A Comparative NMR Study on the Reactions of Hf(IV) Organometallic Complexes with Al/Zn Alkyls

Luca Rocchigiani,*†‡§ Vincenzo Busico,§‡ Antonello Pastore,§‡ and Alceo Macchioni†‡

ABSTRACT

NMR spectroscopy has been exploited to investigate the reactions of Hf(IV) organometallic complexes with trialkylaluminium and dialkylzinc, with the aim of obtaining insights into the elementary steps of coordinative chain transfer polymerization (CCTP). Bis-cyclopentadienyl hafnium dimethyl (Cp₂HfMe₂, 1Me₂) and [N-[2,6-Diisopropylphenyl]-α-[2-isopropylphenyl]-6-(1-naphthenyl)-2-pyridinemethanaminato]hafnium dimethyl (2Me₂) complexes have been chosen as case studies for understanding the differences between poorly performing and highly active CCTP catalysts, in an attempt to assess the effect of the ancillary ligand on the transalkylation rate. 2Me₂ was found to react much faster with both AlEt₃ and ZnEt₂ than 1Me₂, mainly due to a remarkably lower activation enthalpy. In addition, while the ethylation rate was found to depend on the nature of the alkylating agent for 1Me₂, it does not for 2Me₂. This difference in reactivity was observed also in the case of the ion pairs obtained by reacting 1Me₂ and 2Me₂ with [CPh₃][B(C₆F₅)₄]. For the latter species, NMR indicated that two main deactivation pathways, namely anion decomposition and σ-bond methatesis of Hf-alkyl groups, occur.

Introduction

Chain transfer reactions between transition organometallic complexes and main element alkyls play a crucial role in homogeneous olefin polymerization catalysis.¹ Polymeryl-group migration from active sites to co-catalysts, most frequently aluminium alkyls or methylaluminoxane (MAO),²³ is indeed a suitable chain termination process that can be exploited in tuning molecular weight and end-group structures of resulting polyolefins.⁴ This is particularly true in the case of living polymerization,⁵ since chain transfer increases the number of chains produced by each catalytic site and decreases the polydispersity.⁶ This concept is key in coordinative chain transfer polymerization (CCTP, Scheme
1), a reaction protocol based on the addition of chain transfer agents, such as AlR₃, ZnR₂ or MgR₂, to the catalytic pool, aimed at stimulating fast and reversible alkyl exchange between active transition metal and main element. As a matter of fact, when CCTP conditions are attained, chain transfer occurs faster than monomer insertion (k_{CT} >> k_P, Scheme 1) resulting in polymers with extremely narrow molecular weight distributions.

From the mechanistic point of view, the key step of CCTP relies on the formation of binuclear adducts in which polymeryl groups act as bridges between transition metal and main metal centers (Scheme 1). Despite rather intensive research in this area, little is known about adducts between active catalysts for CCTP and main metal alkyls, mainly due to their dynamic nature and low stability in solution. In a few cases, well defined LₙM(μ-R)₂ERₘ (M=transition metal, E=main metal) heterobimetallic adducts have been characterized, including group IV metallocenes, rare earth-metal or bisiminopyridyl V, Fe and Co complexes, but only when E=Al. Recently, we have shown that cationic pyridylamido Hf complexes, which are remarkably active catalysts for CCTP, react with zinc and aluminium alkyls to give heterobimetallic adducts. In the latter ones, the cyclometalated naphthyl group acts as a bridge between hafnium and main metal atoms, closely resembling the proposed intermediate for CCTP. The investigation of degenerative alkyl transfer kinetics revealed that Hf/Zn methyl exchange was faster than Hf/Al one, suggesting that the nature of metal alkyl is key in tuning the fluxionality of such adducts.

Scheme 1. Mechanism of coordinative chain transfer polymerization (M= transition metal, E=main element).

Nuclear Magnetic Spectroscopy has proven to be a suitable technique for mechanistic investigations of homogeneous olefin polymerization and, in the present study, we exploited NMR for studying the reactivity of bis(cyclopentadienyl)- and (pyridylamido)hafnium complexes with ZnR₂ and AlR₃ (R=Me or Et). The main purpose of this work is to compare the behavior of the simplest hafnocene Cp₂HfMe₂ (1Me₂, Scheme 2), which is not a suitable catalyst for chain transfer polymerization, with that of the highly optimized pyridylamido complex (2Me₂, Scheme 2) that is one of the most effective group IV catalysts in CCTP. First, we investigated the reactivity of mixtures containing ZnEt₂ and AlEt₃. Secondly, a kinetic study of their reactions with hafnium dimethyl species was car-
ried out for evaluating the effect of the ancillary ligand on the activation parameters. Then, the reactivity of Zn– and Al–alkyls with cationic metalloccenium species was explored and compared to that of the previously reported pyridylamido cationic complexes. Finally, the thermal decomposition of pyridylamido-Zn/Al heterobimetallic adducts was studied for understanding the role of chain transfer agent in deactivating the catalytic system.

Scheme 2. Hafnium complexes considered in this study.

Results and discussion

1. AlEt₃/ZnEt₂ mixtures

¹H and ¹³C NMR spectra of a 1:1 AlEt₃/ZnEt₂ mixture in toluene-d₈ showed the presence of only one set of signals at room temperature, having chemical shift values equal to the average of those of pure components. This indicates that a fast ethyl exchange process between aluminum and zinc atoms does occur, as already reported for AlMe₃/ZnMe₂ mixtures. Nevertheless, at low temperature the process became slow with respect to the NMR timescale and three different sets of signals separated below 200 K (Figure 1a); they were assigned to a) the ethyl group bound to the Zn atom [δH(CH₂)=0.09 ppm], b) the terminal [δH(CH₂)=0.16 ppm and c) the bridging [δH(CH₂)=0.67 ppm] ethyl groups of the AlEt₃ dimer. The simulation of the VT NMR spectra was hampered by the presence of many signals with different populations and only approximate rate constant values for alkyl exchange were derived in this specific case. For example, coalescence between unbridging methylene signals of AlEt₃ and ZnEt₂ was detected at 210 K and an approximate rate constant of 70 s⁻¹ was calculated (ΔG°=10.3 kcal/mol).
Figure 1. a) VT $^1$H NMR spectra of a 1:1 mixture of AlEt$_3$ and ZnEt$_2$ in toluene-d$_8$; b) $^1$H NOESY NMR spectrum recorded at 185 K.

At 185 K, the $^1$H NOESY NMR spectrum of the mixture (Figure 1b) showed the presence of intense exchange cross peaks, revealing that the alkyl exchange occurs also at rather low temperatures. Interestingly, the bridging ethyl groups of AlEt$_3$ dimer were in exchange with both terminal and Zn-ethyl groups, likely owing to the dissociation/recombination process of the Al dimer.$^{18a,19}$ Additionally, the uniform signal broadening with temperature observed in VT $^1$H NMR spectra suggested the presence of a unique kinetic constant for all the exchanges. This could be explained assuming the dissociation of the AlEt$_3$ dimer as rate determining step, as already suggested for the AlR$_3$/GaR$_3$ exchange.$^{18a}$

2. 1Me$_2$/ER$_n$ mixtures

The reaction of 1Me$_2$ with an excess of ZnEt$_2$ or AlEt$_3$ in benzene-d$_6$ led to the formation of Cp$_2$HfMeEt (1MeEt) and Cp$_2$HfEt$_2$ (1Et$_2$, Scheme 3), as indicated by the appearance of two overlapped signals at $\delta_H=1.45$ ppm ($^3$J$_{HH}=7.8$ Hz, $^1$J$_{CH}=124.6$ Hz) in the $^1$H NMR spectrum. They were assigned to the CH$_3$ groups of the Hf-ethyl moieties, in agreement with previous observations.$^{21}$

Scheme 3. Ethyl transfer from E(Et)$_n$ to 1Me$_2$. 
In contrast with zirconocenes, ethyl transfer reactions occur slowly at room temperature. For instance, 80% conversion of 1Me₂ into 1MeEt and 1Et₂ was obtained after 17 hours in the presence of 30 equivalents of ZnEt₂ at room temperature. 1Me₂ was instead consumed in approximately 85 minutes when 2 equivalents of AlEt₃ were used (Figure 2). Ethylated hafnocenes showed to be remarkably stable in solution up to 350 K, even if traces of ethane (δ_H=0.80 ppm) were detected during the reactions, in particular at temperatures above 320 K.

