Discovery and Development of Pyridine-bis(imine) and Related Catalysts for Olefin Polymerization and Oligomerization

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CONSPECTUS: For over 40 years following the polyolefin catalyst discoveries of Hogan and Banks (Phillips) and Ziegler (Max Planck Institute), chemists traversed the periodic table searching for new transition metal and lanthanide-based olefin polymerization systems. Remarkably, none of these "hits" employed iron, that is, until three groups independently reported iron catalysts for olefin polymerization in the late 1990's. The history surrounding the discovery of these catalysts was only the beginning of their uniqueness, as the ensuing years have proven these systems remarkable in several regards. Of primary importance are the pyridine-bis(imine) ligands (herein referred to as PDI), which produced iron catalysts that are among the world's most active for ethylene polymerization, demonstrated "staying power" despite over 15 years of ligand improvement efforts, and generated highly active polymerization systems with cobalt, chromium, and vanadium. Although many ligands have been employed in iron-catalyzed polymerization, the PDI family has thus far provided the most information about iron's capabilities and tendencies. For example, iron systems tend to be highly selective for ethylene over higher olefins, making them strong candidates for producing highly crystalline polyethylene, or highly linear α-olefins. Iron PDI polymerizes propylene with 2,1-regiochemistry via a predominantly isotactic, chain end control mechanism. Because the first insertion proceeds via 1,2-regiochemistry, iron (and cobalt) PDI systems can be tailored to make highly linear dimers of α-olefins by "head-to-head" coupling, resulting from a switch in regiochemistry after the first insertion. Finally, PDI ligands, while not being surpassed in activity, have inspired the development of related ligand families and complexes, such as pendant donor diimines (PDD), which are also highly efficient at producing linear α-olefins.

This Account will detail a variety of oligomerization and polymerization results achieved with PDI and PDD catalysts. Our studies on ligand modification are discussed, but numerous ligands have been synthesized by others. Computational approaches, identification of catalyst active sites, noninnocent ligand studies, commercialization efforts, and other outstanding research are only briefly mentioned, at most. The reader is directed to review articles where appropriate, in order to address the cursory treatment of these areas.
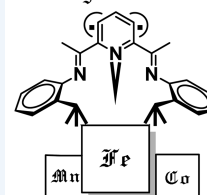
INTRODUCTION

The independent discoveries by Hogan and Banks (Phillips Petroleum) and Ziegler (Max Planck Institute für Kohlenforschung, Mülheim) over 60 years ago are the foundations of transition metal catalyzed olefin polymerization. Highlights of the Phillips discoveries included a commercially robust, chromium-based polyethylene system, as well one of the most valuable patents in the history of the petrochemical industry for "crystalline polypropylene."[1] The Max Planck Institute research, centered on titanium-based catalysts, garnered Ziegler the 1963 Nobel Prize (with Natta), as well as a lucrative royalty stream. The Phillips chromium catalysts, used for making a wide variety of polyethylenes, and the Ziegler−Natta titanium catalysts, used for making high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and isotactic polypropylene (iPP), retain their places of commercial dominance to this day.[2,3]

The heterogeneous, multisite nature of both catalyst systems, the economic potential of commodity plastics, and the growing field of organometallic chemistry made transition metal catalyzed polymerization an exciting area of study, as multiple researchers tried to better understand the catalyst fundamentals and push more systems toward commercial application. Including catalysts for ethylene oligomerization, a variety of catalysts were commercialized in the ensuing decades. For example, vanadium complexes, originally studied by Ziegler, are used for making ethylene/propylene/diene monomer (EPDM) rubber.[4] Nickel catalysts are employed in the Shell higher olefin process (SHOP) for oligomerizing ethylene to linear α-olefins.[5] Idemitsu and SABIC-Linde oligomerize ethylene using zirconium catalysts,[6] and zirconium-based metallocene catalysts have a sizable impact in the polyolefin market.[7] Titanium-based systems have expanded significantly, for example, in the development of constrained geometry catalysts (CGCs)[8] and phenoxy-imine (FI) catalysts.[9] IFP's Alphabutol process, also based on titanium, dimerizes ethylene to produce 1-butene.[10] Chromium catalyst systems, behaving quite differently from the

original Phillips PE catalysts, have been commercialized by Chevron Phillips for ethylene trimerization to 1-hexene[11] and recently by Sasol for ethylene tetramerization to 1-octene.[12] Chevron Phillips and INEOS use variants of Ziegler's original interest, the non-transition-metal, aluminum-catalyzed *aufbaureaktion*, in which ethylene slowly oligomerizes at elevated pressure and temperature in the presence of aluminum alkyls, to produce a full range of linear α-olefins.[13]

The number of commercial catalysts is a small sampling of the types reported in the literature. Among the second row metals, yttrium, niobium, molybdenum, palladium, and perhaps ruthenium and rhodium, can polymerize olefins. On the third row of the transition series, hafnium, tantalum, and tungsten provide examples of olefin polymerization. The lanthanides are also well-known as polymerization catalysts, with examples ranging from lanthanum across the series to lutetium. Returning to the first row, abundant examples exist, including titanium, vanadium, chromium, cobalt, and nickel systems.[14,15]

The preceding "fly-over" survey cannot do justice to the 60-plus years of polyolefin catalysis. Nonetheless, it frames a remarkable observation: in the 45 or so years following the initial discoveries, no significant iron-based catalyst had been reported. Yet, in a brief period in the latter half of the 1990s, three research groups, at The University of North Carolina (UNC), DuPont, and Imperial College, independently discovered that iron could in fact polymerize and oligomerize ethylene with prodigious activity. This Account is a record of my discovery of these iron-based systems while working in Maurice Brookhart's research group at UNC and the subsequent study of related catalysts.

■ DISCUSSION

Three particular catalyst families, two within Brookhart's group and one outside, captured my early imagination as a graduate student (Figure 1). The first systems were Pd complexes
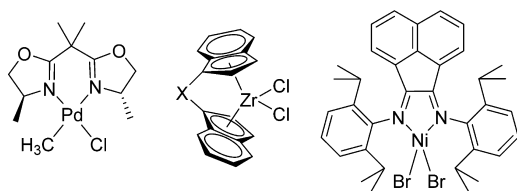

Figure 1. Bis-oxazoline, *ansa*-metallocene, and α-diimine complexes.

bearing C_2-symmetric bisoxazoline ligands for producing isotactic, alternating copolymers of *t*-butylstyrene and CO.[16] This method of polyketone synthesis demonstrated that a
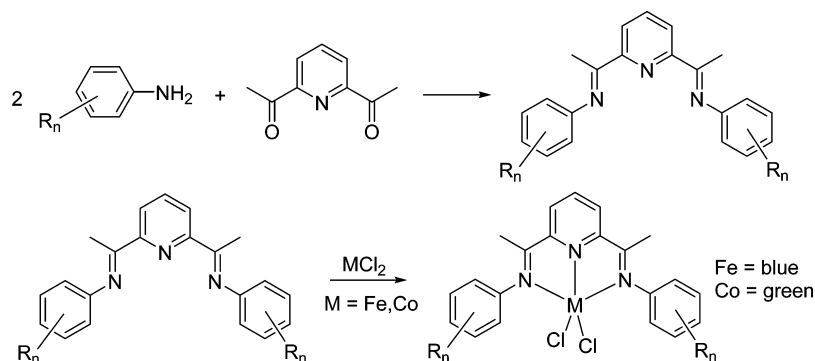
Table 1. Ethylene Polymerization Using PDI Fe and Co Catalysts[a]

complex	pressure (bar)	T (°C)	MW (peak)	productivity (g/mmol cat)
1	40	60	31100	57000
2	40	125	9000	25700
3	1	25	81000	2220
4	1	25	24000	860
5	1	25	1400	1870
6	1	0	b	1360

