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Highly active and selective ethylene oligomerization catalysts: Asymmetric 2,6-bis(imino)pyridyl iron (II) complexes with alkyl and halogen substitutients

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ABSTRACT

A series of asymmetric 2,6-bis(arylimino)pyridines with alkyl and halogen substitutients on different iminoaryl rings and corresponding iron (II) complexes ($[2-(Ar_1N = CCH_3)-6-(Ar_2N = CCH_3)C_5H_3N]FeCl_2$, **3a–3j**) are synthesized and characterized. These Fe(II) complexes are highly active for ethylene oligomerization with high selectivity for linear α -olefins. The oligomer distributions can be tuned by the synergism of alkyl-steric effect and halogen electronic effect, and the production of C_6-C_{16} can reach more than 80% with the highest selectivity being 87.5% for **3 g** ($Ar_1 = 2$ -ethylphenyl, $Ar_2 = 2$ -fluorophenyl), which is 15–30% higher than that catalyzed by their methyl or fluoro-substituted symmetric counterparts.

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Linear α -olefins are essential feedstocks in the preparation of surfactants, plasticizers, synthetic lubricants, fine chemicals, and linear low-density polyethylene (LLDPE). Industrially, linear α olefins are mainly manufactured by oligomerization of ethylene which generally produces wide distributions of linear α -olefins with a range of C_4/C_6 up to C_{20}^+ . This process affords a variety of important chemical intermediates; however, the broad distribution of linear α -olefins does not closely match market demand. For example, the output of C₄ has far exceeded the market demand, and high-molecular-weight α -olefins (C⁺₁₈) have lesser commercial value. As such the development of more selective routes to desired linear α -olefins is currently of industrial and academic interest. One challenge is to design ethylene oligomerization catalysts with higher catalytic activity and selectivity for C₆-C₁₆. Since Ziegler's original work on AlR₃ catalysis of ethylene oligomerization [1], there has been considerable interest in developing new oligomerization-active catalysts. Various transition metals such as nickel, chromium, titanium, zirconium, and others have been proven to be effective oligomerization catalysts [2–15].

In 1998, Brookhart [16,17] and Gibson [18,19] independently reported that bis(arylimino) pyridyl iron and cobalt complexes, when activated by MAO, are highly active for the polymerization and oligomerization of ethylene. The products could be tuned by an alkyl-steric effect, and the presence of one small *ortho* substituent on the aryl groups generates catalysts that selectively oligomerize ethylene

to Schulz–Flory distributions of α -olefins with high productivity and exceptional purity (97–99%), but a little polyethylene with average molecular weight 700 exists inevitably in the oligomers due to alkyl-steric effect [19]. Since these initial developments, various iron and cobalt complexes bearing different alkyl-substituted bis(imino) pyridyl ligands have been reported [20,21]. Recently Qian et al. introduced electron-withdrawing halogen substituents (F, Cl, Br, I) into the iminoaryl ring's ortho positions and found that the corresponding iron and cobalt complexes are also very active for ethylene polymerization or oligomerization [22–24]. The iron and cobalt complexes with two fluoro, one bromo, or one iodo substituent can oligomerize ethylene with high activity and selectivity, yet with no production of polyethylene. However, the proportion of C₄ (~30%) is too high.

Here we designed and synthesized a series of new asymmetric 2,6bis(arylimino)pyridyl iron (II) complexes with alkyl and halogen substitutients on different iminoaryl rings (Scheme 1). The complexes are highly active and selective due to the synergistic steric and electronic effect, which can remarkably increase the proportion of C₆– C₁₆ in oligomers compared with the symmetric alkyl or halogensubstituted complexes.

The new asymmetric 2,6-bis(imino)pyridines (2) can be synthesized by the successive condensation reactions of 2,6diacetylpyridine with an alkyl-substituted aniline and a halogensubstituted aniline (Scheme 2). 2,6-Diacetylpyridine can react with alkyl-substituted aniline to obtain mono(arylimino)pyridine firstly under high temperature or refluxing in toluene, and the mono(imino)pyridine can further react with halogen-substituted aniline to produce asymmetric 2,6-bis(imino)pyridines catalyzed by silica-alumina catalyst support under mild reaction conditions [25].

