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Oligomerization of Ethylene Using New Iron Catalysts Bearing Pendant Donor Modified α-Diimine Ligands

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Stoichiometric Schiff base condensations of sterically bulky primary amines with acenaphthenequinone yield isolable monoimines. In the presence of Fe or other transition metals, the remaining ketone reacts with a second primary amine bearing a pendent donor atom to give asymmetric, tridentate, α-diimine complexes. Upon activation with alumoxanes, these complexes are highly active for the oligomerization of ethylene to linear α-olefins, with turnover numbers (TONs) exceeding 2.5×10^6 mol ethylene/mol Fe. Product purities are high, with 1-hexene and 1-octene exceeding 99% purity in most examples.

Introduction

Following reports from Brookhart,[1] Bennett,[2] and Gibson[3] that disclosed extremely active pyridine bisimine (PBI) iron and cobalt catalysts for the polymerization of olefins, a number of efforts have been made to investigate related catalyst systems.[4] One approach has been the use of PBI ligands on other first-row metals, such as Cr,[5] V,[6] and Ti[7]—all of which have yielded active catalysts. Another approach has been the development of alternative tridentate ligands for Fe and Co. Restricting the discussion to neutral tridentate ligands that coordinate in meridional fashion, some examples of iron and cobalt complexes are shown in Figure 1.

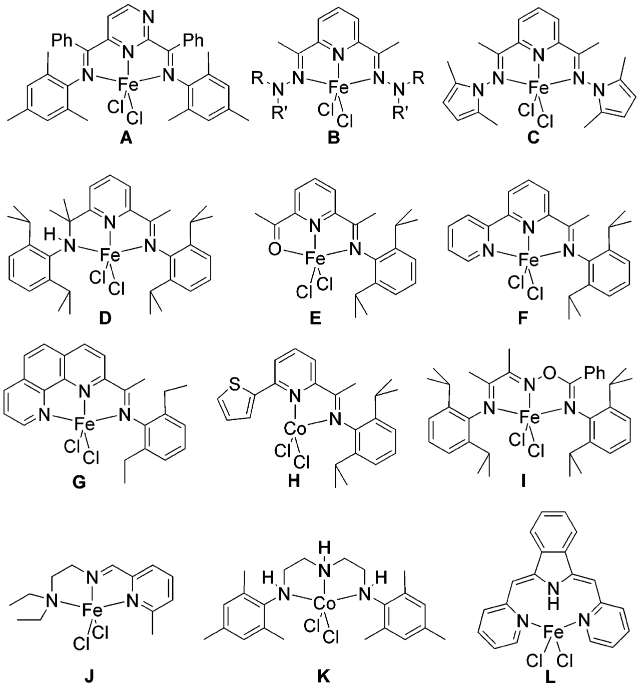

Figure 1. Some precatalyst complexes reported since the initial PBI systems of Brookhart, Bennett, and Gibson.

The first five examples, complexes **A**−**E**, show only slight variations from the PBI species. In complex **A**, the central pyridine ring has been replaced by a pyrimidine ring; the resultant catalyst was reported by Gibson to be somewhat less active than its PBI analogue.[8] Complexes of type **B**, in which dialkyl or diaryl hydrazines were used instead of anilines to generate the PBI structure, exhibited substantially lower activity than the aryl-imino PBI catalysts.[9] Catalyst activity increased, though, when 1-amino-2,5-dimethylpyrrole was used to form the tridentate ligand (complex **C**). The steric similarities of **C** to the parent PBI catalysts are obvious; the lower molecular weight of the polymer made by **C** relative to the 2,6-dimethyl-substituted aryl-imine analogue was noted by both Gibson[9] and Luinstra.[10] Two additional variations of the PBI structure,

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(4) For reviews of non-metallocene systems, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Park, S.; Han, Y.; Kim, S. K.; Lee, J.; Kim, H. K.; Do, Y. *J. Organomet. Chem.* **2004**, *689*, 4263.

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10.1021/om0611406 CCC: $37.00

reported by Gibson[11] and Bennett,[12] respectively, are complexes **D** and **E**. Complex **D**, in which one of the imines has been reduced, exhibited lower activity than its parent PBI species. This was also the case for **E**, in which only one of the ketone groups was converted to the aryl-imine.

