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## Oxide-Bridged Heterobimetallic Aluminum/Zirconium Catalysts for Ethylene Polymerization

Cédric Boulho,<sup>[a,b]</sup> Harmen S. Zijlstra,<sup>[a,b,c]</sup> and Sjoerd Harder\*<sup>[a,b]</sup>

**Keywords:** Sandwich complexes / Heterometallic complexes / Zirconium / Polymerization / Polyethylene

A bimetallic aluminum/zirconium complex  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})$  [ $\text{DIPH-H}_2 = 3,3'$ -bis(2-methylallyl)-(1,1'-biphenyl)-2,2'-diol;  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ] was prepared in good yield by the reaction of  $(\text{DIPH})\text{AlMe}$  with  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{OH}$ . In contrast to Roesky's catalyst,  $\text{Cp}_2\text{Zr}(\text{Me})\text{O}(\text{Me})\text{Al}(\text{DIPP-nacnac})$  { $\text{DIPP-nacnac} = \text{CH}[(\text{CMe})(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N})]_2$ }, it contains no Al–Me functionality and has increased Lewis acidity at Al. Crystal structures and the NMR spectra of the aluminum complex  $(\text{DIPH})\text{AlMe}$  and the bimetallic Al/Zr species reveal in both

cases dimeric complexes. The crystal structure of  $[\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})]_2$  shows a planar  $\text{Al}_2\text{O}_2$  core and a terminal  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{O}$  group. Ethylene polymerization in toluene was studied for the bimetallic complex with a variety of scavengers. Under comparable polymerization conditions, the methylalumoxane-activated species show high activities that are similar to those obtained with  $\text{Cp}^*_2\text{ZrCl}_2$  and Roesky's bimetallic complex  $\text{Cp}_2\text{Zr}(\text{Me})\text{OAl}(\text{Me})(\text{DIPP-nacnac})$ , with a relatively narrow polydispersity index (2.47).

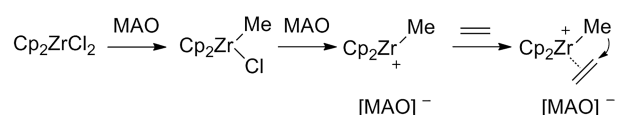
### Introduction

Heterobimetallic catalysis is a rapidly growing field strongly inspired by nature.<sup>[1–6]</sup> Cooperation of two neighboring metals enables attractive new reactivities or physical properties.<sup>[7–9]</sup>

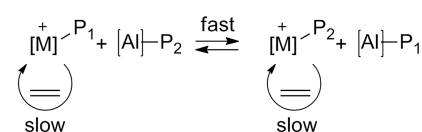
Homogeneous olefin polymerization by metallocenes is an interesting playground for such heterobimetallic catalysts:  $\text{Cp}_2\text{MCl}_2$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ;  $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) type precatalysts are usually activated by a cocatalyst that is generally a compound containing a Lewis acidic boron or aluminum center.<sup>[10–12]</sup> Owing to its capability to fulfil multiple functions, methylalumoxane (MAO) is the most widely used cocatalyst (Scheme 1).<sup>[13–17]</sup> It functions as a methylating agent, a methyl group abstractor, a stabilizer for the cation, and it also scavenges impurities that are fatal for catalytic activity (e.g. water). MAO, or the incorporated trimethylaluminum ( $\text{Me}_3\text{Al}$ ) always present in MAO mixtures, could also act as a chain-transfer agent allowing for an efficient “Aufbaureaktion” at the Al center<sup>[18]</sup> or shuttling the growing polymer chain between different catalytic centers (Scheme 1).<sup>[19–25]</sup>

This interplay between group 4 and group 13 metal centers in olefin polymerization catalysis is well established<sup>[15]</sup>

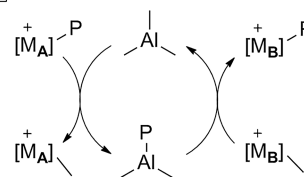
Activation by MAO



“Aufbaureaktion”



Chain shuttling



Scheme 1. The role of MAO and aluminum alkyls in Zr-catalyzed ethylene polymerization (P = polymeryl).

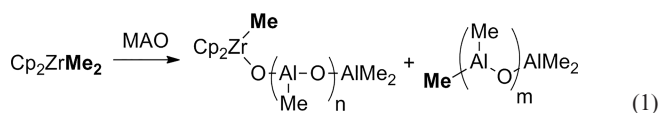
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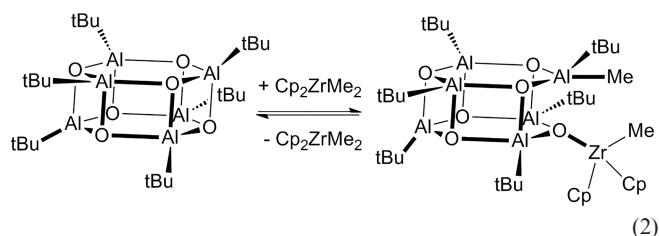
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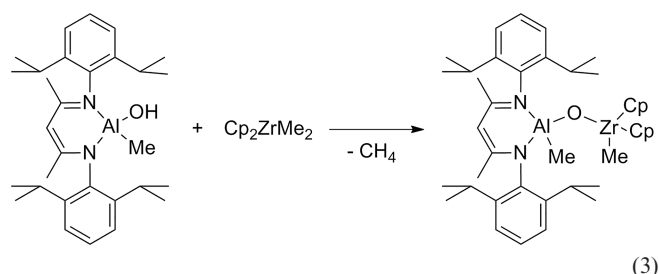
and has led to the design of some interesting heterobimetallic catalysts.<sup>[26–29]</sup> Among the first to propose an Al/Zr bimetallic system in homogeneous Ziegler–Natta olefin polymerization were Giannetti et al.,<sup>[30]</sup> who described the activation of a  $\text{Cp}_2\text{ZrMe}_2$  catalyst by a linear MAO polymer [Equation (1)]. Hitherto, the exact structural nature of MAO is still unknown, but it is more likely that alumoxanes form three-dimensional clusters rather than linear polymers.<sup>[17]</sup>



