone, ethylene, and styrene. Some of these catalysts bear a chemically grafted methylalumoxane (MAO) unit in the backbone of an active metal center, which led to efficient ethylene polymerizations at an unusually low MAO concentration. We attribute this reactivity both to the presence of a chemically grafted (Me)Al—O backbone in the active catalysts (a part of externally added cocatalyst, MAO) and to the enhanced Lewis acidity from the bridging oxygen at the active metal center.

In addition, we have demonstrated the development of heterometallic systems having two catalytically active centers. Such structures could aid in the development of a catalytic system bearing two active centers with different chemistries.

1. Introduction

It is generally assumed that properly designed hetero- and multimetallic systems would provide new reactivity patterns and physical properties that could not be achieved in the similar monometallic systems.[1] Neighboring metals in a multimetallic system are expected to cooperate in promoting reactions, and electronic interactions might lead to distinct physical properties. Cooperative interactions are ubiquitous in biological systems, and nature had constructed numerous multimetallic protein complexes that perform an extraordinary

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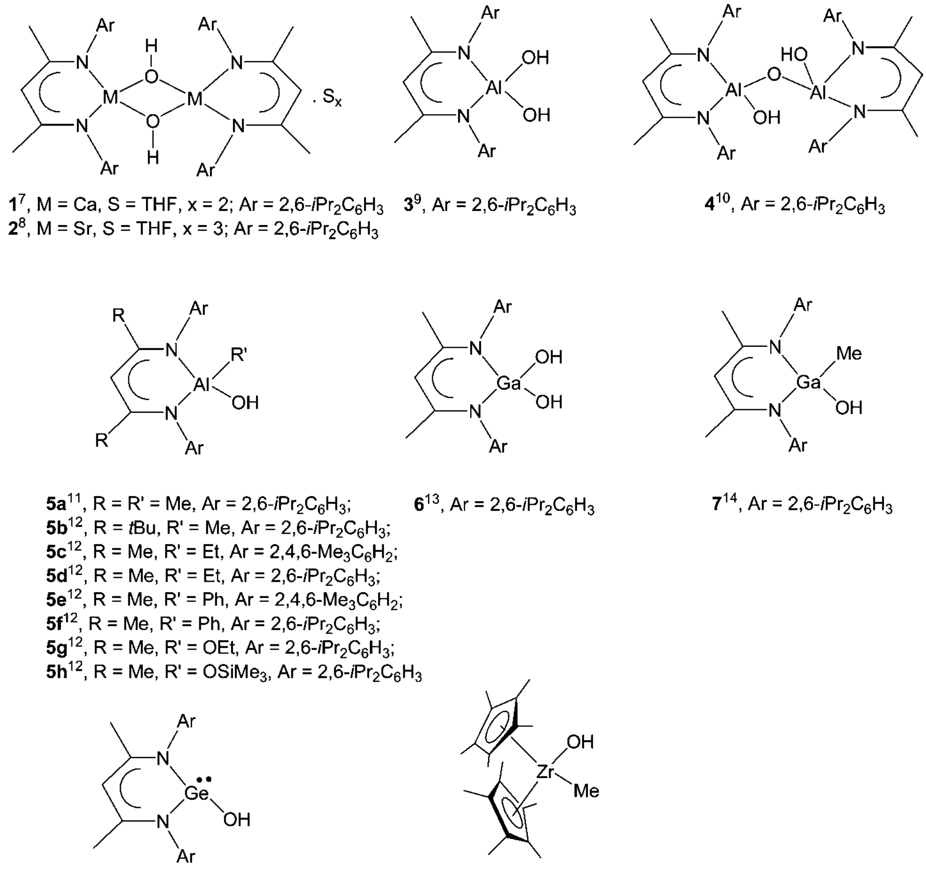
CHART 1. Synthons for Heterometallic Complexes: Main Group and Transition Metal Hydroxides[7−16]



1[7], M = Ca, S = THF, x = 2; Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$
2[8], M = Sr, S = THF, x = 3; Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

3[9], Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

4[10], Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

5a[11], R = R' = Me, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$;
5b[12], R = *t*Bu, R' = Me, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$;
5c[12], R = Me, R' = Et, Ar = $2,4,6\text{-}\mathrm{Me_3C_6H_2}$;
5d[12], R = Me, R' = Et, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$;
5e[12], R = Me, R' = Ph, Ar = $2,4,6\text{-}\mathrm{Me_3C_6H_2}$;
5f[12], R = Me, R' = Ph, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$;
5g[12], R = Me, R' = OEt, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$;
5h[12], R = Me, R' = $\mathrm{OSiMe_3}$, Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

6[13], Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

7[14], Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

8[15], Ar = $2,6\text{-}i\mathrm{Pr_2C_6H_3}$

9[16]

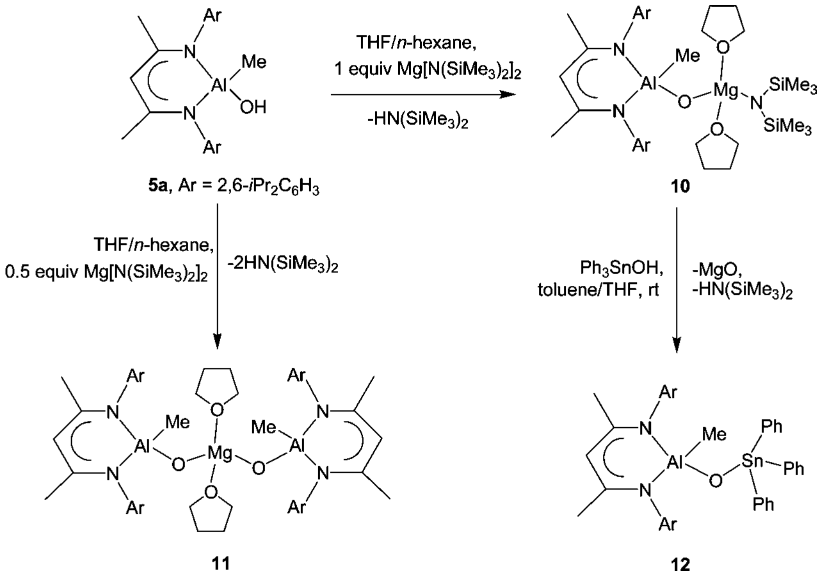
array of catalytic transformations. This has inspired inorganic chemists to persist in developing the area from an inorganic viewpoint. When cooperative interactions are used deliberately in a continual fashion, new and otherwise inaccessible chemistry can be realized, and a new field of supramolecular chemistry[2] could be achieved with a goal to realize even enzyme-like catalytic systems and addressable molecular sensors. Heterometallic complexes in general have enormous potential to revolutionize homogeneous catalytic processes. They can activate both components of a bimolecular reaction simultaneously, overcome entropy barriers associated with bringing two reagents together, and minimize the energy barrier that arises from solvent-shell rearrangements during the reaction by virtue of the cooperative interaction between two different metal centers,[3] and in this way a very important area of "tandem catalysis" has burgeoned in recent years.[4]