![Figure 2](image.png)

**Figure 2.** Concentration *versus* time plot obtained for the reaction of 1Me₂ with 2 equivalents of AlEt₃ in toluene-*d₈* at 298 K.

Kinetic profiles of methyl-to-ethyl transalkylation at variable temperature were obtained by following the evolution of the ¹H NMR spectra with time, as depicted in Figure 2. By a qualitative analysis, it is possible to note that the first ethylation is markedly faster than the second one and the concentration of 1MeEt shows a maximum that is dependent on both temperature and Hf/ERₚ ratio. These observations are consistent with a consecutive reaction pathway, in which 1Et₂ is formed only from 1MeEt and not owing to a double ethylation of 1Me₂.

Table 1 collects kinetic constants obtained for first (k₁) and second (k₂) alkylation of 1Me₂ with ZnEt₂ and AlEt₃ at different reaction temperatures (Experimental Section for details). The results show that the first alkyl exchange reaction is 2-4 times faster than the second, independent of the alkylating agent. On the other hand, the main group metal plays a crucial role since reactions with AlEt₃ are notably faster than those with ZnEt₂. As an example, at 300K kinetic constants obtained in the case of aluminium are twenty times larger than those obtained with zinc.

**Table 1.** Second-order rate constants (M⁻¹ s⁻¹) for first (k₁) and second (k₂) ethylation of 1Me₂ obtained at different temperatures (K) with different alkylating agents.

<table>
<thead>
<tr>
<th>T</th>
<th>k₁</th>
<th>k₂</th>
<th>k₁</th>
<th>k₂</th>
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</thead>
<tbody>
<tr>
<td>ZnEt₂</td>
<td></td>
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<td>(6.6±0.2)·10⁻⁵</td>
<td>(2.7±0.2)·10⁻⁵</td>
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<tr>
<td>267.5</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>273.8</td>
<td>-</td>
<td>-</td>
<td>(1.5±0.3)·10⁻⁴</td>
<td>(4.9±0.8)·10⁻⁵</td>
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</table>
The Eyring analysis of $k_1$ values (Figure 3) allowed the transalkylation activation parameters to be determined. In the case of ZnEt₂, the activation enthalpy is equal to 16.2±0.3 kcal/mol and the activation entropy amounts to $-22±1$ cal/mol·K while, for AlEt₃, a similar $\Delta S^\# (-23±2$ cal/mol·K) and a lower $\Delta H^\# (14.6±0.5$ kcal/mol) are obtained.

![Eyring plots](image)

**Figure 3.** Eyring plots for the ethylation of 1Me₂ with ZnEt₂ and AlEt₃ in toluene-$d_8$.

In the case of Al-alkyls, the complication derived from the formation of Al₆R₆ dimers, which might affect the trans-alkylation kinetics, has to be taken into account. For this reason, reactions of 1Me₂ with variable amounts of AlEt₃ (1:1, 2:1 and 4:1 Al/Hf ratios) were performed. The kinetic model was modified slightly to take into account possible equilibrium effects ascribed to the lower concentration of AlEt₃. Interestingly, rate constant values at 298K are three times larger when hafnocene and aluminium alkyl are equimolar ($k_1=4.83\cdot10^{-3}$ M⁻¹ s⁻¹) while decrease by increasing the concentration of AlEt₃ to reach a plateau at an Al/Hf ratio between 5 and 10 (Supporting Information).

It was also considered worthwhile to perform a reaction between 1Me₂ and a mixture of ZnEt₂/AlEt₃ in a 1:1 molar ratio, with the aim of exploring the role of the fast ethyl exchange between Zn and Al atoms in the alkylation of the transition metal complex. The quantification of the kinetic rate constants gave a $k_1$ value of $2.4\cdot10^{-3}$ M⁻¹ s⁻¹, which is quite similar to the values obtained in the experiment with only AlEt₃ at lower Al/Hf ratios (Supporting Information).

The analysis of the results reveals that the ethylation of 1Me₂ by ZnEt₂ and AlEt₃ is a slow reaction with a rather high activation barrier ($\Delta G^\neq=22.7$ and 21.4 kcal/mol for ZnEt₂ and AlEt₃, respectively) that is composed by a large activation enthalpy (16.2 kcal/mol for ZnEt₂ and 14.6 kcal/mol for AlEt₃) and a negative activation entropy ($-22$ and $-23$ cal/mol·K for ZnEt₂ and AlEt₃, respectively).
The latter values fit nicely with previously reported data on degenerative methyl transfer between 1Me₂ and AlMe₃ and are consistent with an associative mechanism, in which the main element alkyl and metallocene form a heterobimetallic complex featuring one or more bridging alkyl groups. Since similar ΔS‡ values were measured for ZnEt₂ and AlEt₃, it is reasonable to assume that the reaction pathway is the same for both. Moreover, the activation entropy value points out that the dissociation/recombination of AlEt₃ dimer is not rate determining. AlEt₃ dimerization has a modest detrimental effect, as deduced by the slightly higher reaction rates at lower Al/Hf ratios, likely due to a higher amount of Al₂Et₆ dimers that dissociate to monomeric AlEt₃, thus increasing the alkylation efficiency. Concerning the activation enthalpy, the lowest ΔH‡ value observed for AlEt₃ (ΔH‡(Zn-Al)=1.6 kcal/mol) could be related to the higher tendency of the latter of forming dimers with metallocenes and stronger E–Me bonds. The associative transition state should be, in effect, stabilized by Hf–(µ-Me)–Er bridges, whose formation is preferred with Al-alkyls.

Finally, the results obtained on the ethylation of 1Me₂ with a 1:1 AlEt₃/ZnEt₂ mixture are coherent with the proposed mechanistic scenario. The observation of reaction rates similar to those measured with pure AlEt₃ confirms that i) the Al/Zn ethyl exchange is not rate determining and ii) there are no cooperative effects, so that the reaction rate is determined by the alkylation of the most efficient metal–alkyl.

3. 2Me₂/Er₃ mixtures

The reaction of 2Me₂ with 1 equivalent of ZnEt₂ in benzene-d₆ afforded a mixture of stable mono- and bis-ethylated complexes, as seen above for 1Me₂. Four different Hf–ethyl groups were observed in the ¹H NMR spectrum, with methyl groups resonating at δH=1.75, δH=1.72, δH=1.53 and δH=1.44 ppm (¹JHH=8.0 Hz). They were assigned to i) the two diastereotopic (anti and syn with respect to the 2-(Me₂CH)-C₆H₄ substituent) Hf–Et moieties of 2Et₂ and ii) the ethyl groups of the two equally populated diastereoisomeric 2MeEt species (Scheme 4). When 1 equivalent of AlEt₃ was used, the same reactivity was observed. However, some resonances of reaction products appeared slightly broadened, likely due to dynamic processes. Contrary to what was observed with ZnEt₃, the reaction mixture was unstable at room temperature and slow decomposition of AlEt₃ to ethane occurred.
Scheme 4. Transalkylation reaction between $2\text{Me}_2$ and ZnEt$_2$.

Figure 4. A section of the $^1$H NOESY NMR spectrum of the mixture obtained after the reaction of $1\text{Me}_2$ with ZnEt$_2$ (benzene-$d_6$, 297 K).

As far as the reaction rate was concerned, alkyl exchange was very fast with both ZnEt$_2$ and AlEt$_3$ and it was not possible to follow the ethyl transfer by $^1$H NMR spectroscopy. Nevertheless, the phase sensitive $^1$H NOESY NMR spectrum of the reaction mixture (Figure 4, ER$_n$=ZnEt$_2$) revealed the presence of exchange cross peaks between Zn/Al-alkyl and Hf-alkyl resonances, indicating that a fast and reversible transalkylation occurs at equilibrium. This prompted us to explore the reaction kinetics by means of variable temperature $^1$H EXSY NMR, with the aim of obtaining activation parameters to compare with those measured for the reactions of $1\text{Me}_2$.

