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Bimetallic Catalysts

Insight into Oxide-Bridged Heterobimetallic Al/Zr Olefin Polymerization Catalysts

Cédric Boulho,[a, b] Harmen S. Zijlstra,[a, b, c] Alexander Hofmann,[a] Peter H. M. Budzelaar,[b, d] and Sjoerd Harder*[a, b]

Abstract: Reaction of (TBBP)AlMe-THF with [Cp∗Zr(OMe)] gave ([(TBBP)Al(THF)−O−Zr(OMe)Cp∗]− (TBBP = 3,5,5′-tetra-tert-Bu-2,2′-biphenolato). Reaction of [DIPPacnacAl(Me)−O−Zr(Me)Cp∗] with [Me2NH][B(C6F5)4]2 gave a cationic Al/Zr complex that could be structurally characterized as its THF adduct ([(DIPPacnac)Al(Me)−O−Zr(THF)Cp∗]2[B(C6F5)4]2 (DIPPacnac = H[C(Me)=C{2,6-IPr−2−C6H4}]2). The first complex polymerizes ethene in the presence of an alkylaluminoxane scavenger but in the absence of methylalumoxane (MAO). The adduct cation is inactive under these conditions. Theoretical calculations show very high energy barriers (∆G = 40–47 kcal mol−1) for ethene insertion with a bridged AlOZr catalyst. This is due to an unfavorable six-membered ring transition state, in which the methyl group bridges the metal and ethene with an obtuse metal-Me-C angle that prevents synchronized bond-breaking and making. A more likely pathway is dissociation of the Al-O-Zr complex into an aluminate and the active polymerization catalyst [Cp∗ZrMe]2.

Introduction

In recent decades homogeneous olefin polymerization has grown into a well-established field of chemistry.[1] Group 4 metalloence and post-metalloence dichloride precatalysts are activated by a cocatalyst that contains a Lewis acidic aluminum or boron center. In many cases methylalumoxane (MAO) is used for this purpose.[2] MAO functions as a methylating agent, methyl-group abstractor, cation stabilizer, and scavenger for catalyst deactivating impurities such as water.[3] Despite its frequent use and many desirable functions there are severe drawbacks to using MAO. It is a complex mixture of different (undefined) aggregates and unreacted Me3Al that are in dynamic equilibrium. Its composition changes over time, which affects reproducibility. An extreme excess of MAO is needed to achieve optimal polymerization activity (Al/metal ratios up to 20000 have been reported).[4]

To circumvent, or at least minimize, the need for external cocatalysts heterobimetallic polymerization catalysts have been developed. Some heterobimetallic olefin polymerization catalysts contain two polymerization active metals, and therefore still need an activating cocatalyst.[5–7] However, several examples of self-activating catalysts with a built-in Lewis acid have been described.[8–11] Roeksy and co-workers reported heterobimetallic Al/Zr catalyst systems in the form of Al−O−Zr complexes (Scheme 1).[12, 13] These hybrid complexes can catalyze ethene polymerization but are, despite their Al content, only polymerization active in the presence of MAO, albeit with significantly less MAO required to obtain the same activity as the [Cp∗ZrMe2]/MAO system.

Scheme 1. Synthesis of the first hybrid Al−O−Zr catalyst, reported by Roesky et al (see ref. [12a]).

The hybrid Al/Zr catalyst has no vacant coordination sites at either metal center, which explains the need for an alkyl abstracting activator such as MAO to create a polymerization-active species. Upon reaction with MAO three different polymerization pathways are possible (Scheme 2; pathways i–iii). In pathways i and ii polymerization would take place by a hypothetical migratory insertion between the two metal centers.
The mechanisms with the polymer chain at either Al (i) or Zr (ii) could alternate (flip-flop mechanism). Alternatively, only one of them could be operative in combination with a Zr–Al chain-transfer step after each insertion.

Although several different oxo-bridged heterobimetallic olefin polymerization catalysts have been used in olefin polymerization,\textsuperscript{[12c]} reports of mechanistic investigations or proposals of the catalytic cycle are scarce. There is a rare report of mechanistic investigations of the Ti–O–Zr hybrid catalyst [Cp*Zr(Me)–O–Ti(Me)Cp*] by Roesky and co-workers.\textsuperscript{[14]}

$^1$H NMR spectroscopic experiments showed that in the presence of low concentrations of MAO the Ti–O–Zr unit stays intact and methyl-group abstraction occurs at the Ti center. These investigations were carried out at a Ti–O–Zr/Al ratio of 1:10, which is much lower than that used in the polymerization experiments (Ti–O–Zr/Al = 1:78–1:512; best activities at 1:512). Therefore, it remains unclear whether the cluster stays intact under the polymerization conditions and whether there is any cooperativity between the two metals. Furthermore, these findings may not be transferable to the Al–O–Zr systems. The latter complexes only contain one olefin polymerization-active metal (Al undergoes much slower olefin oligomerization in the Aufbau reaction).\textsuperscript{[15]} Therefore, the observed increase in activity described earlier can only be attributed to a cooperative effect between Al and Zr or to breaking the Zr–O bond (see Scheme 2), in which case [DIPPnacnacAl(Me)O]– (DIPPnacnac = HC([(Me)C=N(2,6-iPr$_2$–C$_6$H$_3$)]$_2$) would function as an efficient leaving group. The effect of the leaving group X on the catalytic activity of [Cp$_2$ZrX$_3$] (X = Me or Cl) precatalysts is well established.\textsuperscript{[16]} To investigate the activation mechanism for the heterobimetallic catalysts in more detail a bimetallic Al–O–Zr catalyst with a vacant coordination site would be desirable. This may allow for activation without the MAO cocatalyst, and might provide insight into which of the previously discussed activation pathways (Scheme 2 i–iii) is most likely. We recently reported an attempt to synthesize such complexes by substitu-

tion of the monoanionic DIPPnacnac ligand with a dianionic bipheno
ome (Scheme 3).\textsuperscript{[17]} We used a bipheno
ome ligand (DIPH, see Scheme 3) functionalized with –CH$_2$C(Me)=CH$_2$