Thus, appropriate proximity between two different metals in a heterometallic complex would allow more pronounced chemical communication between the metals. Additionally, it is a synthetic challenge to assemble different metal centers of entirely different chemical properties into a single molecule. Therefore this Account aims to describe several suitable routes to assemble heterometals bound through an oxygen atom with the idea that construction of M−O−M′ will lead to a system in which both metals will be in close proximity to each other. One of the major thrusts for this chemistry is that two different metals are better than one in catalysis owing to the cooperative effect between two metal centers.

2. Assembly of Heterometals: Synthetic Strategy

Hydroxides are well-known building blocks for construction of M−O−M′ motif, and in this way a number of compounds bearing the Si−O−M motif have been prepared.[5] In recent years considerable effort has been ongoing in our laboratory to stabilize terminal hydroxides of main group and transition metals[6] resulting in a number of well-defined hydroxides, **1**−**9** (Chart 1).[7−16] Ready access to these hydroxides (**1**−**9**) opened the possibility to test some of their utility in assembling the heterometals through an oxygen center. The syn-

SCHEME 1. Assembling Magnesium and Tin on an Aluminum Oxide Surface



thetic strategy took advantage of the Brønsted acidic character of the proton in the M(O−H) moiety in assembling a new class of heterometallic complexes. The main group hydroxides can build up new heterometallic complexes with other suitable main group metals, transition metals, or lanthanide metals on a molecular level. Additionally access to the transition metal hydroxide Cp*$_2$ZrMe(OH) (**9**) motivates the possibility to explore **9** in assembling two catalytically active transition metals. The following sections will elucidate this synthetic strategy categorically.

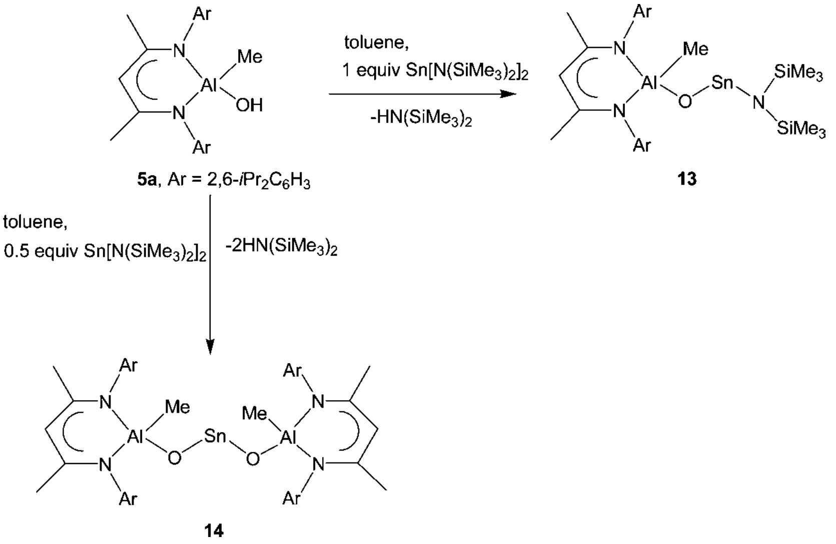
3. Main Group Heterometallic Oxides

There has been a continuously growing interest in the synthesis of heterometallic oxides of main group elements. In this regard, zeolites and aluminosilicates that contain Al−O−Si moieties have found various applications.[17] A facile synthesis of heterometallic compounds containing only main group elements has been designed by utilizing the mild acidity of the aluminum hydroxide LAlMe(OH) [**5a**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$]. The deamination reaction of Mg[N(SiMe$_3$)$_2$]$_2$ leads to heterometallic complexes **10** and **11** where the metal atoms are bridged by oxide groups.[18] The reaction of **5a** with Mg[N(SiMe$_3$)$_2$]$_2$ proceeds in a very controlled manner under elimination of HN(SiMe$_3$)$_2$. The reaction of Mg[N(SiMe$_3$)$_2$]$_2$ with LAlMe(OH) in a 1:1 stoichiometric ratio results in the formation of a compound (**10**) bearing an Al−O−Mg framework (Scheme 1). When Mg[N(SiMe$_3$)$_2$]$_2$ is treated with 2 equiv of LAlMe(OH), it affords compound **11**, with an Al−O−Mg−O−Al framework that proceeds under elimination of 2 equiv of HN(SiMe$_3$)$_2$ (Scheme 1). The Al−O−Mg and (Al−O)$_2$Mg units in these molecules serve as highly soluble model compounds compared with the insoluble spinel (MgAl$_2$O$_4$). Later on, compound **10** was further reacted with Ph$_3$Sn(OH) to yield compound **12** generating the Al−O−Sn motif (Scheme 1).[19] Molecular compounds containing the Al−O−Sn moiety are not very well documented. The reported Al and Sn mixed metallic alkoxides and oxides are dominated by compounds with Sn(IV).[20] Sn(II) and aluminum mixed metallic alkoxides and oxoalkoxides are rarely known, and no pure mixed metallic oxide of Al and Sn(II) was previously reported. Incorporation of the oxide ion between Al and Sn(II) moieties is a synthetic challenge because of no accessible suitable reactive species containing oxides of either Al or Sn reagents. Very recently, we reported a facile route to access mixed heterometallic oxides of Al and Sn(II).[19] A similar deamination reaction of LAlMe(OH) with Sn[N(SiMe$_3$)$_2$]$_2$ leads to the heterometallic complexes **13** and **14** where the metal atoms are bridged by oxide groups. The formation of **13** or **14** is controlled by proper stoichiometric mixing of the precursors (Scheme 2).