The kinetic study was performed by using a 5-fold excess of ER$_n$, in order to promote the exclusive formation of $2\text{Et}_2$ and simplify the NOE spectra (Supporting Information). No exchange between anti and syn ethyl groups of $2\text{Et}_2$ was detected, indicating that the interconversion of the two alkyls on the metal center is very slow (or frozen), as also observed for $2\text{Me}_2$. Second order kinetic rate constants were determined from $^1$H EXSY spectra taking into account the different populations of
the exchanging sites (Experimental Section). In the case of AlEt₃, the temperature window was limited by decomposition, which is faster than the measurement time above 300 K.

Table 2. Second order rate constants (M⁻¹ s⁻¹) for the reversible transalkylation of syn (kₛᵣₚ) and anti (kₐⁿᵗⁱ) ethyl groups of 2Et₂ with ZnEt₂ (Cₜₜ=32.0 mM, Zn/Hf=6) and AlEt₃ (Cₜₜ= 34.0 mM, Al/Hf=5) at different temperatures (T, K).

<table>
<thead>
<tr>
<th>T</th>
<th>kₛᵣₚ</th>
<th>kₐⁿᵗⁱ</th>
<th>kₛᵣₚ</th>
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<td>273.8</td>
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<tr>
<td>300.8</td>
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<tr>
<td>320.6</td>
<td>6.2±0.3</td>
<td>7.1±1.3</td>
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</tr>
<tr>
<td>335.6</td>
<td>9.7±0.3</td>
<td>11.6±4.6</td>
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<tr>
<td>349.6</td>
<td>15.8±2.7</td>
<td>19.3±7.2</td>
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The results reported in Table 2 show that the rate constants of the reversible transalkylation of 2Et₂ are notably larger than those measured for irreversible hafnocene ethylations. For example, at 300 K the reversible ethyl exchange with ZnEt₂ is four orders of magnitude faster than the methyl to ethyl exchange of 1Me₂. Moreover, transalkylation of the two ethyl groups in syn and anti positions occurs essentially with the same reaction rate, indicating that the process is not diastereoselective. The behavior of AlEt₃ and ZnEt₂ is not markedly different; for example, at 300 K rate constant values measured with AlEt₃ are only 2-3 times larger than those obtained with ZnEt₂.

The Eyring analysis of average transalkylation rate constants (Supporting Information) provided an activation enthalpy of 6.3±0.3 kcal/mol for ZnEt₂ and 8.1±0.3 kcal/mol for AlEt₃. For the activation entropy, values of −35±2 and −27±2 cal·mol/K were obtained for ZnEt₂ and AlEt₃, respectively.

The effect of AlEt₃ concentration was explored by performing ¹H EXSY NMR experiments at different concentrations of hafnium complex and AlEt₃ keeping their molar ratio constant, in order to induce the full conversion of 2Me₂ and 2MeEt to 2Et₂. The results showed that, for 2Et₂ at a concentration of 9.5 mM, average rate constants of reversible transalkylation were only 2 times larger than those measured at 34.0 mM (Figure 5). The Eyring analysis of such data allowed a ΔH‡ of 7.5±0.3 kcal/mol and a ΔS‡= −28±3 cal·mol/K to be derived (Supporting Information).

When 2Me₂ was mixed with 1 equivalent of AlEt₃ and 10 equivalents of ZnEt₂, the trend of rate constants was similar to that obtained for pure ZnEt₂ (Figure 5). For example, the average rate constant measured at 300 K is 4.2 M⁻¹ s⁻¹, while that of pure ZnEt₂ is 3.3 M⁻¹ s⁻¹ at the same temperature.
Figure 5. Second order rate constants ($k$, M$^{-1}$s$^{-1}$) for reversibile transalkylation of 2Et$_2$ with AlEt$_3$ (A: C$_{Hf}$=34.0 mM, Al/Hf=5; C: C$_{Hf}$=9.5 mM, Al/Hf=5), ZnEt$_2$ (B: C$_{Hf}$=34.0 mM, Zn/Hf=6) and their mixture (D: C$_{Hf}$=37.9, Zn/Al/Hf=10:1:1) in toluene-d$_8$.

To summarize, it was shown that 2Et$_2$ undergoes fast and reversible ethyl exchange with ER$_n$. Contrary to what observed for cationic species,$^{16}$ cyclometalated naphthyl group does not give ligand exchange with Al/Zn alkyls, suggesting that a coordinative vacancy is necessary to promote the breakage of the Hf–aryl bond. The free activation energy at 298K for reversible ethyl exchange is close to 16.0 kcal/mol for both the alkylating agents. The activation barrier is composed of a large and negative activation entropy ($-27$ and $-35$ cal·mol/K for AlEt$_3$ and ZnEt$_2$, respectively) and a modest activation enthalpy (8.1 and 6.3 kcal/mol for AlEt$_3$ and ZnEt$_2$, respectively). $\Delta S^\ddagger$ values suggest an associative mechanism in which the alkyl is exchanged through the formation of a heterobimetallic adduct at the transition state, as previously inferred above for 1Me$_2$. Also in the present case, $\Delta S^\ddagger$ values measured for AlEt$_3$ and ZnEt$_2$ are not markedly different thus indicating that the dissociation/recombination process of AlEt$_3$ is not rate determining. Higher values of activation enthalpy were obtained for AlEt$_3$ ($\Delta\Delta H^\ddagger$=1.8 kcal/mol), in contrast to those observed with 1Me$_2$. This could be due to the higher Lewis acidity of the Hf atom in the pyridylamido complex that prevents the dimerization with AlEt$_3$ through the establishment of bridging interactions. In such a mechanistic scenario, the more electron-rich ZnEt$_2$ could be favored in the interaction with the postmetallocene complex and undergo transalkylation with a lower activation enthalpy.

4. Metallocenium species/ER$_n$ mixtures

The reactivity of cationic hafnocenes with ER$_n$ was explored using both mononuclear [Cp$_2$HfMe][B(C$_6$F$_5$)$_4$] and binuclear [(Cp$_2$HfMe)$_2$(μ-Me)][B(C$_6$F$_5$)$_4$] [1(μ-Me)1] ion pairs, which can be straightforwardly obtained by reacting 1Me$_2$ with 1 or 0.5 equivalents of [CPh$_3$][B(C$_6$F$_5$)$_4$], respectively. The mononuclear ion pair quickly underwent –C$_6$F$_5$ transfer reactions, especially when Zn al-
kyls were used. Therefore, the attention was focused on 1(µ-Me)1 that, despite it is not likely relevant under polymerization conditions, allowed us to probe collateral reactions occurring at the metal center and tendency of ERs to split hafnocenium dimers.

a) Reactions with AlMe₃. When a 10-fold excess of AlMe₃ was added to a solution of 1(µ-Me)1 in toluene-d₈, the ¹H NMR spectrum of the reaction mixture showed the immediate consumption of the starting hafnium complex and the concomitant formation of two new species in a 1:1 ratio that were assigned to 1Me₂ and [Cp₂Hf(µ-Me)₂MeAlMe₂][B(C₆F₅)₄]⁹⁺ [1(µ-Me)Al]. The ¹H NOESY NMR spectrum of the reaction mixture (Figure 6a) revealed the presence of a selective pattern of chemical exchange involving: i) the cyclopentadienyl rings of both neutral and ionic metallocenes, ii) the methyl groups of 1Me₂ and the bridging ones of 1(µ-Me)Al, iii) the terminal methyl moieties of 1(µ-Me)Al and free AlMe₃. In line with previous observations,²⁵ no exchange was detected between terminal and bridging methyl groups of the bimetallic cation in the 298–338 K temperature range, thus indicating that the AlMe₃ dissociation/recombination in 1(µ-Me)Al is very slow (or frozen). Further evidence of this was obtained from a ¹⁹F,¹H HOESY NMR experiment, which showed the presence of dipolar contacts between the fluorine atoms of the borate anion and the methyl groups of 1Me₂ (Figure 6b) likely due to transferred Overhauser Effect.²⁶

![Figure 6](image-url)

Figure 6. a) A section of the ¹H NOESY NMR spectrum of a toluene-d₈ solution containing 1Me₂, 1(µ-Me)Al and AlMe₃; b) a section of the ¹⁹F,¹H NOESY NMR spectrum of the same mixture.

