Kinetic and Mechanistic Aspects of Propene Oligomerization with Ionic Organozirconium and -hafnium Compounds

Eshuis, Johan J.W.; Tan, Yong Y.; Meetsma, Auke; Teuben, Jan H.; Renkema, Jaap; Evens, George G.

Published in:
Organometallics

DOI:
10.1021/om00037a061

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1992

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 02-01-2019
In \(N,N\)-dimethylaniline the ion complexes \([\text{Cp}^*\text{MMe(THT)}]^+\) \([\text{BPh}_4]^-\) \((\text{M} = \text{Zr}, \text{Hf})\)

Johan J. W. Eshuis, Yong Y. Tan, Auke Meetsma, and Jan H. Teuben

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Jaap Renkema and George G. Evens

DSM Research BV, P.O. Box 18, 6160 MD Geleen, The Netherlands

Received August 23, 1991

In \(N,N\)-dimethylaniline the ion complexes \([\text{Cp}^*\text{MMe(THT)}]^+\) \([\text{BPh}_4]^-\) \((\text{M} = \text{Zr}, \text{Hf})\) oligomerize propene to low molecular weight oligomers. At room temperature for \(\text{M} = \text{Zr}\) a rather broad molecular weight distribution is obtained \((\text{C}_9 \text{ to } \text{C}_{14})\), whereas for \(\text{M} = \text{Hf}\) only one dimer (4-methyl-1-pentene) and one trimer (4,6-dimethyl-1-heptene) are formed. With an increase in reaction temperature the product composition shifts to lower molecular weights, but the specific formation of head-to-tail oligomers is retained. The oligomers are formed by \(\beta\)-Me transfer from the growing oligopropene alkyl chain to the metal center. The molecular weight distribution of the oligomers produced at temperatures between 5 and 45 °C is satisfactorily described by the Flory–Schulz theory.

This allows the calculation of ratios of rate coefficients for propagation \((k_p)\) and termination \((k_t)\). Values for \((\Delta G_p^* - \Delta G_t^*)_{298K}\) were calculated as -1.9 (3) and -1.4 (4) kcal mol\(^{-1}\) for \([\text{Cp}^*\text{ZrMe(THT)}]^+\) \([\text{BPh}_4]^-\) and \([\text{Cp}^*\text{HfMe(THT)}]^+\) \([\text{BPh}_4]^-\), respectively. Both complexes crystallize in the space group \(Pn\alpha2\). with \(a = 31.31 (1)\) Å, \(b = 11.84 (4)\) Å, \(c = 11.08 (4)\) Å, \(V = 4110 (2)\) Å\(^3\), and \(Z = 4\) for \([\text{Cp}^*\text{ZrMe(THT)}]^+\) \([\text{BPh}_4]^-\) and \(a = 31.32 (1)\) Å, \(b = 11.85 (7)\) Å, \(c = 11.029 (1)\) Å, \(V = 4086 (1)\) Å\(^3\), and \(Z = 4\) for \([\text{Cp}^*\text{HfMe(THT)}]^+\) \([\text{BPh}_4]^-\). A molecular modeling study based on the molecular structures using the Alchemy software package suggests that the conformations with the \(\beta\)-Me group in the plane between the \(\text{Cp}^*\) rings are more stable than the conformations with the \(\beta\)-Me group pointing toward one of the \(\text{Cp}^*\) ligands. Inactivation of the catalysts is caused by two different mechanisms. At room temperature allylic C–H activation of monomer and isobutene (formed by a minor \(\alpha\)-Me transfer termination) gives inactive (methyl)alkyl compounds, \([\text{Cp}^*\text{M}(\eta^2-\text{C}_5\text{H}_4\text{H}_3\text{Me})]\) and \([\text{Cp}^*\text{M}(\eta^2-\text{C}_5\text{H}_4\text{H}_3\text{Me})]\) \((\text{M} = \text{Zr}, \text{Hf})\).

At elevated temperatures (>45 °C) catalytically inactive zwitterionic complexes \([\text{Cp}^*\text{M}^-\text{m-C}_6\text{H}_5\text{BPh}_3\text{]+}\) \((\text{M} = \text{Zr}, \text{Hf})\) are formed through aromatic C–H activation. Reactivation of the inactive (methyl)alkyl complexes can be achieved by addition of hydrogen to the oligomerization mixtures.

**Introduction**

Neutral d\(^0\), 14-electron complexes \(\text{Cp}^*\text{LnR}\) \((\text{Ln} = \text{lanthanide or group 3 metal, R = alkyl, H})\) and cationic d\(^1\), 16-electron complexes \([\text{Cp}^*\text{MR}(\text{L})]^+\) \((\text{Cp}^* = \eta^5-\text{C}_5\text{H}_5\text{C}_6\text{H}_4\text{Me}_3\text{H}_3\text{M}, \text{TH} = \text{tetrahydrothiophene})\).

