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On the Quest for New Mixed-Metal μ-Oxo-bridged Complexes: Synthesis of Compounds Containing Transition Metal−Oxygen− Main Group Metal Motifs M−O−M^1 (M = Ti, Zr; M^1 = Al, Ga) without Cyclopentadienyl Ligands[†]

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The reaction of $TiBz_4$ (Bz = benzyl) with LAlMe(OH), L = $(2,6\text{-}i\text{Pr}_2C_6H_3NC(Me))_2CH$, afforded LAlMe($\mu$-O)$TiBz_3$ (**1**) and [LAlMe(μ-O)]$_2TiBz_2$ (**2**), whereas the corresponding reaction with $ZrBz_4$ resulted only in the formation of the trinuclear species [LAlMe(μ-O)]$_2ZrBz_2$ (**3**). The reaction of $(Mes_2Ga(OH))_2 \cdot THF$ (Mes = 2,4,6-$Me_3C_6H_2$) with $Ti(NEt_2)_4$ yielded the cluster compound $TiGa_6O_7(NEt_2)_2(Mes)_6$ (**4**). All compounds have been characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. Additionally, single crystal X-ray structure data of **1**, **3**, and **4** are reported. Compounds **1**−**4** show low catalytic activities in the polymerization of ethylene. Revisiting known μ-oxo-bridged complexes containing the M−O−M^1 (M = Ti, Zr, Hf; M^1 = Al, Ga) skeleton revealed that the application of polynuclear group 13 hydroxides and oxo bridged complexes possesses a potential for the preparation of new polyoxometal clusters.

Introduction

Organometallic polyoxoclusters containing different metals have recently gained increased interest for application in technical processes, as well as from theoretical aspects. These heteropolymetallic compounds may act as suitable model systems for the immobilization of catalysts at oxide surfaces[1] and for the study of their reactivity and properties.[2]

The metal atoms of heteropolymetallic clusters arranged in close proximity to each other may activate substrate molecules cooperatively or simultaneously; the substrate is able to switch between the metal atoms, something that could not be achieved with mononuclear complexes. It is well-known that μ-oxo bridged aluminum−titanium and aluminum−zirconium complexes possess high catalytic activities in olefin polymerization reactions.[3]

Consequently increasing research activities are focused on the synthesis and characterization of mixed metal oxides that can be employed as multifunctional catalysts or precursors for the preparation of heterobi- and -polymetallic heterogeneous catalysts.[4]

[†] Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday.

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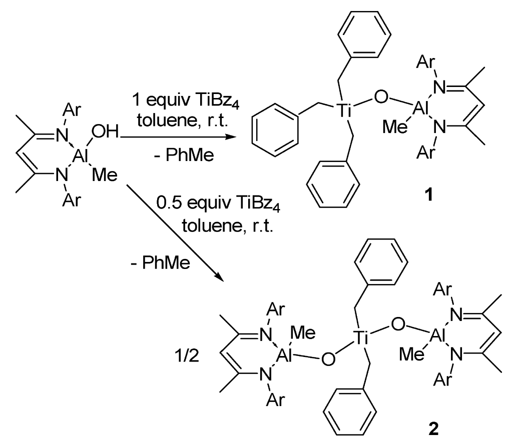
Examples of heterobimetallic μ-oxo-bridged complexes exhibiting M−O−M^1 motifs (M = Ti, Zr, M^1 = Al, Ga) are rare, among them $Cp_2ZrMe(\mu\text{-}O)Al_6O_5(t\text{Bu})_6(Me)$,[3d] $(t\text{Bu})_2Ga(\mu\text{-Neol})_2Ti(\mu\text{-}O)[Ga(t\text{Bu})_2(HNMe_2)]$ ($NeolH_2$ = 2,2-dimethylpropane-1,3-diol)[5] and $L^*TiCl_2(\mu\text{-}O)AlCl_3$ (L* = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine)[6] are known. Recently, we reported a new class of μ-oxo-bridged heterobimetallic complexes containing the M(μ-O)Al core (M = Ti, Zr, Hf).[7] The cyclopentadienyl complexes $CpMX_2(\mu\text{-}O)AlMeL$ (L = NacNac; X = Cl, Me; M = Ti, Zr) possess high catalytic activity in the polymerization of ethylene and are considered as model systems to study the polymerization of olefins. It was suggested that the bridging oxygen plays an important role in the active species, forming a kinetically and thermally stable M(μ-O)Al unit which enhances the Lewis acidity at the metal atoms.[7c] However, the noncyclopentadienyl complexes $LAlMe(\mu\text{-}O)M(NMe_2)_2(\mu\text{-}O)AlMeL$[7f] showed only moderate activity in ethylene polymerization. The complexes $LTiCl_2(\mu\text{-}O)AlMeL$ and $LTiMe_2(\mu\text{-}O)AlMeL$ even were unstable at room temperature.[8]

Therefore, we became interested in new μ-oxo-bridged heterobimetallic systems and quantified the ligand effect on the stability and polymerization activity of heterobimetallic μ-oxo-bridged complexes containing the M(μ-O)Al skeleton. Herein we report on the investigation of the MBz_4−LAlMe(OH) (M = Ti, Zr) and $Ti(NEt_2)_4$−$(Mes_2Ga(OH))_2\cdot$THF systems. We describe the synthesis, characterization, and catalytic activity of new noncyclopentadienyl μ-oxo-bridged bimetallic and trimetallic compounds with an Al−O−M core and a polyoxometal cluster with a $TiGa_6O_7$ skeleton.

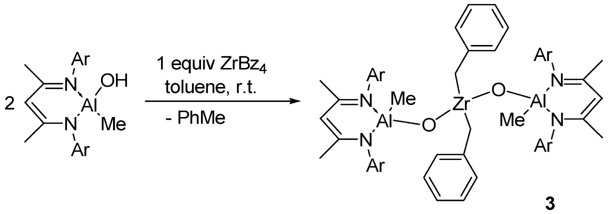
Results and Discussion

For the preparation of μ-oxo-bridged complexes with alkyl functionalities at the Ti(IV) or Zr(IV) atoms we investigated the reaction of MMe_4 with LAlMe(OH) (M = Ti, Zr) as well as that with MBz_4 (Bz = benzyl) and LAlMe(OH). The reaction of the thermally unstable MMe_4 with LAlMe(OH) resulted in the formation of elemental titanium or zirconium. The $TiBz_4$ (Bz = benzyl), stable at room temperature, and LAlMe(OH) afforded $LAlMe(\mu\text{-}O)TiBz_3$ (**1**) and $[LAlMe(\mu\text{-}O)]_2TiBz_2$ (**2**) (Scheme 1). Reactions of 3 to 4 equiv of LAlMe(OH) with $TiBz_4$ resulted in a mixture of **2** and unreacted LAlMe(OH).

Scheme 1. Ar = 2,6-iPr$_2$C$_6$H$_3$



Scheme 2. Ar = 2,6-iPr$_2$C$_6$H$_3$



The analogous reaction of $ZrBz_4$, stable at ambient temperature, with 1 to 4 equiv of LAlMe(OH) resulted in the formation of complex $[LAlMe(\mu\text{-}O)]_2ZrBz_2$ (**3**) (Scheme 2). Compound **3** was obtained as a powder from the reaction in toluene followed by crystallization from n-hexane while crystallization of **3** from DME afforded the $\mathbf{3}\cdot DME_{0.5}$ solvate. Surprisingly, the 1:1 complex could not be detected, the NMR spectrum of the *in situ* 1:1 mixture of $ZrBz_4$:LAlMe(OH) exhibits only resonances for $ZrBz_4$ and **3**.