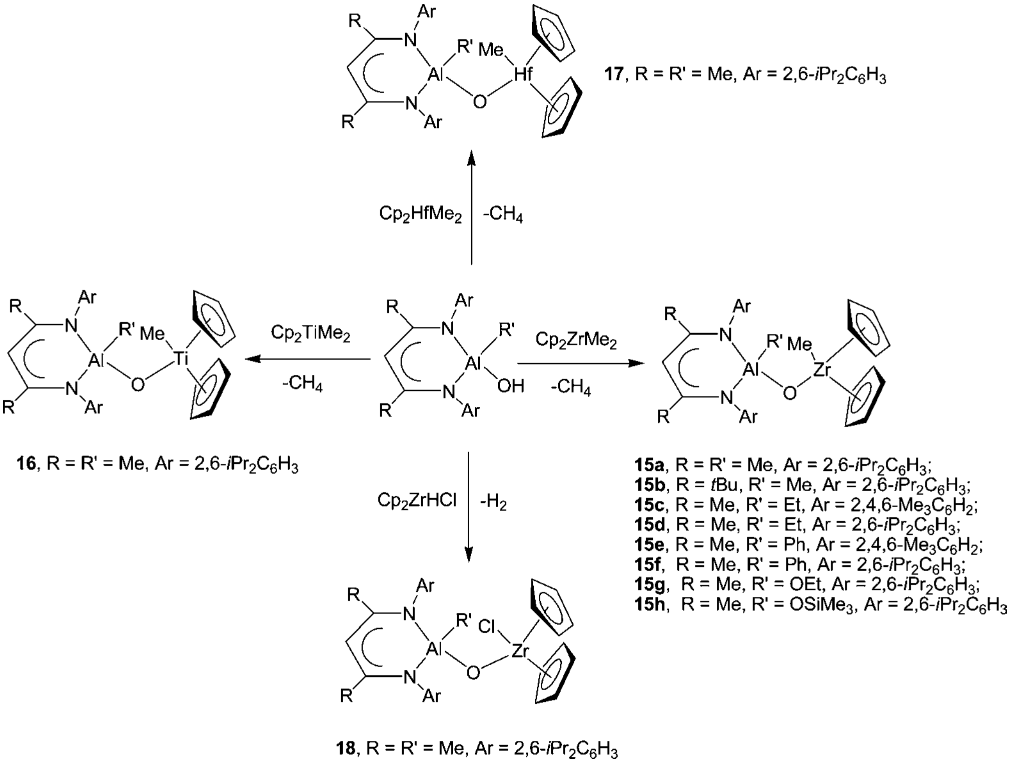
4. Mixed Main Group and Transition Metal Heterometallic Oxides

The synthesis of new transition metal precursors chemically fixed on main group organometallic cocatalysts is a very important subject, which can provide high catalytic activity of the resulting heterometallic compounds with unusual properties. One of the major objectives of this study has been designing a heterometallic system in which a strong Lewis acceptor will be chemically grafted with a catalytically active transition metal center. This section describes the synthetic methodologies adopted in our laboratory during recent years

SCHEME 2. Formation of the Al−O−Sn(II) Motif



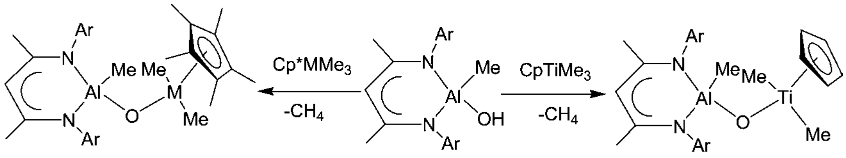
SCHEME 3. Chemical Grafting of Methylalumoxane Core on Metallocene Group 4 Transition Metal Precursors



in achieving the goal of synthesizing heterometallic systems based on the main group element−oxygen−transition metal motif.

Heterometallic Oxides of Aluminum and Group 4 Metallocenes. The first transition metal fixed on main group aluminum through an oxygen center was reported in 2005, when LAlMe(OH) [**5a**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$] was treated with 1 equiv of Cp$_2$ZrMe$_2$ in toluene at 100 °C leading to the formation of O-bridged heterodinuclear complex [LAlMe(μ-O)ZrMeCp$_2$] (**15a**; Scheme 3) in high yield.[11] The driving force for this reaction is the elimination of methane gas. Later on, a series of heterobimetallic complexes of Zr and Al (**15b**−**15h**, Scheme 3) was synthesized adopting similar synthetic methodology.[12] The generality of this reaction was further proven by successful synthesis of heterobimetallic complexes (**16** and **17**, Scheme 3) containing Al−O−Ti and Al−O−Hf cores by treatment of LAlMe(OH) with Cp$_2$TiMe$_2$ and Cp$_2$HfMe$_2$ respectively.[21] Reaction of LAlMe(OH) with a stoi-

SCHEME 4. Preparation of Stable Half-Metallocene Group 4 Transition Metal Compounds



20, M = Ti
21, M = Zr

5a, Ar = 2,6-*i*$Pr_2C_6H_3$

19

chiometric amount of Cp_2ZrHCl in toluene at room temperature results in the formation of O-bridged dinuclear compound [$LAlMe(\mu$-$O)ZrClCp_2$] (**18**; Scheme 3). Clearly the oxophilicity of group 4 metals and Brønsted acidic character of the Al(O−H) moiety resulted in the isolation of these complexes containing an Al−O−M (M = Ti, Zr, or Hf) fragment. The molecular structures of these complexes exhibit a bent Al−O−M core.

Grafting Half-Metallocene Group 4 Metal Precursors on Aluminum Oxide Surfaces. Considerable attention has been devoted to the synthesis, characterization, and catalytic studies of sandwich metallocene complexes; however, homogeneous half-metallocene complexes of group 4 metals bearing terminal methyl groups have received little attention because of the instability of these complexes at ambient temperature. Instability of $Cp'MMe_3$ [$Cp' = C_5H_5$ (Cp) or C_5Me_5 (Cp*); M = Ti or Zr] complexes does not allow them to be used in the polymerization reactions. Preparation of a thermally stable complex bearing one Cp′ and two methyl groups on the metal center remained a synthetic challenge.