The complex is only active for ethene polymerization in combination with a MAO cocatalyst (Zr/Al = 1:1500, activity = 1595 kgPE mol$_{-1}$h$^{-1}$bar$^{-1}$).
al study on ethene polymerization with these heterobimetallic catalysts.

Results and Discussion
Complex synthesis and characterization

Bulky dianionic ligand 3,3′,5,5′-tetrabutylbiphenolato (TBBP)\(^{[16]}\) was chosen for use in the Al–O–Zr hybrid catalyst (Scheme 4). In principal, there are two possible routes to synthesize Al–O–Zr catalysts: deprotonation of a [(TBBP)AlOH] precursor by [Cp\(_{2}\)ZrMe\(_{2}\)] (Scheme 4i) or [Cp\(^{+}\)ZrMe\(_{2}\)], and deprotonation of [Cp\(^{+}\)Zr(Me)(OH)] by [(TBBP)AlMe] (Scheme 4ii). Because [Cp\(^{+}\)Zr(Me)(OH)] is not accessible the latter route is limited to the use of [Cp\(^{+}\)Zr(Me)(OH)].

To probe route i we set out to synthesize [(TBBP)AlOH] by controlled hydrolysis of an alkyl precursor. Although the synthesis and structure of monomeric [(TBBP)AlMe\(_{2}\)THF] is known,\(^{[17]}\) we attempted the synthesis of the THF-free precursor [(TBBP)AlMe] by reacting (TBBP)H\(_{2}\) with Me\(_{3}\)Al. The stoichiometric reaction led to a poorly defined mixture of products, whereas excess Me\(_{3}\)Al gave the [(TBBP)AlMe-AlMe\(_{3}\)] adduct from which coordinated Me\(_{3}\)Al could not be removed. Deprotonation of (TBBP)H\(_{2}\) with the bulkier reagent tBu\(_{3}\)Al in toluene at \(\text{55}^\circ\text{C}\) cleanly gave [(TBBP)AltBu]. The \(^{1}H\) NMR spectrum shows a sharp singlet for the Al–tBu protons at \(\delta = 1.10\) ppm but four separate ligand–tBu signals at \(\delta = 1.63, 1.52, 1.48, \) and \(1.15\) ppm, which is indicative of a symmetric phenolate-bridged dimeric complex. This was confirmed by X-ray structural analysis (Figure 1). The centrosymmetric dimer shows an Al\(_{2}\)O\(_{2}\) core in which the bond lengths range from 1.858(1)–1.878(1) \(\AA\) (average 1.868(1) \(\AA\)), which is likely due to increased steric hindrance in both the biphenolate ligand and alkyl substituent.\(^{[17]}\) Despite the increased steric bulk of TBBP, formation of a dimeric product could not be prevented. As the Cp\(^{+}\)Zr(Me)(Me–O–) substituent is bulkier than a tBu group, isolation of monomeric [Cp\(^{+}\)Zr(Me)(OH)OAl(TBBP)] is not excluded at this stage.

Next, we attempted to prepare THF-free species [(TBBP)AlO\(_{2}\)H] by controlled hydrolysis of [(TBBP)AltBu] in aromatic solvents. However, only undefined product mixtures were obtained. The presence of THF simplified the product spectra enormously: careful hydrolysis of known compound [(TBBP)AlMe\(_{2}\)THF] by water (1 equiv) gave the desired product [(TBBP)AlO\(_{2}\)H] in moderate yield (47\%) after recrystallization from hot toluene. The \(^{1}H\) NMR spectrum in C\(_{6}\)D\(_{6}\) revealed THF signals at \(\delta = 1.11\) and 3.05 ppm that are typical for coordinated THF. The OH signal is shifted far downfield to \(\delta = 11.12\) ppm, which is rather unusual because the OH proton in aluminum hydroxide complexes normally appears in the range \(\delta = 1–3\) ppm.\(^{[12,20–22]}\) An exception to this is the dimer [Mes\(_{3}\)AlO\(_{2}\)H] (Mes = mesityl), which shows an OH signal in the \(^{1}H\) NMR spectrum at \(\delta = 7.69\) ppm.\(^{[23]}\)

The crystal structure of the product revealed a pseudo-C\(_{3}\) symmetric trimer (Figure 2). The various tBu groups in the structure are heavily disordered and the unit cell contains considerable amounts of cocrystallized disordered solvent molecules (circa 27\% of the unit cell), thus its quality only allows for a generalized discussion. The central core of the trimeric aggregate is formed by three Al cations bridged by three hydroxide anions; the biphenolate ligands are bound in terminal positions. Interestingly, the THF ligands are not coordinated to the Lewis acidic Al centers, but instead function as acceptors in hydrogen bridges to the OH groups. The hydrogen atoms of the OH groups could not be located in the difference Fourier map, and have been placed at idealized positions. The short \(O_{\text{THF}}–O_{\text{OH}}\) distances that range from 2.534(7)–2.574(7) \(\text{Å}\) (average: 2.547(6) \(\text{Å}\)) are evidence for O–H–O hydrogen bridges that vary between 1.58 and 1.62 \(\text{Å}\) in length. A very similar structure was found for another trimeric biphenolate aluminum hydroxide complex with cocrystallized THF, [(MCIMP)AlO\(_{2}\)H] (MCIMP = 2,2-methylene-bis(4-chloro-6-isopropyl-3-methylphenolate)).\(^{[24]}\)

