Iron-Based Catalysts with Exceptionally High Activities and Selectivities for Oligomerization of Ethylene to Linear α-Olefins

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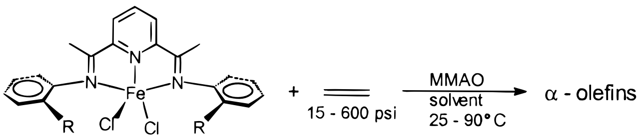
α-Olefins are produced worldwide at a rate of ca. 4 × 10^9 lb/year, predominantly through oligomerization of ethylene.[1] They are used primarily as comonomers for production of linear low-density polyethylene and manufacture of detergents and synthetic lubricants. Catalysts currently used in industry include neutral Ni(II) complexes bearing bidentate monoanionic ligands[1−3] that are the basis for the Shell Higher Olefin Process (SHOP)[2] and aluminum alkyls which find utility in the processes of both Chevron and Amoco.[1a] Additionally, we recently reported that cationic Ni(II) α-diimine complexes are also effective ethylene oligomerization catalysts,[4] and Bazan has reported that certain bis(boratabenzene)zirconium complexes will produce α-olefins from ethylene.[5] Recently the discovery of highly active iron and cobalt ethylene polymerization catalysts that incorporate bulky, tridentate pyridinebisimine ligands was reported by both Gibson[6] and us.[7] We report here that by reducing the steric bulk of these pyridinebisimine ligands the resultant iron catalysts oligomerize ethylene to linear α-olefins with remarkably high activity and selectivity while maintaining desirable oligomer distributions.[6]

Pyridinebisimine complexes **1**−**3** $\{[(2\text{-ArN}{=}C(Me))_2\text{-}C_5H_3N]FeCl_2\}$ (Ar = 2-C_6H_4Me, **1**; 2-C_6H_4Et, **2**; 2-C_6H_4(*i*-Pr), **3**) bearing only a single ortho substituent on each aryl ring were readily prepared by procedures described previously.[7] These complexes, when activated with MMAO[8] in aromatic or aliphatic hydrocarbon solvents, oligomerize ethylene to α-olefins with exceptionally high turnover frequencies (TOFs) and selectivities (Scheme 1). Results are summarized in Table 1.

Turnover frequencies are dependent on catalyst structure, ethylene pressure, and temperature. The methyl-substituted complex **1** exhibits the highest activity with turnover frequencies ranging from 1.0 × 10^5/h at 25 °C and 1 atm to an astonishing 1.8 × 10^8/h (5.0 × 10^6 kg of oligomer/(mol of Fe·h)) at 90 °C and 600 psig. Entries 3 and 4 (60 °C runs) and 6−8 (90 °C runs) clearly show that there is a rate dependence on ethylene pressure, while at 200 psig, entries 2, 3, and 6 demonstrate the increased and sustained activity of the catalysts with increasing temperature.[9] Sterically bulkier catalysts result in somewhat reduced activities as shown by comparing the methyl-substituted catalyst **1** with the ethyl-substituted **2** under similar conditions (entry 4 vs entry 11; 72 × 10^6 vs 20 × 10^6 turnovers/h).

Scheme 1



1 **R = Me**
2 **R = Et**
3 **R = *i*-Pr**

Table 1. Results of Oligomerization of Ethylene with Catalysts **1**−**3**

	cat.[a]	loading (μmol)	reactn length (min)	*P*[b]	*T* (°C)	yield (g)[c]	*K*	TOF (×10^{-6}/h)	solvent	% α-O[d]
1	1	5.7	180	1 atm	25	22.7	.81	0.1	toluene	>95
2	1	0.13	120	200	35	112	.74	15.5	toluene	>99
3	1	0.10	30	200	60	36	.73	25.3	toluene	>99
4	1	0.10	30	400	60	95	.73	72.1	toluene	>99
5	1	0.24	15	300	80	48	.71	28.5	toluene	>99
6	1	0.13	30	200	90	68	.70	38.1	toluene	>99
7	1	0.13	30	400	90	136	.70	75.8	toluene	>99
8	1	0.09	30	600	90	245	.70	177.0	toluene	>99
9	2	2.2	60	1 atm	25	5.0	.81	0.08	toluene	>98
10	2	0.13	30	200	60	31	.79	17.1	toluene	>99
11	2	0.11	30	400	60	31	.79	19.7	toluene	>99
12	2	0.07	30	200	50	24	.82	24.1	hexanes	>99
13	2	0.05	30	400	50	22	.82	29.8	hexanes	>99
14	2	0.05	30	600	50	21	.82	29.5	hexanes	>99
15	3	1.7	60	1 atm	25	4.1	.87	0.08	toluene	>99

[a] All pre-catalysts were activated with MMAO. [b] Pressure, units of psig unless otherwise indicated. [c] The yields were calculated as described in the Supporting Information. [d] % α-olefin content determined by GC and ^{1}H NMR spectroscopy.

The oligomer distribution in all cases is Schulz−Flory,[10] and the *K* value characteristic of this distribution (eq 1) is given for

$$K = k_{\mathrm{prop}}/(k_{\mathrm{prop}} + k_{\mathrm{ch\ transfer}}) = \text{mol of } C_{n+2} \text{ oligomers/mol of } C_n \text{ oligomers} \quad (1)$$

each run in Table 1. Increasing the steric bulk of the ortho substituent leads to an increase in *K*, a trend seen by comparing entries 3 and 10 or 9 and 15. The *K* values do not vary with changes in ethylene pressure, as shown in entries 6−8 and 12−14. The pressure *dependence* of the TOF and the pressure *independence* of *K* suggest that both chain growth and chain transfer are first order in monomer.[11] As the temperature is

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[1] For recent reviews, see: (a) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Publishers: 1996; Vo1. 1; pp 245−256. (b) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; John Wiley & Sons: NewYork, 1992; pp 68−72. (c) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

[2] (a) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (b) Keim, W.; Behr, A.; Limbacker, B.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (c) Keim, W.; Behr, A.; Kraus, G. *J. Organomet. Chem.* **1983**, *251*, 377. (d) Peuckert, M.; Keim, W. *J. Mol. Catal.* **1984**, *22*, 289. (e) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21.