Barron et al. prepared a variety of  $(t\text{BuAlO})_n$  model systems for MAO and structurally characterized these as molecular cages ( $n = 6-9, 12$ ).<sup>[31-33]</sup> These cages [Equation (2)] do not contain highly Lewis acidic low-coordinate Al, but they can activate  $\text{Cp}_2\text{ZrMe}_2$  by so-called latent Lewis acidity: two adjoining four-membered rings open to create a three-coordinate Lewis acidic Al site. The reaction product of  $(t\text{BuAlO})_6$  and  $\text{Cp}_2\text{ZrMe}_2$  has been characterized by multidimensional NMR spectroscopy [Equation (2)].

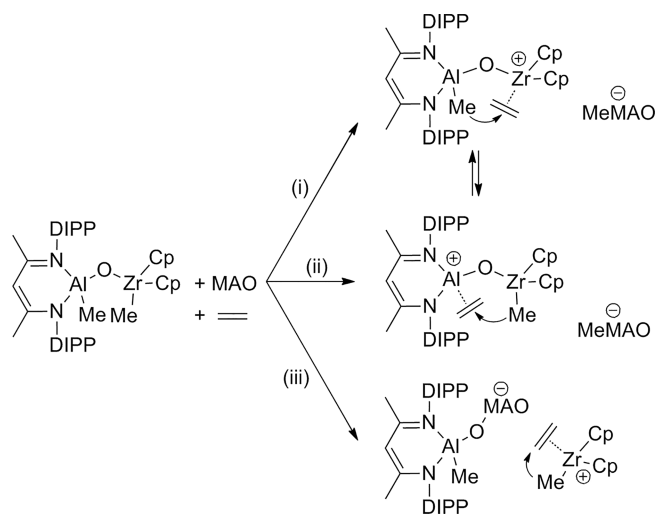


Despite studies on self-activating catalysts with built-in Lewis acidic boron functions,<sup>[26-29]</sup> only very few approaches towards heterobimetallic Zr/Al catalysts have been reported. The first structurally authenticated Al–O–Zr complex was obtained by Roesky and co-workers through reaction of a terminal aluminum hydroxide with dimethylzirconocene through methane elimination [Equation (3)].<sup>[34,35]</sup> The aluminum hydroxide precursor in this reaction is sterically stabilized by the well-known, very protective  $\beta$ -diketiminate ligand DIPP-nacnac ( $\text{CH}\{\text{(CMe)}\text{---}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\}$ ). The obtained Al–O–Zr species can be used as an ethylene polymerization catalyst but still needs to be activated by MAO. Its merit, however, lies in the drastically reduced quantities of MAO needed for activity.



The hybrid Al/Zr species in Equations (1)–(3) all contain the  $(\text{alkyl})\text{Al-O-Zr}(\text{alkyl})$  subunit but have no vacant sites at either metal. The exact mechanism of ethylene polymerization with  $\text{M-O-M}'$  precatalysts is unknown, but it is suggested that they “benefit from chemical communication between the oxide-linked metal atoms, for example, by enhancing the Lewis acidity of the catalytic center or providing a binding site for cocatalysts, such as methylalumoxane

(MAO)”.<sup>[34]</sup> Ethylene polymerization with Roesky’s Al–O–Zr/MAO system could, therefore, proceed through three possible mechanisms (Scheme 2).



Scheme 2. Possible activation mechanisms with an Al–O–Zr precatalyst.

(i) Addition of MAO could result in abstraction of the Zr-bound methyl group, in which case the alkyl group at Al would attack a Zr-bound alkene. Although nucleophilic attack by an Al–Me species is unusual in polymerization catalysis, a similar pathway has been suggested for doubly activated Ti catalysts such as  $[\text{Me}_4\text{CpSiMe}_2(\text{N}t\text{Bu})\text{Ti}^{2+}]_2[\text{MeAl}(\text{C}_6\text{F}_5)_3]_2$ .<sup>[36]</sup>