[a]All complexes activated with MMAO 3A. [b]Very high.

proper ligand choice could overcome the catalyst's tendency to produce syndiotactic chains (e.g., when using achiral 2,2′-bipyridine). The second group of catalysts that sparked my interest was the stereoselective *ansa*-metallocenes, such as those reported by John Ewen[17] and Hans Brintzinger[18] for polymerization of propylene. The third group of catalysts, based on sterically bulky α-diimine ligands bound to Ni and Pd, was becoming a "red-hot" area when I joined the group in 1994. Lynda Johnson had discovered that these catalysts were highly active for olefin polymerization, making them among the first late metal systems to exhibit high activity and to produce high molecular weight polymers. The catalysts were proposed to work based on the concept of using the N-aryl substituents to hinder the approach of olefins to the axial binding sites of the d^8, square planar complexes, therefore favoring propagation over associative chain displacement. A 500+ claim, 500+ example patent was filed by DuPont (who was funding Johnson's work) and UNC.[19,20]

The unifying feature of the three catalyst families in Figure 1 was *ligand design*, the idea that special ligands could be tailored to affect almost every aspect of the polymerization process, including tacticity, molecular weight, catalyst activity, polymer branch content, etc. These concepts dominated my thinking as I began work on the Ni and Pd α-diimine systems, and I speculated that bulky imine ligands might also be used with other coordinatively unsaturated metals to polymerize olefins. Simple electron counting implied that if a similar iron complex could be developed, its two fewer d electrons than nickel could be offset by adding a third donor, that is, by using a tridentate ligand. On a "rainy day" in the summer of 1996, I found a small amount of 2,6-diacetylpyridine in the laboratory and reacted it with some 2,6-diisopropyl aniline to form the crude tridentate ligand. Elsewhere I located an ancient bottle of iron(II) chloride tetrahydrate, rust rather than green colored, and coordinated the ligand to the metal in a THF slurry (Scheme 1).
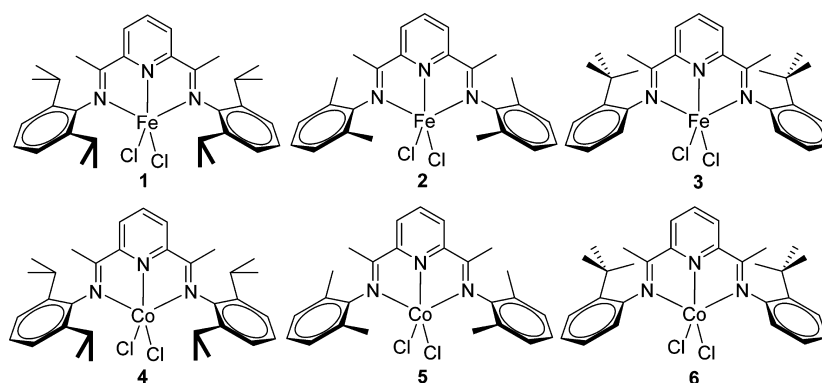
Scheme 1. Synthesis of PDI Fe and Co Complexes

Figure 2. PDI Fe and Co complexes for ethylene polymerization.

Table 2. Ethylene Polymerization at 0°C with Co Complex 6/MMAO

rxn length (min)	M_n	M_w	theoretical $M_n{}^a$
5	200000	400000	390000
10	280000	590000	490000
15	370000[b]	890000	930000

[a]M_n value if $M_w/M_n = 1.0$, determined by dividing yield by catalyst loading. [b]Some PE was insoluble.

The complex, somewhat gray in color rather than the eventual characteristic regal blue, was tested for ethylene polymerization (MMAO activation) at 1 bar of ethylene pressure. Almost immediately, polyethylene began to precipitate and the flask became warm to the touch, indicating rapid polymerization!

Over the ensuing months, multiple ligand variations were synthesized. In addition to the iron complexes, the ligands were bound to cobalt, generating green complexes that were active for polymerization (with MMAO activation). Moving the opposite direction on the periodic table, peach-colored manganese complexes were also formed, but they exhibited no polymerization activity. Observing the inactivity of the

Table 3. Ethylene Oligomerization Using PDI Fe Catalysts[a]

complex	pressure (bar)	T (°C)	yield (g)	k value	productivity (g/mmol cat)
7	14	90	68	0.70	523000
7	41	90	245	0.70	2720000
8	14	50	24	0.82	343000
8	41	50	21	0.82	420000
9	1	25	4.1	0.87	2400

[a]All complexes activated with MMAO 3A. ^{1}H NMR analysis showed >99.0% 1-alkene content for the bulk products but did not take into account branched α-olefins at the 3 and higher positions. Detailed GC analysis was reported in ref 30.

manganese systems prompted me to forego testing with chromium, which delayed the discovery of the active chromium catalysts for a few years. The simple yet quite effective rationale of electron counting had led to the discovery of the iron systems, yet over-reliance on this reasoning forestalled the use of pyridine diimine (PDI) ligands with earlier metals.

Table 1 shows initial results for ethylene polymerization using three ligand variations and their resultant Fe and Co complexes (Figure 2).[21] As with the Ni α-diimine catalysts,[19] a
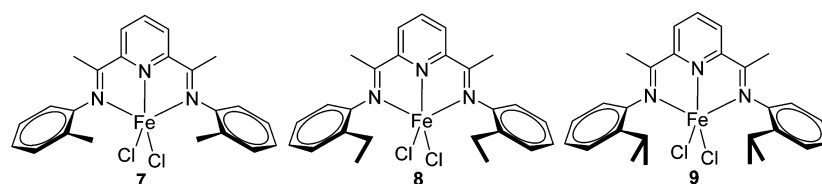

Figure 3. PDI Fe complexes for ethylene oligomerization.
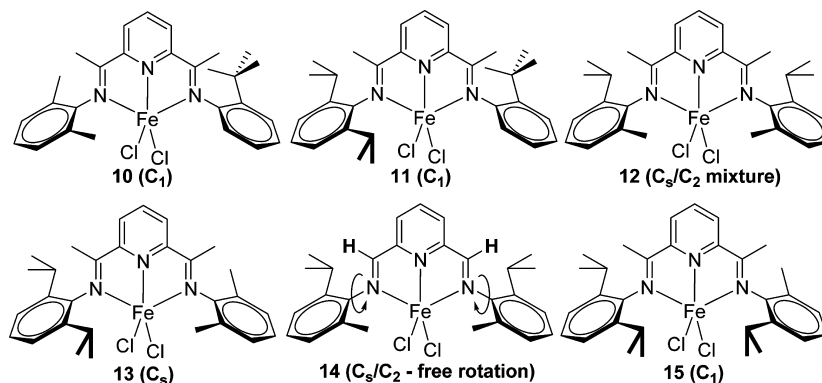