The timescale of fluxionality was suitable for VT ¹H EXSY NMR experiments and kinetic rate constants were determined by applying a two-site exchanging model.²⁴ The results are reported in
Table 3 and show that the exchange of hafnium methyl groups occurs roughly 20 times faster than those of aluminum along the explored temperature range. The Eyring analysis of the data afforded ΔH_f values of 13.7±1.0 and 14.1±1 kcal/mol for the Hf–Me and Al–Me exchanges, respectively, while ΔS_f values of −8±1 and −14.0±1 cal·mol/K were obtained.

Formally, the observed dynamic process suggests that [AlMe_2][B(C_6F_5)_4] ion pairs 27,28 are exchanged between neutral and ionic metallocenes. The obtained activation entropy values indicate that the reaction occurs via associative interchange, likely through the attack of 1Me_2 at the Al atom of the bimetallic 1(μ-Me)Al ion pair; the same conclusion applies to the exchange with AlMe_3, for which similar ΔH_f and ΔS_f were obtained. Activation enthalpy values are rather high for both processes and similar to those obtained in the case of the ethyl exchange on neutral hafnocenes, indicating that such processes are still difficult on cationic species, presumably due to the strong AlMe_3–hafnocene bridging interaction and the large HF–Me bonding energy.

Table 3. Rate constants (M⁻¹ s⁻¹) for 1Me_2/1(μ-Me)Al (k₁) and 1(μ-Me)Al /AlMe_3 (k₂) reversible exchanges as a function of temperature (T, K).

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<tr>
<th>T</th>
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<td>338</td>
<td>(152.0±3.0)</td>
<td>(4.9±0.1)</td>
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b) Reactions with ZnMe_2. Upon mixing a solution of 1(μ-Me)I in toluene-d₈ with 5 equivalents of ZnMe_2, no sign of reaction was observed in the ¹H NMR spectrum thus suggesting that ZnMe_2 has a lower tendency to split the hafnium dimer than that of AlMe_3. In addition, no signs of reversible methyl exchange were detected in the ¹H EXSY NMR spectra. After 2 days at room temperature, the starting homobimetallic ion pair was consumed to give 1Me_2, CH₄ and two new hafnium compounds (a and b) in approximately 1:1 ratio. The latter have three signals each: one signal for Cp resonances located at δH=5.54 and 5.21 ppm (δC=111.1 and 109.9 ppm), a singlet for Hf–CH₂ moieties at δH=0.13 and 1.85 ppm (δC=68.9 and 65.3 ppm) and a signal for Hf–CH₃ groups at δH= −0.35 and −0.42 ppm (δC=25.8 and 36.1 ppm); the relative signal intensities were 20:2:6 and 10:2:3 for a and b, respectively. By monitoring the composition of the reaction mixture as a function of time, it was observed that a formed initially to reach a steady state concentration, while the concentration of b increased as the starting ion pair decreased. ¹H NOE experiments showed the presence of rather strong dipolar contacts between Cp signals and both methyl and methylene resonances of the two species (Supporting Information). In addition, a NOE interaction was detected between methyl and methylene signals of a while, in the case of b, the interaction was notably weaker.
It is possible to hypothesize that the presence of $1\text{Me}_2$ in the reaction mixture arose from the splitting of the starting bimetallic cation, while the formation of Hf-CH$_2$ moieties and the evolution of methane suggest that a $\sigma$-bond metathesis of Hf–Me groups occurred. By compiling all the pieces of information, it can be speculated that $a$ corresponds to a bimetallic dimer featuring a CH$_2$ZnMe moiety, while $b$ could be labeled as a monomeric [Cp$_2$Hf(CH$_2$ZnMe)][B(C$_6$F$_5$)$_4$] fragment. The $^{13}$C chemical shift value of the methyl group in $b$ suggests the presence of an interaction between the Zn–Me moiety and the Hf atom. An higher amount of $b$ was obtained by using a larger amount of ZnMe$_2$ (20 equivalents), suggesting that it is likely formed from the breakage of the dimeric species $a$. No traces of dynamic processes were observed in the NOE spectrum, indicating that no reversible alkyl exchange occurs in the EXSY timescale.

c) Reactions with E(Et)$_n$ When $1(\mu\text{-Me})1$ was mixed in toluene-$d_8$ with an excess of ZnEt$_2$ at 283K, $^1$H NMR spectroscopy revealed the complete disappearance of the starting ion pair with the formation of $1\text{Et}_2$ and other cationic products. The integration of the spectra indicated that all the methyl groups of the starting $1(\mu\text{-Me})1$ were converted into ZnMe$_2$, suggesting a fast and irreversible ethyl transfer to hafnocene. The reaction mixture was unstable under these conditions and $1\text{Et}_2$ was consumed in a further process where ethane and a new species formed. The $^1$H NMR spectrum showed the presence of four Cp resonances ($\delta$H = 5.23, 5.02, 4.94 and 4.79 ppm), an ABX spin system (three doublets of doublets at $\delta$H = 3.43, 3.03 and 1.40 ppm, $J_{HH}=17.0$, 12.0 and 3.5 Hz) and a markedly shielded methyl group ($\delta$H = –2.13 ppm). The ABX spin system was identified as a –CH–CH$_2$ moiety by means of $^1$H,$^{13}$C HSQC NMR spectrum and showed a $\delta$C = 122.1 and $\delta$C = 59.5 ppm for methyne and methylene moieties, respectively. The rather high chemical shift value of the CH moiety lead us to hypothesize the formation of a methyne-bridged bimetallic dimer, likely arising from a double $\sigma$-bond metathesis reaction of Hf-ethyl groups (Scheme 5). $^1$H NOESY NMR experiments (Supporting Information) indicating the presence of selective dipolar interactions between the CHCH$_2$ moiety and the four magnetically non-equivalent cyclopentadienyl groups. The nature of methyl group located at $\delta$H = –2.13 ppm, having a $^{13}$C chemical shift at $\delta$C = 7.0 ppm, is unclear. Given that the latter showed strong NOE contacts only with the Cp rings, it can be speculated that it belongs to an anionic methylzincate fragment undergoing ion pairing with the bimetallic cation.
When the reaction was performed with AlEt₃, a similar pathway was observed. At the end of the reaction, the $^1$H NMR spectrum showed the presence of many products and two ABX spin systems (80:20 ratio) were observed. For the latter, $^1$H and $^{13}$C NMR chemical shift values were rather different to those obtained with ZnEt₂: the first pattern had $\delta_H=3.22$, 0.70, 0.32 ppm and $\delta_C=70.5$, 25.4 ppm while the second had $\delta_H=3.10$, 0.94, 0.50 ppm and $\delta_C=69.8$, 25.2 ppm. Assuming that the same bimetallic cation observed before formed, it can be inferred that the high low-frequency shift of the $^{13}$C NMR resonances of the ABX spin system is due to bridging interactions with the excess of AlR₃ species.