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Scheme 1. Asymmetric 2,6-bis(imino)pyridyl iron (II) complexes.

The Fe(II) complexes can similarly be synthesized according to literature [22,23] with high yields and characterized by IR and EA.

The asymmetric 2,6-bis(arylimino)pyridyl iron (II) complexes, activated by modified methylaluminoxane (MMAO), are highly active catalysts for ethylene oligomerization. The detailed results are summarized in Table 1. The catalytic activity of 3a, 3b and 3g can reach more than 10^6 g mol⁻¹ h⁻¹ atm⁻¹, which are higher than that of methyl or fluoro-substituted symmetric 2,6-bis(arylimino)pyridyl iron (II) complexes. The products are mainly linear α -olefins, with the highest yield of above 98%. The distributions of α -olefins are between C_4 and C_{24} and no polymers were found in the products. The catalytic performances, especially for oligomer distributions, can be tuned by the synergistic steric and electronic effect. The selectivity for C_6-C_{16} can reach more than 80% in oligomers catalyzed by complexes 3a, 3g and 3i, which is 15-30% higher than that catalyzed by methyl or fluoro-substituted symmetric 2,6-bis(imino)pyridyl iron (II) complexes and demonstrates great potential for industrial application.

The influences of the reaction temperature on ethylene oligomerization were investigated with complex 3b, as detailed in Table 1. Elevation of the reaction temperature from 0 to 40 °C results in a sharp decrease in catalytic activity, which may be attributed to catalyst decomposition and decreased ethylene solubility at higher temperature [19]. The temperature also greatly influences the oligomer distributions, as shown in Fig. 1(a). The content of C₄ was increased remarkably as the temperature elevates from 0 to 40 °C, probably due to guicker rates of chain transfer and B-hydrogen elimination than

Table 1 Ethylene oligomerization by complexes 3a-31/MMAO^a.

Run	Complex	Al/Fe	Т	$Oligmer(C_n / \sum c, \%)$			α	LAO ^b	Activity ^c
			(°C)	C ₄	C ₆ -C ₁₆	C ₁₈			
1	3a	1000	20	10.4	81.1	8.5	0.68	96.8	1.43
2	3b	1000	20	18.7	75.9	5.4	0.57	98.7	1.19
3	3b	500	20	6.8	69.5	19.8	0.84	98.2	1.84
4	3b	1500	20	20.0	75.1	4.9	0.69	93.6	1.32
5	3b	2000	20	22.2	74.3	3.5	0.66	87.6	0.82
6	3b	1000	0	7.3	65.4	27.3	0.77	96.5	3.03
7	3b	1000	40	32.7	60.9	6.4	0.71	84.6	0.38
8	3c	1000	20	40.8	59.2	0	0.37	71.4	0.20
9	3d	1000	20	28.9	67.4	3.7	0.54	94.1	0.61
10	3e	1000	20	12.1	76.2	11.7	0.65	92.5	0.52
11	3f	1000	20	8.3	72.0	13.7	0.60	89.8	0.67
12	3g	1000	20	9.3	87.5	3.2	0.58	90.5	1.15
13	3h	1000	20	32.9	67.1	0	0.48	83.2	0.92
14	3i	1000	20	16.3	82.5	1.2	0.45	91.6	0.79
15	3j	1000	20	16.3	79.0	4.7	0.54	89.6	0.68
16	3k	1000	20	9.8	72.9	17.3	0.75	92.8	0.81
17	31	1000	20	37.2	58.3	4.5	0.59	81.9	0.33

Reaction conditions: 10 µmol catalyst; 1 h; 1 atm of ethylene, 30 ml of toluene. ^b Linear α -olefin.

 c 10⁶ g mol⁻¹ h⁻¹ atm⁻¹.

chain propagation at higher temperature [26]. The C_6-C_{16} portion in oligomers can reach more than 75% and the selectivity for linear olefin is higher than 98% at 20 °C.

