Activation of 2,6-Bis(imino)pyridine Iron(II) Chloride Complexes by Methylaluminoxane: An Electrospray Ionization Tandem Mass Spectrometry Investigation

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Received May 4, 2005

The activation of the [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chloride complex (**1**) with methylaluminoxane (MAO) was investigated in tetrahydrofuran (THF) by means of electrospray ionization tandem mass spectrometry (ESI-MS) complemented by UV−visible spectroscopy studies. The four-coordinated cationic methyl iron(II) complex **2** ([LFe-Me]$^+$, L = 2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine) was identified in the ESI-MS experiment. In addition, the cationic monochloride iron(II) complex **3** ([LFe-Cl]$^+$), the product of α-H transfer from **2** to trimethylaluminum (TMA) [LFe-CH$_2$AlMe$_2$]$^+$ (**4**), and the cationic iron hydride complex **5** ([LFe-H]$^+$) were identified. Correlation of the ESI-MS experiments with UV−visible studies revealed that **2** and **3** are present in the THF solution as their solvent adducts.

Introduction

Among the variety of late transition metal complexes introduced in the field of polymerization catalysis almost a decade ago,[1] 2,6-bis(arylimino)pyridine iron(II) chloride complexes were reported to be efficient catalysts for the polymerization of ethylene after activation with methylaluminoxane (MAO).[2] By analogy with metallocene catalysts,[3] it is assumed that the species active in polymerization is a highly reactive monomethylated iron(II) cation ([LFe-Me]$^+$) bearing a weakly coordinating counteranion ([X-MAO]$^-$, X = Cl, Me);[2,4] chain propagation occurs after olefin coordination to the metal center and subsequent insertion into the metal−carbon bond.

As a matter of fact, activation of group 4 metallocene dichlorides with MAO has been an extensively studied subject, and the activation process usually proposed consists of two steps: (1) monoalkylation of the metallocene dichloride by aluminum alkyls present in MAO and (2) abstraction of the remaining chloride by the Lewis acidic MAO species. As a result, a monomethylated metallocene cation with a weakly coordinated counteranion is formed and is accountable for the catalytic activity in olefin polymerization.[3a,5] If excess amounts of MAO are used, the first step can lead to the dialkylation product, which undergoes methyl abstraction by MAO to generate the active species.

With regard to iron complexes, if stable diamagnetic dialkyl and alkyl halogen complexes are known,[6] their paramagnetic counterparts are prompt to decompose via reductive elimination,[7] which significantly restricts the possibility to isolate and characterize the catalytically active components of the polymerization system. Examples of structurally characterized stable paramagnetic iron(II) alkyl or halogeno alkyl complexes are rather scarce and have only been recently reported.[8] Therefore, a different pathway was proposed for the activation of 2,6-bis(imino)pyridine iron(II) chloride

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10.1021/om050351s CCC: $30.25

complexes: (1) abstraction of one of the chlorides followed by (2) transmetalation with an alkylaluminum species, leading to the cationic monomethylated iron catalyst.[9,10] Both monochloride and monoalkyl cationic species are expected to be present in the solution, and their respective concentrations depend on the relative concentration of MAO—an excess of which favors the formation of the monoalkyl species to the detriment of the monochloride cation.

Regardless of the activation pathway, coordinatively unsaturated monoalkyl metal cations are likely to be stabilized by further interactions with other molecules present in the solution: i.e., solvent or cocatalyst. Indeed, bimetallic metallocene species of the type $[Cp_2M(\mu\text{-Me})_2AlMe_2]^+[X\text{-MAO}]^-$ (M = group 4 metal) have been identified and are believed to be the dormant state of the catalytically active $[Cp_2M\text{-Me}]^+[X\text{-MAO}]^-$ ion pair, the position of the equilibrium between these two species governing the catalytic activity.[3a,11] Correspondingly, in the case of 2,6-bis(imino)pyridine iron(II) catalysts, the formation of a heterobinuclear Fe–Al complex via coordination of trimethylaluminum (TMA) to the cationic iron(II) center has been evidenced by paramagnetic ^1H NMR in toluene-d_8,[12] and an equilibrium between active and inactive species identical with that described above was confirmed experimentally in the polymerization of ethene.[13] The actual active species, $[LFe\text{-Me}]^+[X\text{-MAO}]^-$, was thus defined by Britovsek et al. as "a transition state or perhaps a high energy intermediate."[13] Accordingly, to the best of our knowledge, the existence of the mononuclear cationic iron(II) complex $[LFe\text{-Me}]^+[X\text{-MAO}]^-$ has never been shown spectroscopically.[14]

The combination of electrospray ionization techniques and tandem mass spectrometry (ESI-MS) is an intriguing analytical method for the characterization of organic and organometallic compounds.[15] Due to its relatively soft ionization mode, this technique has found new applications in the study of metal complexes,[16] metal-catalyzed reaction mechanisms,[17] polymerization catalysts,[18] and high-throughput screening of homogeneous catalysis.[19] Accordingly, we thought it pertinent to use the aptitude of electrospray to transfer ionic species from a sample solution to the gas phase in order to identify the different products resulting from the activation of the complex [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chloride (**1**) with MAO in a THF solution by tandem mass spectrometry and to attest to the existence of the iron methyl cation.