[3] For other neutral Ni(II)-based catalysts, see: (a) Desjardins, S. Y.; Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *515*, 233. (b) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2203 and references herein.

[4] Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005.

[5] (a) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (b) Barnhart, R. W.; Bazan, G.; Mourey, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082.

[6] Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. These authors report one iron catalyst that produces ethylene oligomers with M_ws of ca. 260−470, but few details are given.

[7] Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.

[8] MMAO is a modified methylaluminoxane activator in which 25% of the methyl groups have been replaced with isobutyl groups. It has the advantage of longer shelf life than MAO.

[9] At constant pressure, the solubility of ethylene in toluene drops substantially with increasing temperature. Thus, rate increases observed by raising the temperature at constant pressure are moderated by the decreasing amounts of ethylene in solution. Significantly greater increases in activity would be expected at *constant* ethylene concentration.

[10] (a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (b) Schulz, G. V. Z. *Phys. Chem., Abt. B* **1935**, *30*, 379. (c) Schulz, G. V. Z. *Phys. Chem., Abt. B* **1939**, *43*, 25.

[11] The first-order dependence of both propagation and chain transfer on ethylene concentration appears to rule out a mechanism in which β-H elimination is followed by *dissociative* displacement. The data are consistent with chain transfer occurring by an *associative* process or by β-H abstraction by monomer in an ethylene alkyl complex.

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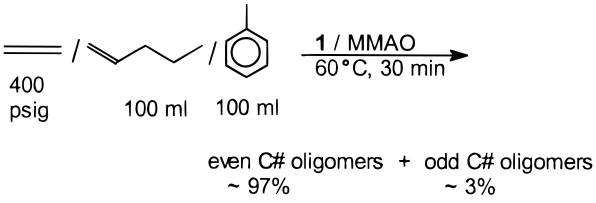
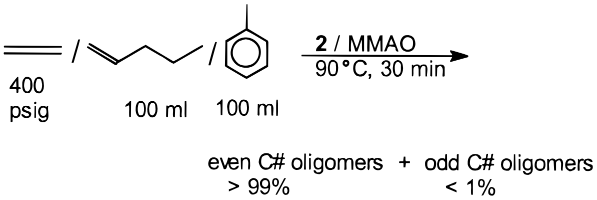
increased, the *K* values decrease as shown in entries 2, 3, and 6. Variations of temperature and substituent allow the *K* values to be adjusted between 0.70 and 0.85, a range that encompasses the most desired values for industrial production of α-olefins.[1a]

GC and ^{1}H NMR analyses confirm that all of the catalysts produce α-olefins (relative to internal olefins) with selectivities greater than 99% at ethylene pressures of 200 psig or higher (see Table 1). At high conversion using methyl-substituted catalyst **1** and after substantial buildup of α-olefins (e.g., >20 million turnovers at 90 °C and 200 psig), isomeric oligomers (up to 2−3%) can be detected. NMR analysis indicates that these are *not* internal olefins or oligomers with vinylidene end groups. Isolation of the total C_{10} fraction followed by hydrogenation and GC analysis of the saturated C_{10} oligomers establishes that these isomeric alkenes are branched α-olefins. Since these isomeric alkenes build up with increasing conversion, they are very likely formed from reincorporation of α-olefin products into oligomers made later in the reaction. To verify reincorporation, the oligomerization was run in a 50:50 volume ratio of 1-pentene to toluene as solvent at 60 °C and 400 psig of C_2H_4 (eq 2). GC analysis revealed that after 35×10^6 turnovers (30 min) ca. 3 mol % of odd carbon number oligomers are formed. This experiment demonstrates α-olefin reincorporation, but the very low fraction of 1-pentene incorporation under these conditions establishes a very high selectivity of catalyst **1** for insertion of ethylene relative to α-olefins.



(2)

The ethyl-substituted catalyst **2** is even more selective in all respects relative to the methyl-substituted catalyst **1**. The α-olefin selectivity in runs 10−14 is estimated as greater than 99.7%. Even at high conversion (>10 million turnovers) there is less than 1% of branched α-olefins present. In an experiment employing 1-pentene/toluene as solvent (eq 3), GC analysis of the products revealed only traces (<1%) of odd oligomers which establishes extremely high selectivity of the ethyl-substituted **2** for insertion of ethylene relative to insertion of α-olefins.



(3)

These iron complexes represent a remarkable new generation of ethylene oligomerization catalysts that have extended the understanding of the important role of ligand sterics in controlling transition metal-catalyzed olefin polymerizations and oligomerizations. The active catalysts reported here are stable over a wide temperature range, and their activities at moderate pressures and temperatures far exceed those of the SHOP and aluminum alkyl processes that require much more severe conditions.[1a] The Schulz−Flory *K* values are predictable and easily manipulated in the desired range, and the selectivities for formation of α-olefins are exceptionally high and exceed those of commerical systems. We are currently investigating mechanistic details as well as modifying the catalysts to gain a better understanding of steric and electronic effects on the behavior of these systems.

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Supporting Information Available: Text detailing synthesis of ligands and complexes and procedure for α-olefin product workup and figures with ^{1}H NMR spectra of α-olefins made at 1 atm and elevated ethylene pressures and GC traces of α-olefins made under various conditions (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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