Figure 4. PDI Fe complexes for propylene polymerization (also complexes **1–3** in Figure 2).

strong correlation of ligand sterics to PE molecular weight was observed and was found to be primarily dependent on the *ortho* substituents of the N-aryl rings. The iron catalysts exhibited higher activities than their cobalt analogues, as well as a tendency toward broad polydispersities (M_w/M_n), which were

Table 4. Propylene Polymerization Using PDI Fe Catalysts[a]

complex	M_n	M_w/M_n	productivity (g/mmol cat)	%[m][4]
1	6500	2.1	1080	55
2	1800	2.3	221	
3	1700	2.1	543	
10	2700	1.8	615	
11	2000	2.2	266	59
12	4100	2.2	1450	67
13	5600	2.2	1910	56
14	1200	1.9	60	
15	5700	1.8	1010	59

[a]Reactions were performed at −20 °C and 1 bar ethylene pressure; activation with MMAO **3A**.

Scheme 2. Catalytic Cycle for PDI Fe-Catalyzed Propylene Polymerization
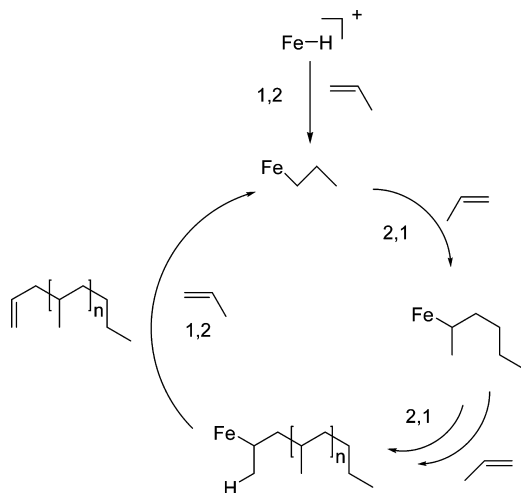
attributed to iron's propensity to exchange alkyl (i.e., polymer) groups with aluminum alkyls in solution. Additional mechanisms for broadening the M_w/M_n have been proposed.[22] The polymers were found by DSC and NMR to contain virtually no branching, in stark contrast to the homopolymers made by "chain-walking" α-diimine Ni and Pd catalysts. One peculiar outlier to the ligand sterics/MW relationship was observed for cobalt complex **6**, with a single *o-t*-butyl group on each aryl ring. Unlike the iron complexes, where a single *t*-butyl group and 2,6-diisopropyl substituents produced similar molecular weights, **6** gave such high MW at 0 °C that the PE was insoluble, even in hot trichlorobenzene. This anomaly was investigated further, with results shown in Table 2.[23] Although the data in Table 2 do not indicate polydispersities characteristic of living polymerization, this could be attributed to mass transport limitations. The PE molecular weights did increase with increasing run length, matching fairly well with the numbers expected for a living system. Whether the catalyst is truly living is a secondary consideration; a more interesting question is how the geometry of the aryl rings in the active species affects catalysis. This question is initially framed by the crystal structure of complex **6**, in which the *t*-butyl groups in the *unactivated* molecule are *syn*-oriented. It is not known whether this orientation persists in the active species nor whether iron and cobalt behave similarly. The implications are interesting, since a *syn* orientation could hinder the approach of olefin from one side of the complex; in a system (such as these) where propagation and termination are both first-order dependent on ethylene concentration, blocking the termination approach would have a huge impact on molecular weight.[24] In the case of **6**, it is plausible that the catalyst produces ultrahigh molecular weight PE due to blocking of an associative termination pathway. As the preceding discussion illustrates, this system raises questions about the fluxional nature of the PDI ligands in catalysis.

Following the initial discoveries at UNC, the university sought patent protection; it was during this process that our industrial colleagues at DuPont were informed of our efforts. To the surprise of both parties, we learned that both groups had independently discovered the same catalysts! Alison
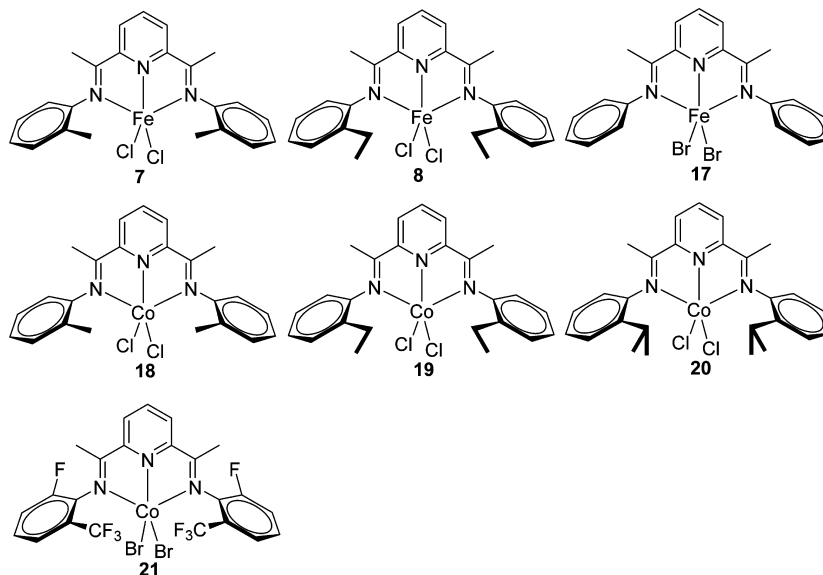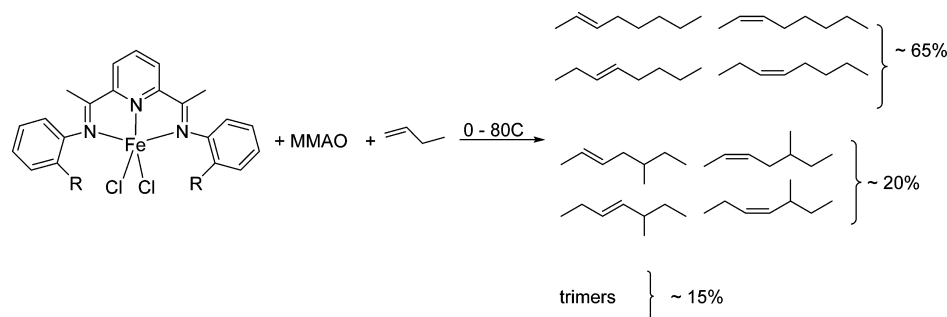

Figure 5. PDI complexes for α-olefin dimerization.

