Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene

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Study of the polymerization of olefins by soluble, well-defined transition metal complexes is an ever-growing area. While most attention has been focused on early transition metal d^0 and lanthanide d^0f^n systems,[1] recently late metal Pd(II)- and Ni(II)-catalyst systems incorporating α-diimine ligands have been reported which convert both ethylene and α-olefins to high molar mass polymers.[2] Unique features of these systems include the ability to produce highly branched polymers from ethylene and to copolymerize ethylene with certain polar monomers using the Pd(II) catalysts. Most late metal systems produce low molecular weight oligomers from ethylene and particularly α-olefins. The key to high polymer production using the aryl-substituted α-diimine systems is the incorporation on the aryl rings of bulky *ortho* substituents that greatly retard the rate of chain transfer. We report here the synthesis of tridentate Fe(II) and Co(II) complexes incorporating bulky substituted arylimine moieties and demonstrate that these are extremely active and long-lived catalysts for the polymerization of ethylene.

The tridentate ligands used in this study are pyridine diimine ligands of general structures **1**−**3** prepared by the Schiff-base condensation of 2 equiv of the desired aniline with 2,6-diacetylpyridine. The precatalysts, formed by addition of the ligand to the appropriate hydrated or anhydrous metal salt (Scheme 1), are neutral Fe(II) and Co(II) complexes $\{[(2,6\text{-ArN}{=}\text{C(Me)})_2\text{C}_5\text{H}_3\text{N}]\text{MX}_2\}$ (Ar = 2,6-$\text{C}_6\text{H}_3(i\text{-Pr})_2$, **1**; 2,6-$\text{C}_6\text{H}_3\text{Me}_2$, **2**; 2-$\text{C}_6\text{H}_4(t\text{-Bu})$, **3**; M = Fe, **a**; Co, **b**; X = Cl^-, Br^-, NO_3-). Figure 1 shows the X-ray crystal structure for 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride (**1a**).[3] The structure for 2,6-bis[1-(2-*tert*-butylphenylimino)ethyl]pyridinecobalt(II) chloride (**3b**) is shown in the Supporting Information.[4] Both complexes are pentacoordinate with pseudo-square-pyramidal geometry, the most notable features being the nearly perpendicular arrangement in both complexes of the aryl rings relative to the square plane as well as the syn conformation of the *tert*-butyl groups in complex **3b**. Complexes **1a**-**b**, **2a**-**b**, and **3a**-**b** are paramagnetic, high-spin species, as indicated by magnetic susceptibility measurements.[5] Both the crystallographic data and the magnetic susceptibility measurements are consistent with the results reported for similar complexes lacking *ortho* substituents on the aryl rings.[6]

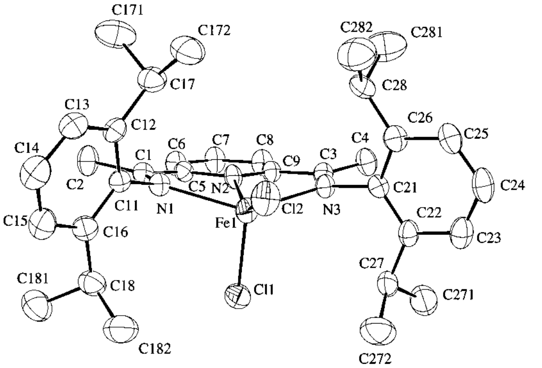
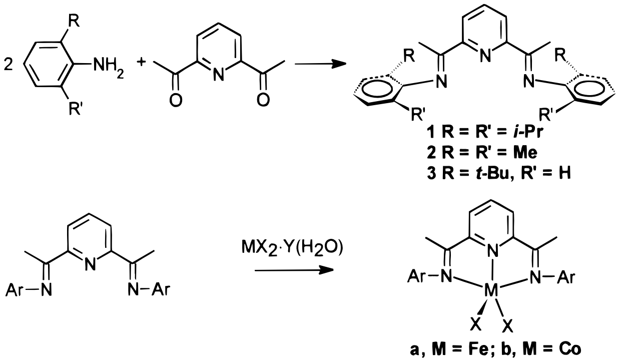


Figure 1. X-ray crystal structure of **1a**. Selected bond distances (Å) and angles (deg): Fe(1)−N(1), 2.222(4); Fe(1)−N(2), 2.091(4); Fe(1)−N(3), 2.225(5); Fe(1)−Cl(1), 2.3173(19); Fe(1)−Cl(2), 2.2627(17); Cl(1)−Fe(1)−Cl(2), 117.58(7); N(1)−Fe(1)-Cl(1), 100.57(12); N(3)−Fe(1)-Cl(1), 102.47(12); N(2)−Fe(1)−Cl(1), 94.52(13); N(1)−Fe(1)−N(3), 140.23(16); N(1)−Fe(1)−N(2), 73.67(16).

