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Heterobimetallic Complexes

Unusual Hafnium–Pyridylamido/ER_n Heterobimetallic Adducts ($ER_n = ZnR_2$ or AlR_3)**

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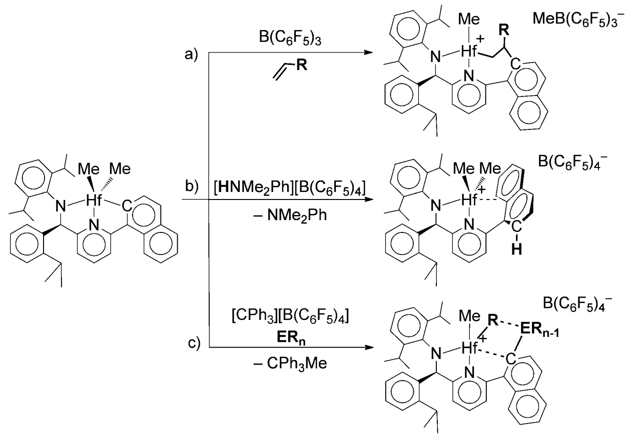
Abstract: *NMR spectroscopy and DFT studies indicate that the Symyx/Dow Hf(IV)–pyridylamido catalytic system for olefin polymerization, $[\{N^-,N,C_{Nph}^-\}HfMe][B(C_6F_5)_4]$ (**1**, Nph = naphthyl), interacts with ER_n (E = Al or Zn, R = alkyl group) to afford unusual heterobimetallic adducts $[\{N^-,N\}HfMe(\mu\text{-}C_{Nph})(\mu\text{-}R)ER_{n-1}][B(C_6F_5)_4]$ in which the cyclometalated Nph acts as a bridge between Hf and E. ^1H VT (variable-temperature) EXSY NMR spectroscopy provides direct evidence of reversible alkyl exchanges in heterobimetallic adducts, with ZnR_2 showing a higher tendency to participate in this exchange than AlR_3. 1-Hexene/ER_n competitive reactions with **1** at 240 K reveal that the formation of adducts is strongly favored over 1-hexene polymerization. Nevertheless, a slight increase in the temperature (to > 265 K) initiates 1-hexene polymerization.*

Discovered by means of high-throughput screening in the framework of a Dow/Symyx collaboration,[1–3] Hf^{IV}–pyridylamido-based olefin polymerization catalysts have several unique features. Initially reported as the first industrially relevant systems to yield highly isotactic polypropylene with solution-process technology,[4–6] they subsequently attracted even greater attention for their propensity to undergo reversible transalkylation with metal alkyls, thereby opening the door to novel olefin block copolymers through "chain shuttling", that is, tandem catalysis under coordinative chain-transfer polymerization (CCTP) conditions.[7–11]

A key feature of the ancillary ligand framework is the *ortho*-metalation of the aryl moiety bound to the pyridine fragment (Scheme 1). It has been demonstrated that the resulting strained Hf^{IV}–aryl bond represents the most reactive site of the cationic catalytic species formed from the activation of the neutral precursors by means of Lewis acids such as $B(C_6F_5)_3$; in fact, compelling evidence indicates that the first monomer insertion occurs at this site (Scheme 1a), thereby modifying the ligand in situ.[12,13] Activation with Brønsted acids such as $[HNMe_2Ph][B(C_6F_5)_4]$,[14] on the other hand, first leads to the protonation of the Hf^{IV}–aryl bond (Scheme 1b), which opens the metallacycle and results in a poorly active cation as long as *ortho*-metalation (with liberation of CH_4) is not restored.



2: E = Zn R = Me n = 2
3: E = Al R = Me n = 3
4: E = Zn R = Et n = 2
5: E = Al R = Et n = 3

Scheme 1. Reactivity of Hf^{IV}–pyridylamido precatalyst with: a) $B(C_6F_5)_3$ and α-olefins; b) $[HNMe_2Ph][B(C_6F_5)_4]$; and c) $[CPh_3][B(C_6F_5)_4]$ and metal alkyls (ER_n; ZnR_2 or AlR_3, R = Me or Et).