The results of the MBz_4−LAlMe(OH) (M = Ti, Zr) system as well as those of the previously reported Cp_2MMe_2−LAlMe(OH)[7a,c] and $M(NMe_2)_4$−LAlMe(OH)[7f] showed that only 1:1 and 1:2 complexes could be isolated.

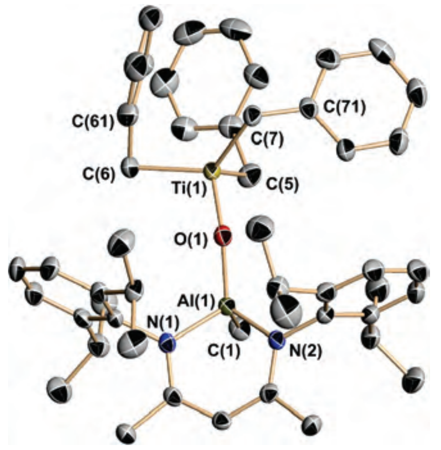


Figure 1. Molecular structure of $LAlMe(\mu\text{-}O)TiBz_3$, **1**, [L = (2,6-$iPr_2C_6H_3$NCMe)$_2$CH)] with selected atoms labeled. Anisotropic displacement parameters are depicted at the 50% probability level. Only one of the two crystallographically independent molecules is shown. For clarity reasons hydrogen atoms are not depicted.

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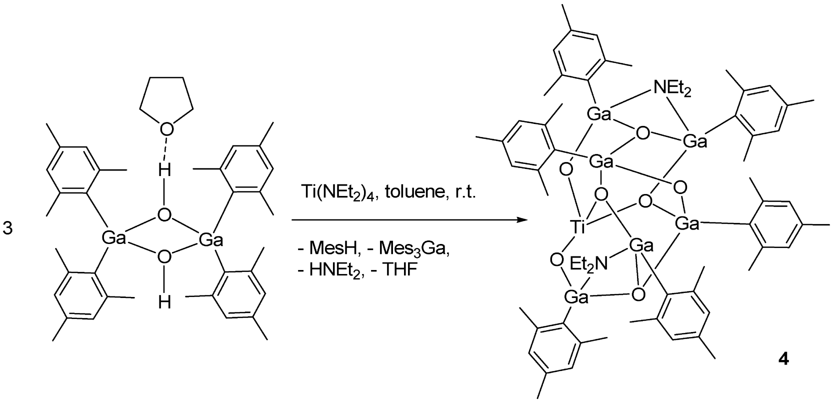
Scheme 3



To prepare a new polyoxometal cluster, we used a gallium hydroxide with less bulky mesityl groups $(Mes_2Ga(OH))_2\cdot THF$ and explored its reaction with MR_4 (R = Bz, NEt_2). It is noteworthy that the corresponding aluminum hydroxide $(Mes_2Al(OH))_2$ is unstable at room temperature. Unfortunately, the reaction of the dimeric gallium hydroxide and MBz_4 gives only unidentifiable products. However, the protocol of 1 and 0.5 equiv of $(Mes_2Ga(OH))_2\cdot THF$ with 1 equiv of $Ti(NEt_2)_4$ in toluene afforded the polyoxometal cluster $TiGa_6O_7(NEt_2)_2(Mes)_6$ (**4**) according to the idealized equation shown in Scheme 3. Compound **4** has been recrystallized from *n*-hexane solution to afford crystals suitable for X-ray structural investigation.

The tendency of $(Mes_2Ga(OH))_2\cdot THF$ to form higher aggregates such as $Mes_6Ga_6O_4(OH)_4$ at room temperature[9] and $(MesGaO)_9$ at elevated temperatures[10] has been described. The reaction of $LTiMe_3$ (L = NacNac) with $(Mes_2Ga(OH))_2\cdot THF$ in toluene afforded the di-μ-oxo bridged complex $LTiMe(\mu\text{-}O)_2TiMeL$ and Mes_3Ga[8] implying oxygen transfer from gallium to titanium, whereas in the reaction depicted in Scheme 3 transfer of the amino substituents from titanium to gallium occurs.

It is noteworthy that Mes_3Ga and unreacted $Ti(NEt_2)_4$ (for a 1:1 ratio of precursors) were detected by NMR spectroscopy in the *in situ* mixture, and $HNEt_2$, MesH, and THF were found in the volatile products.

Characterization of Compounds 1−4. The single crystal structures of **1**, **3**, and **4** (Figures 1 to 5) have been determined by X-ray crystallographic methods. The composition and structure of **2** was deduced from elemental analysis, NMR, and mass spectrometry.

Complexes **1** and **2** are thermally stable (decomp 179 and 187 °C, respectively) and remain unchanged on storage in sealed ampoules for several months at room temperature. The largest ion detected in the mass spectrum of **1** corresponds to $[M - Bz]^+$ (*m*/*z* 705) whereas in the mass spectrum of **2** it is $[M - PhMe]^+$ (*m*/*z* 1088). Further fragments observed in the EI-MS of **1** and **2** are due to the elimination of Bz, PhMe, CH_4, *i*Pr, and $C_6H_3(iPr)_2$ from the molecular ions. The ^1H and ^{13}C NMR data of **1** and **2** are in agreement with the proposed structures (Scheme 1, Figures 1 and 3). The resonance of the CH_2 protons attached to the Ti(IV) atom appears at 2.00 ppm in **1** and at 2.17 ppm in **2** being shifted to low frequency relative to $TiBz_4$ (2.79 ppm).[11]

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and contains two independent molecules in the unit cell with similar structural features (Figure 1).

As expected, **1** contains the aluminum atom bonded through an oxygen atom to titanium. The aluminum atom exhibits a highly distorted tetrahedral coordination site with two nitrogen atoms of the β-diketiminato ligand, the methyl carbon atom, and the (μ-O) atom. The titanium atom also has a distorted tetrahedral coordination sphere comprised of the (μ-O) atom and three CH_2 groups. Moreover, Ti(1) and Ti(2) show close contacts with the carbon atoms of the benzyl group. The shortest contacts are observed between the Ti atoms and the carbon atoms C(61) and C(101) in the β position (2.506 and 2.689 Å, respectively). The contacts $Ti-C_\beta$ range from 2.807 to 3.093 Å (Figure 2). Consequently, the acute C(61)−C(6)−Ti(1) and C(101)−C(10)−Ti(2) angles range from 85.8(1)° to 95.3(2)° while the other $Ti-C_\alpha-C_\beta$ angles range from 101.3(2)° to 116.3(2)°. This implies nonequivalent inter-

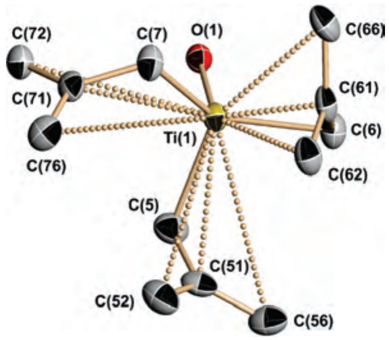


Figure 2. Coordination sphere (4.1 Å) around Ti(1) in **1**. The values in brackets are the corresponding bond lengths for the second molecule. Anisotropic displacement parameters are depicted at the 50% probability level. Selected distances (Å): Ti(1)−C(51) 2.855 (2.689), Ti(1)−C(52) 3.625 (3.315), Ti(1)−C(56) 3.599 (3.416), Ti(1)−C(61) 2.506 (2.807), Ti(1)−C(62) 3.109 (3.651), Ti(1)−C(66) 3.105 (3.354), Ti(1)−C(71) 3.093 (3.036), Ti(1)−C(72) 3.698 (3.758), Ti(1)−C(76) 4.051 (3.856).