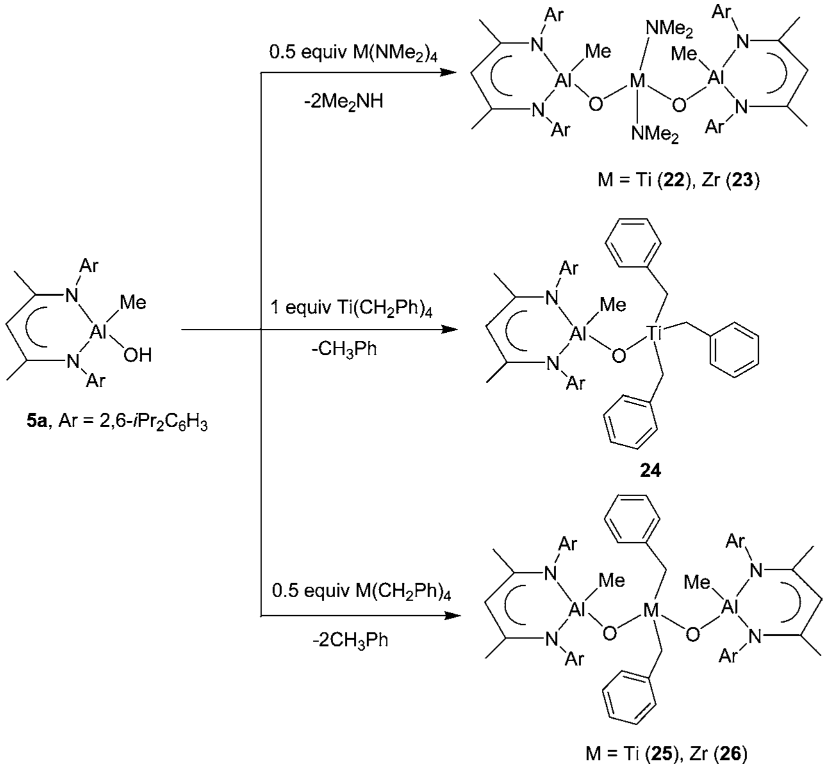
Only recently, we have been successful in establishing a facile route for chemical grafting of half-metallocene group 4 catalyst on an aluminum oxide surface at a molecular level leading to enormous thermal stability in comparison with its parent half-metallocene precursor.[22] The high oxophilicity of titanium in combination with the Brønsted acidic character of LAlMe(OH) [**5a**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$] allowed us to isolate compound **19** (Scheme 4) under methane elimination at low temperature in high yield. The relatively higher thermal stability of Cp^*MMe_3 (M = Ti or Zr) compared with that of $CpTiMe_3$ allowed its reaction with LAlMe(OH) at room temperature to form the oxygen-bridged heterobimetallic compound $LAlMe(\mu$-$O)MMe_2Cp^*$ [M = Ti (**20**) or Zr (**21**); Scheme 4]. The heterobimetallic complexes **19**−**21** exhibit good thermal stability and can be stored for a long period of time at room temperature in the absence of air or moisture, unlike their precursors.

Heterometallic Oxides of Aluminum and Nonmetallocene Group 4 Metal Precursors. There have been ongoing efforts in our laboratory to accomplish models of chemical fixation of nonmetallocene group 4 transition metal precursors on an aluminum oxide surface by taking advantage of the acidic character of LAlMe(OH) [**5a**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$]. For some time, we have been actively involved in the synthesis of a compound bearing an Al−O−M−O−Al trimetallic core with a catalytically active transition metal center (M). Synthesis of complexes bearing the oxygen-bridged trimetallic Al−O−M−O−Al [M = Ti (**22**) or Zr (**23**); Scheme 5] core was accomplished by reacting the monometallic hydroxide LAlMe(OH) with less sterically crowded nonmetallocene group 4 metal precursor $M(NMe_2)_4$ under elimination of Me_2NH.[23] Subsequently we used other nonmetallocene group 4 precursors to accomplish more trimetallic complexes similar to the type discussed above.[24] Reaction of $TiBz_4$ (Bz = benzyl), with LAlMe(OH) affords $LAlMe(\mu$-$O)TiBz_3$ (**24**) and [$LAlMe(\mu$-$O)]_2TiBz_2$ (**25**) depending on reaction stoichiometry (Scheme 5). The analogous reaction of $ZrBz_4$ with LAlMe(OH) results only in the formation of a trimetallic complex [$LAlMe(\mu$-$O)]_2ZrBz_2$ (**26**; Scheme 5).

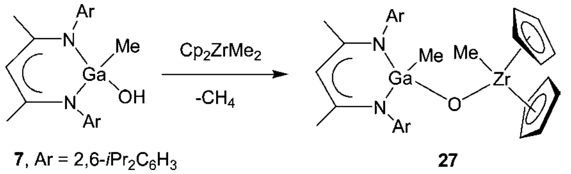
Heterometallic Oxides of Gallium and Group 4 Metals. Although considerable attention was paid to synthesizing and characterizing aluminum-based heterometallic complexes, only very few studies are known dealing with gallium-based oxygen-bridged heterometallic complexes. The first heterobimetallic compound with a Ga−O−Zr core, [$LGaMe(\mu$-$O)ZrMeCp_2$] (**27**) was reported in 2006 using LGaMe(OH) [**7**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$] as a synthon.[14] The reaction of **7** with Cp_2ZrMe_2 in toluene leads to the formation of **27** under methane evolution (Scheme 6). Compound **27** represents the first example of an X-ray characterized molecule with a Ga−O−Zr core.

Assembling Alkaline Earth Metals with Transition Metals. Successful preparation of the organic substituted strontium hydroxide [$LSr(THF)(\mu$-$OH)_2Sr(THF)_2L$] [**2**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$] soluble in common organic solvents allowed us to study the reactivity of the hydroxide groups present in **2**. The strontium hydroxide **2** was used for construction of a heterometallic complex by deamination reaction. Treatment of **2** with 2 equiv of $Zr(NMe_2)_4$ in toluene at −60 °C leads to the intermolecular elimination of 2 equiv of Me_2NH and results in the μ-oxo-bridged complex [$LSr(\mu$-$O)Zr(NMe_2)_3]_2$ (**28**, Scheme 7) as a

SCHEME 5. Nonmetallocene Group 4 Transition Metal Precursors on Aluminum Oxide Surfaces



SCHEME 6. Assembling Gallium and Zirconium



colorless solid.[8] Compound **28** is dimeric in the solid state and contains a $Sr_2Zr_2O_2$ core, and this dimerization results in the formation of a planar four-membered Zr_2O_2 ring.

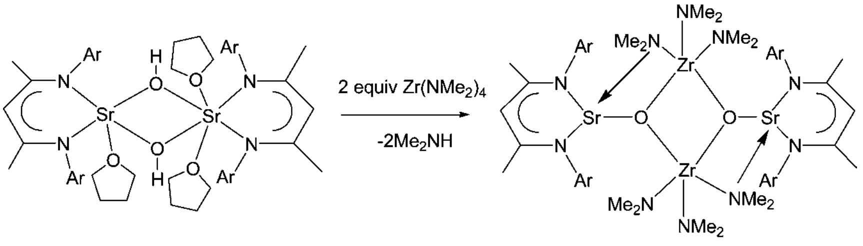
Heterometallic Oxides of Germanium and Transition Metals. The germanium hydroxide LGe(OH) [**8**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$, Chart 1] was used as a precursor building block for chemical fixation of group 4 transition metal precursors.[25] The reaction of **8** with Cp_2MMe_2 [M = Zr or Hf] under methane evolution leads to the isolation and characterization of the first μ-oxo heterobimetallic oxide system [LGe(μ-O)MMeCp_2] [M = Zr (**29**) or Hf (**30**)] of germanium(II) and a group 4 transition metal (Scheme 8). Compounds **29** and **30** were characterized by single-crystal X-ray diffraction studies exhibiting a bent Ge−O−M arrangement (143.8° in **29** and 141.9° in **30**). A distorted tetrahedral geometry can be assigned around the germanium center assuming that a lone pair of electrons occupies the fourth vacant site.