Once again, no chemical exchange between any metallocene species and Al/Zn alkyls was observed, indicating that no reversible alkyl transfer occurs between hafnium and the main group metal and that $\sigma$-bond metathesis is the main active deactivation pathway. This seems to be in agreement with the general tendency of cationic hafnocenes to undergo bond methatesis with different substrates.²⁹

5. Hafnium pyridylamido cationic species

Cationic species derived by the activation of 2Me₂ with [CPh₃][B(C₆F₅)₄] are known to undergo ligand exchange reactions with ZnR₂ or AlEt₃ at low temperature, affording heterobimetallic adducts in which the naphtyl group acts as a bridge between Hf and the main group metal.¹⁶ To investigate the thermal transformation of such species, a sample of the heterobimetallic adduct with ZnMe₂ was synthesized in toluene-$d_8$ and kept at room temperature for 12 hours. The $^1$H NMR spectrum of the solution obtained (Supporting Information) showed the presence of a prevalent set of sharp signals featuring typical fingerprints of pyridylamido hafnium complexes and a broad singlet at $\delta_H=0.73$ ppm. The latter was assigned to BMe₃, reasonably arising from –C₆F₅ transfer reactions between ZnMe₂ and the anion.²⁸,³⁰ In agreement, the $^{19}$F NMR spectrum showed the disappearance of starting borate resonances with the formation of many sets of signals that were assigned to Zn(C₆F₅)₂ ($\delta_F=–118.4$, –153.4 and –160.9 ppm)³⁰ and Hf–C₆F₅ moieties (ortho fluorine at $\delta_F=–119.4$, –121.5, accounting for two F
atoms, and −125.5 ppm). The latter signals showed selective NOE interactions with pyridylamido protons in the $^{19}$F,$^1$H HOESY NMR spectrum, thus confirming that two C₆F₅ rings are bound to the same hafnium atom. Therefore, the complete −C₆F₅ ring transfer to zinc and hafnium atoms (Scheme 6) led to the complete decomposition of borate anion and neutralization of pyridylamido cation. In perfect agreement with the latter hypothesis, a $^{13}$C NMR signal at δc=209.3 ppm, showing long-range scalar correlations with naphthyl protons (Supporting Information), was observed thus confirming that the remetalation of the naphthyl group occurred.

Interestingly, when 2Me₂ was activated with [HNMe₂Ph][B(C₆F₅)₄] to give the dimethyl cation featuring the demetalated naphthyl group and then reacted with ZnMe₂, no reaction took place at room temperature and B(C₆F₅)₄ did not decompose. Reversible methyl transfer between Zn and Hf atoms was shown to occur, but the superimposed methyl groups hampered the quantification of the rate constants by $^1$H EXSY NMR spectroscopy.

![Scheme 6. Thermal evolution of pyridylamidoHfMe/ZnMe₂ adducts.](image)

In the case of the adduct with AlMe₃, the thermal transformation at room temperature was more complex and led to the formation of two prevalent species in a 1:1 ratio, as deduced by the presence of 6 septets due to isopropyl groups in the $^1$H NMR spectrum. The $^{19}$F NMR spectrum showed the appearance of both Al− and Hf−C₆F₅ moieties that, together with the presence of BMe₃ in the $^1$H NMR spectrum, confirmed borate anion decomposition. Different to what was observed with ZnMe₂, an accurate analysis of the long range interactions in the $^1$H,$^{13}$C HMQC spectrum revealed that no remetalation of the naphthyl occurred. The first product showed two doublets located at δH=4.60 and 0.98 ppm ($^3$JHH=7.8 Hz, δc=74.1 ppm) and a Al−Me group falling at δH=−0.88 ppm. A $^{19}$F,$^1$H HOESY NMR spectrum showed that such resonances had selective NOE interactions with one ortho-F atom belonging to a Hf−C₆F₅. The second product showed the presence of an Hf−Me group at δH=1.72 ppm (δc=69.5 ppm) that was dipolarly coupled with another ortho-F of an Hf−C₆F₅ moiety. Full characterization of the complex was hampered by the overlapping of many signals but it was possible to conclude that aluminium has no tendency to detach from the naphthyl group, opening the route for new deactivation pathways including the formation of bridging Hf−CH₂−Al moieties arising from σ-bond metathesis.

6. Conclusions
The reactions of organometallic Hf(IV) complexes with ZnR₂ and AlEt₃ (R = Me or Et) have been explored by means of NMR spectroscopy, with the main purpose of obtaining insights into alkyl transfer processes that are central to coordinative chain transfer olefin polymerization catalysis. The simplest hafnocene 1Me₂ and highly-optimized pyridylamido 2Me₂ have been chosen as a case study, in order to contrast a poorly performing metallocene and an industrially relevant post-metallocene featuring the same transition metal. The main conclusion of this work is that the efficiency of the chain transfer is not arising from the nature of the single transition or main group metal complex, but reflects the matching between them. The investigation of the reactivity of neutral dimethyl species with ER₃ revealed that the ancillary ligand plays a remarkable role in determining both rate and reversibility of alkyl exchange between hafnium and main metal. In fact, metallocene reacts slowly with both ZnEt₂ and AlEt₃ to give methyl to ethyl exchange, while postmetallocene reacts much faster and reversibly. Variable temperature kinetic studies relate this difference to the notably lower activation enthalpy of the reaction with 2Et₂ (ΔH°=8 kcal/mol with ZnEt₂) whereas activation entropy values have shown to be large and negative in all the cases, pointing to an associative reaction mechanism. The nature of chain transfer agent was found to be important only in the case of metallocene ethylation, where the alkyl transfer occurs out of the equilibrium. In this case, AlEt₃ reacts faster than ZnEt₂ due to a lower ΔH° value. On the contrary, pyridylamido precatalysts undergo fast and reversible alkyl exchange with both Al– and Zn–alkyls with comparable activation barriers, reasonably due to the combination of higher Lewis acidity and less steric encumbrance at the metal centre in postmetallocene framework.

As far as cationic species are concerned, homobimetallic 1(µ-Me)1 ion pair reacts with ER₃ affording different products whose structure depends on the nature of both E and R. In the case of AlMe₃, the bimetallic cation is readily split into 1Me₂ and heterobimetallic 1(µ-Me)Al ion pair, which have been found to undergo slow selective chemical exchange formally due to [AlMe₂][B(C₆F₅)₄] ion pairs transfer. ZnMe₂ is instead less electrophilic and does not favor the cleavage of the bimetallic cation. However, it stimulates a very slow σ-bond metathesis reaction leading to the formation of methane and Hf-CH₂-Zn moieties. In the case of ZnEt₂ and AlEt₃, a fast irreversible ethylation of the bimetallic cation occurs but, even at low temperature, rapid metathesis reactions affording ethane and methyne-bridged bimetallic cations take place. Interestingly, none of the formed species exhibit reversible chemical exchange with ER₃, indicating that this kind of process is still difficult for cationic hafnocenes. Heterobimetallic [pyridylamido(Hf)Me(µ-Me)EMe₃₋₁][B(C₆F₅)₄] adducts showed rapid decomposition of the borate anion to BMe₃ as main deactivation pathway. Interestingly, remetalation of the naphthyl group on the Hf atom was observed when E=Zn. This strongly supports that the formation of heterobimetallic adducts with Zn is a reversible reaction, as previously suggested. In the case of the adduct with Al, no remetalation occurs and other decomposition pathways take place leading to the formation of Al-CH₂-Hf moieties.

7. Experimental Section
Materials and methods. All manipulations of air-sensitive materials were performed in flamed Schlenk glassware on a Schlenk line, interfaced to a high-vacuum pump (10⁻⁵ mmHg), or in a nitrogen-filled Vac-Atmosphere glovebox with a high capacity recirculator (<1 ppm O₂ and H₂O). All solvents were preventively distilled after 12 h reflux over Na and freeze-pump-thaw degassed over Na/K alloy. Benzene-d₆ and toluene-d₈ were freeze-pump-thaw degassed over Na/K alloy, vacuum transferred into a Schlenk flask with a PTFE valve and stored over activated molecular sieves.

Bis-cyclopentadienyl-hafnium-dimethyl (1Me₂) was purchased from Strem Chemicals and used as received. [N-[2,6-Diisoproplyphenyl]-α-[2-isoproplyphenyl]-6-(1-naphthalenyl)-2-pyridinemethanaminato]hafnium dimethyl (2Me₂) was obtained as a gift from Dow Chemical and was used as received. [CPh₃][B(C₆F₅)₃] was obtained from Boulder Scientific and used as received. ZnMe₂ (2.0 M solution in toluene), ZnEt₂ (Zn 52% wt.), AlMe₃ (97%) and AlEt₃ (93%) were purchased from Sigma Aldrich and used as received. CAUTION: trio-alkylaluminum and dialkyl-zinc are pyrophoric and must be handled in rigorously dry conditions.

