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## COMMUNICATION

## Access to highly active and thermally stable iron procatalysts using bulky 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine ligands<sup>†</sup>

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Ethylene polymerization was performed using a series of 2-[1-(2,6-dibenzhydrylphenylimino)ethyl]-6-[1-(arylimino)ethyl]-pyridyliron(II) chlorides with the activity in the range of  $10^7$  g PE mol<sup>-1</sup> (Fe) h<sup>-1</sup>, which is the highest observed in iron procatalysts at elevated reaction temperatures such as 80 °C in the presence of MMAO and 60 °C in the presence of MAO, without any trace of ethylene oligomerization.

The emergence of bis(imino)pyridyliron(II) chlorides marked a milestone in iron-based procatalysts for ethylene polymerization and oligomerization.<sup>1</sup> Research papers on bis(imino)pyridyliron(II) chlorides have mushroomed and were reviewed in a number of articles.<sup>2</sup> In addition, there has also been much work focusing on understanding the reactive species<sup>3</sup> as well as self-activating catalysts<sup>4</sup> of bis(imino)pyridyliron derivatives. Previously we reported iron procatalysts using nonsymmetrical bis(imino)pyridines<sup>5</sup> and designed bulky anilines, however, our ongoing project was halted because of concerns about any overlapping research and similar works reported by Gibson et al.<sup>6</sup> Consequently we have turned our attention iron(II) procatalysts employing new ligands such to 2-imino-1,10-phenanthrolines,<sup>7</sup> 2-(2-benzimidazolyl)-1, as 10-phenanthrolines,<sup>8</sup> 2-(benzoxazolyl)-1,10-phenanthrolines,<sup>5</sup> 2-benzimidazolyl-6-(1-(arylimino)ethyl)-pyridines,<sup>10</sup> 6-(quinoxalin-3-yl)-2-iminopyridines,<sup>11</sup> N-((pyridin-2-yl)methylene)-8aminoquinolines<sup>12</sup> and 2,8-bis(1-aryliminoethyl)quinolines.<sup>13</sup> These catalytic systems are useful for either oligomerization or polymerization of ethylene.<sup>2f</sup> Impeding the progress of bis(imino)pyridyliron(II) procatalysts in ethylene polymerization, the critical problems are their deactivation and production

of oligomers at elevated reaction temperatures.<sup>1*a*,6,14</sup> Though impressive bis(imino)pyridyliron procatalysts employing bulky anilines enhanced the thermostability,<sup>15</sup> exploring more bulky anilines is still an attractive subject. In addition, the design of new bis(imino)pyridyliron procatalysts which will perform solely ethylene polymerization with high activity at elevated reaction temperature (suitable for industrial consideration between 60 to 80 °C) is highly beneficial.

In the classical bis(imino)pyridyliron(II) system,<sup>1</sup> the aniline moiety bearing bulky substituents on the 2,6-positions resulted in a lower activity. However, the new iron(II) procatalysts bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(aryl-imino)ethyl]pyridines show high activity up to the range of  $2.2 \times 10^7$  g PE mol<sup>-1</sup> (Fe) h<sup>-1</sup> for solely ethylene polymerization and a unique thermal behavior with best performance in the presence of modified methylaluminoxane (MMAO) at 80 °C, or methylaluminoxane (MAO) at 60 °C.

The stoichiometric condensation reaction of 2,6-diacetylpyridine and 2,6-dibenzhydryl-4-methylphenylamine produced 2,6-bis[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]pyridine (L') as a minor product and 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-acetylpyridine as a major product, which further reacted with various anilines to form nonsymmetrical 2-[1-(2.6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino) ethyl]pyridines (L1-L5) (Scheme 1). The bis(imino)pyridines reacted with iron(II) dichloride to form the corresponding bis(imino)pyridyliron(II) dichlorides in good yields (Scheme 1). All organic and iron complexes were fully characterized, and the molecular structures of representative iron complexes were confirmed as a pseudo-square-pyramidal geometry by the single crystal X-ray diffraction. According to the molecular structure of Fe1 (Fig. 1), the chlorine Cl(2) occupied its apical position, and the square plane is formed with three nitrogen atoms N(1), N(2), N(3)and one chlorine Cl(1) atom. The iron lies 0.513 Å out of the plane of chelating nitrogen atoms, N(1), N(2) and N(3) (crystallographic data of Fe1, Fe3 and Fe5 and molecular structures of Fe3 and Fe5 are available in ESI<sup>†</sup>).

The catalytic behaviour of complex Fe3 was routinely evaluated for the optimum condition in the presence of either MAO or MMAO (Table 1). Under the ambient pressure of ethylene at room temperature, good activity was observed for ethylene polymerization in the presence of MMAO (entries 1–8, Table 1), whereas moderate activity was shown with

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthesis and characterization of organic and complex compounds, detail data of ethylene polymerization under 1 atm ethylene, and crystallographic data and ORTEP drawings for complexes Fe1, Fe3 and Fe5. CCDC 798843 (Fe1), 798844 (Fe3) and 798845 (Fe5). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05373b



Scheme 1 Synthesis of iron complexes Fe', Fe1-Fe5.



