Chapter 1

Late Metal Catalysts for the Polymerization of Ethylene and the Copolymerization of Ethylene with Polar Olefins
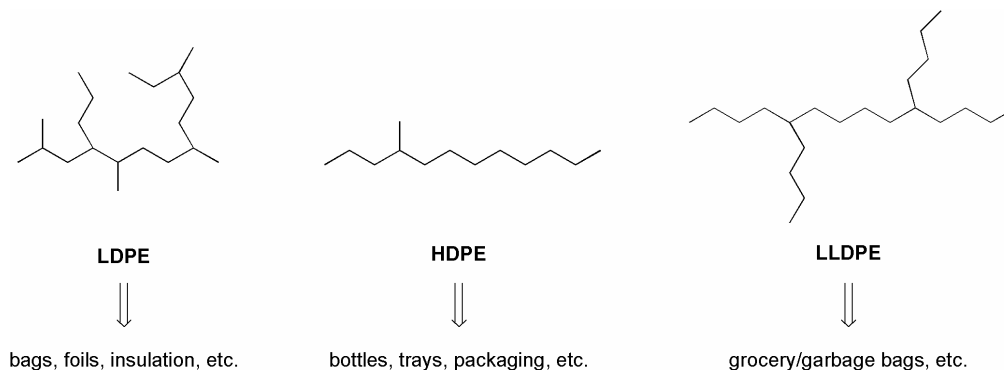
1.1 Abstract

Late metal catalysts for olefin polymerization represent an important field of organometallic research. In this chapter, a brief review of the history of this subject is presented – with particular emphasis on the development of neutral Ni(II) catalysts.

1.2 Introduction

The polyolefin industry represents one of the largest components of the modern industrial chemical market, with over 160 billion tons produced every year. The leading polyolefin is polyethylene, representing 60% of the total output.[1] Polyethylene, along with polypropylene, the second highest volume product, find extensive use in modern life in the bags, bottles, pipes, tubing, and other plastic tools and toys that have become indispensable to modern life.

Historically, polyolefins have been produced using either high-pressure radical-mediated processes or early transition metal-based catalysts.[2] Depending on the conditions used to create the polyolefins, the structural properties can vary a great deal (Figure 1.1). For example, heating ethylene to high temperature under high pressure in the presence of radical initiators produces a highly-branched, polydisperse polymer known as Low Density Polyethylene (LDPE). LDPE finds use in garment bags, foils and wraps, and wiring insulation.

Figure 1.1. The three main types of polyethylene.

LDPE   HDPE   LLDPE

bags, foils, insulation, etc.   bottles, trays, packaging, etc.   grocery/garbage bags, etc.

Polyethylene is also produced with heterogeneous early metal (Ti and Zr) catalysts, in a manner essentially unchanged from the initial reports from Ziegler and

Natta in the late 1950s.[3] The high molecular weight, linear polyethylene formed with these catalysts is known as High Density Polyethylene (HDPE). HDPE is used in applications requiring a tougher plastic than LDPE, such as bottles, trays and food packaging. Intermediate between LDPE and HDPE is Linear Low Density Polyethylene (LLDPE). This is made by the addition of an α-olefin, such as 1-hexene, to the linear polyethylene chain, which disrupts the crystallinity of the polymer to provide a less rigid product. For example, LLDPE finds use in grocery and garbage bags.

The addition of olefins bearing polar functionality (rather than simple α-olefins, *e.g.*, 1-hexene) can also drastically alter the properties of polyolefin plastics. The inclusion of 5-20% of a polar comonomer such as methyl acrylate, acrylic acid or acrylonitrile into a polyethylene base can significantly improve polymer properties such as adhesiveness, wettability and hardness.[4] As a result, these polymers find use in specialty applications, such as frozen food and medical packaging, disposable gloves, coatings for metal and glass, sporting equipment and tubing. Currently, these polymers can only be made with high-temperature, high-pressure radical processes that result in highly branched and amorphous structures.[5] Given the potentially great commercial value of these functionalized polymers, it would be very desirable to produce a linear, crystalline polymer that would combine the durability of HDPE with specialized properties of functionalized polymers (Scheme 1.1).

