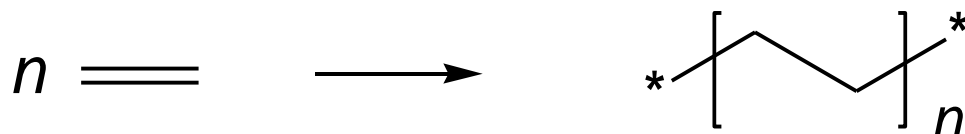


Polymerization & Metathesis

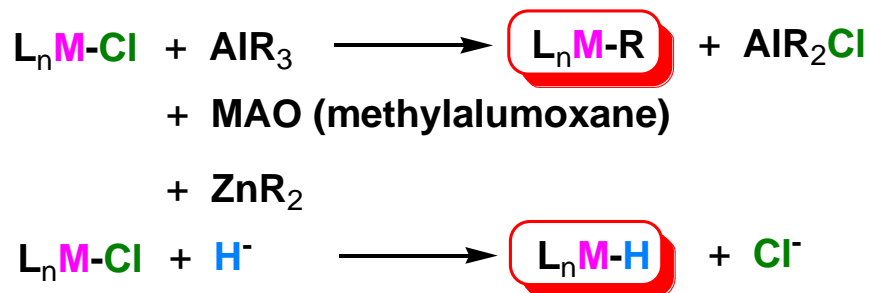
Polymerization is the reaction of an unsaturated organic reactant, typically a C=C, with itself over and over again to produce a polymer chain:



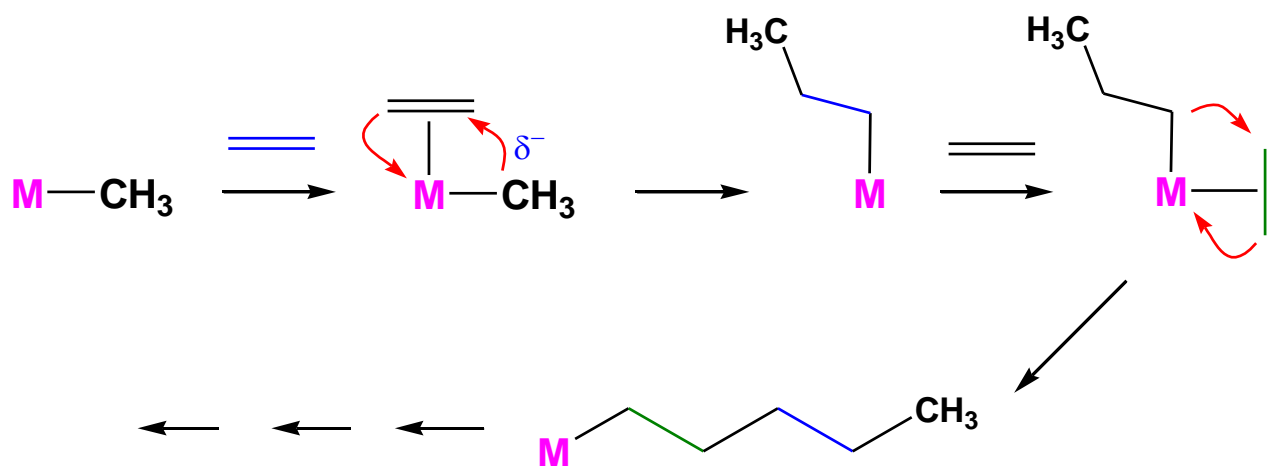
When only a few alkenes couple together to make a short chain, we refer to that as **oligomerization** (oligomers are very short polymers).