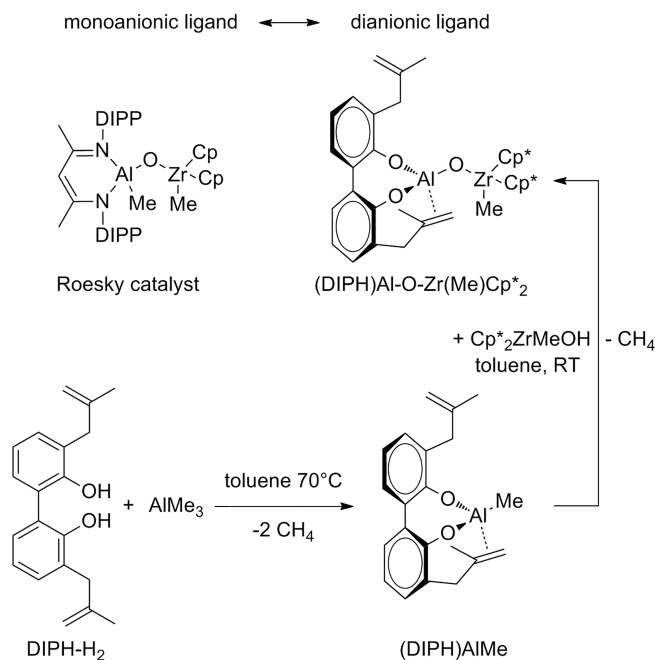
(ii) Addition of MAO could result in abstraction of the Al-bound methyl group, in which case the alkyl group at Zr would attack an Al-bound alkene. In this particular case, the alkene is activated by unusual coordination to Al; however, there is precedence for unsupported alkene–Al coordination in the form of  $(\text{C}_6\text{F}_5)_3\text{Al}(\text{cyclohexene})$ .<sup>[37]</sup>

As pathways (1) and (2) are based on migratory alkene insertion between two metal centers, these could be alternated; otherwise subsequent Al–Zr chain transfer would be needed.

(iii) Addition of MAO could also lead to cleavage of the Zr–O bond, in which case a classical  $[\text{Cp}_2\text{ZrMe}^+]$  ion would be formed. Given the high oxophilicity of Zr,<sup>[38]</sup> this pathway should be less likely. On the other hand, cleavage of a Zr–O bond in a Zr–O–Zr complex by  $\text{Me}_3\text{Al}$  is known.<sup>[39,40]</sup>

Design of a heterobimetallic Al–O–Zr catalyst with a preorganized vacant site could circumvent the use of MAO as a cocatalyst. Substitution of the bidentate monoanionic DIPP-nacnac ligand for a dianionic biphenolate ligand could possibly lead to a complex with such a vacant Al site (Scheme 3). Synthesis of a coordinatively unsaturated species, however, may lead to undesired aggregation. Therefore, we chose potentially weakly coordinating alkene substituents in the 2,2′-positions for metal protection. Owing to the relative weakness of such an interaction, the complex could be regarded as a masked Lewis acid. Our synthetic approach (Scheme 3) involves coupling of an aluminum alkyl with  $\text{Cp}^*\text{Zr}(\text{Me})\text{OH}$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), a route that has

been used by Roesky and co-workers for the syntheses of a large variety of M–O–Zr species (M = Ca, Ti, Hf, Zr).<sup>[41–44]</sup> Herein, we describe a new heterobimetallic Zr/Al complex and evaluate its properties in ethylene polymerization.



Scheme 3. Potential design of a bimetallic Al–O–Zr complex with a dianionic ligand and a (latent) vacant site at Al.

## Results and Discussion

### Synthesis and Characterization of the Al–O–Zr Catalyst

A solution of the 3,3'-bis(2-methylallyl)-(1,1'-biphenyl)-2,2'-diol (DIPH-H<sub>2</sub>) ligand in a noncoordinating solvent (i.e., toluene) was treated with Me<sub>3</sub>Al at room temperature. The first deprotonation proceeded smoothly, but the second deprotonation needed more rigorous reaction conditions (70 °C, 12 h). Removal of all solvents and recrystallization from hot hexane gave the (DIPH)AlMe product in the form of colorless crystals; this product was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and 2D NMR spectroscopy as well as by X-ray crystallography. The <sup>1</sup>H NMR (Supporting Information) spectrum reveals a singlet for the Al–Me proton at  $\delta = -0.78$  ppm, which is in agreement with a terminal methyl group. The CH<sub>2</sub>C(Me)=CH<sub>2</sub> side arms of the DIPH ligand display two different signal sets, which could indicate alkene coordination of one of the two substituents: two AB systems for the benzylic protons ( $\delta = 3.15/3.43$  ppm with  $J = 15.9$  Hz and  $\delta = 3.33/4.06$  ppm with  $J = 14.3$  Hz) and four singlets for the alkene protons ( $\delta = 4.38, 7.73, 4.87,$  and  $4.97$  ppm) are observed. The crystal structure revealed by X-ray diffraction, however, shows another explanation for asymmetry in the DIPH ligand: a dimer is formed in which one of the O atoms of the ligand bridges the Al centers (Figure 1). The dimer has no crystallographic symmetry but is pseudocentrosymmetric. The central (Al–O)<sub>2</sub>

ring is almost planar with a torsion angle of 4.11(6)°, and the two methyl groups on aluminum are oriented *trans* with respect to each other. The average Al–O–Al and O–Al–O angles within the ring measure 100.26(6) and 79.58(5)°, respectively. This results in deviation from a tetrahedral Al coordination geometry. The Al–O bonds within the ring vary from 1.838(1) to 1.854(1) Å and are equivalent to those in similar (Al–O)<sub>2</sub> rings<sup>[45–49]</sup> but are much longer than the terminal Al–O bonds [average: 1.724(1) Å]. The average angle between the aryl planes in the DIPH ligands is 52.9(3)° and is similar to that in other aluminum complexes bearing a diphenolate or 1,1'-bi-2-naphthol (BINOL) ligand.