Experimental Section

General Considerations. All the manipulations were done under an inert argon atmosphere using standard Schlenk techniques. The hydrocarbon and ethereal solvents were refluxed over sodium and benzophenone, distilled, and stored under argon with sodium flakes. All the reagents were purchased from commercially available sources and used without further purification. MAO (30 wt % in toluene solution) was received from Borealis Polymer Oy. The complexes [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chloride (**1**),[2] [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chloride hexafluoroantimonate–acetonitrile ($\mathbf{3}SbF_6^-\cdot CH_3CN$),[9] and [2,6-bis(1-(isopropylimino)ethyl)pyridine]iron(II) chloride (**6**)[20] were synthesized according to published procedures. ^1H NMR spectra were collected at room temperature in $CDCl_3$ with a Varian 200 NMR spectrometer at 200 MHz.

UV–Visible Spectroscopy. UV–vis spectroscopy measurements were carried out with a HP 8453E spectrophotometer and UV–visible ChemStation software. Samples were withdrawn from the catalyst solution (630 μmol/L) and transferred under an argon atmosphere to a gastight rectangular quartz cuvette (10 mm path length) fitted with a silicon septum.

ESI-MS Measurements. The electrospray ionization tandem mass spectrometric study was undertaken with an API-300 triple-quadrupole mass spectrometer from Perkin-Elmer-SCIEX (Toronto, Ontario, Canada). The ESI-MS spectra were acquired by infusing the sample solution directly into the Sciex Turboionspray source at a rate of approximately 30 μL/min. No heating was applied. Nitrogen was used as the nebulizing gas to assist the electrospray process and to provide a relatively inert atmosphere within the ion source. Full MS spectra were acquired every 2 s. The orifice plate, focusing ring, and curtain gas flow were maintained at 30 V, 300 V, and approximately 1.1 L/min, respectively.

Preliminary experiments with **1**/MAO in toluene as the solvent were not satisfactory, probably due to the nonpolar nature of toluene, which is not suitable for the electrospray ionization mode. THF was then chosen as the solvent due to its higher polarity and because polymerization of acrylates proceeds in this solvent with MAO-activated 2,6-bis(imino)pyridine iron(II) complexes.[21] The catalyst solution (63 μmol/L) was prepared by dissolving the iron complex in dry THF followed by the addition of 50 molar equiv of the aluminum activator. The injection system was flushed with dry THF beforehand, and 50 μL of the catalyst solution was injected prior to the measurement, to remove traces of water from the injection line and electrospray source. *Caution!* The activator-to-complex ratio was voluntarily limited to 50 in order to avoid the occlusion of the source and injection system by aluminum oxide, resulting from the hydrolysis of MAO by inherent traces of moisture.

Hydrolysis of 1/MAO in THF. A 38 mg portion of [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chlo-

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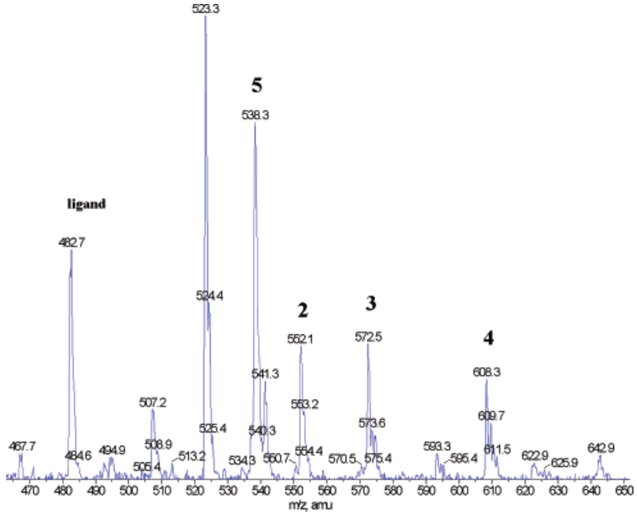

Figure 1. ESI-MS spectrum of **1**/MAO in THF.

