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Iron Catalysts for the Head-to-Head Dimerization of α-Olefins and Mechanistic Implications for the Production of Linear α-Olefins

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A series of pyridine bis-imine iron catalysts previously reported for the oligomerization of ethylene and propylene are now reported as active catalysts for the dimerization of α-olefins to make linear internal olefins. The dimers possess up to 80% linearity, depending on the catalyst structure and the reaction conditions. The dimer byproducts consist almost exclusively of methyl-branched species and only traces of vinylidene (2-alkylalkene), trisubstituted, or α-olefin products. The linear dimers are formed by a unique mechanism that precludes the formation of multiple dimer products. The dimer content is verified by hydrogenation, which produces only a linear paraffin and a methyl-branched paraffin upon GC analysis. The dimer composition is also verified by ^{1}H NMR, which shows >95% disubstituted internal olefin and less than 5% total vinylidene and trisubstituted olefin. Observations regarding the dimer structures are used to elucidate the structures of the branched α-olefin (BAO) byproducts that are made when ethylene is oligomerized by the same catalysts.

Introduction

The dimerization of olefins by metal catalysts has been a widely studied topic,[1] creating interest in diverse areas stretching from pharmaceuticals[2] to the plastics industry.[3] Yet, despite the many catalysts known to dimerize olefins, relatively few of these systems have shown promising commercial viability due to a variety of limiting factors, including competing side reactions, catalyst cost and activity, selectivity for dimer formation, and severity of the reaction conditions. Furthermore, of the catalysts that are selective for dimer preparation, most produce vinylidene (2-alkyl-1-alkene) dimers[4] or di-branched dimers[5] or are unselective in the product distribution (branched vs linear vs vinylidene).[1a,6] There are only a few catalysts known to produce *linear* dimers from α-olefins, and these systems generally exhibit low activity and selectivity. A recent report by Wasserscheid et al. and an earlier report from Beach et al. illustrate this tendency, underscoring the desirability and potential commercial importance of linear olefin dimers.[7] Specifically, although branched dimers are often preferred for the production of chemicals such as fuel additives and synthetic oils, linear dimers may find application in the area of new and/or higher performance alcohol, alkylate, or fine chemical feedstocks.

The synthesis of linear olefin dimers is the result of head-to-head coupling of α-olefins, as shown in Scheme 1. If a metal hydride formed from β-H elimination or catalyst activation is assumed to be the active species,[8] the first step in head-to-head coupling is a primary (1,2) insertion of an α-olefin to generate a metal−primary alkyl species. To make the linear product, the second olefin exhibits opposite (2,1) regiochemistry of insertion, thus forming a secondary metal−alkyl bond. At this juncture, chain transfer leads to a mixture of four linear internal olefin products. In addition to the necessary

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[1] For reviews on olefin dimerization, see: (a) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W., Eds.; VCH: New York, 1996; Vol. 1, pp 258−268. (b) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

[2] See, for example: (a) Albert, J.; Cadena, M.; Granell, J.; Muller, G.; Ordinas, J. I.; Panyella, D.; Puerta, C.; Sañudo, C.; Valerga, P. *Organometallics* **1999**, *18*, 3511. (b) Englert, U.; Haerter, R.; Vasen, D.; Salzer, A.; Eggeling, E. B.; Vogt, D. *Organometallics* **1999**, *18*, 4390.

[3] See, for example, catalyst systems for producing 4-methyl-1-pentene: (a) Matsuno, M.; Kudoh, M.; Imai, H. (Nippon Oil Company) U.S. Pat. 4533781, 1985. (b) Stevens, J. C.; Fordyce, W. A. (Dow) U.S. Pat. 5081231, 1992.

[4] (a) Slaugh, L. H.; Schoenthal, G. W. (Shell) U.S. Pat. 4658078, 1987. (b) Lin, K−F.; Nelson, G. E.; Lanier, C. W. (Ethyl) U.S. Pat. 4973788, 1990. (c) Wu, F.-J. (Ethyl) U.S. Pat. 5087788 1992. (d) (Mitsubishi) Jpn. Pat. 49-64683. (e) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284. (f) van der Heijden, H.; Hessen, B.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 1112. (g) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

[5] (a) Sato, H.; Nogushi, T.; Yasui, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3069. (b) Sato, H.; Tojima, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3079. (c) Anon. *Chem. Br.* **1990**, *26*, 400.

[6] See, for example: (a) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65. (b) Threlkel, R. S.; Kurkov, V. P.; Woo, G. L. (Chevron Research and Technology Company) U.S. Pat. 5196624, 1993. (c) Threlkel, R. S.; Kurkov, V. P. (Chevron Research and Technology Company) U.S. Pat. 5196625, 1993. (d) Mitkova, M.; Tomov, A.; Kurtev, K. *J. Mol. Catal. A: Chem.* **1996**, *110*, 25. (e) Vicari, M.; Polanek, P. (BASF) U.S. Pat. 5849972, 1998. (f) Vicari, M.; Walter, M.; Ulonska, A.; Brox, W.; Keuser, U. (BASF) WO9925668, 1999.