The THF ligands are surprisingly strongly bound; attempts to remove the coordinated THF molecules by heating the complex under high vacuum did not give the desired THF-free complex. Bridging of the hydroxide ion between two Lewis acidic Al\(^{1+}\) centers likely increases its hydrogen-donor ability substantially. However, reaction of [(TBBP)AlO\(_{2}\)H] with Cp\(^{+}\)ZrMe\(_{2}\) did not show any conversion under a variety of conditions. Use of the less-sterically hindered deprotonating agent Cp\(^{+}\)ZrMe\(_{2}\) also gave no noticeable conversion.
Attempted deprotonation of the Al hydroxide complex with the alkylzirconium complex was fruitless, hence we focused on the alternative pathway: deprotonation of \( [\text{Cp}^*\text{Zr}(\text{Me})\text{OH}] \) by an alkylaluminum complex (Scheme 4 ii). Because the reaction with dimeric \( [(\text{TBBP})\text{Al}(\text{Bu})_2] \) did not proceed, even under forcing conditions, we reacted the monomeric complex \( [(\text{TBBP})\text{Al}(@\text{Me}-\text{THF})] \) with \( [\text{Cp}^*\text{Zr}(\text{Me})\text{OH}] \) at room temperature and a smooth conversion to the desired heterobimetallic complex \( [(\text{TBBP})\text{Al}(\text{THF})\cdot\text{Zr}(\text{Bu})\text{Me}] \) was confirmed by X-ray analysis (Figure 3). The complex has no crystallographic symmetry and its main structural parameters are comparable to those of dimeric \( [(\text{DIPH})\text{Al}(@\text{O–Zr}(\text{Me})\text{Cp}^*)_2] \) (Table 1).

The \( \text{Al}–\text{O}(\text{Zr}) \) bond lengths are equal (within standard deviation) but the (\( \text{Al}[(\text{Me})\text{O}]–\text{Zr} \) bond length in the monomer (1.964(1) \( \text{Å} \)) is significantly shorter than in the dimer (2.007(1) \( \text{Å} \)). The \( \text{Al}–\text{O}–\text{Zr} \) angle in the TBBP complex (170.88(7)) is much larger than in the dimeric DIPH analogue (153.7(1)°). This may be due to the increased steric bulk caused by the \( \text{tBu} \) groups in the TBBP ligand. The \( \text{Zr}–\text{O} \) bond lengths in other reported \( \text{Zr}–\text{O}–\text{Ti} \) or \( \text{Zr}–\text{O}–\text{Hf} \) complexes are somewhat larger (range = 1.999(1)–2.026(1) \( \text{Å} \)), \(^{[14, 25, 26]} \) and a reported \( \text{Zr}–\text{O}–\text{Ca} \) complex \(^{[27]} \) has a substantially smaller \( \text{Zr}–\text{O} \) bond length (1.888(1) \( \text{Å} \)) due to the soft ionic \( \text{O}–\text{Ca} \) bond. The \( \text{Zr}–\text{O}–\text{metal} \) angles in other complexes are partially smaller.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( [(\text{TBBP})\text{Al}(\text{THF})]–\text{O}–\text{Zr}(@\text{Me})\text{Cp}^*]_2 )</th>
<th>( [(\text{DIPH})\text{Al}(@\text{O–Zr}(@\text{Me})\text{Cp}^*)_2]_2 )</th>
<th>( [(\text{DIPP} \text{nacnac})\text{Al}(@\text{Me–O–Zr}(@\text{Me})\text{Cp}^*)_2]_2 )</th>
<th>( [(\text{DIPP} \text{nacnac})\text{Al}(@\text{Me–O–Zr}(\text{THF})\text{Cp}^*])_2 [\text{B}(@\text{C} \text{F}_3)_2]_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}–\text{O}(\text{Zr}) )</td>
<td>1.693(1)</td>
<td>1.688(1)</td>
<td>1.710(3)</td>
<td>1.746(3)</td>
</tr>
<tr>
<td>( \text{Zr}–\text{O}(\text{Al}) )</td>
<td>1.964(1)</td>
<td>2.007(1)</td>
<td>1.929(3)</td>
<td>1.911(2)</td>
</tr>
<tr>
<td>( \text{Zr}–\text{Me} )</td>
<td>2.326(2)</td>
<td>2.285(3)</td>
<td>2.287(4)</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Zr}–\text{C}(@\text{Bu}) )</td>
<td>2.286(4)</td>
<td>2.279(3)</td>
<td>2.255(3)</td>
<td>2.247(3)</td>
</tr>
<tr>
<td>( \text{Al}–\text{O}(\text{Al}) )</td>
<td>1.723(1) (^{[26]} )</td>
<td>1.720(2) (^{[26]} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Al}–\text{N} )</td>
<td>–</td>
<td>–</td>
<td>1.920(3)</td>
<td>1.911(3)</td>
</tr>
<tr>
<td>( \text{Al}–\text{O}(\text{Zr}) )</td>
<td>1.708(7)</td>
<td>153.7(1)</td>
<td>158.2(1)</td>
<td>159.2(2)</td>
</tr>
<tr>
<td>( \text{Zr}–\text{C}(@\text{Bu}) )</td>
<td>132.9(1)</td>
<td>133.80(8)</td>
<td>124.4(1)</td>
<td>127.7(2)</td>
</tr>
</tbody>
</table>