Moving further from the original PBI complexes, bipyridine imine complexes of type **F** were reported by Lenges[13] and Gibson.[14] These catalysts are about an order of magnitude less active than the PBI catalysts. This lower activity may be due to "in-plane" steric crowding at the metal center by the terminal pyridine ring, or perhaps due to the inability of the ligand to enforce a coplanar arrangement of the coordinated ethylene with the $Fe{-}C_\alpha$ bond, thus slowing the insertion process. Complex **G**, described by Sun,[15] replaces the bipyridine of **F** with phenanthroline and exhibits a much higher activity than **F**. Perhaps the more rigid strucuture imposed by the phenanthroline backbone is responsible for the high activity. Cobalt complexes of type **H**, reported by Bianchini,[16] possess a terminal sulfur donor that is not bound to the metal in the solid state. In fact, the ligand in **H** appears to bind in bidentate fashion in the activated catalysts, which likely explains why catalytic activity was not reported for the related Fe systems. Complex **I**, disclosed by Johnson,[17] is similar to the PBI catalysts but possesses a more flexible ligand backbone. The activity of **I** was apparently lower than that of the PBI systems. Another flexible ligand structure is present in complex **J**, reported by Nagy.[18] Although the ligand is very simple to prepare, consisting of a single condensation reaction between an aldehyde and a primary aliphatic amine, the catalyst is only moderately active. Complex **K**, which possesses a flexible ligand backbone and no imino groups, was reported by Solan.[19] This activated complex showed modest activity for ethylene oligomerization; the analogous iron system was not successfully prepared. A final example is complex **L**, the phthalimide-based precursor disclosed by Liu.[20] Even though **L** contains significant "in-plane" steric bulk and deviates from the typical two-atom spacer length between the donor atoms, the catalyst is claimed to be as active as the PBI systems. Even more curious is the fact that when the pyridyl rings are replaced with phenyl rings, the catalyst remains highly active, thus raising questions about the ligand binding mode.

Completing the discussion of iron and cobalt PBI catalysts, it is worthwhile to discuss a few inactive systems (Figure 2). For instance, complexes of type **M** could be formed only when X was N−H, resulting in a monoanionic ligand after deprotonation and complexation.[21] When the central donor was changed to S or O, the iron complexes were not successfully prepared.[8] Similarly, when the central pyridine ring was replaced by a five-atom ring such as thiophene or furan, complexation to form species **N** did not occur.[8] The anionic pyrrolide derivative has been reported to bind in a bidentate fashion,[22] but apparently the neutral O and S donor ligands do not participate in this manner. A final inactive example is the iron complex **O**, which has a biscarbene ligand.[23] Despite the activity of this ligand when bound to chromium,[24] the iron system does not polymerize olefins.

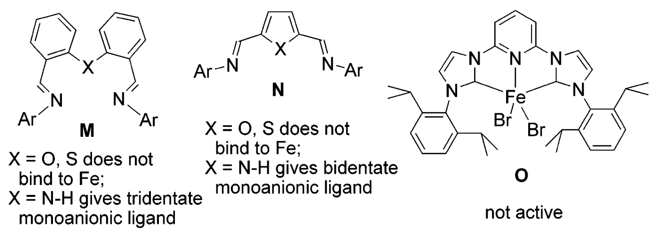
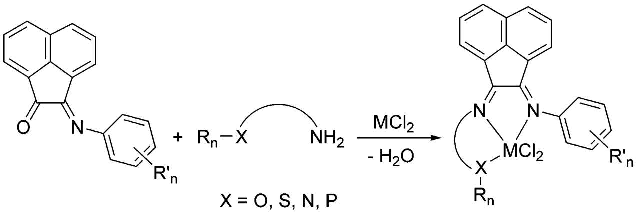


Figure 2. Examples of inactive ligands and catalyst precursors.

Scheme 1



We endeavored to discover additional tridentate ligands, especially when bound to iron, that would yield new catalysts for the oligomerization and polymerization of olefins. By consideration of the α-diimine ligand structure reported by Brookhart for Ni- and Pd-catalyzed polymerization,[25] and the propensity of iron to prefer tridentate ligands for the generation of active catalysts, a new family of complexes bearing pendent donor modified α-diimine ligands was developed. Scheme 1 shows the basic route for preparing these new precatalysts; our concurrent publication provides the synthetic and characterization details for these compounds.[26] This paper will discuss the polymerization results for these new systems, primarily with respect to their high activity for the production of linear α-olefins (C_4-C_{30} ethylene oligomers).

