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# Cationic group IV metal alkyl complexes and their role as olefin polymerization catalysts: The formation of ethyl-bridged dinuclear and heterodinuclear zirconium and hafnium complexes ☆

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## Abstract

Bis(cyclopentadienyl)hafnium diethyl (**1**) reacts with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane at −60 °C with hydride rather than alkyl transfer to give triphenylmethane and the ethyl-bridged dinuclear complex $[(Cp_2HfEt)_2(\mu\text{-Et})][B(C_6F_5)_4]$ (**2**). The complex is less stable than analogous methyl complexes but is stabilized by the presence of excess $Cp_2HfEt_2$. The reaction between $Cp_2HfEt_2$, $[CPh_3][B(C_6F_5)_4]$, and $AlEt_3$ under analogous conditions leads to $[Cp_2Hf(\mu\text{-Et})_2AlEt_2][B(C_6F_5)_4]$ (**3**). The reaction between $Cp_2HfMe_2$ and $AlEt_3$ leads to alkyl ligand exchange to give, successively, $Cp_2Hf(Me)(Et)$ and $Cp_2HfEt_2$. Similar fast ligand exchange reactions take place between $Cp'_2ZrMe_2$ and $AlEt_3$ and can be used for generating the thermally labile complex $Cp'_2ZrEt_2$ as a precursor for cationic polymerization catalysts [$Cp'_2 = Cp_2$, *rac*-$Me_2Si(Ind)_2$]. Polymerization activities of *rac*-$[Me_2Si(Ind)_2Zr(\mu\text{-R})_2AlR_2][B(C_6F_5)_4]$ increase in the order R = Me < Et.

*Keywords:* Zirconium; Hafnium; Olefin polymerization catalyst; Group IV metal alkyl complexes

## 1. Introduction

Cationic Group IV metallocene complexes of the type $[Cp_2MR]^+$ (R = alkyl) have been identified as the catalytically active species in the polymerization of olefins with metallocene-based catalysts [1]. They are highly electron deficient and extremely reactive and have as yet not been isolated or unequivocally characterized but are readily stabilized in solution through adduct formation with any available nucleophile, such as the counter-anion [2], neutral metal alkyls [3,4], or the solvent [5]. We have recently shown that the addition of $Cp_2ZrMe_2$ or $AlMe_3$ to in situ generated $[Cp_2ZrMe]^+$ results in isolable methyl-bridged dinuclear complexes $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ and $[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+$ respectively, and have proposed such species as temporarily inactive resting stages of polymerization catalysts [3]. While methyl bridges are quite common in electron-deficient complexes, they are poor models for the longer alkyl chains formed during the polymerization process, and the question arose whether the behaviour of methyl complexes was of general relevance to the chemistry of active polymerization systems. Ethyl and butyl ligands are more realistic models and offer alternative coordination modes, such as β-agostic bonding, which are not available to methyl systems. We have therefore investigated the behaviour of ethyl compounds and report here the synthesis and characterization of cationic hafnocene complexes with bridging ethyl ligands.

## 2. Results and discussion

The reaction of $Cp_2HfCl_2$ with an excess of ethylmagnesium bromide in diethylether gives $Cp_2HfEt_2$ (**1**) as a colourless solid in good yield. In contrast to its zirconium analogue, **1** is thermally stable at room temperature. The alkylation is sensitive to steric requirements; the bulky complex $\{C_5H_3(SiMe_3)_2\}_2HfCl_2$ did

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☆ Dedicated to Professor Dr. Hans-Herbert Brintzinger on the occasion of his 60th birthday.

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not react with EtMgBr under these conditions and was recovered unchanged.

In general the formation of cationic complexes of the type $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ or $[Cp_2Zr(\eta^2\text{-}CH_2Ph)]^+$ from metallocene dialkyls $Cp_2MR_2$ (M = Zr, Hf; R = $CH_3$, $CH_2Ph$) and $[CPh_3][B(C_6F_5)_4]$ proceeds by the rapid transfer of $R^-$ to $CPh_3^+$ to give $Ph_3CR$ [4b,6,7]. By contrast, **1** reacts with $[CPh_3][B(C_6F_5)_4]$ under hydride abstraction to give exclusively triphenylmethane, ethene and $[Cp_2HfEt]^+$ (Scheme 1). A similar hydride abstraction takes place in the reaction of $CPh_3^+$ with $(C_5H_4SiMe_3)_2HfBu^n_2$ [8]. As was observed in the case of methyl complexes [3], the formally 14-electron hafnium ethyl cation is stabilized by forming an adduct with excess $Cp_2HfEt_2$ to give $[(Cp_2HfEt)_2(\mu\text{-Et})]^+$ (**2**). The bridging ethyl ligands are characterized in the $^1H$ NMR spectrum of **2** by a quartet at $\delta = -0.72$ and a triplet at $\delta = -0.44$ ppm.