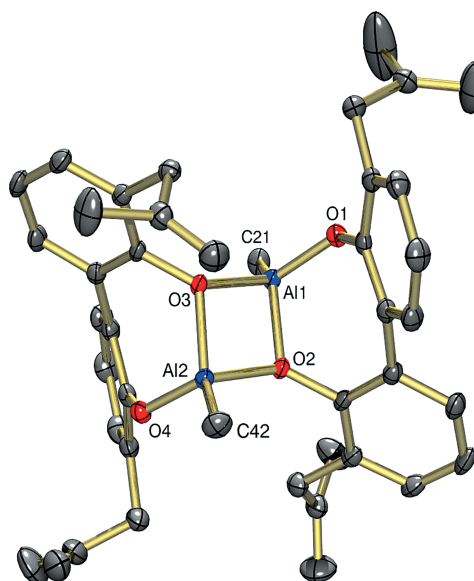


Figure 1. X-ray molecular structure of [(DIPH)AlMe]<sub>2</sub>. Hydrogen atom are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

Notably, the [(DIPH)AlMe]<sub>2</sub> dimer has MAO-like features such as bridging O atoms and terminal methyl groups. Similar to Barron's (*t*BuAlO)<sub>6</sub> model system<sup>[33]</sup> [Equation (2)], it may show latent Lewis acidity by breaking the four-membered (Al–O)<sub>2</sub> ring; however, no reaction or interaction between [(DIPH)AlMe]<sub>2</sub> and Cp\*<sub>2</sub>ZrMe<sub>2</sub> is observed by NMR spectroscopy. This shows that latent Lewis acidity requires structures with annealed four-membered rings that are significantly more strained and, therefore, more reactive.<sup>[33]</sup> The stability of the (Al–O)<sub>2</sub> ring was confirmed by high-temperature NMR spectroscopy studies on [(DIPH)AlMe]<sub>2</sub> in [D<sub>8</sub>]toluene: even at 110 °C no exchange of the two CH<sub>2</sub>C(Me)=CH<sub>2</sub> substituents was found. Lack of exchange means that there is, also at higher temperatures, no cleavage of the (Al–O)<sub>2</sub> ring.

Reaction of Cp\*<sub>2</sub>Zr(Me)OH (2 equiv.) with [(DIPH)AlMe]<sub>2</sub> in toluene gave, at room temperature, complete release of two molecules of methane and led to the formation of the heterobimetallic (DIPH)AlOZr(Me)Cp\*<sub>2</sub> complex as the major product (Scheme 3). The complex is air and moisture sensitive and poorly soluble in most noncoordinating solvents at room temperature; however, it can be solu-

bilized in aromatic solvents upon heating at reflux. Recrystallization from hot toluene gave the product in the form of colorless crystals in good yield (64%). The crystal structure of  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})$  is shown in Figure 2. The complex is crystallographically centrosymmetric and is similar to that of  $[(\text{DIPH})\text{AlMe}]_2$  in that it features an  $(\text{Al}-\text{O})_2$  core and  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{O}$  substituents in *trans* positions. Evidently, exchange of an Al–Me group for a much bulkier Al–O(Me)ZrCp $^*_2$  group does not lead to cleavage of the  $(\text{Al}-\text{O})_2$  cycle. It does lead, however, to an average Al–O distance within the ring [1.856(2) Å] that is slightly longer than that in  $[(\text{DIPH})\text{AlMe}]_2$  [1.845(1) Å]. Table 1 shows the close structural comparison between the two complexes.

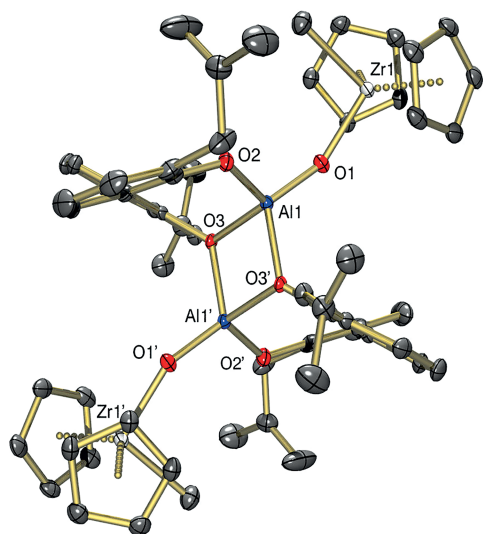


Figure 2. X-ray molecular structure of  $[\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})]_2$ . Hydrogen atoms and Cp $^*$  Me groups are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

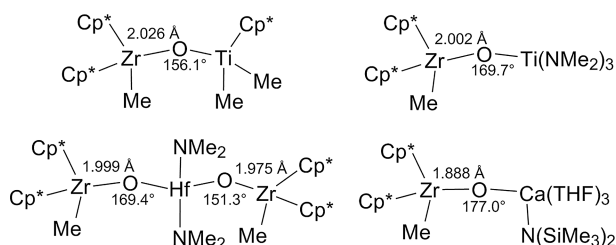
Table 1. Selected bond lengths and angles for the  $[(\text{DIPH})\text{AlMe}]_2$  and  $[(\text{DIPH})\text{AlOZr}(\text{Me})\text{Cp}^*_2]_2$  complexes.<sup>[a]</sup>