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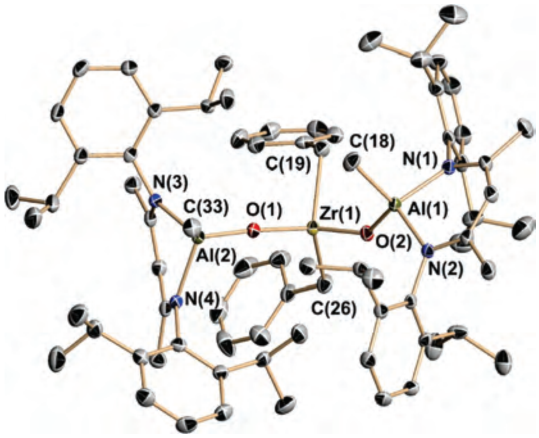

Figure 3. Molecular structure of **3** with selected atoms labeled. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity reasons.

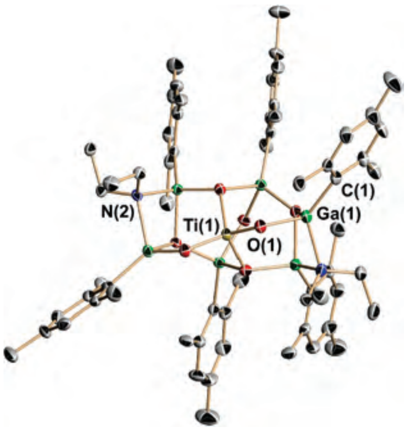

Figure 4. Molecular structure of **4** with selected labeled atoms. Anisotropic displacement parameters are depicted at the 50% probability level. Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity reasons.

actions of the Bz carbon atoms with the titanium atom in **1**. The reported Ti−C$_\beta$ bond lengths in Ti(IV) benzyl complexes are short (2.464(4)−2.647(4) Å) and result in small Ti−C$_\alpha$−C$_\beta$ angles (81.9(2)°−92.5(3)°) (see structures of TiBz$_4$,[12] TiCl$_{3-n}$Bz$_n$(dmpe) (n = 1,2),[13] LTiBz$_2$ (L = *N,N′*-bis(trimethylsilyl)aminobenzylamine),[14] LTiBz$_2$ (L = [OSSO]-type ligand)[15]).

The Al−Me (1.957(2) and 1.959(2) Å), Al−(μ-O) (1.7468(17) and 1.7391(16) Å) bond lengths as well as Ti−(μ-O) distances (1.7506(16) and 1.7483(16) Å) and Al(μ-O)Ti angles (145.4(1)° and 146.5(1)°) compare well with the recently structurally characterized oxygen bridged heterobimetallic compounds of the general formula LAlMe(μ-O)M(R)Cp$_2$ (R = Me, Cl; M = Ti, Zr, Hf).[7] The Ti−CH$_2$ distances (2.112(3)−2.143(2) Å) are also similar to those of the reported Ti(IV) complexes with benzyl ligand (see refs 12–15).

Single crystals of [LAl(Me)(μ-O)]$_2$ZrBz$_2$·DME$_{0.5}$ (**3**) have been obtained by recrystallization from DME. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ (Figure 3).

Both the aluminum and zirconium atoms in **3** exhibit a distorted tetrahedral coordination with [AlN$_2$(Me)(μ-O)] and [Zr(μ-O)$_2$(CH$_2$)$_2$] environments (Figure 3). In contrast to the titanium complex, the zirconium atom shows only weak contacts to the carbon atoms in the β position of the Bz substituent (3.165 and 3.317 Å). Consequently, the C(20)−C(19)−Zr(1) and C(27)−C(26)−Zr(1) angles are larger (113.6(2)° and 121.5(2)°) in comparison to those of the titanium compound **1**. Furthermore, the mean angle Zr−C−C in ZrBz$_4$ is 92° and the average Zr−C$_\beta$ bond length is 2.74 Å.[16] Tetracoordinate zirconium is not common in complexes, and it is only present when the zirconium atom is encapsulated by bulky ligands, for example, in polymeric Cs$_2$Ag$_2$ZrTe$_4$ (ZrTe$_4$ polyhedron),[17] Zr[CH$_2$(CH$_2$NSiMePh$_2$)$_2$]$_2$[18] and Zr[(N*t*Bu)$_2$SiMe$_2$]$_2$[19] (ZrN$_4$ polyhedron), and in ZrCl[N(SiMe$_3$)$_2$]$_3$ (ZrN$_3$Cl polyhedron).[20] Therefore, the tetracoordinate ion in [LAl(Me)(μ-O)]$_2$ZrBz$_2$ (**3**), as well as in the related complex [LAl(Me)(μ-O)]$_2$Zr(NMe$_2$)$_2$,[7f] is the result of two bulky [LAl(Me)(μ-O)] moieties.

The Zr−(μ-O) bond lengths in **3** (1.9132(14) and 1.9143(14) Å) and Al−(μ-O) bond lengths (1.7344(15) and 1.7471(15) Å) are in agreement with those found for [LAl(Me)-(μ-O)]$_2$Zr(NMe$_2$)$_2$ (1.941(2) and 1.944(2) Å),[7f] LAlMe(μ-O)ZrRCp$_2$ (av 1.92 Å) (R = Me, Cl),[7a] and LAlMe(μ-O)TiMeCp$_2$ (1.808(3) Å).[7c] Two types of Al−(μ-O)−Zr bond angles are observed in **3** (175.58(9)° and 141.80(9)°) similar to [LAl(Me)(μ-O)]$_2$Zr(NMe$_2$)$_2$ (166.50(10)° and 173.21(10)°).[7f] The almost linear Al−(μ-O)−Zr bond angle is explained by mutual repulsion of the [LAl(Me)] and [Zr(μ-O)AlMeL] moieties.

Complex **3** is thermally stable (decomp above 130 °C) and remains unchanged on storage in sealed ampoules at room temperature for several months. The ion of highest mass detected in the mass spectrum of **3** is of weak intensity and corresponds to [M − C$_6$H$_3$*i*Pr$_2$ − Bz − PhMe]$^+$ (*m*/*z* 879). Further ions observed in the EI-MS of **3** are mostly due to subsequent loss of Bz, PhMe, and C$_6$H$_3$*i*Pr$_2$ from the molecular ion. The ^{1}H and ^{13}C NMR data of **3** are consistent with the proposed structure (Scheme 2, Figure 3). The ^{1}H NMR resonance of the CH$_2$ group attached to the Zr(IV) atom appears at 1.85 ppm and is shifted to high frequencies in relation to ZrBz$_4$ (1.44 ppm).