As noted, Hf^{IV}–pyridylamido catalysts belong to the very limited class of olefin-polymerization catalysts amenable to CCTP. The process entails reversible chain-transfer reactions with some metal alkyls (ER_n, E = Al or Zn, R = alkyl group, including polymeryl,[15] most likely through the formation of heterobimetallic adducts followed by metathesis of the bridging alkyls.[8,16,17] Despite the importance of this chemistry, to our knowledge, very limited molecular information (if any) is available on the ER_n/Hf^{IV}–pyridylamido interaction(s). Herein, we report the results of a combined NMR spectroscopy and DFT study, which indicate that the Hf^{IV}–aryl bond is still the most reactive site in the presence of ER_n moieties, thus leading to the generation of unusual and

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comparatively stable bimetallic adducts such as $Hf(\mu\text{-}C_{Nph})(\mu\text{-}R)ER_{n-1}$ (Scheme 1 c), rather than more typical $Hf(\mu\text{-}R_2)ER_{n-1}$ adducts.[18,19]

Upon activation with $[CPh_3][B(C_6F_5)_4]$, $[\{N^-,N,C_{Nph}^-\}HfMe_2]$ precatalyst forms two diastereoisomeric ion pairs $[\{N^-,N,C_{Nph}^-\}HfMe][B(C_6F_5)_4]$ (**1a**/**1b**, see the Supporting Information), which differ in the relative orientation of the Hf–Me and 2-$(Me_2CH)C_6H_4$ moieties.[14] **1a**/**1b** undergo ligand exchange with ER_n to afford unusual heterobimetallic adducts **2**–**5** (Scheme 1 c) with yields approaching 70–80 %, as estimated by means of multinuclear and multidimensional low-temperature NMR experiments (see the Supporting Information).[20]

Two pieces of evidence were diagnostic for the transformation of **1a**/**b** into **2** or **3**: 1) the disappearance of the ^{13}C NMR resonances typical of the Hf–C_{Nph} moiety of **1a** and **1b** ($\delta_C = 203.0$ and 199.6 ppm) with the concomitant formation of a new resonance (assigned to C1) at $\delta_C = 166.8$ and 160.8 ppm for E = Zn and E = Al, respectively (Figure 1 a); 2) the presence of two distinct Hf–C resonances (see the Supporting Information), which demonstrates that an alkyl group was transferred from ER_n to **1a**/**1b**. Notably, this reaction did not go to completion when E = Zn, and an equilibrium constant of $9\times10^2\,\mathrm{M}^{-1}$ was estimated in [D$_8$]toluene at 243 K by NMR integration of the resonances of the reagents and products. Adducts **2** and **3** are unusual and represent the first heterobimetallic adducts with a bridging aryl, although aryl-bridged homobimetallic $Me_3Al(\mu\text{-}Ph)AlMe_2$ has been reported.[21]

^1H ROESY NMR spectroscopy provided information about the 3D structures of **2**–**5** in solution. It was found that after the cleavage of the Hf–C1 bond subsequent to the addition of ER_{n-1}, C1 still remained in proximity to Hf. This was clearly indicated by the presence of NOE between H8 and H12 (Figure 1 b) and between H2 and H35 (and H36, which undergoes an exchange process with H35 (see below); Figure 1 c). Furthermore, because NOE contacts were observed between ER_{n-1} moieties and H27, it was concluded that the naphthyl group is slightly tilted out of the plane defined by the pyridyl ring, thus directing the ER_{n-1} attached to it into an *anti* position with respect to the 2-$(Me_2CH)C_6H_4$ substituent of C16 (Figure 1).