[7] (a) Ellis, B.; Keim, W.; Wasserscheid, P. *Chem Commun.* **1999**, 337. (b) Beach, D. L.; Bozik, J. E.; Wu, C.-Y.; Kissin, Y. Y. *J. Mol. Catal.* **1986**, *34*, 345.

[8] As note (35) in ref 9a of this paper reports, the exact nature of chain transfer (β-H elimination to metal vs β-H transfer to monomer) in the iron catalysts reported herein is not known. If hydride abstraction by incoming monomer is the actual mechanism, this process would likely occur with opposite regiochemistry from propagation, to form linear dimers. If abstraction occurs with the same regiochemistry (2,1) as propagation, then the resultant Fe−alkyl complex would produce only branched dimers, or in the analogous propylene polymerization systems, no *n*-butyl groups would be observed at the saturated chain ends. This said, it is worth noting that several theoretical papers on both the Fe and the Co catalysts support a mechanism of β-H transfer rather than β-H elimination. See, for example: (a) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 6479. (b) Margl, P.; Deng, L.; Ziegler, T.. *Organometallics* **1999**, *18*, 5701. (c) Khoroshun, D. V.; Musaev, D. G.; Vreven, T.; Morokuma, K. *Organometallics* **2001**, *20*, 2007.

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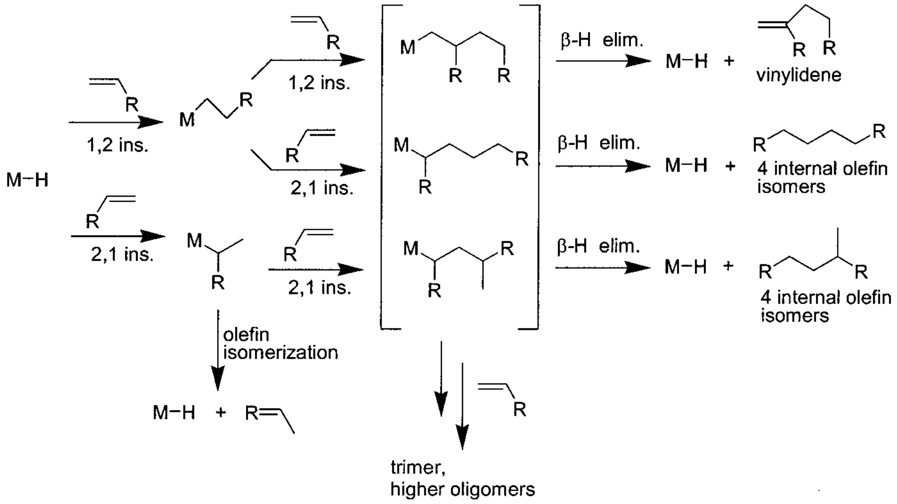
Scheme 1. Pathways for Olefin Dimerization



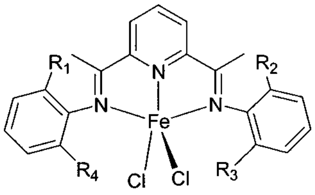


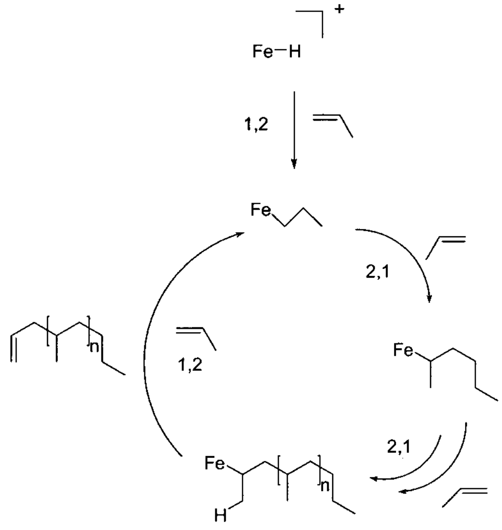
Figure 1. Fe-based precatalysts for propylene polymerization ($R_n = C_1{-}C_4$ alkyl; $R_1 = R_2 = tBu$, $R_3 = R_4 = H$).

switch in regiochemistry that prevents vinylidene or methyl-branched species from forming, Scheme 1 also shows several competing and detrimental side reactions. If the initial olefin insertion is nonregioselective (2,1 insertion), nonlinear dimers will be formed. In addition, initial 2,1 insertion may lead to olefin isomerization, especially if β-H elimination from the resultant secondary metal−alkyl complex is nonregioselective and fast on the dimerization time scale. If β-H elimination/abstraction and resultant product release do not occur rapidly on the dimerization time scale, then significant amounts of oligomer or polymer will be produced. Finally, to prevent product isomerization or reincorporation, a catalyst that is not reactive toward the dimer product is desired.

