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## Alternative Aluminum-Based Cocatalysts for the Iron-Catalyzed Oligomerization of Ethylene

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**Multinuclear aluminum cocatalysts have been obtained by the reaction of various phenols, alcohols or diols with trimethylaluminum and were used *in situ* or as isolated, well-defined species, for the activation of an iron(II) or an iron(III) pre-catalyst for the oligomerization of ethylene. The best cocatalyst candidate involves 2,2'-biphenol (10) in a 10/AlMe<sub>3</sub> ratio of 2/3.**

Organoaluminum compounds play a key role as cocatalysts in ethylene oligomerization and polymerization. For iron-catalyzed ethylene transformations, methylaluminoxanes<sup>1</sup> (MAOs) lead to the most active systems.<sup>2</sup> However, these ill-defined cocatalysts evolve over time and extended storage is limited. Efforts are thus devoted to replace them. In the specific area of iron-catalyzed ethylene polymerization, trialkylaluminum compounds associated to alkyl-abstracting reagents and weakly coordinating anions, most notably boron-based compounds, have long been known as suitable activators.<sup>3</sup> Tetraalkylaluminoxanes R<sub>2</sub>AlOAlR<sub>2</sub>, formed by partial hydrolysis of AlEt<sub>3</sub> or Al*i*Bu<sub>3</sub>, were also reported by Wang et al.<sup>4</sup> Interestingly, non-hydrolytic synthetic routes can generate MAO-like cocatalysts from AlMe<sub>3</sub> and benzophenone or carboxylic acids, which are active in iron-catalyzed ethylene polymerization.<sup>5</sup> Partially hydrolyzed trimethylaluminum supported on silica has been described by Alt and coworkers<sup>6</sup> for iron-bis(imino)pyridine complex heterogenization, Al/Fe ratio was lowered to 8 while maintaining the catalyst active for ethylene polymerization.

However, in the area of iron-catalyzed ethylene oligomerization, the main issue for cocatalysts is not about the product properties but rather the ability to readily activate and trigger the oligomerization process. Focusing on this

transformation, examples of alternative cocatalysts to MAO or MMAO are scarce. Hanton et al.<sup>7</sup> successfully replaced MMAO with AlEt<sub>3</sub> in combination with the perfluoro-borate or -aluminates [Ph<sub>3</sub>C][(B(Ph<sup>F</sup>))<sub>4</sub>] or [Ph<sub>3</sub>C][Al(O*t*Bu<sup>F</sup>)<sub>4</sub>], respectively, to activate the bis(imino)pyridine complex **A** (Figure 1), although the catalytic system appeared to be temperature-sensitive and noticeable catalyst deactivation occurred. More recently, Sun et al.<sup>8</sup> used diethylaluminum chloride as cocatalyst of a benzimidazole(imino)pyridine ferric iron precursor, albeit this system exhibited very low reactivity. In our hands, none of the commercial alkylaluminum compounds AlMe<sub>3</sub>, AlEt<sub>3</sub>, Al*i*Bu<sub>3</sub>, AlCl<sub>2</sub>Et or AlClEt<sub>2</sub> proved to be suitable iron cocatalysts under our oligomerization catalytic conditions (complex **A**, 10 μmol(Fe), 500 eq. Al, 50 °C, 30 bar ethylene). Herein, we report unprecedented aluminum cocatalysts for the iron-catalyzed oligomerization of ethylene. They are formed by reaction of phenols, alcohols or diols with trimethylaluminum and may be used *in situ* or as isolated and easier to handle and keep, well-defined species.<sup>9</sup>

