

Late-Metal Catalysts for Ethylene Homo- and Copolymerization

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1. Introduction and Scope

Polyolefins are a multibillion dollar a year industry with worldwide production in excess of 160 billion pounds and polyethylene alone in excess of 100 billion pounds. Despite this size and the commodity nature of the business, polyolefins are the fastest-growing segment of the polymer industry.^{1,2} Although it has been almost half a century since polyethylene's commercialization, polyolefins remain highly technology-driven.^{3–8}

The three major classes of polyethylene are described by the acronyms HDPE, LDPE, and LLDPE.⁵ High-density polyethylene (HDPE) is a linear, semi-crystalline ethylene homopolymer ($T_m \approx 135$ °C) prepared by Ziegler–Natta and chromium-based coordination polymerization technology. Linear low-density polyethylene (LLDPE) is a random copolymer of ethylene and α -olefins (e.g., 1-butene, 1-hexene, or 1-octene) produced commercially using Ziegler–

Natta, chromium, and metallocene catalysts. Low-density polyethylene (LDPE) is a branched ethylene homopolymer prepared in a high-temperature and high-pressure free-radical process. The extreme conditions of LDPE polymerizations demand considerable capital investment, so there have been few new plants in recent years, essentially capping this capacity. Copolymers of ethylene with functionalized olefins such as methyl (meth)acrylate, (meth)acrylic acid, and vinyl acetate are also important commercial polymers. These copolymers are prepared by free-radical processes similar to those used for LDPE production.⁹ Incorporation of the polar functionality is relatively random. The acid or ester functionality may be converted to their respective salts, leading to polymers bearing ionic cross links. These polyolefin ionomers are used in applications requiring extreme toughness (e.g., golf ball covers) or superior sealing properties (e.g., bacon packaging).

There have been many rapid advances in the catalysis of olefin polymerization, including the “metallocene revolution”.^{10–30} Metallocene-based catalysts are dramatically different from previous generations of catalysts. For example, their homogeneous nature leads to lower polydispersities and more uniform incorporation of α -olefin comonomers than obtained with Ziegler–Natta catalysts. The resulting improvements in the properties of the polymers produced by metallocenes—clarity, strength, and lower hexane-extractables—usually come at a higher price, so market penetration has not been as great as was originally predicted. These single-site catalysts have been reviewed or commented upon elsewhere.^{10–30}

The high oxophilicity of early transition metal catalysts (titanium, zirconium, or chromium) causes them to be poisoned by most functionalized olefins, particularly the commercially available polar comonomers. However, there are examples of copolymerizations with special substrates^{31–40} or with very high levels of a Lewis acid incorporated into the polymerization system to protect the polar functionality through complexation.^{41–43} Alternative routes to polar copolymers involving metathesis of cyclic olefins and functionalization of the resulting unsaturated polymer or metathesis of polar cycloolefins followed by hydrogenation to remove the resulting unsaturation have been published.^{44,45} The cost of these multistep



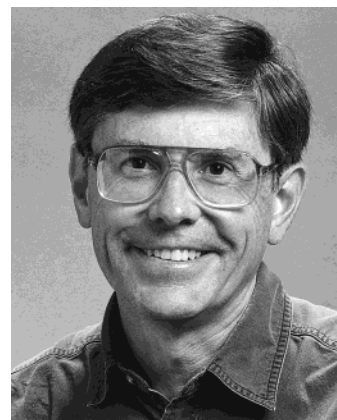
Steve Ittel, born in Hamilton, OH (1946), received his B.S. degree in Chemistry from Miami University in 1968. After two years of studying photochemical smog in the greater New York City area for the USPHS, he attended Northwestern University where he received his Ph.D. degree in Inorganic Chemistry in 1974 with Jim Ibers. Joining DuPont's Central Research, he was involved in the elucidation of fluxional processes in five- and seven-coordinate molecules. After work on C–H activation and diamagnetic and paramagnetic agostic M–H–C interactions, he moved to Research Management. Never straying far from the scientific edge, he has been involved in small-molecule catalysis including hydrocarbon oxidation, fluoro–organometallic chemistry, and olefin hydrocyanation. The molecules started getting a little bigger as his interests turned toward elastomeric polypropylene, catalytic chain transfer in free-radical polymerizations, and most recently ethylene polymerization with polar comonomers. Other interests having both technical and nontechnical aspects include book preservation and bonsai. He has 80 publications, 18 patents or published patent applications, and a book to his credit.



Lynda Johnson grew up in Minnesota and Iowa. She received her B.A. degree in Chemistry and Mathematics from Wartburg College in Waverly, IA, in 1986. While an undergraduate, she was introduced to organometallic chemistry by doing summer research with Bob Angelici at Iowa State University. Johnson received a NSF graduate fellowship to pursue this interest and attended graduate school at Caltech, where she studied olefin metathesis with Bob Grubbs. After receiving her Ph.D. degree in Chemistry in 1992, she spent two years as a NSF postdoctoral fellow with Maurice Brookhart at the University of North Carolina, studying olefin insertion polymerizations catalyzed by late metals. At the end of 1994, Johnson joined DuPont Central Research. She is currently a senior research chemist at DuPont developing ethylene polymerizations with polar comonomers. In 1992 and 1998, respectively, she was a recipient of the Caltech McCoy Award and the ACS Cooperative Research Award.

routes would preclude commercialization of all but the most valuable polymers. Therefore, copolymers of functionalized olefins with ethylene are still produced commercially by free-radical polymerizations.⁴⁶

The lower oxophilicity and presumed greater functional-group tolerance of late transition metals relative to early metals make them likely targets for the



Maurice Brookhart (born 1942) grew up in the mountains of western Maryland and attended Johns Hopkins University in Baltimore where he received his A.B. degree in Chemistry in 1964. He carried out his doctoral work in physical organic chemistry at UCLA under the direction of Saul Winstein. After finishing his Ph.D. degree in 1968, he spent six months as a National Science Foundation postdoctoral fellow at UCLA followed by a year of study at Southampton University as a NATO postdoctoral fellow. Brookhart joined the University of North Carolina faculty in 1969 and is currently a William R. Kenan, Jr. professor in the Department of Chemistry. He has spent research leaves in Rennes (1981), Oxford (1982–83), and most recently as a Visiting Miller Professor at UC–Berkeley (Fall, 1996) and an Iberdrola Visiting Professor in Seville (Spring, 1997). Brookhart served as Associate Editor of *Organometallics* (1990–96) and received the 1992 ACS Award in Organometallic Chemistry and a 1994 ACS Cope Scholar Award. Brookhart's research interests span mechanistic, synthetic, and structural organometallic chemistry. Most recently, efforts have focused on the development and mechanistic understanding of late-transition-metal complexes for olefin polymerizations and employing carbon–hydrogen bond-activation processes in catalytic transformations of small molecules.

development of catalysts for the copolymerization of ethylene with polar comonomers under mild conditions. In contrast to the wealth of information describing olefin polymerizations based on early transition metals, until recently there were relatively few reports of late transition metal catalysts for the polymerization of ethylene and α -olefins. This is because late metal catalysts generally exhibit reduced activities for olefin insertion relative to early-metal catalysts, and β -hydride elimination typically competes with chain growth, resulting in the formation of dimers or oligomers. In fact, this is the basis for the Shell Higher Olefin Process (SHOP). This generalization has been changing recently, and those changes are the subject of this review.

This review covers families of catalysts based largely on chelating nitrogen-based ligands that are active for the homopolymerization of ethylene and the copolymerization of ethylene with α -olefins and polar comonomers. Late metal catalysts not active for ethylene polymerization are not included, but when a system is active for ethylene polymerizations, its activity for polymerizations beyond ethylene are included. Catalyst syntheses, structures, activities, and chain-growth mechanisms and the influence of these factors on the structures of the resulting polymers are discussed.

Subjects specifically excluded are cycloolefin polymerizations catalyzed by "naked nickel" catalysts, palladium-catalyzed ethylene/carbon monoxide alternating copolymerizations, metathesis polymerizations of cyclic olefins, and diene polymerizations

utilizing cationic, coordinatively unsaturated complexes. The use of cationic palladium and nickel catalysts for the insertion polymerization of styrene, substituted cyclopropenes,⁴⁷ and particularly norbornene derivatives have been reviewed recently,^{48–60} as have the alternating copolymerization of olefins and carbon monoxide by palladium(II) and nickel(II) complexes^{61–63} and the polymerization of dienes by nickel allyl catalyst precursors.^{64–66} In the present review, there is no intention to be comprehensive about catalysts specific to ethylene conversion to α -olefins, for instance the Ni(II) complexes bearing P–O ligands used in Shell's SHOP process, but many examples are included in that they relate mechanistically to the subject of this review.

It should be realized that throughout this review, the term "catalyst" often refers to a catalyst precursor that must be activated to achieve the desired polymerization. Some of the discrete cationic complexes will polymerize ethylene without adjuvants, but more often, catalyst activators or cocatalysts are required and there is a final chemical transformation that converts the catalyst precursor to its active form.

There have been several recent overviews of the area of olefin polymerization. Academic reviews of the α -diimine chemistry^{67–69} complement other, more industrial perspectives.^{70–72} The considerable additional activity in a number of industrial and academic laboratories has generated a body of literature of sufficient size that a review is now appropriate. It should be noted, however, that a very high percent of the information appears in the patent literature. With free, on-line patent databases, this material should now be readily available to most research labs in the world. We have gone to some length to guide the reader through the patents. In larger patents with many examples, the examples are often in random order so example numbers are included in the tables to guide the reader to the particular experiment; they are indicated as E-###.

2. Neutral Ligands

2.1. Palladium and Nickel

The area of ethylene polymerization with late metal catalysts was rejuvenated when Brookhart and his group reported a family of new cationic Pd(II) and Ni(II) α -diimine catalysts (trademarked the Versipol catalyst system by DuPont) for the polymerization of ethylene, α -olefins, and cyclic olefins and the copolymerization of nonpolar olefins with a variety of functionalized olefins.^{73–81} These catalysts are now the focus of a joint development effort between the University of North Carolina at Chapel Hill and DuPont, and as can be seen from the scope of this review, they are being pursued at many other companies and universities.

Three key features of the original α -diimine polymerization catalysts are (1) highly electrophilic, cationic nickel and palladium metal centers; (2) the use of sterically bulky α -diimine ligands; and (3) the use of noncoordinating counterions or the use of reagents thought to produce noncoordinating counterions.⁷³ The electrophilicity of the late metal center

in these cationic complexes results in rapid rates of olefin insertion. The use of bulky ligands favors insertion over chain transfer. The use of noncoordinating counterions provides an accessible coordination site for the incoming olefins. Of these three features, only the last seems to be a requirement for the late transition metal catalysts. For example, the chemistry has been extended to additional metals, the ligands now include anionic species, and the steric bulk may be reduced if conditions are modified appropriately. Catalysts that feature all of these attributes except steric bulk often are olefin oligomerization catalysts.^{82–84} There are reports of ethylene polymerization by ligand-free palladium systems which are not well characterized, and it is unclear what species are responsible for the ethylene polymerization.^{85,86}

2.1.1. α -Diimines

The easily varied steric and electronic properties of the α -diimine ligands are an important feature of the nickel α -diimine catalyst systems. The α -diimine ligands are well-known to stabilize organometallic complexes.^{87–89} Their synthesis involves the condensation of a diketone with 2 equiv of an alkyl- or arylamine, often catalyzed by a Lewis or Bronsted acid. α -Diimines with heteroatom backbone substituents have been synthesized from bis(imido) chloride precursors.¹⁰⁷ Using these synthetic routes, the backbone and aryl substituents are readily varied, enabling the preparation of arrays of ligands with independent control over the steric and electronic effects at the metal center. Simple arrays can be extended to exhaustive libraries using techniques well-developed in the pharmaceutical industry.^{90,91} A variety of approaches to the synthesis of polymer-bound ligands for polymerization catalysts have been disclosed,^{92–101} and elegant solid-phase techniques for synthesizing, screening, and encoding nickel and palladium catalysts based upon α -diimines and other ligands have been developed.^{102–104} The development of sound analytical techniques for characterization of the resulting polymers is more problematic, but advances are being made. For instance, electrospray ionization mass spectrometry provides implicit encoding of the catalyst identities by the mass of the catalyst residue remaining on the polymer chain.¹⁰⁵ Short-column chromatographic techniques allow molecular weight determinations or compositional determinations in periods of as little as 10 s, although 30 s is closer to the norm.¹⁰² The syntheses of free ligands are not discussed in detail in this review, but their syntheses can usually be located in the papers or patents referenced herein. In fact, the α -diimine ligands do not need to be preformed before complexation; combining the dione, aniline, and metal salt in mixed aqueous/organic systems can lead directly to (DAB)NiX₂ complexes.¹⁰⁶

The simplest catalyst precursors are the metal dihalides. A number of routes have been developed into these and other catalyst precursors. These methods and the routes to particular complexes of nickel and palladium bearing α -diimine ligands are summarized in Table 1.^{91,107–112} The easiest involve

Table 1. Reported Syntheses of α -Diimine Complexes of Ni and Pd

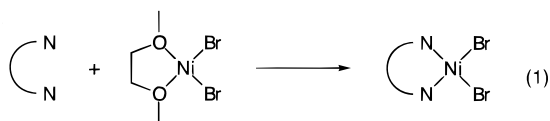
metal precursor	DAB	reactants	product	ref ^a
(DME)NiBr ₂	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	ligand addition	(DAB)NiBr ₂	75, 76 E-29
	(2,6- <i>i</i> -PrPh) ₂ DABH ₂			75, 76 E-28
	(2,6-MePh) ₂ DABH ₂			75, 76 E-30
	(2,6- <i>i</i> -PrPh) ₂ DABAn			75, 76 E-31
	(2,6-MePh) ₂ DABAn			75, 76 E-32
	(2,6-MePh) ₂ DABMe ₂			75, 76 E-33
	(2- <i>t</i> -BuPh) ₂ DABMe ₂			75, 76 E-185
	(2- <i>t</i> -BuPh) ₂ DABAn			75, 76 E-186, 456
	(2,5- <i>t</i> -BuPh) ₂ DABAn			75, 76 E-187
	(2,6- <i>i</i> -PrPh) ₂ DAB(4-F-Ph) ₂			75, 76 E-278
	(2-CF ₃ Ph) ₂ DABMe ₂			75, 76 E-280
	(2,5- <i>t</i> -BuPh) ₂ DABAn			75, 76 E-457
	(2- <i>i</i> -Pr-6-MePh) ₂ DABMe ₂			75, 76 E-475
	(2,6-MePh) ₂ DABSCH ₂ CH ₂ S			107, E-23
	(2,6- <i>i</i> -PrPh) ₂ DABSCH ₂ CH ₂ S			107 E-24
	(Ph) ₂ DABSCH ₂ CH ₂ S			107 E-25
	(2,6-MePh) ₂ DABSC ₆ H ₄ S			107 E-26
	(2,6-MePh) ₂ DAB(OMe) ₂			107 E-27
	(2,6-MePh) ₂ DABOCH ₂ CH ₂ O			107 E-28
	(2,6-MePh) ₂ DABOCH(CH ₂ OMe)CH ₂ O			107 E-29
	(2,6-MePh) ₂ DABNMeCH ₂ CH ₂ O			107 E-30
	(2,6-Me-4-MeOPh) ₂ DAB(N-2,6-Me-4-MeOPh) ₂ CO			107 E-32
	(2,6-MePh) ₂ DABNMeCH ₂ CH ₂ NMe			107 E-33
	(2,6-MePh) ₂ DAB(SC ₃ N ₂ H ₃) ₂			107 E-83
	(2,6-MePh) ₂ DAB(NH-2,6-MePh) ₂			107 E-85
	(2,6-MePh)(<i>i</i> -Pr)DABcam			112
	(2,6-MePh)(2-MePh)DABcam			112
	(2,6- <i>i</i> -PrPh)(2- <i>i</i> -PrPh)DABcam			112
	(2,6- <i>i</i> -PrPh)(2-MePh)DABcam			112
	Mes ₂ DABEt(CH ₂ CH ₂ Ph)			91
	Mes ₂ DABEt((CH ₂) ₃ O(CH ₂) ₂ OMe)			91
	DAB-polystyrene			91
	DAB-PEG-polystyrene			91
	(2- <i>i</i> -Pr ₃ Si)Ph)DABAn			110
	(4-Me-2-(<i>i</i> -Pr ₃ Si)Ph)DABPhen			110
	(2-(MePh ₂ Si)Ph)DABPhen			110
	(2-adamantyl)Ph)DABPhen			110
	(2-(Ph ₃ Si)Ph)DABPhen			110
	(2-(3,5-Me ₂ adamantyl)Ph)DABPhen			110
	(4-PhPh)DABPhen			110
(COD)PdCl ₂	(2,6-MePh)(<i>i</i> -Pr)DABcam	ligand addition	(DAB)PdCl ₂	112
	(2,6-MePh)(2-MePh)DABcam			112
	(2,6-MePh)(Ph)DABcam			112
(DAB)NiCl ₂	(2,6- <i>i</i> -PrPh)(2- <i>i</i> -PrPh)DABcam	MgMe ₂	(DAB)NiMe ₂	112
(DAB)PdCl ₂	(2,6-MePh)(Ph)DABcam	LiCuMe ₂	(DAB)PdMe ₂	112
CODPdMeCl	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	ligand addition	(DAB)PdMeCl	75, 76 E-1, 34
	(2,6- <i>i</i> -PrPh) ₂ DABH ₂			75, 76 E-2, 35
	(2,6-MePh) ₂ DABMe ₂			75, 76 E-3
	(2,6-MePh) ₂ DABMe ₂			75, 76 E-4
	(4-MePh) ₂ DABMe ₂			75, 76 E-5
	(4-MePh) ₂ DABH ₂			75, 76 E-6
	(2,6- <i>i</i> -PrPh) ₂ DABAn			75, 76 E-36
	(Ph) ₂ DABMe ₂			75, 76 E-37
	(2,6-EtPh) ₂ DABMe ₂			75, 76 E-38
	(Mes) ₂ DABMe ₂			75, 76 E-39
	(2,6- <i>i</i> -PrPh) ₂ DABSCH ₂ CH ₂ S			107 E-34
	(Mes) ₂ DABEt(CH ₂ CH ₂ Ph)			91
	DAB-polystyrene			91
	DAB-PEG-polystyrene			91
(DAB)PdMeCl	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	Me ₂ Mg	(DAB)PdMe ₂	75, 76 E-10
	(2,6- <i>i</i> -PrPh) ₂ DABH ₂			75, 76 E-11
	(2,6-MePh) ₂ DABH ₂			75, 76 E-12
(COD)PdMe ₂	(2- <i>t</i> -BuPh) ₂ DABAn	ligand addition	(DAB)PdMe ₂	75, 76 E-462
	(2,5- <i>t</i> -BuPh) ₂ DABAn			75, 76 E-463
Ni(acac) ₂	(2,6- <i>i</i> -PrPh) ₂ DABH ₂	Me ₂ Mg	(DAB)NiMe ₂	75, 76 E-13
	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂			75, 76 E-463, 109
(DAB)PdMeCl and diethylether	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	NaBAF	[(DAB)PdMe] ₂ (μ -Cl) ⁺ BAF ⁻	75, 76 E-7,9
	(2,6- <i>i</i> -PrPh) ₂ DABH ₂			75, 76 E-8
(DAB)PdMeCl and MTBE	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	AgNO ₃ + LiX X = C(SO ₂ CF ₃) ₃ , N(SO ₂ C ₂ F ₅) ₂ , B(C ₆ F ₅) ₄ , BAF, SO ₃ C ₄ F ₉ , NSO ₂ (CF ₂) ₂ SO ₂	[(DAB)PdMe(MTBE)] ⁺ X ⁻	108