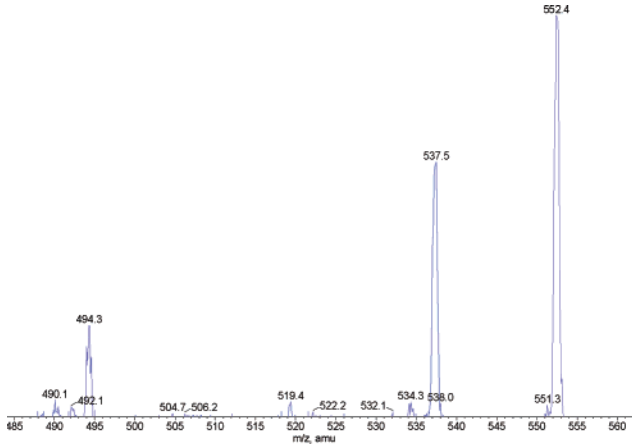

Figure 2. ESI-MS/MS spectrum of the mass-selected ion **2** from the activation of **1** with MAO in THF. Collision energy 30 eV.

ride (**1**; 63 μmol) was dissolved in 100 mL of THF ([Fe] = 6.3 μmol/L). A 50 molar equiv amount of MAO (30 wt % in toluene, 0.7 mL) was then added to the complex solution. After the mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo, the residue was dissolved in 10 mL of regular CH_2Cl_2, and 10 mL of 1 M HCl was added. After another 1 h of stirring, the organic phase was separated from the aqueous phase, and the latter was further extracted with 2 × 5 mL of CH_2Cl_2. The different organic phases were gathered together and dried over magnesium sulfate, and the solvent was removed in vacuo to afford nearly 30 mg (99%) of 2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine (yellow powder). The ^{1}H NMR spectrum matched the values reported in the literature.[2]

Results and Discussion

Activation with MAO. A priori, despite the precautions taken during the sample preparation and transfer, the mass spectrum obtained (Figure 1) reveals that the species present in the solution seem to be particularly sensitive to traces of moisture and/or other contaminants, as exemplified by the presence of the ligand peak at *m/z* 482 (ligand + H^+). It is important to notice that, under the same conditions, **1** alone gave only a small signal corresponding to the ligand peak and that MAO alone did not give any significant signal. The origin of the base peak at *m/z* 523 and of the second most prominent signal at *m/z* 538 will be discussed later in the paper.

A peak centered at *m/z* 552 corresponding to the molar mass of [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]Fe^+-Me (**2**) could be reproducibly observed in the ESI-MS spectrum of **1**/MAO. The fragmentation pattern of this ion was further studied by collision-induced dissociation (CID) at the collision energy of 30 eV (Figure 2). The fragment at *m/z* 537 correlates to the loss of a methyl group, followed by the loss of one isopropyl group from the ligand (*m/z* 494). The nature of the *m/z* 552 peak was additionally confirmed by comparing its isotopic fingerprint (Figure 3, left) to a computer-generated theoretical plot (Figure 3, right). Analogously, the *m/z* 572 ion corresponds unambiguously to LFe^+-Cl (**3**) (fragments obtained by CID at *m/z* 536 (**3** − Cl); 521 (−Me); 506 (−Me)).[22] The presence of **3** is explained by the low MAO concentration used for the ESI-MS experiments.

MAO is synthesized by controlled hydrolysis of TMA, which is present to a certain extent as a free or MAO-bound species in the cocatalyst solution.[3a] Considering that both MAO and TMA are efficient alkylating agents,

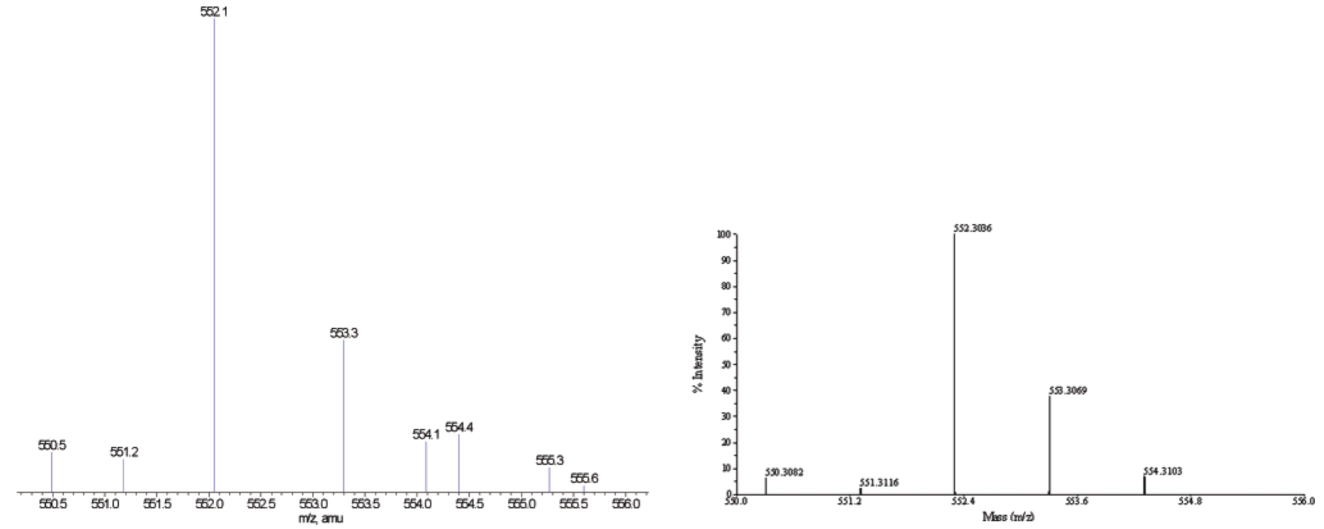

Figure 3. Isotopic fingerprint of the ion **2** issued from the ESI-MS spectrum of **1**/MAO in THF (left) and a computer-generated theoretical plot corresponding to **2** (right).