5. Mixed Main Group Lanthanide Metal Heterometallic Oxides

There is widespread interest in the heterometallic chemistry of lanthanides containing main group elements as heteroatoms. The heterometallic complexes of lanthanides and main group elements are good catalysts for the polymerization of olefinic monomers such as methyl methacrylate (MMA), lactones, and cyclic carbonates. Synthesis of a new class of compounds containing a Ln−O−Al moiety has been accomplished by the reaction of LAlMe(OH) [**5a**, L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$] with a series of Cp_3Ln compounds.[26] The terminal Al−OH group exhibits selective reactivity, and the complexes LAlMe(μ-OH)LnCp_3 [Ln = Sm (**31**), Dy (**32**), or Er (**33**)], LAlMe(μ-O)LnCp_2(THF) [Ln = Yb (**34**), Dy (**35**), or Er (**36**)], and LAlMe(μ-O)YbCp_2 (**37**) were obtained as shown in Scheme 9. The formation of the Al−O−Ln unit has been found to be a multistep process (Scheme 9) especially when the reactions are carried out in a noncoordinating solvent like toluene. The first step is formation of an adduct LAlMe(μ-OH)LnCp_3, which subsequently eliminates CpH in the second step to generate Al−O−Ln compounds in the presence of a coordinating solvent like THF.

In view of the extensive interest in the chemistry of lanthanide compounds containing hetero-main group atoms, we

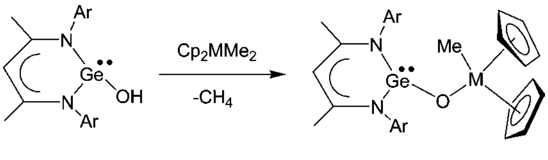
SCHEME 7. Formation of the Sr−O−Zr Core



2, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

28

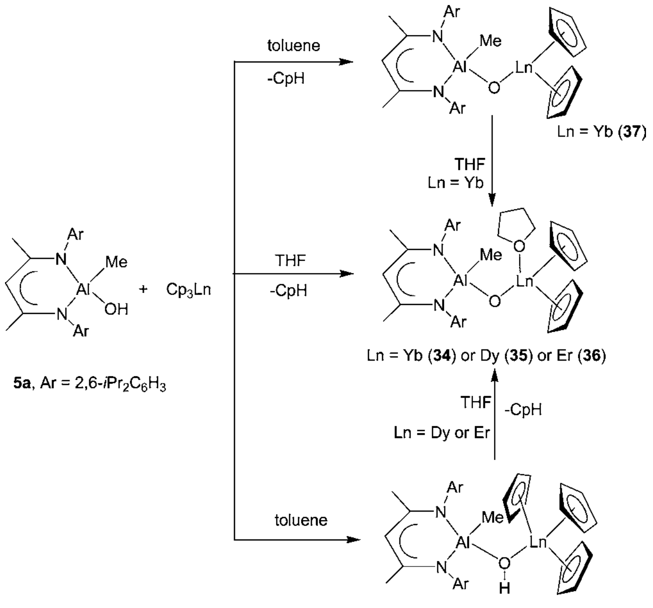
SCHEME 8. Germanium(II) Fixed at a Transition Metal Oxide Site



8, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

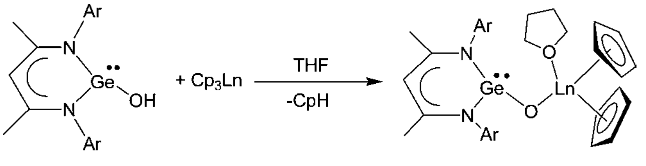
29, M = Zr;
30, M = Hf

SCHEME 9. Construction of Molecular Compounds with Aluminum and Lanthanides



Ln = Sm (**31**) or Dy (**32**) or Er (**33**)

SCHEME 10. Lanthanides on Germanium(II)



8, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Ln = Yb (**38**) or Y (**39**)

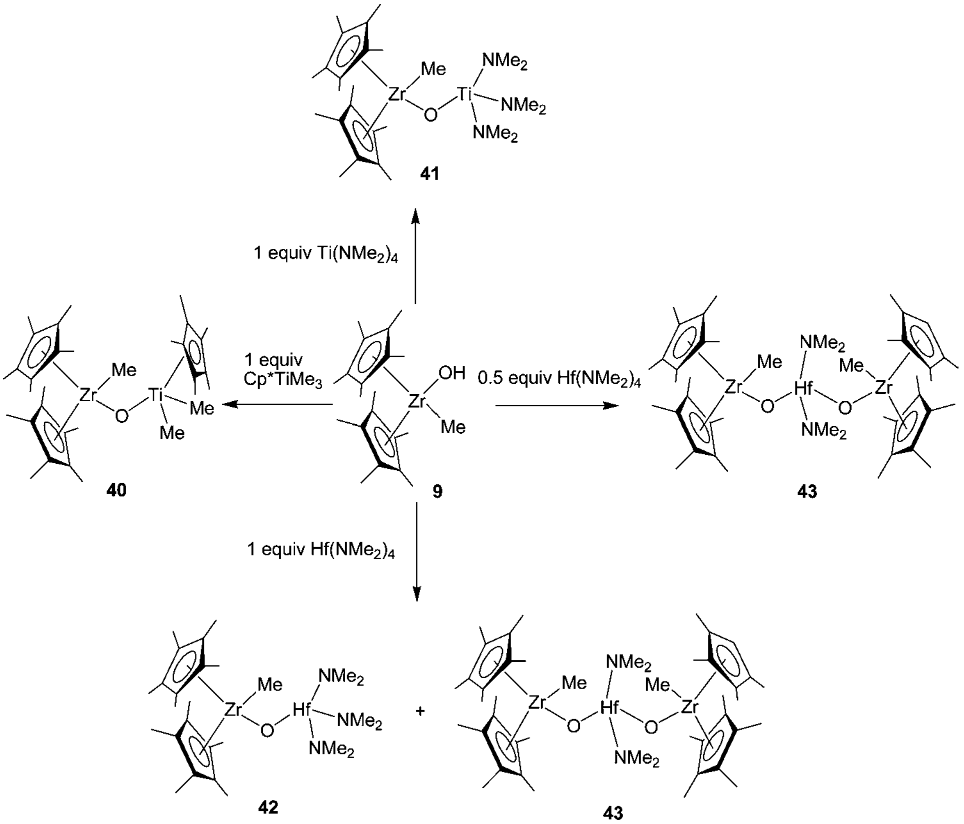
prepared LGe(μ-O)MCp$_2$(THF) [M = Yb (**38**), Y (**39**); L = CH{N(Ar)(CMe)}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] as shown in Scheme 10, and compounds **38** and **39** are the only examples of a Ge−O−Ln linkage bearing a germanium(II) center.[27] The N−Ge−N bond angles in these complexes are found to be less than 90°, which may be attributed to the stereochemically active lone pair of electrons demanding higher angular volume for its accommodation.