Adducts **2** and **3** show large variations in the ^1H chemical shifts of the Hf–Me groups. The H35 signals are low-frequency shifted ($\delta_H = -0.20$ and 0.24 ppm for **2** and **3**, respectively) with respect to those of the dimethyl precursor ($\delta_H = 0.96$ and $\delta_H = 0.71$ ppm), whereas the H36 signals are located at rather high frequencies ($\delta_H = 0.94$ and 1.81 ppm for **2** and **3**, respectively). These observations reflect the peculiar structure of the heterobimetallic adducts; the naphthyl group, which is indeed tilted towards H35, is likely responsible for the shielding observed. The same phenomenon has been reported for the mono-inserted product (Scheme 1 a, $\delta_H = 0.06$ ppm)[12] and the product derived from activation with ammonium salts (Scheme 1 b, $\delta_H = -0.25$ and $\delta_H = -0.49$ ppm).[14] As far as H36 is concerned, the chemical shift in complex **2** is only 0.2 ppm higher than in the dimethyl precursor, whereas the change observed for **3** is much more pronounced. The other methyl group of **2** (H37) exhibits a resonance at the same chemical shift as that of free $ZnMe_2$. In the case of **3**, only the H38 resonance ($\delta_H = -0.44$ ppm) falls at a chemical shift value similar to that of $AlMe_3$, whereas H37 ($\delta_H = -1.34$ ppm) is more shielded, likely owing to the interaction with the pyridine ring (see Figure S29).

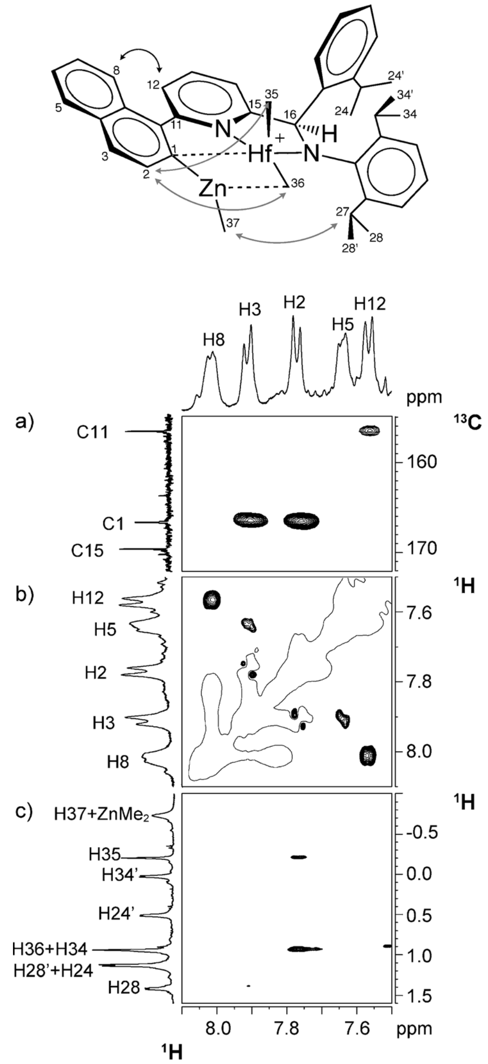
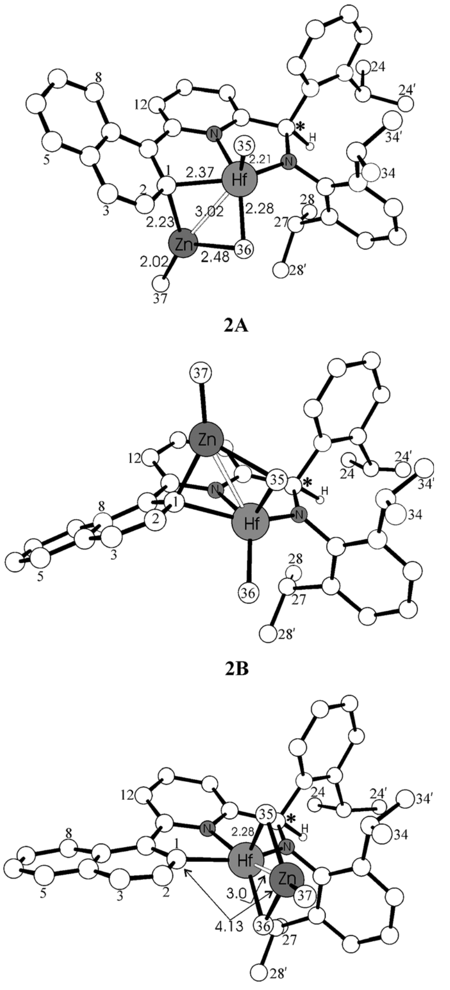


Figure 1. a) A section of the $^1H,^{13}C$ HMBC NMR spectrum of **2** (250 K, [D$_8$]toluene/[D$_5$]chlorobenzene 1:1 v/v) showing C1/H2 and C1/H3 long-range correlations. Two sections of the ^1H ROESY NMR spectrum of **2** (250 K, [D$_8$]toluene/[D$_5$]chlorobenzene 1:1 v/v) show the H8/H12 (b) and H2/H35 (c) NOE interactions. Atom labeling relates to the sketch shown above the spectra.