¹H, ¹³C inversion recovery, ¹³C {¹H} COSY, ¹H NOESY, ¹H EXSY, ¹H,¹³C HMQC, ¹H,¹³C HSQC, ¹H,¹³C HMBC, ¹⁹F and ¹⁹F,¹H HOESY NMR experiments were performed on a Bruker Avance DRX 400 equipped with a QNP probe or on a Bruker Avance III 400 equipped with a ¹H, BB smartprobe. Referencing by residual solvents is relative to TMS. The actual concentration of the samples was estimated from integration relative to an external standard.

In situ reactions and NMR data. Dimethyl precursors/ERₐ mixtures were generated within the glovebox, by dissolving the suitable amount of 1Me₂ or 2Me₂ in approximately 0.7 ml of benzene-d₆ or toluene-d₈ and by injecting the required volume of ZnR₂ or AlEt₃ with a micrometric syringe. Immediately after mixing, the tube was sealed, transferred out of the glovebox and inserted into a cold bath. 1(µ–Me)₁ was synthesized in situ, by loading the suitable amount of 1Me₂ and 0.5 equivalents of [CPh₃][B(C₆F₅)₃] into a J Young NMR tube and adding approximately 0.7 ml of toluene-d₈. Further reactions of 1(µ–Me)₁ with ERₐ were performed as described above. 2(C₆F₅)₂ was obtained by activating 2Me₂ with 1.0 equivalents of [CPh₃][B(C₆F₅)₃] in toluene-d₈ and by reacting the formed ion pair with 5 equivalents of ZnMe₂ at room temperature.

**1Me₂.** ¹H NMR (400 MHz, benzene-d₆, 298K): δ=5.65 (s, Cp), −0.33 ppm (s, Me). ¹³C {¹H} NMR (100.55 MHz, benzene-d₆, 298K): δ=110.0 (s, Cp), 36.4 ppm (s, Me).

**2Me₂.** ¹H NMR (400 MHz, benzene-d₆, 298K): δ=5.65 (s, Cp), 1.41 (t, ³J_Hf=7.7 Hz, CH₂Me), 0.89 ppm (q, ³J_Hf=7.7 Hz, CH₂Me), −0.40 ppm (s, Me). ¹³C {¹H} NMR (100.55 MHz, benzene-d₆, 298K): δ=110.0 (s, Cp), 49.0 (s, CH₂Me), 36.6 (s, Me), 16.0 (s, CH₂Me).

**1Et₂.** ¹H NMR (400 MHz, benzene-d₆, 298K): δ=5.66 (s, Cp), 1.43 (t, ³J_Hf=7.8 Hz, CH₂Me), 0.89 ppm (q, ³J_Hf=7.8 Hz, CH₂Me). ¹³C {¹H} NMR (100.55 MHz, benzene-d₆, 298K): δ=110.0 (s, Cp), 49.1 (s, CH₂Me), 16.1 (s, CH₂Me).
[(Cp₂HfMe)₂(μ-Me)][B(C₆F₅)₄] (1(μ–Me)1). ¹H NMR (400 MHz, toluene-d₈, 298K): δ=5.51 (s, Cp), −0.32 (s, HfMe), −1.21 ppm (s, Hf(μ-Me)). ¹³C{¹H} NMR (400 MHz, toluene-d₈, 298K): δ=111.7 (s, Cp), 40.0 (s, HfMe), 22.6 ppm (s, Hf(μ-Me)). ¹⁹F NMR (376.65 MHz, toluene-d₈, 298K): δ=−131.8 (brd, o-F B(C₆F₅)₄), −162.1 (t, ³JₕF= 20.8 Hz, ρ-F B(C₆F₅)₄), −166.1 ppm (m, m-F B(C₆F₅)₄).

[Cp₂Hf(μ-Me)₂AlMe₂][B(C₆F₅)₄] (1(μ–Me)Al). ¹H NMR (400 MHz, toluene-d₈, 298K): δ=5.37 (s, Cp), −0.07 (s, HfMe), −0.75 ppm (s, AlMe). ¹³C{¹H} NMR (400 MHz, toluene-d₈, 298K): δ=113.4 (s, Cp), 36.0 (s, HfMe), −7.05 ppm (s, AlMe). ¹⁹F NMR (376.65 MHz, toluene-d₈, 298K): δ=−131.8 (brd, o-F B(C₆F₅)₄), −162.1 (t, ³JₕF= 20.8 Hz, ρ-F B(C₆F₅)₄), −166.1 ppm (m, m-F B(C₆F₅)₄).

1(μ–Me)1+ ZnMe₂. ¹H NMR (400 MHz, toluene-d₈, 298K): δ=5.54 (s, Cp (a)), 5.21 (s, Cp (b)), 1.85 (s, CH₂ (b)), 0.13 (s, CH₂ (a)), −0.35 (s, Me (a)), −0.42 ppm (s, Me (b)). ¹³C{¹H} NMR (400 MHz, toluene-d₈, 298K): δ=111.1 (s, Cp (a)), 109.9 (s, Cp (b)), 68.9 (s, CH₂ (a)), 65.3 (s, CH₂ (b)), 36.1 (s, Me (a)), 25.8 ppm (s, Me (b)). ¹⁹F NMR (376.65 MHz, toluene-d₈, 298K): δ=−131.5 (brd, o-F B(C₆F₅)₄), −162.1 (t, ³JₕF= 20.8 Hz, ρ-F B(C₆F₅)₄), −165.9 ppm (m, m-F B(C₆F₅)₄).

1(μ–Me)1+ ZnEt₂. Selected ¹H NMR resonances (400 MHz, toluene-d₈, 298K): δ=5.23 (s, H4), 5.02 (s, H2), 4.94 (s, H3), 4.79 (s, H1), 3.43 (dd, ³JₜH=16.4, 12.0 Hz, H6), 3.03 (dd, ³JₜH=12.0 Hz, H5a), 1.40 ppm (overlapped with 1ET₂, H5b). Selected ¹³C{¹H} NMR resonances (100.55 MHz, toluene-d₈, 298K): δ=122.2 (s, C6), 107.2 (s, C4), 105.9 (s, C2), 105.7 (s, C3), 105.1 (s, C1), 59.5 ppm (s, C5). ¹⁹F NMR (376.65 MHz, toluene-d₈, 298K): δ=−131.6 (brd, o-F B(C₆F₅)₄), −162.2 (t, ³JₕF= 20.8 Hz, ρ-F B(C₆F₅)₄), −166.1 ppm (m, m-F B(C₆F₅)₄).

1(μ–Me)1+ AlEt₃. Selected ¹H NMR resonances (400 MHz, toluene-d₈, 298K): δ=5.87 (s, Cp), 5.36 (s, Cp), 5.46 (s, Cp), 5.84 (s, Cp), 3.07 (dd, ³JₜH=17.2, 11.2 Hz, CH), 0.89 (m, CH2), 0.43 ppm (m, CH2). Selected ¹³C{¹H} NMR resonances (100.55 MHz, toluene-d₈, 298K): δ=114.3 (s, Cp), 113.5 (s, Cp), 105.1 (s, Cp), 104.6 (s, Cp), 69.8 (s, CH), 25.2 ppm (s, CH2).

[N-[2,6-Diisoproplyphenyl]-α-[2-isoproplyphenyl]-6-(1-naphthalenyl)-2-pyridinemethanaminate]hafnium dimethyl (2Me). ¹H NMR (400 MHz, benzene-d₆, 298K): δ=8.58 (d, ³JₜH=7.7 Hz, H2), 8.25 (d, ³JₜH=8.6 Hz, H8), 7.82 (dd, ³JₜH=7.7 Hz, H3), 7.72 (dd, ³JₜH=7.6 Hz, ⁴JₜH=2.0 Hz, H5), 7.50 (d, ³JₜH=8.0 Hz, H12), 7.34 (m, H24), 7.29 (m, H6+H7), 7.15 (m, H30+H31), 7.07 (m, H21+H29), 7.00 (m, H22+H23), 6.82 (t, ³JₜH=8.0 Hz, H13), 6.57 (s, H16), 6.55 (d, ³JₜH=8.0 Hz, H14), 3.83 (sept, ³JₜH=6.8 Hz, H27), 3.37 (sept, ³JₜH=6.8 Hz, H33), 2.89 (sept, ³JₜH=6.9 Hz, H19), 1.38 (d, ³JₜH=6.8 Hz,
H34'), 1.37 (d, $^3J_{HH}$=6.8 Hz, H28), 1.18 (d, $^3J_{HH}$=6.8 Hz, H20), 1.14 (d, $^3J_{HH}$=6.8 Hz, H34), 0.96 (s, H35), 0.70 (s, H36), 0.69 (d, $^3J_{HH}$=6.8 Hz, H20'), 0.39 ppm (d, $^3J_{HH}$=6.8 Hz, H28').