There are typically three parts to most polymerizations:

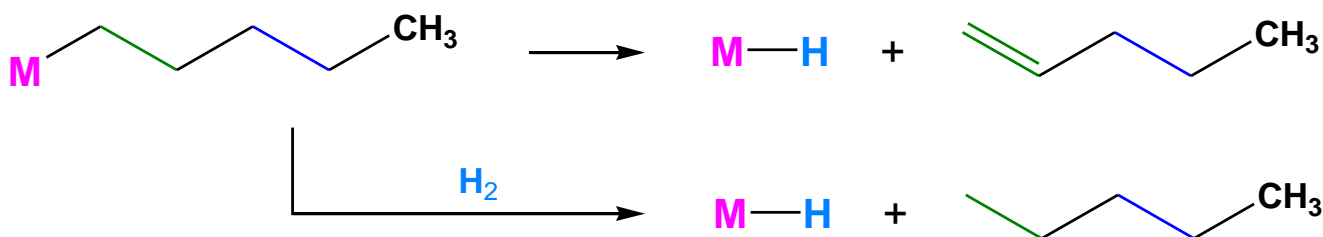
Initiation: generating the active catalyst from a less active catalyst precursor



Propagation: the polymer chain growth portion of the reaction that occurs over and over again



Termination: a reaction step that stops the polymer chain growth



In a good polymerization catalyst the initiation step generates as much active catalyst as possible and the propagation step occurs as often as possible, while the termination step is unlikely to happen. For early transition metal catalysts the β -hydride elimination step that can cause termination is not that favorable.

A **Living Catalyst** is typically a polymerization catalyst in which all the transition metal complexes present are the same and already in an active catalytic state (no initiation step). When the substrate is added all the catalyst molecules start the polymer chain growing steps at the same time and same rate. This means that at any point the polymer chains growing off each and every catalyst are all essentially the same length. This leads to polymers that have a M_w/M_n value very close to 1.0.

What is M_w/M_n ? The average molecular weight of a polymer can be defined by M_n and M_w . M_n is the simple average of total mass of the chains divided by the number of chains. The weight average molecular weight M_w is the summation of the *square* of the molecular weights divided by the summation of the molecular weights of all the molecules present. In M_w more "weight" is provided to the higher molecular weight polymers, while M_n treats all of them the same. The basis for M_w is that the larger molecules contribute more to the properties of the polymer so they should have more importance. M_w is always greater than M_n and the narrower the distribution, the closer M_n and M_w are. The ratio of M_w to M_n is a measure of the distribution of different length polymer chains. This ratio is referred to as the **dispersivity**. As the distribution narrows, the dispersivity approaches a minimum value of 1.0. Such a polymer referred to as **mono disperse**. Alternately as M_w/M_n for a polymer increases (10 or 20) it is referred to as **poly-disperse**. A standard (narrow) Schultz-Flory statistical M_w/M_n polymer distribution is equal to 2.0.

Some History: Ziegler-Natta Polymerization Catalysis

The German chemist Karl Ziegler (1898-1973) discovered in 1953 that when $\text{TiCl}_3(\text{s})$ and AlEt_3 are combined together they produced an extremely active *heterogeneous* catalyst for the polymerization of ethylene at atmospheric pressure. Giulio Natta (1903-1979), an Italian chemist, extended the method to other olefins like propylene and developed variations of the Ziegler catalyst based on his findings on the mechanism of the polymerization reaction. The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium, and zirconium, typically activated by alkyl aluminum compounds. Ziegler and Natta received the Nobel Prize in Chemistry for their work in 1963.

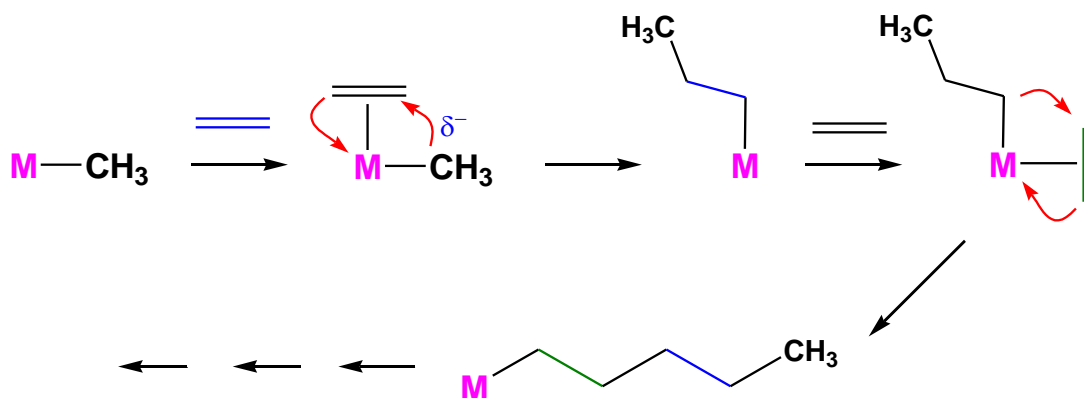
The following is a short excerpt taken from Luigi Cerruti (International Journal for Philosophy of Chemistry, 1999, vol 5, 3-41) on the initial work on the oligomerization and polymerization of ethylene:

In June 1953, they [Ziegler's research group] investigated chromium, whose compounds gave some butene but also a small amount of material with high molecular weight. This result was encouraging. At the end of October, Breil, another of Ziegler's collaborators, came to zirconium: a rapid and complete polymerization occurred. Moreover, the infrared spectra demonstrated that the polymer was *linear*. When the turn of titanium came up, the result was again striking. The reaction was so fast that the vessel became hot, and the product was partially decomposed. Thus, the problem was passed to Heinz Martin, who was looking for the mildest possible conditions of polymerization. Since it was apparent that the system Ti/Al-alkyl was very active, Martin tried the simplest possible conditions: no higher pressure at all and no external heating (Ziegler *et al.* 1955b, 543-544). The result of the trial was that Martin burst in Ziegler's office waving a glass flask and crying: "*Es geht in Glass!*"

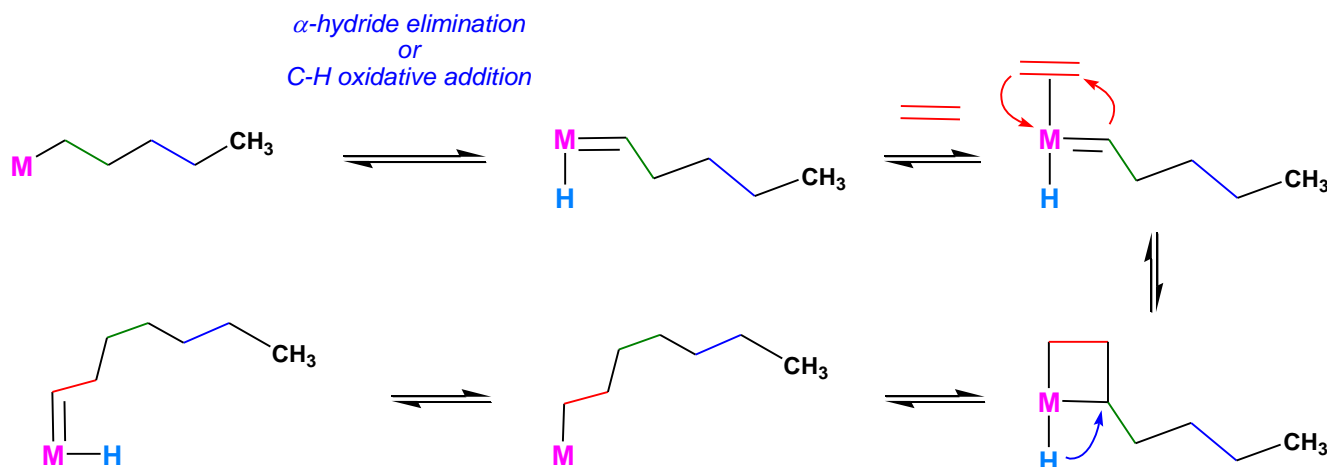
The third generation of Ziegler-Natta catalysts were developed in 1960 with Shell's patent for a heterogeneous catalyst for propylene polymerization based on TiCl_4 supported on MgCl_2 . Montecatini and Mitsui independently patented catalysts prepared from TiCl_4 , MgCl_2 and an electron donor, and activated by a mixture of trialkyl-Al with another electron donor in 1968. Industrial plants based on these catalysts came online in the 1980's. These third generation catalysts brought a 50-fold increase in activity, so much so that the *removal* of the catalyst from the final product was no longer necessary.

Cossee (migratory insertion) vs. Green-Rooney (alkylidene metallacycle) Propagation Mechanisms

The commonly accepted mechanism for polymer chain growth on a transition metal catalyst is the very simple migratory insertion mechanism initially proposed by Piet Cossee (Royal Shell labs) in 1964.