\(^{[a]} \) Average of two independent molecules in the asymmetric unit. \(^{[b]} \) Average value.
As part of our studies on Al/Zr hybrid catalysts, we also converted the original Roesky system \([	ext{(DIPPnacnac)Al(Me)}–\text{Zr(Me)CP}]\) into a catalyst with a vacant coordination site by an NMR-scale reaction with \([\text{PhMe}_2\text{NH}]^+\text{[B(C}_6\text{F}_5]_2\text{O}]^-\) in \(\text{D}_2\text{O}\)toluene or \(\text{C}_6\text{D}_6/\text{D}_2\text{O}\)THF (80:20). Monitoring the reaction by \(^1\text{H} \text{NMR}

spectroscopy showed that the Zr–Me signal disappeared upon formation of \(\text{CH}_3\). The Al–Me signal observed at \(\delta = -0.44 \text{ ppm (CP}_2\text{D}_6/\text{D}_2\text{O}\)THF, 80:20\) was maintained (which indicated the formation of a vacant coordination site at the Zr center) but shifted downfield by \(\Delta \delta = 0.28 \text{ ppm compared to its neutral analogue (} \delta = -0.72 \text{ ppm). We could not isolate the Lewis base free cation–anion pair, but we could crystalize the THF-stabilized salt \([\text{(DIPPnacnac)Al(Me)}–\text{Zr(THF)CP}]^+\text{[B(C}_6\text{F}_5]_2\text{O}]^-\). The crystal structure shows the cation–anion complex with methyl-group abstraction at the Zr center and stabilization of the cation by THF coordination (Figure 4).

The complex shows no crystallographic symmetry and its structural parameters are closely comparable to those in the neutral complex \([\text{(DIPPnacnac)Al(Me)}–\text{Zr(Me)CP]}\) (shown in Table 1 for comparison). The Zr–O(Al) and Zr–Cp bond lengths are slightly shortened because of the cationic nature of the Zr center. The Zr–O(Al) bond length (1.911(2) \(\text{Å}\)) is shorter than in the TBBP and DIPH complexes (1.964(1) and 2.007(1) \(\text{Å}\), respectively). On the other hand, the Al–O(Zr) bond is somewhat elongated upon methyl-group abstraction. The Al–O(Zr) bond (1.746(3) \(\text{Å}\)) is also substantially longer than in complexes with dianionic ligands at Al (average bond length = 1.691(1) \(\text{Å}\), most likely due to the anionic nature of this aluminate unit. The Al-O-Zr bond angle (159.2(2)\(^\circ\)) lies between the values for the other complexes, and because the Zr center is sterically shielded by four ligands there are no Zr-\([\text{B(C}_6\text{F}_5]_2\text{O}]^-\) interactions.

**Table 2.** Ethene polymerization by different Al/Zr hybrid catalysts (toluene (20 mL), [Zr] = 19 \(\mu\text{M}\), ethene (5 bar), 30 °C, 15 min).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Scavenger (Al/Zr)</th>
<th>Activity (kg(\text{PE/mmol}_{\text{Al}})h(^{-1})bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>none</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>Me(_2\text{Al}) (300)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>Et(_2\text{Al}) (300)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>iBu(_2\text{Al}) (300)</td>
<td>1180(^{10})</td>
</tr>
<tr>
<td>5</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>iBu(_2\text{Al}) (300)</td>
<td>1070(^{10})</td>
</tr>
<tr>
<td>6</td>
<td>([\text{ITBBP}]/\text{Al(THF)}–\text{Zr(Me)CP}^*])</td>
<td>rBu(_2\text{Al}) (300)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>([\text{DIPPnacnac}]/\text{Al(Me)}–\text{Zr(THF)CP}^*]\text{[B(C}_6\text{F}_5]_2\text{O}]^-)</td>
<td>iBu(_2\text{Al}) (300)</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>([\text{DIPPnacnac}]/\text{Al(Me)}–\text{Zr(THF)CP}^*]\text{[B(C}_6\text{F}_5]_2\text{O}]^-)</td>
<td>iBu(_2\text{Al}) (300)</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^{10}\) \(M_6 = 302 \times 10^4 \text{ g mol}^{-1}\); \(M_6 = 960 \times 10^4 \text{ g mol}^{-1}\); PDI = 3.17. \(M_6 = 440 \times 10^4 \text{ g mol}^{-1}\); \(M_6 = 1336 \times 10^4 \text{ g mol}^{-1}\); PDI = 3.03.