	$[(\text{DIPH})\text{AlMe}]_2$	$[\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})]_2$
Bond length [Å]		
(Al–O) $_2$ core	[1.846(1)]	[1.856(2)]
Al–O	[1.724(1)]	1.720(2)
Al–O(Zr)	–	1.688(1)
(Al)O–Zr	–	2.007(1)
Zr–Me	–	2.285(3)
Al–Me	1.922(2)	–
Zr–Cp $^*$	–	2.279(3)
Bond angle [°]		
O–Al–O core	79.60(5)	79.28 (7)
Al–O–Al core	[100.26(6)]	100.72(8)
Al–O–Zr	–	153.7(1)
Cp $^*$ –Zr–Cp $^*$	–	133.80(8)

[a] Average values are given in square brackets.

Although several complexes of the form  $\text{Cp}_2\text{Zr}(\text{Me})\text{OAl}(\text{Me})\text{L}$  are known (L = monoanionic ligand), the current Zr/Al complex contains a bulkier Cp $^*$  ligand and no Al–alkyl moieties. Hitherto, four Cp $^*_2\text{Zr}(\text{Me})\text{O}-\text{M}$  com-

plexes have been structurally characterized (M = Ca, Ti, Hf, Zr; Scheme 4).<sup>[41–44]</sup>



Scheme 4. Selected geometrical parameters in Cp $^*_2\text{Zr}-\text{O}$ -metal complexes.<sup>[41–44]</sup>

Except for the calcium complex, all of these Zr–O–M complexes are bent [ $\angle(\text{Zr}-\text{O}-\text{M}) = 151.3(1)–169.7(6)^\circ$ ]. The Zr–O–Al bending angle in  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})$  is at the lower end of the range [ $153.7(1)^\circ$ ] and is likely due to an attractive C–H $\cdots$ C( $\pi$ ) interaction between a Me group of Cp $^*$  with the  $\pi$  system of the DIPH ligand [ $d(\text{H}\cdots\text{C}) = 2.83$  Å;  $\angle(\text{C}-\text{H}\cdots\text{C}) = 131.4^\circ$ ]. The Zr–O distance of 2.007(1) Å lies in the range of that in other Cp $^*_2\text{Zr}(\text{Me})\text{O}-\text{M}$  complexes (Scheme 4).

The  $^1\text{H}$  NMR spectrum of  $\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})$  in deuterated benzene (Supporting Information) reveals a singlet for the Zr–Me protons at  $\delta = -0.22$  ppm, which appears close to the methyl signal of the Cp $^*_2\text{ZrMeOH}$  reagent ( $\delta = -0.18$  ppm), owing to its similar chemical environment. The methyl protons are less shielded than those in Cp $^*_2\text{ZrMe}_2$  ( $\delta = -0.55$  ppm) because of the higher electron deficiency at the metal center. Two different signals for the two Cp $^*$  ligands indicate a chiral tetracoordinate aluminum center and, thus, the dimeric structure of the compound in solution. This feature also leads to the appearance of an AB system ( $\delta = 3.78/3.86$  ppm with  $J = 17.2$  Hz) and an AX system ( $\delta = 3.58/4.31$  ppm with  $J = 15.3$  Hz) for the four protons in the benzylic position, four singlets for the alkene protons ( $\delta = 5.01, 5.06, 5.27,$  and  $5.30$  ppm), and two signals for the adjacent methyl groups ( $\delta = 1.93$  and  $2.03$  ppm). Raising the temperature up to  $110^\circ\text{C}$  did not lead to coalescence of signals or to decomposition, which indicates the dimeric nature also at higher temperatures.

### Reactivity in Ethylene Polymerization

The  $[\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})]_2$  dimer was tested in olefin polymerization under standardized conditions (20 mL of toluene,  $9.6\ \mu\text{M}$  [Zr], 5 bar ethylene,  $20^\circ\text{C}$ , 15 min; 1 bar = 0.1 MPa). Without the use of a cocatalyst, no activity was observed (Table 2, entry 1). Addition of aluminum alkyls as scavengers for impurities such as water was considered. The choice of the scavenger is crucial and should, in our case, only have the role of purification of the gases and solvents used. Addition of aluminum alkyls of increasing bulkiness  $\text{AlMe}_3 < \text{Al}i\text{Bu}_3 < \text{Al}t\text{Bu}_3$  (Table 2, entries 2–4) gave, under no circumstance, significant activities. However, activation of the  $[\text{Cp}^*_2\text{Zr}(\text{Me})\text{OAl}(\text{DIPH})]_2$  dimer with MAO gave a high activity in ethylene polymerization. The re-

Table 2. Polymerization of ethylene by different Zr/Al alkyl systems.