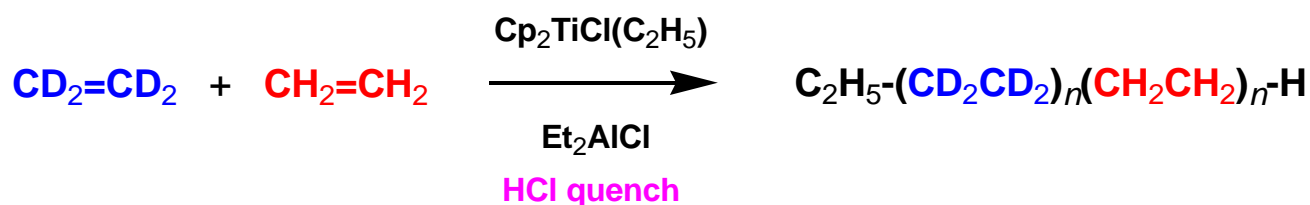


However in 1978 Malcolm Green and John Rooney proposed a rather different mechanism based on the recently reported Schrock alkylidenes:



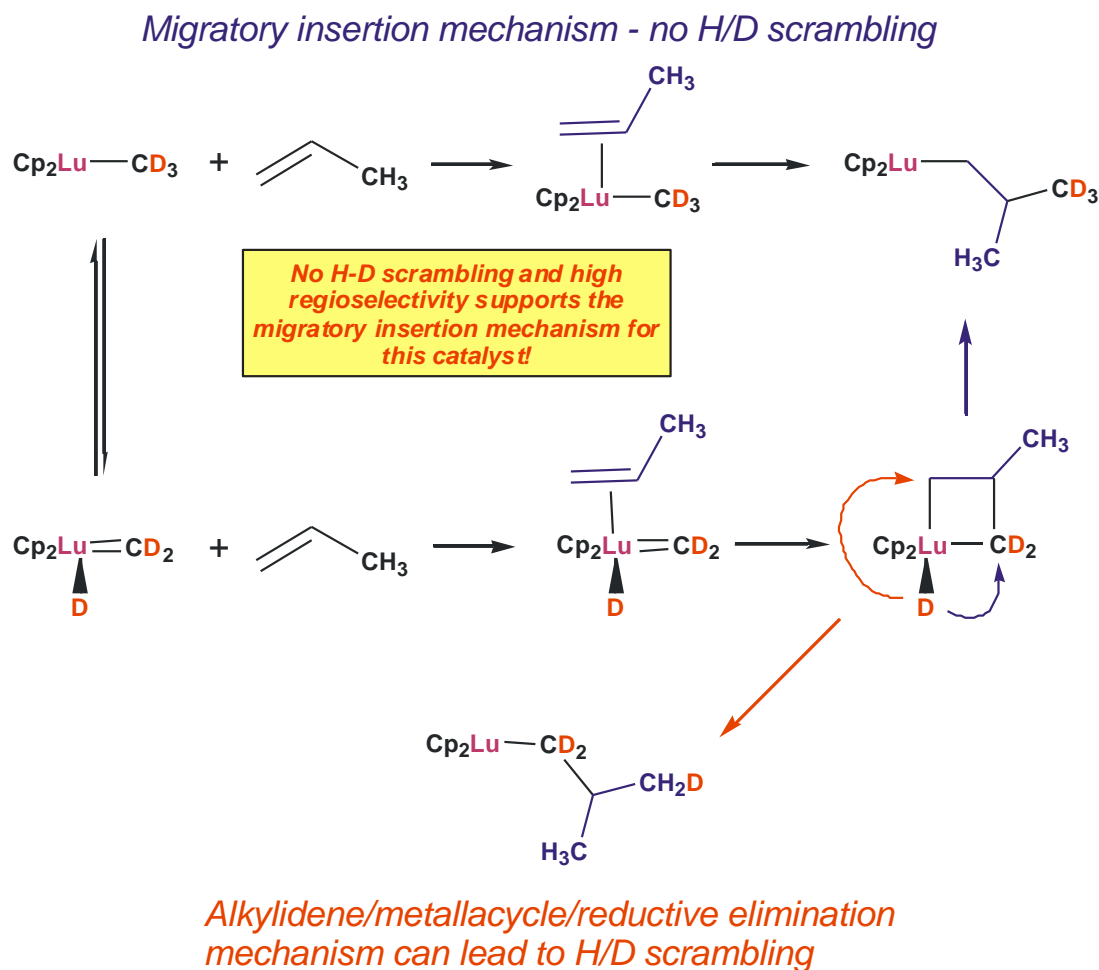
At the time this mechanism was very “sexy” since alkylidenes were relatively new and quite the “rage”. A number of organometallic researchers performed some rather elegant mechanistic studies to figure out which mechanism was operating in a variety of polymerization catalysts.