**Figure 4.** Crystal structure of \([\text{(DIPPnacnac)Al(Me)}–\text{Zr(THF)CP}^*]\text{[B(C}_6\text{F}_5]_2\text{O}]^-\); the anion is not shown, and the hydrogen atoms and Pt groups have been omitted for clarity. Selected bond distances and angles are shown in Table 1. of a Lewis acidic alkylaluminum reagent (Me\(_2\text{Al}\) or Et\(_2\text{Al}\) that could simultaneously function as a scavenger for impurities, but no polymerization activity was observed (Table 2, entries 2 and 3). However, addition of iBu\(_2\text{Al}\) gave a polymerization-active system with an activity of 1180 kg\(\text{PE/mol}_{\text{Al}}\)h\(^{-1}\)bar\(^{-1}\) (Table 2, entry 4). This activity is slightly lower than that for the previously reported dimer \([\text{DIPH}]/\text{Al–Zr(Me)CP}^*]\) in the presence of MAO (1595 kg\(\text{PE/mol}_{\text{Al}}\)h\(^{-1}\)bar\(^{-1}\)). Decreasing the Al/Zr ratio from 300 to 30 only gave a small decrease in activity (1070 kg\(\text{PE/mol}_{\text{Al}}\)h\(^{-1}\)bar\(^{-1}\); Table 2, entry 5), which shows the effectiveness of iBu\(_2\text{Al}\) as a cocatalyst. Interestingly, no polymerization activity was observed upon addition of rBu\(_2\text{Al}\) (Table 2, entry 6). The fact that polymerization activity was only observed in the presence of iBu\(_2\text{Al}\) suggests that the alkylaluminum species is more than just a scavenger for impurities. The size of the alkyl group in the cocatalyst is critical: it needs to be large enough to shift the monomer–dimer equilibrium to the side of the Lewis acidic monomer, but small enough to
leave the Lewis acidic Al center accessible for activation. Smith reported accurate measurements on \( R_2\text{Al}, c\rightarrow 2 R_2\text{Al} \) equilibria in hydrocarbon solutions and found that the monomer percentages increased in the order \( R = \text{Me} (0.02\%) < \text{Et} (0.35\%) < \text{nPr} (1.78\%) < \text{nBu} (2.64\%) < \text{Bu} (95.23\%) < \text{iBu} (100\%) \); values for 0.1 M hydrocarbon solutions at 20 °C.\(^{126}\) It is apparent that \( \text{Bu}_2\text{Al} \), which is predominantly monomeric in solution but is less bulky than \( \text{Bu}_3\text{Al} \), is the optimal cocatalyst. At this stage, it is unclear whether \( \text{Bu}_2\text{Al} \) extracts the THF ligand to leave a cationic \( \text{Al}^{+} \)-\( \text{O}^{-} \)-\( \text{Zr} \) catalyst with a vacant coordination site or whether the \( \text{Zr} \)-\( \text{O}^{-} \) bond is broken to generate \( [\text{Cp}^+\text{ZrMe}]^+ \) and \( [\text{Bu}_2\text{Al}^{+} \rightarrow \text{Al}(\text{THF})^+] \).

Experiments that used \( [\text{DIPPnacnac}]\text{Al}(\text{Me})^{-} \rightarrow \text{O}^{-} \text{ZrCP}_{3} \)\(^+\), \( [\text{B}(\text{C}_6\text{H}_{3})_{3}]^- \) prepared in situ in the presence (or absence) of the scavenger \( \text{Bu}_2\text{Al} \) did not produce a polymerization-active species (Table 2, entry 7). Likewise, use of the crystalline, well-defined, cation–anion pair \( ([\text{DIPPnacnac}]\text{Al}(\text{Me})^{-} \rightarrow \text{O}^{-} \text{THF})\text{ZrCP}_{3} \)\(^+\), \( [\text{B}(\text{C}_6\text{H}_{3})_{3}]^- \) in the presence (or absence) of \( \text{Bu}_2\text{Al} \) did not lead to polymerization (Table 2, entry 8). Therefore, it seems likely that the high activities observed for ethene polymerization with the Roesky system—\( [\text{DIPPnacnac}]\text{Al}^{+}\text{Me}^{-} \rightarrow \text{O}^{-} \text{MeZrCP}_{3} \) activated by MAO\(^{12a}\)—cannot be explained by a mechanism in which the \( \text{Al}^{+} \)-\( \text{O}^{-} \)-\( \text{Zr} \) species is still intact (see Scheme 2i and ii). Thus, we initiated a DFT study to probe the feasibility of a heterobimetallic mechanism that involves cooperation between both metal centers.

**DFT calculations**

Minima and transition states were optimized at the B3-LYP/SV(P) level and final energies were calculated at the M06-2X/TZVP level with corrections for free energies at 298 K (see experimental for further details). Ethene complexes and insertion transition states according to the pathways i–iii shown in Scheme 2 were derived for the full system \( [\text{TBBP}]\text{Al}(\text{THF})^{-} \rightarrow \text{O}^{-} \text{Zr(Me)}\text{Cp}^+\) (see Figure 5 and Table 3).

The two alternative bimetallic ethene complexes (A and B) are rather close in energy, with ethene coordination to Al (B) preferred by 4.1 kcal mol\(^{-1}\). This is likely due, in part, to the steric hindrance from the Cp\(^*\) ligands, but that is not the whole story because even in the simplified model system with Cp groups at Zr (see the Supporting Information) we calculated a preference of about 3 kcal mol\(^{-1}\) for ethene binding at Al. We believe that a second contribution comes from the unfavorable zwitterionic nature of complex A, in which Al and Zr carry formal charges of +1 and +1, respectively. Ethene binds only weakly in both the bimetallic complexes (A and B) and