Entry	Catalyst	Scavenger	Al/Zr	Activity [kg <sub>PE</sub> mol <sub>Zr</sub> <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> ]	M <sub>n</sub> <sup>[a]</sup> [10 <sup>-3</sup> g mol <sup>-1</sup> ]	M <sub>w</sub> <sup>[b]</sup> [10 <sup>-3</sup> g mol <sup>-1</sup> ]	PDI
1	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	none	0	0	–	–	–
2	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	AlMe <sub>3</sub>	1500	0	–	–	–
3	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	Al <i>i</i> Bu <sub>3</sub>	1500	0	–	–	–
4	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	Al <i>i</i> Bu <sub>3</sub>	1500	0	–	–	–
5	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	MAO	600	479	48	119	2.47
6	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	MAO	1500	1595	160	402	2.51
7	[Cp* <sub>2</sub> Zr(Me)OAl(DIPH)] <sub>2</sub>	MAO	3000	917	22	76	3.52
8	Cp* <sub>2</sub> ZrCl <sub>2</sub>	MAO	1500	1529	–	–	–
9	Cp <sub>2</sub> Zr(Me)OAl(Me)(DIPP-nacnac)	MAO	1500	1270	–	–	–

[a] M<sub>n</sub> = Number-averaged molecular weight. [b] M<sub>w</sub> = Weight-averaged molecular weight.

sulting polymers were isolated as a white powder and were dried under high vacuum (0.1 mbar, 60 °C).

The maximum activity was found at an Al/Zr ratio of about 1500, which indicates the need for MAO as a cocatalyst in this reaction (see Figure 3). Any further increase in the Al/Zr ratio, however, led to decreased polymerization activity. In contrast, Cp\*<sub>2</sub>ZrCl<sub>2</sub>/MAO is normally also very active at high MAO concentrations,<sup>[50]</sup> but bell-shaped curves have been described for other zirconocene/MAO catalyst systems.<sup>[10,51–53]</sup>

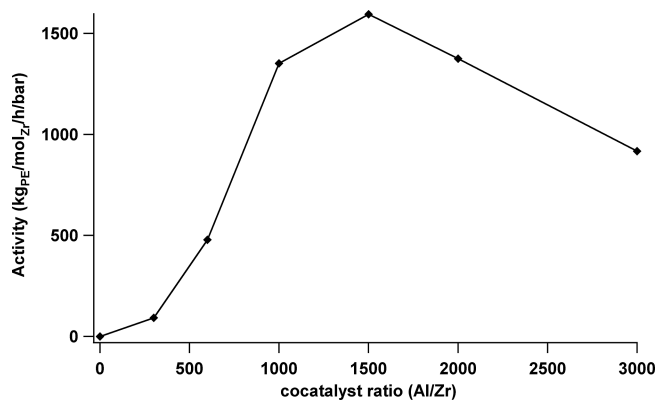


Figure 3. Activity of [Cp\*<sub>2</sub>Zr(Me)OAl(DIPH)]<sub>2</sub> with different amounts of the MAO cocatalyst. Reaction conditions: Toluene (20 mL), [Zr] = 9.6 μM, 5 bar ethylene, 20 °C, 15 min.

The polymer characteristics strongly depend on the amount of cocatalyst. From Al/Zr = 600 to 1500 the polydispersity index (PDI) remains similar (2.47–2.51) and only the average molecular weight increases from 119 × 10<sup>3</sup> to 402 × 10<sup>3</sup> g mol<sup>-1</sup>, which indicates that MAO stabilizes the active species. For higher Al/Zr ratios, the average molecular weight decreases to 76 × 10<sup>3</sup> and the PDI increases to 3.52, which indicates that MAO deactivates the active species. This decay can be explained by the competition between ethylene and the excess amount of MAO for the vacant site on zirconium, as stated by Müllhaupt and co-workers and by Rempel.<sup>[54–56]</sup> However, as noted by Fink et al., MAO contains ample amounts of unreacted Me<sub>3</sub>Al, and increasing the MAO concentration simultaneously leads to an increased Me<sub>3</sub>Al content.<sup>[51]</sup> As Me<sub>3</sub>Al is known to block free metal coordination sites, diminished reactivity at high MAO concentrations could be equally well due to

a higher Me<sub>3</sub>Al content. This is in line with the isolation of low-molecular-weight polymers at high MAO concentrations: Me<sub>3</sub>Al may function as a chain-transfer reagent as in the “Aufbaureaktion” (Scheme 1).<sup>[20,57–59]</sup>

For comparison, we also tested the activities of Cp\*<sub>2</sub>ZrCl<sub>2</sub> and Roesky’s catalyst, Cp<sub>2</sub>Zr(Me)OAl(Me)(DIPP-nacnac), under the same standardized polymerization conditions. It was found that the activity of [Cp\*<sub>2</sub>Zr(Me)OAl(DIPH)]<sub>2</sub>/MAO was comparable to that of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO and to that of Cp<sub>2</sub>Zr(Me)OAl(Me)(DIPP-nacnac)/MAO (Table 2, entries 8 and 9).