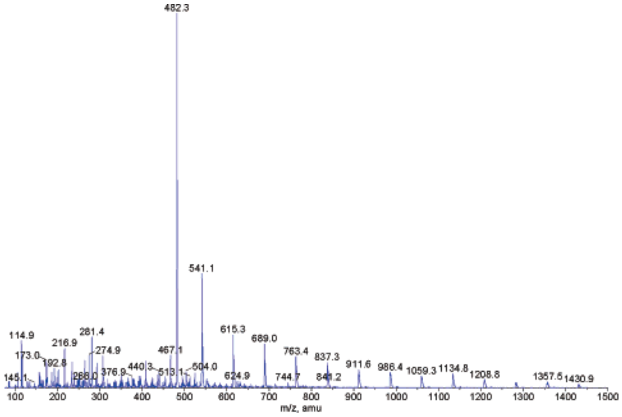

Figure 4. ESI-MS spectrum of the products of the reaction of **1** with TMA in THF.

it is conceivable that **1** will react with TMA to form neutral monoalkyl chloride and/or dialkyl iron(II) complexes.[7,12a] The possibility that **2** and **3** could simply be the result of in-source CID of these neutral mono- and dialkylation products was therefore envisaged. When 50 equiv of TMA was added to a solution of **1** in THF, a color change was immediately observed (see below), confirming that a reaction took place. The nature of the obtained products was subsequently investigated by ESI-MS (Figure 4). A succession of peaks with decreasing intensities starting at *m/z* 541 and separated by intervals of 73−75 atomic mass units (amu) was retrieved, which is more likely to be the result of TMA oligomerization in the presence of traces of moisture, forming aluminoxane oligomers. Apart from these TMA oligomers and the ligand signal (*m/z* 482), none of the peaks recovered from the ESI-MS of **1**/MAO (Figure 1) were detected, suggesting that no cationic species are formed by the reaction of **1** with TMA and thus confirming that **2** and **3** are actual products resulting from the MAO activation process.

Another control experiment was carried out with the MAO-activated [2,6-bis(1-(isopropylimino)ethyl)pyridine]iron(II) chloride complex (**6**), recently reported to perform the polymerization of various acrylate monomers.[20,21] The sample was prepared in THF and transferred to the MS in the same way as for **1**/MAO. Similarly, the mass spectrum exhibited a complicated and variable distribution of products, but a peak centered at *m/z* 316 corresponding to the cationic iron(II) monomethylated complex could be reproducibly observed, as well as peaks at *m/z* 336 (monochloride cation), 302, and 287 (analogues of the *m/z* 538 and 523 peaks obtained with **1**, see below). Mass selection of the *m/z* 316 ion and its fragmentation by CID gave the loss of one methyl (*m/z* 301) followed by the loss of iron (*m/z* 245).

UV−Visible Spectroscopy. In general, the position of absorption bands of transition metal complexes in the visible region is related to a ligand to metal charge transfer (LMCT).[9,23] It is then subject to variations depending on the electron configuration at the metal center and also reflects the changes occurring in the coordination sphere of the metal.[23] In the case of **1**, the deep royal blue THF solution turns to light purple after the addition of MAO, whereas the emerald green color obtained after the reaction with TMA suggests in this case the presence of different species. In view of that, a complementary UV−vis spectroscopy study was undertaken to confirm the observations made in the ESI-MS measurements (Figure 5).

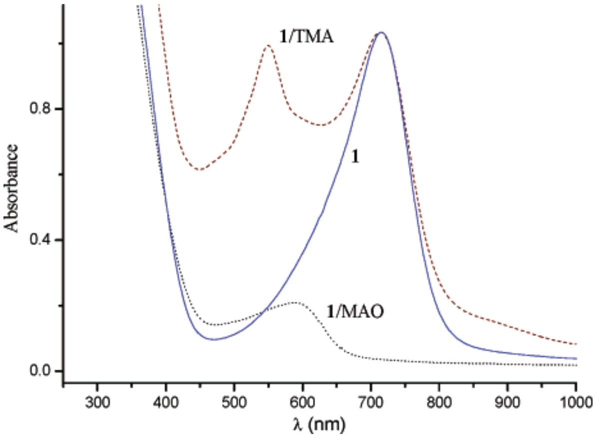

Figure 5. UV−vis spectra of **1** (solid line), **1**/MAO (dotted line), and **1**/TMA (dashed line) in THF at room temperature. [Fe] = 630 μmol/L; [Al]/[Fe] = 50.