Scheme 1



The active catalysts are generated in situ in toluene by the addition of modified methylalumoxane (MMAO, ≥ 300 equiv) to the precursors in the presence of ethylene (Scheme 1). Data for the polymerizations of ethylene are summarized in Table 1.[7] All of the catalysts reported convert ethylene to highly linear polyethylene (PE) as determined by differential scanning calorimetry (T_m values 133−139 °C).[8] In contrast to the Ni(II)- and Pd(II)-diimine catalysts, no branching is observed, even with the bulkiest ligands at high temperatures and low ethylene pressures. However, the polymer molecular weights vary dramatically with modifications in ligand, metal, and concentration of activator. Like the Ni(II) and Pd(II) systems, increasing the steric bulk of the *ortho* aryl substituents increases molecular weight. For example, the tetraisopropyl-substituted Fe system (**1a**/MMAO, Table 1, entry 1) yields a polymer with a peak MW of 71K, while the

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[2] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

[3] Crystal data of **1a**: triclinic, $P\bar{1}$, blue; $a = 8.7953(6)$ Å, $b = 9.8587(6)$ Å, $c = 20.9583(13)$ Å; $V = 1646.45(18)$ Å^3; $Z = 2$; $R = 0.060$; GOF = 2.52.

[4] Crystal data of **3b**: triclinic, $P\bar{1}$, gold; $a = 12.7329(7)$ Å, $b = 15.7633(8)$ Å, $c = 15.8220(8)$ Å; $V = 3138.5(3)$ Å^3; $Z = 4$; $R = 0.084$; GOF = 2.90.

[5] Magnetic susceptibilities (μ_{eff}, BM) were determined for the following complexes: **1a**, 5.54; **2a**, 5.22; **3a**, 5.00; **1b**, 4.55; **2b**, 4.67; **3b**, 4.65. See Supporting Information for experimental details.

[6] (a) Edwards, D. A.; Edwards, S. D.; Martin, W. R.; Pringle, T. J.; Thornton, P. *Polyhedron* **1992**, *11*, 1569. (b) Goldschmied, E.; Stephenson, N. C. *Acta Crystallogr.* **1970**, *B26*, 1867. (c) Reiff, W. M.; Erickson, N. E.; Baker, W. A., Jr. *Inorg. Chem.* **1969**, *8*, 2019.

[7] Nearly equivalent activities are observed when the corresponding Fe(III) complexes (prepared from ligands **1**−**3** and the corresponding FeX_3 hydrates) are activated with MMAO.

[8] All methyl groups visible by ^{13}C NMR are attributable to end groups; there are less than 0.4 methyl branches per 1000 carbons. Heat of fusion data from the DSC traces indicates very high crystallinity (226 J/g vs 170 J/g for commercial HDPE).

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Table 1. Results of Ethylene Polymerization by 1a-b, 2a-b, and 3a-b in Toluene

entry	catalyst[a]	loading (μmol)	pressure (psig)	temp (°C)	reaction length (min)	yield (g)	peak[b] MW	TOF[c]($\times 10^{-6}$/h)
1	**1a**	1.1	15	25	50	3.09	71 000	0.12
2	**2a**	1.2	15	25	50	2.78	33 000	0.10
3	**3a**	1.3	15	25	50	2.88	81 000	0.10
4	**1a**	0.6	15	0	50	1.35	19 000	0.09
5	**2a**	0.6	15	0	50	1.17	15 000	0.08
6	**3a**	0.7	15	0	50	1.36	56 000	0.09
7	**1b**	1.4	15	25	50	1.20	24 000	0.04
8	**2b**	1.6	15	25	50	2.99	1 400	0.08
9	**3b**	1.2	15	25	50	1.00	183 000	0.04
10	**1b**	0.8	15	0	50	0.45	43 000	0.02
11	**2b**	0.9	15	0	50	0.59	3 700	0.03
12	**3b**	1.0	15	0	50	1.36	v. high[d]	0.06
13	**1b**	8.0	200	50	12	17.5	11 300	0.39
14	**1b**	7.9	400	50	12	17.5	9 700	0.40
15	**1b**	8.0	600	50	12	21.6	8 900	0.48
16	**1a**	0.6	200	60	10	12.8	26 600	4.8
17	**1a**	0.5	400	60	10	17.3	27 600	7.0
18	**1a**	0.5	600	60	10	28.5	31 100	11.8
19	**1a**	1.3	600	90	10	46.6	17 400	7.6
20	**2a**	4.2	600	125	10	107.6	9 000	5.5

[a] All of the precursor complexes were activated with MMAO. [b] Entries 1−6 exhibit bimodal molecular weight distributions. [c] Entries 1−6 and 19−20 are likely mass transport limited. [d] The sample was not soluble.