$^{13}$C $^1$H NMR (100.55 MHz, benzene-$d_6$, 298K): δ=171.2 (s, C15), 165.0 (s, C11), 148.0 (s, C26), 147.4 (s, C18), 147.0 (s, C32), 146.2 (s, C25), 144.7 (s, C10), 141.5 (s, C17), 141.4 (s, C13), 136.4 (s, C9), 134.8 (s, C2), 131.4 (s, C4), 130.8 (s, C24), 130.6 (s, C5), 130.5 (s, C3), 128.5 (s, overlapped with C6D6, C22), 127.6 (s, C6 or C7), 127.4 (s, C23), 126.7 (s, C30), 126.2 (s, C7 or C6), 126.1 (s, C21), 125.8 (s, C31), 125.2 (s, C29), 124.9 (s, C8), 121.1 (s, C12), 120.2 (s, C14), 77.4 (s, C16), 67.6 (s, C36), 63.5 (s, C35), 29.4 (s, C33), 29.3 (s, C19), 28.8 (s, C27), 28.1 (s, C28), 26.5 (s, C34'), 26.1 (s, C34), 25.8 (s, C20), 24.4 (s, C28'), 23.7 ppm (s, C20').

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$^{13}$C $^1$H NMR (100.55 MHz, benzene-$d_6$, 298K): δ=8.66 (d, $^3J_{HH}$=7.7 Hz, H2 syn or anti), 8.65 (d, $^3J_{HH}$=7.7 Hz, H2 syn or anti), 8.26 (d, overlapped with HfEt2, H8 syn+anti) 7.81 (d, $^3J_{HH}$=7.7 Hz, H3 syn+anti), 7.72 (d, overlapped with HfEt2, H5 syn+anti), 7.52 (d, overlapped with HfEt2, H12 syn+anti), 7.35 (m, overlapped with HfEt2, H24 syn+anti), 7.29 (m, overlapped with HfEt2, H6+H7 syn+anti), 6.85 (t, overlapped with HfEt2, H13 syn+anti), 6.57 (s, overlapped with HfEt2, H16 syn+anti), 6.55 (d, overlapped with HfEt2, H14 syn+anti), 3.75 (sept, overlapped with HfEt2, H27 syn+anti), 3.37 (sept, overlapped with HfEt2, H33 syn+anti), 2.89 (sept, overlapped with HfEt2, H19 syn+anti), 1.75 (t, $^3J_{HH}$=8.0 Hz, H36 syn), 1.53 (t, $^3J_{HH}$=8.0 Hz, H37 anti), 1.50 (m, H35 syn), 1.39 (overlapped with HfEt2, H34'+H28 syn+anti), 1.28 (overlapped with HfEt2, H36 anti + H20+H34 syn+anti), 1.05 (m, overlapped with HfEt2, H35 syn), 1.04 (s, H35 anti), 0.84 (m, overlapped with HfEt2, H36 anti), 0.70 (m, overlapped with HfEt2, H37 syn+H20' syn+anti), 0.36 ppm (overlapped with HfEt2, H28' syn+anti).

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**syn/anti** [N-[2,6-Diisopropylphenyl]-α-[2-isopropylphenyl]-6-(1-naphthalenyl)-2-pyridinemethanamino]hafnium methyl-ethyl (2MeEt). Selected $^1$H NMR resonances (400 MHz, benzene-$d_6$, 298K): δ=8.66 (d, $^3J_{HH}$=7.7 Hz, H2 syn or anti), 8.65 (d, $^3J_{HH}$=7.7 Hz, H2 syn or anti), 8.26 (d, overlapped with HfEt2, H8 syn+anti) 7.81 (d, $^3J_{HH}$=7.7 Hz, H3 syn+anti), 7.72 (d, overlapped with HfEt2, H5 syn+anti), 7.52 (d, overlapped with HfEt2, H12 syn+anti), 7.35 (m, overlapped with HfEt2, H24 syn+anti), 7.29 (m, overlapped with HfEt2, H6+H7 syn+anti), 6.85 (t, overlapped with HfEt2, H13 syn+anti), 6.57 (s, overlapped with HfEt2, H16 syn+anti), 6.55 (d, overlapped with HfEt2, H14 syn+anti), 3.75 (sept, overlapped with HfEt2, H27 syn+anti), 3.37 (sept, overlapped with HfEt2, H33 syn+anti), 2.89 (sept, overlapped with HfEt2, H19 syn+anti), 1.75 (t, $^3J_{HH}$=8.0 Hz, H36 syn), 1.53 (t, $^3J_{HH}$=8.0 Hz, H37 anti), 1.50 (m, H35 syn), 1.39 (overlapped with HfEt2, H34'+H28 syn+anti), 1.28 (overlapped with HfEt2, H36 anti + H20+H34 syn+anti), 1.05 (m, overlapped with HfEt2, H35 syn), 1.04 (s, H35 anti), 0.84 (m, overlapped with HfEt2, H36 anti), 0.70 (m, overlapped with HfEt2, H37 syn+H20' syn+anti), 0.36 ppm (overlapped with HfEt2, H28' syn+anti).
[N-[2,6-Diisopropylphenyl]-α-[2-isopropylphenyl]-6-(1-naphthalenyl)-2-pyridinemethanaminate]hafnium diethyl (2Et2). ¹H NMR (400 MHz, toluene-­d₈, 298K): δ=8.62 (d, ³J_HH=7.7 Hz, H2), 8.20 (d, ³J_HH=8.2 Hz, H8), 7.76 (d, ³J_HH=7.7 Hz, H3), 7.68 (dd, ³J_HH=7.4 and 1.9 Hz, H5), 7.50 (d, ³J_HH=8.0 Hz, H12), 7.30 (m, H24), 7.26 (m, H6+H7), 7.13 (dd, ³J_HH=7.4 and 1.9 Hz, H31), 7.07-7.00 (m, H29+H30+H21+H22+H23), 6.91 (t, ³J_HH=7.8 Hz, H13), 6.54 (s, H16), 3.68 (sept, ³J_HH=6.8 Hz, H27), 3.68 (sept, ³J_HH=6.8 Hz, H27), 3.34 (sept, ³J_HH=6.8 Hz, H33), 2.87 (sept, ³J_HH=6.8 Hz, H19), 1.72 (t, ³J_HH=8.0 Hz, H36), 1.44 (m, H38+H35b), 1.39 (d, ³J_HH=6.8 Hz, H34'), 1.34 (d, ³J_HH=6.8 Hz, H28), 1.18 (d, ³J_HH=6.8 Hz, H20), 1.15 (d, ³J_HH=6.8 Hz, H34), 1.08 (m, H35a), 0.98 (m, H37b), 0.76 (m, H37a), 0.66 (d, ³J_HH=6.8 Hz, H20'), 0.30 ppm (d, ³J_HH=6.8 Hz, H28'). ¹³C{¹H} NMR (100.55 MHz, toluene-­d₈, 298K): δ=205.0 (s, C1), 170.3 (s, C15), 164.1 (s, C11), 147.2 (s, C26), 146.5 (s, C18), 146.1 (s, C32), 145.9 (s, C25), 144.0 (s, C10), 141.1 (s, C17), 140.3 (s, C13), 135.4 (s, C9), 134.2 (s, C2), 130.5 (s, C4), 130.1 (s, C24), 129.6 (s, C5), 129.5 (s, C3), 127.5 (s, overlapped with C7D8, C22), 126.6 (s, C6 or C7), 126.5 (s, C23), 125.6 (s, C30), 125.2 (s, C21 or C29), 125.0 (s, overlapped with C7D8, C7 or C6), 124.8 (s, C31), 124.3 (s, C29 or C21), 123.9 (s, C8), 120.2 (s, C12), 119.1 (s, C14), 79.2 (s, C37), 76.6 (s, C16), 74.7 (s, C35), 28.5 (s, C19), 28.4 (s, C33), 28.0 (s, C27), 26.9 (s, C28), 25.9 (s, C34'), 25.2 (s, C34), 25.0 (s, C20), 23.7 (s, C28'), 22.8 (s, C20'), 11.7 (s, C38), 11.3 ppm (s, C36).