Scheme 3. α-Olefin Dimerization Catalyzed by PDI-Fe

Table 5. α-Olefin Dimerization Using PDI Fe and Co Catalysts[a]

complex	olefin	amt. (g)	T (°C)	productivity (g/mmol cat)	% dimer	% linear	D/I ratio
7	1-C_6	135	40	4190	83	66	~20
7	1-C_4	250	30	7160	82	70	~20
8	1-C_6	34	30	790	87	71	~20
17	1-C_6	67	50	2640	96	29	~1
18	1-C_4	250	30	1840	99	97	0.70
19	1-C_4	1080	30	2070	99	98	0.72
20	1-C_4	250	30	250	97	98	0.47
21	1-C_6	34	0	180	86	72–92	b

[a]Complexes activated with MMAO **3A** (except **21**, ref 33). D/I = mass ratio of (dimerized + trimerized AO)/isomerized AO and is conversion dependent. [b]Not determined.

Bennett at DuPont Central Research had also been studying iron and cobalt catalysts for a number of months. Her work had been focused on ethylene polymerization and on attempts to generate a discrete catalyst active site, while my work had been aimed at understanding the effects of the ligand on the product molecular weight and on the polymerization of propylene. We combined our efforts, with our first publication appearing as a poster at the OMCOS 9 conference in Göttingen in July of 1997.[25] Our second publication, a POLY preprint for the Spring, 1998, ACS Convention in Dallas[26] brought another development, because it was this disclosure that caught the attention of Vernon Gibson, who informed us that his group had also independently discovered the same catalyst systems. The studies in Gibson's lab were initiated by George Britovsek, with funding provided by BP. Both Alison and I gave talks at the ACS Convention that spring (overlapping each other!), and we published a joint communication.[21] The initial studies from Gibson's group were also published at that time,[27] and *C&E News* discussed the discoveries of all three groups as its "News of the Week."[28]

Returning to our laboratory studies, we continued to acquire a better understanding of the PDI catalysts' characteristics. One unique feature was the enormous selectivity of ethylene to higher olefins, as evidenced by the almost complete lack of comonomer incorporation by either the Fe or the Co catalysts. In fact, with the exception of propylene, the polymerization systems were largely inert to all higher olefins. There have been reports of copolymers in the literature and one disclosure claiming to incorporate alkene-functionalized ligands into ethylene/ligand copolymers.[29] A *bona fide* iron-based copolymerization system (e.g., for making LLDPE), despite these reports, has yet to be confirmed.

The iron PDI systems' reluctance to incorporate C_4+ olefins proved advantageous for the next discovery, ethylene oligomerization. Noting the dependence of the PE molecular
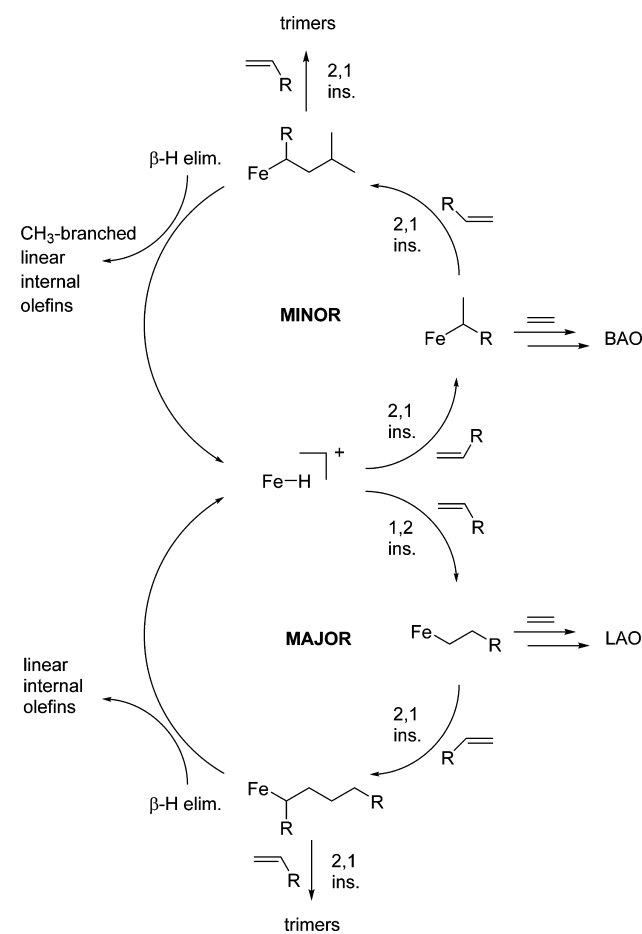
Scheme 4. Catalytic Cycle for PDI Fe-Catalyzed α-Olefin Dimerization

Table 6. Propylene Oligomerization Using PDI Co Catalysts[a]

complex	C$_3$ mass (g)	T (°C)	prod. (g/mmol Co)	% C$_6$	% Linear C$_6$ in C$_6$ fraction	% 1-C$_6$ in C$_6$ fraction	% C$_9$	% linear C$_9$
18	400	30	8050	58.5	99.0	8	28.4	96.0
19	400	30	7780	45.5	99.7	22	32.4	91.6
20	400	30	4930	69.5	99.9	59	25.1	75.9
21	1 bar	−20	649	77.5	>99	90	19.5	63

[a]All complexes were activated with MMAO **3A**, except complex **21** (MAO, ref 33).

Scheme 5. Proposed Catalytic Cycle for PDI Co-Catalyzed Propylene Oligomerization
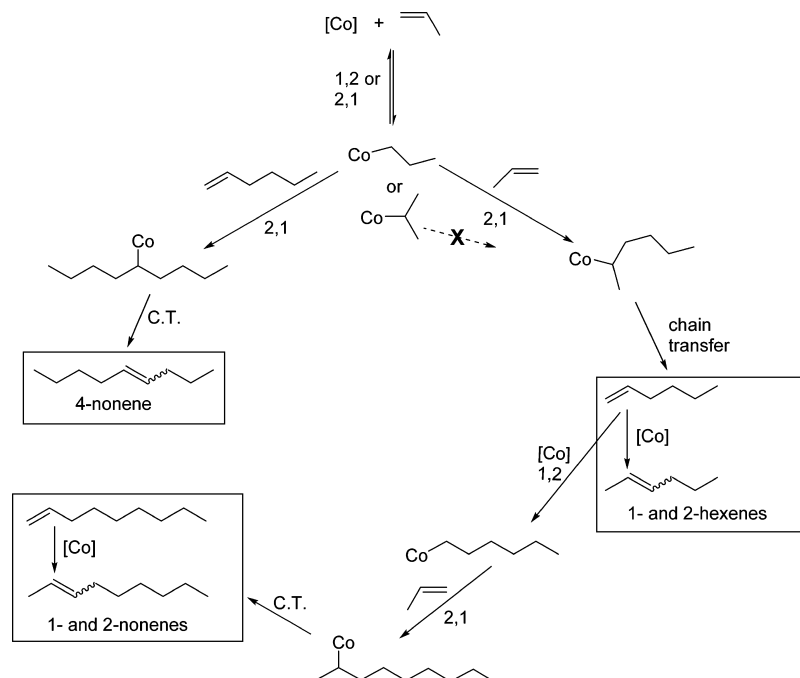
weight on ligand sterics, I examined the effects of reducing the size and number of the N-aryl *ortho*-substituents on the Fe PDI complexes (Figure 3). Upon activation with MMAO, particularly at elevated ethylene pressures, these complexes showed astonishingly high activities for ethylene oligomerization, with product purities exceeding those of commercial systems (Table 3).[30] It was noted, however, that reduction of the ligand steric bulk did allow small amounts of comonomer incorporation, which explained the trace amounts of branched products formed by the oligomerization systems. When this reincorporation was pushed to the limit by running the reaction in 1-pentene solvent, up to several percent of odd carbon number oligomers were formed. These oligomers would later be better characterized, but a better understanding of the regiochemistry of olefin insertion was needed.