In THF, **1** shows a broad absorption band in the visible region at 715 nm, slightly bathochromic compared to the value reported in CH_2Cl_2 (695 nm).[9] After the addition of 50 equiv of MAO, the original broad absorption totally disappears to step aside to a unique less intense band at 588 nm, indicating that the entire catalyst precursor **1** was consumed during the reaction. Conversely, the addition of 50 equiv of TMA did not witness the disappearance of the 715 nm peak arising from **1** but resulted in the formation of a new absorption of similar intensity centered on 550 nm, which is most plausibly due to a neutral five-coordinated dimethyl [$LFeMe_2$] or monomethyl [LFeMeCl] complex. Indubitably, different species are formed when **1** is reacted with TMA as compared to MAO.

Nature of the Activation Products in THF. The exact nature of the species formed during the activation process has been discussed by two different groups,[12,24] and although experimental results tend to support that the methyl cation is the actual polymerization catalyst,[9,13] direct spectroscopic evidence of its existence has been lacking. Earlier studies on the structural determination of the catalytically active species have mainly been carried out by means of paramagnetic ^{1}H NMR[12] and EPR[12b,24] spectroscopy, and the latest report states that the addition of MAO to a 2,6-bis(imino)pyridine iron(II) chloride complex in toluene forms various cationic bimetallic species of the type $[LFe^{II}(\mu\text{-Me})(\mu\text{-L*})AlMe_2]^+[Me\text{-MAO}]^-$ (L* = Cl, Me depending on the amount of MAO), in which iron is exclusively in the +2 oxidation state.[12b,c]

As a matter of fact, the detection of **2** and **3** by ESI-MS as the activation products of **1** with a low amount of MAO (50 equiv) does not give any further indication concerning the activation pathway for 2,6-bis(imino)pyridine iron(II) chloride complexes (see above) but

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[22] The *m/z* value found in the literature for $\mathbf{3}SbF_6^-\cdot CH_3CN$ measured by FAB mass spectrometry is 572 amu.[9]

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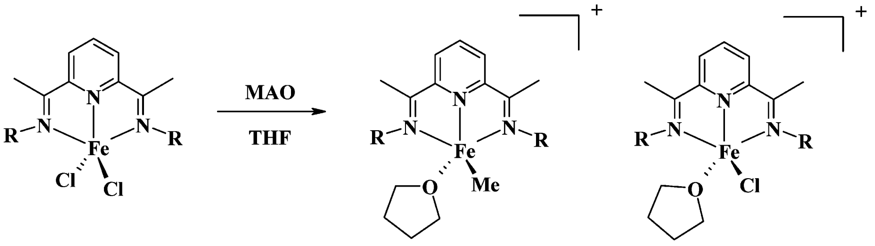
Scheme 1. Activation Products of 1 with MAO in THF: 2·THF and 3·THF



R = 2,6-diisopropylphenyl (1)
isopropyl (6)

2.THF

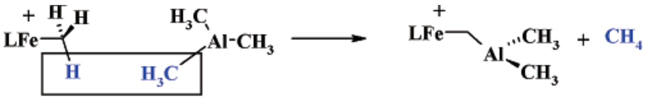
3.THF

shows unambiguously that **2** is a relatively stable species under the current experimental conditions. Donor molecules such as THF are known to stabilize cationic metal alkyl[25] and hydride[25c] complexes by coordination, and in fact, **3** and its cobalt analogue have been isolated as an acetonitrile and a THF adduct, respectively, for which single-crystal structure determinations could be undertaken.[9]

This encouraged us to carry on with complementary UV−vis measurements to further study the nature of **2** in the present system. In a control experiment, [2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine]iron(II) chloride hexafluoroantimonate−acetonitrile (**3**SbF_6^-·CH_3CN) prepared according to the literature[9] was used as a model compound for a four-coordinated 2,6-bis(imino)pyridine iron(II) cation. The UV−vis spectra displayed a broad absorption at 584 nm in THF, while it is reported to absorb at 540 nm in CH_2Cl_2.[9] It is reasonable to assume that the red shift is due to replacement of CH_3CN with THF. Furthermore, when **1** was activated with MAO in toluene, the UV−vis spectrum exhibited a faint broad absorption around 530 nm, in accordance with the value reported in the literature.[9] After the addition of 10 equiv of THF, λ_{max} was red-shifted to a sharper band of a similar intensity at 599 nm. This phenomenon cannot be ascribed solely to the increase of solvent polarity but also to the different nature of the species observed; if a bimetallic Fe−Al complex is formed in toluene, a monometallic solvent adduct is dominating in THF.[26] Accordingly, after activation, **2** and **3** are likely to be present in the solution as THF adducts, **2**·THF and **3**·THF (Scheme 1), while the application of a declustering potential in the ion source converts both **2**·THF and **3**·THF to free **2** and **3**.[18] Undeniably, THF had a significant role in stabilizing **2** in a monometallic form.