<table>
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<tr>
<th>Table 3. Relative free energies (298 K, 1 bar) for ethene insertion into Me–Me bonds (M = metal) for paths i–iii shown in Scheme 2 (see also Figure 5).</th>
</tr>
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<tbody>
<tr>
<td><strong>Bimetallic system</strong></td>
</tr>
<tr>
<td>( [\text{TBBP}]\text{Al}(\text{Me})^{-} \rightarrow \text{O}^{-} \text{ZrCP}_{3} )(^+)</td>
</tr>
<tr>
<td>( [\text{TBBP}]\text{Al}(\text{Me})^{-} \rightarrow \text{O}^{-} \text{Zr(C}_6\text{H}_5\text{)}\text{Cp}^+)(^+) (A)</td>
</tr>
<tr>
<td>Insertion TS Me(^{+})Al(^{-}) (B)</td>
</tr>
<tr>
<td>( [\text{TBBP}]\text{Al}(\text{THF})^{-} \rightarrow \text{O}^{-} \text{Zr(Me)}\text{Cp}^+)(^+)</td>
</tr>
<tr>
<td>( [\text{TBBP}]\text{Al}^{-} \rightarrow \text{O}^{-} \text{Zr(Me)}\text{Cp}^+)(^+) (C)</td>
</tr>
<tr>
<td>Insertion TS Me(^{+})Zr (E)</td>
</tr>
</tbody>
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<tr>
<th><strong>Monometallic system</strong></th>
<th>( \Delta G ) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{Cp}^+\text{ZrMe}]^+)</td>
<td>9.32</td>
</tr>
<tr>
<td>( [\text{Cp}^+\text{ZrMe(C}_6\text{H}_5\text{)}]^+) (C)</td>
<td>0.00</td>
</tr>
<tr>
<td>Insertion TS (F)</td>
<td>7.79</td>
</tr>
</tbody>
</table>

Figure 5. Calculated core geometries (the phenolate \( \text{Bu} \) and \( \text{Cp}^+\text{Me} \) groups have been omitted for clarity) of the complexes and transition states in paths i–iii shown in Scheme 2. Bond lengths (Å), angles (°).
the monometallic complex (C), which is evident from the rather long M–C distances (> 2.5 Å for Al, > 2.8 Å for Zr) and from the ethene C=C bond length, which is only 0.01 Å longer than in free ethene when calculated at the same level of theory.

For the monometallic system [Cp*ZrMe(C₅H₅)]⁺ (C) the insertion free-energy barrier is only 7.8 kcal mol⁻¹, which agrees with the observation that the [Cp*ZrX₃]/MAO system is an active polymerization catalyst.²⁹ For the bimetallic system there are two issues: 1) removal of the THF molecule that is coordinated to the Al atom of the precatalyst, and 2) olefin insertion into the resulting unsaturated system. The calculated free-energy cost for THF removal is 20.8 kcal mol⁻¹, which suggests that this is not an easy process, but it could be performed in the presence of a strongly Lewis acidic scavenger. Subsequent ethene complexation to Al is slightly exergonic (4.6 kcal mol⁻¹). Alternatively, the methyl group could migrate from Zr to Al (5.6 kcal mol⁻¹), after which ethene coordination to Zr is again slightly exergonic (4.1 kcal mol⁻¹). In either case, the subsequent olefin insertion is difficult: the two transition states for bimetallic insertion following paths i and ii (Scheme 2) are more than 39 kcal mol⁻¹ above the most-stable olefin complex (Table 3). These high barriers correspond to reactions that would be very slow under ambient conditions. Clearly these mechanisms cannot be responsible for the observed polymerization activity. Unfortunately it is not possible to put paths i and ii on a common scale with path iii (Scheme 2) because we do not know exactly how the [(TBBP)AlO]⁻ fragment would be removed from the precatalyst to yield [Cp*ZrMe]⁺ in the latter pathway. Nevertheless, it seems justified to assume that polymerization happens at a monometallic Zr species.

Next, we considered why bimetallic insertion is so strongly disfavored. The steric bulk of the Cp⁺ and TBBP ligands appears unimportant because the barriers calculated for model systems with unsubstituted Cp ligands are rather similar to those for the full system (see Table S3 in the Supporting Information), which also implies that less-hindered systems are unlikely to follow bimetallic insertion mechanisms. We believe that an important reason is the rather obtuse M-CH₃-C angle enforced by the six-membered-ring transition state. During insertion, the CH₃ cone has to tilt to form a new C=C bond while breaking the existing M–C bond. The larger the M-CH₃-C angle is forced to be, the more the existing bond has to break before the new bond can start to form. Despite strong folding of the cyclic transition state, the two bimetallic transition states show much larger M-CH₃-C angles (85° and 102°) than the simple monometallic [Cp*ZrMe]⁺ system (72°). Figure 6 shows the Wiberg bond indices for three relevant transition states; the bond indices for the bonds forming to and breaking from the migrating methyl group are of particular interest. In [Cp*Zr(Me)–C₅H₅]⁺ these two numbers add to 1.0, which indicates a smooth transition of the Zr–Me bond into the C–C–Me bond. In contrast, for the two bimetallic systems the two indices total well below 1.0, which indicates a loss of net bonding of the methyl group.

Our DFT calculations show that the activation energies for heterobimetallic ethene insertion are so high that it is unlikely that this reaction will proceed at temperatures below 100 °C. This contrasts with the high activity for the system [(TBBP)Al(THF)–O–Zr(Me)Cp⁺]/iBu₃Al in ethene polymerization at 30 °C. Therefore, it is likely that polymerization proceeds through a mechanism in which the Zr–O bond is broken and a classical [Cp*ZrMe]⁺ ion is formed (cf. Scheme 2 iii).