Scheme 1.1. The desired copolymerization of ethylene with functionalized olefins.

X = CO_2Me, CN, etc.
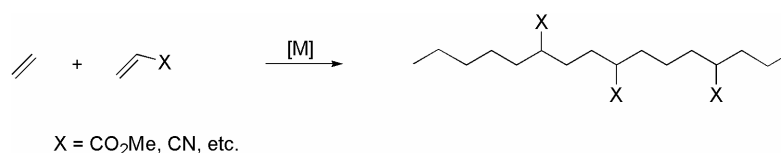
Unfortunately, treatment of the oxophilic early metals typically used in Ziegler-Natta polymerizations with oxygenated or polar monomers tends to inhibit the catalysts. Accordingly, there has been much interest in recent years in late transition metal-based catalysts. The tendency of these metals to make well-defined homogenous complexes suggests that they may offer greater control over polymer properties (such as molecular weight, polydispersity, and branching) than ill-defined early metal systems can provide. In addition, they possess an advantage over their less functional group-tolerant early metal counterparts in the possible copolymerization of ethylene with polar olefins.
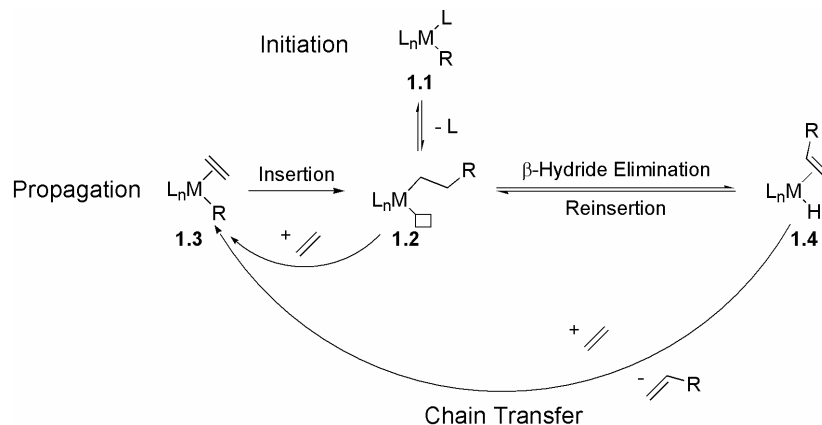
1.3 The Mechanism of Olefin Polymerization

Before beginning a discussion about developments in late transition metal-catalyzed olefin polymerization, a word about the mechanism of olefin polymerization is required. A simplified mechanism representative of most systems to be considered can be proposed. Any deviations from this general mechanism will be mentioned when appropriate.

The catalytic cycle typically begins with dissociation of a neutral ligand from the metal-alkyl precatalyst (**1.1**, Scheme 1.2). This leads to a metal complex with an empty site which is capable of binding olefin (**1.2**). Olefin association leads to olefin/alkyl complex (**1.3**). ^{1}H NMR experiments suggest that this complex is often the resting state.[6] Olefin insertion into the metal-alkyl bond, the key step of polymer propagation, leads back to an unsaturated metal-alkyl complex (**1.2**), which can then bind ethylene. In this way, the polymer chain continues growing until chain transfer occurs. This typically proceeds via a reversible β-hydride elimination to give olefin/hydride complex **1.4**. This

complex may undergo hydride reinsertion to continue polymerization along the same polymer chain, or the olefin-terminated polymer chain may be displaced by another olefin to release the polymer chain, and begin the polymerization process anew.