Table 1 (Continued)

metal precursor	DAB	reactants	product	ref ^a
(DAB)PdMe ₂	(2,6- <i>i</i> -Pr ₂ Ph) ₂ DABMe ₂ (2,6-MePh) ₂ DABH ₂ (2- <i>t</i> -BuPh) ₂ DABAn	H ⁺ (OEt ₂) ₂ BAF	[(DAB)PdMe(Et ₂ O)] ⁺ BAF	73, 75, 76 E-17 73, 75, 76 E-18 73, 75, 76 E-462
(DAB)PdMeCl and CH ₃ CN	(2,6-MePh) ₂ DABMe ₂ (4-MePh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (Ph) ₂ DABMe ₂ (2,6-EtPh) ₂ DABMe ₂ (2,6-EtPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABSCH ₂ CH ₂ S	NaBAF NaBAF AgSbF ₆ AgSbF ₆ NaBAF AgSbF ₆ NaBAF	[(DAB)PdMe(MeCN)] ⁺ - BAF ⁻ or SbF ₆ ⁻	75, 76 E-15 75, 76 E-16 75, 76 E-48 75, 76 E-49 75, 76 E-50 75, 76 E-50 107 E-35
[(COD)PdMe- (MeCN)] ⁺ SbF ₆ ⁻	(4-Me ₂ NPh) ₂ DABMe ₂ (2- <i>t</i> -BuPh) ₂ DABMe ₂ (Np) ₂ DABMe ₂ (Ph ₂ CH) ₂ DABH ₂ (2-PhPh) ₂ DABMe ₂ (Ph) ₂ DAB(<i>cyclo</i> -CMe ₂ CH ₂ CMe ₂)	ligand addition	[(DAB)PdMe(MeCN)] ⁺ - SbF ₆ ⁻	75, 76 E-40 75, 76 E-54 75, 76 E-55 75, 76 E-56 75, 76 E-57 75, 76 E-58
(DAB)PdMeCl	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABH ₂ (Mes) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABMe ₂	AgSbF ₆ AgBF ₄ AgPF ₆ AgSbF ₆ AgSbF ₆ AgSbF ₆ AgOSO ₂ CF ₃	[(DAB)PdMe(Et ₂ O) _{<i>n</i>}] ⁺ - SbF ₆ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ , or OSO ₂ CF ₃	75, 76 E-41 75, 76 E-42 75, 76 E-43 75, 76 E-44 75, 76 E-45 75, 76 E-46 75, 76 E-47
(DAB)NiMe ₂	(2,6-MePh) ₂ DABMe ₂ (2,6-MePh) ₂ DABH ₂	H ⁺ (OEt ₂)BAF	[(DAB)]NiMe(Et ₂ O)] ⁺ BAF ⁻	75, 76 E-19 75, 76 E-20
[(DAB)PdMe- (Et ₂ O) _{<i>n</i>}] ⁺ SbF ₆ ⁻	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	CH ₂ =CHCO ₂ Me	[(DAB)Pd(CH ₂ CH ₂ CH ₂ - CO ₂ Me)] ⁺ SbF ₆ ⁻	75, 76 E-59
(DAB)PdMeCl + CH ₂ =CHCO ₂ Me	(2,6- <i>i</i> -PrPh) ₂ DABH ₂ (2,6- <i>i</i> -PrPh) ₂ DABH ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABH ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABH ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂	AgSbF ₆ NaBAF NaBAF NaBAF NaBAF NaBAF NaBAF NaBAF NaBAF	[(DAB)Pd(CH ₂ CH ₂ CH ₂ - CO ₂ Me)] ⁺ BAF ⁻ or SbF ₆ ⁻ (<i>t</i> -Bu acrylate) (<i>t</i> -Bu acrylate) (<i>t</i> -Bu acrylate) FOA FOA	75, 76 E-60 75, 76 E-328 75, 76 E-329, 113, 114 75, 76 E-330, 113, 114 75, 76 E-331, 113, 114 75, 76 E-332, 113, 114 75, 76 E-333, 113, 114 75, 76 E-334, 113, 114 75, 76 E-334, 113, 114
(DAB)PdMeCl + styrene 4- <i>t</i> -Bu-styrene pentafluoro- styrene	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABH ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂	NaBAF	[(DAB)Pd(η^3 -CH ₂ EtAr)] ⁺ BAF ⁻	75, 76 E-493 75, 76 E-494 75, 76 E-495
[(DAB)NiMe- (OEt ₂)]BAF + 4- <i>t</i> -Bu-styrene	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	NaBAF	[(DAB)Ni(η^3 -CH ₂ EtAr)] ⁺ BAF ⁻	75, 76 E-496
(DABH ₂)PdMeCl	(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	B(C ₆ F ₅) ₃ , CH ₂ =CHCO ₂ Me	[(DAB)Pd(CH ₂ CH ₂ - CH ₂ CO ₂ Me)] ⁺ [B(C ₆ F ₅) ₃ Cl] ⁻	75, 76 E-61
[(allyl)Ni(μ -X)] ₂ (X = Cl or Br)	(Mes) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABMe ₂ (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABAn (Mes) ₂ DABAn (Mes) ₂ DABAn (Mes) ₂ DABA (Mes) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABA (Mes) ₂ DABAn (2,6- <i>i</i> -PrPh) ₂ DABAn (Mes) ₂ DABAn (2,6- <i>i</i> -PrP) ₂ DABAn (Mes) ₂ DABAn	NaBAF	[(DAB)Ni(η^3 -allyl)] ⁺ BAF ⁻ allyl = (η^3 -C ₃ H ₅) (η^3 -C ₃ H ₅) (η^3 -H ₂ CCHCHMe) (η^3 -H ₂ CCHCHPh) (η^3 -H ₂ CCHCHMe ₂) (η^3 -C ₃ H ₅) (η^3 -H ₂ CCHCHMe) (η^3 -H ₂ CCHCHPh) (η^3 -H ₂ CCHCHMe ₂) (η^3 -H ₂ CCHCHMe) (η^3 -H ₂ CCHCHPh) (η^3 -H ₂ CCHCHMe) (η^3 -C ₃ H ₅) (η^3 -H ₂ CCHCHMe) (η^3 -H ₂ CC(CO ₂ Me)CH ₂) (η^3 -H ₂ CC(CO ₂ Me)CH ₂) (η^3 -H ₂ CCHCH(CO ₂ Et)) (η^3 -H ₂ CCHCH(CO ₂ Et)) (η^3 -H ₂ CCHCHCl) (η^3 -H ₂ CCHCHCl)	75, 76 E-497 75, 76 E-498 75, 76 E-499 75, 76 E-500 75, 76 E-501 75, 76 E-502 75, 76 E-503 75, 76 E-504 75, 76 E-505 75, 76 E-506 75, 76 E-507 75, 76 E-508 75, 76 E-509 75, 76 E-510 75, 76 E-511 75, 76 E-512 75, 76 E-513 75, 76 E-514 75, 76 E-515

^a E-### represents the example number in those references which are patents with a large number of examples.

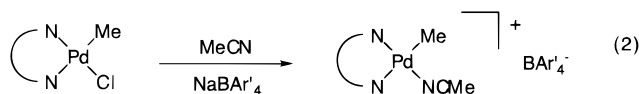
the addition of the appropriate ligands to preformed starting materials; for instance, the displacement of dimethoxyethane from (dme)NiBr₂ as shown in eq 1.



This reaction illustrates the simple displacement of labile ligands from precursor complexes. Rather than convert (DAB)PdCl₂ to metal alkyls, it is often easier to utilize alkyl-containing precursors. Thus, (COD)-PdMeCl is a useful precursor to the (DAB)PdMeCl series. (DAB)PdMe₂ has been synthesized both by reacting (DAB)PdMeCl with MgMe₂ and by adding the α -diimine ligand to (COD)PdMe₂. The dimethyl complexes of nickel have also been synthesized by reacting Ni(acac)₂ or NiBr₂ with MgMe₂ in the presence of ligand.

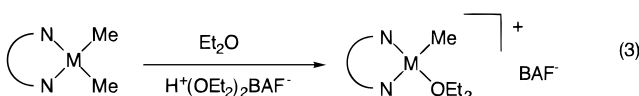
Generally, it is the cationic form of organometallic complexes that is of interest in polymerizations. Reaction of halo complexes with methyl aluminoxanes in the presence of ethylene or other olefins is presumed to form cationic, catalytically active species. This route has been used to screen α -diimines and other ligands for activity and is discussed below.

Syntheses of discrete cationic α -diimine complexes of palladium and nickel are well developed. DAB complexes containing halo ligands can be reacted with a variety of salts of noncoordinating anions to yield cationic organometallic species. For instance, the reaction in eq 2 illustrates chloride abstraction with NaBAF.^{73,113,114} The resulting complexes are



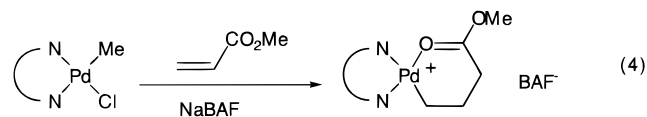
typically stabilized by relatively weak donor ligands such as acetonitrile. The acetonitrile complexes are stable, easily handled, and are useful precursors for preparative-scale polymerizations. Attempts to make palladium-ether adducts by chloride abstraction with NaBAF resulted in the formation of chloride-bridged dimers $\{[(N-N)PdMe]_{2-\mu-Cl}\}BAF$.^{75,76} This was attributed to the weak basicity of diethyl ether, though it would appear that MTBE is more successful in filling the vacant coordination site.¹⁰⁸

A more successful route to cationic palladium and nickel ether adducts is through protonation of the nickel and palladium dimethyl precursors with H⁺(OEt₂)₂BAF⁻ in the presence of diethyl ether,⁷³ illustrated by eq 3. The ether ligand is extremely



labile, making these precursors ideal for the low-temperature NMR mechanistic studies discussed below. Protonation of the dimethyl complex in the presence of an olefin to yield the olefin adduct has been successful only at low temperatures.

Halide metathesis with noncoordinating anions in the presence of olefins was attempted as a synthetic route to methyl olefin complexes. While the observed product was identified at low temperatures, the product was not isolated. In the case of methyl acrylate, the reaction results in the formation of a chelate complex which is isolated as the salt of a noncoordinating anion, as shown in eq 4. This chelate



is a useful catalyst precursor. Chelate complexes of nickel as well as palladium have been prepared by addition of the acrylates to the ether-stabilized cationic alkyl complexes. In the case of methyl acrylate, protonation of (DAB)Ni(CH₂=CHCO₂Me) with H⁺(OEt₂)₂BAF⁻ also leads to chelate formation.^{75,76}

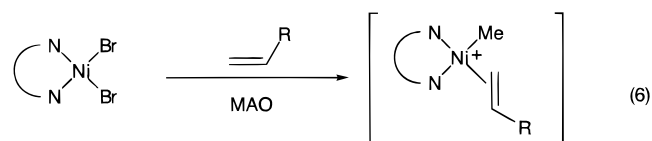
In polymerization reactions, cationic allyl complexes [(DAB)Ni(η^3 -allyl)]⁺ have found considerable utility. They are readily synthesized by the reaction illustrated in eq 5. The substituents on the allyl



group can be varied and it is often advantageous to do so.

In analogy with the synthesis of neutral complexes bearing α -diimine ligands, diimine addition to preformed cations such as [(COD)PdMe(MeCN)]⁺SbF₆⁻ is a useful route to cationic complexes. Nonetheless, it has seldom been utilized.

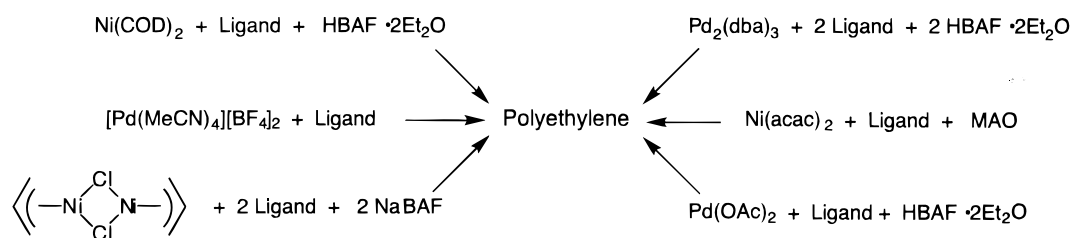
Attempts to observe the methyl olefin complex by reacting dihalo precursors with MAO have not been successful, although the cationic methyl complex is expected to be a critical intermediate (eq 6) in the



polymerizations. Instead of the methyl olefin complex, the olefin insertion product is observed. This in situ generation of the active catalyst with MAO is a useful method for preparative-scale polymerizations with nickel and to some extent with palladium.

2.1.2. Other Ligands

While the major focus of recent efforts has been on the use of α -diimine ligands with N–N chelation, there has been considerable research on alternative classes of ligands. These may be alternative N–N chelators or completely different classes of ligands. Anionic ligands such as the P–O systems utilized in Shell's catalysts for ethylene oligomerization to α -olefins will be dealt with in section 3. Table 2 summarizes cationic complexes of Ni and Pd bearing neutral ligands other than α -diimines for which olefin polymerization activity has been reported.^{115–143} Most of these ligands are bidentate, although some are

Scheme 1. Reactions Utilized for the Rapid Screening of Ligands for Ethylene Polymerization Catalysts^a

^a All of the screening reactions were carried out in the presence of ethylene.

potentially tridentate and others are clearly tridentate. While many of the catalyst precursors have been isolated and characterized, many more were discovered through screening processes that rely upon facile syntheses of the active species in situ. Often this initial screening provided guidance as to which metal complexes warranted preparative-scale synthesis and characterization. To achieve thorough screening, the development of a variety of robust and sensitive screening methods was often necessary, since the performance of individual ligands was often screen-dependent. It was found that no single screen was adequate to catch all ligands, but a battery of screens probably caught most. Typical rapid-screening procedures are illustrated by, but not limited to, the equations shown in Scheme 1.^{75,76,108,115–117,142–146}

Another reaction shown to lead to active catalysts is the combination of (DAB)Ni(COD) with MAO under reaction conditions,¹⁴⁷ although there is some indication that oxygen promotes this activity.^{75,76} The use of β -diketonate complexes of nickel as catalyst precursors leads to a halide-free system, and the MAO is proposed to participate in the ligand-exchange process. The order of mixing is important: addition of MAO to a solution of Ni(acac)₂ and DAB yields an active system, while addition of Ni(acac)₂ to a solution of DAB/MAO is far less active.¹⁴⁵ In addition, other routes to in situ catalyst formation have been reported.¹⁰⁸

These screening methods identified a range of interesting ligands that were successful in promoting olefin polymerization. The ligands are classified in Table 2 according to their donor functionality: N–N, N–O, N–X, P–O, Monodentate-N, and Other (which includes those species where a likely mode of coordination remains unclear). Related species are grouped close together for comparison. However, it should be realized that due to the screening nature of the polymerizations and the small reactor volumes utilized, productivities of the catalysts are often variable and condition-dependent and therefore have not been included in this table. Screening procedures often include temperature ramps and/or a range of other variables because it is unclear, for example, what the optimum operating temperature of any given species will be. For example, in a given array of catalysts, one may have its optimum activity at 25 °C and taper off with increasing temperature while another might not initiate until 75 °C. Screens that measure the final mass of polymer give little information about activity, with productivity being the more important feature. Screens that measure heat of reaction often give little information about polymerization produc-

tivities, since they are unable to differentiate between polymer and oligomer formation.