Recent reports on a series of iron catalysts capable of polymerizing propylene sparked our interest in olefin dimerization[9] (Figure 1). The iron catalysts described therein possess bulky, alkyl-substituted aryl rings, and they polymerize propylene in 2,1 fashion to make isotactic polypropylene with allyl end groups at the unsaturated chain ends (Scheme 2). However, the polymers also contain *n*-butyl end groups at the saturated chain ends, resulting from a switch in the regiochemistry of propagation from 1,2 to 2,1 (head-to-head) following the initial propylene addition step. With the observation of this desirable regiochemical constraint, it was decided to investigate the ability of variations of these iron catalysts for making linear dimers from α-olefin feedstocks.

First, however, to prejudice the catalysts toward lower molecular weight products, catalysts with less bulky

Scheme 2. Propagation Mechanism for Propylene Polymerization by Fe Catalysts



ligands were selected (Figure 2). This reasoning agrees with previous observations that for ethylene[10] as well as propylene[9a,11] polymerization the molecular weight of the products is largely dependent on the size of the ortho substituents at the 2 and 6 positions of the aryl rings of the ligand. Herein we report a series of highly active iron catalysts that are effective for the dimerization of α-olefins to form linear internal olefins.

Results and Discussion

Relationship Between α-Olefin Production and Olefin Dimerization. Complexes **1**−**6**, shown in Fig-

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[9] (a) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120. (b) Pellecchia, C.; Mazzeo, M.; Pappalardo, D. *Macromol. Rapid Commun.* **1998**, *19*, 651.

[10] (a) Small, B. L.; Brookhart, M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1998**, *39*, 213. (b) 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. (c) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (d) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (e) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728. (f) Bennett, A. M. A. *Chemtech* **1999**, *29* (7), 24. (g) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6* (12), 2221.

[11] Small, B. L. University of North Carolina Doctoral Dissertation, *Diss. Abstr. Int., B*, **1999**, *59* (12), UMI order number DA9914912.

Table 1. Results for the Dimerization of α-Olefins

entry	cat.	loading (mg)	Co-cat.[a]	Al/Fe ratio	α-olefin monomer	amount (mL)	react. length	react. temp (°C)	% conv	yield (g)	% dimer	% linear internal[b]	% methyl branched
1	**1**	1.0	MMAO	810	C6	20	3 h	25	21	2.8	92	76	23
2	**1**	1.0	MMAO	810	C6	20	3 h	0	9	1.2	85	81	18
3	**2**	5.9	MMAO	440	C6	50	1 h	30	28	9.4	87	71	28
4	**1**	11.7	MMAO	420	C6	200	2 h	65	29	39	85	63	36
5[c]	**4**	4.3	MMAO	660	C6	100	2 h	20	8	5.6	95	34	65
6	**4**	6.0	MMAO	480	C6	100	1 h	50	44	30	96	29	70
7	**1**	10.5	MMAO	480	C6	200	5 h	40	70	94	83	66	33
8	**5**	10.5	MMAO	510	C6	200	1 h	40	64	86	85	65	34
9	**5**	6.8	MMAO	390	C6	100	2 h	0	33	22	83	80	19
10	**5**	6.3	MMAO	430	C5, C6[d]	47, 53	1 h	40	65	43	85	64	35
11	**3**	5.5	MMAO	490	C6	100	1 h	40	36	24	90	71	28
12	**5**	26.5	MMAO	80	C6	200	16 h	50	76	102	85	63	36
13	**1**	15.3	MMAO	220	C10	100	2 h	45	74	55	85	66	33
14	**1**	10.0	MMAO	100	C6	100	16 h	50	70	47	87	67	32
15	**1**	10.0	TEA, $F_{15}B$/25 mg	70	C6	200	2 h	30	43	59	93	70	29
16	**1**	50.0	MMAO	250	C20−24[e]	1 kg	26 h	50	31	310	84	68	31
17	**1**	10.0	TIBAL, $F_{15}B$/25 mg	120	C6	200	2 h	40	36	49	94	67	32
18	**1**	30.0	MAO−IP	105	C4	400	70 min	40	57	145	85	68	31
19	**1**	100.0	MAO	100	C4	2300	3 h	40	43	629	85	69	31
20	**6**	14.0	MMAO	250	C6	100	24 h	40	8	5.3	95	74	25
21	**1**	100.0	MMAO	85	C4	2300	3 h	40	57	785	83	68	31

[a] MMAO = modified methylalumoxane (25% of methyl groups replaced by isobutyl groups); TEA = triethylaluminum; $F_{15}B$ = trispentafluorophenylborane; TIBAL = tri-isobutylaluminum; MAO-IP = methylalumoxane − improved process, which shows increased activity relative to MAO in certain benchmarking trials by the producer. [b] Percent of dimer that is linear [c] Catalyst **4** causes substantial isomerization of the nondimerized olefin. [d] Co-dimerization using 1-pentene and 1-hexene in equimolar amounts. GC analysis revealed that equimolar amounts (±5%) of each monomer were incorporated into the resultant dimers and trimers. [e] Chevron Phillips' C_{20-24} alpha-olefin mix.