(1) In this paper the following abbreviations are used: \(\text{Cp}^* = \eta^5-\text{C}_5\text{H}_5\text{C}_6\text{H}_4\text{Me}_3\text{H}_3\text{M, Cp} = \eta^5-\text{C}_5\text{H}_5\text{Me}, \text{Cp}^* = \eta^5-\text{C}_5\text{H}_5\text{C}_6\text{H}_4\text{Me}_3\text{H}_3\text{M, TH} = \text{tetrahydrothiophene).}


5. One of the most striking features of a number of catalytic systems based on \([\text{Cp}^*\text{MR}]^+\) \((\text{M} = \text{Lu, R = alkyl}), [\text{Cp}^*\text{MMe(THT)}]^+\) \((\text{M} = \text{Zr}, \text{Hf}), \text{and } [\text{Me}_2\text{Si}(\text{BuC}_6\text{H}_4\text{Me})_2\text{ScR}] (\text{R = hydride})\) is their propensity to terminate chain growth by \(\beta\)-alkyl elimination instead of the more commonly encountered \(\beta\)-H elimination.

Our group has focused on the more fundamental aspects of the initiation, propagation, and termination steps in olefin oligomerization and polymerization with ion group 4 complexes \([\text{Cp}^*\text{MMe(THT)}]^+\) \([\text{BPh}_4]^-\) \((\text{M} = \text{Ti, Zr, Hf})\). We have shown that these compounds \((\text{M} = \text{Zr, Hf})\) are effective catalysts for the polymerization of ethene and that
they oligomerize propene. The catalytic systems show a remarkable difference in selectivity toward propene. Whereas the zirconium compound at room temperature produces oligomers up to C_{24}, the hafnium compound only gives one dimer (4-methyl-1-pentene) and one trimer (4,6-dimethyl-1-heptene) under the same conditions. Labeled propene CH_2=CH-CD_3 was used to demonstrate that β-Me elimination is the dominant termination which accounts for over 97% of the products obtained. Termination of chain growth by β-H transfer to the metal takes place as well but is a minor pathway (<3%).

In this paper we report the effect of temperature on the initiation, propagation, and termination reactions and correlate the results to differences in activation parameters. Further, the inactivation of the catalysts was determined at various temperatures and methods developed to reactivate the catalysts.

Results and Discussion

Effect of Temperature on Oligomerization. Products. As described earlier, both complexes [Cp*,ZrMe(THT)]^+[BPh_4]^- (1) and [Cp*,HfMe(THT)]^+[BPh_4]^- (2) oligomerize propene at room temperature in N,N-dimethylaniline. The Hf complex gives exclusively the dimer 4-methyl-1-pentene, and the trimer, 4,6-dimethyl-1-heptene. The Zr complex gives a much broader distribution with oligomers up to C_{24}. At higher temperatures the formation of the lower oligomers is clearly favored (Figure 1). This was especially evident for the hafnium compound, where above 55 °C the dimer 4-methyl-1-pentene forms more than 95% of the oligomerization products. For the zirconium-based catalyst this level of selectivity is not achieved within the temperature range studied. At lower temperatures broad distributions are obtained for both the Zr and Hf compounds (oligomers up to C_{30} and C_{31}, respectively). Oligomer distributions for various temperatures are listed in Table I. Similar effects (i.e. decreasing polymer molecular weight with increasing temperature) have been observed in other Ziegler–Natta type polymerizations. Although the shift toward lower molecular weight with increasing temperature can be partially attributed to the decrease in propene concentration, lower molecular weights are also expected on thermodynamic grounds. Unfortunately, at temperatures where selectivity for dimerization for 2 exceeds 95% (i.e. at temperatures above 60 °C, Table I), the catalyst is inactive after about 15 productive cycles due to reaction of the cationic catalyst with the anion (vide infra).

Effect of Temperature on Oligomerization. Kinetics. At 25 °C, over 97% of the products resulting from the catalytic oligomerization of propene with [Cp*,MMe(THT)]^+[BPh_4]^- (1, M = Zr, 2, M = Hf) can be explained by the reactions shown in Scheme I. For such a (homogeneous) oligomerization reaction with single initiation, propagation, and termination steps with k_i, k_p, and k_t, remaining constant throughout the oligomerization and in which inactivation of the catalyst is negligible, the Flory–Schulz distribution is valid:

\[ m_p = P a^P \ln^2 \alpha \]  

with \( m_p \) denoting the weight fraction of oligomer with degree of oligomerization \( P \) and \( \alpha \) denoting the probability of the propagation step with \( P \).