In general, the most productive catalysts shown in Table 2 are based upon N–N and N–O ligands. The productivities can be appreciable, but as a broad generalization, catalysts bearing α -diimine ligands remain the most active. Discrete palladium catalysts with bis(pyrazoyl)methane ligands have been synthesized and investigated mechanistically. They provide linear, low molecular weight materials.¹³⁰ In this one case, it has been reasonably demonstrated that activation with MAO, which leads to high polymer, is probably the result of ligand abstraction from the metal.

2.2. Ethylene Polymerization

2.2.1. General Features of α -Diimine-Mediated Polymerizations

Ethylene polymerizations for rapid screening purposes have been described above. These polymerizations can be catalyzed by α -diimine-derived catalysts or by a host of other ligand systems. This section will focus on polymerizations run under more controlled conditions utilizing isolated complexes of Ni and Pd bearing α -diimine ligands because these are the most thoroughly described in the literature at present. These catalysts are among the most active, and they display features that will be used as reference standards in subsequent discussions.

In a typical preparative-scale polymerization with nickel α -diimine-derived catalysts, a rapidly stirred suspension of the nickel dibromide complex ($\sim 1 \times 10^{-6}$ mol) in toluene is saturated with ethylene and then activated by addition of MAO (100–1000 equiv).^{73,148–149} Activities as high as 3×10^6 TO/mol of Ni·h at 35 °C have been reported, but catalyst deactivation during the course of the polymerization yields optimum productivities in the tens to hundreds of kilograms of PE/mole of Ni. Molecular weights can be varied from oligomers to high polymer ($M_w \approx 30\,000$ to $>1\,000\,000$) by varying the catalyst structures and polymerization conditions. Using the same parameters, the resulting polyethylene microstructures can be varied from strictly linear to highly branched, resulting in polymers ranging from highly crystalline to totally amorphous. However, under a given set of conditions, polymers derived from the nickel α -diimine catalysts are generally less branched than polymers derived from their palladium analogues.^{73,148}

The Ni α -diimine catalysts may be supported on a wide range of inorganic oxide supports,¹⁵⁰ but silica

Table 2. Neutral Ligand Complexes of Ni and Pd

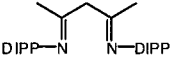
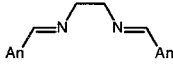

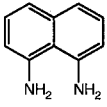
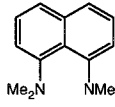
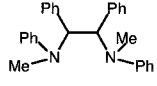
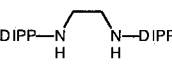
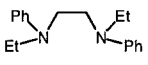
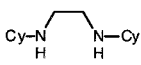
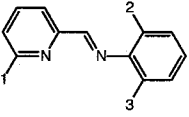
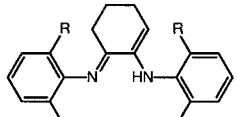
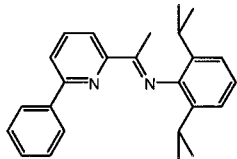
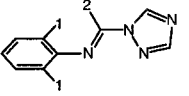
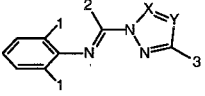
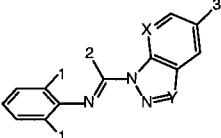
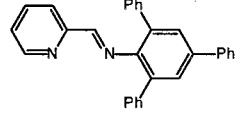
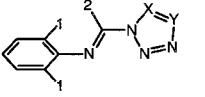
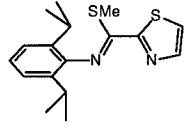
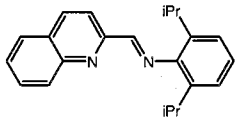
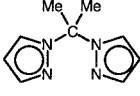
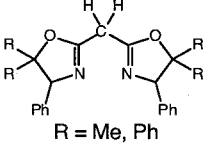
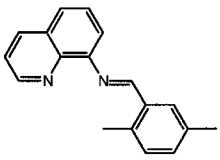
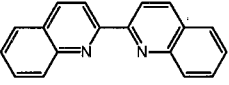
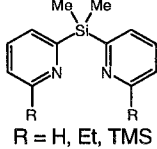
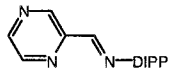
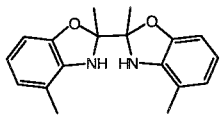
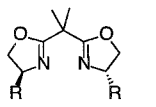
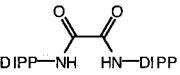
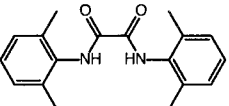
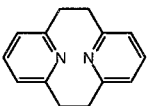
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		<table border="0"> <tr> <td>1</td> <td>2</td> <td>X, Y</td> <td></td> </tr> <tr> <td>iPr</td> <td>1Np</td> <td>CH, CH</td> <td>120 E-42</td> </tr> <tr> <td>iPr</td> <td>Ph</td> <td>N, CPh</td> <td>120 E-43</td> </tr> </table>	1	2	X, Y		iPr	1Np	CH, CH	120 E-42	iPr	Ph	N, CPh	120 E-43																																																									
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	118		116 E-98		140																																																																		
	116 E-107 E-178		116 E-181		257																																																																		

Table 2 (Continued)

Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
	116 E-6		116 E-5		116E-14
	116 E-33, E-133		116 E-32, E-130 123		116E-15 E-35 E-40 E-136
	116 E-57		116 E-51		116 E-60
	116 E-185		116 E-23 E-141-143		116 E-89
	116 E-29, E-151-6		116 E-27, E-147-50		116E-61
	116 E-43		116 E-49		116 E-39, E-157-9
	116 E-56		116 E-36		116 E-95
	116 E-3		116 E-184 E-138-140		116 E-104
	116 E-141 E-142 E-143		116 E-144 E-145 E-146		116 E-53 E-176
	116 E-105		116 E-106		116 E-37
	116 E-46		116 E-44		135
	139				

Table 2 (Continued)

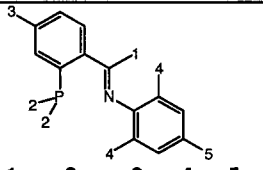
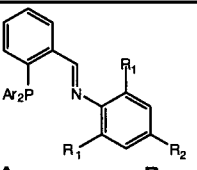
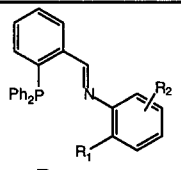
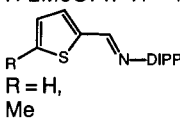
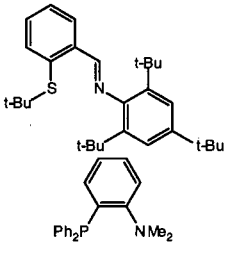
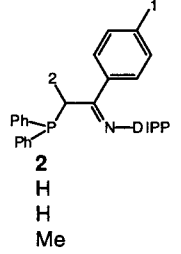
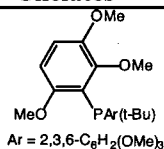
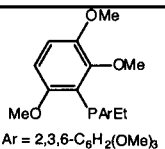
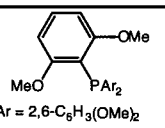
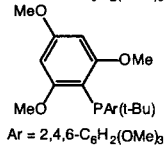
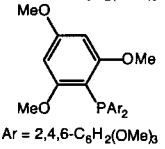

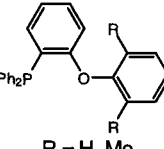
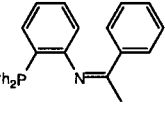
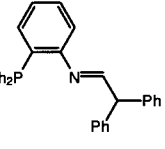
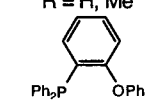
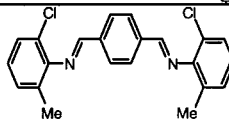
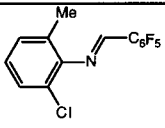
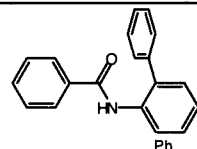
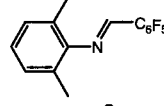
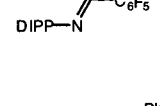
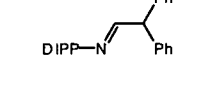
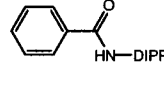
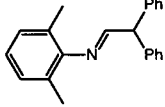
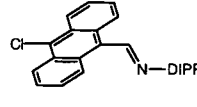
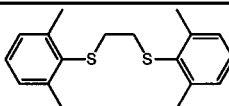
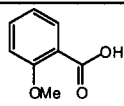
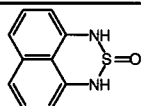
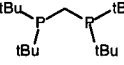
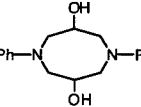
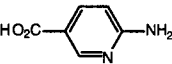
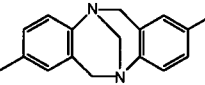
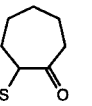
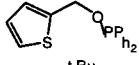
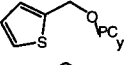
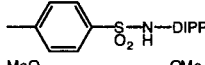
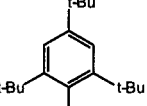
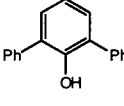
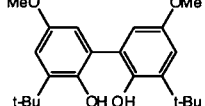
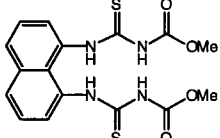
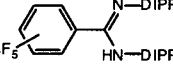
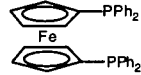
Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
N-X Chelates					
					129
1	2	3	4	5	
H	Ph	H	tBu	tBu	
H	Ph	OMe	iPr	H	120
H	Ph	H	iPr	H	120 E-12
Me	Ph	H	iPr	H	120 E-13
Ph	Ph	H	iPr	H	120 E-14
H	Cy	H	iPr	H	120
Me	Cy	H	iPr	H	120
Ph	Cy	H	iPr	H	120
H	Ph	H	H	H	122
H	Ph	H	Me	H	122
H	Ph	H	iPr	H	122
H	3MeOPh	H	iPr	H	122
H	2MeOPh	H	H	Cl	122
H	2MeOPh	H	H	H	122
H	2MeOPh	H	H	OMe	122
H	2MeOPh	H	iPr	H	122
					
R = H, Me	116 E-162 116 E-173		140	1 H CF ₃ H	120 E-15
			136	Me H	116 E-16
P-O Chelates					
	116 E-48		116 E-30		116 E-47
Ar = 2,3,6-C ₆ H ₂ (OMe) ₃		Ar = 2,3,6-C ₆ H ₂ (OMe) ₃		Ar = 2,6-C ₆ H ₃ (OMe) ₂	
	116 E-55		116 E-24, E-124-129		116 E-54
Ar = 2,4,6-C ₆ H ₂ (OMe) ₃		Ar = 2,4,6-C ₆ H ₂ (OMe) ₃		Ar = 2-C ₆ H ₄ (OMe)	
	140		140		140
R = H, Me					
	136				
Monodentate Nitrogen					
	116 E-200		116 E-103		116 E-55
	116 E-198 E-199		116 E-196 E-197		116 E-93
	116 E-28		116 E-97		116 E-186

Table 2 (Continued)

Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
Other or Unknown Coordination					
	116 E-100		116 E-64		116 E-63
P(<i>t</i> -Bu) ₃ P(<i>i</i> -Pr) ₂ (<i>t</i> -Bu)	138, 124		124, 143		116 E-38
	116 E-45		116 E-102		116 E-96
	116 E-34		116 E-160		116 E-41
	116 E-58		116 E-62		116 E-66
	116 E-66		116 E-42		136

appears to be a support of choice.^{151,152} The supporting procedure generally includes the use of MAO or some other aluminum reagent to provide alkylation and generation of the cationic site. The nickel catalysts may also be supported on polymeric supports such as polycyclopentene.¹⁵³ Acidic supports such as montmorillonite clays do not need to be activated with MAO, presumably because the strong-acid nature of the support is sufficient to activate the catalyst.^{153,154} Polymerization on the clays can lead to polyolefin-exfoliated anisotropic nanocomposites with large interlayer spacings.¹⁵⁵

The palladium α -diimine catalysts yield high molecular weight polyethylene that is unlike that observed with nickel. The products from palladium-catalyzed polymerizations are amorphous, highly branched polyethylenes with densities as low as 0.85.^{73,114,156–158} Glass-transition temperatures are in the range of -30 to -70 °C. It should be noted that these highly branched polyethylenes are produced without the intermediacy of α -olefins. Higher molecular weight, highly branched polymers contain no residual α -olefins, thereby indicating that the catalysts are not making olefins and then incorporating them into high polymer to achieve the branching. The ability to form such highly branched polymers from ethylene alone without the intermediacy of α -olefins is unprecedented.¹⁵⁹ A more detailed description of the branching and its analysis will be presented below.

These unusual branched structures give rise to unique polymer properties.^{160–165} For example, the topologies of the polyethylenes vary from linear with moderate branching to hyperbranched structures. For the most highly branched systems, the overall branching number and the distribution of short-chain branches can change very little while the architecture

or topology of the polyethylene can be varied from elastomeric, semicrystalline polymers with moderate branch lengths to hyperbranched oils. In the high molecular weight oils, none of the polymer chains are beyond the polyethylene chain entanglement length. This control of topology can be attributed to a catalytic mechanism referred to as "chain walking", which is described in the next section. Synthesis of related polymers by copolymerization of ethylene with an appropriate mixture of commercial α -olefins yields a polymer that in many respects mimics the polymers derived from chain walking.¹⁶⁶ Nonetheless, it is possible to differentiate not only the structure of these polymers, but also the end-use performance. The highly branched polymers are useful as base stocks or additives for lubricants,^{75,76,167} especially when they contain polar functionality (vide infra).¹⁶⁸

To obtain a particular set of polyethylene properties, it is often advantageous to blend two different polymers. This can be achieved through in-reactor blending by combining two nickel or palladium α -diimine catalysts or by combining a nickel or palladium α -diimine catalyst with an early transition metal or metallocene catalyst.^{169–172} A specific example would be the combination of a metallocene catalyst (which makes a crystalline polyethylene) with a nickel α -diimine catalyst (which makes a rubber phase). The resulting dispersion of polyethylene elastomer in the crystalline polyethylene phase would result in a system less likely to break under stress.^{173–174} This single-step approach would be less expensive than extruder blending the rubbery phase from the nickel catalysts into a crystalline polymer after the polymerization step.¹⁴⁶

There are a number of catalyst mixtures for synthesizing LLDPE from ethylene only dating back to Ziegler.^{175,176} Introduction of nickel to traditional

titanium-based Ziegler–Natta catalysts gives reduced-density products; the nickel dimerizes ethylene to butene, while the titanium incorporates the butene at low levels yielding polyethylenes with low levels of ethyl branches. The approach was confirmed in later work with mixed nickel/chromium catalysts by observing the effect of increased nickel concentrations.^{177,178} The strategy was further developed by combining discrete homogeneous nickel catalysts for α -olefin synthesis with chromium, titanium, or metallocene catalysts for α -olefin incorporation.^{179–190} The successful commercialization came with Phillips' introduction of hexene copolymers from an ethylene-only feed.¹⁹¹ Their catalyst mix simultaneously synthesizes hexene and copolymerizes it with ethylene. The same approach can now be accomplished by nickel-only systems.¹⁹² The ideal situation occurs when the activities of the two catalysts are matched so that most of the α -olefin is consumed.¹⁹³

There is a great deal of versatility in the mode of polymerization available with the α -diimine catalyst systems. Homogeneous versions of the Ni diimine catalysts can be utilized in solution polymerization of ethylene, but when higher density, less-soluble polymers are desired, slurry polymerization can be employed.^{75,76,194} Gas-phase polymerizations are best carried out with the catalyst supported on inorganic or organic supports to control the particle morphology of the resulting polymer. The phase in which the polymerization is carried out can have a pronounced effect on the polymer properties through modification of the local concentration of ethylene.

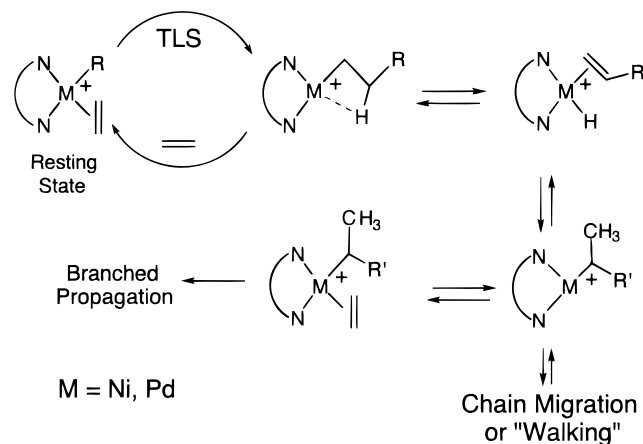
The productivities of the catalysts, a complex function of the catalyst activity, lifetime, initiation, and decay, are intimately tied to ligand structure, cocatalyst, temperature, olefin concentration, and other factors, as are the polymer molecular weights, molecular weight distributions, and degrees of branching.^{70,195–200} This has been found to be true for both homogeneous and supported systems, and the relationships can be quite different for analogous supported and unsupported species.²⁰¹ Molecular weights can be controlled independently by addition of hydrogen, silanes, or CBr_4 .²⁰² A correlation between polymerization activity and changes in the UV–vis absorption spectra of the nickel α -diimine catalysts activated with MAO has proven to be a useful tool.^{198–199} These studies have shown that the catalysts are stabilized by the presence of olefin.^{75,203}

2.2.2. Mechanism

Most mechanistic and theoretical work published to date has been directed at the α -diimine complexes of nickel and palladium. For that reason, mechanistic work is discussed at this point in the review. While details will differ for the particular metal and ligand set, all of the pertinent details are covered with these two systems. The details then can be drawn upon where appropriate for other systems.