## Conclusions

It was attempted to generate an Al–O–Zr complex with an open, Lewis acidic, coordination site at aluminum by reaction of the biphenolate methylaluminum (DIPH)AlMe complex with Cp\*<sub>2</sub>Zr(Me)OH. Despite potential intramolecular coordination by the CH<sub>2</sub>C(Me)=CH<sub>2</sub> side arms in the 2,2’-positions of the biphenolate ligand, the (DIPH)AlMe precursor crystallized as a dimer, in which the O atom of biphenolate bridges the Al cations and Al is four coordinate. Further reaction with Cp\*<sub>2</sub>Zr(Me)OH gave a very similar [(DIPH)Al–O–Zr(Me)Cp\*<sub>2</sub>]<sub>2</sub> dimeric complex. This complex represents the first example of a Cp\*<sub>2</sub>Zr(Me)–O–Al complex containing the bulkier Cp\* ligand and is the first Zr/Al hybrid catalyst that does not contain an alkyl group at Al. [(DIPH)Al–O–Zr(Me)Cp\*<sub>2</sub>] is not only dimeric in the solid state but also in solution. On account of its dimeric existence, there is no vacant site at Al. As found by high-temperature NMR spectroscopy measurements, dimers are also prevalent in solution at higher temperatures and deaggregation could not be observed. The general features of the Al–O–Zr unit show similarities with other bimetallic M–O–Zr (M = Ti/Hf) species and displays a similar Zr–O bond length and M–O–Zr angle. Without the addition of a cocatalyst, the complex is inactive in ethylene polymerization. Also, the addition of alkylaluminum scavengers such as Me<sub>3</sub>Al, *i*Bu<sub>3</sub>Al, and *t*Bu<sub>3</sub>Al did not result in any activity. However, upon activation with methylalumoxane, this complex is highly active in ethylene polymerization (1595 kg<sub>PE</sub> mol<sub>Zr</sub><sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>, M<sub>n</sub> = 160 × 10<sup>3</sup> g mol<sup>-1</sup>, polydispersity index: 2.51).

## Experimental Section

**General Considerations:** All experiments were performed under a nitrogen atmosphere by using standard Schlenk line and glove box techniques. The solvents were dried on alumina columns and were degassed by bubbling nitrogen through the solvent reservoir. The ligand and MAO (5% in toluene) were prepared according to the literature.<sup>[60,61]</sup> Trimethylaluminum was bought from Aldrich and was used as received. Ethylene (N4.5) was bought from Air Liquid and was used as received. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and 2D NMR spectra were recorded with a Bruker DPX300 spectrometer operating at 300.13 MHz (for <sup>1</sup>H) and 75.48 MHz (for <sup>13</sup>C). Molecular-weight distributions of the polyethylenes were determined by gel permeation chromatography (GPC) versus polystyrene standards by using dichlorobenzene as eluent at 135 °C. Crystals were measured with a Bruker diffractometer with a Nonius-Kappa CCD area detector.

**(DIPH)AlMe:** The DIPH-H<sub>2</sub> ligand (345 mg, 1.17 mmol) was dissolved in toluene (5 mL), and the solution was cooled down to –30 °C. Trimethylaluminum (120 μL, 1.25 mmol) was added dropwise, and the mixture was stirred for 5 min. The resulting solution was stirred at room temperature for 2 h and then at 70 °C overnight. The solution was concentrated to about 1 mL, hexane (5 mL) was added, and the slurry was heated to reflux until all solids were dissolved. Colorless crystals of (DIPH)AlMe were formed upon cooling the solution to 5 °C. The crystals were washed with hexane (2 × 3 mL) and dried under vacuum to give (DIPH)AlMe (188 mg, 0.56 mmol, 48%). <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 6.85–7.40 (m, Ar), 4.97, 4.87, 4.73, 4.38 (s, 1/1/1/1 H, =CH<sub>2</sub>), 4.06 (d, J = 14.2 Hz, 1 H, ArCH<sub>2</sub>), 3.43 (d, J = 15.9 Hz, 1 H, ArCH<sub>2</sub>), 3.33 (d, J = 14.2 Hz, 1 H, ArCH<sub>2</sub>), 3.15 (d, J = 15.9 Hz, 1 H, ArCH<sub>2</sub>), 1.70, 1.50 (s, 3/3 H, ArCH<sub>2</sub>CMe), –0.78 (s, 3 H, Al-Me) ppm. <sup>13</sup>C NMR (75.48 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 154.0, 146.0 (Ar), 145.5, 144.1 (ArCH<sub>2</sub>C), 133.4, 132.7, 131.2, 131.2, 130.9, 130.9, 130.2, 128.6, 125.7, 120.8 (Ar), 113.1, 112.1 (=CH<sub>2</sub>), 39.6, 37.4 (ArCH<sub>2</sub>), 22.7, 22.3 (ArCH<sub>2</sub>CMe), –16.3 (AlMe) ppm. C<sub>42</sub>H<sub>46</sub>Al<sub>2</sub>O<sub>4</sub> (668.77): calcd. C 75.43, H 6.93; found C 74.95, H 6.87.