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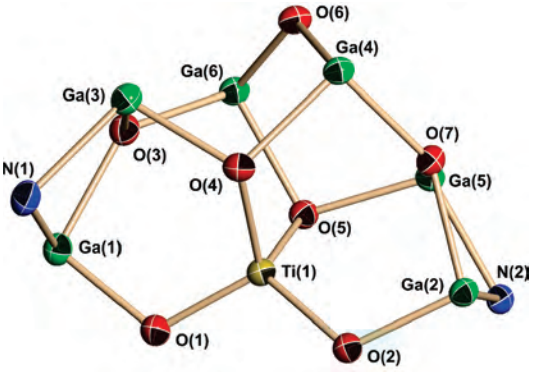

Figure 5. $TiGa_6O_7N_2$ core of **4**. Ellipsoids represent 50% probability levels. Hydrogen atoms are omitted for clarity.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$. It contains two crystallographically independent molecules $TiGa_6O_7(NEt_2)_2(Mes)_6$ in the lattice with almost identical conformation (Figure 4). The core of the molecule consists of a $TiGa_6O_7N_2$ cluster, where the titanium is connected to all gallium atoms via two μ- and two μ_3-bridging oxygen atoms. The two amino nitrogen atoms are bound to two gallium atoms each, one of them being incorporated in the cluster by one μ- and one μ_3-oxygen atom, the other by two μ_3-oxygen atoms. Additionally, each gallium atom is bound to one Mes group.

Four oxygen atoms form a highly distorted tetrahedral environment around the Ti(1) and Ti(2) atoms with two shorter Ti−(μ-O) bond lengths (1.763(3), 1.767(3) Å and Ti(2)−O(9) 1.751(3) Å) and two longer Ti−(μ_3-O) distances (1.888(3), 1.893(3) Å and Ti(2)−O(11) 1.901(3), Ti(2)−O(12) 1.909(3) Å) (angles see Tables 1 and 2). The Ti−(μ-O) bond lengths in cluster **4** are longer than those in $(t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Neol})_2\mathrm{Ti}(\mu\text{-O})[\mathrm{Ga}(t\mathrm{Bu})_2(\mathrm{HNMe}_2)]$ (NeolH_2 = 2,2-dimethylpropane-1,3-diol),[5] (Ti−O 1.725(9) Å, Ga−O 1.94(1) Å) which has only one Ti(μ-O)Ga bond, and two Ti(μ-OR)Ga bonds. Therefore, the latter are different from those of **4**. As a consequence, the Ti−(μ-O) bond in **4** is weaker than in the above-mentioned complex, while the Ga−(μ-O) bond strength is similar (Table 1).

The coordination geometry around the gallium atoms is that of a distorted tetrahedron with Ga−O distances in the range of 1.813(3) to 1.994(3) Å. Longer distances are observed for the Ga−(μ_3-O) bonds and shorter ones for the Ga−(μ-O) bonds. The Ga−N and Ga−C bond lengths are in a narrower range, 1.989 to 2.021 Å (av 2.009 Å) and 1.944(4) to 1.959(6) Å (av 1.953 Å), respectively. The reported Ga−N and Ga−C distances are typical for the Ga−(μ-N)[21] and Ga−C bonds.[9,22] The O−Ga−O and O−Ga−N angles are smaller than the C−Ga−O and C−Ga−N ones because of mutual repulsion of the ligands. The Mes group is sterically more demanding than the oxygen and nitrogen atoms.

The deviation of the Ga−O−Ga angles is caused by the different environment of the oxygen atoms. The smallest Ga−O−Ga angles are observed for the Ga(μ-O)(μ-NEt_2)Ga moiety (95.1(1)° to 95.7(1)°) while the largest Ga−O−Ga angles (135.3(2)° to 136.3(2)°) are found within the Ga(μ_3-O)Ga unit, where one gallium atom belongs to the Ga(μ-O)(μ-N)Ga moiety. The range of Ga−O−Ga angles, as well as that of the Ga−O distances, is close to those of $Mes_6Ga_6O_4(OH)_4$[9a] and $(Mes_2Ga(OH))_2\cdot THF$[9b] while the Ti−O−Ga angles in **4** are slightly larger than the Ti−(μ-O)−Ga angle (106.8(3)°) in $(t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Neol})_2\mathrm{Ti}(\mu\text{-O})[\mathrm{Ga}(t\mathrm{Bu})_2(\mathrm{HNMe}_2)]$.[5]

Compound **4** is stable at room temperature under an inert atmosphere. The biggest ion found in the mass spectrum of **3** corresponds to the $[M - Mes - 6\,Me]^+$ cation (*m/z* 1228). Further ions are due to loss of Me, Et, and Mes substituents and of CH_4 from the molecular ion (see Supporting Information). The ^1H NMR spectrum of **4** contains the expected six resonances of the aromatic protons of the six Mes groups (6.81−6.24 ppm) and nine resonances for the Me protons (1.92 to 2.85 ppm). The relative intensities for aromatic and Me protons is 1:4.5, as expected for **4**. The ethyl groups of NEt_2 give rise to four quintets (3.89, 2.87, 2.76, 2.67 ppm) and two triplets (0.83, 0.37 ppm) because of the nonequivalence of the Et groups in **4**.

Conclusion

We have investigated the MBz_4−LAlMe(OH) system (M = Ti, Zr) and prepared the heterobimetallic complexes LAlMe(μ-O)$TiBz_3$ (**1**), $[LAlMe(\mu\text{-}O)]_2TiBz_2$ (**2**), and $[LAlMe(\mu\text{-}O)]_2ZrBz_2$ (**3**) which are stable at room temperature. Titanium complexes containing more than two LAlMe(μ-O) moieties are not formed from these precursors, instead 1:1 and 1:2 compounds have been obtained. The polynuclear complex $TiGa_6O_7(NEt_2)_2(Mes)_6$ (**4**) was isolated from the reaction of $Ti(NEt_2)_4$ with $(Mes_2Ga(OH))_2\cdot THF$.

In general, the activity of complexes for the polymerization of ethylene is not increased by replacement of the Bz or NEt_2 group at the transition metal atom by the bulky [LAl(Me)O] or (MesGaO) moieties (see Supporting Information). Furthermore, we have compared the stability and polymerization activities of all literature reported and herein investigated μ-oxo bridged complexes (Table 3).

Several conclusions can be drawn from the results of Table 3. Compounds **B** and **C**, containing the bulky NacNac ligand attached to the titanium as well as to the aluminum center, are unstable and decompose in solution. The heterobimetallic complexes **A** and **D**−**Y** with less bulky ligands, such as Cp, NMe_2, or Bz, on the transition metal are stable. Complex **F** contains a bulky ligand on the Ti(IV) center and a small $\{OAlCl_3\}$ moiety connected to the titanium atom. Furthermore, only 1:1 complexes (**A**, **E**, **I**−**K**, **N**, **O**−**Y**) have been obtained from $LM^1Me(OH)$ (M^1 = Al, Ga) and cyclopentadienyl complexes Cp_2MMe_2 (M = Ti, Zr, Hf) or $Cp_2Zr(H)Cl$. However, MR_4 compounds containing less bulky R groups (Bz, NMe_2) than Cp allowed the preparation of stable 1:2 complexes (**G**, **H**, **L**, **M**). Hydrolysis of cyclopentadienyl complexes LAl(μ-S)$_2MCp_2$ (M = Ti, Zr) afforded the 1:1 complexes LAl(OH)(μ-O)M(SH)Cp_2 (**E**, **I**) while hydrolysis of $[(t\mathrm{Bu})_2\mathrm{Ga}(\mathrm{Neol})_2]_2\mathrm{Ti}(\mathrm{NMe}_2)_2$ resulted