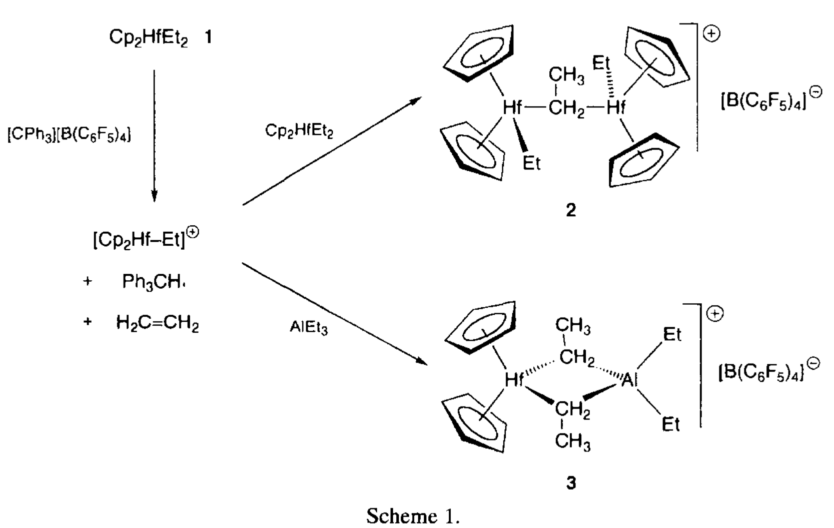
Some of the ethene liberated in this process would be expected to be consumed by insertion into Hf–Et bonds, and indeed the NMR spectra of **2** contain a minor component which appears to have terminal *n*-butyl as well as ethyl ligands. Since ethene insertion is slow under the low-temperature conditions employed for generating **2**, signals due to free ethene can also be identified.

We have shown earlier that complexes such as $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+$ establish dissociation equilibria to give $[Cp_2ZrMe]^+$ and $Cp_2ZrMe_2$ [3]. Such a dissociation process is expected to be favoured by larger alkyl ligands and leads to the decomposition of **2** in chlorinated solvents at temperatures at which the analogous methyl complex is still stable. The stability of **2** is significantly enhanced by the addition of excess **1**.

The reaction between $[CPh_3][B(C_6F_5)_4]$ and $Cp_2HfEt_2$ in the presence of $AlEt_3$ at −60 °C leads to the formation of the heterodinuclear complex $[Cp_2Hf(\mu\text{-Et})_2AlEt_2][B(C_6F_5)_4]$ (**3**). As was observed in the case of **2**, this compound is less stable in chlorinated solvents than its methyl analogue. The stability is enhanced by the presence of an excess of $AlEt_3$, an indication that the decomposition process is initiated by the dissociation of the hafnium–aluminium complex. Complex **3** has counterparts in lanthanide chemistry [9], including the crystallographically characterized $(C_5Me_5)_2Sm(\mu\text{-Et})_2AlEt_2$ [10].

The formation of compounds with bridging ethyl ligands, such as **2** and **3**, closely mirrors the chemistry of the methyl complexes reported earlier [3] and supports the assumption that complexes with bridging alkyl ligands are important in polymerization catalysis as resting stages of the active species during the chain growth process. Cationic polymerization catalysts containing metal triethyl compounds as cleaning or "activating" agents are known, such as $Cp'_2ZrMe_2/[HNMe_2Ph][B(C_6F_5)_4]/BEt_3$ and $Me_2Si(Ind)_2ZrCl_2/[CPh_3][B(C_6F_5)_4]/AlEt_3$ [11], although the stabilizing role of the metal alkyl additives through the formation of alkyl-bridged species with the active centre was apparently not realized.