\[ \frac{\alpha}{(1 - \alpha)} = \frac{k_p}{k_t} [C_3H_6] \]

Values for \( m_p \) can be determined from gas chromatographic analysis of the oligomerization reactions. According to (a), a plot of \( \ln (m_p/P) \) versus \( P \) yields a straight line with slope in \( \alpha \). With our oligomerization reactions two assumptions have to be made to allow the application of the Flory–Schulz theory. Inactivation of the catalyst should be slow relative to the insertion, propagation, and termination steps, and termination reactions other than β-Me elimination (e.g. β-H elimination) have to be negligible. At the temperature range studied (5–95 °C) oligomerization products due to β-H elimination accounted for less than 3% of the total propene consumption.

---


Table II. $\alpha$ Values and $k_p/k_i$ Ratios for Propene Oligomerization with 1 and 2 as a Function of Temperature

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>$\alpha$ of 1</th>
<th>$\alpha$ of 2</th>
<th>$k_p/k_i$ of 1</th>
<th>$k_p/k_i$ of 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.96 (5)</td>
<td>0.77 (2)</td>
<td>36.2 (6)</td>
<td>20.9 (1.3)</td>
</tr>
<tr>
<td>15</td>
<td>0.85 (3)</td>
<td>0.59 (5)</td>
<td>25.2 (7)</td>
<td>15.1 (1.0)</td>
</tr>
<tr>
<td>25</td>
<td>0.63 (3)</td>
<td>0.39 (2)</td>
<td>17.3 (5)</td>
<td>11.2 (2)</td>
</tr>
<tr>
<td>35</td>
<td>0.41 (6)</td>
<td>0.22 (2)</td>
<td>11.4 (5)</td>
<td>8.3 (5)</td>
</tr>
<tr>
<td>45</td>
<td>0.26 (11)</td>
<td>0.11 (2)</td>
<td>9.5 (3)</td>
<td>6.1 (9)</td>
</tr>
</tbody>
</table>

$k_p$ = rate constant for propagation, $k_i$ = rate constant for termination.

Table III. Values for $(\Delta H_p^* - \Delta H_i^*)$, $(\Delta S_p^* - \Delta S_i^*)$, and $(\Delta G_p^* - \Delta G_i^*)_{298K}$ for the Oligomerization of Propene with 1 and 2

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$(\Delta H_p^* - \Delta H_i^*)$</th>
<th>$(\Delta S_p^* - \Delta S_i^*)$</th>
<th>$(\Delta G_p^* - \Delta G_i^*)_{298K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-7.5 (1)</td>
<td>-18.7 (5)</td>
<td>-19 (3)</td>
</tr>
<tr>
<td>2</td>
<td>-5.5 (2)</td>
<td>-13.8 (6)</td>
<td>-1.4 (4)</td>
</tr>
</tbody>
</table>

Therefore it is reasonable to neglect this termination step in a first approximation. At temperatures above 45 °C inactivation is no longer negligible, leading to deviations from the Flory–Schulz distribution. Good correlations were obtained over the temperature range from 5 to 45 °C (Figure 2), indicating that for these temperatures our assumptions were valid. An important conclusion that can be derived from the Flory–Schulz behavior is that \([\text{Cp}^*\text{MMe(THT)}]^+\)[BPh$_4^-]$ act as true single-site catalysts. Table II contains the $\alpha$ values together with the corresponding $k_p/k_i$ ratios for propene oligomerization at five different temperatures for both catalytic systems. The $k_p/k_i$ ratios strongly depend on the reaction temperature and decrease with increasing temperature. The ratios are related to the differences in entropy and to the enthalpy of activation for propagation and $\beta$-methyl elimination via

$$k_p/k_i = \exp\left[-\frac{(\Delta H_p^* - \Delta H_i^*)}{R} - \frac{(\Delta S_p^* - \Delta S_i^*)}{R}\right]$$

(c)

Plots of ln $(k_p/k_i)$ versus $1/T$ for 1 and 2 yield straight lines with slope $-(\Delta H_p^* - \Delta H_i^*)/R$ and $(\Delta S_p^* - \Delta S_i^*)/R$ as the y intercept. These plots are shown in Figure 3, while the values of $(\Delta H_p^* - \Delta H_i^*)$, $(\Delta S_p^* - \Delta S_i^*)$, and $(\Delta G_p^* - \Delta G_i^*)_{298K}$ are listed in Table III. Although the experimental results indicate that $\Delta G^*_{298K}$ for 2 is smaller than for 1, the calculated values do not permit a definite conclusion due to the experimental error.