**Scheme 1.2.** General mechanism for olefin polymerization.

Examination of this mechanism reveals some important features of transition metal-catalyzed olefin addition polymerization. The observed rate of olefin polymerization depends partially on initiation, which is the rate at which the neutral ligand ("L") dissociates. The rate of polymerization also depends upon the relative rates of rebinding the neutral ligand and olefin binding. A catalyst that demonstrates a higher affinity for binding ethylene over the neutral ligand will feature a higher rate of polymerization. Also, it should be noted that the molecular weight of the resulting polymer depends upon the rate of chain transfer. Any factor that can slow either β-hydride elimination from alkyl complex **1.2**, or olefin exchange with olefin/hydride complex **1.4** serves to increase polymer molecular weight.

1.4 SHOP Catalysts

The first important development in late-metal catalysts for ethylene polymerization was the discovery by Keim and coworkers in the late 1970s that neutral Ni complexes of certain [P,O]-chelating ligands are excellent catalysts for the oligomerization of ethylene to short-chain α-olefins (Figure 1.2).[7] These catalysts comprise a component of the Shell Higher Olefin Process (SHOP), a multi-stage industrial process for the production of C_{11-15} terminal alcohols for various industrial uses, such as detergents.[8] One of the chief benefits of using Ni, a late transition metal, is demonstrated by the fact that the ethylene oligomerization by catalyst **1.5** can be performed in emulsion in 1,4-butanediol, allowing for simple isolation of the product.[9] It would not be possible to use an early metal catalyst in such a protic solvent.

Figure 1.2. Some SHOP catalysts for ethylene oligomerization.
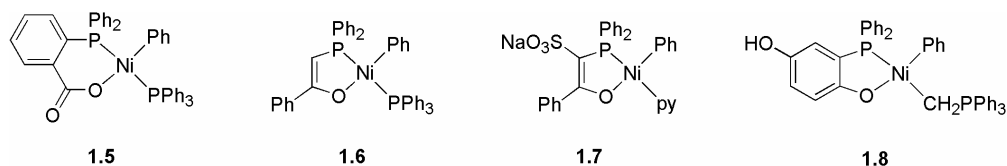
The catalysts depicted in Figure 1.2 are typically used in the production of oligomers of ethylene. However, under appropriate conditions, these catalysts are also capable of forming high-molecular weight polyethylene. For example, catalyst **1.6** provides oligomers at 50 °C and 50 atm of ethylene in toluene, but forms high polymer under the same conditions in hexane.[10] It was further demonstrated that polymerizations could be performed at much lower pressures (3–5 atm) if a phosphine scavenger, *e.g.*, Rh(acac)(C₂H₄)₂, Ni(cod)₂ or trimethylamine-*N*-oxide, is used. This strongly suggests that there is a phosphine-assisted step in the rapid chain transfer that occurs during

ethylene oligomerization. This was further confirmed when the phosphine ligand of catalyst **1.6** was replaced with much more weakly-bound ligands such as pyridine (**1.7**) and phosphorus ylides (**1.8**).[11] The origin of this effect is not entirely clear, but it is likely due to the fact that phosphine inhibits the binding of ethylene, slowing ethylene insertion, and allows chain transfer to occur.

Despite being both tolerant to the presence of polar functionality and active for ethylene polymerization, [P,O]-chelated Ni complexes are incapable of the copolymerization of ethylene with vinyl-functionalized olefins such as methyl methacrylate or vinyl acetate.[9] This is attributed to coordination of the Lewis basic oxygen to the metal center. However, olefins in which the functionality is removed from the olefin by two or more methylene units can be incorporated in a polyethylene chain.[9] The demonstration that [P,O]-chelating Ni complexes are capable not only of ethylene polymerization, but also the copolymerization of ethylene with some functionalized olefins was a major breakthrough.
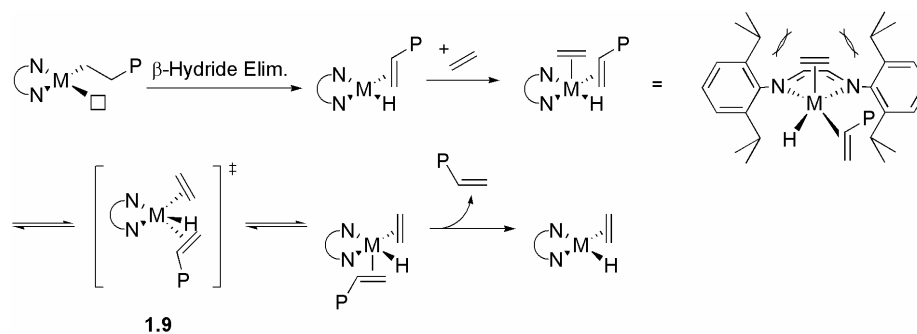
1.5 Cationic Group 10 Diimine Catalysts