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**, **3**, and **4**[a]

1	3	4
Ti(1)−O(1) 1.7506(16)	Zr(1)−O(1) 1.9143(14)	Ti(1)−O(1) 1.763(3)
Ti(1)−C(5) 2.112(3)	Zr(1)−O(2) 1.9132(14)	Ti(1)−O(2) 1.767(3)
Ti(1)−C(7) 2.135(2)	Zr(1)−C(19) 2.265(2)	Ti(1)−O(4) 1.888(3)
Ti(1)−C(6) 2.143(2)	Zr(1)−C(26) 2.289(2)	Ti(1)−O(5) 1.893(3)
Al(1)−O(1) 1.7391(16)	Al(1)−O(2) 1.7344(15)	Ga(1)−O(1) 1.860(3)
Al(1)−N(2) 1.897(2)	Al(1)−N(2) 1.9088(18)	Ga(1)−O(3) 1.921(3)
Al(1)−N(1) 1.8998(19)	Al(1)−N(1) 1.9249(18)	Ga(1)−C(1) 1.956(4)
Al(1)−C(1) 1.957(2)	Al(1)−C(18) 1.947(2)	Ga(1)−N(1) 2.021(4)
O(1)−Ti(1)−C(5) 104.3(1)	O(2)−Zr(1)−O(1) 116.5(1)	O(1)−Ti(1)−O(2) 114.8(1)
O(1)−Ti(1)−C(7) 103.4(1)	O(1)−Zr(1)−C(19) 106.7(1)	O(1)−Ti(1)−O(4) 108.0(1)
C(5)−Ti(1)−C(7) 111.0(1)	C(19)−Zr(1)−C(26) 109.8(1)	O(1)−Ga(1)−O(3) 99.2(1)
O(1)−Ti(1)−C(6) 105.6(1)	O(2)−Al(1)−N(2) 111.5(1)	O(1)−Ga(1)−C(1) 119.9(2)
C(5)−Ti(1)−C(6) 106.9(1)	O(2)−Al(1)−N(1) 112.4(1)	C(1)−Ga(1)−N(1) 127.0(2)
C(7)−Ti(1)−C(6) 123.9(1)	N(2)−Al(1)−N(1) 96.5(1)	O(3)−Ga(6)−O(5) 97.0(1)
O(1)−Al(1)−N(1) 110.4(1)	O(2)−Al(1)−C(18) 111.1(1)	
N(2)−Al(1)−N(1) 97.2(1)	N(2)−Al(1)−C(18) 114.3(1)	
O(1)−Al(1)−C(1) 116.2(1)	Al(2)−O(1)−Zr(1) 175.6(1)	
N(1)−Al(1)−C(1) 110.2(1)	Al(1)−O(2)−Zr(1) 141.8(1)	
Al(1)−O(1)−Ti(1) 145.4(1)	C(20)−C(19)−Zr(1) 113.6(2)	
C(51)−C(5)−Ti(1) 105.7(1)	C(27)−C(26)−Zr(1) 121.5(2)	
C(61)−C(6)−Ti(1) 85.8(1)		
C(71)−C(7)−Ti(1) 116.3(1)		

[a] Symmetry transformations used to generate equivalent atoms #1 of **3**: $-x + 1$, $-y + 2$, $-z + 1$.

Table 2. Range of Angles (deg) in **4**

angle	min	max	average
O−Ti−O	105.8(1)°	114.8(1)°	109.4°
Ti−O−Ga	107.0(2)°	116.1(2)°	112.1°
O−Ga−O	94.0(1)°	104.0(1)°	98.1°
O−Ga−N	84.5(1)°	106.5(1)°	94.6°
O−Ga−C	110.9(1)°	127.9(2)°	120.3°
C−Ga−N	112.0(2)°	127.0(2)°	121.2°
Ga−O−Ga	95.1(1)°	136.3(2)°	113.5°
Ga−N−Ga	88.8(1)°	89.7(2)°	89.2°

in the 1:2 complex $(t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-Neol})_2\mathrm{Ti}(\mu\text{-O})[\mathrm{Ga}(t\mathrm{Bu})_2(\mathrm{HNMe}_2)]$ (**Q**) (NeolH_2 = 2,2-dimethylpropane-1,3-diol). Reaction of the dinuclear gallium hydroxide containing the Mes group led to the formation of a 1:6 complex (**R**). Another 1:6 complex $\mathrm{Cp}_2\mathrm{ZrMe}(\mu\text{-O})\mathrm{Al}_6\mathrm{O}_5(t\mathrm{Bu})_6(\mathrm{Me})$ (**P**) was obtained by the reaction of $\mathrm{Cp}_2\mathrm{ZrMe}_2$ and $[t\mathrm{BuAl}(\mu\text{-O})]_6$. Thus, combination of the aluminum and gallium compounds bearing substituents of a reasonable size are opening a route to new polyoxometal clusters.

When the activity of complexes with the $\mathrm{LAl(Me)}(\mu\text{-O})$ moiety is compared, it is obvious, that the cyclopentadienyl titanium and zirconium 1:1 complexes $\mathrm{Cp}_2\mathrm{MR}(\mu\text{-O})\mathrm{AlMeL}$ (R = Me, Cl, M = Ti, Zr, L = $(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NC(Me)})_2\mathrm{CH}$) (**A**, **J**, **K**) exhibit the best activities in the polymerization of ethylene upon activation with MAO. The catalytic activity of these complexes was studied in detail in ref 7a,e. As depicted in Table 3, the catalytic activity depends on the type of the transition metal (Ti, Zr containing complexes are more active than Hf complexes), the ligand attached to this metal, as well as from the subtituents that bind to the aluminum atom. Namely, replacement of the Cp ligand (complexes **A**, **J**, **K**) by the Bz (**D**, **G**, **M**), NMe_2 (**H**, **L**), and L* = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine) (**F**) decreases the catalytic activity. This could be explained by the higher stability of active species supported by the Cp ligand. Replacement of the Me group on the aluminum atom by the more bulky Et, Ph groups increases the shielding of the transition metal center and decreases the activity (compare activities of complexes **J** and **Y**, **V**). The increase of shielding might be responsible for hampering the interaction between the metal complexes and the activator (complex **G** has low activity only by heating) and/or for the lower activity of the intermediates. Furthermore, introduction of a second [LAl(Me)O] moiety, four (MesGaO) species, and replacement of the [LAl(Me)O] on the more bulky $[\mathrm{Al}_6\mathrm{O}_5(t\mathrm{Bu})_6(\mathrm{Me})]$ also increases the shielding of the transition metal center resulting in a decrease of the catalytic activity (compare activities of complexes **A**, **D** and **G**, **H**, **R**; complexes **J**, **K** and **L**, **M**, **P**).