The reaction of iBu₃Al with [(TBBP)Al(THF)–O–Zr(Me)Cp⁺] was followed by 'H NMR spectroscopy. Addition of iBu₃Al to a solution of [(TBBP)Al(THF)–O–Zr(Me)Cp⁺] in C₆D₆ immediately resulted in the formation of a variety of undefined species, which indicated decomposition of [(TBBP)Al(THF)–O–ZrMeCp⁺]. Unambiguous assignment of the signals is difficult, but slow cooling of the solution gave colorless crystals of [(TBBP)Al(iBu₃)] (determined by crystal-structure analysis; see the Supporting Information). Therefore, we propose a mechanism in which monomeric Lewis acidic iBu₃Al coordinates to the Al–O–Zr unit, which is quite flexible and can bend (Scheme 5).

![Figure 6. Wiberg bond indices for forming and breaking bonds in the transition states of [Cp*ZrMe–C₅H₅]⁺ and the two bimetallic systems. The number in italics is the sum of the two bond indices to the Me group.](image-url)
the side product of the last step shown in Scheme 5, could be isolated in its dimeric form (see above). Although biphenolate alkylaluminums were recently found to be active cocatalysts in ethene oligomerization,[30] our previous findings[31] indicate that the dimer ([TBBP]AlBu$_2$) itself should not be an activator.

Conclusion

Exchange of the monoanionic [β-diketiminate ligand DIPPnacnac] in Roesky's hybrid catalyst ([DIPPnacnac)Al(Me)−O−Zr(Me)Cp$_3$] for a dianionic biphenolate ligand TBBP gave a complex with a free coordination site at Al. The complex could only be obtained by reaction of [TBBP]AlMe-THF and [Cp$_2$Zr(η-$C_6$H$_5$)O] and therefore the vacant coordination site is occupied by a THF molecule. The main geometric parameters in ([TBBP]Al(THF)−O−Zr(Me)Cp$_3$)$_2$ are similar to those reported for the THF-free dimeric complex [DIPP]Al−O−Zr(Me)Cp$_3$)$_2$.[17]

The reaction of Roesky's hybrid catalyst ([DIPPnacnac)Al(Me)−O−Zr(Me)Cp$_3$] with [PhMe$_2$NH]$_2$ [B(C$_6$F$_4$)$_3$] results in abstraction of the methyl group at Zr. Isolation of the cation ([DIPPnacnac)Al(Me)−O−Zr(Me)Cp$_3$]$,^+$ which has a free coordination site, proved difficult but the THF adduct ([DIPPnacnac)Al(Me)−O−(THF)ZrMeCp$_3$]$,^+$ [B(C$_6$F$_4$)$_3$]$^-$ was characterized by X-ray crystallography and $^1$H NMR spectroscopy. Although the bond lengths to Zr are slightly contracted, methyl-group abstraction does not lead to major changes in the geometry.

The THF-stabilized complex ([TBBP]Al(THF)−O−Zr(Me)Cp$_3$)$_2$ is only active in ethene polymerization in the presence of Bu$_3$Al (30 equiv). The bulkier cocatalyst Bu$_4$Al showed no activity, probably on account of its reduced Lewis acidity. Less-bulky alkylaluminum cocatalysts (Me$_2$Al or Et$_2$Al) also showed no activity, probably due to the fact that these occur mainly as dimers with strongly reduced Lewis acidity. Ours is the first example of a defined Al/Zr system that does not need to be activated by MAO.

The THF-stabilized complex ([DIPPnacnac)Al(Me)−O−(THF)ZrMeCp$_3$]$,^+$ [B(C$_6$F$_4$)$_3$]$^-$ is not active in ethene polymerization in the presence or absence of an $Bu_3$Al scavenger. Interestingly, the THF-free cation ([DIPPnacnac)Al(Me)−O−Zr(Me)Cp$_3$]$^+$, prepared in situ, is also inactive in ethene polymerization in the presence of an alkylaluminum scavenger. Because activation of the Roesky catalyst with [PhMe$_2$NH]$_2$ [B(C$_6$F$_4$)$_3$] gave a defined Al/Zr cationic species that did not show activity in ethene polymerization, it is likely that another route explains the activity found for the [(DIPPnacnac)Al(Me)−O−Zr(Me)Cp$_3$]/MAO system.

Indeed, DFT calculations on Al/Zr hybrid catalysts show that the transition state for ethene insertion (a six-membered ring containing both metals) is too high in energy (40–47 kcal mol$^{-1}$) to proceed at room temperature. This is due to a rather large metal-Me$_2$C angle (>85°) that is enforced by the six-membered-ring transition state. This results in a mismatch between the bond-breaking and bond-making processes, and explains the unrealistically high activation energy (compared to about 8 kcal mol$^{-1}$ for [Cp$_2$ZrMe]$^+$). Wiberg bond indices confirm that the six-membered-ring transition states for Al/Zr catalysts show substantial bond breaking without significant conomitant bond formation, which results in a loss of total bond energy.

Instead, it is proposed that addition of an alkylaluminum cocatalyst (or MAO) to Al/Zr hybrid catalysts induces cleavage of the Zr−O bond resulting in the active ethyene polymerization catalyst [Cp$_2$ZrMe]$^+$. The ease or extent of activation is determined by the nature of the leaving group [LAl(Me)O]$^−$ or [LAl(THF)O]$^−$ (L = monoanionic ligand, L$^-$ = dianionic ligand). Differences in leaving-group ability may explain why in some cases $Bu_3$Al would be sufficient for activation, whereas in other cases more Lewis acidic MAO is needed. The activity of the system is regulated by equilibria that are controlled by interactions between the active catalyst [Cp$_2$Zr(polymeryl)]$^+$ and hitherto unknown anionic species.