**Cp\*<sub>2</sub>Zr(Me)OAl(DIPH):** The (DIPH)AlMe complex (77.8 mg, 0.23 mmol) was dissolved in toluene (5 mL), and the solution was cooled down to –30 °C. A solution of Cp\*<sub>2</sub>Zr(Me)OH (96 mg, 0.24 mmol) in toluene (5 mL) was slowly added dropwise. The resulting bright yellow solution was stirred at room temperature overnight, dried under vacuum, and washed with hexane (2 × 5 mL). The resulting solid was recrystallized (hot toluene), which gave a white crystalline material suitable for single-crystal X-ray diffraction. Washing these crystals with hexane and drying them in vacuo afforded a white solid (108 mg, 0.15 mmol, 66%), m.p. 225 °C (decomp.). <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 6.9–7.5 (m, Ar), 5.30, 5.27, 5.07, 5.01 (s, 1/1/1/1 H, =CH<sub>2</sub>), 4.31 (d, J = 15.3 Hz, 1 H, ArCH<sub>2</sub>), 3.86, 3.78 (AB sys., J = 17.2 Hz, 1/1 H, ArCH<sub>2</sub>), 3.58 (d, J = 15.3 Hz, 1 H, ArCH<sub>2</sub>), 2.03, 1.93 (s, 3/3 H, ArCH<sub>2</sub>CMe), 1.61, 1.55 (s, 15/15 H, Cp\*), –0.32 (s, 3 H, Zr-Me) ppm. <sup>1</sup>H NMR (300.13 MHz, [D<sub>8</sub>]toluene): δ = 6.9–7.4 (m, Ar), 5.26, 5.01, 4.93 (s, 2/1/1 H, =CH<sub>2</sub>), 4.24 (d, J = 15.8 Hz, 1 H, ArCH<sub>2</sub>), 3.80, 3.73 (AB system, J = 17.1 Hz, 1/1 H, ArCH<sub>2</sub>), 3.50 (d, J = 15.8 Hz, 1 H, ArCH<sub>2</sub>), 2.03, 1.91 (s, 3/3 H, ArCH<sub>2</sub>CMe), 1.57, 1.51 (s, 15/15 H, Cp\*), –0.32 (s, 3 H, Zr-Me) ppm. <sup>13</sup>C NMR (75.48 MHz, [D<sub>8</sub>]toluene): δ = 154.5, 147.7 (Ar), 146.0, 142.3 (ArCH<sub>2</sub>C), 133.4, 133.4, 133.1, 131.6, 130.9, 129.9, 128.0, 127.8, 125.6, 119.9 (Ar), 117.2 (Cp\*), 117.0 (=CH<sub>2</sub>), 116.9 (Cp\*), 112.4 (=CH<sub>2</sub>), 39.8, 38.3 (ArCH<sub>2</sub>), 28.4 (ZrMe), 23.2, 22.9 (ArCH<sub>2</sub>CMe), 11.3, 11.2 (Cp\*)

ppm. C<sub>82</sub>H<sub>106</sub>Al<sub>2</sub>O<sub>6</sub>Zr<sub>2</sub> (1424.13): calcd. C 69.16, H 7.50; found C 67.49, H 7.58.

**Crystal Structure Determinations:** The crystal structures were solved by direct methods (SHELXS-97)<sup>[62]</sup> and refined with SHELXL-97.<sup>[63]</sup> All geometry calculations and graphics were performed with PLATON.<sup>[64]</sup> The hydrogen atoms were placed on calculated positions and were refined isotropically in a riding mode.

**[(DIPH)AlMe]<sub>2</sub>:** Measurement at –120 °C (Mo-K<sub>α</sub>), C<sub>42</sub>H<sub>46</sub>Al<sub>2</sub>O<sub>4</sub>, triclinic, *a* = 9.7065(6) Å, *b* = 12.7659(8) Å, *c* = 16.4191(6) Å, *a* = 104.414(3)°, *β* = 91.587(4)°, *γ* = 111.001(5)°, *V* = 1824.15(19) Å<sup>3</sup>, space group *P* $\bar{1}$ , *Z* = 2,  $\rho_{\text{calcd.}}$  = 1.218 g cm<sup>–3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 0.121 mm<sup>–1</sup>, 56889 measured reflections, 10149 independent reflections (*R*<sub>int</sub> = 0.051), 7369 reflections observed with *I* > 2σ(*I*), *θ*<sub>max</sub> = 29.5°, *R* = 0.0508, *wR*<sub>2</sub> = 0.1254, GOF = 1.05, 440 parameter, min./max. residual electron density –0.42/+0.49 e Å<sup>–3</sup>.

**[Cp\*<sub>2</sub>Zr(Me)OAl(DIPH)]<sub>2</sub>:** Measurement at –120 °C (Mo-K<sub>α</sub>), C<sub>82</sub>H<sub>106</sub>Al<sub>2</sub>O<sub>6</sub>Zr<sub>2</sub>, triclinic, *a* = 10.4060(8) Å, *b* = 13.4310(5) Å, *c* = 14.5640(8) Å, *a* = 114.022(4)°, *β* = 103.013(5)°, *γ* = 95.904(5)°, *V* = 1767.66(19) Å<sup>3</sup>, space group *P* $\bar{1}$ , *Z* = 1,  $\rho_{\text{calcd.}}$  = 1.338 g cm<sup>–3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 0.373 mm<sup>–1</sup>, 45512 measured reflections, 8121 independent reflections (*R*<sub>int</sub> = 0.047), 6976 reflections observed with *I* > 2σ(*I*), *θ*<sub>max</sub> = 27.5°, *R* = 0.0315, *wR*<sub>2</sub> = 0.0970, GOF = 1.17, 428 parameter, min./max. residual electron density –0.50/+0.52 e Å<sup>–3</sup>.

CCDC-1042668 (for [(DIPH)AlMe]<sub>2</sub>) and -1042669 (for [Cp\*<sub>2</sub>Zr(Me)OAl(DIPH)]<sub>2</sub>) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H NMR, <sup>13</sup>C NMR, and 2D NMR spectra of (DIPH)AlMe and (DIPH)Al–O–Zr(Me)Cp\*<sub>2</sub> and high-temperature GPC analyses of polyethylenes.

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