Experimental Section

All operations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a MBraun MB-150B inert atmosphere glovebox. The solvents toluene, *n*-hexane, $\mathrm{Et}_2\mathrm{O}$, THF, and DME were dried over Na/benzophenone and distilled under nitrogen prior to use. $\mathrm{C}_6\mathrm{D}_6$ was dried over K and degassed. The compounds LH with the ligand L = $[2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{NC(Me)}]_2\mathrm{CH}$,[23,24] LAlMe(OH),[7b] $(\mathrm{Mes}_2\mathrm{Ga(OH)})_2\cdot\mathrm{THF}$,[9] TiBz_4, and ZrBz_4[11] were prepared by methods known from the literature. The purity of all compounds was checked by ^{1}H and ^{13}C NMR spectra. TiCl_4 (Aldrich 95%) was distilled prior to use in a dry and O_2-free N_2 atmosphere. Solutions of BzMgCl (1.0 M in $\mathrm{Et}_2\mathrm{O}$), MAO (10 wt %) in toluene, $\mathrm{Ti(NEt}_2)_4$ (Acros Organics, 98%), and AlMe_3 (Aldrich, 98%) were used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 and Varian INOVA-600 spectrometers. Positive chemical shifts are reported in δ ppm to high frequency of $\mathrm{Me}_4\mathrm{Si}$ with the resonance of the residual protons of the solvent as the reference signal. Assignment of the resonances was made by ^{1}H ^{13}C correlation and according to reference 25. Chemical shifts of proton resonances correlating with carbon resonances are shown in brackets.

Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analyses were carried out at the

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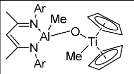
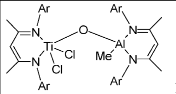
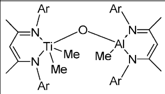
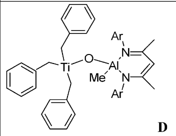
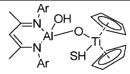
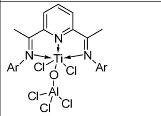
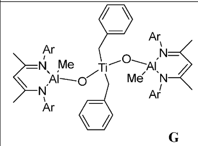
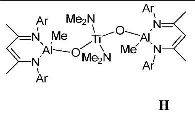
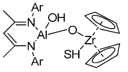
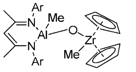
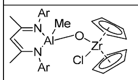
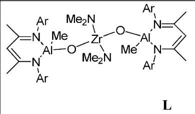
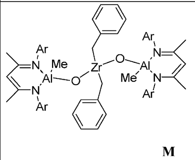
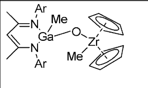
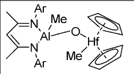
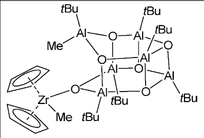
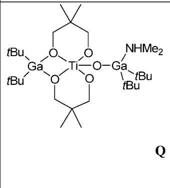
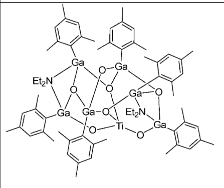
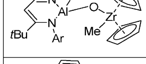
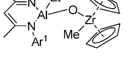
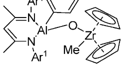
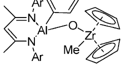
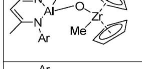
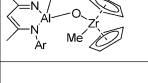
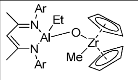
Table 3. Heterobimetallic and Polymetallic Complexes Containing Group 4 (M = Ti, Zr, Hf) and Group 13 (M^1 = Al, Ga) Elements with M(μ-O)M^1 Motifs[a]

Complex	Activity	Complex	Activity
 **A**	high.[7c]	 **B**	complex is unstable.[8]
 **C**	complex is unstable.[8]	 **D**	low.
 **E**	n.r.[7d]	 **F**	n.r. [6] moderate [*]
 **G**	not active at room temp.; low at 85°C.	 **H**	low.[7f]
 **I**	n.r.[7d]	 **J**	high.[7a]
 **K**	high.[7a]	 **L**	low.[7f]
 **M**	low.	 **N**	n.r.[7b]
 **O**	low.[7c]	 **P**	low. [3d]
 **Q**	n.r. [5]	 **R**	low.
 **S**	n.r.[7g]	 **T**	n.r.[7g]
 **U**	n.r.[7g]	 **V**	moderate.[7g]
 **W**	n.r.[7g]	 **X**	n.r.[7g]
 **Y**	moderate.[7g]		

[a] Magnitude of activity: low ~10^3−10^4; moderate ~10^5; high ~10^6 g (polymer)/mol catalyst·h·bar, all complexes were activated with MAO. The activities are compared at room temperature for the best compatibility. n.r. = not reported. * indicates complex **F** was obtained from L*$TiCl_3$ and 2 equiv of MAO, activity of L*$TiCl_3$ upon activation with 500 equiv of MAO is 2.67 × 10^5 g (polymer)/mol catalyst·h·bar at 70 °C.

Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were determined in sealed capillary tubes under nitrogen on a Büchi B540 melting point apparatus. Melting points of the polymers were measured on a Netzsch STA 409 PC spectrometer.

Compound [LAlMe(μ-O)]$TiBz_3$ (1). A solution of LAlMe(OH) (0.45 g, 0.95 mmol) and $TiBz_4$ (0.39 g, 0.95 mmol) in toluene (40 mL) was stirred for 3 d at room temperature. After removal of all volatiles *n*-hexane was added (20 mL), the solution filtered, concentrated, and stored at ambient temperature to yield **1** (0.65 g, 86%) as red crystals which were filtered off, washed with *n*-hexane (2 × 2 mL), and dried in vacuo. Mp 179 °C (decomp). ^{1}H NMR (500.2 MHz, C_6D_6, rt), δ_H (ppm) = 7.18−7.10 (m, aryl-*H*), 7.06−7.03 (m, aryl-*H*), 6.89 (m, aryl-*H*), 6.45−6.43 (m, aryl-*H*), 4.91 (s, 1H, C(CH_3)C*H*C(CH_3)), 3.70 (sept, 2H, *J* = 6.80 Hz, C*H*(CH_3)$_2$), 3.36 (sept, 2H, *J* = 6.70 Hz, C*H*(CH_3)$_2$), 2.00 (s, 6H, TiCH_2Ph), 1.56 (s, 6H, C(CH_3)CHC(CH_3)), 1.51 (d, 6H, *J* = 6.80 Hz, CH(CH_3)$_2$), 1.35 (d, 6H, *J* = 6.80 Hz, CH(CH_3)$_2$), 1.17 (d, 6H, *J* = 6.70 Hz, CH(CH_3)$_2$), 1.12 (d, 12H, *J* = 6.80 Hz, CH(CH_3)$_2$), −0.08 (s, 3H, Al−CH_3). ^{13}C NMR (125.707 MHz, C_6D_6, rt), δ_C (ppm) = 170.9 (*C*(CH_3)CH*C*(CH_3)), 144.9 (aryl-*C*), 144.1 (aryl-*C*), 140.3 (aryl-*C*), 129.1 (aryl-*C* 7.06−7.03), 128.7 (aryl-*C*, 6.45−6.43), 127.7 (aryl-*C* 7.15), 125.2 (aryl-*C* 7.11), 124.7 (aryl-*C*, 7.17), 123.1 (aryl-*C*, 6.89), 97.6 (C(CH_3)*C*HC(CH_3), 4.91), 80.8 (Ti-CH_2Ph, 2.00), 29.2 (*C*H(CH_3)$_2$, 3.70), 27.9 (*C*H(CH_3)$_2$, 3.36), 26.3 (*C*H_3, 1.35), 24.91 (*C*H_3, 1.51), 24.89 (*C*H_3, 1.17 or 1.12), 24.84 (*C*H_3, 1.17 or 1.12), 23.5 (C(*C*H_3)CHC(*C*H_3), 1.56), −8.7 (Al−CH_3, −0.08), Elemental analysis for $C_{51}H_{65}AlN_2OTi$: calcd: C, 76.80; H, 8.16; N, 3.51; found C, 76.87; H, 8.19; N, 3.43.