In recent years, one of the most dramatic discoveries in the field of late metal catalysis has been that of Brookhart and coworkers, of cationic diimine complexes of Ni and Pd that are highly active catalysts for ethylene polymerization (1.1×10^4 g PE (mmol cat.)$^{-1}$ (hr)$^{-1}$) (Scheme 1.3).[12] It was observed that the molecular weight of the resultant polymer had a direct correlation with the size of the aryl substituents on the imine ligand. This was attributed to the effect of the steric encumbrance of the aryl groups on the rate of chain transfer to monomer (Scheme 1.4). The presence of substituents situated above the square planar Ni or Pd coordination center prevents chain transfer to monomer by

slowing association of ethylene. These bulky groups may also make displacement difficult by disfavoring the transition state (**1.9**) required to replace the polymer chain with ethylene.

Scheme 1.3. Group 10 diimine catalysts for olefin polymerization.

R = H, Me
Ar = Mes, 2,6-diisopropylphenyl, 3,5-bis(triflouromethyl)phenyl
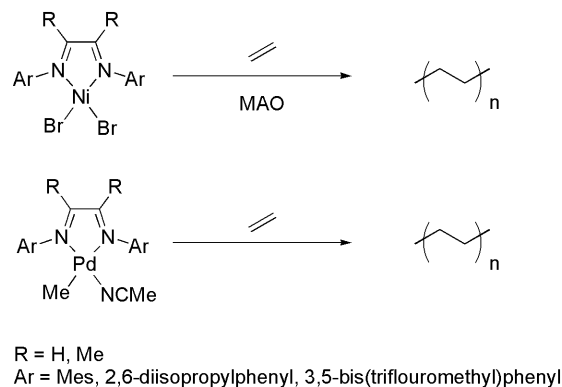
**Scheme 1.4.** Large ligands decrease the rate of chain transfer.

Group 10 diimine catalysts have been the subject of computational studies which suggest that β-hydride elimination from the coordinatively unsaturated metal complex does not readily occur.[13] Instead, there is direct concerted β-hydrogen transfer from polymer to monomer via a transition state similar to **1.9**. Whether or not this is the case,

in this and following mechanisms, β-hydride elimination will be depicted as a discrete step for the sake of clarity, but the possibility of a concerted mechanism should be noted.

The polymers produced by group 10 diimine catalysts generally show a fairly high degree of branching, though this can vary depending on the conditions and the metal used. The degree of branching is directly related to the rate of β-hydride elimination. This is because branching is caused by multiple β-hydride elimination and reinsertion events, with intervening olefin rotation (Scheme 1.5).