Results and Discussion

The last 10 years have witnessed the discovery of a large number of catalyst systems for the oligomerization of ethylene to linear α-olefins.[27] PBI iron catalysts, due to their extremely high activity, reluctance to incorporate higher olefins, and commercially relevant product distributions based on the

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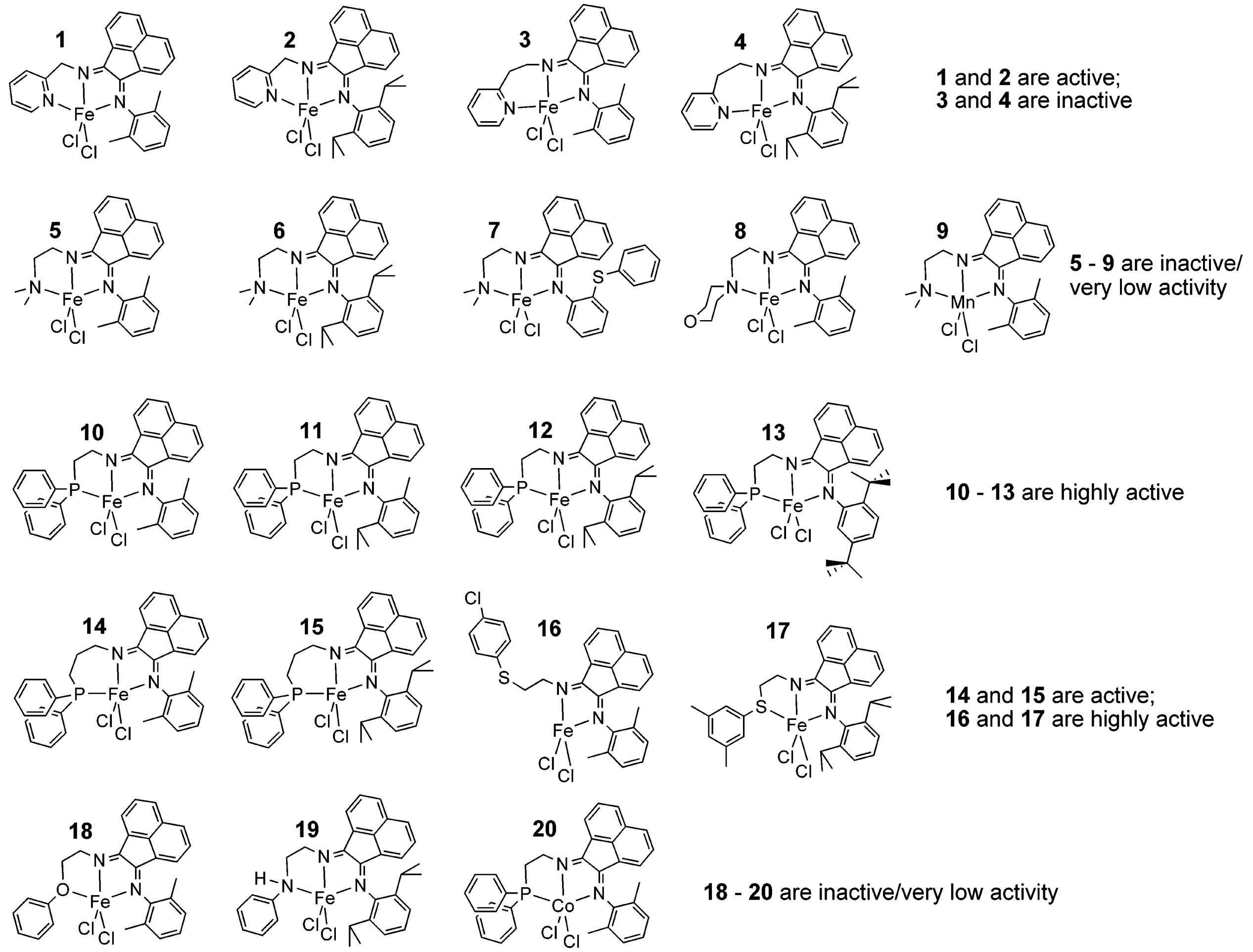

1 and **2** are active;
3 and **4** are inactive

5 - **9** are inactive/
very low activity

10 - **13** are highly active

14 and **15** are active;
16 and **17** are highly active

18 - **20** are inactive/very low activity

Figure 3. Precatalyst complexes **1**−**20**. Note that **16** exists in the solid state as a chloride-bridged dimer.