**Fig. 1** ORTEP drawing of complex **Fe1** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

MAO (entry 17, Table 1). The increasing temperature resulted in deactivation (entries 3, 5–8, Table 1) due to unstable active species and lower ethylene solubility.<sup>6,11c,12</sup>

Considering industrial application of highly exothermal polymerization, the critical factor is to maintain good activity within industrial operation temperature<sup>13</sup> such as around 60 °C for UHMPE (ultra high molecular weight polyethylene) or 80 °C even higher for common polyolefins. Then the evaluation was carried out under 10 atm ethylene (entries 9–16 and 18–23, Table 1), and the best performance was obtained with **Fe3**/ MMAO at 80 °C and Al/Fe molar ratio of 2000 (entry 15, Table 1), and **Fe3**/MAO at 60 °C and Al/Fe molar ratio of 1500 (entry 22, Table 1), respectively. At the Al/Fe molar ratio of 1500, polyethylenes with high molecular weights and narrow distributions were obtained as observed in our work<sup>16</sup> and by Brookhart,<sup>1a</sup> Gibson *et al.*<sup>14b</sup> A unique feature is that polyethylenes with narrow molecular distributions were noticeable

 Table 1
 The catalytic behaviour of complex Fe3<sup>a</sup>

Entry	Cocat.	Pres. atm	$T/^{\circ}\mathrm{C}$	Al/Fe	Activity <sup>b</sup>	${M_{ m w}}^c/{ m kg\ mol^{-1}}$	$M_{ m w}/M_{ m n}^{c}$	$T_{\rm m}{}^d/^{\circ}{ m C}$
1	MMAO	1	20	1000	0.67	39.0	23.6	129.3
2	MMAO	1	20	1500	1.04	47.0	31.6	125.1
3	MMAO	1	20	2000	1.64	5.8	7.5	123.0
4	MMAO	1	20	2500	1.29	42.2	31.5	124.7
5	MMAO	1	0	2000	1.44	47.8	17.4	130.0
6	MMAO	1	40	2000	1.12	2.1	3.6	118.0
7	MMAO	1	60	2000	0.37	1.1	2.3	98.0
8	MMAO	1	80	2000	0.17	1.0	2.0	67.3
9	MMAO	10	20	1500	2.45	374.7	88.7	130.0
10	MMAO	10	20	2000	3.20	365.0	49.5	127.5
11	MMAO	10	20	2500	2.85	131.3	15.6	129.1
12	MMAO	10	40	2000	5.07	39.7	13.5	124.6
13	MMAO	10	60	2000	7.80	21.8	6.3	130.0
14	MMAO	10	70	2000	9.51	15.7	3.8	128.3
15	MMAO	10	80	2000	11.9	17.7	4.3	129.3
16	MMAO	10	90	2000	6.67	11.0	2.9	134.0
17	MAO	1	20	2000	0.26	93.2	70.2	127.0
18	MAO	10	20	1000	2.00	299.0	19.3	135.7
19	MAO	10	20	1500	3.44	355.5	34.8	134.0
20	MAO	10	20	2000	2.43	338.0	44.3	134.7
21	MAO	10	40	1500	3.07	187.3	19.2	134.3
22	MAO	10	60	1500	9.95	166.5	10.9	136.7
23	MAO	10	80	1500	4.89	53.1	4.93	133.0

<sup>*a*</sup> General conditions: 1.5 µmol Fe; 30 min; 30 mL toluene for 1 atm ethylene, and 100 mL toluene for 10 atm ethylene. <sup>*b*</sup> 10<sup>6</sup> g mol<sup>-1</sup> (Fe) h<sup>-1</sup>. <sup>*c*</sup> Determined by GPC. <sup>*d*</sup> Determined by DSC.

at elevated temperature, but the bimodal or multimodal polyethylenes were produced at 40  $^{\circ}$ C and lower reaction temperature due to multi-active species formed in the catalytic system.

Subsequently, polymerization behaviors of all iron procatalysts were exploited using MAO at 60 °C and Al/Fe molar ratio of 1500 under 10 atm ethylene (Table 2). The activities decreased in the order of Fe1 > Fe2 > Fe3 consistent with increase in the bulk of the ortho-substituent in the imino groups, whilst random effects of the additional para-methyl in the imino groups were observed within Fe1 and Fe4, Fe2 and Fe5. However, the procatalyst Fe' displayed moderate activity due to steric bulk. As a reference, the 2,6-bis [1-(2,6-diisopropylphenylimino)ethyl]pyridyliron(II) chloride (FeR) displayed good activity in polymerization, but with a little (likely ignorable) oligomers. Fe1-Fe5 showed sole polymerization without any trace of oligomers being observed, and higher activities were observed for Fe1, Fe2 and Fe5 than FeR. The molecular weights and distributions of resultant polyethylenes controllably relied on the nature of ligands used.