**Scheme 1.5.** "Chain running" leads to branched polymer.
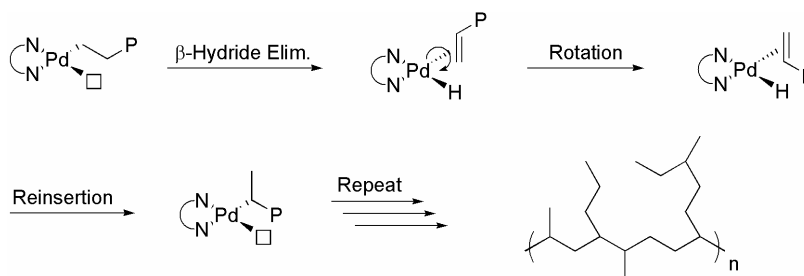
There is a significant difference in the degree of branching obtained by Ni and Pd complexes. When Pd catalysts are used, extensive branching is nearly always observed (~100 branches per 1000 carbon atoms), with long branches and even branches on branches.[14] This branching behavior is indicative of frequent β-hydride elimination by Pd diimine catalysts. Nickel catalysts allow for more control over branching (from 1–100 branches per 1000 carbon atoms) through variation of polymerization conditions. Methyl branches are observed almost exclusively, suggesting a lower rate of β-hydride elimination for Ni than for Pd. The degree of branching in a Ni-catalyzed polymerization varies directly with polymerization pressure and inversely with ethylene pressure.[15] The higher degree of branching observed with increasing temperature is attributed to

increased β-hydride elimination. The lower degree of branching observed with increasing ethylene pressure is attributed to an increased rate of ethylene binding relative to β-hydride elimination.

Subsequent to the discovery of the group 10 complexes, a related class of pyridine diimine compounds of Co and Fe (Scheme 1.6) were reported to be capable of polymerizing ethylene to a highly linear product at rates even higher than those observed for Ziegler-Natta systems (3.3×10^5 g polymer (mmol. cat.)$^{-1}$ (hr)$^{-1}$).[16]

Scheme 1.6. Fe and Co catalysts for the addition polymerization of olefins.

M = Fe, Co
R = H, Me
Ar = Mes, 2,6-diisopropylphenyl
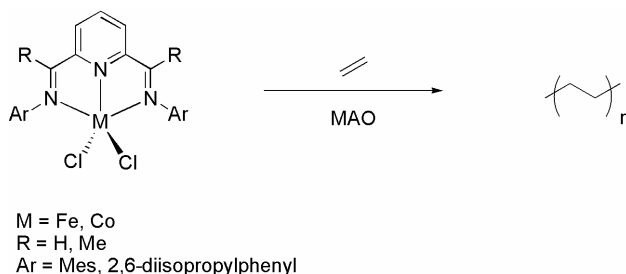
Though the demonstration of ethylene homopolymerization by the late metal catalysts developed by Brookhart and others was an extremely important development, it was overshadowed by the observation that the Pd catalysts are also capable of incorporating up to 20% of a vinyl functionalized comonomer, *e.g.,* methyl acrylate (MA).[17] This was the first time that these monomers could be directly incorporated into polyethylene via a metal-mediated process. However, in meeting the ultimate goal of incorporation of functional groups into the backbone of a linear polyethylene chain, the diimine catalysts fell short. Like ethylene homopolymers produced by the Pd catalysts, the ethylene/MA copolymers are highly branched. Furthermore, it was found that the

ester functionality is found only at chain ends, never in the polymer backbone (Scheme 1.7).

Scheme 1.7. The ethylene/MA copolymer produced by Brookhart's diimine catalysts.
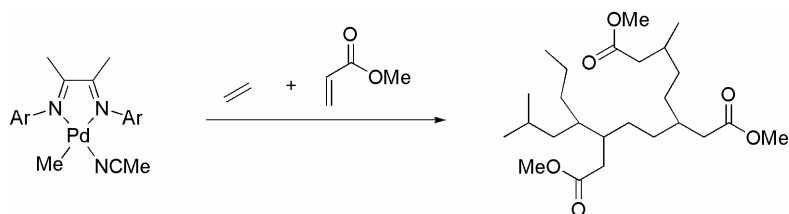
Extensive mechanistic studies on these catalysts have revealed the cause of this behavior (Scheme 1.8).[18] Methyl acrylate binds to the free site of a molecule of catalyst (**1.10**). 2,1-Insertion of MA into the Pd–C bond leads to intermediate four-member chelate **1.11**. Instead of inserting ethylene to continue polymerization, Pd-enolate **1.11** undergoes β-hydride elimination to give olefin/hydride complex **1.12**. Rotation of the olefin, followed by 1,2-insertion of the hydride, leads to five-member chelate complex **1.13**. This process repeats, giving six-member chelate complex **1.14**, which is a stable, isolable compound. Complex **1.14** can perform further polymerization, but because of the process depicted in Scheme 1.8, the polymer chain always grows away from the ester, leaving the functionality at chain ends. Nonetheless, Brookhart's discovery was revolutionary, and suggested that late metal catalysts may be the solution to the problem of functionalized polymerization.