Schulz−Flory constant K ($K = \mathrm{mol}_{\mathrm{C}n+2}/\mathrm{mol}_{\mathrm{C}n}$), have been at the forefront of these discoveries. Iron is also attractive for preparing α-olefins for other reasons. Unlike early transition metals, iron possesses little intrinsic ability for polymerizing ethylene by itself, which should minimize the formation of polyethylene coproducts. And, unlike nickel, iron is less likely to isomerize product olefins to undesirable internal olefin species.[28] Thus, it came as a very pleasant surprise to discover a new family of highly active iron oligomerization systems based on the route shown in Scheme 1.

Using the metal-template synthesis method, 20 different precatalyst complexes were prepared and screened for polymerization activity. Figure 3 shows each of these complexes, which have been grouped according to their structural similarities and their catalytic activities. The notes next to each subgroup in Figure 3 provide general details on catalyst activity. Table 1 contains more specific data on the catalyst behavior and, if applicable, product distribution for each system.

The data in Table 1 were obtained using a 500 mL Zipperclave reactor, typically charged with 200 mL of cyclohexane or heptane, the cocatalyst, and a methylene chloride solution of the complex. Details can be found in the Experimental Section. Slow activation of some of the complexes, coupled with sustained activity after 30 or 60 min, resulted in longer reaction times to maximize the catalyst productivities. The results in the table disclose some important trends relating catalyst structure to both activity and product distribution. Beginning with systems **1** and **2**, consisting of triaza (NNN)-ligated complexes, moderately active catalysts with sustained activities were generated, resulting in the production of high-purity α-olefins. Gas chromatographic analysis of these products indicated a curious product distribution that showed significant deviation from Schulz−Flory behavior, with a nonconstant K value ($K = \mathrm{mol}_{\mathrm{C}n+2}/\mathrm{mol}_{\mathrm{C}n}$). For example, for entry **1** the lower K value of 0.46 refers to the $\mathrm{mol}_{\mathrm{C}10}/\mathrm{mol}_{\mathrm{C}8}$, while the higher value is for the $\mathrm{C}_{18}/\mathrm{C}_{16}$ molar ratio, thus pointing to a large increase in K with increasing carbon number. There are at least two plausible explanations for this type of variance. First, it is possible that as the carbon number increases, the K value could increase due to the increased likelihood of product olefins to reincorporate. If these reincorporation steps do not induce chain transfer, an increasing K value would be expected. In fact, it has been reported that for PBI complex **21**, shown in Figure 4, reincorporation does lead to a gradual deviation from ideal

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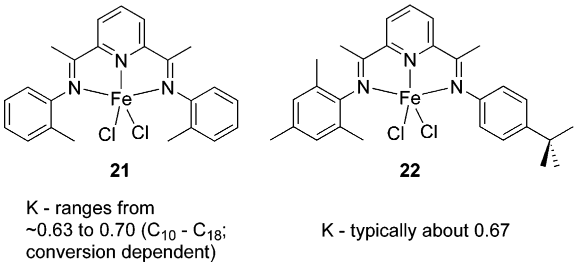
(27) Although a comprehensive review on emerging α-olefin catalyst technologies is not available, the following references, as well as other citations in this report, provide a reasonable overview: (a) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641. (b) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166. (c) Chen, Y.; Chen, R.; Qian, C.; Dong, X.; Sun, J. *Organometallics* **2003**, *22*, 4312. (d) Tang, X.; Sun, W.-H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1570. (e) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784. (f) Döhring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. In *Organometallic Catalysts and Olefin Polymerization: Catalysts for a New Millennium*; Springer-Verlag: Berlin, 2001; pp 127−136.

(28) Although Fe-catalyzed isomerization is well-known in the literature, it generally does not compete with chain propagation as well as Ni. See, for example, ref 6(e). For $\mathrm{Fe(CO)_5}$-catalyzed isomerization, see: Bingham, D.; Hudson, B.; Webster, D.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521.

