

## Sequential Reduction And Alkyl Exchange Reactions Of Bisiminopyridine Dialkyliron(II) With Trimethylaluminum.

M. Ángeles Cartes, Antonio Rodríguez-Delgado, Pilar Palma, Eleuterio Álvarez and Juan Cámpora.\*

*Instituto de Investigaciones Químicas, CSIC – Universidad de Sevilla. c/ Américo Vespucio, 49, 41092, Sevilla, Spain.*

**Summary:** *The sequence of reactions ensuing when 2,6-bisiminopyridine Fe(II) dialkyl complexes  $[Fe(CH_2SiMe_3)_2(BIP)]$  react with trimethylaluminum is described in detail. The first step is the reduction of the dialkyl to the corresponding monoalkyl complex  $[Fe(CH_2SiMe_3)(BIP)]$ . In the presence of an excess of trimethylaluminum, these undergo exchange of the remaining  $CH_2SiMe_3$  group for methyl, and ultimately the methyliron fragment is displaced from the complex, leading to previously known paramagnetic aluminum compounds. The diethyl aluminum complex  $[AlEt_2(iPr)BIP]$  was obtained when triethylaluminum was used instead of trimethylaluminum.*

### Introduction

The study of iron and cobalt complexes with 2,6-bis(imino)pyridine (BIP) ligands as catalysts for olefin polymerization has attracted much interest since their discovery in 1998.<sup>1</sup> As a result, the main factors controlling their performance and selectivity are now reasonably well understood.<sup>2</sup> However, the investigation of the mechanistic aspects of these catalysts proved very challenging, and the true nature of the active species involved in these catalytic systems is still being debated.<sup>3</sup>

By analogy with other homogeneous olefin polymerization catalysts, early mechanistic proposals postulated that activation of  $[MX_2(BIP)]$  with organoaluminum co-catalysts leads to coordinatively unsaturated cationic Fe(II) or Co(II) alkyl species.<sup>4</sup> This proposal received a strong experimental support from Chirik, who synthesized iron<sup>5</sup> and cobalt<sup>6</sup> complexes of type  $[M(R)(S)(iPr)BIP]^+$  (S is a solvent molecule or no ligand; the superscript on the BIP ligand refers to the aryl substituents on the imine groups, see Scheme 1) and confirmed that these complexes do in fact behave as single-component catalysts for ethylene polymerization. However, one of the difficulties for this classic activation scheme is that, while the reaction of paramagnetic dihalide complexes  $[MX_2(BIP)]$  with organoaluminum compounds is complex and difficult to study, the better-behaved organolithium or -magnesium reagents seldom lead to straightforward alkylation.<sup>7</sup> Frequently, the outcome of such reactions is simultaneous alkylation *and* reduction, the main products being unusual neutral or anionic monoalkyl species  $[M(R)(BIP)]^{0/-}$ .<sup>8-10</sup> This distinct reactivity of BIP complexes suggested that activation of iron or cobalt dihalide precursors by organoaluminum compounds could also involve redox changes.<sup>8,9</sup> Although the intermediacy of neutral or even anionic intermediates in the polymerization reaction seems at the first sight unusual, combined structural, spectroscopic and theoretical studies have shown that the above-mentioned reduced species  $[M(R)(BIP)]^{0/-}$  are properly described as M(II) complexes containing singly or doubly reduced BIP radical-anion ligands,<sup>5b,9,11</sup> therefore the redox changes are ligand- rather than metal-centered processes. Since the electronic

state and the steric environment of the metal center in isoelectronic cationic, neutral and anionic monoalkyl species is very similar, **it is conceivable that differently charged species could play some role in the polymerization process.**

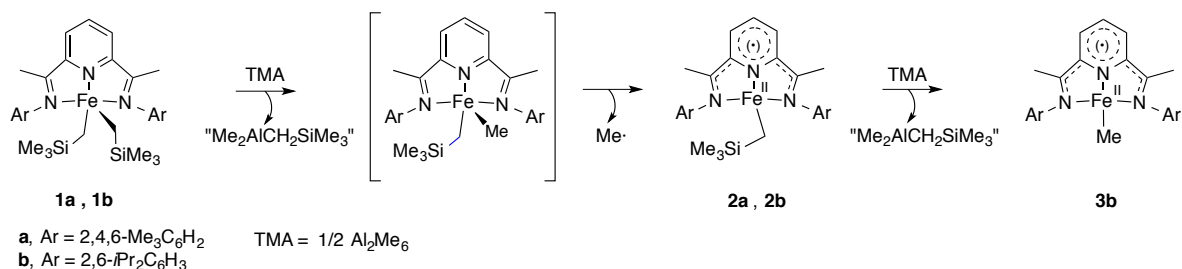
So far, no stable alkyliron or alkylcobalt complexes have been isolated from the reactions of iron or cobalt precursors with organoaluminum reagents. For example, Gambarotta studied the reaction of the iron complexes  $[\text{FeCl}_2(\text{}^i\text{PrBIP})]$  or  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{}^i\text{PrBIP})]$  with trimethyl- or triethylaluminum (henceforth TMA and TEA, respectively), but this led to the isolation of  $[\text{AlMe}_2(\text{}^i\text{PrBIP})]$  and other paramagnetic, NMR-silent aluminum compounds that are catalytically inactive, rather than to iron alkyl species.<sup>12</sup> In consequence, studies on activation processes have relied on *in situ* spectroscopic studies.<sup>13-16</sup> These led to different and sometimes contradictory results. Thus, using ESI mass spectrometry, Leskelä and co-workers identified the formation of the cationic alkyl species  $[\text{FeMe}(\text{THF})(\text{}^i\text{PrBIP})]^+$  when the corresponding halide precursor complex was treated with MAO in THF,<sup>13</sup> but a combined Mossbauer and UV-VIS analysis of the MAO activation products in more usual non-polar solvents led Gibson to propose that this process involves oxidation rather than reduction, producing Fe(III) species.<sup>14</sup> This conclusion has found support in theoretical contributions.<sup>17</sup> Using NMR, Bryliakov and Talsi showed that interaction of iron<sup>15</sup> and cobalt<sup>16</sup>  $[\text{MX}_2(\text{BIP})]$  complexes with MAO or aluminum trialkyls leads to different types of products depending on the M / Al ratio and the nature of the organoaluminum compounds. Whilst MAO gives rise to cationic bimetallic species  $[\text{M}(\mu\text{-X})(\mu\text{-Me})\text{AlMe}_2(\text{BIP})]^+$  (where X = Cl or Me), TMA and other aluminum trialkyls cause the reduction of the complexes, affording neutral compounds  $[\text{M}(\mu\text{-X})(\mu\text{-R})\text{AlR}_2(\text{BIP})]$  that are significantly less stable than the cationic species generated with MAO and decompose at room temperature to ultimately yield iron-free aluminum complexes, consistently with Gambarotta's results.<sup>12,15c</sup> Both neutral and cationic bimetallic species can be seen as adducts of the corresponding complexes  $[\text{M}(\text{X})(\text{BIP})]^{+/0}$  with a trialkylaluminum unit. Considering that both MAO and aluminum trialkyls are efficient activators, and the previously-mentioned similarity of the metal center in cationic and neutral monoalkyl complexes, it was suggested that different cocatalysts could lead to different (cationic or neutral) active species, at least in the case of iron complexes.<sup>5b,15c</sup> This could help explain the strong influence of co-catalysts in the molecular weight distribution of polyethylenes obtained with the latter catalysts.