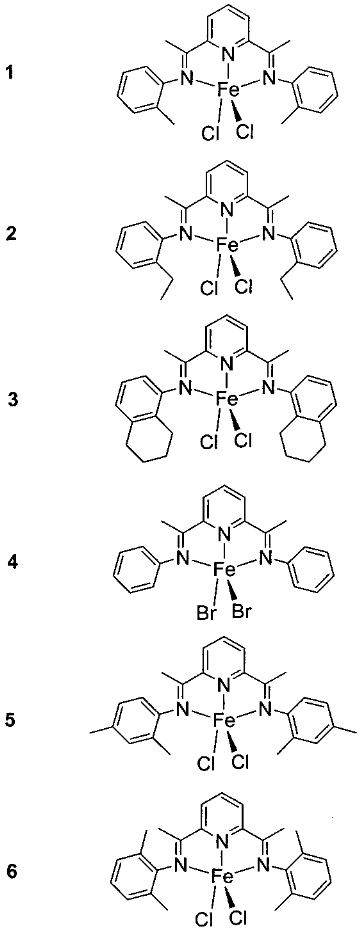

Figure 2. Fe-based precatalysts for α-olefin dimerization.

ure 2, when activated with various alumoxanes or Lewis acid/trialkylaluminum combinations, are active for the dimerization of α-olefins. Complexes **1**, **2**, **4**,[10d] and **5**[10g] have been reported, upon activation, to oligomerize ethylene to linear α-olefins; complex **6** has been noted as an ethylene[10c] and propylene[9a] polymerization precatalyst. The synthesis for complex **3** is reported herein. Table 1 presents the results for a variety of dimerization reactions. In a typical experiment, the iron complex and the neat olefin were added to a flask or a stainless steel reactor under inert atmosphere, followed by addition of the alumoxane or trialkylaluminum/borane cocatalyst at or near room temperature. Surprisingly, addition of the cocatalyst often resulted in large and rapid exotherms, indicative of fast initial reaction rates. The heats of reaction were controlled by an external water bath or by internal cooling coils. The reaction temperatures shown in Table 1 reflect the maximum temperatures that the reactions were allowed to reach. In most cases, these temperatures were maintained for 15−30 min with cooling, until substrate depletion caused a gradual drop in the temperature. External heating was then used to maintain the desired temperature. The activity of the catalysts toward higher olefins, expressed by the exothermicity of the reactions, was unanticipated, especially considering the almost total lack of α-olefin comonomer incorporation exhibited by the closely related ethylene polymerization and oligomerization systems.[12] In fact, when ethylene is polymerized in the presence of 1-hexene comonomer by alumoxane-activated complex **6** shown in Figure 2, the level of comonomer incorporation is at best only a few percent.[12] These observations raised an important question about why the ethylene polymerization systems show such low affinity for higher olefins while the

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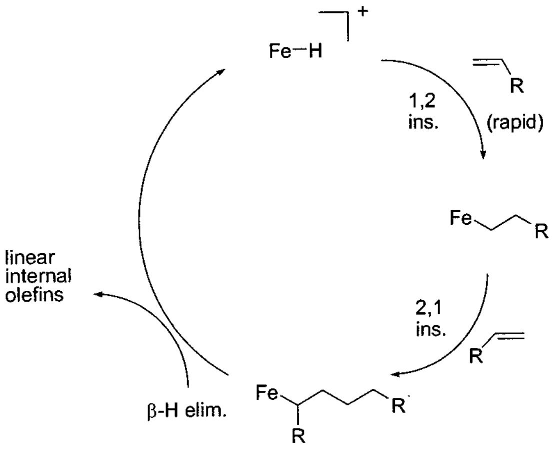
(12) Researchers at DuPont and BP have reported several examples of low comonomer incorporation using supported versions of these catalysts: (a) Bennett, A. M. A.; Feldman, J.; McCord, E. (DuPont) WO9962967, 1999. (b) Kimberley, B. S.; Maddox, P. J.; Partington, S. R. (BP) WO9946302, 1999.

Scheme 3. Catalytic Cycle for Linear Dimerization of α-Olefins



dimerization catalysts react readily with them. This apparent contradiction between the two catalyst groups may be explained by two factors. First, in the dimerization cycle (Scheme 3), approximately 50% of the olefin insertion steps proceed via "Fe−H" species.[8] Apparently, addition of α-olefins to the iron hydride (first insertion) is much faster than addition to iron alkyls, resulting in an increase in the rate of reaction. This contrast in rates is not unpredictable, since a true iron hydride species could not exhibit a stabilizing agostic interaction and would thus be more susceptible to olefin insertion, as has been noted by several researchers studying a variety of transition metal hydride complexes.[13] Furthermore, the catalysts discussed herein possess less sterically encumbered aryl rings, thereby facilitating greater ease of α-olefin approach to the catalyst. This effect of decreasing the size of the aryl ring substituents has already been demonstrated by several iron catalysts reported to produce linear α-olefins from ethylene.[10d,g] In those systems, which include complexes **1** and **2**, several percent of isomeric alkenes were formed in the reactions. These alkenes were shown by NMR to be predominantly branched α-olefins (BAOs) and *not* vinylidenes or internal olefins. The BAOs were produced by reincorporation of α-olefins made earlier in the reaction; catalyst **2**, as expected due to its larger ortho substituents, exhibited less BAO formation than catalyst **1**, thus demonstrating the increased affinity of nonbulky catalysts toward higher α-olefins.