Compound [LAlMe(μ-O)]$_2$$TiBz_2$ (2). This compound was synthesized by the procedure described for **1** in a 2:1 molar ratio from LAlMe(OH) (0.88 g, 1.85 mmol) and $TiBz_4$ (0.38 g, 0.92 mmol). Yield 0.54 g. Mp 187 °C (decomp). ^{1}H NMR (500.2 MHz, C_6D_6, rt), δ_H (ppm) = 7.17−7.15 (m, aryl-*H*), 7.10−7.08 (m, aryl-*H*), 6.93 (m, aryl-*H*), 6.80 (m, aryl-*H*), 6.74 (m, aryl-*H*), 5.13 (s, 2H, C(CH_3)C*H*C(CH_3)), 3.78 (sept, 4H, *J* = 6.80 Hz, C*H*(CH_3)$_2$), 3.22 (sept, 4H, *J* = 6.80 Hz, C*H*(CH_3)$_2$), 2.17 (s, 4H, TiCH_2Ph), 1.60 (s, 12H, C(CH_3)CHC(CH_3)), 1.28 (d, 12H, *J* = 6.80 Hz, CH(CH_3)$_2$), 1.26 (d, 12H, *J* = 6.80 Hz, CH(CH_3)$_2$), 1.13 (t, overlapping d + d, 24H, CH(CH_3)$_2$) −0.51 (s, 6H, Al−CH_3). ^{13}C NMR (125.707 MHz, C_6D_6, rt), δ_C (ppm) = 170.6 (*C*(CH_3)CH*C*(CH_3)), 147.5 (aryl-*C*), 144.8 (aryl-*C*), 144.3 (aryl-*C*), 141.4 (aryl-*C*), 127.3 (aryl-*C,* 7.17−7.15), 124.8 (,aryl-*C*, 7.10−7.08), 124.7 (aryl-*C,* 7.17−7.15), 121.6,(aryl-*C* 6.80), 99.5 (C(CH_3)*C*HC(CH_3), 5.13), 73.6 (Ti-*C*H_2Ph, 2.17), 28.5 (*C*H(CH_3)$_2$, 3.78), 28.2 (*C*H(CH_3)$_2$, 3.22), 26.3 (*C*H_3, 1.28 or 1.26), 26.0 (*C*H_3, 1.28 or 1.26), 24.7 (*C*H_3, 1.13), 24.6 (*C*H_3, 1.13), 24.0 (C(*C*H_3)CHC(*C*H_3), 1.60), −11.3 (Al−CH_3, −0.51). Elemental analysis for $C_{74}H_{102}Al_2N_4O_2Ti$: calcd: C, 75.25; H, 8.64; N, 4.75; found: C, 75.31; H, 8.69; N, 4.71.

Compound [LAl(Me)(μ-O)]$_2$$ZrBz_2$ (3). Toluene (40 mL) was added to LAlMe(OH) (1.12 g, 2.4 mmol) and $ZrBz_4$ (0.55 g, 1.2 mmol). The resulting solution was stirred for 3 d at room temperature; after removal of the solvent *n*-hexane was added (50 mL). Small amounts of insoluble (ca. 0.1 g, **3** according to NMR) were filtered off, the *n*-hexane solution concentrated and left at 0 °C for 4 d, during which time a white solid consisting of small needles deposited. Yield of **3** 0.92 g (65%). Compound **3** can be recrystallized from DME giving X-ray quality needles of **3**·DME. Elemental analysis and further characterization was done for **3**·$DME_{0.5}$. The compound turns dark above 130 °C, melting at 197−198 °C with decomp. ^{1}H NMR (599.74 MHz, C_6D_6, rt), δ_H (ppm) = 7.16−7.13 (m, aryl-*H*), 7.10−7.07 (m, aryl-*H*), 7.03 (m,

Table 4. Crystallographic Data and Structure Refinement Details for **1**, **3**, and **4** at 100 K and Mo Kα Radiation[a]

	1	**3**	**4**
empirical formula	$C_{51}H_{65}AlN_2OTi$	$C_{76}H_{107}Al_2N_4O_3Zr$	$C_{62}H_{86}Ga_6N_2O_7Ti$
CCDC no	664927	664925	664926
M_r	796.93	1269.84	1437.55
crystal size/mm	0.2 × 0.2 × 0.05	0.4 × 0.2 × 0.05	0.1 × 0.05 × 0.02
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	18.312(4)	12.2881(9)	12.9331(12)
b/Å	23.545(5)	17.1318(13)	14.5324(14)
c/Å	21.309(4)	19.858(2)	35.544(3)
α/°	90	111.6850(10)	81.7410(10)
β/°	98.56(3)	93.8700(10)	81.7230(10)
γ/°	90	109.3090(10)	77.0610(10)
V/Å^3	9090.0(10)	3579.3(5)	6399.9(10)
Z	8	2	4
$\rho_{\mathrm{calcd.}}$/g·cm^{-3}	1.165	1.178	1.492
μ/mm^{-1}	0.245	0.226	2.656
F(000)	3424	1362	2944
scan range Θ/°	1.42 to 26.42	1.91 to 25.05	1.45 to 25.41
completeness to $\Theta_{\max}$/%	99.3	99.5	99.4
index ranges	$-22 \le h \le 22$ $0 \le k \le 29$ $0 \le l \le 26$	$-14 \le h \le 14$ $-20 \le k \le 18$ $0 \le l \le 23$	$-15 \le h \le 15$ $-17 \le k \le 17$ $0 \le l \le 42$
total reflections	77407	37690	107136
unique reflections	18557	12607	23474
R(int)	0.0521	0.0289	0.0720
data/restrains/parameters	18557/0/1031	12607/42/827	23474/15/1474
goodness-of-fit on F^2	1.037	1.059	1.012
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0530, 0.1372	0.0370, 0.0924	0.0417, 0.0809
$R1$, $wR2$ (all data)	0.0821, 0.1499	0.0459, 0.0962	0.0745, 0.0916
max./min. el. dens. [e·Å^{-3}]	0.603, −0.416	0.773, −0.412	0.615, −0.712

[a] $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, weight $= 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (max\ (F_o^2, 0) + 2F_c^2)/3$; for **1**, $A = 0.0903$, $B = 0.00$; for **3**, $A = 0.0468$, $B = 2.3106$.; for **4**, $A = 0.0321$, $B = 9.3272$.