Table IV. Selected Bond Distances (Å) and Angles (deg) for \([\text{Cp}^*\text{ZrMe(THT)}]^+\)[BPh$_4^-]$ (1) and \([\text{Cp}^*\text{HfMe(THT)}]^+\)[BPh$_4^-]$ (2)

<table>
<thead>
<tr>
<th>Compd</th>
<th>Bond Distances</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^c$Cnx denotes Cp$^*$ ring centroid; C1x = C1–C5, C2x = C11–C15.
arranged in the plane between the two Cp* ligands. The M–C25 distances of 2.242 (8) Å in 1 and 2.233 (9) Å in 2 are at the short side of the range of values reported for M–CH3 (M = Zr, Hf) distances (average 2.292 (49) Å (M = Zr), 2.275 (49) Å (M = Hf)) but agree well with Zr–CH3 distances in other cationic zirconium complexes (cf. 2.240 (4) Å in (CM6Et5)2ZrMe(C2H5)235 and 2.256 (10) Å in [Cp2ZrMe(THT)]+) [BPh4]–.35

On the basis of the strong similarity between zirconium and hafnium, both with respect to size and chemical properties, one expects compounds with almost identical structures. At first view this is the case, but there are a few differences, even when one realizes that the accuracy of the determination for 2 is not very high. Whereas the zirconium atom is placed symmetrically between the two cyclopentadienyl ligands (Zr–Cp* = 2.23 (3) Å, Zr–Cp* = 2.23 (4) Å, C1–C1 in plane through C1–C5, C1–C2 = plane through C11–C15), the distances of the hafnium atom to the rings are different: Hf–Cp* = 2.34 (4) Å vs Hf–Cp* = 2.14 (8) Å. The other difference is the M–S distance in 1 and 2. The Zr1–S1 distance (2.730 (4) Å) is typical for early-transition-metal sulfur bonds.34,14-16 The Hf1–S1 distance (2.626 (4) Å) is significantly shorter. These are the only clear differences between both structures. The bond lengths and angles within the ligands are equal and different.

Refractions in the plane between the two Cp* ligands. The structures. At first view this is the case, but there are a few differences, even when one realizes that the accuracy of the determination for 2 is not very high. Whereas the zirconium atom is placed symmetrically between the two cyclopentadienyl ligands (Zr–Cp* = 2.23 (3) Å, Zr–Cp* = 2.23 (4) Å, C1–C1 in plane through C1–C5, C1–C2 = plane through C11–C15), the distances of the hafnium atom to the rings are different: Hf–Cp* = 2.34 (4) Å vs Hf–Cp* = 2.14 (8) Å. The other difference is the M–S distance in 1 and 2. The Zr1–S1 distance (2.730 (4) Å) is typical for early-transition-metal sulfur bonds.34,14-16 The Hf1–S1 distance (2.626 (4) Å) is significantly shorter. These are the only clear differences between both structures. The bond lengths and angles within the ligands are equal and different.

Refractions in the plane between the two Cp* ligands. The structures. At first view this is the case, but there are a few differences, even when one realizes that the accuracy of the determination for 2 is not very high. Whereas the zirconium atom is placed symmetrically between the two cyclopentadienyl ligands (Zr–Cp* = 2.23 (3) Å, Zr–Cp* = 2.23 (4) Å, C1–C1 in plane through C1–C5, C1–C2 = plane through C11–C15), the distances of the hafnium atom to the rings are different: Hf–Cp* = 2.34 (4) Å vs Hf–Cp* = 2.14 (8) Å. The other difference is the M–S distance in 1 and 2. The Zr1–S1 distance (2.730 (4) Å) is typical for early-transition-metal sulfur bonds.34,14-16 The Hf1–S1 distance (2.626 (4) Å) is significantly shorter. These are the only clear differences between both structures. The bond lengths and angles within the ligands are equal and different.

Refractions in the plane between the two Cp* ligands. The structures. At first view this is the case, but there are a few differences, even when one realizes that the accuracy of the determination for 2 is not very high. Whereas the zirconium atom is placed symmetrically between the two cyclopentadienyl ligands (Zr–Cp* = 2.23 (3) Å, Zr–Cp* = 2.23 (4) Å, C1–C1 in plane through C1–C5, C1–C2 = plane through C11–C15), the distances of the hafnium atom to the rings are different: Hf–Cp* = 2.34 (4) Å vs Hf–Cp* = 2.14 (8) Å. The other difference is the M–S distance in 1 and 2. The Zr1–S1 distance (2.730 (4) Å) is typical for early-transition-metal sulfur bonds.34,14-16 The Hf1–S1 distance (2.626 (4) Å) is significantly shorter. These are the only clear differences between both structures. The bond lengths and angles within the ligands are equal and different.