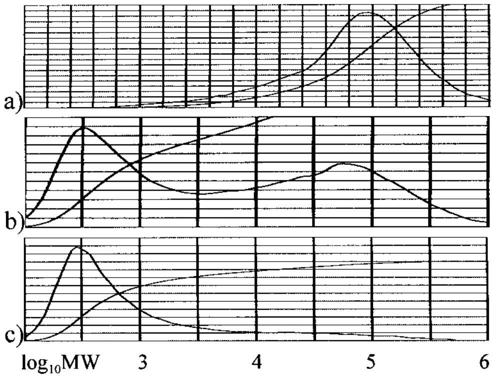

Figure 2. Activator effect on molecular weight (catalyst **1a**/MMAO, 25 °C, 15 min, 1 atm ethylene): (a) 300 equiv of Al, $M_N = 20\,900$, $M_W = 135\,000$; (b) 1500 equiv of Al, $M_N = 709$, $M_W = 52\,400$; (c) 4500 equiv of Al, $M_N = 390$, $M_W = 9570$.

tetramethyl system (**2a**/MMAO, entry 2) shows the peak MW at 33K.[9] For comparison of the cobalt analogues, see entries 7 and 8. Generally, the iron systems produce higher molecular weight materials relative to their cobalt analogues (entries 1 vs 7 and 2 vs 8), but the *tert*-butyl-substituted systems do not exhibit this trend (entry 3 vs 9).

For the iron systems in particular, increasing the amount of activator leads to broadened polydispersities and bimodal behavior (Figure 2). This observation is consistent with the proposal that chain transfer to aluminum is a viable route for the formation of low molecular weight materials early in the polymerization.[10,11] Thus, by using large amounts of activator or short reaction times, predominantly low molecular weight polymers are made (see GPC trace c, Figure 2).

In the case of the iron catalysts, the turnover frequencies (TOFs) increase with ethylene pressure as shown by the 60 °C runs (entries 16−18) where TOFs are 4.8×10^6/h at 200 psig, 7.0×10^6/h at 400 psig, and 11.8×10^6/h at 600 psig, thus establishing that the rate of chain growth is dependent on ethylene concentration. In contrast, the TOFs of the cobalt analogues at 50 °C show little dependence on ethylene pressure under these conditions−3.9×10^5/h at 200 psig, 4.0×10^5/h at 400 psig, and 4.8×10^5/h at 600 psig (entries 13−15). The activities of the iron catalysts are remarkably high; TOFs of greater than 10^7/h can be achieved at 60 °C and 600 psig C_2H_4 (entry 18) which corresponds to 3.3×10^5 kg PE/mol Fe•h! These activities are thus comparable to the most active Ziegler−Natta systems.[12] The cobalt complexes generally exhibit activities that are an order of magnitude lower than their iron analogues. The catalysts are stable at elevated temperatures as demonstrated by runs 19 and 20. In these cases activation with an increased catalyst loading resulted in rapid exotherms to 90 and 130 °C, respectively. These temperatures remained constant for the duration of each run.

In summary, using the previously examined Ni(II) and Pd(II) α-diimine catalysts as a guide, we have prepared new iron(II) and cobalt(II) catalysts based on tridentate pyridine bis-imine ligands in which the imine moieties are bulky *ortho*-substituted aryl imines. These catalysts are robust and extremely active for polymerization of ethylene to linear, high-density polyethylene. To the best of our knowledge, these are the first reported iron-based homogeneous catalysts for ethylene polymerization. Mechanistic studies are in progress.

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Supporting Information Available: Crystal structure data for **1a** and **3b**, syntheses of ligands and complexes, magnetic susceptibility data, polymerization procedures, and polymer characterization data (selected GPC and DSC traces; ^{13}C NMR data) (30 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(9) Bimodal behavior is sometimes observed with a low MW fraction due to chain transfer (see text). If a distinct low MW fraction is not observed, then low molecular weight shoulders or tails are seen. Thus, the best measure of the molecular weight of the high MW fraction is the peak MW. See Supporting Information for sample gpc traces.

(10) As an alternative explanation for bimodal behavior, a referee suggested the existence of two catalytic species whose ratios vary with changing Al:Fe ratios. However, we have shown by ^{1}H NMR that the end groups of the low M_N materials are saturated, which supports chain transfer via transmetalation.

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