The speed of the dimerization reaction combined with the ability of the less sterically hindered iron catalysts to produce BAOs prompted a revisitation of the BAO question; namely, what are the nature and location of the branches formed by the Fe-based α-olefin catalysts? Scheme 4 depicts several processes that may occur during α-olefin synthesis. Beginning with the iron hydride species, the catalyst may insert ethylene to form the Fe−ethyl complex, or an α-olefin (if present) to form a different Fe−alkyl species. If an α-olefin is selected, it can add in either primary (1,2) or secondary (2,1) manner, generating the new complexes shown. Primary addition will result in a linear Fe−alkyl complex, while secondary addition will lead to the formation of a branch point. Successive addition(s) of ethylene to either species followed by chain transfer would generate the linear α-olefin (LAO) and BAO products, respectively. On the basis of the results for propylene polymerization, though, initial insertion of an α-olefin into the iron hydride is expected to proceed in 1,2 fashion, resulting in a linear product if no further α-olefins are incorporated. However, it has also been reported that the regioregularity of the propylene polymerization catalysts decreases with decreasing steric bulk of the ligands,[9a,11] so it was not possible to rule out significant amounts of initial 2,1 insertions of α-olefins into the Fe−H bond.

Alternatively, higher olefins could incorporate into the growing ethylene-based chains at some other point during oligomer formation. For example, if the iron catalyst were to first add a molecule of ethylene to form the Fe−ethyl complex, subsequent addition of a higher olefin could form two new complexes, depending on the regiochemistry of insertion. On the basis of the propylene polymerization data,[9] the predicted regiochemistry would be predominantly 2,1 to give the Fe−secondary alkyl complex; 1,2 addition would yield the β-branched Fe−alkyl species. At this point in the pathway, alignment of the experimental data with the suggested mechanism becomes problematic. If it is assumed that chain transfer may occur at any point along the way, then some of the complexes will undergo this process without adding another molecule of ethylene. These chain transfer steps would produce increased amounts of internal olefins from the secondary olefin insertion (more likely) intermediates or vinylidene buildup from the intermediates possessing primary Fe−alkyls. However, since no vinylidenes and only very small amounts ($<0.5\%$) of internal olefins are detected in the α-olefin products, a mechanism proposing significant amounts of reincorporation of α-olefins in the middle of the oligomer chains seemed unlikely.

The low level of internal olefin products and the total absence of vinylidene species pointed toward the mechanism proposed in Scheme 4 (indicated by the asterisks along the reaction pathway); that is, the majority of the branches formed in the α-olefins made by the iron catalysts rest at the saturated ends of the chains and away from the double bonds. To test this proposal, it was helpful to directly compare some α-olefins made by complex **1** to some α-olefins produced by a typical aluminum-based α-olefin catalyst.[14] In Scheme 5 the major impurities contained in 1-decene made by an aluminum−alkyl catalyst are shown. They are 2-ethyl-1-octene, formed by 1,2 addition of 1-butene to an aluminum−hexyl complex or by 1,2 addition of 1-octene to an aluminum−ethyl complex, and 2-butyl-1-hexene, made by the 1,2 addition of 1-hexene to an aluminum−butyl complex. Chain transfer from these Al−alkyl species produces two distinct, 10-carbon, vinylidene isomers in the C_{10} fraction. Scheme 5 also shows the 10-carbon BAO species expected to be made by the iron catalysts, assuming that reincorporation of α-olefins occurs predominantly at the iron hydride (first insertion) stage. These molecules are 7-methyl-1-nonene, 5-methyl-1-nonene, and 3-methyl-1-nonene, resulting from an initial 2,1 insertion of 1-butene,