One of the simplest studies involved the use of deuterated ethylene mixed with regular ethylene:



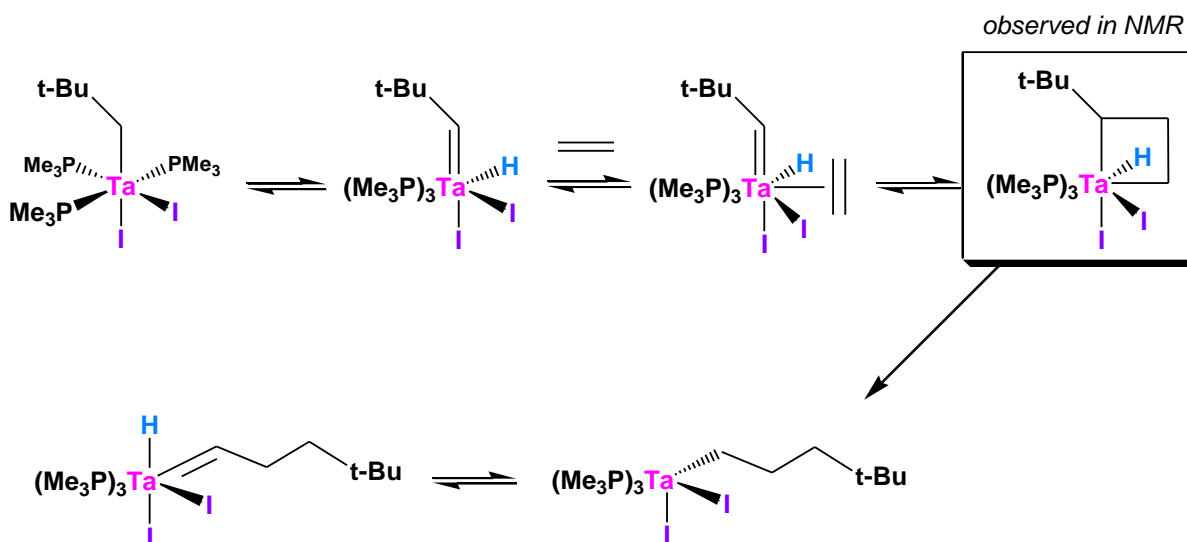
If the migratory insertion mechanism was working, one should *NOT* get any scrambling of the deuteriums and hydrogens in the polyethylene chain (easily confirmed by ^1H and ^2H NMR). However, if the polymerization was working by the Green-Rooney metallacycle mechanism, the α -hydride elimination and subsequent H-alkyl reductive elimination steps would lead to some scrambling of the H and D atoms. But no H/D scrambling was observed, leading to conclusion that the polymerization was NOT working via the alkylidene-metallacycle mechanism, supporting the simpler migratory insertion pathway.

Patricia Watson at Dupont performed another elegant study in 1984 using deuterium labeling:

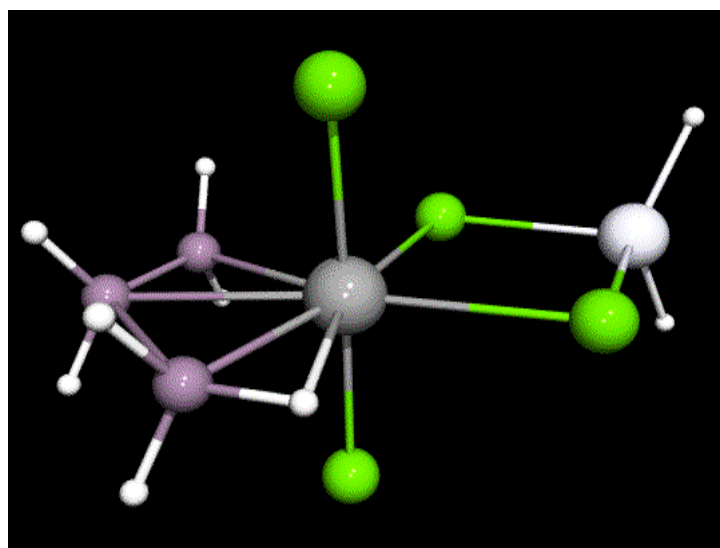


The bottom line is that most mechanistic studies have clearly pointed to the **migratory insertion** mechanism, certainly for the highly active Group IV metals (Ti & Zr), for the lanthanides and actinides, and the new late transition metal systems discovered by Brookhart and Gibson.

One proven exception is Schrock's Ta alkylidene living catalyst that is believed to work via the metallacycle mechanism:



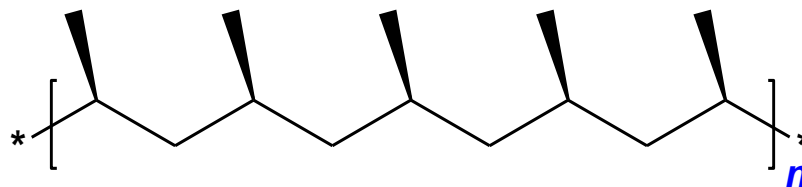
An interesting aspect of the migratory insertion reaction is that the most active polymerization catalysts typically need to have an extra empty orbital after the coordination of the alkene to the M-alkyl unit. Bercaw has proposed that this is because the alkyl group needs to form an agostic C-H bond interaction with the empty orbital on the metal to tilt the localized sp³ alkyl orbital away from the metal and more towards the alkene ligand to promote the migratory insertion. A transition-state structure from a quantum mechanical calculation showing this interaction is shown above.



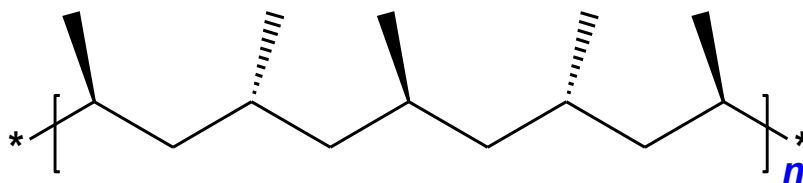
Polypropylene & Stereochemistry

The polymerization of propylene is slower and more complicated than ethylene due to increasing steric factors and the generation of stereochemistry on the polymer chain:

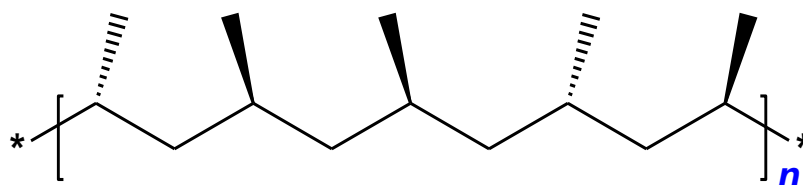
isotactic



syndiotactic

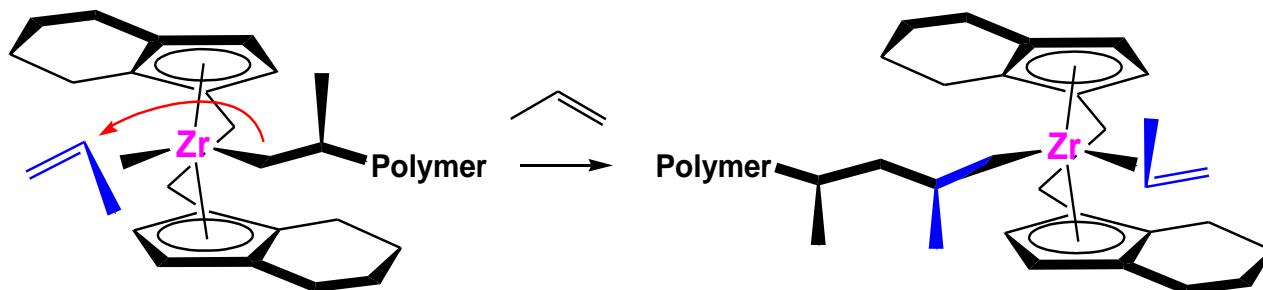


atactic (random)