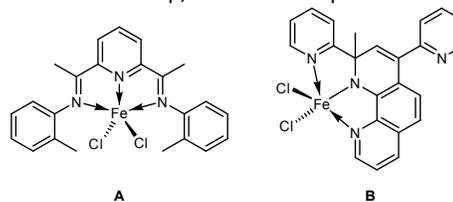


Fig 1 Iron(II) and iron(III) complexes used as precatalysts

We observed that the well-known complex **A** is activated by a solution of phenol **1** as additive and AlMe<sub>3</sub> (molar PhOH/Al = 1/1, prepared prior to use, see SI) under 30 bar of ethylene pressure and produces linear alpha olefins (up to 9.3×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>, Figure 2 and Table 1). A plot of cumulative ethylene uptake over 1 h reveals slight catalyst deactivation (see ESI). A Schulz-Flory distribution of oligomers with *K* = 0.70 was obtained, with no solid polymer (Table 1, entry 1). Different phenols (**2-3**) and alcohols (**4-5**) were then evaluated in combination with AlMe<sub>3</sub>, for the activation of the iron complex but resulted in either lower activity in oligomerization

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† Electronic Supplementary Information (ESI) available: Syntheses, procedure for catalyst evaluation and ethylene uptakes. See DOI: 10.1039/x0xx00000x

of ethylene for 2,6-di-*tert*-butylphenol, 4-phenylphenol or cyclohexanol compared to phenol (up to  $6.7 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 1, entries 2-4), or, surprisingly, no activity as with *tert*-butanol (Table 1, entry 5). Little influence of the different cocatalysts was observed on the distribution of oligomers with  $K = 0.67$ - $0.69$ .

We also considered the use of diols in a molar ratio diol/ $\text{AlMe}_3 = 1/2$ . Under our catalytic conditions, activation of complex **A** with  $\text{AlMe}_3$  and 1,2-ethanediol **6** afforded a rapidly deactivating system while with the longer 1,4-butanediol **7**, a stable and active catalytic system was obtained (activities of  $2.9 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$  and  $12.9 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , respectively, Table 1, entries 6 and 7). In comparison, tertiary and benzyl diols such as 1,1,2,2-tetraphenyl-1,2-ethanediol **8** and 2,2'-biphenyldimethanol **9** led to inefficient cocatalysts (Table 1, entries 8 and 9). More interestingly, 2,2'-biphenol **10** or pyrocatechol **11** associated with  $\text{AlMe}_3$  afforded the most effective cocatalytic systems for the iron(II)-catalyzed ethylene oligomerization (up to  $55.9 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$  and  $22.7 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , respectively, Table 1, entries 10 and 11). A controlled exotherm was observed ( $< 15 \text{ }^\circ\text{C}$ ) and linear alpha olefins were formed, with selectivities around  $K = 0.69$ - $0.70$ , along with waxes. Under the same operating conditions, complex **A** and MAO as cocatalyst led to extremely fast ethylene consumption. The non-controllable exothermicity of the reaction under these conditions led to more than 60 wt% of polymer and a Schulz-Flory distribution of oligomers ( $K = 0.69$ , Table 1, entry 16).

The two other isomeric dihydroxybenzene compounds **12** and **13** in combination with  $\text{AlMe}_3$  presented no activation ability (Table 1, entries 12 and 13), suggesting that the position of the hydroxyl groups should favor chelating geometries. Replacing one (**14**) or both (**15**) hydroxyl by amino groups led also to catalyst activation with slightly lower activities but good stability over 1 h (Table 1, entries 14 and 15).

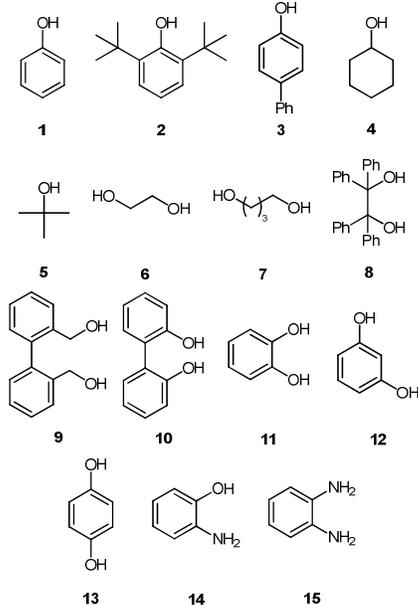


Fig 2 Phenols, alcohols and diols used as additives (addit.)