6. Hetero-Transition Metal Assembly

The assembly of different transition metals on a molecular level could be advantageous in view of the development of a bimodal catalytic system bearing more than one catalytically active center with different catalytic activity. Therefore the attractive possibility of bringing two catalytic centers in close constrained proximity offers the potential for significantly enhanced catalytic efficiency. In this section, we will address suitable synthetic routes to the heterometallic complexes in which two catalytically active transition metal centers are connected by an oxygen atom.

Assembly of two catalytically active metal centers through an oxide linkage was possible recently by using the Brønsted acidic character of the proton in the Zr(O−H) moiety of Cp$^*_2$ZrMe(OH) (**9**). The first heterobimetallic complex, Cp$^*_2$ZrMe(μ-O)TiMe$_2$Cp* (**40**, Scheme 11), bearing two catalytically active metal centers was synthesized recently by reacting **9** with Cp*TiMe$_3$ (Cp* = C$_5$Me$_5$) at room temperature under elimination of methane.[16] The first report of oxo-bridged trimetallic complexes of only transition metals was accomplished by introducing sterically less demanding transition metal precursors.[28] At first it was thought that synthesis of Cp$^*_2$ZrMe(μ-O)Ti(NMe$_2$)$_3$ (**41**) might lead to the formation of a trimetallic complex by further reaction of **41** with **9**. Compound **41** does not undergo further reaction with **9** to form a heterotrimetallic complex, which can probably be attributed to the steric demand imposed by the bulky Cp* ligands of **9**, hindering further transformation of **41** into a trimetallic complex. However, the reaction of Hf(NMe$_2$)$_4$ with Cp$^*_2$ZrMe(OH) (**9**) proceeds in a different way. The reaction of Cp$^*_2$ZrMe(OH) in toluene with Hf(NMe$_2$)$_4$ in a 1:1 stoichiometric ratio yields a colorless heterobimetallic compound Cp$^*_2$ZrMe(μ-O)Hf(NMe$_2$)$_3$ (**42**) along with another minor product in a 4:1 molar ratio.

SCHEME 11. Construction of Hetero-Transition Metal Assembly



The minor compound was formulated as a trimetallic complex **43** after its exclusive preparation using $Cp^*_2ZrMe(OH)$ and $Hf(NMe_2)_4$ in a 2:1 stoichiometric ratio (Scheme 11).

7. Polymerization Catalysis

One of the most exciting developments in the areas of homogeneous catalysis in recent years has been the intense exploration and commercialization of new polymerization technologies based on design of new catalysts for olefin polymerization, and as a result, the design and synthesis of a vast number of single-site homogeneous catalysts have been developed in the last few decades.[29,30] Shortly after the famous discovery of the polymerization catalyst by Ziegler and Natta for the polymerization of various α-olefins to produce many of the polyolefin products commonly termed "plastics", the seminal work by Sinn and Kaminsky introduced methylalumoxane (MAO) as a cocatalyst to generate highly active catalysts for the polymerization of ethylene and propylene.[30] Due to the use of a high amount of MAO, high temperature, and poorly understood cocatalyst MAO system, efforts have been made to develop MAO-free catalyst systems.[31] Specifically designed transition metal complexes (catalyst precursors) chemically fixed with main group organometallic compounds (cocatalysts) might provide high catalytic activity with low cocatalyst to catalyst precursor ratio. Additionally, a catalytic system in which a strong Lewis acceptor is chemically grafted can in turn make the catalytically active metal center more electrophilic in nature thereby activating the nucleophilic monomers more easily. Keeping these issues in mind, a number of heterometallic compounds based on the M−O−M′ motif were tested to check the efficacy of these compounds as catalysts for ring-opening polymerization and olefin polymerization reactions. Three types of monomers were used for this study, namely, ε-caprolactone, ethylene, and styrene.

Ring-Opening Polymerization of ε-Caprolactone. The synthesis of mixed main group and lanthanide based heterometallic oxides **31**−**39** (Schemes 9 and 10) allowed us to test the efficacy of some of these compounds for ring-opening polymerization reaction of lactones.[26] Ring-opening polymerization of lactones is an important process since the polymer is biodegradable and of practical application. The catalytic property of complexes **32**, **34**, **35**, and **37** for the polymerization of ε-caprolactone was preliminarily investigated. These complexes exhibited living catalyst activity with almost quantitative yield and narrow polydispersities (M_w/M_n) on the order of 1.5−1.7 at ambient temperature in THF or toluene.