This improved understanding of olefin regiochemistry was obtained by studying propylene polymerization. First, reflecting upon the reports of Ewen[17] and Brintzinger,[18] we made a variety of different PDI ligands possessing different symmetry, to determine whether the PDI complexes could be induced to polymerize propylene by an enantiomorphic site control mechanism, rather than the already observed chain end control mechanism.[31] As shown in Figure 4, four of these ligands possessed different groups on the N-aryl rings, which represented the first syntheses of "non-symmetrical" PDI ligands. The ligand symmetries are listed in Figure 4, but in the case of complex **12**, the assignment depended on X-ray data. Ultimately, these synthetic efforts failed to overcome the

Scheme 6. Ligand Alkylation for PDI Vanadium Complex
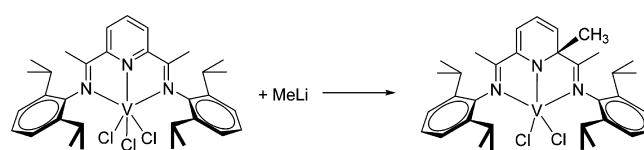
intrinsic chain end control mechanism, as ¹³C NMR analysis of the methyl pentad regions for the polymers indicated moderate isotacticity with stereoerrors characteristic of chain end control (Table 4). Wisely undeterred by my unsuccessful attempts to achieve site control, Cámpora resolved complex **12** into its *rac-* and *meso-*diastereomers several years later,[32] reporting that the *rac-* isomer was more active and showed a slight enhancement in polymer isotacticity due to site control contributions. Although the enhancement was not large, it showed that properly tailored PDI ligands could be used to "impart enantioselectivity to other catalytic reactions."

Examination of the ¹³C NMR spectra indicated that propagation occurs in these systems via 2,1 regiochemistry, making them the first isopreferred catalysts to operate by 2,1 enchainment. Analysis of the saturated polymer end groups indicated that the first insertion is primary (1,2) but the regiochemistry switches once the initiating Fe−H has been converted to an Fe-alkyl, likely indicative of the steric congestion around the active site. This switch in regiochemistry generates an *n*-butyl end group. Finally, analysis of the unsaturated chain ends showed exclusive production of allyl
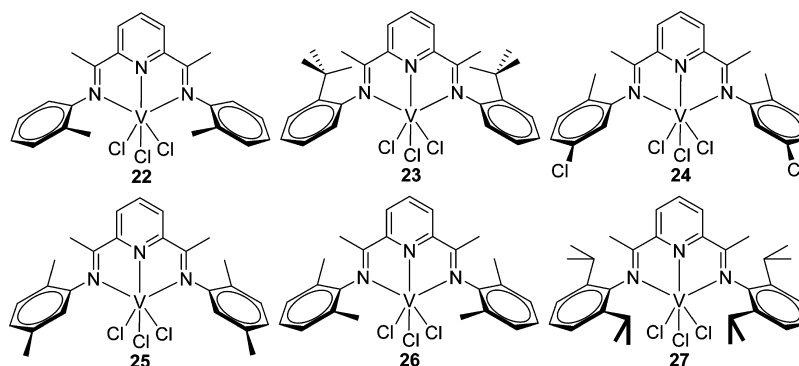
Figure 6. PDI vanadium complexes.

Table 7. Ethylene Oligomerization and Polymerization Using PDI V Catalysts[a]

complex	productivity (g/mmol cat)	% purity 1-hexene	% liquids
22	29600	94.7	98.3
23	3110	86.7	71.0
24	58100	94.4	98.1
25	33400	94.9	98.4
26	26700	b	9.8
27	4280	86.7	14.3

[a]Complexes activated with MAO, 60 °C, and 17 bar ethylene pressure. [b]Not determined.

end groups, implying that β-H elimination occurs exclusively toward the *least* sterically hindered carbon. These observations are depicted in the catalytic cycle (Scheme 2), and provide circumstantial evidence supporting iron PDI's "steric disdain" for incorporating higher olefins.

The switch in regiochemistry between first and second insertion, combined with the observation that less hindered N-aryl groups employed in ethylene oligomerization could incorporate small amounts of comonomer, opened a new avenue of research, olefin dimerization. In studies performed at Chevron Phillips Chemical Company (CPChem), we tested catalysts that had been reported for ethylene oligomerization, as well as other similar complexes (Figure 5), and found that they were highly active for linear (head-to-head) dimerization of higher olefins (Scheme 3, Table 5).[33] When the steric bulk was reduced relative to the polypropylene systems, some of the regiospecificity of the initial insertion was lost, which resulted in about 25−35% of the dimers possessing methyl branches. These methyl branches were the result of initial 2,1 insertion, followed by 2,1 insertion and chain termination. This observation gave an improved understanding of the branches formed during ethylene oligomerization; they were being formed by higher olefin incorporation, but only by 2,1 insertion, and only