Table 1. Oligomerization of ethylene catalysed by complex **A** in combination with  $\text{AlMe}_3$  and different alcohols, phenols and diols as additives (addit.)<sup>a</sup>

entry	addit. (addit./ $\text{AlMe}_3$ ratio)	$m_{\text{C}_2\text{H}_4}$ (g) <sup>b</sup>	activity <sup>c</sup>	$K^d$
1	<b>1</b> (1/1)	9.3	9.3	0.70
2	<b>2</b> (1/1)	3.6	3.6	0.67
3	<b>3</b> (1/1)	4.6	4.6	0.67
4	<b>4</b> (1/1)	6.7	6.7	0.69
5	<b>5</b> (1/1)	<1	0 <sup>d</sup>	-
6	<b>6</b> (1/2)	2.9	2.9	0.66
7	<b>7</b> (1/2)	12.9	12.9	0.69
8	<b>8</b> (1/2)	<1	0 <sup>e</sup>	-
9	<b>9</b> (1/2)	<1	0 <sup>e</sup>	-
10 <sup>f</sup>	<b>10</b> (1/2)	23.3	55.9	0.70
11	<b>11</b> (1/2)	22.7	22.7	0.69
12	<b>12</b> (1/2)	<1	0 <sup>d</sup>	-
13	<b>13</b> (1/2)	<1	0 <sup>d</sup>	-
14	<b>14</b> (1/2)	11.0	11.0	0.70
15	<b>15</b> (1/2)	11.6	11.6	0.67
16 <sup>g</sup>	MAO	62.0	740	0.69

<sup>a</sup> Complex **A** (10  $\mu\text{mol}$ ),  $\text{AlMe}_3$  (500 eq.), toluene (25 mL),  $P_{\text{C}_2\text{H}_4} = 30 \text{ bar}$ ,  $T = 50 \text{ }^\circ\text{C}$ , reaction time 1 h. <sup>b</sup> mass of ethylene introduced. <sup>c</sup>  $\times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ . <sup>d</sup>  $K = \text{Schulz-Flory coefficient} = k_{\text{prop}} / (k_{\text{prop}} + k_{\text{ch transfer}}) = \text{mol of } C_{n+2} \text{ oligomers} / \text{mol of } C_n \text{ oligomers}$ . <sup>e</sup> No ethylene uptake considered ( $< 1 \text{ g}$ ). <sup>f</sup> Reaction time: 25 min. <sup>g</sup> Reaction time: 5 min,  $\text{Al/Fe} = 500$ .

Considering the reaction of the diols with  $\text{AlMe}_3$ , different multinuclear aluminum species could be obtained depending on the stoichiometry of the reactants.<sup>10</sup> We therefore tested different **10**/ $\text{AlMe}_3$  molar ratios (Table 2) at constant  $\text{Al/Fe}$  molar ratio (500) and observed a maximum of activity for the 2/3 **10**/ $\text{AlMe}_3$  molar ratio (up to  $125.5 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entries 1-6) along with a non negligible exotherm ( $+40 \text{ }^\circ\text{C}$ , see ESI). Increasing the molar ratio **10**/ $\text{AlMe}_3$  and thus the relative number of hydroxyl groups led to a sharp decrease of the activation ability of the cocatalytic mixture (Table 2, entry 4), until no activity was detected for **10**/ $\text{AlMe}_3 = 1/1$  or more (Table 2, entries 5-6). At the optimum **10**/ $\text{AlMe}_3$  molar ratio of 2/3, the  $\text{Al/Fe}$  ratio could be lowered to 250 without significant alteration of the catalyst activity ( $100 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entry 7). At a  $\text{Al/Fe}$  ratio of 100, a lower catalyst activity was observed ( $83.7 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entry 8), but the reaction temperature was perfectly controlled and the ethylene consumption was stable. Lowering the  $\text{Al/Fe}$  ratio to 50 led to a decrease of activity and progressive deactivation of the catalytic system ( $9.6 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entry 9). Associated to complex **A**, pyrocatechol **11** used in a ratio **11**/ $\text{AlMe}_3 = 2/3$  led to a lower activity compared to the ratio 1/2 ( $10.2 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$  vs  $22.7 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entry 10 and Table 1, entry 11, respectively).