aryl-*H*), 6.82 (m, aryl-*H*), 6.69 (m, aryl-*H*), 5.03 (s, 2H, C(CH$_3$)C*H*C(CH$_3$)), 3.62 (sept, 4H, J = 6.71 Hz, C*H*(CH$_3$)$_2$), 3.31 (s, 4H, C*H*$_2$, DME), 3.17 (sept, 4H, J = 6.71 Hz, C*H*(CH$_3$)$_2$), 3.10 (s, 6H, C*H*$_3$, DME), 1.85 (s, 4H, ZrC*H*$_2$Ph), 1.55 (s, 12H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.27 and 1.26 (overlapping d + d, J = 6.71 Hz, J = 6.71 Hz), 1.15 (d, 12H, J = 6.71 Hz, CH(C*H*$_3$)$_2$), 1.10 (d, 12H, J = 6.80 Hz, CH(C*H*$_3$)$_2$), −0.56 (s, 6H, Al−C*H*$_3$). ^{13}C NMR (125.707 MHz, C$_6$D$_6$, rt), δ_C (ppm) = 170.32 (*C*(CH$_3$)CH*C*(CH$_3$)), 146.69 (aryl-*C*), 144.74 (aryl-*C*), 144.20 (aryl-*C*), 141.22 (aryl-*C*), 128.40 (aryl-*C*, 7.03), 127.49 (aryl-*C*, 6.69), 127.25 (aryl-*C*, 7.14), 124.74 (aryl-*C*, 7.08), 124.70 (aryl-*C*, 7.13), 121.35 (aryl-*C*, 6.82), 99.04 (C(CH$_3$)*C*HC(CH$_3$), 5.03), 72.19 (*C*H$_2$, DME, 3.31), 59.35 (Zr-*C*H$_2$Ph, 1.85), 58.71 (*C*H$_3$, DME, 3.10), 28.54 (*C*HC*H*$_3$)$_2$, 3.62), 28.19 (*C*HC*H*$_3$)$_2$, 3.17), 26.14 (*C*H$_3$, 1.27 or 1.26), 26.00 (*C*H$_3$, 1.27 or 1.26), 24.77 (*C*H$_3$, 1.15), 24.63 (*C*H$_3$, 1.10), 23.77 (C(*C*H$_3$)CHC(*C*H$_3$), 1.55), −11.36 (Al-Me, − 0.56). Elemental analysis for **3**·DME$_{0.5}$, $C_{76}H_{107}Al_2N_4O_3Zr$ calcd: C, 71.82; H, 8.43; N, 4.41; found: C, 72.32; H, 8.59; N, 4.14.

Compound $\mathbf{TiGa_6O_7(NEt_2)_2(Mes)_6}$ (4). A toluene solution (20 mL) of Ti(NEt$_2$)$_4$ (0.73 g, 2.2 mmol) was added drop by drop to the toluene suspension of (Mes$_2$Ga(OH))$_2$·THF (1.565 g, 2.2 mmol) at room temperature. The resulting suspension was stirred at room temperature for 5 d. During this time all solid dissolved. Then, all volatiles were removed under vacuum, and the residue dissolved in *n*-hexane (60 mL). The *n*-hexane solution was filtered off from small amounts of solid (ca. 0.05−0.1 g), concentrated to 30 mL, and left undisturbed at room temperature. Small needles of **4** were formed from a *n*-hexane solution during 7 d at room temperature. The solid was filtered off and washed with *n*-hexane (3 × 4 mL). An additional crop of **4** was obtained by further concentrating this solution. Yield of **4** 0.48 g. Mp 295 °C, (decomp). ^{1}H NMR (599.74 MHz, C$_6$D$_6$, rt), δ_H (ppm) = 6.81 (s, 2H, aryl-*H*), 6.76 (s, 2H, aryl-*H*), 6.69 (s, 2H, aryl-*H*), 6.68 (s, 2H, aryl-*H*), 6.60 (s, 2H, aryl-*H*) 6.24 (s, 2H, aryl-*H*), 3.89 (q, 2H, J = 7.3 Hz, NC*H*$_2$CH$_3$), 2.87 (q, 2H, J = 7.2 Hz, NC*H*$_2$CH$_3$) overlapping with 2.85 (s, 6H, C*H*$_3$), 2.76 (q, 2H, J = 6.7 Hz, NC*H*$_2$CH$_3$), 2.69 (s, 12H, C*H*$_3$) overlapping with 2.66 (q, 2H, J = 7.0 Hz, NC*H*$_2$CH$_3$), 2.60 (s, 6H, C*H*$_3$), 2.32 (s, 6H, C*H*$_3$), 2.16 (s, 6H, C*H*$_3$), 2.09 (s, 6H, C*H*$_3$), 2.08 (s, 6H, C*H*$_3$), 1.92 (s, 6H, C*H*$_3$), 0.83 (t, 6H, J = 7.0 Hz, NCH$_2$C*H*$_3$), 0.37 (t, 6H, J = 7.1 Hz, NCH$_2$C*H*$_3$). ^{13}C NMR (125.707 MHz, C$_6$D$_6$, rt), δ_C (ppm) = 147.17 (*aryl*), 146.00 (*aryl*), 145.59 (*aryl*), 144.81 (*aryl*), 143.89 (*aryl*), 139.24 (*aryl*), 138.54 (*aryl*), 137.80 (*aryl*), 137.04 (*aryl*), 136.77 (*aryl*), 134.57 (*aryl*), 128.68 (*aryl*), 128.53 (CH of *aryl*, 6.81 ppm), 128.38 (CH of *aryl*, 6.76 ppm), 127.53 (CH of *aryl*, 6.68 ppm), 127.47 (CH of *aryl*, 6.60 ppm), 127.23 (CH of *aryl*, 6.24 ppm), 126.38 (CH of *aryl*, 6.69 ppm), 41.38 (N*C*H$_2$CH$_3$, 2.87 and 2.66 ppm), 40.60 (N*C*H$_2$CH$_3$, 3.89 and 2.76 ppm), 26.47 (*C*H$_3$, 2.69 ppm), 25.85 (*C*H$_3$, 1.92 ppm), 25.48 (*C*H$_3$, 2.85 ppm), 25.03 (*C*H$_3$, 2.60 ppm), 25.01 (*C*H$_3$, 2.69 ppm), 23.95 (*C*H$_3$, 2.32 ppm), 21.28 (*C*H$_3$, 2.16 ppm), 21.14 (*C*H$_3$, 2.09 or 2.08 ppm), 21.11 (*C*H$_3$, 2.09 or 2.08 ppm), 13.51 (NCH$_2$*C*H$_3$, 0.83 ppm), 10.86 (NCH$_2$*C*H$_3$, 0.37 ppm). Elemental analysis of $C_{62}H_{86}Ga_6N_2O_7Ti$, calcd: C, 51.76; H, 5.98; N 1.95; found: C, 52.06, H 5.99, N 1.87.

X-ray Crystallography. The selected bond distances and angles are presented in Table 1. Crystallographic data and structure determinations of **1**, **3**, and **4** are summarized in Table 4. The data for **1**, **3**, and **4** were collected from shock-cooled crystals at 100(2) K.[26] The data for **1** and **3** were collected on a Bruker SMART-APEX II diffractometer with a D8 goniometer, for **4** on a Bruker TXS-Mo rotating anode with an APEX II detector on a D8 goniometer. The Bruker SMART-APEX II diffractometer employed graphite-monochromated Mo Kα radiation (λ = 71.073 pm). The Bruker TXS-Mo rotating anode employed INCOATEC Helios mirror optics as radiation monochromator. The data of **1**, **3**, and

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4 were integrated with SAINT,[27] and an empirical absorption (SADABS) was applied.[28] The structures were solved by direct methods (SHELXS-97)[29] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[30] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained as equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints. In **3**, half an uncoordinated DME solvent molecule per zirconium atom is present in the lattice.

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Supporting Information Available: X-ray crystallographic data files in CIF format; EI-MS data for **1**, **2**, **3**, and **4** and notes for the preparation of **3** and **4**; data for polymerization of ethylene with **1**, **2**, **3**, and **4** as catalysts and MAO as cocatalyst (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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