A clear picture of the geometrical features of **2**–**5** was provided by full quantum mechanical (QM) modeling studies (see the Supporting Information). The structures obtained by DFT calculations for **2**, which nicely agree with the ^1H NOESY and ^1H ROESY results, are shown in Figure 2.

QM calculations allowed us to estimate the relative stability of the heterobimetallic adducts with respect to the more typical $M(\mu\text{-}R_2)ER_{n-1}$ adducts, the roles of Zn and Al (by comparison of **2** and **3**), the alkyl effect (by comparison of **4** and **5**), and last but not least, the competing reaction with olefins (ethene, propene, and 1-hexene) at the Hf–C_{aryl} bond. A complete set of the energy values with respect to **1a**/**1b** is



2A

2B

2C

Figure 2. QM-optimized structures of complexes **2**. Complexes **2 A** and **2 B** correspond to the adducts with $ZnMe_2$ *anti* and *syn* with respect to the 2-$(Me_2CH)C_6H_4$ bonded to the stereogenic carbon center (marked *), whereas **2 C** corresponds to the traditional $M(\mu\text{-}R_2)ER_{n-1}$ product. For the sake of clarity, H atoms are omitted. Distances are reported in Å.

reported in Table S5 in the Supporting Information. Remarkably, for all of the structures (**2**–**5**), the unusual heterobimetallic adducts are more stable than the typical ones by 9–12 kcal mol^{-1}.

Furthermore, methyl exchange between hafnium and E was directly investigated for **2** and **3** by means of ^{1}H EXchange SpectroscopY (EXSY) NMR experiments performed at low and variable temperatures (see the Supporting Information). A clean Me35/Me36 exchange cross-peak was observed in the ^{1}H EXSY spectra when E = Zn (**2**), a result that can be plausibly ascribed to a Hf/Zn transmethylation process. VT ^{1}H EXSY experiments performed in the 243–269.8 K range gave an estimated $\Delta G^{\neq}$ value of 16 ± 4 kcal mol^{-1}. The same exchange process was not observed in the case of E = Al (**3**), even at slightly higher temperatures (276.4–299.3 K), thus indicating that Zn has a higher propensity for acting as a transalkylating agent than Al.

By means of DFT calculations, we were able to identify the transition states (TS) of the two processes (see Figure S30), and we obtained a $\Delta G^{\neq}$ value for **2** of 16.6 kcal mol^{-1}, which is in excellent agreement with the experimental results. A higher $\Delta G^{\neq}$ value (28.9 kcal mol^{-1}) was calculated for **3**, a result that explains why the exchange process was not observed experimentally.

Incidentally, intra-$AlMe_3$ exchanges (Me36/Me37, Me36/Me38, and Me37/Me38) were observed for **3** with a $\Delta G^{\neq}$ value of 15 ± 3 kcal mol^{-1}. Compound **2** also showed Me35/Me37 exchange and an intra-$ZnMe_2$ (Me36/Me37) exchange but unfortunately, reliable $\Delta G^{\neq}$ values for these processes could not be obtained owing to an overlapping of the Me37 resonance with that of free $ZnMe_2$. Our observations further demonstrate that the most reactive fragment of Hf^{IV}–pyridylamido precatalysts is the Hf–aryl bond, and add to the previously known chemistry a new and intriguing piece of evidence involving the formation of bimetallic adducts with ER_n species (Scheme 1 c).