Refractions in the plane between the two Cp* ligands. The structures. At first view this is the case, but there are a few differences, even when one realizes that the accuracy of the determination for 2 is not very high. Whereas the zirconium atom is placed symmetrically between the two cyclopentadienyl ligands (Zr–Cp* = 2.23 (3) Å, Zr–Cp* = 2.23 (4) Å, C1–C1 in plane through C1–C5, C1–C2 = plane through C11–C15), the distances of the hafnium atom to the rings are different: Hf–Cp* = 2.34 (4) Å vs Hf–Cp* = 2.14 (8) Å. The other difference is the M–S distance in 1 and 2. The Zr1–S1 distance (2.730 (4) Å) is typical for early-transition-metal sulfur bonds.34,14-16 The Hf1–S1 distance (2.626 (4) Å) is significantly shorter. These are the only clear differences between both structures. The bond lengths and angles within the ligands are equal and different.
so are the M–C25 bonds. The coordinated THT ligands are oriented out of the C25–M–S1 plane (dihedral angle between the C25–M–S1 plane and the THT C21–S1–C24 plane 44.2° in 1 and 44.4° (9°) in 2; angle between the M–S vector and the THT C21–S1–C24 plane 43.3° (6°) in 1 and 43.4° (8°) in 2). It is tempting to consider the short Hf–S bond as the result of a considerable interaction of the lone electron pair on sulfur and the asymmetric position of the hafnium atom between the Cp* ligands do not lead to the short Hf–S distance and the asymmetric position of the SOC.

The C–C bond lengths and angles within the Cp* ligands are normal geometry. That this is not normally observed for the inequivalent distances of the Zr-centroid distances are equal and lie as expected (viz. room temperature) indicate that the cationic Hf-isobutyl complex is more stable than the methyl complex. Therefore the tendency of [Cp*2YMe–C(THF)] to undergo β-methyl elimination has to be kinase in origin. A possible explanation might be that in complexes with bulky Cp* groups on the β-Me substituent of the growing chain in the equatorial plane of the Cp*–M wedge that contains the Zr LUMO (structure A) is more favorable than an orientation with the β-Me group pointing toward one of the Cp* rings (structure B) due to steric interactions. In this way, transfer of the methyl group from a growing oligomer chain to the metal is kinetically favored over β-H transfer. Similar steric arguments were used by Bercaw et al. to explain the presence of an agostic interaction in Cp*2ScCH2CH2 and the absence of such an interaction in Cp*2ScCH2CH2CH2. Minimization of the potential energy of [Cp*2ZrCH2(CH2)2CH2CH2CH2] (the compound that produces 4-methyl-1-pentene upon β-methyl elimination) with the ALCHEMY II software package indeed suggests that conformation A is about 4 kcal.mol−1 more stable than B. The main reason for the difference appears to be the close contact of the β-Me group with the Cp* methyl groups in conformation B, which is absent in conformation A. If the calculated energy difference is real, then, as a result of the lower energy of A, over 99% of the molecules will be in this conformation, as predicted by the Boltzmann distribution (T = 298 K). This percentage is reflected in the distribution of oligomeric products arising from the two different termination steps (β-Me elimination: 97%; β-H elimination: 3%). Therefore the activation energy for β-H transfer starting from B has to be comparable to the activation energy for β-Me transfer starting from A. The propensity for β-Me transfer then is due to differences in ground-state energy of the two conformations.

Figure 4. Perspective ORTEP view with adopted numbering scheme of [Cp*2ZrMe(THT)]+ (hydrogen atoms omitted for clarity). All atoms are represented by their thermal vibrational ellipsoids drawn to encompass 50% of the electron density.


Catalyst Inactivation. The catalysts are slowly inactivated during the oligomerization. For example at room temperature turnover numbers are 150 and 370 mol of \( \text{C}_8\text{H}_8\) per mol of \( \text{M} \) for 1 and 2, respectively. To identify the inactivation process, the following experiment was carried out. Propene was oligomerized at 25 °C with either 1 or 2 as the catalyst. After monomer uptake had ceased, the volatiles were pumped off and \( \text{D}_2\text{O} \) was added. Gas (1 equiv) was liberated (Toeppler pump) that was shown by GC and MS to consist of a mixture of propene-\( d_1 \) and isobutene-\( d_1 \) (\( \text{M} = \text{Zr}, \text{C}_8\text{H}_8/\text{C}_4\text{H}_8 = 0.3/0.7; \text{M} = \text{Hf}, \text{C}_8\text{H}_8/\text{C}_4\text{H}_8 = 0.4/0.6 \)). These results indicate that both catalysts 1 and 2 are inactivated by formation of allyl and 2-methylallyl complexes, respectively, presumably by allylic C-H activation. The same type of inactivation has been observed in the reaction of propene with lanthanide complexes \( \text{Cp}^{*} \text{LuMe}_2 \) [2b] [\{\text{Me}_2\text{Si}(\text{C}_6\text{H}_5)_2\} \text{LuH}_2\}], [24] and [\text{Cp}^{*} \text{LnH}_2] (\text{Ln} = \text{La}, \text{Nd}, \text{Sm})]. This emphasizes the close resemblance of cationic group 4 compounds and the isoelectronic lanthanide complexes.