From Table 1 and Fig. 1(b), it can be seen that Al/Fe molar ratio can also affect the catalytic behavior. However, the effects of Al/Fe molar ratio on catalytic activity are not as evident as reaction temperature. The catalytic activity of complex 3b remains at a high level when the Al/Fe molar ratio was increased from 500 to 1500, but decreases as the Al/Fe molar ratio further increases to 2000. Also with the increase of Al/Fe Molar ratio, the production of C₄ increases while the selectivity for longer-chain oligomers decreased, which may be attributed to quicker rates of chain transfer.

The steric alkyl substuituent has profound effect on oligomer distribution (Fig. 2). As shown in Fig. 2(a), with halogen substituents



Scheme 2. Synthesis of asymmetric 2,6-bis(imino)pyridines and corresponding Fe(II) complexes.



Fig. 1. The effect of reaction conditions on oligomer distribution obtained from complex 3b, (a) reaction temperatures, and (b) Al/Fe molar ratio.

being the same and alkyl substitutents different in complex 3b (methyl) and 3g (ethyl), 3b produces significantly more C₄ than 3b, which could be attributed to the smaller alkyl-steric effect and subsequently quicker rates of chain transition or β -hydrogen elimination. Moreover, similar trends also exist in 3c/3h (Fig. 2(b)) and 3d/3i (Fig. 2(c)), which is in accordance with the catalytic behavior of symmetric alkyl-substituted 2,6-bis(arylimino)pyridyl iron (II) complexes. The steric effects apparently also work in asymmetric 2,6-bis(imino)pyridyl iron (II) complexes, and can be used to inhibit the production of the low-molar-mass oligomers (C₄).

Electronic effects have important influences on the catalytic performance. Qian et al. found that the catalytic performance of symmetric 2,6-bis(imino)pyridyl iron (II) complexes with halogen groups in ligands can be improved evidently compared with that having alkyl ones [22,23]. The electron-withdrawing halogen groups can also exert influences on catalytic behaviors of the asymmetric 2,6bis(imino)pyridyl iron (II) complexes. It was found that the complexes with only one fluoro atom on imino-N aryl ring's ortho positions have higher oligomerization activity (Table 1). The introduction of electron-withdrawing group can increase the electrophilicity of the central metal Fe and the coordination of ethylene, which would enhance the catalytic activity [22,23]. However, the catalytic activity decreased as more fluoro atoms were introduced into the phenyl ring of the imino nitrogen, which is similar to the symmetric 2,6-bis(imino)pyridyl iron (II) complexes with multifluoro atoms on aryl ring [27] and the titanium complexes with β enaminoketonato ligands or β -diiminato ligands [28,29]. A possible explanation is that the stronger electron-withdrawing fluoro atoms would weaken the electron donation ability of the ligand, which would make the active species decompose more easily during the polymerization [30,31].

The electronic effect of halogen groups is also demonstrated in oligomer distributions (Fig. 3). When one of the methyl groups on the iminoaryl rings of complex 3k was substituted by a fluorine atom (3b), much more C_4 and much less C_{18}^+ are produced (Fig. 3(a)). Furthermore, when comparing complexes 3a, 3b, 3d and 3l, which are with gradually enhanced electron-withdrawing effect, a similar trend is clearly seen (Fig. 3(b)). Similar results are also observed in the complexes 3f, 3g, 3i and 3l as shown in Fig. 3(c). So the electronic effect of halogen can be utilized to inhibit the production of high-molecular oligomers.



Fig. 2. The steric effect on oligomer distribution, (a) 3b and 3g, (b) 3c and 3h, and (c) 3d and 3i.



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Fig. 3. The electronic effects on oligomer distribution, (a) 3b and 3k, (b) 3a, 3b, 3d and 3l, and (c) 3f, 3g, 3i and 3l.

In summary, a series of asymmetric bis(arylimino) pyridyl iron complexes with alkyl and halogen substitutients on different iminoaryl rings of ligands are synthesized and characterized. These complexes were found to catalyze ethylene oligomerization with high activity and selectivity. Incorporation of steric alkyl and electronwithdrawing halogen groups on different imino aryl rings led to the augmentation of the more useful C_6-C_{16} portion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.07.003.

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