Table 1. Selected Oligomerization Results for Complexes 1−21

precat./amt[a] (*μ***mol)**	MMAO Al:TM	C_2 pressure (bar)	T_{av}/T_{max}	run length (min)	yield[b] (g)	productivity[c] (g prod/mmol cat.)	K[d] (mol C_{12}/mol C_{10})	C_6 purity (%)	C_8 purity (%)
1/12	500	68	50/53	120	44	3700	0.44−0.63	99.0	98.7
2/7.2	300	68	45/50	60	50	7000	0.46−0.66	99.3	98.9
3/7.8	500	27	30	30	n.a.				
4/7.0	500	27	30	30	n.a.				
5/8.3	500	27	30	30	n.a.				
6/7.4	500	68	45/46	30	15	1300	0.72	97.6	97.4
7/7.1	500	27	30	30	n.a.				
8/7.6	500	27	30	30	n.a.				
9/16	500	44	35	60	n.a.				
10/3.2	500	68	50/65	60	122	38 100	0.39−0.48	99.6	99.1
11/3.1	500	68	50/63	60	108	35 200	0.49−0.61	99.4	99.1
12/1.8	300	82	50/52	90	124	70 600	0.60	99.4	99.3
13/5.7	500	27	45/45	30	15	2700	polymer/wax		
14/6.3	500	27	40/46	60	21	3300	0.61	98.6	98.7
15/5.8	500	44	35/37	30	6.4	1100	∼0.60	n.d.	n.d.
16/5.2	500	68	50/68	60	110	21 400	0.65	99.5	99.3
17/3.2	500	68	50/50	60	116	36 500	0.85	n.d.	98.9
18/7.5	500	27	30	30	n.a.				
19/6.8	500	68	30	30	n.a.				
20/6.4	500	44	35	30	n.a.				
21/0.43	300	68	50/60	30	39	106 000	0.68	99.2	98.7

[a] Standard reaction conditions and methods are described in the Experimental Section. [b] Product amounts were estimated for reactions in which a true Schulz−Flory K value could not be determined. [c] Although it is possible to derive a time-averaged catalyst activity by dividing the productivity by the run length, the varying run lengths and the probable first-order rate of catalyst deactivation make this a less useful number than the time-independent productivity. Initial activities determined at very short run lengths can yield quite high numbers; however, the intent of this study was to assess the ability of the catalysts to sustain reasonable activities (i.e., catalyst stability). The data in Table 2 clearly show how initial activity can vary greatly from time-averaged activity. [d] The variation in K values is shown for the C_8−C_{18} fractions.



21

22

K - ranges from ~0.63 to 0.70 (C_{10} - C_{18}; conversion dependent)

K - typically about 0.67

Figure 4. Complex **22** deviates little from Schulz−Flory behavior.

Schulz−Flory behavior and slightly lower product purity,[29] while for complex **22**, placing both *ortho*-methyl groups on the same aryl ring appears to lessen the amount of reincorporation and in turn reduce the amount of variance in K. This possibility appeared at first unlikely in our systems, since significant amounts of reincorporation would generally be expected to cause increased amounts of branching. Although it is possible that higher olefins could incorporate exclusively into an “Fe−H” initiator in 1,2 fashion, thereby giving only linear products, any 2,1 insertions would lead to branching.[30] Scheme 2 illustrates how 1,2 incorporation of a higher α-olefin into an Fe−H bond would not result in increased branch content. Despite the relatively high level of reincorporation necessary to change the K value this significantly, the products nevertheless possess high purities and very little branching.

Alternatively, divergence from the expected value for K can result from the presence of two active catalyst sites. Viewed as a kinetic expression, K is a ratio of the relative rates of propagation and termination, $K = k_{prop}/(k_{prop} + k_{term})$. Two active catalysts, each with its own respective rates for these values, would produce a lower K value for the lighter olefins and a higher K value for the heavier olefins upon blending of the products.[31] This is essentially what is observed for **1** and **2** (and **10** and **11**).