With the aim of contributing to clarify the role of aluminum alkyls as reducing agents, we have investigated the interaction of thermally stable dialkyls  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{BIP})]$  with TMA at room temperature as a well-defined model for the **interaction of iron BIP complexes with aluminum alkyls, a highly relevant process for olefin polymerization.** In this contribution, we show that these reactions take place through a sequence of consecutive reduction and alkyl exchange steps involving neutral iron monoalkyls  $[\text{Fe}(\text{R})(\text{BIP})]$  (R =  $\text{CH}_2\text{SiMe}_3$  or Me), which could be isolated or detected under the appropriate experimental conditions.

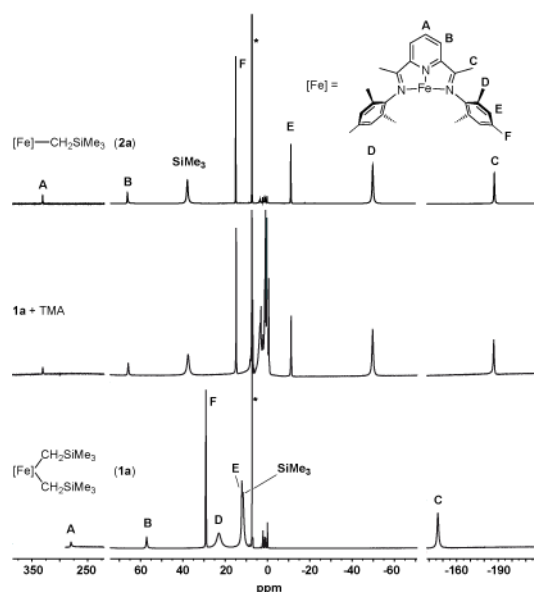
## Results and Discussion

Some time ago, we studied the interaction of the iron dialkyl complex  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{}^{\text{Mes}}\text{BIP})]$  (**1a**) with trimethylaluminum (TMA).<sup>18</sup> Using  $^1\text{H}$  NMR, we observed that the reaction of **1a** with one equivalent of TMA (i. e.,  $0.5 \text{ Al}_2\text{Me}_6$ ) in  $\text{C}_6\text{D}_6$ , leads to a single product, **2a**, moderately stable in solution at room temperature. This result was considered relevant because ethylene was rapidly polymerized when bubbled through the resulting solution. In that report, we suggested that complex **2a** could be a bimetallic Fe/Al complex on the basis of the similarity of some of its main  $^1\text{H}$  signals with those of the species reported by Bryliakov and Talsi.<sup>15b</sup> However, we later found

closer similarity with the spectra of the monoalkyl complexes  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(^{\text{Et}}\text{BIP})]^{10\text{a}}$  and  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(^{\text{iPr}}\text{BIP})]$ ,<sup>19</sup> reported by Chirik, and this led us to conclude that **2a** could be a member of the same family of monoalkyl compounds, as shown in Scheme 1. Our efforts to isolate **2a** from the reaction of **1a** and TMA were initially thwarted by the facile decomposition of the product during the workup. However, after a number of attempts, we found that **2a** is obtained in high yield (up to 90 %) when stoichiometric amounts of **1a** and TMA are combined in toluene at room temperature and the resulting mixture is evaporated under vacuum in order to minimize the exposure of the product to the aluminum byproducts during the workup. As shown in Figure 1, the NMR spectrum of the crystalline sample of **2a** confirms that this is the same observed in the NMR experiment.