It is possible to monitor ethylene chain growth at cationic α -diimine nickel and palladium centers by low-temperature NMR spectroscopy.^{73,204,205} Under these conditions, the alkyl ethylene complex on the left of Scheme 2 is the catalyst resting state. (This is

Scheme 2. Mechanism for Ethylene Polymerization and Polymer Branch Formation with Ni and Pd α -Diimine Complexes^a



^a TLS is the "turnover-limiting step".

in sharp contrast to early metal catalyst systems where such intermediates are not observed.) The turnover-limiting step is the migratory insertion reaction of the alkyl ethylene complex, and as a result, the chain growth is zero-order in ethylene. The barriers to migratory insertions as measured by low-temperature NMR spectroscopy in the palladium systems lie in the range of 17–18 kcal/mol with systems bearing the bulkiest ligands exhibiting the lowest insertion barriers. Barriers for the insertions in the nickel complexes are substantially lower and in the range of 13–14 kcal/mol. The barrier differences ($\Delta\Delta G^\ddagger$'s) of ca. 4–5 kcal/mol account quantitatively for the much higher activities of the nickel complexes and are in line with expectations of differences between first-row and second-row insertion barriers.

Increased steric bulk of the diimine ligand aryl substituents leads to an increase in the ground-state energy of the resting-state species relative to the migratory insertion transition state in nickel species.²⁰⁵ Consequently, lower migratory insertion barriers were expected with bulkier diimine substituents. Consistent with the observations for the palladium systems, the barriers to insertion in the nickel methyl ethylene complexes were quite similar to barriers for subsequent insertions. Also comparable to the palladium systems, the barrier to propylene insertion in the nickel methyl propylene complex was similar to the insertion barrier in the methyl ethylene complex. The much lower turnover frequencies observed for α -olefin polymerizations relative to ethylene polymerizations in the nickel systems were a consequence of the agostic catalyst resting state after methyl migration. As a result, chain growth is first-order in α -olefin.

The formally 14-electron cationic alkyl species generated following migratory insertion have been shown to have β -agostic interactions. Trapping of the initially formed primary alkyl species by ethylene followed by insertion results in chain growth without the introduction of a branch in the polymer. Alternatively, prior to trapping and insertion, the agostic metal alkyl species can undergo a series of β -hydride

Scheme 3. Two Possible Modes of Chain Transfer: (A) Associative Displacement from the Olefin Hydride Intermediate Requiring β -Hydride Elimination before Ethylene Coordination; (B) Direct β -Hydride Transfer to Monomer from the Alkyl-Olefin Resting State

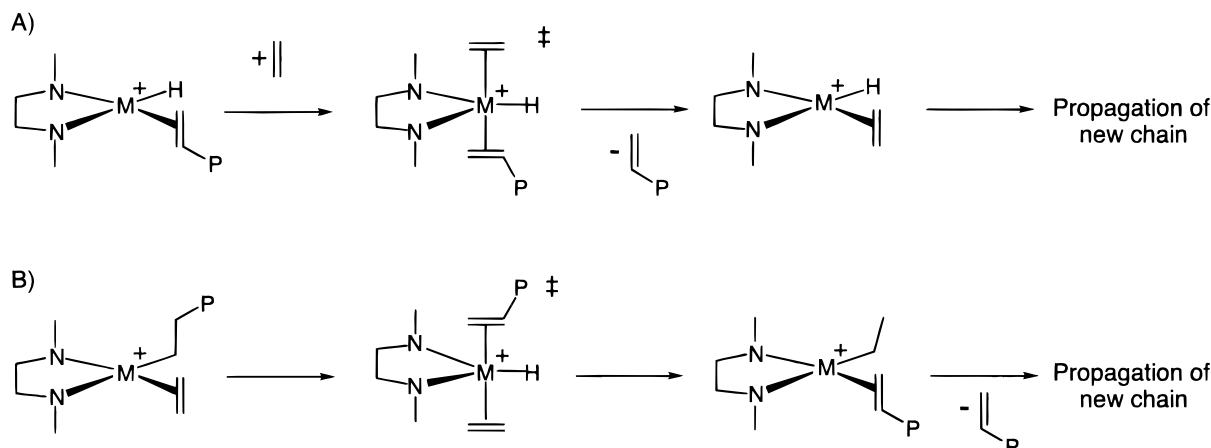


Table 3. Effect of Catalyst Structure and Conditions^a on Branched Polyethylenes Produced by [(DAB)Pd(CH₂CH₂CH₂CO₂Me)][BAF]

DAB	pressure (atm)	total turnovers	M_n ($\times 10^{-6}$)	M_w/M_n	branches (per 1000 C)
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	2	30 000	297	3.5	102
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	11	48 500	490	2.7	100
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	29	28 500	496	3.0	98
(2,6-MePh) ₂ DABMe ₂	11	13 250	445/28	<i>b</i>	106

^a 0.01 mmol catalyst, 100 mL CH₂Cl₂, 25 °C ^b Bimodal distribution.

eliminations and re-additions which results in the metal migrating or “walking” along the polymer chain. This process has been observed in a simple three-carbon model system.²⁰⁵ Trapping of these species followed by insertion results in the introduction of a branch into the growing polymer chain. This process is shown in Scheme 2. For example, migration one carbon down the chain followed by trapping and insertion introduces a methyl branch. Longer chain walks introduce longer branches. The observation of branches-on-branches indicates that palladium catalysts can migrate past tertiary carbon atoms.

Unlike most late metal catalysts, chain transfer in these α -diimine systems is quite slow relative to chain propagation, and thus, high molecular weight polymer is produced. It is clear that the key to slowing chain transfer is introduction of steric bulk in the axial sites of the square plane. Crystallographic results demonstrate that the aryl rings of the square-planar α -diimine complexes lie roughly perpendicular to the square plane, and the ortho substituents are then positioned above and below the plane. As the steric bulk of either the backbone substituents or the ortho substituents increases, the plane of the aryl ring becomes more rigidly locked perpendicular to the coordination plane, and thus, the ortho substituents block the axial sites more effectively.^{88,196,206}

Initially, chain transfer was proposed to occur via associative displacement of the unsaturated polymer chain from an olefin hydride intermediate by monomer (Scheme 3A).⁷³ The bulky ortho substituents were proposed to block axial approach of monomer and retard the rate of displacement. Alkyl ethylene model systems established that indeed exchange of

free and bound ethylene did occur by an associative process and exchange rates were dramatically retarded by bulky ortho substituents.⁷³

A somewhat different proposal for chain transfer has been advanced based on calculations concerning the nickel systems.^{207–211} It suggests that chain transfer occurs from the resting state through direct β -hydrogen transfer to monomer (Scheme 3B). The transition state for this process places the olefinic units in axial sites, and thus, the barrier to chain transfer is increased by positioning bulky groups in these sites. Increasing steric bulk makes this state increasingly unstable relative to the four-coordinate ethylene alkyl adduct.²¹² Note that in each case the transition state is quite similar and involves, in essence, a bis-olefin hydride species with olefinic units in the crowded axial positions. No experimental evidence is yet available to distinguish between these two possible chain-transfer pathways. Calculations on palladium systems²¹⁶ do not support direct chain transfer to monomer.^{213–218} Other theoretical studies concur with these conclusions.^{219,220}

Platinum complexes show none of the catalytic activity found in palladium and nickel complexes. This chemical inertness makes platinum a useful model for the more active catalysts.^{221–223} There has been a suggestion that platinum complexes of chiral α -diimines might lead to stereoselective olefin polymerization.²²⁴ Chiral camphor-based ligands have been employed in palladium complexes for ethylene polymerization, but there was no mention of stereoselectivity in hexene polymerizations.¹¹²

There is a readily observed difference between the behavior of palladium catalysts and nickel catalysts, as illustrated in Tables 3 and 4. These differences are reflected in theoretical calculations.^{225,226} The

Table 4. Effect of Catalyst Structure and Conditions on Branched Polyethylenes Produced by (DAB)NiBr₂ Activated with MAO

DAB	pressure (atm)	temp (°C)	TOF ^a (×10 ⁻⁴ /h)	M _n (×10 ⁻³)	branches (per 1000 carbon)
(2,6- <i>i</i> -PrPh) ₂ DABH ₂	1	0	21	110	7
(2,6- <i>i</i> -PrPh) ₂ DABAn	1	0	19	650	24
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	1	0	11	520	48
(2,6-MePh) ₂ DABMe ₂	1	0	6	170	20
(Ph) ₂ DABAn	15	35		oligomers	<i>b</i>
(Ph) ₂ DABAn	56	35		oligomers	<i>b</i>
(2,6- <i>i</i> -PrPh) ₂ DABAn	1	25	19	170	65
(2,6- <i>i</i> -PrPh) ₂ DABAn	15	25	180	470	30
(2,6- <i>i</i> -PrPh) ₂ DABAn	30	25	230	490	20
(2,6- <i>i</i> -PrPh) ₂ DABAn	42	25	190	510	5
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	1	25	77	850	30
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	1	50	56	260	67
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	1	65	68	180	80
(2,6- <i>i</i> -PrPh) ₂ DABMe ₂	1	80	9	150	90

^a TOF determined by weighing solid polymer. ^b 85% linear α -olefins

polyethylenes produced by the palladium catalysts are always highly branched, typically exhibiting ~100 methyl-ended branches per 1000 methylene groups, indicating high rates of chain walking relative to insertion. For palladium, the apparent branching is independent of the reaction pressure (Table 3). However, the morphology of the polymer does vary with pressure with amorphous viscous oils produced at low pressures and amorphous rubbery solids at higher pressures.^{160–163}

Similar data for nickel-based catalysts and the effects of α -diimine substituents are presented in Table 4.^{73,148} As with the palladium catalysts, reduction in steric bulk of either the backbone substituents or the ortho substituents of the *N*-aryl ring reduces the molecular weight of the polyethylene. In contrast to palladium, the total number of branches for the resulting ethylene homopolymers is also reduced with decreasing steric bulk of the ligand substituents, with the number of branches always being lower than that observed for palladium. When the steric effects are reduced significantly, the increased chain-transfer rates lead to the production of linear α -olefins instead of high molecular weight polymer. The selectivity for linear α -olefins increases with increasing pressures.^{148,227–229}

As ethylene pressure is increased, the number of branches per 1000 methylene groups decreases while catalyst productivity and molecular weight are largely unaffected. (It should be noted that under the experimental conditions chosen, diffusion of ethylene into the solution under mass-transfer conditions can have a pronounced effect on the actual ethylene concentration in solution.) The sensitivity of branching to ethylene pressure is consistent with a competition between ethylene trapping and “chain walking”. At higher ethylene pressures trapping is favored, resulting in the formation of fewer branches.

As temperature increases, branching increases and the polymer molecular weight and melting point decrease. At 80 °C, a completely amorphous ethylene homopolymer ($T_m = -12$ °C) is produced. This is consistent with higher reaction temperatures favoring unimolecular chain running relative to bimolecular trapping and insertion, resulting in a more highly branched microstructure. This effect seems to be greater than can be attributed to a decrease in ethylene concentration at the higher temperatures.

Thus, it not surprising that it is possible to compensate for increased pressures by increasing temperature to maintain the same branching level.²³⁰

The use of noncoordinating counterions is important to high-polymer formation. Anions such as BAF yield polymers with higher molecular weights than those of polymers prepared with complexes incorporating more coordinating counterions such as BF₄⁻ and triflate. Several different commercial versions of MAO also serve as useful counterions as do inorganic materials such as montmorillonite clays.^{75,76,231,232} Discrete aluminoxanes also have been employed.²³³ The trend is similar to that observed in metallocene polymerizations with noncoordinating counterions.^{234–237} The high solubility of organometallic cations stabilized with BAF is particularly advantageous for low-temperature NMR elucidation of the mechanism of olefin insertions and other processes.²³⁸

Mechanistic aspects of both the Ni and Pd diimine catalysts systems have been addressed using density functional, molecular orbital, and molecular mechanics calculations in an extensive series of papers.^{207–212,225,226} It is beyond the scope of this review to present a comprehensive account of this complex body of work, but a few features should be noted. In general, calculations have been consistent with the experimental observations available. Calculated barriers to insertion in the [(diimine)Pd(olefin)R]⁺ complexes are in reasonable agreement with experiment. For example, the calculated barrier to insertion in [(2,6-*i*-PrPh)₂DABMe₂]Pd(C₂H₄)CH₃]⁺ is 14.1 kcal/mol,²¹⁴ which compares favorably with the experimentally determined barrier of 17.3 kcal/mol. The barrier to insertion in the Ni analogue was calculated to be 13.2 kcal/mol, which is very close to the measured barrier of 13.5 kcal/mol.²⁰⁹ Other calculations significantly underestimate this barrier.²¹⁴

The intermediate cationic alkyl complexes are predicted by all groups to be β -agostic alkyl species in agreement with experimental observations. A surprising experimental finding was that the β -agostic propyl complex [(diimine)Pd C₃H₇]⁺ was more stable as the isopropyl agostic species than as the *n*-propyl agostic species.²⁵⁶ Calculations on both a simple model system and on the N-(2,6-*i*-Pr)₂C₆H₃-substituted diimine complex (experimental system) are in accord with this observation.²¹⁴ Formation of

these secondary alkyl complexes is necessary to incorporate branches in the polymers, so the stabilities of secondary relative to primary alkyl complexes play a significant role in determining the extent of branching in these polymers. The β -agostic isopropyl isomer in the Ni system has been calculated to be slightly more stable than the *n*-propyl isomer,²¹⁰ although the opposite conclusion was also reached.²¹⁴ No experimental determination has yet been made. Barriers to β -hydride elimination/re-addition reactions (chain walking) in the agostic alkyl intermediates have been predicted, but appropriate experimental numbers are not yet available for comparison. The barriers for 1,2-shifts in the Pd complexes are calculated to be significantly lower than those for nickel complexes. Coupled with the higher insertion barriers for Pd, these calculations are consistent with the much higher branching observed in the Pd-catalyzed polyethylenes. Ethylene and propylene binding energies have been calculated for several species, but no experimental binding energies are available. A major mechanistic question which has not yet been resolved concerns the mode of chain transfer.

2.2.3. Polyethylene Structure Analysis

Until this point, the observed branching structures in polyethylenes have been discussed only briefly. Elucidation of the structures took considerable effort and involved a combination ¹³C NMR techniques with the syntheses of specific polymer structures.^{160,239–241} A ¹³C NMR spectrum of a typical highly branched polyethylene is shown in Figure 1. Using ¹³C NMR

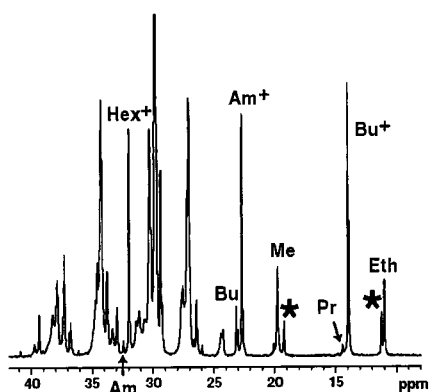


Figure 1. Typical ¹³C NMR spectrum of a highly branched polyethylene. The two peaks indicated by the asterisk (*) represent branches containing a *sec*-butyl end—the shortest branch-on-branch observed in polyethylenes.

spectroscopy, it is possible to quantify all of the linear branches emanating from the polymer backbone from methyl to pentyl. Another quantifiable resonance is attributable to the cumulative resonances of all branches hexyl and longer together with the ends of the polymer chains if they are at least hexyl. In addition to these branches, it has been possible to quantify a pair of resonances attributable to a branch terminated with a *sec*-butyl group. This is the smallest branch-on-branch possible in an ethylene polymerization.