To test the possibility of reincorporation, two experiments were performed. First, the oligomerization was performed using complex **10** and a 50:50 blend of 1-pentene and *n*-pentane as the solvent (see Experimental Section). The products were found to contain about 2.3% (by mass) odd carbon number species in the C_{11}−C_{16} range.[32] At first, this amount seems a bit low to explain the significant drift in K. However, under these conditions, 1-pentene is the primary olefin that is reincorporated, whereas under normal conditions the effect of olefin reincorporation would increase with each successive carbon number, owing to the cumulative effect of having additional olefins available (e.g., 1-hexene may contain a 1-butene molecule, but 1-octene may contain 1-butene or 1-hexene, etc.).[30a] Further, these odd-numbered olefins in the 1-pentene experiment were predominantly linear, thus showing that reincorporation need not significantly affect the branch content for this catalyst. It also occurred to us that if the broadening of the distribution

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(29) De Boer, E. J. M.; Deuling, H. H.; Van Der Heijden, H.; Meijboom, N.; Van Oort, A. B.; Van Zon, A. U.S. Pat. 6710006 (Shell), 2004.

(30) Several 1-hexene dimerization experiments using the oligomerization-active complexes in Figure 3 showed very little activity, thus pointing to the sluggishness of higher olefin reincorporation. However, these experiments are not definitive because it may only be the second insertion step that is slow. These results are contrasted with the highly active PBI Fe and Co dimerization systems: (a) Small, B. L.; Marcucci, A. J. *Organometallics* **2001**, *20*, 5738. (b) Small, B. L. *Organometallics* **2003**, *22*, 3178.

(31) A number of mechanisms have been proposed for the generation of two active sites from a single precursor complex. It has been suggested that the ligand of complex **21** fluctuates between C_2 and C_{2v} symmetry on the oligomerization time scale, effectively creating two different active sites, each with its own K value. In addition to the “reincorporation” mechanism, symmetry interconversion cannot be ruled out as an additional K-broadening mechanism. Thus, it is not the asymmetry of complex **22** that prevents K broadening, but rather the inability of the “locked” 2,6-disubstituted aryl ring to interconvert to a species of different symmetry. See: Ionkin, A. S.; Marshall, W. J.; Adelman, D. J.; Fones, B. B.; Fish, B. M.; Schiffhauer, M. F. *Organometallics* **2006**, *25*, 2978. For additional references on the topic of ligand symmetry and ethylene polymerization, see: Bianchini, C.; Giambastiani, G.; Rios, I. G.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391, and references therein.

(32) This carbon range was chosen because the MMAO is produced in heptane, and the internal standard for the reaction was *n*-nonane, thus making the quantification of C_7 and C_9 olefins difficult.

(33) (a) Ban, H. T.; Kase, T.; Murata, M. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 3733. (b) Reardon, D.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 786.

Scheme 2

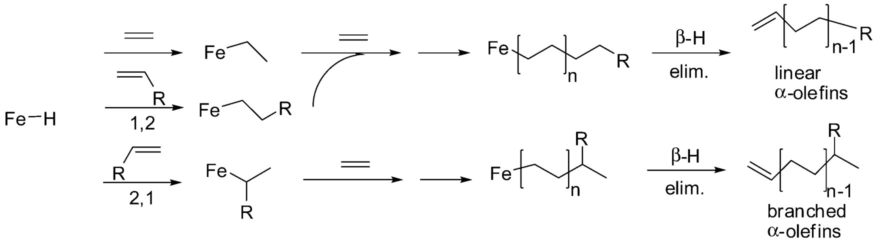

Table 2. Deviation from Schulz−Flory Behavior with Increasing Conversion[a]

K	5 min	20 min	30 min	45 min	60 min
nC$_{10}$/nC$_8$	0.48	0.45	0.44	0.44	0.44
nC$_{12}$/nC$_{10}$	0.49	0.47	0.46	0.47	0.47
nC$_{14}$/nC$_{12}$	0.50	0.50	0.50	0.51	0.51
nC$_{16}$/nC$_{14}$	0.54	0.53	0.55	0.55	0.56
nC$_{18}$/nC$_{16}$	0.55	0.56	0.59	0.60	0.61
total product g (C$_8$−C$_{20}$)	11.5	29.1	40.3	44.4	47.3
1-hexene % purity	99.2	99.5	99.6	99.6	99.6
1-octene % purity	99.0	99.3	99.3	99.3	99.3
1-decene % purity	98.1	98.5	98.6	98.6	98.6

[a] Conditions: 50 °C, 68 bar, complex **10** activated with MMAO (500:1 Al:Fe), cyclohexane solvent.