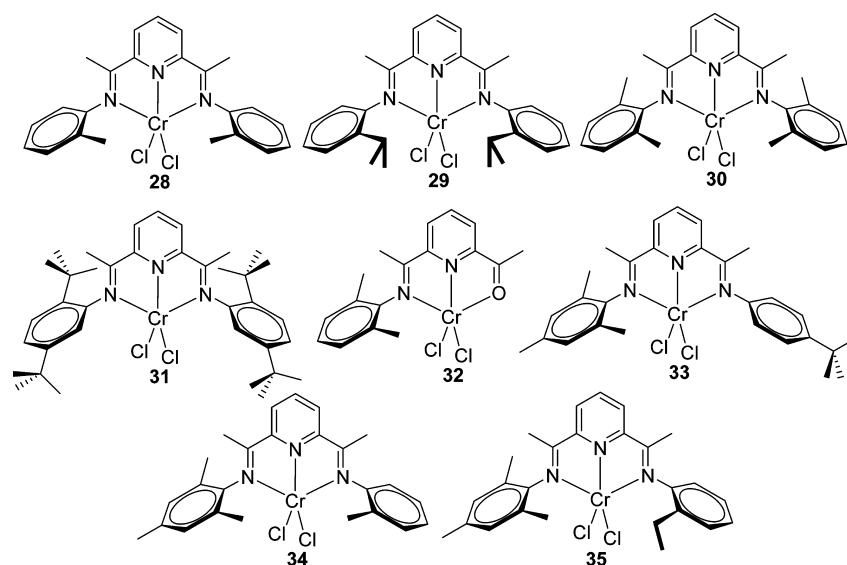**Scheme 7. Catalytic Cycle for PDI V-Catalyzed α-Olefin Dimerization**
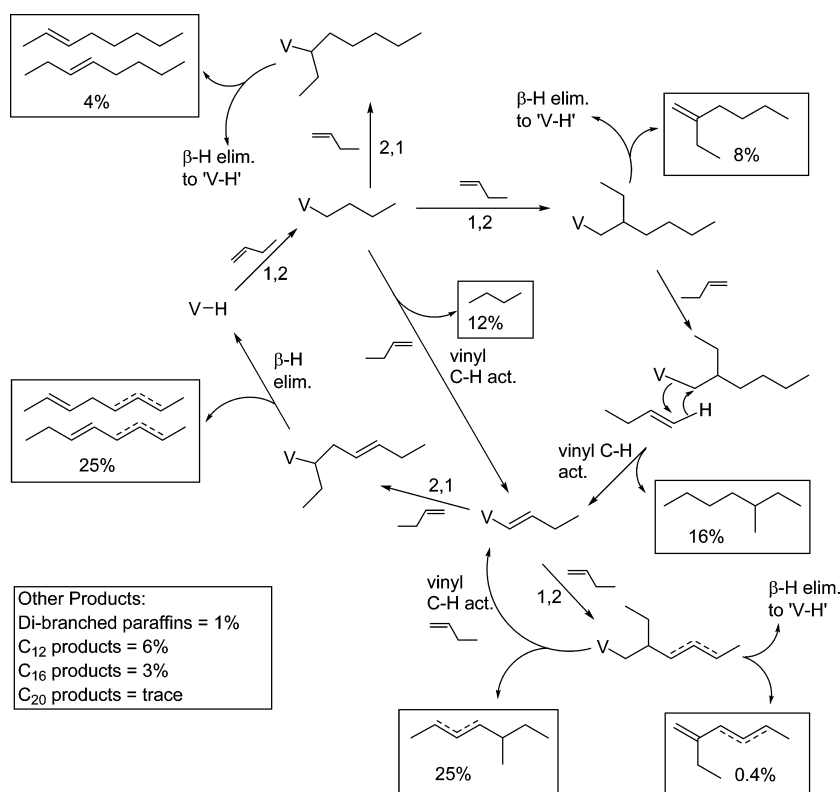
Figure 7. PDI (except **32**) Cr complexes.

into "Fe−H" species. We were able to use the ratio of linear to branched dimers (2:1 to 3:1) to more accurately assess the amount of comonomer incorporation during ethylene oligomerization. It became apparent that most comonomer incorporation was never being observed since it happened with 1,2 regiochemistry at Fe−H, producing linear Fe-alkyls, which would insert only ethylene (Scheme 4). De Bruin reported an interesting theoretical study of linear dimerization;[34] however, the proposal that trimer byproducts form via insertion of olefin dimers into Fe-butyl species appears to go against the steric preference of the system. It seems more likely that trimer products are formed by straightforward chain growth from Fe-*iso*-octyl intermediates that sometimes add a third molecule of 1-butene before terminating.

We observed during our dimerization studies that some of the α-olefin feed was being isomerized, presumably due to 2,1 insertions followed by β-H elimination to the internal olefin. With iron, these reactions were not highly competitive with dimerization, but with the cobalt PDI systems, isomerization was often the dominant reaction (see Table 5, complexes 18−20). In fact, 2,1 initial insertion led almost exclusively to isomerization, such that the dimers were very highly linear. To overcome the limitations of isomerization, the cobalt systems were tested with propylene, which in the case of the iron had produced a Schulz−Flory mix of oligomers. With cobalt, however, the catalysts produced an extremely linear mixture of dimers and trimers via step growth (Table 6).[35] The catalytic cycle, shown in Scheme 5, made a somewhat odd, but rational, mixture of 1- and 2-hexene, 1-, 2-, and 4-nonene, and small amounts of higher olefins, an unprecedented mixture for propylene oligomerization. Gibson later reported several studies involving propylene oligomerization and α-olefin dimerization using complex **21**.[36]

In the preceding discussion, it was noted that our testing of PDI ligands on the earlier transition metals was halted by the inactivity of manganese. However, in 1999 Gambarotta disclosed that vanadium PDI complexes were quite active,[37] demonstrating that catalysis was not limited to iron and cobalt. Gambarotta's report also provided an introduction to the ligand-centered chemistry that could occur on PDI ligands, especially when exposed to alkylating agents present in

Table 8. Ethylene Oligomerization and Polymerization Using PDI Cr Catalysts[a]

complex	C₂ pressure (bar)	T (°C)	MW_peak	productivity (g/mmol cat)	major products
28	27	80	40000	*b*	1-butene
29	1	35	*c*	*b*	1-butene
30	1	35	830	760	wax/PE
31	27	100	11000	7600	PE
32	27	80	1540	7880	wax/PE
33	1	40	350	*b*	1-butene
34	27	60	150	8630	linear α-olefins, $k = 0.60$
35	27	60	160	5700	linear α-olefins, $k = 0.65$