 Table 2
 Ethylene polymerization using MAO<sup>a</sup>

Entry	Procat.	Activity $10^6 \text{ g mol}^{-1}$ (Fe) $\text{h}^{-1}$	$M_{\rm w}^{\ \ b}/{ m kg}~{ m mol}^{-1}$	$M_{ m w}/M_{ m n}^{\ b}$	$T_{\rm m}{}^c/{}^{\circ}{ m C}$
1	Fe1	13.1	313.7	16.4	134.0
2	Fe2	12.4	260.0	8.8	132.3
3	Fe3	9.95	166.5	10.9	136.7
4	Fe4	4.89	443.1	23.4	133.7
5	Fe5	22.3	99.8	8.3	132.7
6	Fe'	0.76	285.2	7.2	134.4
7	FeR	5.71	101.6	14.1	133.3

<sup>*a*</sup> Conditions: 1.5 μmol of Fe; 100 mL toluene; 30 min. <sup>*b*</sup> Determined by GPC. <sup>*c*</sup> Determined by DSC.

 Table 3 Ethylene polymerization using MMAO<sup>a</sup>

Entry	Procat.	Activity 10 <sup>6</sup> g mol <sup>-</sup> (Fe) h <sup>-1</sup>	$M_{\rm w}^{\ \ b}/{ m kg\ mol^{-1}}$	$M_{ m w}/M_{ m n}^{\ b}$	$T_{\rm m}{}^c/{}^{\circ}{ m C}$
1	Fe1	21.5	7.6	1.6	129.3
2	Fe2	19.4	6.5	1.5	131.0
3	Fe3	11.9	17.7	4.3	129.3
4	Fe4	22.4	25.5	5.1	129.7
5	Fe5	5.10	294.9	12.2	133.7
6	Fe'	Trace	_		
7	FeR	4.80	178.5	22.7	130.0
<i>a</i> <b>c</b>	1	5 1 C E A1	E 2000 + + 1	1 .	

<sup>a</sup> Condition: 1.5 µmol of Fe; Al/Fe: 2000; total volume: 100 mL; reaction time: 30 min: reaction temperature: 80 °C. <sup>b</sup> Determined by GPC. c Determined by DSC.

Extensively, all procatalysts were investigated under 10 atm ethylene in the presence of MMAO with Al/Fe molar ratio of 2000 at 80 °C (Table 3). A similar catalytic behaviour was observed for these iron complexes. Comparison with systems employing MAO, the optimum temperature with MMAO illustrated 20 °C higher up to 80 °C, the commonly used industrial temperature. Fe1-Fe5 performed sole polymerization without any trace of oligomers being observed, but Fe' showed a negative response to ethylene polymerization while FeR showed good activity in ethylene polymerization. Generally Fe1-Fe4 showed higher activities than FeR. In comparison with MAO, different influences by the para-methyl were within Fe1 and Fe4, Fe2 and Fe5 due to plausible electronic effects. Considering the industrial application of 2.6-bis(imino)pyridyliron(II) procatalysts in ethylene polymerization, with the best of our knowledge, the current iron complexes bearing the nonsymmetric 2,6-bis(imino)pyridines have the high potential relying on not only the high activity maintained at elevated reaction temperature but also obtaining polyethylenes with controllable molecular weights and distributions. In addition, there is an important advantage of obtaining polyethylenes without any trace of ethylene oligomerization.

Within iron procatalysts bearing the nonsymmetric 2,6bis(imino)pyridines, the bulk of one 2,6-dibenzhydrylaniline was helpful in stabilizing the complexes. The nonsymmetrically spherical environment, besides the active species commonly obtained within 2,6-bis(imino)pyridyliron procatalysts, oriented the orderly spaces for ethylene coordination and growing stretch polymer chain, therefore, the combined influences resulted in active species favorable for ethylene coordination and chain propagation. This represents a success of fine-tuning 2,6-bis(imino)pyridyliron dichlorides, and the catalytic activities were improved from analogues bearing symmetrical ligands such as Fe' and FeR (represents common 2,6-bis(imino)pyridyliron dichlorides).<sup>1,15,17</sup>

In summary, the 2-[1-(2,6-dibenzhydrylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyliron(II) procatalysts showed high activities in ethylene polymerization at 80 °C with MMAO and 60 °C with MAO, without any trace of oligomers. Beyond the high activity and industrially suitable temperature, the molecular weights and distributions of resultant polyethylenes could be controllable. The iron procatalysts are worthy of further investigation, and are potentially applicable for industrial consideration.

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