Ethylene Polymerization Studies. Some of these oxygen-bridged heterometallic compounds were found very active as catalysts in ethylene polymerization. All polymerization reactions were carried out under extremely mild conditions at room temperature and at ambient pressure using methylalumoxane (MAO) as cocatalyst. The highest activity (activity = g polyethylene/(mol catalyst·h)) on the order of 10^6 was observed for the complexes of the type [LAlMe(μ-O)MRCp$_2$] (**15a**, **16**, and **18**; Scheme 3) in ethylene polymerization.[11,21] The catalyst **15a** exhibited 2 orders of magnitude higher catalytic activity in ethylene polymerization than that of a standard metallocene catalyst such as Cp_2ZrMe_2 under identical reaction conditions. Slightly lower activity (on the order of 10^5) in ethylene polymerization was observed for the following heterobimetallic complexes: LAlMe(μ-O)TiMe$_2$Cp (**19**),[22] LAlMe(μ-O)TiMe$_2$Cp* (**20**),[22] Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* (**40**),[16] and Cp*$_2$ZrMe(μ-O)Ti(NMe$_2$)$_3$ (**41**).[28] Moderate activity (on the order of 10^4) was observed for LAlMe(μ-O)HfMeCp$_2$ (**17**),[21] [LAlMe(μ-O)]$_2$Ti(NMe$_2$)$_2$ (**22**),[23] [LAlMe(μ-O)]$_2$Zr(NMe$_2$)$_2$ (**23**),[23] and [Cp*$_2$ZrMe(μ-O)]$_2$Hf(NMe$_2$)$_2$ (**43**),[28] and low activity (on the order of 10^3) in the ethylene polymerization was observed for LAlMe(μ-O)Ti(CH$_2$Ph)$_3$ (**24**)[24] and [LAlMe(μ-O)]$_2$Zr(CH$_2$Ph)$_2$ (**26**).[24] Thus, the highest activity is observed for the heterobimetallic complexes in which a metallocene-based active metal center is grafted on the aluminum oxide surface. Also it is worth noting that these complexes exhibit very high activity even at unusually low MAO concentration; for example, LAlMe(μ-O)ZrMeCp$_2$ (**15a**) exhibits activity on the order of 10^6 at a cocatalyst to catalyst ratio of only 136. This observation could probably be attributed to the presence of a chemically grafted (Me)Al—O backbone in the catalysts, a part of externally added cocatalyst MAO.

Preliminary Investigation on the Active Catalytic Species. We have not carried out detailed mechanistic study, and the exact mechanism for the formation of the catalytically active species involved is not yet fully established. To unravel the initiation process of the polymerization reaction an *in situ* NMR investigation was carried out with the heterobimetallic catalyst Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* (**40**).[16] An attempt was made to monitor the active catalytic species formed during the activation of Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* with MAO by ^{1}H NMR spectroscopy at room temperature. Preliminary investigation of the ^{1}H NMR (MAO/**40** = 10) exhibited a clear downfield shift of the Ti—Me (from 0.22 to 0.45 ppm) with concomitant broadening of the Ti—Me resonance. The initial 2:1 relative intensity of Ti—Me protons compared with that of Zr—Me protons in Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* is reduced to 1:1 after the addition of MAO. This suggests that one of the methyl groups attached to the Ti center interacts with Al of MAO probably by forming a monocationic bridged complex of the type [Cp*$_2$ZrMe(μ-O)TiMeCp*]$^+$[(μ-Me)MAO]$^-$. The resonance for the bridged methyl is observed at −0.3 ppm. The methyl protons of the MAO resonate at −0.73 ppm. The resonances for methyl protons of the Cp* rings remain unchanged. The resonances for Zr—Me protons remain unaffected with a slight downfield shift (from 0.4 to 0.5 ppm), indicating that the Zr—Me does not interact with Al of MAO at least at such a low concentration of MAO. This study indicates that in the case of Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* the M—O—M′ unit remains intact at least at low MAO concentration. However, the catalysis is usually carried out at much higher MAO concentration, and it remains an open question to be addressed whether at a higher concentration of MAO (during the catalytic cycle) the M—O—M′ unit stays intact.

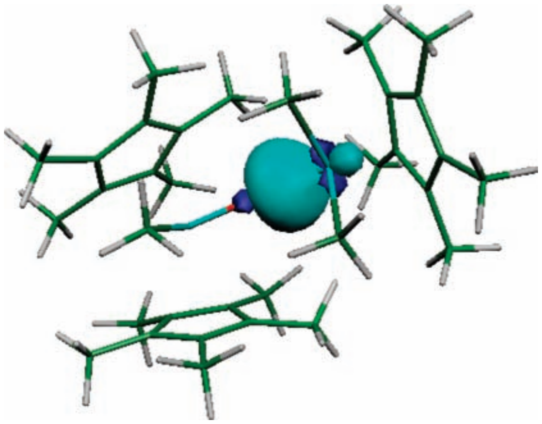
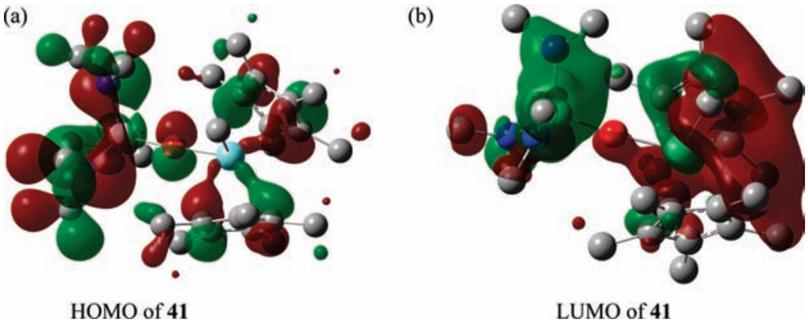


FIGURE 1. Shape of the bonding orbital between zirconium and oxygen in Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* (**40**).

Effect of Oxygen Bridging. Polymerization data show that some of these complexes bearing the M—O—M′ motif are extremely active in ethylene polymerization. This may be attributed to the bridging oxygen, which might draw excess electron density associated with M—O or M′—O bonds leaving the active metal center strongly Lewis acidic. To elucidate the effect of oxygen bridging, we carried out detailed computational study on Cp*$_2$ZrMe(μ-O)TiMe$_2$Cp* (**40**).[16] The NBO analysis shows that the bonds formed between the metal atoms and the oxygen lead to a significant buildup of electron density on the oxygen atom of the corresponding bond (Figure 1).

Styrene Polymerization Studies. Some of these catalysts were found active in styrene polymerization.[21,22,28] All polymerization reactions were carried out at room temperature using methylalumoxane (MAO) as cocatalyst. These complexes show high activity at ambient temperature in toluene when activated with MAO. The activity values of catalyst



HOMO of **41**

LUMO of **41**

FIGURE 2. Computed molecular orbital picture of (a) HOMO and (b) LUMO in $Cp^*_2ZrMe(\mu\text{-}O)Ti(NMe_2)_3$ (**41**).

increase gradually with MAO to catalyst ratio. The catalyst $LAlMe(\mu\text{-}O)TiMe_2Cp^*$ (**20**)[22] exhibits the best catalytic activity (on the order of 10^5), which may be attributed to the formation of a more stable cationic intermediate compared with other catalysts.