[a]Complexes activated with MMAO **3A**. [b]Productivities not be determined when the major product was butene. [c]Not determined.
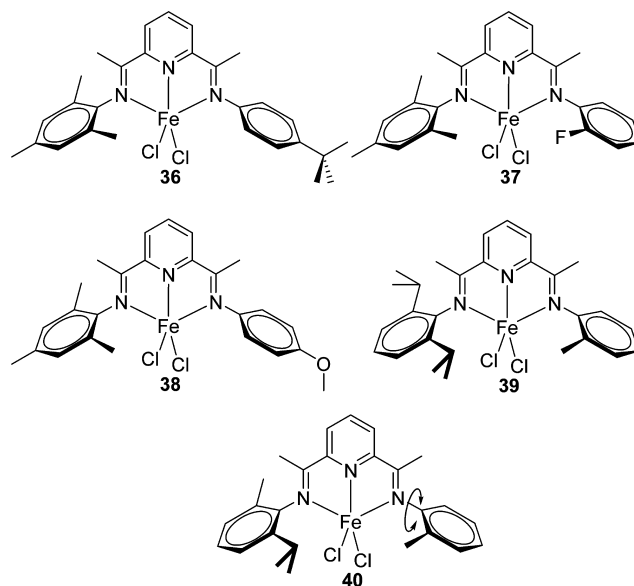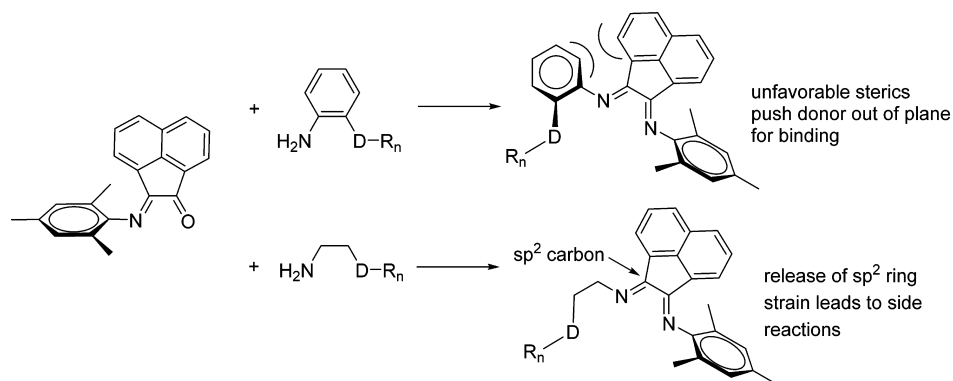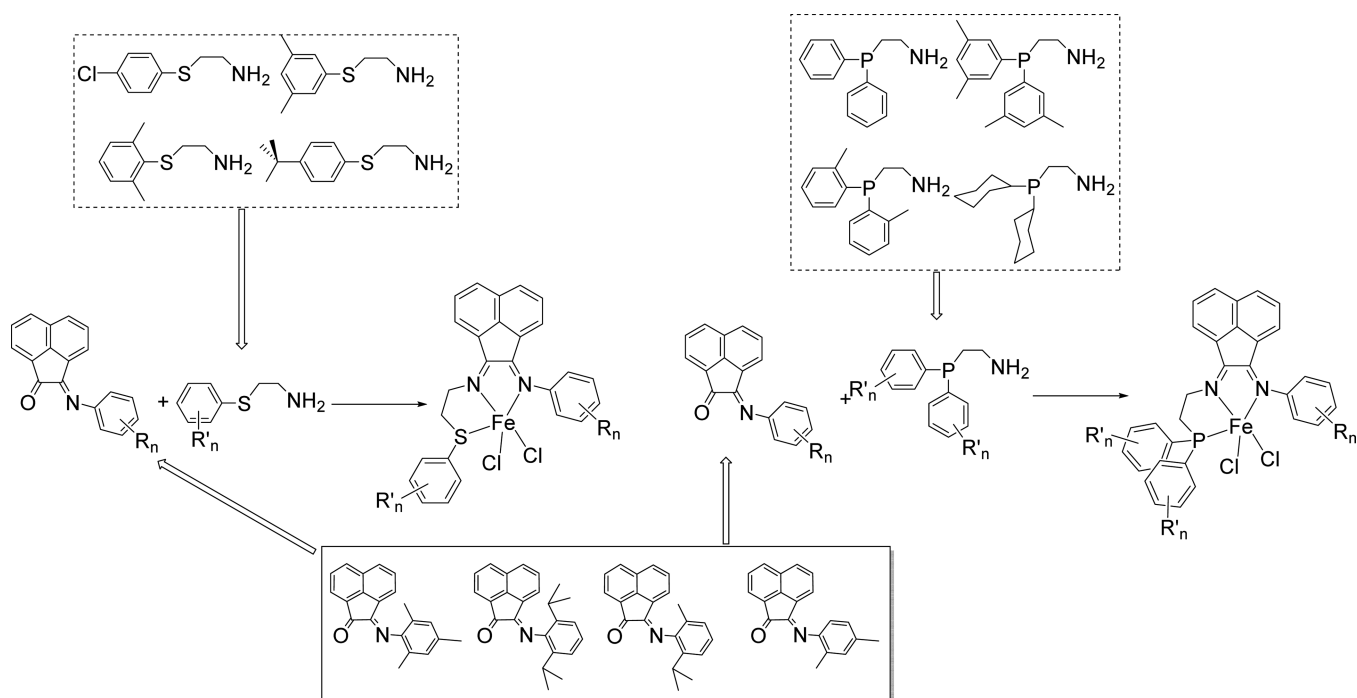

Figure 8. Asymmetric PDI Fe complexes for ethylene oligomerization.

alumoxanes (Scheme 6). A variety of additional PDI vanadium catalysts were evaluated by my colleague at the time, Roland

Scheme 8. Challenges in Preparing Pendant Donor Diimine (PDD) Complexes

unfavorable sterics push donor out of plane for binding

release of sp² ring strain leads to side reactions

Scheme 9. Synthesis of Pendant Donor Diimine (PDD) Complexes

Schmidt.[38] Although the vanadium oligomerization systems showed high activity (Figure 6, Table 7), their tendency to make PE side products and their lower product purity made them noncompetitive with their iron PDI analogues. As part of our α-olefin dimerization studies, we did evaluate vanadium complex **22**, which produced dimers selectively upon MMAO activation. Remarkably, the dimers were a mixture of alkanes, alkenes, and dienes. The mechanistic cycle in Scheme 7 was proposed, in which the regiochemistry of propagation is closely tied to the mechanism of termination, and termination routinely occurs via vinyl C–H bond activation.[39]

The vanadium catalysis prompted us to bypass manganese and bind the PDI ligands to chromium, giving either Cr(II) or Cr(III) salts. Like vanadium, chromium produced potent oligomerization and polymerization systems. An initial result for chromium PDI catalysis was reported by Gambarotta;[40] full papers were authored both by Esteruelas[41] and by us, along with Mike Carney, our collaborator at the University of Wisconsin—Eau Claire.[42] Figure 7 shows a variety of chromium PDI complexes, and Table 8 summarizes their polymerization results.

In Figure 5, several nonsymmetrical (i.e., different aryl groups at each imine) PDI ligands are shown. A few years after these types of complexes were tested for propylene polymerization, researchers at Shell developed new methods for preparing asymmetric ligands and tested them for ethylene oligomerization.[43] Three examples (complexes **36**–**38**) are shown in Figure 8. It was reported for some of these complexes that the activity was comparable to the symmetrical PDI analogues, the Schulz–Flory k value exhibited less drift, and the overall product purity was increased relative to the symmetric complex **7**. It is likely that rotation of the tolyl groups in **7** makes both the syn ("up–up") and anti ("up–down") species present during catalysis, generating a bimodal oligomer distribution. The presence of both species was demonstrated by Ionkin, who crystallized complex **7** and found about 72% of the molecules to be in the up–up conformation.[44] This leads to an interesting conclusion, that the ligands bearing different, that is, asymmetric, aryl groups (e.g., **36**) may be more likely to exhibit single-site behavior during catalysis. In an extreme example of non-single-site behavior, Bianchini observed simultaneous ethylene polymerization and Schulz–Flory oligomerization with
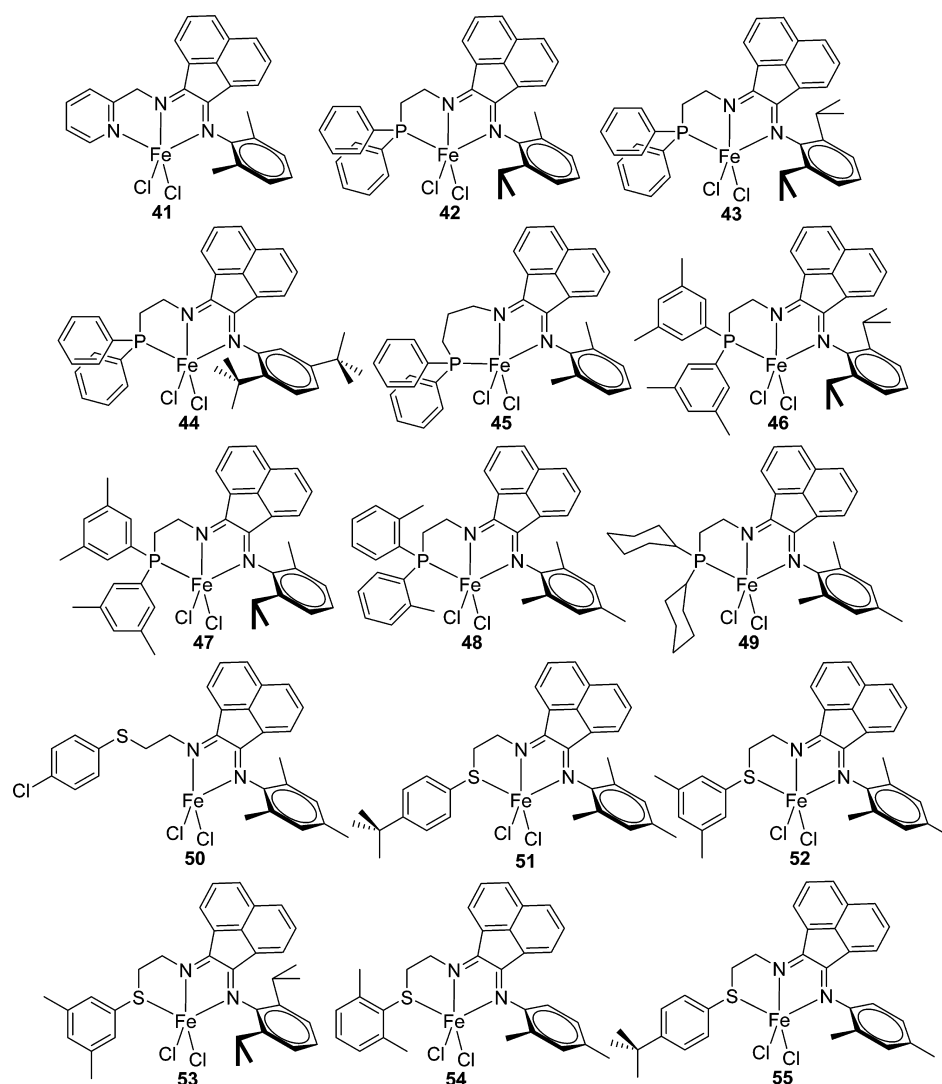
Figure 9. PDD Fe and Co complexes.