Scheme 1

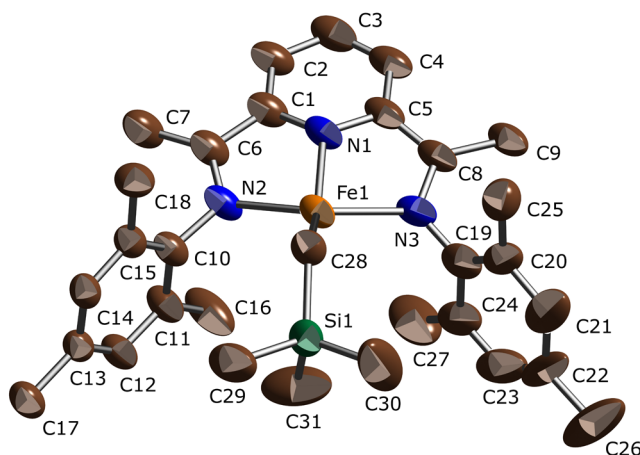


**Figure 1.** <sup>1</sup>H NMR spectrum of **1a** (bottom) and effect of adding one equivalent of TMA (middle). The spectrum of a pure sample of **2a** is shown in the top. The residual signal of the solvent (C<sub>6</sub>D<sub>6</sub>) is marked with an asterisk.

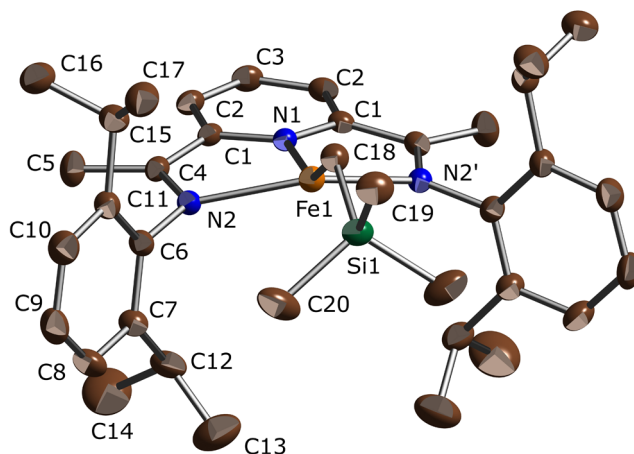
The essentially quantitative reaction of **1a** with TMA suggested that this reaction could be extended to related complexes. As mentioned before, Gambarotta studied the reaction of the bulkier dialkyl complex  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(^{\text{iPr}}\text{BIP})]$  (**1b**) with a large excess (10 equiv) of TMA, showing it leads to the compound  $[\text{AlMe}_2(^{\text{iPr}}\text{BIP})]$ .<sup>14</sup> However, we found that if this reaction is carried out using the procedure devised for the synthesis of **2a**, the previously described monotrimethylsilyl derivative  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(^{\text{iPr}}\text{BIP})]$  (**2b**)<sup>19</sup> is obtained in good yield.

Since the crystal structure of **2b** had not been previously reported, the identities of both monoalkyl derivatives **2** were confirmed with X-ray diffraction studies (Figures 2 and 3). The molecule of **2a** has no symmetry elements but **2b** has a crystallographically imposed symmetry mirror. Apart from that, the main bond lengths and

angles are very similar in both molecules, and close to those in the related monoalkyl  $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(^{\text{Et}}\text{BIP})]$ .<sup>19</sup> Thus, they both exhibit lengthened imino C=N and contracted 2,5-pyridyl C-CN bonds with regard to the free BIP ligand, that can be considered as diagnostic of mono-electronic reduction to  $[\text{BIP}]^-$ .<sup>5b,11b</sup> The 4-coordinated Fe center can be described as approximately square planar, severely distorted by the departure of the Fe-C bond from the mean coordination plane. Interestingly, the varying degree of steric hindrance exerted by the  $^{\text{Mes}}\text{BIP}$ ,  $^{\text{Et}}\text{BIP}$ <sup>19</sup> or  $^{\text{iPr}}\text{BIP}$  ligands has little effect on this distortion, as the angle formed by the central pyridine ring, the iron center and the metal-bound carbon atom is almost the same in the three compounds (ca. 149°).



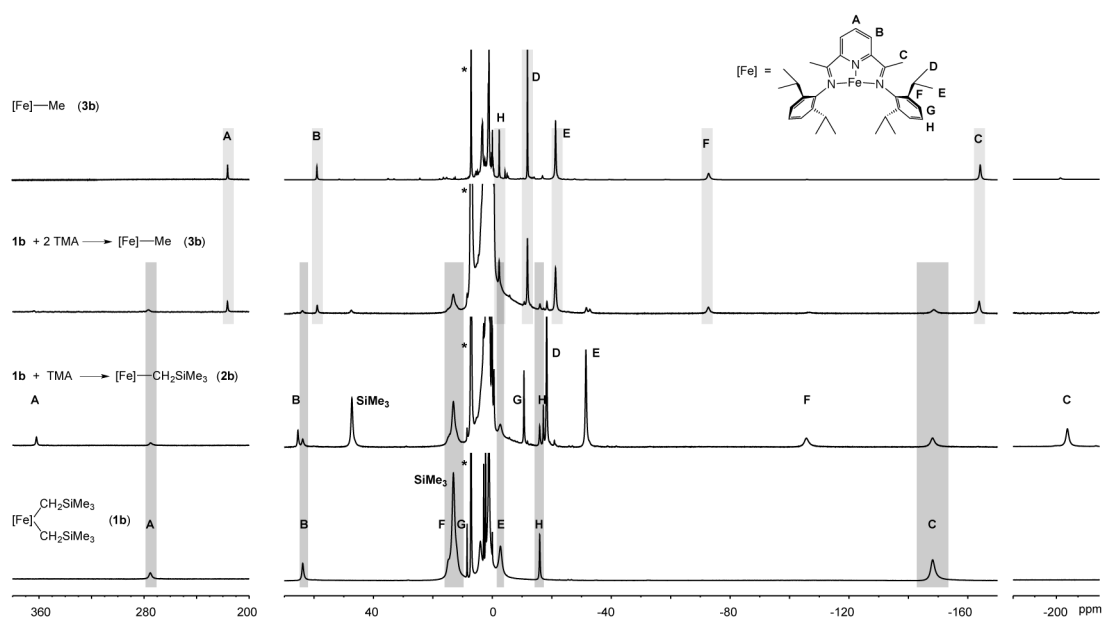
**Figure 2.** X ray crystal structure of compound **2a**. Selected bond lengths (Å) and angles (deg): Fe(1)-N(1), 2.007(5); Fe(1)-C(28), 2.050(5); Fe(1)-N(2), 2.103(5); Fe(1)-N(3), 2.110(6); C(1)-C(6), 1.440(9); C(6)-N(2), 1.323(8); C(5)-C(8), 1.436(10), C(8)-N(3), 1.325(7); N(1)-Fe(1)-C(28), 148.5(2); N(2)-Fe(1)-N(3), 136.68(19).