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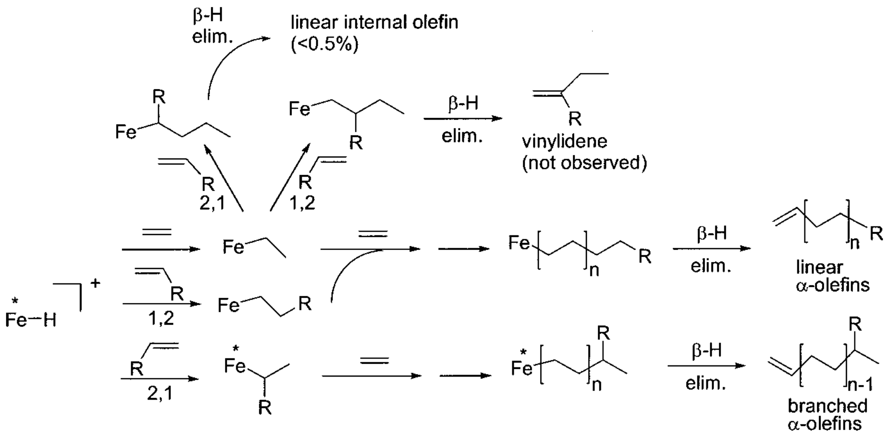
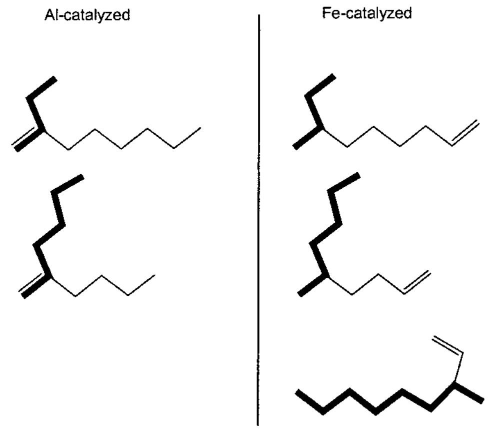
(13) See: Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394, and references therein.

(14) Neutral trialkylaluminum compounds are used in the commercial ethylene oligomerization processes of Chevron Phillips (CPC) and BP. The GC analysis described in the text was performed on CPC commercial samples.

Scheme 4. Formation of Branches in Fe-Catalyzed α-Olefin Production



Scheme 5. Comparison of Al- and Fe-Catalyzed C_{10} α-Olefin Fractions



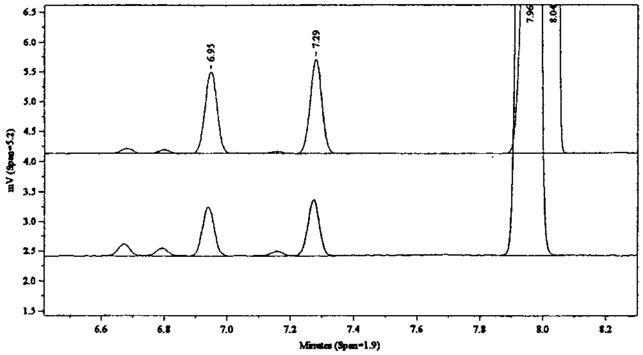


Figure 3. Gas chromatograms comparing hydrogenated C_{12} fractions made by Al (top) and Fe (bottom) catalysts.

1-hexene, or 1-octene, respectively. (Note that there are now three species to consider, since the butene, hexene, and octene initiated products all have unique structures.) Upon comparison of the set of known structures from the aluminum-catalyzed process to the set of proposed molecules from the iron-catalyzed process, it occurred to us that hydrogenation of the two sets of olefins should lead to an identical set of two saturated products for the C_{10} fractions made by each catalyst. In fact, upon analysis by gas chromatography, every hydrogenated fraction should contain the same set of byproduct signals for both the Fe-catalyzed and the Al-catalyzed processes. Figure 3 indicates the success of this experiment; the identical sets of paraffinic signals in the hydrogenated C_{12} products are shown as an example for strong support of the branching mechanism proposed for the iron catalysts in Scheme 4. Identical sets of signals for the major impurities were also found upon comparing other saturated fractions from the two catalytic processes.

From a catalyst selectivity standpoint, the buildup of BAO products in the production of linear α-olefins by the iron catalysts coupled with the proposed mechanism indicate that the initial chain growth step in this process is not highly selective for ethylene over higher olefins. Also, the initial insertion of higher olefins is not extremely regioregular, since the BAOs are formed after a 2,1 "regio-mistake" in the first insertion. Despite the lack of selectivity (1,2 vs 2,1 and ethylene vs higher olefins) in the first insertion, successive chain growth steps that involve insertion into Fe–alkyls are highly selective for ethylene. These observations provide the rationale for the high rate of the olefin dimerization reactions. In the presence of ethylene and α-olefins, the Fe–alkyl species are highly selective for ethylene and produce α-olefin products, either branched or linear. If no ethylene is present, though, the Fe–alkyl complexes will incorporate a second α-olefin in highly regioregular 2,1 fashion to form the dimer. Since the incorporation of the second α-olefin to form the dimer is expected to be slower than the first step, some substrate isomerization would naturally be expected from this process. It is beneficial to take a closer look at the dimerization data in Table 1 to consider this possibility and others.