We then checked that this combination **10**/ $\text{AlMe}_3$  (2/3) is not specific to the iron complex **A** by testing the iron(III) complex **B** (Figure 1).<sup>11</sup> We activated the latter using a  $\text{Al/Fe}$  molar ratio of 250 at  $80 \text{ }^\circ\text{C}$  and observed a short distribution of oligomers (wt %): 76%  $C_4$  (97% 1- $C_4$ ), 13%  $C_6$  (90% 1- $C_6$ ), 13%  $C_{8+}$  and 2% of polyethylene with an activity comparable to the one obtained with MAO at 200 eq. ( $2.6 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$  vs  $2.2 \times 10^5 \text{ g} \cdot (\text{mol}(\text{Fe}) \cdot \text{h})^{-1}$ , Table 2, entries 11 and 12).

Table 2. Iron-catalyzed oligomerization of ethylene with various addit./AlMe<sub>3</sub> molar ratios<sup>a</sup>

entry	addit. (addit./AlMe <sub>3</sub> ratio)	time (min)	m <sub>C<sub>2</sub>H<sub>4</sub></sub> (g) <sup>b</sup>	activity <sup>c</sup>	K <sup>d</sup>
1	<b>10</b> (1/5)	60	23.2	23.2	0.66
2	<b>10</b> (1/2)	25	23.3	55.9	0.69
3	<b>10</b> (2/3)	12	25.1	125.5	0.70
4	<b>10</b> (4/5)	60	15.7	15.7	0.67
5	<b>10</b> (1/1)	60	<1	0 <sup>e</sup>	-
6	<b>10</b> (5/1)	60	<1	0 <sup>e</sup>	-
7 <sup>f</sup>	<b>10</b> (2/3)	15	25.1	100.0	0.67
8 <sup>g</sup>	<b>10</b> (2/3)	18	25.1	83.7	0.66
9 <sup>h</sup>	<b>10</b> (2/3)	50	8.0	9.6	0.65
10 <sup>i</sup>	<b>11</b> (2/3)	60	10.2	10.2	0.68
11 <sup>j,i</sup>	<b>10</b> (2/3)	60	5.1	2.6	n.d. <sup>j</sup>
12 <sup>j</sup>	MAO (200 eq.)	120	8.8	2.2	n.d. <sup>j</sup>

<sup>a</sup> Complex **A** (10 μmol), AlMe<sub>3</sub> (500 eq.), toluene (25 mL), P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 30 bar, T = 50 °C. <sup>b</sup> mass of ethylene introduced. <sup>c</sup> ×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>. <sup>d</sup> K = Schulz-Flory coefficient = k<sub>prop</sub>/(k<sub>prop</sub> + k<sub>ch transfer</sub>) = mol of C<sub>n+2</sub> oligomers / mol of C<sub>n</sub> oligomers. <sup>e</sup> No ethylene uptake considered (<1 g). <sup>f</sup> AlMe<sub>3</sub> (250 eq.). <sup>g</sup> AlMe<sub>3</sub> (100 eq.). <sup>h</sup> AlMe<sub>3</sub> (50 eq.). <sup>i</sup> Complex **B** used as catalyst precursor (20 μmol) and T = 80 °C. <sup>j</sup> K not determined, a short distribution of oligomers was observed (see text).

<sup>1</sup>H NMR spectroscopy revealed, after addition of a diol such as **11** to AlMe<sub>3</sub> at -70 °C in deuterated benzene, broad signals between 0.1 and -0.3 ppm that may be attributed to organoaluminum oligomers<sup>12</sup> and sharp singlets at -0.12, -0.34 and -0.79 ppm that were attributed to the trinuclear aluminum complex **16** (Figure 3), by comparison with an authentic sample prepared according to the literature.<sup>13</sup> Using a similar procedure, the reaction of 2,2'-biphenol with AlMe<sub>3</sub> led to a new compound, characterized by <sup>1</sup>H and <sup>13</sup>C NMR that was tentatively ascribed to the trinuclear species **17** by analogy with complex **16**. No further characterization could however be obtained.