**Figure 3.** X ray crystal structure of compound **2b**. Selected bond lengths (Å) and angles (deg): Fe(1)-N(1), 1.992(3); Fe(1)-C(18), 2.025(4); Fe(1)-N(2), 2.190(2); N(2)-C(4), 1.316(3); C(4)-C(1), 1.443(4); N(1)-Fe(1)-C(18), 149.06(14); N(2)-Fe(1)-N(2)', 142.04(11). Symmetry operation to generate equivalent atoms:  $x, -y+1, z$ .

Monitoring the reaction of **1b** with TMA in  $\text{C}_6\text{D}_6$  by  $^1\text{H}$  NMR improved our understanding of the reaction of the iron and aluminum alkyls (Scheme 1 and Figure 4). The reaction of **1b** with an equivalent amount of TMA proceeds more sluggishly than in the case of **1a**, as the conversion into **2b** is ca. 50 % 10 min after mixing the reagents and reaches 60 % after 30 min (note that NMR experiments are significantly more diluted than preparative reactions, which explains why the latter become nearly complete in a short time). A significant decay of the intensity of the **2b** signals was observed at longer reaction times. Increasing the TMA / **1b** ratio to 2:1 led to the appearance of a new paramagnetic species, identified as the monomethyl complex  $[\text{Fe}(\text{Me})(^{\text{iPr}}\text{BIP})]$ , **3b**, by

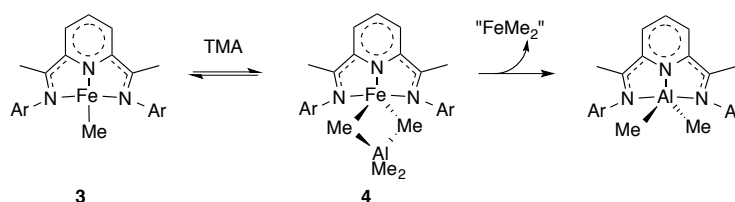
comparison with the spectrum of an authentic sample of this compound independently prepared as described in the literature.<sup>10a</sup> Most likely, this product arises from the alkyl exchange between **2b** and TMA. However, signals of **2b** are almost inappreciable in this experiment whilst significant amounts of **1b** (ca. 15 %) remained unreacted. This indicates that the alkyl exchange between **2b** and TMA proceeds faster than the initial reduction of **1b** to **2b**. In an independent experiment, we reacted a pure sample of **2b** with 1 equiv. of TMA in C<sub>6</sub>D<sub>6</sub>. The spectrum of the reaction mixture showed the formation of **3b**, confirming that, as represented in Scheme 1, this complex can be formed from **1b** in a stepwise manner, *i. e.*, *via* **2b**. In contrast, treating the mesityl derivative **1a** with two equivalents of TMA does not afford the corresponding methyl derivative, **3a**. Monitoring this reaction by NMR showed that the signals of **2a** lose intensity and fade away within minutes. Very likely **3a** is initially formed, but it rapidly decomposes in the presence of free TMA. We confirmed that also **3b** has a similar behavior, as its <sup>1</sup>H spectrum becomes broader and decays in the presence of TMA, a large excess (Al/Fe = 50) causing its immediate disappearance. The instability of both monomethyl complexes in the presence of TMA is consistent with the previously mentioned results by Gambarotta.<sup>12</sup>



**Figure 4.** <sup>1</sup>H NMR monitoring of the reaction of **1b** with 1 and 2 Eq of TMA. From bottom to top: 1) Spectrum of **1b** with signal assignments; 2) Reaction with 1 equiv of TMA, 30 min after mixing, showing signal assignments for **2b**; 3) Reaction with 2 Eq of TMA, 5 min after mixing; 4) Spectrum of **3b** with signal assignments. Shaded bars highlight the signals of **1b** and **3b** in the reaction mixtures. The residual signal of the solvent (C<sub>6</sub>D<sub>6</sub>) is marked with an asterisk.