Since complexes of type **2** and **3** dissociate more readily, and since it has been shown that the rate of olefin insertion into a Ti–Et bond is ca. $10^2$ times faster than the insertion into Ti–Me [12], it is to be expected that ethyl complexes of type **3** are more active catalysts than their methyl analogues. In order to test this assumption, propene was polymerized using a *rac*-$Me_2Si(Ind)_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ catalyst in the presence of 1 to 100 equivalents of $AlEt_3$. Zirconium ethyl complexes are thermally unstable and are not directly available as catalyst precursors; instead the reaction relies on the observation that zirconium methyl complexes undergo rapid ligand exchange with aluminium triethyl at the reaction temperature employed (20 °C). This ligand exchange can be conveniently followed at −40 °C and shown to proceed stepwise via



Scheme 1.

Table 1
Propene polymerizations with *rac*-$Me_2Si(Ind)_2ZrMe_2$ / $[CPh_3][B(C_6F_5)_4]$/$AlEt_3$ [a]

| Entry | $AlEt_3$ ($\mu$mol) | Polymer yield (g) | Productivity ($10^6$ g PP/ (mol $Zr^+$)·$[C_3H_6]$·h) | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | 5 | 0.587 | 20.13 ± 0.55 | 14000 | 2.9 |
| 2 | 10 | 0.601 | 20.57 ± 0.44 | 8600 | 2.6 |
| 3 | 25 | 0.667 | 22.67 ± 0.41 | 8600 | 2.5 |
| 4 | 50 | 0.605 | 20.77 ± 0.52 | 6700 | 2.5 |
| 5 | 100 | 0.346 | 11.83 ± 0.44 | 5650 | 2.2 |
| 6 | 250 | 0.232 | 7.97 ± 1.21 | 6100 | 2.3 |
| 7 | 500 | 0.129 | 4.45 ± 0.85 | 6100 | 2.2 |

[a] At 1 bar $C_3H_6$ pressure, 20 °C, 5.0 $\mu$mol $Me_2Si(Ind)_2ZrMe_2$, 5.0 $\mu$mol $[CPh_3][B(C_6F_5)_4]$, 20 ml toluene, stirring speed 100 rev $min^{-1}$. Polymerizations were terminated by methanol injections after 30 s. Polymer yields and productivities are the averages of three runs under identical conditions.

$Me_2Si(Ind)_2Zr(Me)(Et)$ as the intermediate [13]. The polymerization results are collected in Table 1, and a comparison between zirconium methyl and ethyl catalysts is depicted in Fig. 1.

The results show the expected decrease in activity as the aluminum concentration increases, in line with the assumption of a dissociation equilibrium (Eq. (1)) which is shifted by higher $AlEt_3$ concentrations towards the dormant species **4**. It is also evident that the activities are higher than those of the corresponding methyl complexes.

$$\underset{\mathbf{4}}{[Me_2Si(Ind)_2Zr(\mu\text{-}Et)_2AlEt_2]^+} \rightleftharpoons [Me_2Si(Ind)_2ZrEt]^+ + AlEt_3 \qquad (1)$$

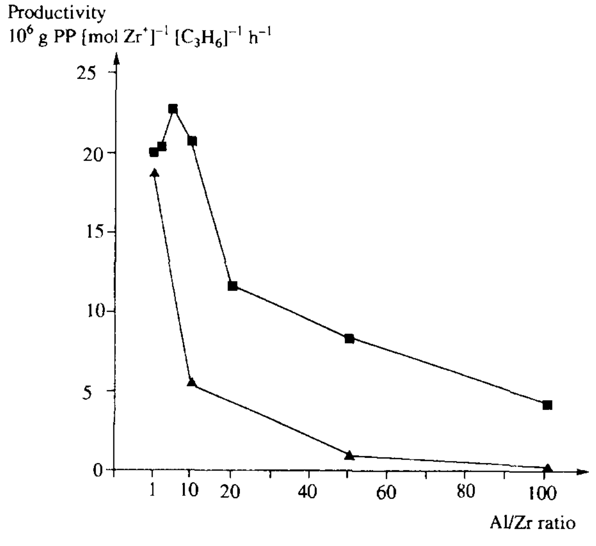


Fig. 1. Propene polymerization activities of *rac*-$Me_2Si(Ind)_2ZrMe_2$ / $[CPh_3][B(C_6F_5)_4]$/$AlR_3$ catalysts at 1 bar, 20 °C, as a function of the aluminium alkyl concentration. $AlR_3$ = $AlEt_3$ (■), $AlMe_3$ (▲). Values for $AlMe_3$ taken from [3] were recalculated on the basis of improved propene solubility data [14].