Especially, the formation of the methallyl complexes is noteworthy, since isobutene is only formed in very small amounts by \( \beta \)-hydrogen elimination during the oligomerization of propene.\(^6\) Apparently, isobutene is a very efficient trapping agent for [\text{Cp}^{*} \text{MR}]\(^+\) (\( \text{M} = \text{Zr}, \text{Hf} \)). To test this hypothesis, a solution of 1 was exposed to isobutene (5-fold molar excess). Reaction with \( \text{D}_2\text{O} \) after the excess olefin had been pumped off liberated 1 equiv of gas that was identified as \( \text{CH}_3\text{D} \) by NMR spectroscopy. These results strongly suggest that [\text{Cp}^{*} \text{MR}]\(^+\) (\( \text{M} = \text{Zr}, \text{Hf} \)) indeed reacts with isobutene to give a methallyl complex. Vinylic C-H activation producing a complex of the type \( \text{C}_8\text{H}_8=\text{CH}==\text{CH}-\text{C}_8\text{H}_5\text{Me} \), as has been observed in the reaction of \( \text{Cp}^{*} \text{ScCH}_3 \) with isobutene,\(^{26}\) can be excluded since \( \text{Cp}^{*} \text{Zr}==\text{CH}-\text{C}_8\text{H}_5\text{Me} \) would produce \( \text{CDH}==\text{CH}==\text{CH}-\text{C}_8\text{H}_5\text{Me} \), upon reaction with \( \text{D}_2\text{O} \).

Addition of hydrogen (10-fold molar excess) to the oligomerization reaction mixture after olefin uptake had ceased restored catalytic activity. Hydrogenolysis of the \( \text{M} \)-allyl bond results in the formation of a metal hydride that can reinitiate the oligomerization. The resulting hydrogen however competes with the insertion reaction by hydrogenolyzing the \( \text{M}-\text{C} \) bond to give a methallyl complex.

At higher temperatures a different inactivation occurs. After an oligomerization had been carried out at 55 °C with either 1 or 2 as the catalyst, the mixture was quenched with \( \text{D}_2\text{O} \) after propene uptake had ceased and all volatiles had been pumped off. No propene, isobutene, or other gaseous products were observed. A possible explanation might be that at these temperatures the catalysts decompose by metalation of one of the phenyl rings of the anion with extrusion of alkane to give zwitterionic complexes of the type \( \text{Cp}^{*} \text{M}^{+}=\text{m}-\text{C}_8\text{H}_8-\text{BPh}_3^{-} \), as recently described by Turner et al. (eq 9). Analogous metalation of aromatic \( \text{Cp}^{*} \text{M}^{+}-\text{R}^{+} \) \( \text{BPh}_3^{-} \) \( \text{C}_8\text{H}_8 \) or growing oligomer chain \( \text{M} = \text{Zr}, \text{Hf} \) rings has been observed in the reaction of \( \text{Cp}_2\text{LuMe} \) and \( \text{Cp}_2\text{ScMe} \) with benzene to give \( \text{Cp}_2\text{LuMe}_2 \) and \( \text{Cp}_2\text{ScC}_8\text{H}_8 \), respectively, and methane.\(^{26}\)


TE-SD thermostated water bath and were observed to be constant to within ±0.1°C.

General Remarks for Oligomerization Reactions. All oligomerization reactions were carried out with 50 mL of 4.0 mM solutions of 1 or 2 in PhNMe₂ at 1 atm of olefin pressure. Olefin uptake profiles were monitored using a Brooks 8500 TR mass flow meter on the gas feed line and recorded for analysis. Reactions were quenched with H₂O (D₂O) after monomer uptake had ceased. Propene concentrations at various temperatures were determined from experiments in which 50 mL of PhNMe₂ was saturated with propene under oligomerization conditions but in the absence of catalyst.