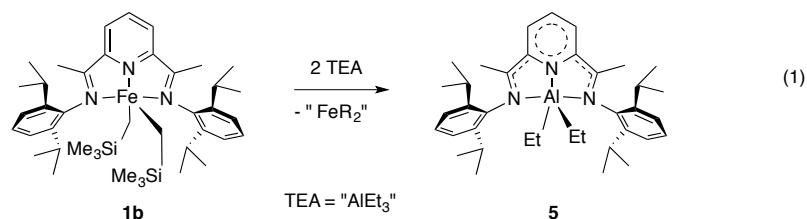
The diamagnetic region close to 0 ppm in the <sup>1</sup>H NMR spectra of solutions of **2a**, **2b** or **3b** directly generated from **1a**, **1b** or **2b** and TMA is complex and consistently show several signals that can be reasonably assigned to the AlCH<sub>2</sub>SiMe<sub>3</sub> moiety of silyl-containing aluminum species. For example, the spectrum of Al(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> consists of two signals at δ 0.0 and -0.55 ppm.<sup>20</sup> The complexity of this region can be explained assuming that the hypothetical compound [Al(Me)<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>] disproportionates into a mixture of silyl-containing alkyls. The fact that similar Al-containing products are observed in the reactions of TMA with compounds **1** and **2** suggests that both processes involve Fe/Al alkyl exchange, but in the former case the resulting mixed iron alkyls [Fe(Me)(CH<sub>2</sub>SiMe<sub>3</sub>(BIP))] undergo Fe-Me homolysis, as depicted in Scheme 1. This outcome is not surprising, as most complexes of the type [MR<sub>2</sub>(BIP)] are unstable and decompose with either M-C bond homolysis or alkyl migration to the BIP ligand.<sup>19,21,22</sup> The successive formation of complexes **2** and **3** can therefore be seen as a

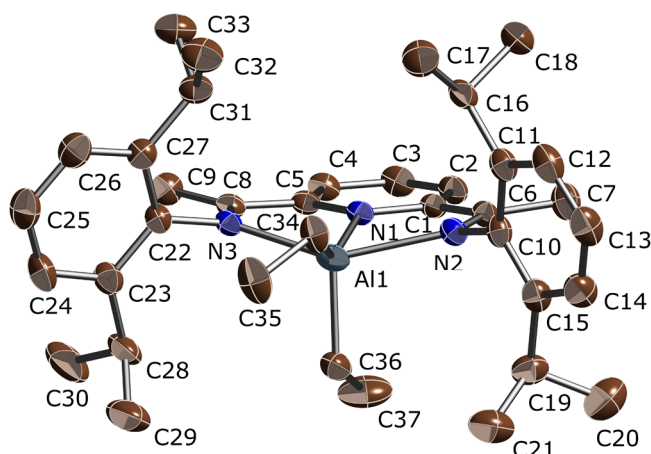
series of alkyl exchange reactions, probably involving bimetallic intermediates similar to those observed by Bryliakov and Talsi.<sup>15</sup> This raises the question of why we did not detect such intermediates in our experiments. These authors showed that **3b** reacts with TMA at 253 K affording the bimetallic derivative  $[\text{Fe}(\mu\text{-Me})_2\text{AlMe}_2(\text{}^{i\text{Pr}}\text{BIP})]$ , **4b**,<sup>15c</sup> but we did not observe this nor any new products when **3b** was treated with excess of TMA at room temperature. In order to address this point, we revisited the reaction of **3b** with TMA at low temperature. We confirmed that, as reported by Bryliakov and Talsi, **3b** is cleanly transformed into **4b** by reaction with 10 Equiv of TMA at 253 K. However, only partial conversion was observed with a TMA / **3b** ratio 5:1, which indicates that either the formation of **4b** is slow, or it is a reversible process requiring excess of TMA to shift the equilibrium. Increasing the temperature should accelerate the reaction of **3b** and TMA, therefore a rapid exchange between iron monoalkyls and bimetallic adducts and a low association constant (because dissociation is entropy-driven) could be the causes that prevent detection of the latter at room temperature. However, the intermediacy of adducts of type **4** can readily explain the instability of the methyl complexes in the presence of TMA (Scheme 2).



**Scheme 2**

To conclude our study, we briefly investigated the interaction of **1b** with two equivalents of TEA, as a possible route for the corresponding monoethyl derivative,  $[\text{FeEt}(\text{}^{i\text{Pr}}\text{BIP})]$ . This compound was not obtained, but instead the green, NMR-silent aluminum complex **5** was isolated in 45 % yield (Eq. 1). The crystal structure of **5** is shown in Figure 4. This compound is analogous to the methyl derivative isolated by Gambarotta from the reaction with excess of TMA, which is best described as an Al(III) complex containing a reduced BIP<sup>-</sup> radical anion. In agreement with this proposal, the lengths of the imino C=N bonds and the C-C bonds connecting these to the central Py ring (C1-C6 and C5-C8) are elongated and contracted, respectively, in comparison with those in the free <sup>iPr</sup>BIP ligand. The main difference between the structures of the dimethyl complex and **5** is in the geometry of the Al center, which is bipyramidal trigonal in the former and square pyramidal in the latter with one of the ethyl groups occupying the apical position. The facile formation of compound **5** confirms that displacement of the iron center from BIP complexes by aluminum alkyls is a quite general process and plays an important role in the deactivation of iron-based olefin polymerization catalysts.





**Figure 5.** X ray crystal structure of compound **5**. Selected bond lengths (Å) and angles (deg): Al(1)-N(1), 1.9582(16); Al(1)-N(2), 1.972(2); Al(1)-N(3), 2.1345(18); Al(1)-C(34), 1.972(2); Al(1)-C(36), 1.984(3); C(6)-N(2), 1.311(2); C(8)-N(3), 1.327(2); C(1)-C(6), 1.456(3); C(5)-C(8), 1.450(3); N(1)-Al(1)-C(34), 142.72(10); N(1)-Al(1)-C(36), 103.36(9); N(2)-Al(1)-N(3), 145.36(7); C(34)-Al(1)-C(36), 113.47(11).