(higher *K*) were due to reincorporation, this broadening should become more pronounced with increasing product concentration in the reactor. With this in mind, the second experiment (with no 1-pentene present) involved periodic sampling of the reaction through a sampling port on the reactor. Table 2 shows the results from this experiment. At 5 min into the reaction, when about 25% of the total products had formed, the *K* values ranged from 0.48 (n_{C10}/n_{C8}) to 0.55 (n_{C18}/n_{C16}). At the end of the reaction (60 min), the values ranged from 0.44 to 0.61, thus demonstrating the effect that reincorporation has on causing deviations from Schulz−Flory behavior. Remarkably, though, these reincorporation reactions do not adversely affect the product quality, as shown by the outstanding purities that were maintained with increasing product composition in the reactor.

When the length of the spacer between the central imine and the pyridine donor was increased by one carbon (compare complexes **1** and **2** with **3** and **4**), catalyst activity was completely suppressed. The spacing between donor atoms in **3** and **4** is identical to that in compounds **M** in Figure 2, suggesting that the extension of the spacer causes too much crowding around the metal center, which suppresses catalyst activity.

Varying the pendent donor slightly, complexes **5**−**9** were made to compare the effects of dialkyl-amino donors. Remarkably, only complex **6** showed any measurable activity. Whether the inactivity of **5**, **7**, and **8** is due to unfavorable sterics of the dialkyl-amino donor or perhaps due to the poor coordinating ability of this species is unknown. Manganese derivative **9** was also made and tested for polymerization activity and, not surprisingly, was found to be inactive. Manganese renders the fewest examples of polymerization-active systems among the group III−VIII first-row metals.[5c,32]

When a diphenylphosphino substituent with a two-carbon spacer was used as the pendent donor, producing an NNP donor set, dramatic increases in catalyst activity were observed. Activated complexes **10**−**12** were highly active catalysts for the production of high-purity linear α-olefins. System **10**, with methyl groups in the *ortho* positions of the aryl-imine, produced 99.6% 1-hexene in the C$_6$ fraction, with a *K* value that varied between 0.39 and 0.48 over the C$_8$−C$_{18}$ carbon range. The lower *K* value range of this experiment relative to the similar reaction described in Table 2 is likely due to the higher initial temperature of the experiment in Table 1. Increasing the steric bulk of the aryl-imino group (complex **11**) caused an increase in the *K* value, resulting in the production of heavier products. This trend relating product molecular weights to ligand steric bulk has been documented for a number of iron, cobalt, and nickel polymerization catalysts.[1−3,25] As with **10**, complex **11** also exhibited a variable *K* value. However, with two isopropyl groups at the aryl-imino *ortho* positions, the *K* value was a true constant (complex **12**). Complex **12** was the most active of any of the catalysts in this report, with a total turnover number of about 2.5 × 10^6 mol C$_2$/mol Fe. Combining this outstanding activity with high product purities (99.4% 1-hexene, 99.3% 1-octene) and a commercially relevant *K* value of about 0.60 makes complex **12** a particularly interesting catalyst system. Finally, when *tert*-butyl groups were introduced at the *ortho* and *meta* positions (complex **13**), catalyst activity decreased and the system converted from oligomerization to polymerization.

The next modification made was to extend the length of the spacer between the central donor and the pendent phosphine, similar to that done for the pendent pyridine donor complexes **3** and **4**. Similar to **3** and **4**, systems **14** and **15** exhibited dramatically reduced activities relative to **10** and **12**. Clearly, increasing the length of the tether between the central and pendent donors is detrimental to catalyst performance.

Success with the NNP-ligated systems implied that other soft donors might be used to generate active catalysts. In fact, it was also found that sulfur-based donors (NNS) could be used to generate highly active catalysts from complexes such as **16** and **17**. Complex **16** exists in the solid state as a halide-bridged bimetallic dimer or as a monometallic complex with a molecule of solvent coordinated; in either case, the sulfur is not bound to the metal.[26] However, it is almost certain that the active catalyst contains bound sulfur, since highly active catalysts would not be expected from a bidentate α-diimine iron system.[34−36] When the sulfur donor is made more electron-rich in complex **17**, the sulfur binds more closely to the metal center in the solid state.[26] Like the phosphine-modified complexes **10**−**13**, systems **16** and **17** exhibit very high activities, with extremely high product purities. These systems also demonstrate the effects that ligand sterics have on the product distribution.