Other Species Detected. Further analysis of the spectrum in Figure 1 afforded a deeper insight into the reaction mixture. Apart from the formation of TMA adducts, another side reaction reported for MAO-activated metallocene catalysts consists of α-H transfer from a metallocenium−methyl bond to an Al-Me group, resulting in the formation of methane and a M−CH_2−Al bimetallic complex.[27,28] The peak centered on *m/z* 608 corresponds to the structure $[LFe\text{-}CH_2AlMe_2]^+$ (**4**), as confirmed by CID, giving two prominent fragments at *m/z* 593 (loss of CH_3) and at *m/z* 578 (loss of a second CH_3). Seemingly, the α-H transfer from **2** to TMA is a prominent side reaction under the applied experimental conditions (Scheme 2). This also indirectly proves that **2** and TMA are in close vicinity, even in THF solution.

Scheme 2. α-H Transfer from 2 to TMA Leading to 4



4

L = 2,6-bis(imino)pyridine

The origin of the ions at *m/z* 538 (**5**), 523 (base peak in Figure 1), and 507 is more delicate to establish, as *m/z* 538 could arise from two different cations: an iron(II) hydride $[LFe\text{-}H]^+$ and $[(LMe)Al\text{-}Me]^+$ (LMe = 2-imino-6-aminopyridine). Since the peak pattern centered on *m/z* 538 includes also different species, notably the *m/z* 541 peak derived from TMA (see above), the isotopic identification of **5** is rendered awkward. In any event, the observation of **5** is directly linked to the combined presence of **1** and MAO in the THF solution, as it does not appear in the TMA-treated sample (Figure 4). Selection of the *m/z* 538 ion in the first quadrupole and its fragmentation by CID gave signals at *m/z* 523 and 507 (Figure 6). It is then reasonable to deduce that the

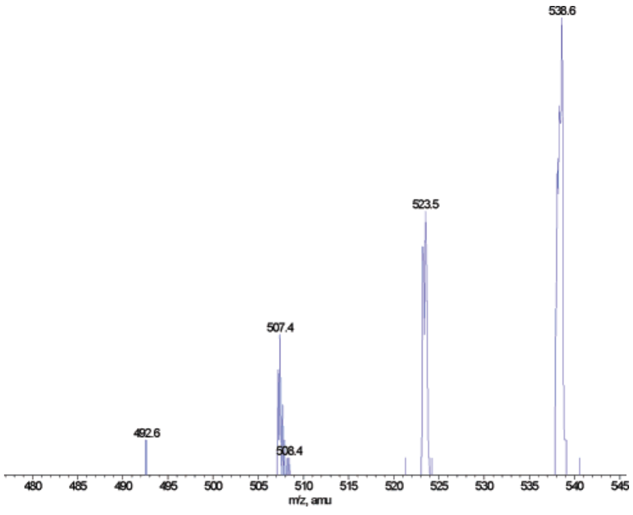


Figure 6. ESI-MS/MS spectrum of the mass-selected ion **5** from the activation of **1** with MAO in THF, showing that the *m/z* 523 and 507 ions are the products of in-source CID of **5** (collision energy 30 eV).

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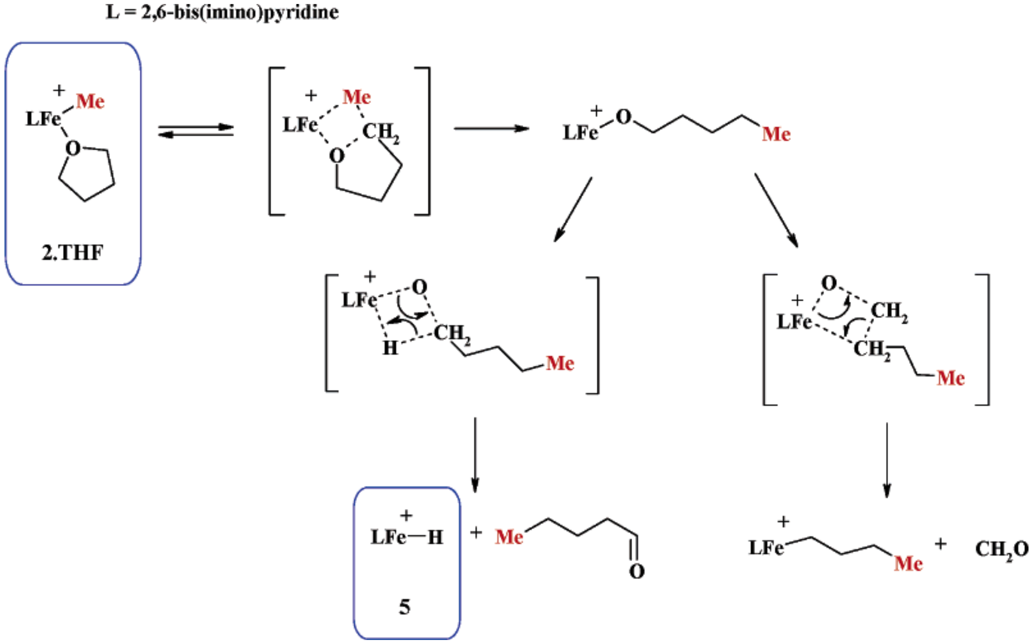
(25) (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718−1719. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410−7411. (c) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892−2903.