Whereas we observed in the case of $[Me_2Si(Ind)_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ that the catalyst productivity at 20 °C decreased significantly if the Al-to-Zr ratio was increased from 1 : 1 to 10 : 1 [3], the behaviour of **4** shows a plateau between ratios of 1 : 1 and 10 : 1. We believe this reflects the fact that the productivities of these very active catalysts at only 1 bar olefin pressure are diffusion limited in this region. Polymer begins to precipitate after only a few seconds, and after ca. 30 s stirring has become so inefficient that longer polymerization times would not produce meaningful results. Studies at higher olefin pressures and lower catalyst concentrations are in progress.

## 3. Experimental details

### *3.1. General procedures*

All reactions were carried out under inert gas using standard vacuum line techniques. Solvents were distilled under nitrogen from sodium-benzophenone [diethylether, petroleum ether (bp 40–60 °C)] or sodium (toluene). NMR solvents were stored over 4A molecular sieves under nitrogen or argon and degassed by several freeze–thaw cycles. *rac*-$Me_2Si(Ind)_2ZrMe_2$ [15] and $[CPh_3][B(C_6F_5)_4]$ [4b] were prepared as described. The latter was recrystallized from dichloromethane as $[CPh_3][B(C_6F_5)_4] \cdot CH_2Cl_2$. The dichloromethane of crystallization is lost by passing a concentrated solution of $[CPh_3][B(C_6F_5)_4]$ in $CH_2Cl_2$ into a large amount of rapidly stirred petroleum ether from which the trityl salt precipitates as a finely divided solvate-free yellow solid. NMR spectra were recorded on a JEOL EX270 instrument modified for low-temperature experiments.

### *3.2. Synthesis of $Cp_2HfEt_2$ (1)*

To a solution of EtMgBr (73 mmol) in 150 ml diethyl ether at room temperature was added 5.75 g $Cp_2HfCl_2$ (15 mmol) in small portions. Towards the end of the addition some magnesium halide was seen to precipitate. The yellow solution was stirred overnight to give a red mixture which was taken to dryness, extracted with 100 ml petroleum ether and filtered. Cooling to −20 °C gave **1** as colourless crystals (3.0 g, 54%). Anal. Calc. $C_{14}H_{20}Hf$: C, 45.8; H, 5.5. Found: C, 45.85; H, 5.2. $^1H$ NMR ($CD_2Cl_2$, −60 °C): $\delta$ −0.06 (q, 4H, Hf-$CH_2$, $^3J_{HH}$ = 7.6 Hz), 1.24 (t, 6H, $CH_3$, $^3J_{HH}$ = 7.6 Hz), 6.04 (s, 10 H, Cp). $^{13}C$ NMR (67.8 MHz, $CD_2Cl_2$, −60 °C): 15.81 ($CH_3$, $^1J_{CH}$ = 123.9 Hz), 49.31 (Hf-$CH_2$, $^1J_{CH}$ = 112.9 Hz), 110.13 (Cp).

### 3.3. Synthesis of $[(Cp_2HfEt)_2(\mu\text{-}Et)][B(C_6F_5)_4]$ (2)

$Cp_2HfEt_2$ (60 mg, 0.16 mmol) and $[CPh_3][B(C_6F_5)_4]$ (174 mg, 0.18 mmol) were dissolved in separate Schlenk tubes in 0.5 ml $CD_2Cl_2$ each. Both solutions were cooled to −78 °C. The solution of **1** was then transferred to an NMR tube, followed by the solution of $[CPh_3][B(C_6F_5)_4]$. The sample was inserted into the spectrometer at −60 °C and characterized at that temperature. $^1H$ NMR ($CD_2Cl_2$, −60 °C): $\delta$ −0.72 (q, 2H, $\mu$-C$H_2$CH$_3$, $^3J_{HH} = 5.6$ Hz), −0.44 (t, 3H, $\mu$-CH$_2$C$H_3$, $^3J_{HH} = 5.6$ Hz), 0.72 (q, 4H, HfC$H_2$CH$_3$ terminal, $^3J_{HH} = 7.6$ Hz), 1.38 (t, 6H, HfCH$_2$C$H_3$ terminal, $^3J_{HH} = 7.6$ Hz), 6.15 (s, 20H, Cp).