Experimental Section

General considerations

All experiments were performed under a nitrogen atmosphere by using standard Schlenk line and glovebox techniques. The solvents were dried on alumina columns and were degassed by bubbling nitrogen through the solvent reservoir. $Bu_3$Al,[31] (TBBP)H$_2$,[18] (TBBP)AlMe-THF,[19] (DIPPnacnac)AlMe−O−Zr(Me)Cp$_3$,$^{[32]}$ and MAO[34] were prepared according to reported literature procedures. Me$_2$Al (97%) and $Bu_3$Al were purchased from Sigma Aldrich, and [PhMe$_2$NH]$_2$ [B(C$_6$F$_4$)$_3$] was purchased from Boulder Scientific; all these reagents were used as received, except $Bu_3$Al which was distilled prior to use. Ethene (purity 4.5) was purchased from Air Liquid and used as received. NMR spectra were recorded with a Bruker DPX (300 MHz) andBruker Avance III HD (400 MHz) spectrometer. Molecular-weight distributions of the polymers were determined by gel-permeation chromatography (GPC) versus polystyrene standards by using dichlorobenzene as the eluent at 135°C. Crystals were measured with a Bruker diffractometer equipped with a Nonius-Kappa charged-coupled device (CCD) area detector or an Agilent Supernova with an Atlas52 CCD detector; Nova (Cu) and Nova (Mo) X-ray microscopes were used.

Synthetic procedures

Synthesis of [TBBP]Al(OH)$^-$: [TBBP]AlMe-THF (998 mg, 1.91 mmol) was dissolved in THF (20 mL), and the solution was cooled to 100°C. Water (35 μL, 1.94 mmol) was added via microsyringe, and the resulting solution was stirred for 10 min. The mixture was warmed to RT and stirred overnight. Evaporation of the solvent gave a white solid, which was dissolved in hot toluene (10 mL) and recrystallized at 4°C to give [TBBP]Al(OH)$^-$ as a colorless crystalline material (475 mg, 0.905 mmol, 47%). $^1$H NMR (300 MHz, C$_6$D$_6$): δ = 11.12 (s, 1H; AlOH), 7.49 (d, $^3$J(H,H) = 2.4 Hz, 2H), 7.16 (brm, 2H), 3.05 (brm, 4H; THF), 1.81 (s, 18H; C(CH$_3$)$_3$), 1.29 (s, 18H; C(CH$_3$)$_3$), 1.11 ppm (brm, 4H; THF); $^1$C NMR (75 MHz, C$_6$D$_6$): δ = 153.6 (Ar), 141.2 (Ar), 139.0 (Ar), 132.6 (Ar), 128.8 (Ar), 122.9 (Ar), 67.9 (THF), 36.0 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 32.0 (C(CH$_3$)$_3$), 31.9 (C(CH$_3$)$_3$), 25.3 ppm (THF); elemental analysis calcd (%) for C$_{39}$H$_{54}$AlO$_4$: C 73.25, H 9.41; found: C 73.52, H 9.50.

Synthesis of [TBBP]AlBu$_2$: (TBBP)H$_2$ (420 mg, 1.02 mmol) was dissolved in toluene (20 mL), and AlBu$_3$ (221 mg, 1.11 mmol) was added dropwise. The resulting solution was heated to 55°C and stirred overnight. The solvent was evaporated and the residue was washed with hexane (2×10 mL) to give [TBBP]AlBu$_3$ as a white solid (398 mg, 0.40 mmol, 79%). $^1$H NMR (300 MHz, C$_6$D$_6$): δ = 7.63
The hydrogen atoms were placed at calculated positions and were refined isotropically in a riding mode. Specific information regarding the refinement of each structure can be found in the Supporting Information.

Crystal-structure determination

Crystal data can be found in the Supporting Information (Table S1). The crystal structures were solved by using the Olex software package[35] through direct methods (SHELXT)[36] and refined with SHELXL.[37] All geometry calculations and graphics were performed with PLATON.[38] The hydrogen atoms were placed at calculated positions and were refined isotropically in a riding mode. Specific information regarding the refinement of each structure can be found in the Supporting Information.

Theoretical calculations

The system is rather large, but simplification by deleting the Me and Rb substituents is likely to introduce artefacts. Therefore, we modeled the complete system, which limited the size of the basis set employed. The structures of the olefin complexes and insertion transition states were fully optimized at the B3-LYP[43]/def-SVP[44] level (def-SVP[45] and Stuttgart ECP[46] on Zr) by using Turbomole 6.5[47] coupled to an external optimizer.[48] Vibrational analyses (analytical Hessians) were used to verify the nature of each stationary point. Improved single-point energies were calculated at the M06-2X[49]/TZVP[50] level (def-TZVP basis[51] and Stuttgart ECP[52] on Zr) by using Gaussian 09.[53] The final free energies were obtained by combining the M06-2X energies with gas phase (298 K, 1 bar) thermal corrections, in which the T∆S term was scaled by 0.67 to account for reduced entropy in solution.[54] Wiberg bond indices were calculated for the transition states.[55] The [Cp[ZrMe]4]+C4H4 system was included for comparison. All xyz coordinates are listed in the Supporting Information.

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Keywords: alkene polymerization - aluminum - bimetallic catalysis - synthetic methods - zirconium