On the basis of the NMR analysis of branching and the distribution of various branches, it is possible to

determine relative probabilities of insertion or migration from each possible type of carbon atom in the backbone. This information can then be used to simulate probable structures of the resulting polymers. Typical examples are given in Figure 2.²⁴² It

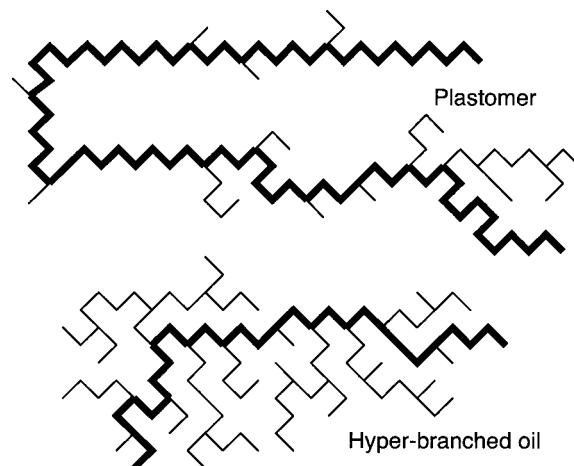
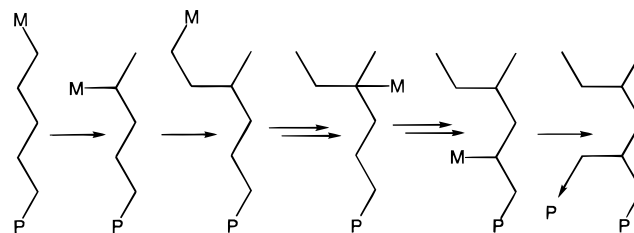


Figure 2. Computer simulations of typical 100 carbon-atom fragments of a polyethylene plastomer and a polyethylene hyperbranched oil. The simulations are calculated from probabilities of various migrations and insertions that are back-calculated from observed NMR spectra. The heavy line is the longest chain through the structure, but it does not necessarily contain either the first or last ethylene inserted. By chance, the hyperbranched structure contains three equal C₃₀ “longest chains”.

should be noted that the structures shown are small fragments of the typical polymers to aid viewing. The longest carbon chain through the structure is highlighted, but this longest chain does not necessarily contain either the first or last ethylene inserted.

The route to the branch-on-branch is complex, as is illustrated in Scheme 4. Each arrow represents either a 1,2-migration (β -hydride elimination and insertion at the opposite carbon atom) or an insertion. After migrating to the tertiary carbon atom, the catalyst could migrate to the primary carbon atom, but this would produce only an ethyl branch. Migration back down the chain produces a branch-on-branch. Despite the multistep nature of this process, up to 40% of all ethyl groups and 10% of all methyl groups in some palladium-catalyzed polyethylenes can be present in *sec*-butyl groups. Ethylene is not observed to insert at tertiary carbon atoms nor at secondary carbon atoms adjacent to a tertiary center, though it will insert at a primary alkyl adjacent to a tertiary center. With this reasonably simple set of rules, the observed structures can be explained. Nonetheless, the particular rates of the various steps

Scheme 4. Mechanism for *sec*-Butyl Branch Formation



are dependent upon the catalyst structure and the polymerization conditions.

The mechanism shown for formation of branch-on-branch structures is also important to the understanding of the distribution of *n*-alkyl branches. The number of branches of a given branch length decreases with increasing branch length. This fits nicely with the competition between ethylene insertion and the chain-walking mechanism. The more time the catalyst spends in chain walking since the last insertion, the more likely that an ethylene insertion will intervene. For some nickel catalysts, the decrease is nearly monotonic, but for palladium catalysts, there can be a disproportionately high number of ethyl and butyl branches. This might seem to indicate formation of α -olefins followed by incorporation of those olefins into the polymer backbone. Nonetheless, there is no observed residual unreacted α -olefin from these polymerizations. An alternative mechanism that nicely explains the extra even-numbered branches is one analogous to the *sec*-butyl branch formation shown in Scheme 4. When the catalyst migrates to the tertiary center, instead of migrating down to the main polymer chain as shown, it migrates up to the primary carbon atom where it undergoes another insertion to continue the polymer chain; an ethyl branch results. This type of mechanism will yield only even-carbon branches. The observed distribution is the cumulation of chain-walking back from the end of a polymer chain, which gives even and odd branches, and this mechanism, which gives only even. It is clear that the random walk leads to the statistical distribution of all of the observed branches.

These two chain-walking mechanisms have an impact upon the distribution of branches. Two consecutive methyl branches must have an even number of methylenes between them. This holds true for any odd-carbon branches because they can only be formed by having the metal center back down the chain by an odd number of carbon atoms. This mechanism would also seem to argue that there must be an odd number of methylenes between two even-carbon branches, but the fact that the catalyst has the ability to walk to any spot on the polymer backbone and insert one or more ethylenes means that this is not true. Thus, if there are an even number of methylene carbon atoms between two consecutive branches, at least one of them must contain an odd number of carbon atoms. This mechanistic argument has been nicely confirmed in the case of nickel-catalyzed

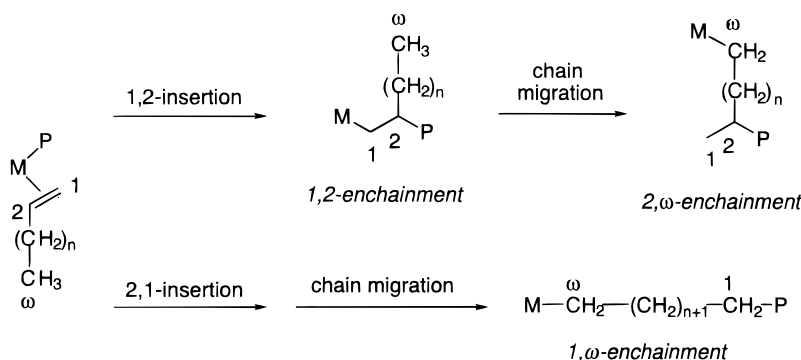
polymers containing moderate levels of branching; in this particular sample, branching levels were not high enough to observe branching-on-branching.²⁴³ With nickel-catalyzed polyethylenes at lower levels of branching, sequences involving two branches separated either by two or four methylene backbone carbons were reported to have at least one methyl branch in this sequence.²⁴³ Clusters of short-chain branches, that is branches separated by only one methylene carbon, are relatively rare unless the branching density becomes very high.

2.3. α -Olefin Polymerization

The quantification of linear branches in the polyethylenes above has been particularly helpful in the elucidation of the structures of polymers of α -olefins produced by the nickel and palladium α -diimine catalysts. Polymerizations of α -olefins with both Ni and Pd catalysts yield high molecular weight polymers. Polymerization rates and productivities are significantly lower than those observed with ethylene. The resulting polymers have unusual properties that can be traced back to their unexpected microstructures. For instance, [(2,6-*i*-PrPh)₂DABH₂]PdMe-(OEt₂)BAF yields a polypropylene which is an amorphous elastomer ($M_n = 15\ 000$) with a T_g of $-43\ ^\circ\text{C}$ rather than the expected $-5\ ^\circ\text{C}$ observed in isotactic or atactic polypropylene;²⁴⁴ this is the behavior expected of an ethylene/propylene rubber. The DAB-NiBr₂ catalysts where DAB = (2,6-*i*-PrPh)₂DABAN and (2-*t*-BuPh)₂DABAN, activated with MAO, yield polymers with $M_n = 190\ 000$ and $60\ 000$ and $T_g = -24$ and $-55\ ^\circ\text{C}$, respectively. Normal polypropylenes of any tacticity should have 333 methyl branches per 1000 carbon atoms, but these three polymers have 210, 270, and 160 methyl branches, respectively.^{73,148,239} The source of "ethylene" in these polymers can come only from 1,3-insertion of propylene. The ¹³C NMR spectra of poly(4-methyl-1-pentene) and polypropylene polymerized with a palladium catalyst appear remarkably similar, though there are no linear segments in poly-4-methyl-1-pentene exceeding four carbons while the polypropylene has segments of six or more methylenes. Both contain methyl- and isopropyl-ended branches.

The chain-walking described above for ethylene can lead to outcomes for α -olefins which are markedly different than those expected;⁶ this is shown in Scheme 5. Insertions that occur in a 1,2-manner

Scheme 5. Routes to the Observed 1,2-, 1, ω -, and 2, ω -Enchainment of α -Olefins



followed by another immediate insertion lead to a structure similar to that observed for early metal catalysts. A 1,2-insertion followed by migration to the opposite end of the olefin yields a 2, ω -insertion and a methyl branch on the polymer backbone. There is also significant 2,1-insertion and subsequent chain walking to give 1, ω -enchainments which resemble linear polyethylene segments.

In contrast to chain growth during ethylene polymerization, insertions of α -olefins into secondary methylene carbons generally do not occur. Rather, the catalyst walks until it forms a primary metal carbon bond before inserting an olefin larger than ethylene. Therefore, branches of intermediate length are generally not observed. It is also possible to quantify the preference of the catalyst for α -olefin insertion at a methylene attached to a secondary carbon relative to a methylene attached to a tertiary carbon atom. Thus, polymerization of higher α -olefins such as hexadecene leads to polymers resembling normal linear polyethylene with largely methyl branches and occasional presumed tetradecyl branches.²³⁹ The length of the linear segments from 1, ω -insertions increases with the chain length of the α -olefin and results in higher polyethylene-like melting points. For instance, a poly(1-octadecene) has from 45 branches/1000 C ($T_m = 56^\circ\text{C}$) to 33 branches/1000 C ($T_m = 78^\circ\text{C}$) depending upon the catalyst.^{75,148}

Although there is normally a preference after a 1,2-insertion for subsequent addition at the end of the longer branch, in propylene polymerizations there is no longer branch. As a result, propylene polymerizations are generally slower than polymerizations of higher α -olefins, in marked contrast to metallocene or Ziegler–Natta catalysts.

Ethylene copolymerizations with α -olefins relax some of the constraints imposed upon α -olefin homopolymerizations, since while α -olefins insert only at primary palladium alkyl bonds, ethylene will insert at secondary palladium–alkyl bonds as long as they are not adjacent to a tertiary carbon atom. Thus, for an α -olefin with n carbon atoms, the spectrum of the resulting copolymer shows a superposition of resonances for a “normal” ethylene polymerization with a spectrum containing not only $n - 2$ branches but also $n - 3$ (and presumably $n - 1$) branches, etc. Ethylene can be inserted into any carbon of the α -olefin.

While a variety of α -olefins have been copolymerized with ethylene,^{75,76,245–247} dienes generally poison the catalysts by repeatedly forming stable allyl intermediates which are very slow to reinitiate. Exceptions to this include very long dienes such as 1,13-tetradecadiene^{246a} or blocked dienes such as 3,3-dimethyl-1,5-hexadiene or 2-methyl-4-thia-1,6-heptadiene.^{75,76} Like dienes, styrene inhibits ethylene polymerization presumably by forming a stable π -benzyl intermediate, but 4-phenyl-1-butene copolymerizes due to the added chain length and 2,3,4,5,6-pentafluorostyrene copolymerizes because it does not form a stable π -benzyl complex.^{246b}

2.4. Living α -Olefin Polymerization

Polydispersities of the α -olefin polymerizations are generally low, and at low temperatures (-10°C) and

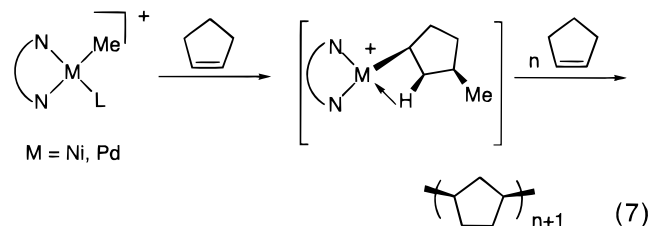
low monomer concentrations (less than one molar), it is possible to achieve living polymerization of α -olefins with the α -diimine nickel catalysts.^{75,148} For example, the number-average molecular weight of polypropylene increases linearly with time and propylene conversion and the resulting polypropylene has a narrow molecular weight distribution (for example, $M_n = 160\,000$, $M_w/M_n = 1.13$). Insertions are largely syndiotactic at -78°C as a result of a chain-end control mechanism.²⁴⁸

The living nature of the nickel-catalyzed α -olefin polymerizations coupled with the propensity for chain straightening of longer α -olefins can be utilized to prepare block copolymers with well-defined architectures. For example, the synthesis of α -olefin A – B – A block copolymers where the semicrystalline A blocks are made up of poly(1-octadecene) and the B block is composed of a more highly branched, amorphous, random copolymer of propylene and 1-octadecene enabled the preparation of thermoplastic elastomeric polyolefins.^{75,148}

2.5. Cycloolefin Polymerization

The palladium and nickel complexes will catalyze the polymerization of cyclic internal olefins. Polymerization of cyclopentene by both the nickel and palladium catalysts results in the formation of new polycyclopentenes which have a crystalline form that differs from that of the highly isotactic polycyclopentenes produced by zirconium metallocene catalysts.^{249,250} The new polycyclopentenes have weight-average molecular weights as high as 251 000 yet are melt-processable to strong, clear films. They have a broad melting transition with end-of-melting point temperatures ranging from 241 to 330 $^\circ\text{C}$. In contrast, polycyclopentenes prepared with metallocene catalysts have low molecular weights ($M_n \leq 2000$) and in general are not melt-processable.^{251–253} Hydro-oligomerizations to yield low molecular mass species coupled with ^{13}C NMR analysis^{254,255} indicated that the late-metal-catalyzed polycyclopentenes exhibit *cis*-1,3-enchainment and range in tacticity from atactic to partially isotactic.²⁵⁰

A study utilizing ^1H NMR indicates a stabilized β -agostic cyclopentyl resting state for both the palladium and nickel catalysts (eq 7). This is in contrast

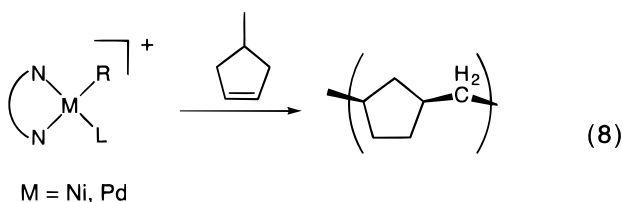


with the alkyl olefin resting state observed after insertion of ethylene, α -olefins, and internal acyclic olefins. A similar agostic structure has been observed in a palladium isopropyl complex.²⁵⁶ For the isopropyl complex, NMR line-shape analysis suggests that two independent processes occur with very similar activation barriers. They are interchange of the agostic and nonagostic methyl groups and exchange of

hydrogen atoms within the agostic methyl group, which is best regarded as an in-place methyl group rotation.

It has been demonstrated that the activated forms of the α -diimine catalysts are more stable to storage if combined with an olefin such as cyclopentene to form the stable agostic C–H–M interaction.²⁵⁷ This is true whether the catalyst is homogeneous or supported.^{203,258}

In the case of cyclopentene polymerization, the insertions at secondary alkyls are the only possible mode of chain growth; no insertions adjacent to tertiary carbons are observed. For substituted cyclopentenes, there are more options in the polymerization.²⁵⁹ For instance, with 4-methylcyclopentene, insertion generally takes place on the unsubstituted side of the ring. This leaves a *cis*-C–H bond available for chain walking to the methyl group. The next insertion takes place at the primary carbon atom, giving a methylenecyclopentane polymer as illustrated in eq 8. A similar behavior is observed for



ethylcyclopentene resulting in an alternating ethylene/cyclopentene polymer. Cyclopentylcyclopentene provides a polycyclopentene having a new tacticity.²⁵⁹

2.6. Polar Comonomer Polymerization

The cationic palladium α -diimine complexes are remarkably functional-group tolerant. Ethylene polymerizations can be carried out in the presence of ethers, organic esters, and acids, but nitriles tend to inhibit polymerizations.^{75,76} In addition, polymerizations have been carried out in the presence of air and in the presence of an aqueous phase.^{75,76,108} Aqueous emulsion and suspension polymerizations using these catalysts have been developed as a route to microspheres of polymer for adhesives as well as for other applications.^{260–263} Preparation of elastomers is often complicated by difficult solvent removal, so polymerizations in supercritical CO₂ have been investigated.²⁶⁴ It is also possible to combine the activity of the palladium catalysts with other polymerization techniques such as living-free-radical polymerizations.²⁶⁵ One interesting observation is that the

addition of 2,6-di(*tert*-butyl)phenol to the reaction medium for ethylene copolymerizations with polar monomers decreases the formation of palladium metal, making the polymers lighter in color.²⁶⁶

This functional-group tolerance extends to comonomers bearing polar functionality. The cationic palladium α -diimine complexes will catalyze the copolymerization of ethylene and α -olefins with commercially significant, functionalized olefins such as acrylates in an unprotected form to give high molecular weight, random copolymers under mild conditions.^{75,76,113,114,168,266–268} The primary comonomers have been acrylates and other olefinic carboxylates,^{113,114} including the epoxy-substituted glycidyl acrylate and the parent acrylic acid.^{75,76} Polymerizations with nickel catalysts and low levels of methyl acrylate give relatively linear polymers with very low levels of polar comonomer incorporation.^{269,270} Other demonstrated polar comonomers include methyl vinyl ketone, CO, crotonaldehyde, and 4-pentenoates.^{75,76,113,114} The range of monomers is discussed in more detail below. The composition of the various copolymers is dependent upon the feed concentrations of both ethylene and the polar comonomer.^{73–76,271}

A typical structure of an ethylene/methyl acrylate (E/MA) copolymer is very similar to an ethylene homopolymer produced by the same α -diimine palladium catalysts, see Figure 3. The EMA copolymers are amorphous, highly branched materials with about 100 branches per 1000 carbon atoms and with glass-transition temperatures typically ranging from -50 to -70 °C.^{113,114,239,272} Simultaneous RI and UV detection GPC indicates that they are true copolymers with the ester groups randomly and evenly distributed throughout the entire distribution of polymer chain lengths. NMR spectroscopy indicates that most of the ester groups are located at the ends of branches but that the proportion of the ester groups directly attached to the polymer backbone increases with increasing ethylene pressure.