## Conclusions

We have shown that the interaction of thermally stable iron(II) bis(trimethylsilylmethyl) complexes **1a,b** with TMA involves three distinct stages. The dialkyl complexes are first reduced to the mono(trimethylsilyl)methyl derivatives **2a,b**. These are robust enough, and can be isolated in good yields when **1a** or **1b** and TMA are reacted in 1:1 ratio. Presumably, the initial reduction of the Fe center is not directly induced by the organoaluminum compound but is due to the intrinsic instability of mixed alkyl intermediates arising from  $\text{CH}_2\text{SiMe}_3/\text{Me}$  exchange, which rapidly decomposes undergoing Fe-Me bond homolysis. The  $\text{CH}_2\text{SiMe}_3$  group that remains in **2a** and **2b** is readily exchanged with a second equivalent of TMA, a process that leads to methyl complexes (**3**). An excess of TMA causes the displacement of iron from the BIP ligand, affording NMR-silent dialkylaluminum-BIP complexes. The latter process probably constitutes a main deactivation route for the iron polymerization catalysts. Complexes **3** react further with organoaluminum compounds such as TMA or the products resulting from the alkyl exchange, affording NMR-silent aluminum species. This prevented their isolation from the reaction mixtures, although the formation more stable derivative **3b** (but not **3a**) was observed using NMR spectroscopy. A similar process takes place when TMA is replaced with higher aluminum alkyls, and complex **5**, the ethyl analogue of the previously known compound  $[\text{AlMe}_2(\text{IPr}^{\text{BIP}})]$ , was isolated from the reaction of **1b** with two equivalents of TEA. The sequence of reactions of the dialkyls **1** with TMA can be regarded as a series of alkyl exchanges between the BIP-containing species and the aluminum alkyls, and probably involve the formation of Fe/Al bimetallic species as intermediates. As reported previously by Bryliakov, Talsi *et al.*, the **reduced, electrically neutral Fe/Al bimetallics** are thermally unstable and can only be detected at low temperature. Therefore, reduced monoalkyl species  $[\text{Fe}(\text{R})(\text{BIP})]$  are the most relevant products arising from the interaction between Fe(II) BIP complexes and aluminum alkyls at the room temperature and, in consequence, they are likely to play some role in catalyst systems generated from Fe(II) precursors and TMA or other trialkylaluminum compounds. In an ensuing paper we will be analyzing the role of these reduced species in the mechanism of ethylene polymerization catalyzed by iron complexes.

## Experimental

All manipulations were carried out under oxygen-free argon atmosphere using conventional Schlenk techniques, or a nitrogen filled glove box. Solvents were rigorously dried and degassed before using. TMA and TEA were purchased from Aldrich and used as received. Compounds **1a** and **1b** were prepared according to literature procedures.<sup>18-19</sup> Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared and UV-Vis spectra were recorded, respectively, on a Bruker Vector 22 and Perkin-Elmer Lambda 12 or Lambda 750 spectrophotometers and NMR spectra on Bruker DRX 300, 400 or 500 MHz spectrometers. The resonances of the solvent were used as the internal standard but chemical shifts were reported with respect to TMS. Magnetic susceptibilities were measured at 298 K using a Sherwood magnetic balance model MSB-Auto, and were corrected for the diamagnetic contributions estimated from Pascal's constants.<sup>23</sup>

**[Fe(CH<sub>2</sub>SiMe<sub>3</sub>)<sup>(Mes)</sup>BIP], 2a.** To a solution of complex **1a** (627 mg, 1 mmol) in toluene (30 mL), stirred at room temperature, 1.1 mL of a 1 M solution of TMA in toluene (1 mmol "AlMe<sub>3</sub>" / mL, 1.1 Eq) was added dropwise. During the addition, the color of the mixture changed from purple to green. The stirring was continued for 5 min and then the solution was evaporated to dryness. The residue was extracted in pentane (2 x 30 mL) and the solution was filtered through a pad of celite. The resulting green solution was concentrated to 1/3 of the original volume (approx. 20 mL) and stored at -20 °C. The product was isolated as a green solid by filtration, washed with cold pentane and dried under vacuum. Yield, 500 mg, 90 %. X-ray quality crystals were obtained by recrystallization from hexane. Anal. Calcd for C<sub>31</sub>H<sub>42</sub>N<sub>3</sub>FeSi: C, 68.87; H, 7.83; N, 7.77. Found: C, 68.80; H, 8.17; N, 7.85.  $\mu_{\text{eff}}$  (298 K) = 4.3  $\mu_{\text{B}}$ . UV-VIS (Et<sub>2</sub>O):  $\lambda_{\text{max}}$  360 nm ( $\epsilon = 4994$ ),  $\lambda_{\text{max}}$  479 nm ( $\epsilon = 2825$ ),  $\lambda_{\text{sh}}$  640 nm ( $\epsilon = 1285$ ),  $\lambda_{\text{sh}}$  687 nm ( $\epsilon = 1202$ ). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -187.3 ( $\Delta\nu_{1/2} = 178$  Hz, 6H, MeCN), -50.0 ( $\Delta\nu_{1/2} = 172$  Hz, 12H, *o*-Me<sub>mes</sub>), -11.3 ( $\Delta\nu_{1/2} = 42$  Hz, 4H, *m*-CH<sub>mes</sub>), 14.8 ( $\Delta\nu_{1/2} = 24$  Hz, 6H, *p*-Me<sub>mes</sub>), 33.7 ( $\Delta\nu_{1/2} = 214$  Hz, 9H, SiMe<sub>3</sub>), 66.0 ( $\Delta\nu_{1/2} = 96$  Hz, 2H, 3,3'-H<sub>Py</sub>), 331.8 ( $\Delta\nu_{1/2} = 234$  Hz, 1H, 4-H<sub>Py</sub>).