Despite the activity of NNP complexes **10**−**13** and NNS complexes **16** and **17**, aryl-modified pendent donor complexes

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(34) For an example of a very low activity bidentate α-diimine iron catalyst, see example 212 in: Brookhart, M.; Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett; A. M. A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Wang, L.; Yang, Z.-Y. U.S. Pat. 5866663 (DuPont), 1999.

(35) Bidentate salen-type Fe complexes have been reported to oligomerize ethylene in the presence of ethylalumoxane (EAO) at 200 °C and 18 bars of ethylene pressure. However, under these conditions the catalysis is almost certainly due to free TEA in the EAO: Mingxing, Q.; Mei, W.; Ren, H. *J. Mol. Catal. A: Chem.* **2000**, *160*, 243.

(36) Contrary to earlier reports, it has been recently shown that (bipy)$_2$FeEt$_2$ is not a catalyst precursor for the insertion polymerization of olefins: Yang, P.; Chan, B. C. K.; Baird, M. C. *Organometallics* **2004**, *23*, 2752.

18 and **19**, bearing oxygen and nitrogen donors, respectively, were not active for oligomerization. This finding indicates that the phosphorus and sulfur donor atoms are responsible for enhanced catalyst activity and not the mere presence of aryl substituents on the donor atoms. In the case of **18**, oxygen may simply be too poor a ligand to bind to iron; the inactivity of complex **19** falls in line with NNN-ligated complexes **5**−**8**. Complex **20** was also examined to compare the effect of changing the metal from iron to cobalt. Although PBI systems typically drop about an order of magnitude in activity upon moving from Fe to Co, system **20**, which is the cobalt analogue of iron complex **10**, exhibited no discernible activity.

Finally, to provide a suitable benchmark for these new systems, we compared their activity to complex **21** (Figure 4), one of the most active PBI catalysts. Under conditions similar to those employed throughout Table 1, catalyst **21** was shown to be about 1.5 times more active than pendent donor catalyst system **12**, thereby confirming the very high activity of these new pendent donor systems.

In conclusion, a new class of tridentate α-diimine complexes has been reported. When activated with alumoxanes, they are highly active for ethylene oligomerization and can produce a wide range of high-purity α-olefins. It is evident from these results that further studies will likely result in a number of new synthetic and catalytic opportunities.

Experimental Section

Materials and Methods. Heptane and cyclohexane were purchased from Aldrich or acquired from internal company resources, degassed, and pumped repeatedly in a circular loop over a molecular sieve bed. MMAO-3A (Al 7% by wt) was purchased from Akzo Nobel.

Product Analysis. A Hewlett-Packard 6890 Series GC System with an HP-5 50 m column with a 0.2 mm inner diameter was used for α-olefin characterization. An initial temperature of 35 °C and a rate of 2.4 °C/min were used to raise the temperature to 52 °C, followed by a rate of 15.0 °C/min to raise the temperature to 157 °C. A final ramp rate of 22.5 °C/min was used to reach the final temperature of 250 °C. ChemStation from Hewlett-Packard was used to analyze the collected data.

Ethylene Oligomerization/Polymerization. A 500 mL Zipperclave reactor from Autoclave Engineers was used for the oligomerization and polymerization reactions. The catalyst was dissolved in a small amount of dichloromethane in an NMR tube, which was then sealed and bound to the stirrer shaft of the clean, dry reactor. The reactor was evacuated, then charged with the solvent (typically 200 mL) and the aluminum cocatalyst/scavenger. The desired pressure of ethylene was introduced, and the reactor stirrer was started, resulting in breakage of the NMR tube and catalyst activation. Ethylene was fed "on demand" using a TESCOM regulator, and the reactor temperature was maintained by internal cooling. Reactions were terminated by slowly venting the reactor over a few minutes.

Ethylene/1-Pentene Co-oligomerization. The reaction was performed in the same manner as above, except the solvent was a 50:50 v/v mixture of *n*-pentane and 1-pentene. The reaction was run at a constant pressure of 68 bar, and the products in the C_{11}−C_{16} range were analyzed by gas chromatography. This range, which contains three even and three odd carbon number species, was found to contain about 2.3% of the odd-numbered products. On a fraction by fraction basis, i.e., comparing the amount of C_{11} to C_{12}, C_{13} to C_{14}, and C_{15} to C_{16}, each even−odd pair contained about 2.3% of the odd-carbon species as well. The odd-carbon species were estimated to be greater than 90% linear.

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