The ethylene methyl acrylate system is amenable to low-temperature NMR mechanistic studies with all of the critical intermediates visible spectroscopically.^{113–114} Acrylate insertion occurs predominantly in a 2,1-fashion, yielding a strained four-membered chelate ring in which the carbonyl oxygen atom is coordinated to the palladium atom. This insertion is followed by a series of β -hydride eliminations and re-additions expanding the ring stepwise to the six-membered chelate complex; this is the catalyst resting state shown in Scheme 6.

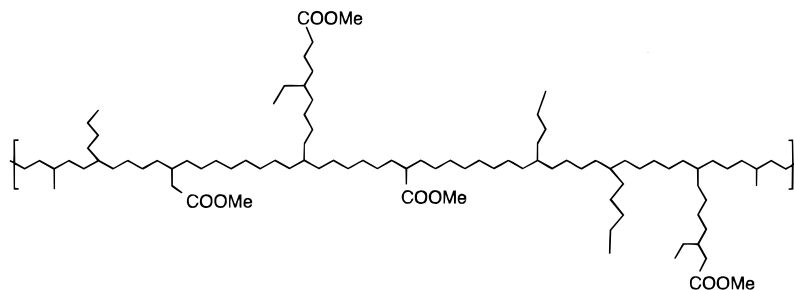
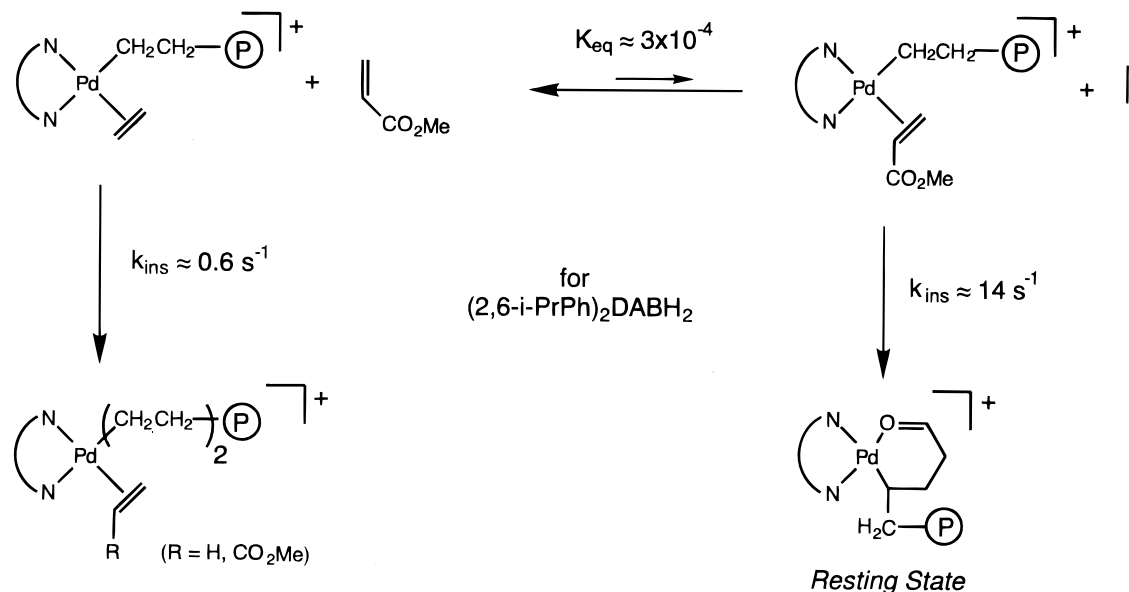


Figure 3. Representative structure of a highly branched random copolymer of ethylene and methyl acrylate produced by palladium catalysts.

Scheme 6. Illustration of Results from Low-Temperature NMR Mechanistic Studies of the Copolymerization of Ethylene and Methyl Acrylate^{114 a}


^a Rate and equilibrium constants are at 35 °C.

The strong binding of oxygen to the palladium center in the chelate resting state retards the rate of chain growth relative to the rate of homopolymerization of ethylene. The equilibrium between the chelate complex and the alkyl olefin species necessary for insertion of monomer and chain propagation has been quantitatively assessed and strongly favors the chelate complex even at high ethylene pressure.

The relative ratios of incorporation of ethylene and methyl acrylate into the copolymers are governed by both the equilibrium ratio of the alkyl ethylene and alkyl methyl acrylate complexes and their relative rates of migratory insertion (Curtin–Hammett kinetics) as illustrated in Scheme 6. While the rate of migratory insertion of methyl acrylate is somewhat faster than that of ethylene at low temperature, there is an overwhelming preference for binding ethylene to the electrophilic Pd(II) center relative to the electron-deficient olefin, methyl acrylate (Scheme 6). Thus, to achieve significant incorporation of methyl acrylate into the copolymer, very large (MA):C₂H₄ ratios must be used. A consequence of increasing MA concentrations is that the overall rate of polymerization decreases due to increased concentrations of the chelate complex. Decreasing the steric bulk of the diimine ligand or incorporating more electron-donating substituents on the diimine increase acrylate incorporation, probably through improved binding of MA to the catalyst center.

While a wide range of monomers have been incorporated in ethylene copolymerizations with the palladium α -diimine catalysts, there are also a variety of monomers which slow homopolymerization and are not incorporated into the polymer chain and others which inhibit all polymerization. There is a general trend that removing the polar functionality from the vicinity of the double bond lessens the rate penalty experienced in the copolymerizations. A superior approach is to place a group which blocks double-bond isomerization between the olefinic group and

the desired functionality; this approach prevents the catalyst from chain walking to that functionality.

The catalysts tolerate carboxyl functionality, so a variety of acrylates have been copolymerized with ethylene using the α -diimine catalysts; these acrylates include CH₂=CHCO₂R (where R = H, Me, Et, *t*-Bu, CH₂CH₂OH, CH₂CH₂(CF₂)₉CF₃, OCH₂(CF₂)₆-CF₃, or -(CH₂)₂SiCl₃).^{75,76,156,247} Comonomers such as 10-undecenylate or 4-pentenoate esters exemplify the use of longer chains which can be copolymerized not only by the palladium α -diimine catalysts, but also by nickel α -diimine catalysts and neutral nickel catalysts bearing anionic ligands.^{152,156,247,273} Copolymerizations of ethylene with diethyl allylmalonate, methyl 3,3-dimethyl-4-pentenoate, 2,2-dimethylpent-4-enoic acid, and methyl 2,2-dimethyl-4-pentenoate exemplify the blocked chain strategy.²⁴⁷ Tolerance of organic ester functionality is not limited to carboxylates. Carbonate esters such as vinyl ethylene carbonate^{246,247} and allyl methyl carbonate^{246,247} are copolymerized; neutral nickel catalysts discussed below have also been used to copolymerize phosphonate esters such as CH₂=CH(CH₂)₂P(O)(OC₂H₅)₂ with ethylene.²⁷³ Vinyl ethers can be a problem for α -diimine catalysts, sometimes undergoing preferential cationic homopolymerization, but vinyl ethyl ether has been copolymerized using nickel ylide catalysts,²⁷³ and both 2,3-dihydrofuran and 2,2-dimethyl-4-vinyldioxolane have been copolymerized with ethylene using heterosubstituted α -diimine catalysts.²⁴⁶

Sulfones such as allyl-2-methylallyl sulfone and allyl phenyl sulfone and ketones such as 5-hexen-2-one, 2-allyl-2-methyl-1,3-cyclopentanedione, and methyl vinyl ketone have been copolymerized.²⁴⁷ Ethers such as 2,2-dimethyl-4-vinyldioxolane,¹⁰⁷ 2-methyl-2-(3-butenyl)-1,3-dioxolane, and 2,2-dimethyl-4-pentenyl methyl ether²⁴⁷ and even epoxides such as 3,3-dimethyl-5-hexene-1,2-epoxide have been copolymerized.²⁴⁷

Ethylene polymerizations may be carried out in alcohols, indicating their tolerance for this functionality. Olefinic alcohols such as 5-hexenol or 10-undecenol provide examples of the longer-chain protection approach,^{273–275} and 2,2-dimethyl-4-pentenol provides an example of a blocking group in the chain.²⁴⁷

Fluoro-functionalized monomers where the fluoro group is accessible to the catalyst (as opposed to fluoroalkyl acrylates) are also effective in ethylene copolymerizations. Allylpentafluorobenzene, $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{C}_6\text{F}_{13}$ and $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$, and $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_2\text{CO}_2\text{Et}$ ^{75,76,247} are copolymerized using palladium α -diimine catalysts, and $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{CF}_3)_3$ or $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}_3\text{F}_9$ ²⁷³ provides examples of copolymerizations utilizing neutral nickel catalysts. Silanes such as $\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_2\text{SiCl}_3$ or $\text{CH}_2=\text{CH}_2(\text{CH}_2)_6\text{SiCl}_3$ will copolymerize with ethylene and can be cross-linked after polymerization through exposure to moist air.^{247,273} Siloxanes have also been copolymerized.²⁷³ While allyl and vinyl ethers may be problematic, allyl 1,1,1,2,2-pentafluoroethyl ether will undergo ethylene copolymerization.²⁴⁷ Normal amides such as acrylamide inhibit polymerization, but $\text{FSO}_2\text{CF}_2\text{CON}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$ will copolymerize.²⁴⁷ Vinyl acetate completely inhibits polymerization, but 4-penten-1-yl acetate can be copolymerized.²⁴⁷

Nitriles, amides, and amines generally inhibit polymerization either as solvents or monomers. This is thought to be through nitrogen competition for the olefin binding site. Nonetheless, both 4-pentenitrile and $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C}(\text{O})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ have been copolymerized with ethylene using the anionic ligand complexes of nickel discussed below.²⁷³

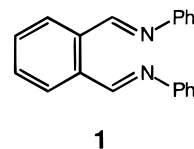
It is possible to incorporate low levels of acrylics into ethylene polymers using nickel α -diimine catalysts without a large penalty in polymerization rate. A reaction medium containing 1% methyl acrylate was polymerized with ethylene in the presence of $\text{NiMeBr}[(2,6\text{-}^i\text{PrPh})_2\text{DABMe}_2]$ and NaBAF to give a copolymer showing M_w of about 10^5 ($M_w/M_n = 3.9$) and an acrylate content of 0.1 mol %.²⁶⁹

2.7. Other Metals

With the advent of the nickel and palladium α -diimine catalyst systems, it was reasonable to extend the diimine chemistry to cobalt and iron.^{75,76} Low to moderate activity was observed in a limited number of cases, but the observation led to a broader search for catalytic activity. In addition to complexes of nickel and palladium, other late metal complexes that catalyze insertion polymerization of olefins include ruthenium,^{276,277} cobalt,^{75,76,132,139,278–282} rhodium,^{283–291} platinum, and copper.^{292,293} Iron has been shown to polymerize ethylene when ligated with α -diimine ligands, but the polymerizations are poor compared with nickel and palladium.^{75,76} In addition to these references, a substantial body of literature on the use of tridentate ligands on iron and cobalt has appeared recently and will be covered in section 2.7.1. There is also a considerable body of literature on the use of late metals to polymerize acrylates and styrene, but those atom-transfer radical polymerizations are beyond the scope of this review.

Cationic, electrophilic, cyclopentadienyl-based cobalt complexes such as $[(\text{C}_5\text{Me}_5)(\text{P}(\text{OMe})_3)\text{CoCH}_2\text{-CHR-}\mu\text{-H}]^+$ catalyze the living polymerization of ethylene.^{278–280,294} Other than the nickel and palladium α -diimine systems, these are the best mechanistically characterized late-metal catalysts.^{278,295} NMR investigation of ethylene polymerization by $[(\text{C}_5\text{Me}_5)(\text{P}(\text{OMe})_3)\text{CoCH}_2\text{CH}_2\text{-}\mu\text{-H}]^+$ using $^{13}\text{C}_2\text{H}_4$ allowed the observation of the intermediate ethyl ethylene complex, $[(\text{C}_5\text{Me}_5)(\text{P}(\text{OMe})_3)\text{Co}(^{13}\text{C}_2\text{H}_4)\text{CH}_2\text{-CH}_3]^+$. This was the first case in which an alkyl ethylene complex was detected as an intermediate in a polymerizing system. From a kinetic analysis at -70°C , the first-order rate constant for the β -alkyl migratory insertion reaction was determined to be $1.8 \times 10^{-3} \text{ s}^{-1}$. This value is compared to similar values for β -hydride migration in $[(\text{C}_5\text{Me}_5)(\text{P}(\text{OMe})_3)\text{-Co}(\text{C}_2\text{H}_4)\text{H}]^+$ and both β -hydride and β -ethyl migration in the analogous rhodium complexes. Generation of $[(\text{C}_5\text{Me}_5)(\text{P}(\text{OMe})_3)\text{Co}(\text{CH}_2\text{CHR-}\mu\text{-H})][\text{BAF}]$ [$\text{R} = (\text{CH}_2)_4\text{SiEt}_3$ or $(\text{CH}_2)_4\text{SiMe}_2\text{Cl}$] through an olefin hydrosilation sequence provides a route to silyl-end-capped polyethylenes with narrow molar mass distributions. Controlled termination of the polymerization results in end-functionalized polyethylenes.²⁹⁶ Investigation of these complexes led to the observation of a parallel between the structure and dynamics of alkene-, polyene-, and polyenyl-transition-metal hydride complexes and the activation energy of related alkyl complexes to migratory insertion. Those factors that favor bridging hydride structures over terminal hydride structures also facilitate alkyl migration. This correctly suggests that alkyl ethylene complexes whose hydride analogues are bridged should undergo rapid migratory insertion and serve as polymerization catalysts for olefins.²⁸⁰

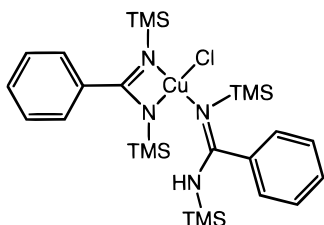
Polymerizations with α -diimine complexes of cobalt have been investigated.^{75–76} They are clearly less active than their nickel analogues.²⁸¹ Theoretical investigation of the related cobalt iminopyridines have been carried out along with calculations on cobalt and iron complexes bearing tridentate bis(imino)pyridine ligands.²⁹⁷ There is also a report of an interesting cobalt complex of **1** which polymerizes ethylene.²⁸¹



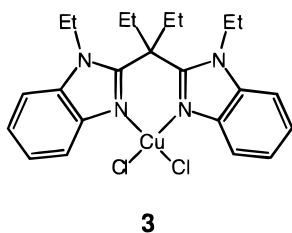
Rhodium-catalyzed polymerization of ethylene was reported very early in the history of organometallic chemistry,²⁸³ but the more recent hard-ligand triaza-cyclononane complexes of rhodium ($\text{Cn} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) are the best characterized.²⁸⁴ At room temperature, ethylene is slowly polymerized by $[(\text{Cn})\text{RhMe}(\text{H}_2\text{O})(\text{OH})]^+$ in water and more rapidly in acetone. At 50°C , the disappearance of the methyl resonance in the presence of ethylene is first order in ethylene and in rhodium. The polymerization rate profile versus pH in water indicates that $[(\text{Cn})\text{RhMe}(\text{OH}_2)(\text{OH})]^+$ is the most effective catalyst, $[(\text{Cn})\text{RhMe}(\text{OH}_2)_2]^{+2}$ is much slower, and

$CnRhMe(OH)_2$ is not a catalyst. One polyethylene sample formed in water had a M_w of 5100 and a polydispersity index of 1.6; the average turnover rate was 1 per day.²⁸⁴ It is possible to copolymerize ethylene with polar comonomers such as methyl acrylate with the rhodium catalysts.²⁹¹ In addition to the Cn ligands, softer trithiocyclononane ligands support the polymerization of ethylene on both rhodium and platinum.²⁸⁸

Copper ethylene chemistry is well developed,²⁹⁸ but reports of polymerizations based upon copper are rare. The amidinate ligand, *N,N*-ditrimethylsilylbenzamidinato, has been reported to support copper-catalyzed ethylene polymerizations.²⁹¹ It is prepared from hexamethyldisilazane, benzonitrile, and trimethylsilyl chloride. The resulting copper chloride complex, **2**, when activated with methylaluminumoxane, produced polyethylene with $M_w = 820\,000$ and $T_m = 138\text{ }^\circ\text{C}$.²⁹² In another patent,



ethylene was polymerized with 2,2'-bis[2-(1-ethylbenzimidazol-2-yl)biphenyl]copper(II), **3**, and methylaluminumoxane cocatalyst to give polyethylene melting at $139\text{ }^\circ\text{C}$ and having a $M_n = 4900$.²⁹¹ The oxidation

**3**

states and the active catalytic species in both of these copper systems are unknown.