**[Fe(CH<sub>2</sub>SiMe<sub>3</sub>)<sup>(Pr)</sup>BIP], 2b.** To a solution of complex **1b** (1.56 g, 2.5 mmol) in 30 mL of toluene, stirred at room temperature, 2.5 mL of a 1 M solution of TMA in the same solvent (2.5 Eq "AlMe<sub>3</sub>") were added at room temperature. The color of the mixture changed from purple to green. After 5 min, the volatiles were removed under vacuum, the residue was extracted in pentane (3 x 20 mL) and the solution was filtered through a pad of celite. The green solution was concentrated to ca. 1/3 of its original volume and stored at -20 °C for several days. The product forms a green microcrystalline material that was filtered, washed with cold pentane and dried under vacuum. Yield, 1.15 g, 77%. X-ray quality crystals were obtained by recrystallization from toluene/pentane. Anal. Calcd for C<sub>37</sub>H<sub>54</sub>N<sub>3</sub>FeSi·0.5C<sub>7</sub>H<sub>7</sub>: C, 72.51; H, 8.71; N, 6.26. Found: C, 72.04; H, 8.17; N, 6.35.  $\mu_{\text{eff}}$  (298 K) = 4.0  $\mu_{\text{B}}$ . IR (Nujol mull), 1581 ( $\nu_{\text{C=N}}$ ). UV-VIS (Et<sub>2</sub>O):  $\lambda_{\text{max}}$  353 nm ( $\epsilon = 4919$ ),  $\lambda_{\text{max}}$  465 nm ( $\epsilon = 2538$ ),  $\lambda_{\text{sh}}$  589 nm ( $\epsilon = 478$ ). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -203.6 ( $\Delta\nu_{1/2} = 178$  Hz, 6H, MeCN), -105.6 ( $\Delta\nu_{1/2} = 421$  Hz, 2H, CHMe<sub>2</sub>), -31.7 ( $\Delta\nu_{1/2} = 102$  Hz, 6H, CHMeMe), -18.4 ( $\Delta\nu_{1/2} = 41$  Hz, 6H, CHMeMe), -17.4 ( $\Delta\nu_{1/2} = 28$  Hz, 2H, *p*-CH<sub>Ar</sub>), -10.8 ( $\Delta\nu_{1/2} = 31$  Hz, 4H, *m*-CH<sub>Ar</sub>), 65.8 ( $\Delta\nu_{1/2} = 79$  Hz, 2H, 3,3'-H<sub>Py</sub>), 364.2 ( $\Delta\nu_{1/2} = 211$  Hz, 1H, 4-H<sub>Py</sub>).



**[AlEt<sub>2</sub>(<sup>i</sup>PrBIP)], 5.** A solution of complex **1b** (1.60 g, 2.25 mmol) in toluene (30 mL), stirred at room temperature, was treated with 4.5 mL of a 1 M solution of TEA in the same solvent (4.5 Eq “AlEt<sub>3</sub>”). The color of the mixture changed from purple to green. After stirring for 5 min, the solution was taken to dryness, and the residue was extracted in pentane. The solution was filtered through a pad of celite, concentrated to ca. 1/3 of the original volume and stored at -20 °C. The product formed crystals that were appropriate for X-ray diffraction. Yield, 570 mg, 45 %. Anal. Calcd for C<sub>37</sub>H<sub>53</sub>N<sub>3</sub>Al: C, 78.40; H, 9.48; N, 7.41. Found: C, 78.41; H, 9.92; N, 7.22. IR (Nujol mull): 1581 (νC=N).

### **NMR Monitoring the reactions of iron alkyl complexes with TMA. General procedure.**

*General procedure:* Samples of the iron complexes were weighed in the glove box, dissolved in the required amount of C<sub>6</sub>D<sub>6</sub> and placed in NMR tubes capped with septa. A 0.1 M stock solution of TMA (containing 1 Eq “AlMe<sub>3</sub>” per mL) was prepared in the same solvent, and a sample was placed in a septum-capped vial. The <sup>1</sup>H NMR spectrum of the pure samples was recorded. The required amount of the TMA solution was taken with a gas-tight syringe from its vial, and injected into the tube of the corresponding complex. The NMR tube was sealed with a small amount of silicone grease and parafilm and gently shaken before placing into the NMR probe.

*Monitoring the reaction of complexes 1 - 3 with TMA at room temperature:* Samples containing 10 μmol of the complexes in C<sub>6</sub>D<sub>6</sub> were prepared as described and treated with 100 or 200 μL of the TMA solution (Al/Fe = 1 or 2, respectively). For the reaction of **3b** with 50 Eq of TMA, a 1 N solution of this reagent was used.

*Monitoring the reaction of 3b with TMA at low temperature:* Two samples containing 4.5 mg of **3b** (8 μmol) in toluene-d<sub>8</sub> were prepared in the glove box and placed in septum-capped NMR tubes. A 0.2 N solution of TMA in the same solvent was similarly prepared. The **3b** samples were cooled to 193 K (-80 °C) in an acetone – dry ice bath, and the prescribed amount of the TMA solution (200 or 400 μL, Al/Fe = 5 or 10, respectively) was added. The septa were sealed with silicone grease and parafilm and the tubes were transferred to the pre-cooled NMR probe.

### **Associated Content**

Experimental for the X-ray crystal structure analyses and crystallographic information files for **2a**, **2b** and **5**. These data are available free of charge via the Internet at <http://pubs.acs.org>.

### **Acknowledgements**

This work was supported by the Government of Spain (project number CTQ2012-30962), the Junta de Andalucía (project number FQM5074) and the European Union (EU) (FEDER funds). MAC thanks CSIC for a predoctoral research fellowship (I3P program).