Since olefin and ER_n are always present together in CCTP (including the "chain shuttling" variant), and often in conventional catalytic olefin polymerizations as well, it is of interest to explore the reactivity of the discovered heterobimetallic adducts with olefins and compare in particular the propensity of ER_n and olefins to react with **1**. We opted for 1-hexene as an easy-to-handle olefin, and analysis was limited to **2**, which features the simplest NMR spectra. Interestingly, when 2–3 equivalents of 1-hexene were added to a solution containing complex **2** and 5 equivalents of free $ZnMe_2$, no reaction took place over a period of 3 h at 250 K. This led us to hypothesize a detrimental effect of $ZnMe_2$ on the catalytic activity. On the other hand, when 30 more equivalents of olefin were added, a rather slow polymerization occurred, which consumed all of the 1-hexene and transformed most of the $ZnMe_2$ in solution into ZnP_2 (P = polymeryl chain), which is a clear sign of CCTP (see the Supporting Information). Upon adding even more 1-hexene (up to 180 equivalents), polymerization occurred rapidly in the NMR tube and $ZnMe_2$ was again transformed into ZnP_2. All this points to a competition between $ZnMe_2$ and the monomer for reaction with **1**.

Competitive experiments were carried out by reacting the starting dimethyl precursor with $[CPh_3][B(C_6F_5)_4]$ in the presence of 200 equivalents of 1-hexene and 35 equivalents of $ZnMe_2$ at 240 K with the aim of trapping reaction intermediates.[22] Under these experimental conditions, the reaction proceeded with the exclusive formation of **2**, with no sign of polymerization. This can be ascribed to the higher Zn/Hf ratio, which favors the formation of heterobimetallic adducts. It was only upon raising the temperature to 265 K that the consumption of 1-hexene and the concomitant transformation of $ZnMe_2$ into ZnP_2 were observed. As shown in Figure 3, the rates of the latter processes are similar, which points to a CCTP process.

These experimental results agree with the QM results of Table S5 and Scheme S3, which indicate that the free energy values for the α-olefin mono-inserted products are higher than those of the bimetallic adducts.

In conclusion, we have shown that ER_n alkylating agents 'unlock' the Hf–aryl bond of Hf–pyridylamido precatalysts,

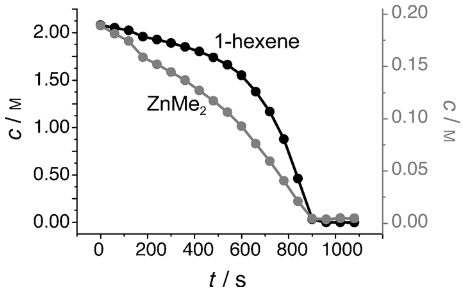
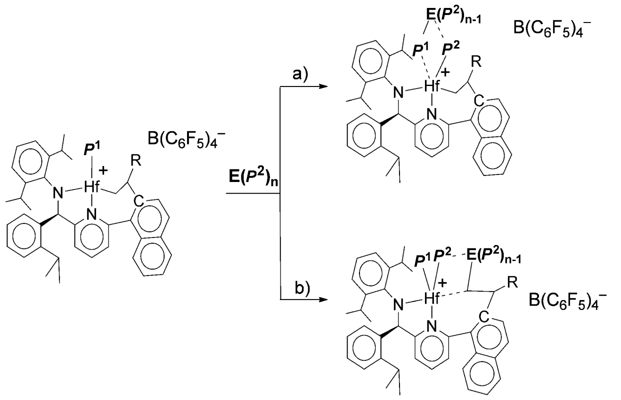


Figure 3. Parallel consumption of 1-hexene and $ZnMe_2$ at 265 K.



Scheme 2. Possible pathways for transalkylation in the mono-inserted active species (P^1 and P^2 = Polymeryl chains).

thereby leading to the formation of unusual heterobimetallic adducts in which the aryl, along with an alkyl group R, acts as a bridge between Hf and E. Such adducts were fully characterized from a structural standpoint by means of NMR spectroscopy and DFT investigations. Moreover, it was demonstrated that the adducts mediate the alkyl exchange between Hf and E, and the tendency of this exchange to occur (Zn > Al) was quantified by ^1H EXSY experiments. Olefin/ER_n competitive experiments indicated that the formation of heterobimetallic species was preferred over olefin mono-insertion into the Hf–aryl bond to yield the catalytic active species for olefin polymerization; the latter process is thus disfavored by adduct formation. Whether structurally analogous adducts can form between ER_n and polymerization-active olefin mono-inserted Hf^{IV} species, thus possibly providing an alternative pathway for transalkyation (Scheme 2), remains to be seen. Further studies on this are in progress.

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