2.7.1. Tridentate Bis(imine) Ligands

A series of pyridyl bis-imine complexes of cobalt and iron exhibit very high activities for ethylene polymerization.^{97,137,299–322} A crystal structure indicates a five-coordinate pseudo-square-pyramidal conformation. As observed for the α -diimine complexes, the aryl groups on the imine nitrogen atoms are roughly perpendicular to the ligand coordination plane. The protective bulk of the ortho substituents above and below the metal center is again critical to the molecular weight of the resulting ethylene polymerizations (vide infra). In contrast to the nickel and palladium systems, there is no chain walking and the polyethylene is strictly linear with very high density.³²¹

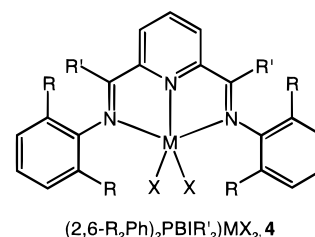
The nomenclature that will be used for the pyridine bis(imine) (PBI) complexes, **4**, is related to that used

Table 5. Iron and Cobalt Complexes Bearing Pyridylbis(imine) Ligands

ligand	Co	Fe
(2,6- <i>i</i> -PrPh) ₂ PBIME ₂ ^a	299 E-7, 16, 17 309 E-3	299 E-5,8,9 309 E-1
(2-Cl-6-MePh) ₂ PBIME ₂	299 E-10	
(Mes) ₂ PBIME ₂	299 E-11	
(2-PhPh) ₂ PBIME ₂	299 E-12	
(2,6- <i>i</i> -PrPh) ₂ PBIH ₂	299 E-13	299 E-12
(2- <i>t</i> -BuPh) ₂ PBIME ₂	299 E-14	299 E-15
(2,6- <i>i</i> -PrPh) ₂ (4-CF ₃ -PBI)Me ₂	299 E-36	299 E-51
(2,6- <i>i</i> -PrPh) ₂ PBI(SMe) ₂	299 E-41	
(2,6- <i>i</i> -PrPh) ₂ PBI(C ₃ N ₂ H ₃)		299 E-59
(2,6-MePh) ₂ PBIME ₂		315 E-6 299 E-8
(Ph) ₂ PBIME ₂		299 E-7
(2- <i>t</i> -BuPh) ₂ PBIME ₂		315 E-8 299 E-4
(2,3-MePh) ₂ PBIME ₂		309 E-6
(2,4-MePh) ₂ PBIME ₂		309 E-7
(Mes) ₂ PBIME ₂		309 E-9
(2,6-MePh) ₂ PBIH ₂		309 E-10
(2,6-EtPh) ₂ PBIH ₂		309 E-11
(1-Np) ₂ PBIH ₂		309 E-12
(Mes) ₂ PBIH ₂		309 E-28, 29
(PhNH) ₂ PBIH ₂		309 E-30
(Ph ₂ N) ₂ PBIH ₂		309 E-31
(Ph ₃ C) ₂ PBIH ₂		309 E-31

^a One manganese complex was also reported, see ref 309 E-2.

for the α -diimine complexes. Substituents on the



pyridine ring will be indicated appropriately. The compounds reported in the literature are summarized in Table 5.

In addition to the PBI complexes, several additional classes of ethylene polymerization catalysts based upon tridentate ligand complexes of iron have been developed. These include the furan, **5**,³²³ and pyrrole, **6**,³²⁴ derivatives. The oxidation state of the

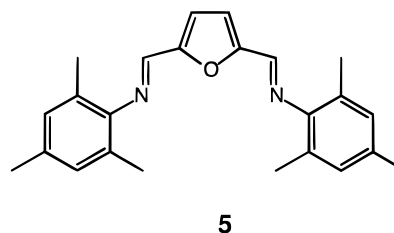
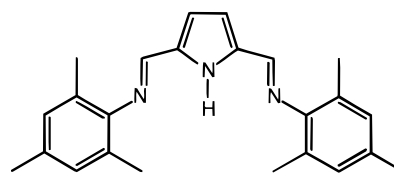
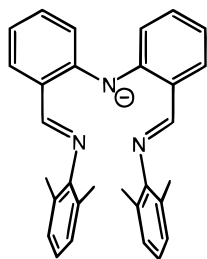
**5****6**

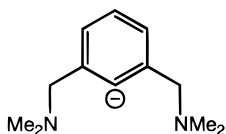
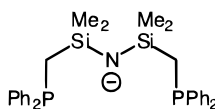
Table 6. Catalyst Activity for a Series of $M[(2,6-i\text{PrPh})_2\text{PBIH}_2]\text{Cl}_2$ Complexes of Cobalt and Iron

metal	ethylene pressure (atm)	activity (kg of PE/g of M/h)
Co	7	140
	41	140
Fe	7	1860
	41	4220
	340	11900

pyrrole derivative is not clear from the description. In the case of the ligand **7**, the oxidation state of iron is III, the ligand being monanionic.¹³⁹ Additional

**7**

tridentate anionic ligands include amine, **8**, and phosphine, **9**, species.³²⁵

**8****9**

The active species for the PBI complexes is not as well characterized as in the nickel and palladium systems. It is assumed to be a cationic alkyl complex formed by reaction of the dihalo precatalyst with a cocatalyst such as methylaluminoxane (MAO). The resulting active species polymerizes ethylene at unusually high rates to form linear high-density polyethylene. Even at ethylene pressures as low as 1 atm, the polymerization is extremely exothermic and the crystalline polymer product rapidly precipitates from solution. Computational chemistry is proving to be of utility in understanding the mechanistic aspects of this chemistry.^{297,326-328} Lower barriers to insertion, relative to the nickel α -diimine complexes, support the higher activity.

The activity of the cobalt PBI systems (Table 6) does not change markedly with ethylene pressure. The iron PBI catalysts are at least an order of magnitude more active than their cobalt analogues, and their activity increases with increasing ethylene pressure.³²¹ Catalysts based upon ketimine ligands ($R' = \text{Me}$) are approximately an order of magnitude more active than catalysts based upon aldimine ligands ($R' = \text{H}$).³²¹ The catalysts are thermally stable and display good activities and reasonable lifetimes at elevated temperatures (100 °C). Electron-withdrawing substituents in the para position of the pyridine ring do not change the overall productivity

Table 7. Product Molecular Weight for Ethylene Polymerizations Catalyzed by a Series of $\text{Co}(\text{PBI})\text{Cl}_2$ Complexes

PBI ligand	M_w
(2-PhPh) ₂ PBIME ₂	α -olefins
(2-Me-2-CIPh) ₂ PBIME ₂	900
(Mes) ₂ PBIME ₂	17 500
(2- <i>t</i> -BuPh) ₂ PBIME ₂	31 000
(2,6- <i>i</i> -PrPh) ₂ PBIME ₂	46 000
(2,6- <i>i</i> -PrPh) ₂ PBIH ₂	18 500

of the catalyst significantly. The more electrophilic metal center might exhibit enhanced activity which is offset by destabilization of the active species leading to lower thermal stability and shorter catalyst lifetime.²⁹⁷

In the PBI cobalt and iron complexes, the steric bulk around the metal center is key to retarding chain transfer in order to obtain high molecular weight polymer. Reduction of ligand bulk by reducing the size of the ortho substituents on the imine aryl group or by using the formyl instead of the acetyl pyridine precursors causes a decrease in the molecular weight of the resulting polyethylene. Table 7 shows the results obtained for a series of cobalt catalysts with different ligands.

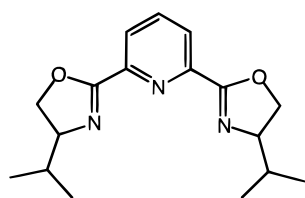
In general, the iron PBI catalysts produce higher molecular weight polyethylene than their cobalt analogues. Hydrogen effectively controls molecular weight.³²⁹ Chain transfer to aluminum also occurs and can make interpretation of molecular weight distributions difficult, although the effect of ligand bulk on molecular weight remains clear. The aluminum chain transfer gives rise to a low molecular weight fraction superimposed upon the normal molecular weight distribution. Aluminum chain transfer predominates at high concentrations of aluminum activator and short reaction times yielding a bimodal molecular weight distribution.^{316,321} Longer run times and lower concentrations of MAO cocatalyst result in monomodal, narrow-dispersity, very high molecular weight polymer. The PBI catalysts can be combined with other catalysts such as nickel α -diimines or metallocenes to yield in-reactor blends of polyethylenes.¹⁹³

The iron PBI catalysts homopolymerize propylene and also copolymerize propylene with ethylene but the polymerizations are sluggish.^{301,310,330-334} Regio-regular 2,1-propylene insertion is observed, with chain transfer resulting in 1-propenyl end groups. The regioregularity of the catalysts decreases with decreasing steric bulk on the ligands. No chain transfer to aluminum is observed. The polypropylene is enriched in isotactic pentads, and it was demonstrated that this occurs through chain-end control. These are the first late metal systems known to polymerize propylene in an isotactic fashion and the first report of formation of isotactic polypropylene via 2,1-insertion.³³³

With the PBI catalysts, the incorporation of ligands with significantly reduced bulk, typically only a single ortho substituent on the imine aryl group, and the absence of chain walking produces high-quality α -olefins. The PBI oligomerization catalysts are extremely productive, even relative to the polymer-

ization catalysts, with turnover frequencies as high as 100 000 kg/g of Fe/h recorded.^{335–336} This far exceeds values reported for catalysts used in current commercial processes.³³⁷ The oligomers consist of 97–99% linear α -olefins with no detectable internal olefin and only trace amounts of branched olefin. The Schulz–Flory distribution of olefins can be tailored by varying the reaction temperature and ligand sterics. Catalysts bearing ligands with larger ortho substituents shift the molecular weight distribution of oligomers to higher values, although this is achieved at the expense of catalyst activity. The oligomerizations can be operated effectively over a wide range of temperatures and at pressures significantly lower than the current 100–200 atm. range, which should allow significant savings in capital investment. The high catalyst activity should allow once-through oligomerizations, obviating the need for catalyst recycle or removal. In addition, it is possible to combine these catalysts with metallocene catalysts to make bimodal polymers or LLDPE directly from ethylene by producing the α -olefins in situ.^{193,338}

Extension of the tridentate catalysts to ruthenium through the use of pyridylbis(oxazoline)pyridine (pybox, **10**) ligands gives (pybox)RuX₂(ethylene) where X = Cl or I. In hydrocarbon solvents at 25–60 C° at



pybox, **10**

ethylene pressures of 6–12 atm, the yields were 0.28–2.14 kg of polyethylene/mol of Ru/h.²⁷⁷ The combination of high molecular weights and low productivities indicate that a small fraction of the ruthenium was active. Attempts to reproduce this work have been unsuccessful.³³⁹ The copolymerization of ethylene with α -olefins by these catalysts was also reported and is apparently facilitated by the larger coordination sphere of ruthenium.

3. Anionic Ligands

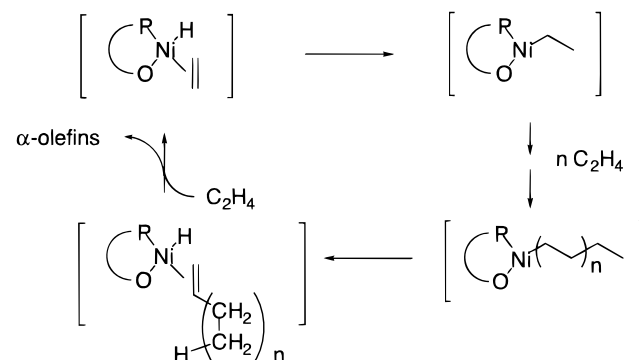
3.1. Nickel

Shell's very successful Shell Higher Olefin Process for the production of linear α -olefins is an excellent example of the utility of Ni(II) complexes bearing anionic ligands for ethylene oligomerization.^{340–355} These catalysts are very selective for the insertion of ethylene versus α -olefins, and β -hydride elimination is competitive with olefin insertion, giving high-quality, linear α -olefins (C₆–C₂₀) from ethylene. The active species is presumed to be a nickel(II) olefin hydride complex, which is generated in situ by reacting bis(1,5-cyclooctadiene)nickel(0) with the acid of the phosphine–carboxylate ligand. Related complexes are so easily prepared that they can be used

as experiments for undergraduate laboratories.³⁵⁶ The nickel catalyst oligomerizes ethylene at $\sim 3,000$ TO/h to form linear α -olefins of greater than 98% purity. The distribution of olefin molecular weights is essentially a Schulz–Flory distribution.^{357–359} A unique feature of the process is the use of a two-phase system for product isolation.^{360–362} The partitioning of the catalyst into the diol phase and the olefins into a hydrocarbon phase facilitates product isolation and catalyst recycle.

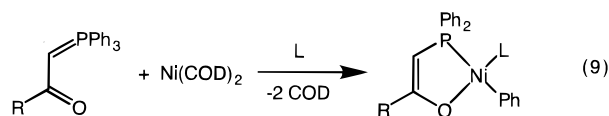
The proposed mechanism for the formation of linear α -olefins is shown in Scheme 7. Ethylene

Scheme 7. Proposed Mechanism for the Formation of Linear α -Olefins



insertion into the nickel–hydride bond generates an ethyl complex. Additional ethylene insertions yield nickel alkyls of various lengths, and subsequent β -hydride elimination produces an α -olefin hydride complex. Chain transfer in these systems likely occurs by associative olefin exchange between free ethylene and nickel-ligated α -olefin, regenerating the nickel–hydride ethylene complex. Due to the selectivity of these systems for ethylene insertion, the formation of branched species by reinsertion of the α -olefin product is minimal.³⁶³ Nonetheless, α -olefins have been deliberately co-oligomerized with ethylene using the SHOP catalyst, and the nature of the resulting products has been determined.³⁶³ There is a slight dependence on α -olefin chain length on the ability of the α -olefin to insert into the metal–carbon bond. There is a far greater dependence of chain propagation and termination on the nature of the alkyl group attached to nickel.³⁶³

Higher molecular weight oligomers and polymers are obtained when ethylene is reacted with P–O chelate catalysts synthesized by the oxidative addition of phosphorus ylides to zerovalent nickel compounds in the presence of triphenylphosphine or other ligands.^{273,352,364–369} As shown in eq 9, the catalysts are easily prepared from keto–ylides by oxidative addition of a P–Ph bond to a nickel(0) precursor like Ni(COD)₂.^{370–374} In this manner, a wide



range of catalysts with various substituents and

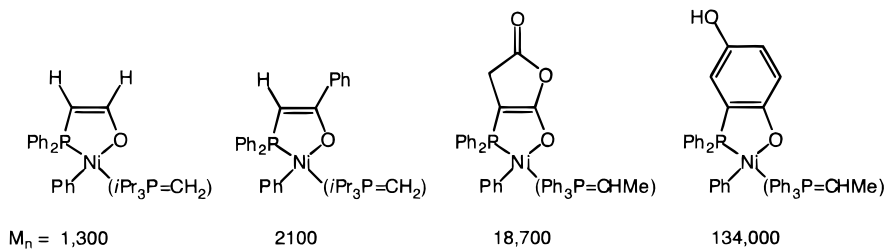


Figure 4. Effect of catalyst variation on the molecular weight of the resulting polymer.

ligands may be prepared. The one difficulty is that it is more difficult to insert an olefin into the Ni–aryl bond than into subsequent Ni–alkyl bonds. The utility of these catalysts has been well-reviewed.^{375,376}

The reactions of these complexes with ethylene are solvent-dependent, with linear α -olefins produced in toluene solution and linear, high molecular weight polyethylene formed in hexane suspension.^{364–365} The molecular weights of the linear α -olefins were increased by increasing the electron density and the steric bulk of the substituents on phosphorus.^{364–365}

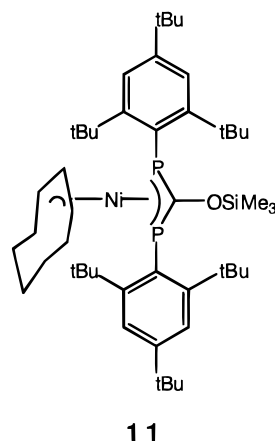
The coordination of a strongly donating ligand such as triphenylphosphine to the P–O chelate catalysts is an important factor in limiting the molecular weight of the products.^{368,369} Removal of the triphenylphosphine by addition of a variety of phosphine “sponges” and employing weaker bases such as pyridine to stabilize the nickel complexes allowed the synthesis of polyethylenes with weight-average molecular weights ranging from 8000 to 350 000. MAO has been utilized as a cocatalyst for the nickel P–O systems, although its role simply may be phosphine scavenging.³⁷⁷

These nickel catalysts are functional-group tolerant, allowing the homopolymerization of ethylene in the presence of polar additives or copolymerization of ethylene with α -olefins bearing a functional group in a position remote from the olefin. Active monomers have already been discussed (vide supra). Levels of functionalized olefin incorporation were low, and attempts to copolymerize ethylene with commercially significant monomers such as methyl acrylate or vinyl acetate were unsuccessful. Block copolymers of ethylene with ethylene/CO were prepared by initiation of polymerizations under ethylene and switching to E/CO feed.^{273,368,369} Varying the ligand in a series of ylide-stabilized, modified SHOP catalysts (Figure 4) gave a range of oligomers and polymers varying from linear α -olefins to HDPE ($M_n > 1.0 \times 10^6$) and with turnover frequencies as high as 50 000 TO/mol Ni·h.¹⁸⁶

Ethylene/propylene copolymers made with these nickel catalysts contain up to 6 mol % propylene.¹⁸⁶ When the nickel catalysts were combined with supported chromium catalysts, branched polyethylene (5.0 methyl-ended branches per 1000 carbon atoms) was produced by the chromium copolymerizing ethylene with the α -olefins that were produced in situ by the nickel catalyst.¹⁸⁶ Like the catalysts above, nickel catalysts with anionic ligands may themselves be supported on inorganic supports^{378,379} and polymeric supports.^{92–96}

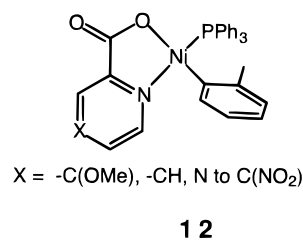
In addition to P–O-based systems, other neutral nickel complexes capable of polymerizing ethylene

included the diphosphallyl complex, **11**. Polymeriza-



tions based upon these ligands required the sterically bulky substituent shown to produce linear high molecular weight polyethylene.³⁸⁰

Electronic effects on nickel-catalyzed oligomerizations/polymerizations have been delineated through the use of a series of substituted pyridine carboxylate complexes, **12**.^{381,382} The electron-rich methoxy-



X = -C(OMe), -CH, N to C(NO₂)

substituted catalyst gave mostly linear olefins (56% α) with only 10–20% of the product consisting of higher molecular weight polyethylene. The electron-deficient nitro-substituted catalyst produced between 80% and 100% of high molecular weight HDPE under similar conditions. In addition, the nitro-substituted catalyst gave the highest activities of the four derivatives. A two-pathway reaction mechanism was proposed, and it was speculated that both pathways might operate concurrently under some conditions. Similar electronic effects were also observed in ethylene/CO copolymerizations; the percent polyketone formed varied from 100% with the nitro complex to 10–20% with the methoxy complex. The remaining portion of the isolated product consisted of ethylene oligomers.