Scheme 1.8. The mechanism of ethylene/MA copolymerization by Pd diimine catalysts.
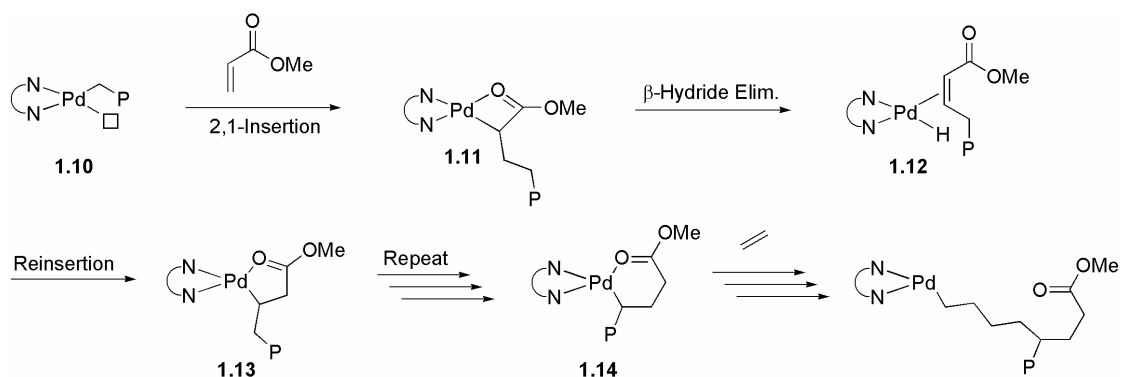

1.6 Neutral Ni Salicylaldimine Catalysts

Contemporarily with Brookhart's development of cationic Ni and Pd catalysts for olefin polymerization, our group began work on novel neutral Ni catalysts for the same. This work derived some inspiration from the example of the SHOP catalysts. However, after Brookhart's report of ethylene/MA copolymerization demonstrated that such a process was indeed possible, it gave new importance to the development of neutral catalysts. It was hoped that novel neutral catalysts could have the same tolerance of polar olefins, with the additional benefit of being inherently less electron-deficient than cationic catalysts, and thus less likely to form deactivating chelate complexes such as **1.11** with electron-rich olefins such as MA.

Combining the lessons learned from both the SHOP catalysts and Brookhart's diimine catalysts, Ni complexes of bulky salicylaldimine (sal) ligands were found to be excellent catalysts for the homopolymerization of ethylene (**1.15**, Figure 1.3).[19] These catalysts were highly active with and without added cocatalysts, *e.g.*, Rh(acac)(C$_2$H$_4$)$_2$, Ni(cod)$_2$ B(C$_6$F$_5$)$_3$ (up to 1.2×10^6 g polymer (mol. cat.)$^{-1}$ (hr)$^{-1}$). Just as with Ni and Pd diimine catalysts, there is a strong correlation between steric bulk and the molecular

weight of the resulting polymer. Anthracenyl-substituted catalyst **1.16** provided the highest molecular weight (3.47 x 10^6 amu). An even greater increase in polymerization rate was obtained with replacement of the phosphine with a weakly binding ligand such as pyridine or acetonitrile (**1.17**). These catalysts show extremely high activity (up to 4.4x10^6 g polymer (mol. cat.)$^{-1}$ (hr)$^{-1}$).[19]