[N-[2,6-Diisopropylphenyl]-α-[2-isopropylphenyl]-6-(1-naphthalenyl)-2-pyridinemethanaminate]hafnium bis-perfluorophenyl (2(C₆F₅)₂). Selected ¹H NMR resonances (400 MHz, toluene-­d₈, 298K): δ=8.17 (d, ³J_HH=8.7 Hz, H8), 8.01 (d, ³J_HH=7.9 Hz, H2), 7.54 (d, H3+H5+H24), 7.48 (m, ³J_HH=7.7 Hz, H3), 7.30 (m, H24), 7.26 (m, H6+H7), 7.13 (dd, ³J_HH=7.4 and 1.9 Hz, H31), 7.07-7.00 (m, H29+H30+H21+H22+H23), 6.91 (t, ³J_HH=7.8 Hz, H13), 6.60 (d, ³J_HH=7.8 Hz, H14), 6.54 (s, H16), 3.68 (sept, ³J_HH=6.8 Hz, H27), 3.68 (sept, ³J_HH=6.8 Hz, H27), 3.34 (sept, ³J_HH=6.8 Hz, H33), 2.87 (sept, ³J_HH=6.8 Hz, H19), 1.72 (t, ³J_HH=8.0 Hz, H36), 1.44 (m, H38+H35b), 1.39 (d, ³J_HH=6.8 Hz, H34'), 1.34 (d, ³J_HH=6.8 Hz, H28), 1.18 (d, ³J_HH=6.8 Hz, H20), 1.15 (d, ³J_HH=6.8 Hz, H34), 1.08 (m, H35a), 0.98 (m, H37b), 0.76 (m, H37a), 0.66 (d, ³J_HH=6.8 Hz, H20'), 0.30 ppm (d, ³J_HH=6.8 Hz, H28'). ¹³C{¹H} NMR (100.55 MHz, toluene-­d₈, 298K): δ=205.0 (s, C1), 170.3 (s, C15), 164.1 (s, C11), 147.2 (s, C26), 146.5 (s, C18), 146.1 (s, C32), 145.9 (s, C25), 144.0 (s, C10), 141.1 (s, C17), 140.3 (s, C13), 135.4 (s, C9), 134.2 (s, C2), 130.5 (s, C4), 130.1 (s, C24), 129.6 (s, C5), 129.5 (s, C3), 127.5 (s, overlapped with C7D8, C22), 126.6 (s, C6 or C7), 126.5 (s, C23), 125.6 (s, C30), 125.2 (s, C21 or C29), 125.0 (s, overlapped with C7D8, C7 or C6), 124.8 (s, C31), 124.3 (s, C29 or C21), 123.9 (s, C8), 120.2 (s, C12), 119.1 (s, C14), 79.2 (s, C37), 76.6 (s, C16), 74.7 (s, C35), 28.5 (s, C19), 28.4 (s, C33), 28.0 (s, C27), 26.9 (s, C28), 25.9 (s, C34'), 25.2 (s, C34), 25.0 (s, C20), 23.7 (s, C28'), 22.8 (s, C20'), 11.7 (s, C38), 11.3 ppm (s, C36).
(H6+H12), 7.16 (m, H7), 6.87 (m, overlapped with other aromatic resonances, H13), 6.75 (s, H16),
6.53 (d, 3JHH=7.8 Hz, H14), 3.25 (sept, 3JHH=6.8 Hz, H27), 3.03 (sept, 3JHH=6.8 Hz, H33), 2.53 (sept,
3JHH=6.8 Hz, H19), 1.26 (d, 3JHH=6.8 Hz, H13), 0.24 (d, 3JHH=6.8 Hz, H34), –0.03 ppm (d, 3JHH=6.8 Hz, H28’).

Selected 13C{1H} NMR resonances (100.55 MHz, toluene-d8, 298K): δ=209.5 (s, C1), 171.9 (s, C15),
165.4 (s, C11), 148.6 (s, C26), 147.8 (s, C18), 146.5 (s, C32), 143.0 (s, C10), 142.4 (s, C13), 130.7 (s, C3),
130.2 (s, C2), 124.1 (s, C8), 120.8 (s, C14), 120.4 (s, C12), 77.4 (s, C16), 29.0 (s, C33), 28.5 (s, C19),
28.3 (s, C27), 26.7 (s, C34’), 25.9 (s, C20), 25.0 (s, C28), 23.9 (s, C28’), 23.7 (s, C34), 22.0 ppm (s, C20’).

19F NMR (376.65 MHz, toluene-d8, 298K): δ=–119.4 (brd, o–F –C6F5), –121.4 (brd, o–F –C6F5), –125.5 (brd, o–F –C6F5), –151.3 (t, 3JFF=19.4 Hz, p–F –C6F5), –151.9 (t, 3JFF=19.4 Hz, p–F –C6F5), –160.9 (m, m–F –C6F5), –161.5 ppm (m, m–F –C6F5).

**Kinetic measurements.** Slow ethylation reactions were performed in J–Young tubes containing cold mixtures of 1Me2 and alkylation agent, which were inserted into the NMR probe and allowed to equilibrate at the desired instrumental temperature. The composition of the reaction mixture was monitored by means of 1H NMR spectroscopy by acquiring a series of spectra as a function of time. Concentration versus time plots were obtained by referencing to an external standard and fitted by means of COPASI software package. The reaction plots were interpolated with a two-reactions kinetic model of the type:

\[
\text{Cp}_2\text{HfMe}_2 + \text{E(Et)} \rightarrow k_1 \rightarrow \text{Cp}_2\text{HfMeEt} + \text{E(Me)}
\]

\[
\text{Cp}_2\text{HfMeEt} + \text{E(Et)} \rightarrow k_2 \rightarrow \text{Cp}_2\text{HfEt}_2 + \text{E(Me)}
\]

where E(Et) and E(Me) are the total concentration of ethyl and methyl groups bound to Al or Zn atoms. Due to the presence of a large excess of alkylation agent, equilibrium effects were neglected. At higher temperatures, a decomposition reaction was added to the kinetic model to take into account the formation of ethane and improve the quality of the fitting.

Fast and reversible exchange rates between 2Et2 and E(Et)n were quantified by means of two-dimensional 1H EXSY NMR spectroscopy, by using the pfg version of the standard 1H NOESY se-
sequence (noesygptp). Different values of spectral width, relaxation delay, mixing time ($\tau_M$) and number of transients were used according to the sample nature and concentration. Microscopic rate constants ($k'$, s$^{-1}$) were calculated from the integration of the 2D spectra by using the software EXSYCALC$^{33}$ and converted into second order rate constants ($k$, M$^{-1}$ s$^{-1}$) correcting by the actual molar concentration of the exchanging sites. At least two experiments with different $\tau_M$ values were acquired and the rate constant values (with relative standard deviations) were obtained from the average of all the values.

T1 values for the exchanging resonances were measured by means of $^1$H inversion recovery experiments and, in all cases, no differences in T1 were observed.

Supporting Information. Additional kinetic experiments and NMR spectra.

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The authors declare no competing financial interests.

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![](image)

References


20) At the coalescence temperature, \( k = \frac{\pi \Delta v_0}{\sqrt{2}} \) (\( \Delta v_0 \) is the distance in Hz between the signals in the completely resolved spectrum).


23) It is known that the average E–Me bond energy is larger for Al compared with that of Zn (65.5 vs. 42.3 kcal/mol): O’Neill, M. E.; Wade, K. in *Comprehensive organometallic chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E.W. eds; Pergamon Press, Oxford (1982).


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