While the P–O ligands were discovered first and are the most studied neutral nickel polymerization catalysts at this point in time, several new classes

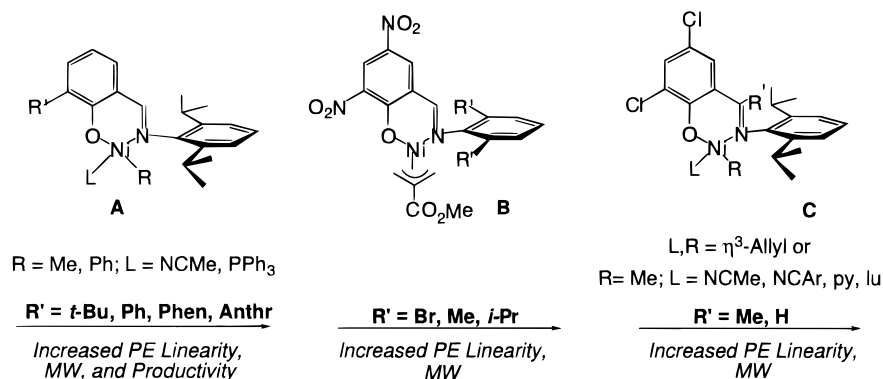


Figure 5. Examples of the effect of substituent variation in salicylaldiminato Ni(II) complexes.

of anionic ligands have been introduced. New salicylaldimine complexes, additional P–O ligands, and other classes of ligands are summarized in Tables 8 and 9.^{383–414} These new ligands center primarily around N–N and N–O chelates. Most feature the steric bulk expected to achieve high molecular weights.

The series of salicylaldiminato complexes of Ni(II) polymerize ethylene with high activities and are the best studied of these new systems.^{383–398} The availability of many sites for substitution makes these catalysts particularly versatile, and some of the effects of substituent variation are illustrated in Figure 5. The base- or allyl-stabilized catalyst precursors shown in Figure 5 are often initiated by Lewis acid cocatalysts such as $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{B}(\text{Ph})_3$, although derivatives of catalyst **A** in Figure 5 where $R' = \text{aryl}$ are able to function as single-component catalysts.^{383,386,391} Apparently the bulky aryl substituent promotes ligand (L) dissociation, enabling ethylene to bind and insert.³⁹¹

As with other imine-based late-metal polymerization catalysts, the N-aryl ring lies roughly perpendicular to the square plane of the molecule in these salicylaldiminato complexes and large ortho substituents on this ring increase the catalyst productivity.^{383–386} Increasing the steric bulk of the N-aryl ortho substituents also increases the linearity and molecular weight of the resulting polyethylene.^{383–386} Bulky substituents adjacent to the phenoxide group increase catalyst lifetime by slowing or preventing decomposition to the corresponding bis(salicylaldiminato)Ni complexes.^{383,385,391} Catalysts with bulky aryl substituents lying adjacent to the phenoxide substituent are especially productive, yielding polyethylenes with high molecular weights and high linearities (Figure 5A).^{383–386,391} Polyethylene with increased branching can be produced by replacing the ortho alkyl substituents on the N-aryl ring by halogens or by changing the imine backbone substituent from hydrogen to methyl. Productivities remain roughly constant with these variations; however, decreased polymer molecular weights are observed (Figure 5B,C).³⁸³ A large number of *sec*-butyl-ended branches have been identified in these highly branched polymers.³⁸³ As with the α -diimine catalysts, this indicates that these neutral nickel catalysts are capable of walking past a tertiary carbon atom to form branches on branches. Finally, similar to the pyridine carboxylate-based nickel systems, the

placement of electron-withdrawing substituents such as halogens and, particularly, nitro groups on the phenoxide ring increases the productivity of the salicylaldiminato catalysts (Figure 5B,C).^{383–386}

In addition to ethylene, these salicylaldiminato-based nickel catalysts will homo- and copolymerize styrene and norbornene and copolymerize ethylene and α -olefins such as 1-hexene and 1-octene.³⁸³ To demonstrate the functional-group tolerance of these neutral catalysts, ethylene homopolymerizations have been carried out in the presence of ethers, ketones, esters, alcohols, amines, and even water.^{384–391} In addition, copolymerizations of ethylene with functionalized norbornenes such as 5-norbornen-2-ol and 5-norbornene-2-yl acetate and α -olefins such as ethyl-4-pentenoate have been reported along with copolymerizations of norbornene with functionalized norbornenes.^{383,384,391} In addition, claims to the combination of differently substituted salicylaldiminato nickel catalysts and combinations of these catalysts with other olefin polymerization catalysts such as metallocenes to produce in-reactor blends of polymers have appeared.⁴¹⁷

3.2. α -Olefin Polymerization

Most of the nickel catalysts with anionic ligands discussed above will only dimerize α -olefins. Notable exceptions are the oligomerization of α -olefins by the aminobis(imino)phosphorane nickel catalyst (**13**).⁴¹⁸

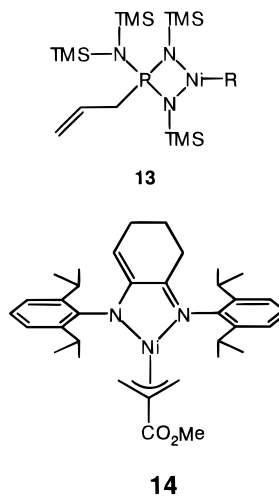
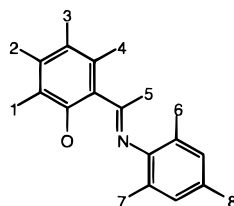


Table 8. Anionic Ligands for Complexes of Ni and Pd

Ligand	Ref.	Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
P-O Chelates							
	374		369, 273		407		406
1 Me Ph Ph		2 H H SO ₃		1 Ph OMe Ph Ph		2 H Ph Ph SO ₃ Na	
			92 93	R₁ Ph Me Me Tol		R₂ Ph Ph Me Tol	
		1 = polystyrene 2 = polystyrene				R 1,4-C ₆ H ₄ (CH ₂) ₄ (CH ₂) ₆ (CH ₂) ₈ 1,3-C ₆ H ₄ 2,3-Nb (C ₅ H ₄) ₂ Fe (C ₅ H ₄) ₂ Fe 1,4-C ₆ H ₄	
	401,402,403		352,367		413		183
	408		408		411		409
	410		374,373		374		413, 414
		Ar = Ph, Tol		Ar = Ph, Tol		R₁ H tBu tBu tBu	R₂ Me tBu tBu tBu
						R₃ iPr Ph Ph iPr	R₄ Ph Ph Ph Ph
P-N Chelates							
	394 E-8		394 E-6,7		399		399
				R = Ph, Cy		Combinations of R ₁ = Me, tBu, R ₂ = Hx, Bz, AE R ₁ , R ₂ = CH ₂ CH ₂ NPhCH ₂ CH ₂ , (CH ₂) ₅ R ₃ = Ph, 2-Py, Mes, 4-CF ₃ C ₆ H ₄ , CpFeC ₅ H ₄ , 2-quin R ₄ = Ph, Cy	
N-O Chelates							
	395		383 E-29 383 E-28 384 E-44 386		381,382		383 E-490
1 CH CH CH N		2 H CO ₂ H benzo H		R = Me, iPr	X = -C(OMe), -CH, N, C(NO ₂)		
	395		383 E-489		383 E-36		
N-N Chelates							
	396		396		383 E-38		383 E-37
	383 E-17		397		383 E-18		383 E-34 385
	383 E-492 383 E-493		383 E-39		419-423, 427		
Ar = 4-MePh Ar = 2-MePh							

Table 8 (Continued)

Ligand	Ref.	Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
Other							
	383 E-496		383 E-498		380		412
	383 E-497		383 E-35 383 E-494		383 E-495		416
	395		395		381,382		
	400		396		396		

Table 9. Nickel Complexes of Salicylaldimine Ligands^a

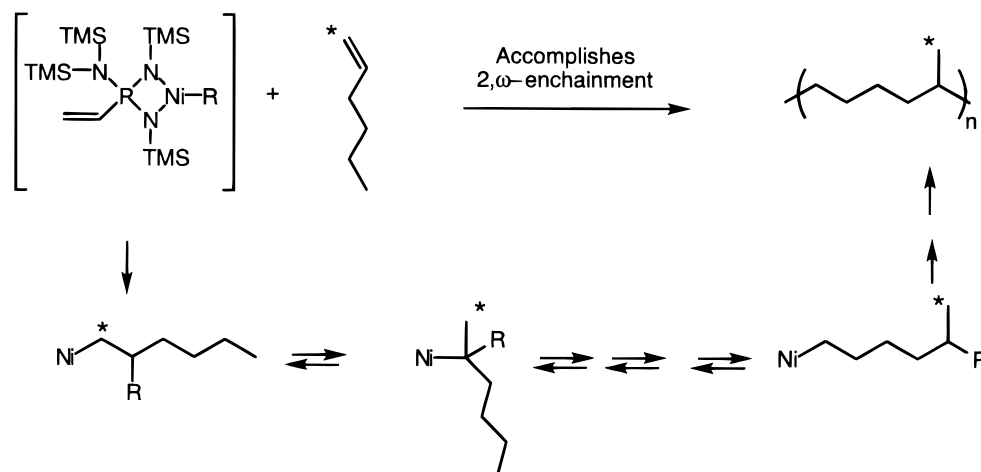
1	2	3	4	5	6	7	8	ref
<i>t</i> -Bu		<i>t</i> -Bu			<i>i</i> -Pr	<i>i</i> -Pr		383 E-20
<i>t</i> -Bu		<i>t</i> -Bu			Me	Me		383 E-21
<i>t</i> -Bu		<i>t</i> -Bu			Br	Br	F	383 E-22
NO ₂		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		383 E-23
NO ₂		NO ₂			<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	383 E-24
NO ₂		NO ₂			Me	Me		383 E-25
NO ₂		NO ₂			Br	Br	Me	383 E-26
Cl		Cl			<i>i</i> -Pr	<i>i</i> -Pr		383 E-31, E-500-2
Cl		Cl			Me	Me		383 E-32
		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		383 E-33
Cl		Cl		Me	<i>i</i> -Pr	<i>i</i> -Pr		383 E-469, E-470
Cl		Cl		Me	Me	Me		383 E-471
		Cl		Me	<i>t</i> -Bu			383 E-472
Br		Br			<i>i</i> -Pr	<i>i</i> -Pr		383 E-473, E-503
Br		Br		Me	<i>i</i> -Pr	<i>i</i> -Pr		383 E-474
Br		Br		Me	Me	Me		383 E-475
Br		Br		Me	<i>t</i> -Bu			383 E-476
<i>t</i> -Bu		<i>t</i> -Bu			<i>t</i> -Bu			383 E-477
NO ₂		NO ₂			<i>t</i> -Bu			383 E-482
NO ₂		NO ₂			Me	Cl		383 E-483
I		I			<i>i</i> -Pr	<i>i</i> -Pr		383 E-485
	OMe		OMe		<i>i</i> -Pr	<i>i</i> -Pr		383 E-486
					<i>i</i> -Pr	<i>i</i> -Pr		384 E-2, 386
<i>t</i> -Bu					<i>i</i> -Pr	<i>i</i> -Pr		384 E-4,5, 386
Ph					<i>i</i> -Pr	<i>i</i> -Pr		384 E-6, 386
9-Phen					<i>i</i> -Pr	<i>i</i> -Pr		384 E-14, 386
9-An					<i>i</i> -Pr	<i>i</i> -Pr		384 E-15, 386
O(Pr ₃ Si)					<i>i</i> -Pr	<i>i</i> -Pr		384 E-19
OSiPh ₂ - <i>t</i> -Bu					<i>i</i> -Pr	<i>i</i> -Pr		384 E-20
		OMe			<i>i</i> -Pr	<i>i</i> -Pr		384 E-26, 386
		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		384 E-27, 386
Cl		Cl			<i>i</i> -Pr	<i>i</i> -Pr		384 E-28
		CF ₃			<i>i</i> -Pr	<i>i</i> -Pr		384 E-31
NO ₂		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		384 E-33
<i>t</i> -Bu		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		384 E-36, 398
Ph		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		384 E-38, 398
9-An					<i>i</i> -Pr	<i>i</i> -Pr	NO ₂	384 E-47, 398
Phen		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		398
9-An		NO ₂			<i>i</i> -Pr	<i>i</i> -Pr		398

^a Unless otherwise noted, substituents 1–8 are hydrogen.

In addition, the amino–imino nickel catalyst **14** and the nitro-substituted salicylaldimine catalyst shown in Figure 5B are active for propylene polymerization

and oligomerization, respectively.³⁸³

The nickel aminobis(imino)phosphorane catalyst polymerizes linear and singly branched α -olefins to

Scheme 8. 2, ω -Enchainment of α -Olefins by Aminobis(imino)phosphorane Nickel Catalyst

give polymers with degrees of polymerization between 10 and 20, with the degree of polymerization falling off with an increase in α -olefin chain length (average $M_n \approx 1000$).^{419–427}

The resulting polymer is composed exclusively of 2, ω -coupling of the olefins with linear α -olefins forming polymers containing only methyl branches.⁴¹⁹ In the case of 1-hexene labeled at the 1-position, the label is found in the methyl branch. The proposed mechanism shown in Scheme 8 involves exclusive 1,2-insertion of the α -olefin to give the sterically crowded primary nickel alkyl, which does not further insert α -olefin.⁴¹⁹ Insertions take place only at primary alkyls with no β -branches so the metal chain walks until reaching the ω -carbon atom of the α -olefin, yielding a primary alkyl with no β -branching. It can then insert another equivalent of α -olefin, thus continuing the chain propagation. The diminishing probability of finding a chain end with increasing molecular weight and the competing chain transfer to monomer accounts for the drop in degree of polymerization as the length of the α -olefin is increased.

4. Summary

Ethylene polymerization and copolymerization using late metal catalysts has blossomed in the last several years. While the commercial impact remains to be seen, the investment of research effort by both academic and industrial laboratories is rapidly increasing. Several clear trends have emerged:

(1) Late metal catalysts that possess high electrophilicity and/or steric hindrance remain the focus for producing high molecular weight polymer.

(2) The detailed mechanistic picture developed around the cationic α -diimine nickel and palladium catalysts provides a mechanistic rationale for the above choice of physical attributes.

(3) The functional-group tolerance of late metal catalysts is evident, particularly in the copolymerization of ethylene and methyl acrylate by the α -diimine palladium catalysts.

(4) Late metal catalysts enable the synthesis of new classes of polymers unavailable through other means of polymerization. These range from stiff, strong

engineering polymers such as polycyclopentene to soft, elastomeric polymers of highly branched polyethylene and chain-straightened poly(α -olefins).

(5) The ability to predictably prepare linear low-density polyethylenes from ethylene alone represents an opportunity to design ethylene homopolymers for target applications.

5. Glossary

acac	acetylacetonate
AE	aminoethyl
An	9-anthryl
Ar'	3,5-bis(trifluoromethyl)phenyl
BAF	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
Bu	butyl
Bz	benzyl
Camph	backbone based upon <i>d</i> -camphorquinone
Cn	1,4,7-triazacyclononane
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cy	cyclohexyl
DAB	1,4-diazabutadiene or α -diimine
DIPP	2,6-diisopropylphenyl
dme	1,2-dimethoxyethane
E	ethylene
Et	ethyl
FOA	fluorinated octyl acrylate
GPC	gel permeation chromatography
Hx	hexyl
HDPE	high-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
Lu	2,6-lutidine
MA	methyl acrylate
MAO	methylaluminoxane
Me	methyl
Mes	mesityl
M_n	number-average molecular weight
MTBE	methyl- <i>tert</i> -butyl ether
M_w	weight-average molecular weight
Nb	norbornyl
Np	naphthyl
PBI	2,6-pyridylbis(imine)
PD or P/I	polydispersity, M_w/M_n
PE	polyethylene
Ph	phenyl
Phen	phenanthroline

Pr	propyl
py	pyridyl
quin	quinoline
RI	refractive index
T_g	glass transition temperature
T_m	melting temperature
To	Tolyl
tmeda	<i>N,N,N,N</i> -tetramethylethylenediamine
TMS	trimethylsilyl
TO	turnovers, the number of moles of monomer polymerized per mole of metal in the catalyst

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