### **References**

- (1) a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523-2524. b) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143-7144.
- (2) a) Ma, J.; Feng, C.; Zhao, K. Q.; Sun, W. H.; Redshaw, C.; Solan, G. A. *Inorg. Chem. Front.* **2014**, *1*, 14. b) Li, L.; Gomes, P. T. In *Olefin Upgrading Catalysis with Nitrogen-based Metal Complexes, State of the Art and Perspectives.*; Giambastiani, G., Cámpora, J., Eds.; Springer: Dordrecht, 2011; Vol. II, p 77-198. c) Bianchini, C.; Giambastiani, G.; Guerrero-Rios, I.; Montovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391-1418.
- (3) Bryliakov, K. P.; Talsi, E. P. *Coord. Chem. Rev.* **2012**, *256*, 2994-3007.
- (4) a) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; Mc. Tavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728-8740. b) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 6479-6487.
- (5) a) Bowkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 9660-99661. b) Tondreau, A. M.; Milsman, C.; Patrick, A. D.; Hoyt, H. M.; Lobkovsky, E.; Weighardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 15046-15059.
- (6) Hojilla Atienza, C. C.; Milsman, C.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 8143-8147.
- (7) a) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442-5448. b) Gibson, V. C.; Redshaw, C.; Solan, G. *Chem. Rev.* **2007**, *107*, 1745-1776.
- (8) a) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. N. N.; Horton, A. D.; Budzelaar, P. H. M. *Angew. Chem. Int. Ed.* **2001**, *40*, 4719-4722. b) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2002**, 2252-2253. c) Kleigrewe, N.; Steffen, W.; Blömker, T.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G.; Wasilike, J.-C.; Wu, G.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13955-13968. d) Humphries, M. J.; Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 2039-2050. e) Steffen, W.; Blömker, T.; Kleigrewe, N.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2004**, 1188-1189.
- (9) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298-6300.
- (10) a) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406-3408. b) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019-13029.
- (11) a) Knijnenburg, Q.; Budzelaar, P. H. M.; Hettterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur J. Inorg. Chem.* **2004**, 1204-1211. b) Bart, S. C.; Chopek, K.; Bill, E.; Bowuwkamp, M. W.; Lobkovsky, E.; Neese, F.; Weighardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901-13912.
- (12) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204-17206.
- (13) Castro, P. M.; Lahtinen, P.; Axenov, K.; Viidnoja, J.; Kotiaho, T.; Leskelä, M.; Repo, T. *Organometallics* **2005**, 3664-3670.
- (14) Britovsek, G. J. P.; Clentsmith, G. K. B.; Gibson, V. C.; Goodgame, D. M. L.; Mc. Tavish, S. J.; Pankhurst, Q. A. *Catal. Commun.* **2002**, 207-211.
- (15) a) Bryliakov, K. P.; Semikolenova, N. V.; Zudin, V. N.; Zakharov, V. A.; Talsi, E. P. *Catal. Commun.* **2004**, *5*, 45-48. b) Bryliakov, K. P.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Organometallics* **2004**, *23*, 5375-

5378. c) Bryliakov, K. P.; Talsi, E. P.; Semikolenova, N. V.; Zakharov, V. A. *Organometallics* **2009**, *28*, 3225-3232.
- (16) Soshnikov, I. E.; Semikolenova, N. V.; Bushmelev, A. N.; Bryliakov, K. P.; Lyakin, O. Y.; Redshaw, C.; Zakharov, V. A.; Talsi, E. P. *Organometallics* **2009**, *28*, 6003-6013.
- (17) a) Cruz, V. L.; Ramos, J.; Martínez-Salazar, J.; Gutiérrez-Oliva; Toro-Labbé, A. *Organometallics* **2009**, *28*, 5889-5895. c) Racoules, R.; de Bruin, T.; Rayaboud, P.; Adamo, C. *Organometallics* **2008**, *27*, 3368-3377.
- (18) Cámpora, J.; Naz, A. M.; Palma, P.; Álvarez, E. *Organometallics* **2005**, *24*, 4878-4881.
- (19) Fernández, I.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 109-118.
- (20) Tessier-Youngs, C.; Beachley, O.; Oliver, J. P. *Inorg. Synth.* **1986**, *24*, 92-93.
- (21) Zhu, D.; Janssen, F. F. B. J.; Buzelaar, P. H. M. *Organometallics* **2010**, *29*, 1897-1908.
- (22) a) Pérez, C. M.; Rodríguez-Delgado, A.; Palma, P.; Álvarez, E.; Gutiérrez-Puebla, E.; Cámpora, J. *Chem. Eur. J.* **2010**, *16*, 13834-13842. b) Sandoval, J. J.; Palma, P.; Álvarez, E.; Rodríguez-Delgado, A.; Cámpora, J. *Chem. Commun.* **2013**, *49*, 6791-6793.
- (23) Bain, G. A.; Berry, J. F. *J. Chem. Ed.* **2008**, *85*, 532-536.

## For Table of Contents

### Sequential Reduction And Alkyl Exchange Reactions Of Bisiminopyridine Dialkyliron(II) With Trimethylaluminum.

M. Ángeles Cartes, Antonio Rodríguez-Delgado, Pilar Palma, Eleuterio Álvarez and Juan Cámpora.\*

*The reaction of bisiminopyridine dialkyliron complexes with aluminum trialkyls under controlled conditions allows observing the successive stages of a complex process that sequentially leads to reduction, alkyl exchange and, ultimately, displacement of the iron center from the tridentate ligand.*