Discussion of Dimerization Data. Table 1 shows that catalysts **1**–**6** can dimerize a variety of α-olefins to form product mixtures that consist primarily of linear internal olefin dimers and monomethyl-branched dimers. The catalysts are active over a wide temperature range, from 0 to 80 °C, but the activity decreases with decreasing temperature (<30 °C). As the catalysts' activities decrease at lower temperatures (see entries 2 and 9), their selectivity for forming linear product increases, irrespective of the catalyst or olefin used. This higher linear selectivity at lower temperatures points to an increased selectivity for primary (1,2) olefin insertion in the first dimerization step, a result consistent with the data earlier reported for propylene polymerization at low temperatures.[9a] Figure 4 plots data collected for catalyst **1**, clearly exhibiting the lower selectivity for linear product at higher temperatures. As the catalysts' activities increase at higher temperatures, the lifetimes of the catalysts appear to decrease; conversion levels up

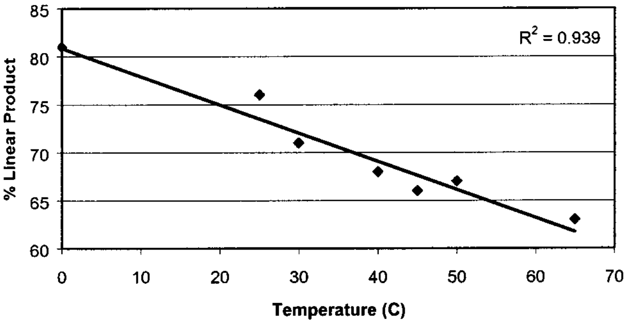


Figure 4. Dependence of linearity on temperature.

to 70% and higher were achieved in the 30−50 °C range (entries 7, 12−14). Additionally, catalyst productivities were found to be quite high with relatively low levels of alumoxane present. Entry 21 shows that with an Al: Fe ratio of only 85:1 complex **1** produces almost 8000 g product/g Fe complex, which represents a total turnover number of 75 000 mol 1-butene/mol Fe.[15]

Catalysts **1**−**3** and **5** produce mostly linear internal dimers, but complex **4**, which bears no alkyl substituents on the aryl rings, gives approximately the opposite distribution, with methyl-branched internal olefins as the predominant species (entries 5 and 6). Unlike the other catalysts, complex **4** also promotes substantial isomerization in the undimerized substrate, thus producing internal olefins. This isomerization may be explained in two ways. First, the nonbulky aryl rings of complex **4** may allow the initial insertion to proceed rapidly in comparison to the second insertion, which causes the rate of β-H elimination following the initial insertion to become even more competitive with the second step (olefin addition). Also, since the first step seems more likely to proceed with 2,1 regiochemistry, reversible β-H elimination at this stage will result in more isomerized product. Regardless of the exact reason for increased isomerization by complex **4**, the increase in methyl-branched dimers from this catalyst further shows that the regioregularity of the first olefin insertion step decreases with decreasing steric bulk on the ligand. Consideration of this trend prompted the question of what would happen if a bulkier catalyst were used for the dimerization. Thus, catalyst **6**, previously reported to polymerize both ethylene[10c] and propylene,[9a] was used to dimerize 1-hexene. Although a mild increase in selectivity was observed (74% linear at 40 °C, entry 20), the catalyst activity dropped precipitously (<10% conversion after 24 h).

Conclusion

A new group of iron-based catalysts, previously reported for the polymerization or oligomerization of ethylene or propylene, have been found to possess several characteristics that make them attractive catalysts for the linear (head-to-head) dimerization of higher α-olefins. A unique and predominant mechanism exists for these systems, in which the initial olefin undergoes 1,2 insertion, which is followed by a 2,1 insertion of the second olefin, resulting in organometallic complexes that undergo chain transfer to produce linear dimers. Byproducts in the reaction are methyl-branched heptenes and olefin trimers, with generally less than 2% vinylidene or trisubstituted olefin species formed. Study of this new reaction has also provided insights into the mechanism of iron-catalyzed α-olefin production. The branches in the α-olefin byproducts are now known to occur almost exclusively at the saturated chain ends, thereby rendering a relatively unhindered olefinic chain end. Elucidation of these unique mechanisms for linear dimerization and ethylene oligomerization further illustrate the diverse and growing number of chemistries for late transition metal catalysts.

Experimental Section

Materials. Anhydrous THF and methanol were purchased from Aldrich and used without further purification. Anhydrous cyclohexane was purchased from Aldrich and stored over molecular sieves. 1-Butene, 1-hexene, 1-decene, and the C_{20-24} α-olefin mixture were obtained as commercial grades of Chevron Phillips' Normal Alpha Olefins (NAOs). 1-Pentene was purchased from Aldrich. All α-olefins were dried over molecular sieves. MMAO-3A and MAO-IP were purchased from Akzo Nobel. MAO was obtained from Albemarle Corporation. Tris(pentafluorophenylborane), 2,6-diacetylpyridine, iron(II) chloride tetrahydrate, and all substituted anilines were purchased from Aldrich and used without further purification. NMR spectra were obtained using a Varian Unity Plus 300 MHz spectrometer.