(26) Referring to the metallocene literature, it was shown that the formation of a bimetallic Zr−TMA complex in CH_2Cl_2 by addition of TMA to a monometallic zirconocenium species was expressed by a progressive hypsochromic shift of the MLCT band; see: Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1459−1464.

Scheme 3. Proposed Reaction Mechanism of the Ring Opening of THF in 2·THF and Subsequent β-H Elimination Leading to the Formation of 5



m/*z* 523 and 507 ions are formed by in-source CID of the *m*/*z* 538 ion.

In these experiments, $[\mathrm{LFe\text{-}H}]^+$ can be formed via different pathways from the in situ generated cationic species. At the latest in the gas phase, the inherent moisture and protons in the ESI-MS spectrometer are accountable for the formation of an iron hydride, and their presence can also explain the intensive ligand-H^+ peak in the spectra. As the appearance of $[\mathrm{LFe\text{-}H}]^+$ is strictly connected to **1**/MAO, other explanations can also be considered. When THF-d_8 was employed as the solvent, a spectrum similar to Figure 1 was retrieved; in particular, **2** was observed at *m*/*z* 552. The spectrum also revealed some important differences. In fact, the *m*/*z* 539 ion belonging to the isotopic pattern of **5** centered on *m*/*z* 538 witnessed an intensity increase of about 10% compared to the experiment in regular THF. Furthermore, signals at *m*/*z* 524 and 508 were detected, matching a 1 amu increase of the 523 and 507 masses. Accordingly, the origin of the *m*/*z* 538 ion can, at least *to a certain extent*, be attributed to hydride transfer from THF, leading to the formation of **5** ([**5**-D] in THF-d_8).

As demonstrated above, the coordination of THF to the cationic metal center in **2** is dominant. It renders its α-carbon susceptible to a nucleophilic attack from the methyl ligand, instigating the formation of a new cationic 2,6-bis(imino)pyridine iron(II) pentoxide via the ring opening of the THF cycle (Scheme 3).[29] This iron alkoxide cation is further prone to undergo β-H and/or β-butyl transfer, at least in the gas phase, leading to the formation of iron hydride (major product) and iron butyl cations, respectively.[30] In fact, this process is confirmed by the detection of a small signal at *m*/*z* 594 ($[\mathrm{LFe\text{-}butyl}]^+$) present in the peak pattern of the *m*/*z* 593 ion (Figure 1).

On the other hand, ions matching *m*/*z* 538 could originate from aluminum complexes, generated by reactions between TMA and the free ligand. The synthesis of *N*,*N*,*N*-pyridyliminoamide dimethylaluminum complexes ($[(\mathrm{LMe})\mathrm{Al\text{-}Me_2}]$) was reported to occur by reacting TMA with 2,6-bis(imino)pyridine in refluxing toluene. This stable aluminum complex is prompt to undergo methyl abstraction in the presence of a strong Lewis acid, yielding $[(\mathrm{LMe})\mathrm{Al\text{-}Me}]^+$, a robust catalyst for ethylene or polar monomer polymerization.[31] Bearing in mind that MAO is able to abstract a methyl group from methylaluminum species,[32] the possibility that the $[(\mathrm{LMe})\mathrm{Al\text{-}Me}]^+$ complex could form in THF by reaction of the free ligand and aluminum species was checked. **1** and 50 equiv of MAO were reacted for 1 h at room temperature in THF under the same conditions as during the sample preparation. After hydrolysis of the solution, only the original 2,6-bis(1-((2,6-diisopropylphenyl)imino)ethyl)pyridine ligand was recovered, without any trace of *N*,*N*,*N*-pyridyliminoamide. Similarly, a simple ligand−TMA adduct could be formed which, in the presence of MAO, would generate the $[\mathrm{LAl\text{-}Me_2}]^+$ ion. However, if the appearance of the *m*/*z* 538 ion in

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(27) (a) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375−2381. (b) Kaminsky, W.; Strübel, C. *J. Mol. Catal. A: Chem.* **1998**, *128*, 191−200. (c) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911−3921.