Bimodal Catalytic Activity. Homogeneous "tandem catalysis" has received attention as an alternative approach to branched polyethylenes.[4] Since this type of polymerization requires intermolecular processes, it was speculated that the spatial proximity between two metallic centers might perform such functions more efficiently.[4c] The synthesis of heterometallic complexes (**40**−**43**, Scheme 11) bearing two catalytically active transition metal centers introduced the attractive possibility to test their bimodal catalytic activity in ethylene and styrene polymerization. The oxygen-bridged hybrid metallocene−nonmetallocene compound $Cp^*_2ZrMe(\mu\text{-}O)Ti(NMe_2)_3$ (**41**) exhibits bimodal activity in olefin polymerization when activated with MAO.[28] It produces polyethylene largely by the zirconium center and also polymerizes styrene predominantly by the titanium center as revealed by the control experiments carried out with $Cp^*_2ZrMe_2$ and $Ti(NMe_2)_4$ as catalysts. DFT calculations were performed on the supposed cationic intermediates to understand the catalytic process. The molecular orbital picture of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) clearly reveals that the two metallic centers are quite different in terms of the distribution of electron density (Figure 2). The calculations reveal that a cation generated on titanium is sterically more accessible for monomer binding, though it is energetically less favorable than that generated on the zirconium center. The thermodynamic data unravels that the formation of the Zr-centered cation or the Ti-centered cation is feasible energetically; however, the energy difference between the neutral compound and the Ti-centered cation is 3.5 times higher than that with the Zr-centered cation (Figure 3). Thus, it seems reasonable to think that in the polymerization process the zirconium centered cation being energetically more favorable predominantly takes control on the ethylene polymerization performed at a relatively lower MAO to catalyst ratio, and the titanium-centered cation being sterically favored predominantly takes control on the styrene polymerization performed at a relatively higher MAO to catalyst ratio.

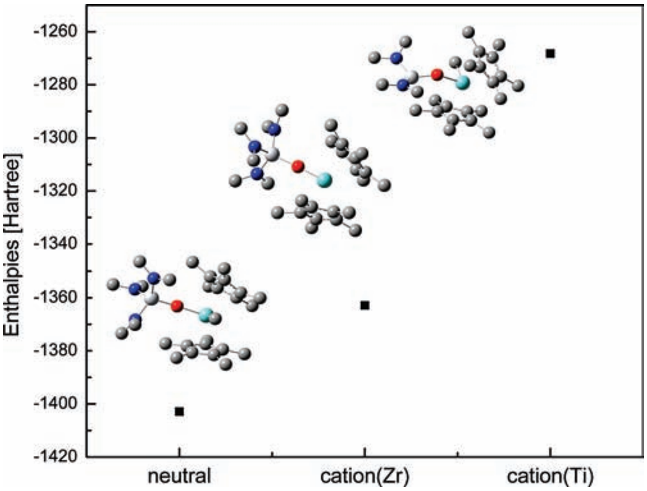


FIGURE 3. Enthalpy differences between the neutral molecule $Cp^*_2ZrMe(\mu\text{-}O)Ti(NMe_2)_3$ (**41**) and corresponding Ti- and Zr-centered cationic species.

8. Summary and Outlook

We have demonstrated a new synthetic route by which a plethora of heterometals can be assembled through an oxygen atom. The synthetic strategy takes advantage of unprecedented syntheses of a number of well-defined hydroxide precursors of the type LMR(OH) [M = Al, Ga, or Ge; R = alkyl, aryl, or lone pair of electrons; L = $CH\{N(Ar)(CMe)\}_2$, Ar = 2,6-$i Pr_2C_6H_3$], $[LSr(\mu\text{-}OH)]_2 \cdot (THF)_3$, and $Cp^*_2ZrMe(OH)$. The Brønsted acidic character of the proton in the M(O−H), Sr(O−H), or Zr(O−H) moiety allows construction of a new class of heterometallic complexes bearing the M−O−M′ motif, and some of them proved to be excellent candidates for polymerization of ε-caprolactone, ethylene, or styrene. It was observed that these catalysts are very active in ethylene polymerization at unusually low MAO concentration, and this may be attributed to the presence of a chemically grafted (Me)Al—O backbone, a part of externally added cocatalyst MAO, in the most active catalysts. Also the bridging oxygen plays an important role in enhancing the Lewis acidity at the active metal center. In addition to it, the development of a heterometallic system having two catalytically active centers extends the possibility to explore the system for two different catalytic reactions, thus a single system would be able to perform two different catalytic reactions, particularly if two such catalytic processes can be integrated in such a way that one center will produce starting materials for the other catalytic center so that one could achieve the goal of a multistep catalytic process by a single system.

It is hoped that this Account will generate interest among chemists to design and synthesize new catalytic systems bearing more than one covalently attached catalytically active center, which is one of the almost unexplored areas of research to be addressed in order to achieve unprecedented control over the polymer microstructure generating new polymers with improved properties. We strongly believe that the outcome of this work will initiate more research in this area leading to the development of new catalytic systems. These new catalytic systems not only will be very attractive for electronic structure calculations for obtaining further insight by investigating the molecular orbitals, bonds, and electron density around the active metal center but also will result in basic knowledge and better understanding of designing active homogeneous catalysts, which is one of the most important areas in organometallic chemistry. New synthetic methods for novel classes of compounds will contribute in the development of inorganic chemistry.

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BIOGRAPHICAL INFORMATION

Swadhin K. Mandal was born in Nadia in 1973. He is currently an assistant professor at the Indian Institute of Science Education and Research—Kolkata in the area of Chemical Sciences since 2007. He received his early chemistry education from the University of Kalyani and obtained his doctoral degree in 2002 under the supervision of Prof. S. S. Krishnamurthy at the Indian Institute of Science, Bangalore. He has been a postdoctoral fellow in the department of chemistry at the University of California, Riverside, with Prof. Robert C. Haddon and also an Alexander von Humboldt fellow at the University of Göttingen with Prof. Herbert W. Roesky. His research interests include areas covering organometallic catalysis, main group chemistry, molecular-based magnetic radical conductors, and nanobiology.

Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He devotes his time to both scientific research and popularizing chemistry to the general public. He is well-known through both his scientific publications and science education experiments. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontier lecturer at Texas A & M University at College Station, University of Texas at Austin, and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists "Leopoldina" in Halle, the Russian Academy of Sciences, Associé étranger de l'Académie des Sciences, Paris, and the Academia Europaea in London. He has served as the Vice President of the German Chemical Society and the President of the Academy of Sciences of Göttingen. He has received many awards, for example, the Leibniz award, le Grand Prix de la Maison de la Chimie, ACS awards in Inorganic and Fluorine Chemistry, the Stock memorial award, and the French Alexander von Humboldt award. Around 1100 research publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and material sciences.

FOOTNOTES

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