Figure 1.3. Ni(sal) catalysts for the polymerization of olefins.


| 1.15 | 1.16 | 1.17 |
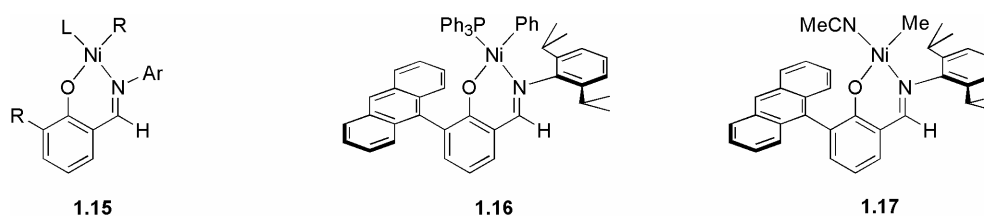
These Ni(sal) catalysts display remarkable tolerance of polar functional groups, *e.g.,* esters, alcohols and water, even polymerizing ethylene in aqueous emulsion.[20] Furthermore, they also incorporate a small percentage of functionalized norbornenes and α-olefins with polar functionality distant from the C–C double bond (Scheme 1.9). However, to date, they have been unable to incorporate any amount of vinyl functionalized olefin such as MA. In fact, attempts to form polymer in the presence of these olefins results in catalyst deactivation.

Scheme 1.9. Neutral Ni catalysts incorporate functionalized olefins into polyethylene.
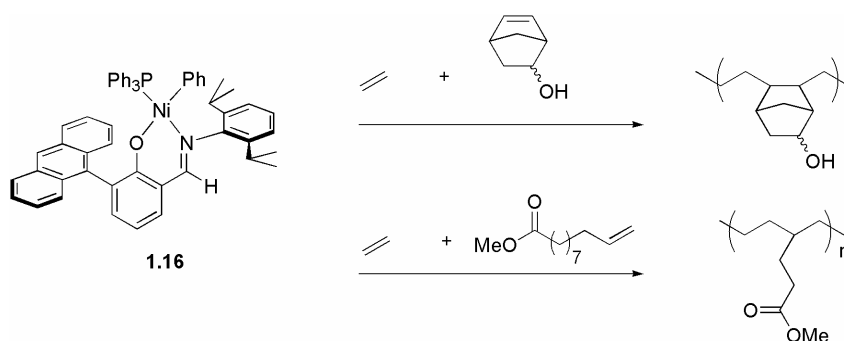
Although both Ni and Pd form catalytically active complexes with diimine ligands, we have found that of the two metals, only sal complexes of Ni are active catalysts for olefin polymerization.[19c] This is unfortunate because, in the case of diimine complexes, only Pd complexes are active for ethylene/polar monomer copolymerization. However, attempts to homopolymerize ethylene with Pd(sal) complexes proved unsuccessful. From these reactions, free phenolic sal compounds are isolated, leading to the proposed mechanism of deactivation presented in Scheme 1.10.[19c] In this mechanism, ethylene polymerization proceeds in a normal fashion, until irreversible reductive elimination of the phenol occurs from olefin/hydride complex **1.18**. This difficulty was determined to be insurmountable, and thus no further research was devoted to Pd(sal) complexes.