Reaction of 1 with Isobutene. A solution of 162 mg (0.21 mmol) of 1 in 10 mL of PhNMe₂ was exposed to 5 equiv isobutene on a vacuum line. After 1 h, excess of isobutene was pumped off and 0.2 mL of D₂O (excess) added by vacuum transfer. Volatiles (0.20 mmol, 95% equiv) were collected by Toeppler pump and analyzed (NMR spectroscopy). ¹H NMR (CD₃OD): δ 4.74 (sexet, 4H, τ(CH₃)= 1.1 Hz, 2 H, CH₂), 1.59 (t, 4H, = 1.1 Hz, 5 H, —(CH₂CH₂)), [HNEt₂⁺][B(C₆D₅)₄⁻]. A suspension of 1.25 mL (9.0 mmol) NEt₂ in 25 mL of water was acidified with concentrated hydrochloric acid to pH = 1. The resulting solution was then added to a stirred solution of NaBH₄ (3.00 g) in 100 mL of water, causing the precipitation of [HNEt₂⁺][B(C₆D₅)₄⁻]. The ammonium salt was filtered off, washed thoroughly with water, dried and redissolved from acetone to afford 2.11 g (4.8 mL, 59%) of colorless crystals. The product was shown by NMR spectroscopy to be >95% duretted. ¹H NMR (acetone-d₆): δ 3.32 (q, J₆H= 1.7 Hz, 6 H, N—CH₂), 1.23 (t, J₃H= 7.3 Hz, 9 H, —CH₂—), NF not found (−10 to +30 ppm).

[Cp*⁺H₂Me(THT)]⁺[B(C₆D₅)₄⁻]. A mixture of 1.114 g (2.38 mmol) Cp*⁺H₂Me(THT) and 1.015 g (2.30 mmol) of [HNEt₂⁺][B(C₆D₅)₄⁻] in 15 mL of THT was stirred at room temperature for 2 h, during which time the solution gradually turned yellow and yellow microcrystalline material precipitated. The suspension was warmed until all solids had dissolved, filtered, and slowly cooled to room temperature, depositing large yellow crystals of [Cp*⁺H₂Me(THT)][B(C₆D₅)₄⁻]. Yield: 1.491 g (1.67 mmol, 73%). ¹H NMR (THF-d₈): δ 2.74 (m, 4 H, α-CH₂—), free THT), 1.96 (s, 30 H, C₆H(C₆H₃), 1.81 (m, 4 H, β-CH₂—, free THT), 0.17 (s, 3 H, H—CH₂—). IR (cm⁻¹): 2728 (w), 2288 (s), 2253 (vs), 1608 (m), 1547 (m), 1520 (m), 1344 (w), 1310 (m), 1262 (s), 1252 (s), 1211 (m), 1202 (m), 1187 (s), 1136 (w), 1084 (m), 1022 (s), 955 (m), 885 (m), 862 (vs), 835 (m), 826 (m), 806 (m), 795 (m), 745 (m), 731 (m), 669 (m), 648 (m), 640 (m), 596 (m), 540 (vs), 517 (m), 475 (m), 453 (m), 422 (vs).

Thermolysis of [Cp*⁺H₂Me(THT)]⁺[B(C₆D₅)₄⁻]. A solution of 20.5 mg (0.023 mmol) [Cp*⁺H₂Me(THT)]⁺[B(C₆D₅)₄⁻] in 10 mL of PhNMe₂ degassed under vacuum by three freeze-pump-thaw cycles and heated at 55 °C for 2 h. Volatiles were collected by Toeppler pump (0.023 mmol, 1.00 equiv) and analyzed by MS. M⁺ = 17 (CH₂D, 100%).

X-ray Crystal Structure Determination of [Cp*⁺ZrMe(THT)]⁺[BPH₄]⁻ (1) and [Cp*⁺H₂Me(THT)]⁺[BPH₄]⁻ (2). Suitable crystals were grown by slow diffusion of pentane into a concentrated solution of 1 in THF and by slowly cooling a hot, concentrated solution of 2 in THF. The sample crystals were glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Although for 1 an X-ray structure determination was thwarted by persistent crystal twinning, a successful characterization was executed ultimately with a small, weakly scattering crystal. Unit cell parameters and their standard deviations were determined from a least-squares treatment of the setting angles of 22 reflections in the range 9.07° < θ < 13.34° for 1 and 13.99° < θ < 17.85° for 2 and checked for the presence of higher merical symmetry. The space group was derived from the observed systematic absences. The crystal system was identified as orthorhombic, space group Pnma, for both 1 and 2; the E statistics showed unambiguously an acentric space group. This choice was confirmed by the solution and successful refinement in this.