### 3.4. Synthesis of $[Cp_2Hf(\mu\text{-}Et)_2AlEt_2][BC_6F_5)_4]$ (3)

$Cp_2HfEt_2$ (**1**) (50 mg, 0.13 mmol) and $[CPh_3][B(C_6F_5)_4]$ (157 mg, 0.16 mmol) were dissolved separately in 0.4 ml $CD_2Cl_2$ each. The solution of **1** was transferred to an NMR tube and cooled to −78 °C, followed by the addition of 0.13 mmol $AlEt_3$ in $CD_2Cl_2$ and the cold solution of $[CPh_3][B(C_6F_5)_4]$. The NMR spectrum of the mixture was recorded at −60 °C and showed that complete reaction had occurred to give **3**. In the absence of **1**, triethylaluminum reacts only very slowly with $[CPh_3][B(C_6F_5)_4]$ under these conditions. $^1H$ NMR ($CD_2Cl_2$, −60 °C): $\delta$ 0.173 (q, br, 8H, bridging and terminal C$H_2$CH$_3$), 1.07 (t, br, 6H, CH$_2$C$H_3$ terminal), 1.81 (t, br, 6H, $\mu$-CH$_2$C$H_3$), 6.45 (s, 10H, Cp). $^{13}C$ NMR (67.8 MHz, $CD_2Cl_2$, −60 °C): $\delta$ −0.575 ($CH_2$ terminal), 8.07 ($CH_3$ terminal), 9.26 ($CH_2$ bridging), 18.89 ($CH_3$ bridging), 113.13 (Cp).

### 3.5. Ligand exchange reactions of $AlEt_3$ with $Cp_2HfMe_2$ and rac-$Me_2Si(Ind)_2ZrMe_2$

A solution of $Cp_2HfMe_2$ in $CD_2Cl_2$ at room temperature reacts with a five-fold excess $AlEt_3$ to give a mixture of $Cp_2HfMe_2$, $Cp_2HfEt_2$, and $Cp_2Hf(Me)(Et)$. After 24 h, $Cp_2HfEt_2$ is the major species present. There is no ligand exchange between $AlEt_3$ and $\{C_5H_3(SiMe_3)_2\}_2HfMe_2$. $Cp_2Hf(Me)(Et)$, $^1H$ NMR (270 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 0.057 (s, 3H, Hf-CH$_3$), 1.29 (t, 3H, HfCH$_2$C$H_3$, $^3J_{HH} = 6.92$ Hz). Other resonances are obscured by the diethyl complex. *rac*-$Me_2Si(Ind)_2ZrMe_2$ and $AlEt_3$ react at −40 °C to give *rac*-$Me_2Si(Ind)_2Zr(Me)(Et)$. At higher temperatures decomposition takes place, possibly involving an unstable diethyl complex. *rac*-$Me_2Si(Ind)_2Zr(Me)(Et)$, $^1H$ NMR (270 MHz, $CD_2Cl_2$, −40°C): $\delta$ −1.32 (s, 3H, Zr-CH$_3$), 0.87 (t, 3H, ZrCH$_2$C$H_3$, $^3J_{HH} = 7.6$ Hz), 0.98 (s, 6H, SiCH$_3$). Other alkyl ligand resonances are obscured.

### 3.6. Propene polymerizations

All polymerizations were carried under 1 bar propene. $AlEt_3$ was injected into 20 ml toluene and allowed to equilibrate with the propene atmosphere at 20 °C. $[CPh_3][B(C_6F_5)_4]$ (5 $\mu$mol) in toluene was then injected, immediately followed by 5 $\mu$mol *rac*-$Me_2Si(Ind)_2ZrMe_2$. The polymerizations started immediately. Polymer began to precipitate after a few seconds. The reactions were terminated after 30 s by methanol injection. Work-up was as described before [3]. The polypropene obtained was highly isotactic. Productivities were determined using propene solubilities in toluene calculated according to [14]. For Fig. 1 productivity values taken from [3] were recalculated on the basis of these improved data.

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