Preliminary tests showed that activated by the well-defined cocatalyst **16**, complex **A** led to oligomerization of ethylene with an activity up to 18.1×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup> (Table 3, entry 1). Linear alpha olefins were obtained in a full range of C<sub>4</sub>-C<sub>24</sub> according to a Schulz-Flory distribution (K = 0.68). It is noteworthy that cocatalyst **16** led to a more active catalytic system than the *in situ* equivalent (18.1×10<sup>5</sup> vs. 10.2×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>, Tables 3, entry 1 and Table 2, entry 10, respectively).<sup>‡</sup> Reduction of the cocatalyst to iron ratio from 250 to 10 was reached by increasing the amount of iron complex used for the catalytic tests (to 150 μmol). The activity of this catalytic composition was one order of magnitude lower than when the cocatalyst to iron ratio was 250 (1.1×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>, Table 3, entry 2). The cocatalyst **17** proved also to activate catalyst precursor **A**, with an activity up to 23.2×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>, Table 3, entry 3) and a similar selectivity with K = 0.68. These large multinuclear structures may favor the formation of counterions that form stable ion pairs with cationic iron(II)-alkyl species likely to be considered as the active species in iron-catalyzed oligomerization or polymerization in the presence of MAOs.<sup>14</sup>

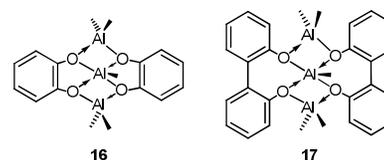


Fig 3 Trinuclear aluminum complexes

Table 3. Activation of iron complex **A** by well-defined cocatalysts **16** and **17**<sup>a</sup>

entry	cocatalyst	cocatalyst/Fe ratio	m <sub>C<sub>2</sub>H<sub>4</sub></sub> (g) <sup>b</sup>	activity <sup>c</sup>	K <sup>d</sup>
1	<b>16</b>	250	18.1	18.1	0.68
2 <sup>e</sup>	<b>16</b>	10	17.2	1.1	0.67
3	<b>17</b>	250	23.2	23.2	0.68

<sup>a</sup> Complex **A** (10 μmol), toluene (25 mL), P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 30 bar, T = 50 °C, 60 min. <sup>b</sup> mass of ethylene introduced. <sup>c</sup> ×10<sup>5</sup> g•(mol(Fe)•h)<sup>-1</sup>. <sup>d</sup> K = Schulz-Flory coefficient = k<sub>prop</sub>/(k<sub>prop</sub> + k<sub>ch transfer</sub>) = mol of C<sub>n+2</sub> oligomers / mol of C<sub>n</sub> oligomers. <sup>e</sup> Complex **A** (150 μmol).

## Conclusions

To conclude, we have established that reactions of phenol-, alcohol- and diol-derivatives with AlMe<sub>3</sub> lead to a new generation of cocatalysts, as easy-to-handle materials that promotes the iron complex-catalyzed oligomerization of ethylene. Aromatic diol derivatives are more efficient than phenol or alcohol compounds in the activation process. Among all, the best candidate is the 2,2'-biphenol with an optimum 2,2'-biphenol/AlMe<sub>3</sub> ratio of 2/3. Along with non-isolated mixtures, well-defined isolated cocatalysts were also successfully engaged leading to activation of iron(II) complex showing the potential of our system. Whether the cocatalysts were used *in situ* or isolated, activities remained lower than with MAO. While the nature of the active species for MAO-activated catalysts remains speculative, the development of such well-defined species,<sup>15</sup> as promising alternatives, supports further theoretical investigations by DFT to better understand the essential role of the cocatalyst in the activation step.<sup>16</sup> Further investigations will be focused on the determination of the role of each aluminum atom of the trinuclear structure in the activation process.

## Notes and references

<sup>‡</sup> It should be noted that Al/Fe ratios are different between the two experiments: Al/Fe = 750 for the well-defined cocatalyst **16**, Al/Fe = 250 for the cocatalyst formed *in situ*. This also suggests that all non-equivalent aluminum atoms do not have the same reactivity.

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