| Table VII. Details on the Structure Determination of 1 and 2 |
|-------------|----------------|----------------|
| color      | orange/yellow | yellow         |
| chem formula| C₃H₇ZrCl₂ | C₃H₇ZrCl₂ |
| fw         | 784.11        | 781.38        |
| crystal syst | orthorhombic | orthorhombic |
| space group, No. | 26 | 26 |
| a, Å       | 31.31 (1)     | 31.32 (1)     |
| b, Å       | 11.84 (4)     | 11.83 (1)     |
| c, Å       | 11.084 (4)    | 11.029 (1)    |
| V, Å³      | 4110 (2)      | 4096 (1)      |
| Z          | 4             | 4             |

of 1, 41 (of 61) hydrogen atom positions could be located on a difference Fourier map. At this stage of the refinement of 2, the hydrogen atom positions of the analogous Zr compound were introduced and refined. The remainder for both 1 and 2 were calculated at idealized geometric positions. Thereby the found hydrogen atoms served to determine the conformation of all methyl groups. All the hydrogen atoms were replaced afterward at idealized positions, by using sp<sup>3</sup> or sp<sup>2</sup> hybridization at the C atom as appropriate and a fixed C–H distance of 1.0 Å. Hydrogen atoms were refined in the riding mode with a fixed C–H bond length of 1.0 Å, given one common fixed isotropic thermal parameter, and used in the structure factor calculations but not refined. Full-matrix least-squares refinement (based on $F_o$) with anisotropic thermal parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged satisfactorily, giving the corresponding final discrepancy indices summarized in Table VII. Weights were introduced in the final refinement cycles. In the final refinement the nonpositive atoms were returned to isotropic thermal displacement parameters. The polarity of the structures was tested with $i\Delta f''$ and $-i\Delta f''$ values, giving only marginally different $R$ values. For 1 the temperature factors of C12 were nonpositive definite and some atoms showed unrealistic temperature factors, suggesting some degree of disorder, which is in line with the weak scattering power of the crystals investigated. For 2 the temperature factors of C26 were nonpositive definite. In the case of 1, five reflections with $w(||F_o|-|F_c||) > 12$ were excluded from the final refinement cycle. The mismatch could be ascribed to an instrumental error. In the case of 2, a bad agreement ($w(||F_o|-|F_c||) > 10$) was observed for 38 reflections. The mismatch is probably due to a small misoriented fraction of the crystal used in this study. Crystal data and experimental details of the structure determination are compiled in Table VII. Scattering factors were as given by Cromer and Liberman.<sup>35</sup> Anomalous dispersion factors, taken from Cromer and Mann.<sup>34</sup> Potential energy minimization calculations were carried out on the hypothetical cationic species [Cp*<sub>2</sub> ZrCl<sub>2</sub> C(CH<sub>3</sub>)<sub>4</sub> C(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> using geometrical data from the crystal structure of 1 (the THT ligand was omitted and not further taken into account during the calculation), and C–C and C–H bond lengths and angles for the 2,4-dimethylpentyl ligand were taken from data supplied with the ALCHEMY program. For the Cp*<sub>2</sub> Zr moiety, the distance between the metal center and the α-carbon atom of the alkyl ligand was kept fixed, while the α-carbon was confined to the plane symmetrically between the Cp* ligands. To minimize the energy of the ion, the position of the pentyl ligand in the Cp*<sub>2</sub> Zr wedge and bond distances and angles in the pentyl ligand were varied. A conformation with the β-methyl group of the pentyl ligand in the plane between the Cp* ligands (structure A) appeared to be about 4 kcal-mol<sup>–1</sup> more stable than the conformation with the β-hydrogen atom in that plane (structure B).

Acknowledgment. We thank DSM Research BV for generous financial support of this investigation.

Registry No. 1, 131494-61-6; 2, 131494-63-8; [Cp*<sub>2</sub> HfMe(THT)]<sup>+</sup> [B(C<sub>6</sub>D<sub>6</sub>)<sub>4</sub>]<sup>–</sup>, 137167-65-8; Cp*<sub>2</sub> HfMe<sub>2</sub>, 116437-01-5; [HNEt<sub>3</sub>]<sup>+</sup> [B(C<sub>6</sub>D<sub>6</sub>)<sub>4</sub>], 137167-67-0; C<sub>2</sub>H<sub>4</sub>, 115-07-1; (C<sub>3</sub>H<sub>2</sub>)<sub>2</sub>, 16813-72-2; (C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>, 13987-01-4; (C<sub>3</sub>H<sub>6</sub>)<sub>2</sub>, 6842-15-5; (CH<sub>3</sub>)<sub>4</sub>, 15220-87-8; (C<sub>2</sub>H<sub>6</sub>)<sub>2</sub>, 50295-91-5; (C<sub>3</sub>H<sub>6</sub>)<sub>2</sub>, 106855-49-6; (C<sub>3</sub>H<sub>8</sub>)<sub>2</sub>, 77111-45-6; isobutene, 115-11-7.

Supplementary Material Available: For 1 and 2, tables of fractional atomic coordinates and equivalent isotropic thermal parameters, thermal displacement parameters, bond distances and angles, and torsion angles (24 pages); listings of structure factors (38 pages). Ordering information is given on any current masthead page.