Scheme 1.10. Proposed mechanism of deactivation of Pd(sal) complexes during attempted ethylene homopolymerization.
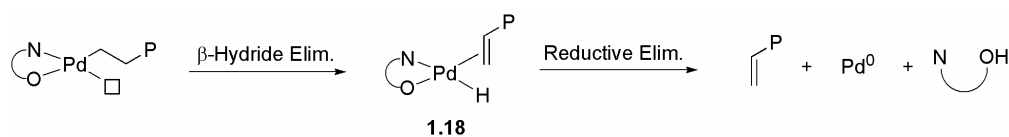
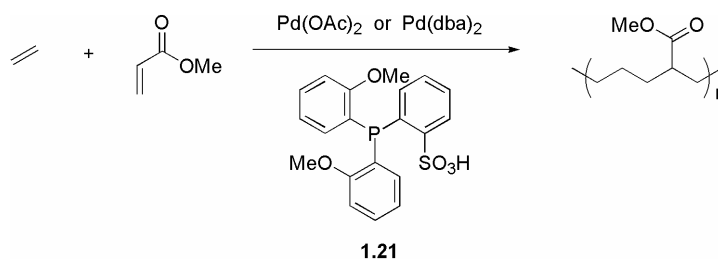### 1.7 Further Developments

Since our initial report of neutral Ni catalysts for ethylene polymerization, a number of similar catalysts have been synthesized, with varying degrees of polymerization and oligomerization activity.[21] Of particular interest are a series of Ni catalysts featuring anilinotropone (**1.19**) and anilinoperinaphthenone (**1.20**) ligand frameworks, presented by Brookhart and coworkers.[22] These catalysts (Figure 1.4) are similar to our Ni(sal) catalysts, and display similar catalytic activities.

Figure 1.4. Some neutral Ni catalysts reported by Brookhart and coworkers.

R = Phenyl, naphthyl

1.19   **1.20**
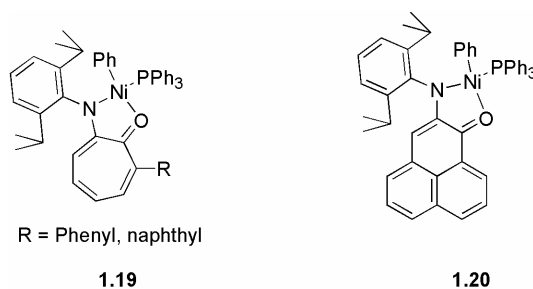
There have been a number of reports of copolymerization of ethylene with acrylates – especially methyl methacrylate (MMA) – by late metal-mediated processes.[23] However, upon review, it seems that some of these reports involve radical polymerization. There has also been a report of Cu-catalyzed addition copolymerization of ethylene with MMA,[24] though this too seems to be a radical reaction, especially considering the tendency of Cu to catalyze radical processes.[25] Beyond transition metal catalysis, Sen and coworkers have demonstrated controlled and living acrylate/alkene polymerizations via low temperature ATRP processes.[26]

Most promising is a report by Drent and coworkers of the copolymerization of ethylene and methyl acrylate by a Pd complex of a phosphine/sulfonate ligand (**1.21**, Scheme 1.11), with up to 17% acrylate incorporation.[27] The nature of this ligand seems to suggest that it plays an important role in the special reactivity of this catalyst, but whether it is the *ortho*-methoxy groups on the phosphine moiety, the sulfonate moiety, or some combination of the two, is unclear. Surprisingly, given the potential importance of this discovery, it was released with little fanfare and subsequent reports have not appeared. Nonetheless, independent studies have confirmed that the copolymerization is reproducible,[28] and at present, this catalyst seems to be the most successful so far.

Scheme 1.11. Drent's Pd catalyst for ethylene/MA copolymerization.

1.21

1.8 Conclusion

The development of late metal catalysts for the polymerization of ethylene and other olefins represented an important advance in transition metal catalysis. Furthermore, the demonstration by Brookhart and coworkers of a Pd diimine catalyst capable of copolymerizing ethylene with polar olefins was significant, even if the polymers formed were not the linear products desired. Likewise, the neutral Ni(sal) complexes presented by our lab are excellent catalysts for ethylene polymerization. However, their inability to perform the same copolymerization as the Pd diimine complexes was problematic. It is with the investigation of the cause of their deactivation in the presence of polar olefins that this story begins.

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