Synthesis of Ligand 3, 2,6-Bis[1-(5,6,7,8-tetrahydronaphthylimino)ethyl]pyridine (3′). 2,6-Diacetylpyridine (1.0 g, 6.1 mmol) and 1-amino-5,6,7,8-tetrahydronaphthalene (3.6 g, 24.5 mmol) were dissolved in a round-bottom flask, to which 50 mL of anhydrous methanol were added. Three drops of glacial acetic acid were added, and the flask was sealed. After stirring the solution for 2 days, a yellow solid was collected and recrystallized from methanol to give 760 mg (30%) of the desired **3′**. ^{1}H NMR (C_6D_6): δ 8.48 (d, 2), 7.30 (t, 1), 7.10 (m, 2), 6.85 (d, 2), 6.56 (d, 2). ^{13}C NMR (C_6D_6): δ 166.0, 156.0, 150.5, 138.4, 137.7, 127.0, 126.2, 124.9, 122.5, 115.4, 30.4, 26.0, 23.8, 23.6, 16.0.

Syntheses of Complexes 1−6. All of the complexes reported herein were made by methods previously reported, namely, the addition of a slight excess of the ligand to iron(II) chloride tetrahydrate in THF. After precipitation with pentane, the complexes were isolated by filtration, dried in vacuo, and analyzed for C, H, and N.[15] Data for complex **3** are reported as follows. Anal. Calcd for $C_{33}H_{39}N_3FeCl_2O$ (contains 1 equiv of THF, see ref 15): C, 63.88; H, 6.34; N, 6.77. Found: C, 63.05; H, 6.08; N, 6.41.

Dimerization of 1-Hexene and Liquid Monomers. A two-necked flask with a stirbar was fitted with a reflux condenser on one neck and a thermocouple with the appropriate adapter on the other neck. The apparatus was heated under vacuum, then filled with nitrogen. The condenser was then removed under positive nitrogen flow, and the precatalyst was added quickly. The flask was back-filled three times with nitrogen and charged with the liquid monomer. Stirring was begun in order to effectively slurry the sparingly soluble precatalyst in the neat monomer. After several minutes, the cocatalyst was added via syringe, and the reactions were performed using a slight nitrogen purge. Many of the reactions were activated at or near room temperature, but the exother-

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(15) To calculate an accurate turnover number (TON), the formula weight of the precatalyst is needed. A closer look at some of the analytical data (CHN analysis) for some of the less sterically bulky complexes, such as those reported in ref 10d, seemed to indicate the presence of an equivalent of THF in the isolated solids. CHN analysis indicated that an equivalent of THF is present in complexes **1**−**5**, and it is here noted that a formula weight of 540.3 was determined for **1** and subsequently used in the TON calculation. Complex **1** was also analyzed by ICP, which gave the expected 10.3% iron content, indicating the presence of THF.

mic nature of the reaction often caused the temperature to rise significantly. Temperatures were monitored using a thermocouple, and the temperatures listed in the table represent the maximum temperatures achieved in the reaction. In some cases the exotherm was controlled by a water bath. After reaching the maximum temperature in each reaction, a cooling process was observed due to substrate depletion, and heating was required to maintain the desired reaction temperature.

Dimerization of 1-Butene. A Zipperclave reactor of appropriate size was heated under vacuum at 50 °C for several hours. The reactor was cooled to room temperature under nitrogen. The precatalyst was then quickly added to the reactor, and the reactor was resealed and placed under vacuum. A dual-chambered glass sample charger was then attached to the injection port of the reactor. From the first chamber an initial portion of cyclohexane internal standard was added to blanket the catalyst. From the second chamber more cyclohexane internal standard (usually about 10 mL) and the cocatalyst were added. The reactor was then charged with liquid butene and was further pressurized with at least 100 psi of nitrogen to keep the butene in the liquid phase. The reaction was stirred rapidly, and the temperature was monitored using a thermocouple. External cooling and heating were used to maintain the desired reactor temperature.

Product Analysis. The aluminum cocatalysts were neutralized by pouring the liquid products into a water wash. After removal of the cocatalysts, the products were analyzed by gas chromatography (GC). A Hewlett-Packard 6890 Series GC System with an HP-5 50 m column with a 0.2 mm inner diameter was used for dimer as well as α-olefin characterization. Chrom Perfect Version 4 from Justice Laboratory Software was used to analyze the collected data. GC analysis showed clear separation of the linear from the branched species, and hydrogenation of the products confirmed these results. ^{13}C NMR and ^{1}H NMR were used to confirm the internal olefin content in the products.

The conversions and yields were determined by comparing the product to the internal standard integrals and by assuming equal response factors of the standard and the products. For the hexene dimerization experiments, unreacted 1-hexene was the internal standard, and for the butene experiments cyclohexane was used.

Hydrogenation of Olefinic Products. The olefinic products in both the dimerization and the α-olefin reactions were hydrogenated in a Zipperclave reactor at 115 °C and 400 psig hydrogen using HTC Ni 500 catalyst from Crosfield.

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Supporting Information Available: GC trace for hydrogenation of 1-butene dimer; ^{1}H NMR spectrum for 1-butene dimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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