(28) Additionally, interactions between $\mathrm{Cp_2ZrMe^+}$ and TMA were observed in the gas phase by Fourier transform ion cyclotron resonance mass spectroscopy; see: Siedle, A. R.; Newmark, R. A.; Schroepfer, J. N.; Lyon, P. A. *Organometallics* **1991**, *10*, 400−404.

(29) According to our unpublished results, MAO-activated 2,6-bis(imino)pyridine iron(II) chloride complexes are able to provide, although to a minor extent, the ring-opening polymerization of THF in the presence of acrylate monomers, which further supports the feasibility of the reaction discussed here.

(30) (a) Fiedler, A.; Schröder, D.; Scharwz, H.; Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1996**, *118*, 5047−5055. (b) Kirkwood, D. A.; Stace, A. J. *Int. J. Mass Spectrom. Ion Processes* **1997**, *171*, 39−49.

(31) (a) It was, however, demonstrated that this aluminum complex is not the species active in the **1**/MAO-catalyzed ethylene polymerization,[2a] as it produces low molar mass polyethylene with low catalytic activity; see: Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523−2524. (b) Baugh, L. S.; Sissano, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1633−1651.

(32) Kim, J. S.; Wojcinski, L. M., II; Liu, S.; Sworen, J. C.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 5668−5669.

Figure 1 is connected to the formation of an aluminum complex, the CID spectrum from *m/z* 538 should exhibit a signal of reasonable intensity at *m/z* 508 (ligand + Al). Whereas such a signal is indeed observed in Figure 6, it is of minor intensity compared to the ion at *m/z* 507, indicating that formation of an aluminum complex in the gas phase is not totally excluded but is of lesser importance.

Conclusion

Electrospray ionization tandem mass spectrometry represents a powerful and straightforward tool for the analysis of complicated mixtures of reaction products, in particular when traditional separation and analytical methods are not applicable because of the instability of the products. In the present study, the use of ESI-MS facilitated a direct insight into the various products formed by the reaction of a 2,6-bis(arylimino)pyridine iron(II) chloride complex with MAO in THF. Several conclusions can be drawn from these experiments. First of all, the cationic iron methyl complex $[LFe\text{-}Me]^+$ (**2**), claimed to be the actual catalytically active species in the polymerization of olefins,[4] was identified. To the best of our knowledge, the detection of **2** by ESI-MS is the first direct spectroscopic evidence of the existence of such a cationic 2,6-bis(imino)pyridine iron(II) methyl complex after MAO activation.[33] It was also confirmed that, at low MAO/Fe ratios, the activation reaction of **1** by MAO is not complete, as the cationic monochloride complex $[LFe\text{-}Cl]^+$ (**3**) was detected.

The signals at *m/z* 538 and 523 are the most prominent peaks in the ESI-MS spectrum and appear only with **1**/MAO. The signal at *m/z* 538 was attributed to an iron hydride species $[LFe\text{-}H]^+$ (**5**) formed, *at least partly*, via hydride transfer from THF to **2**. On the basis of these facts, it can assumed that **2**·THF is a major activation product of **1** by MAO in THF: in this particular case of relative MAO concentration, polar donor solvent, and gas-phase mass spectrometry. It is interesting to notice that the presence of **5** in the ESI-MS spectrum gives also a direct proof of the existence of such a species, which is considered to be a central reaction intermediate in the catalytic cycle of olefin polymerization, and has so far only been deduced from the analysis of polymer end groups[2] or from the addition of H_2 to a propylene polymerization reaction yielding to lowered molar mass and increased activity.[10] Despite the fact that **2** and **3** can be described as solvent-stabilized ion pairs rather than bimetallic TMA adducts as established by UV−vis, the presence of the bimetallic species $[LFe\text{-}CH_2\text{-}AlMe_2]^+$ (**4**) is an indirect proof that the iron methyl cation and aluminum alkyls can come into close vicinity in THF.

Acknowledgment. This work has been financed by the University of Helsinki and the Academy of Finland, projects 0204408 and 77317 (Centre of Excellence, Bio- and Nanopolymer Research Group).

OM050351S

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[33] The ability of **2**·THF to promote olefin polymerization is not addressed here. In any event, isolated cationic methyl zirconocenes stabilized by coordination with THF were found to catalyze the polymerization of olefins.[25] Similarly, diethyl ether adducts of cationic nickel and palladium α-diimine methyl complexes are active catalysts for olefin polymerization.[1b] In addition, olefin polymerization with cationic metallocenes in the presence of coordinating ligands such as PPh_3 has been reported; see: Beck, S.; Prosenc, M. H.; Brintzinger, H. H. *J. Mol. Catal. A: Chem.* **1998**, *128*, 41−52.