Table 9. Ethylene Oligomerization and Polymerization Using PDD Fe and Co Catalysts[a]

complex	C_2 pressure (bar)	T (°C)	yield (g)	productivity (g/mmol cat)	k (C_{12}/C_{10})	% 1-C_6 purity
41	68	50	44	3700	0.44–0.63	99.0
42	68	50	108	35200	0.49–0.61	99.4
43	82	50	124	70600	0.60	99.4
44	27	45	15	2700		b
45	27	40	21	3300	0.61	98.6
46	68	50	49	11900	0.72	
47	68	50	149	55600	0.60	99.6
48	68	42	8.9	1970	0.82	
49	68	50	23	7300	0.86	
50	68	50	110	21400	0.65	99.5
51	68	50	149	91600	0.72	99.8
52	68	50	55	26900	0.72	99.3
53	68	50	116	35500	0.85	
54	68	35	14	2700	0.74	
55	68	50	~40	20100	0.24–0.61	

[a]Complexes activated with MMAO **3A**; k value ranges indicate drift upward from C_8 to C_{18}. [b]PE/wax.

complex **39**, presumably due to the presence of two sterically different faces available for olefin approach.[45] One could

envision combining the product distribution effects of free rotation or oscillation (e.g., in **7**) and ligand asymmetry (e.g., in **39**) to give a complex such as **40**, which would provide four unique faces for ethylene approach.

The potential of PDI iron complexes for ethylene oligomerization prompted multiple researchers to investigate alternatives to the PDI structure. Chevron Phillips, formerly Chevron Chemical Company, where I have been employed since 1998, was no exception to this trend. In 2003, I recalled prior studies from Maurice Brookhart's lab, in which Dan Tempel had prepared monoimines from acenaphthenequinone and bulky anilines and had then made asymmetric α-diimine ligands by condensing the free ketone with a different aniline.[46] Supposing that one of these anilines could be substituted at the *ortho* position with a pendant donor; it seemed plausible that new tridentate ligands could be prepared. First, a larger scale route to monoimines was developed, using slow addition of aniline to the dione, rather than tedious chromatographic separation. The monoimines could then be reacted with the pendant donor-containing amines (Scheme 8). This approach caused two problems. First, aryl imines could not rotate into the plane of the acenaphthene backbone, thus preventing coordination of the pendant donor. Switching from an aromatic amine to an aliphatic amine revealed the second problem,

which was the inability to isolate clean ligands when aliphatic amines were used. An explanation of this difficulty was provided by Ragaini.[47]

These difficulties were overcome in conjunction with Mike Carney's laboratory, by using iron halide salts to precipitate the ligands. The success of the "templating" approach allowed formation of a variety of tridentate iron complexes (Scheme 9).[48−50] When we screened these systems for ethylene oligomerization, many proved to be exceptionally active. Figure 9 shows a selection of the complexes that are active; Table 9 summarizes oligomerization results. Compared with the original PDI complexes, the PNN and SNN pendant donor diimine (PDD) systems exhibit lower activity, but their selectivity for ethylene is even greater than the PDI catalysts, giving unprecedented product purities.

CONCLUSION

Although my work has been focused on olefin oligomerization, PDI and more recently PDD ligands have been studied in a variety of reactions.[51] Concerning their potential for producing linear α-olefins, the reader is directed to reviews by Sun and Redshaw[52] and by Breuil and Olivier-Bourbigou.[53] In the latter reference, the authors conclude, "none of the ligands mentioned here [oligomerize] ethylene with similar or higher activities than [PDI] iron complexes... The [second] highest activities were observed by Small and coworkers for [PDD] ligands." Clearly, these systems possess attractive activities, and it is worth noting that the polymer coproduct concerns described in the literature[54] were at one time problematic for all of the currently practiced α-olefin processes. Regarding commercial polyethylene applications, the extreme selectivity of iron PDI for ethylene has allowed these systems to find use as hybrid catalysts, in which the iron component produces a linear medium molecular weight homopolyethylene matrix that is intimately mixed with a high molecular weight copolymer produced by an early transition metal catalyst. The copolymer enhances the mechanical properties, such as impact strength at low temperatures or stress crack resistance, of the blend.[14a,55]

In summary, PDI and related catalysts have been used in a variety of chemistries, but their commercial promise is still developing. In an unexpected twist, some 15 years or so after beginning his work on metallocenes, Ewen cited the PDI systems as emerging new catalysts.[56] This bit of gracious "irony", from a chemist who had positively influenced my career, was, and is, kindly appreciated.

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Notes

The authors declare no competing financial interest.

Biography

Dr. Brooke L. Small received his B.S. degree in chemistry at Texas A&M in 1994 and completed his Ph.D. studies at The University of North Carolina in 1998, under the direction of Maurice Brookhart. He joined Chevron (now Chevron Phillips) in 1998, and in addition to PDI and PDD catalysts, he has also worked on the development of metallocene-based synthetic lubricants and selective ethylene trimerization and tetramerization. He has authored or coauthored about 20 papers, holds over 30 U.S. patents, and enjoys working with academic collaborators.

DEDICATION

This Account is dedicated to Maurice Brookhart on the occasion of his retirement.

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