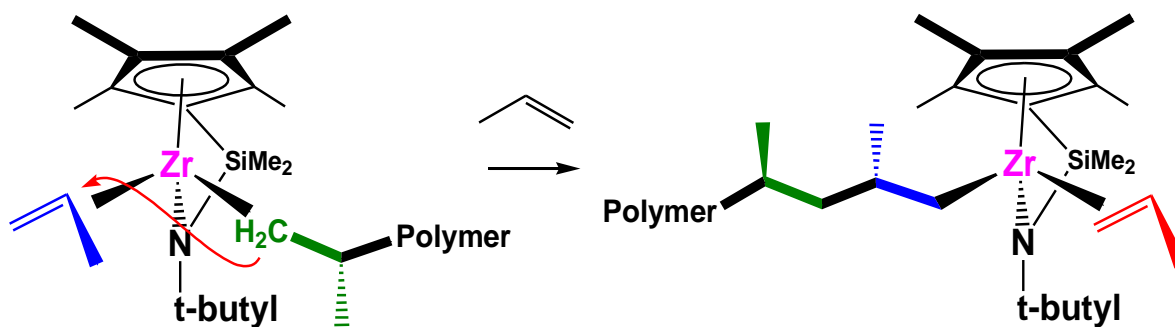


The steric environment around the metal center has a DRAMATIC impact on what kind of stereochemistry one obtains.

C_2 symmetry (chiral) - Isotactic polymer

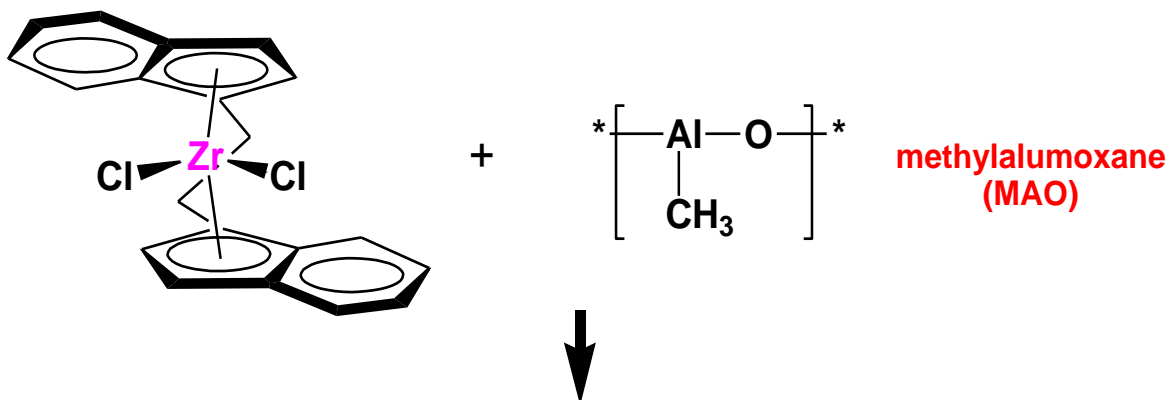


Bulky-Small Catalyst environment - Syndiotactic polymer



A catalyst with small ligands that offer little steric directing effect, like Cp_2TiCl_2 , will generate **atactic** polypropylene.

In 1985 Walter Kaminsky discovered that the combination of methylalumoxane and the Zr catalyst shown below generated a highly active catalyst for isotactic polypropylene.



Almost as active as Ziegler-Natta hetero catalyst

> 95% isotactic polypropylene

High MW and narrow polymer MW distribution
(semi-living catalyst)

meso isomer gives atactic polypropylene

Some History: Kaminsky, Bercaw & Metallocene Polymerization

The fourth generation of polymerization catalysts, based on metallocene compounds, is now evolving towards industrial success. Their origin is very interesting, because it was “accidental.” Kaminsky has described the incident with these words:

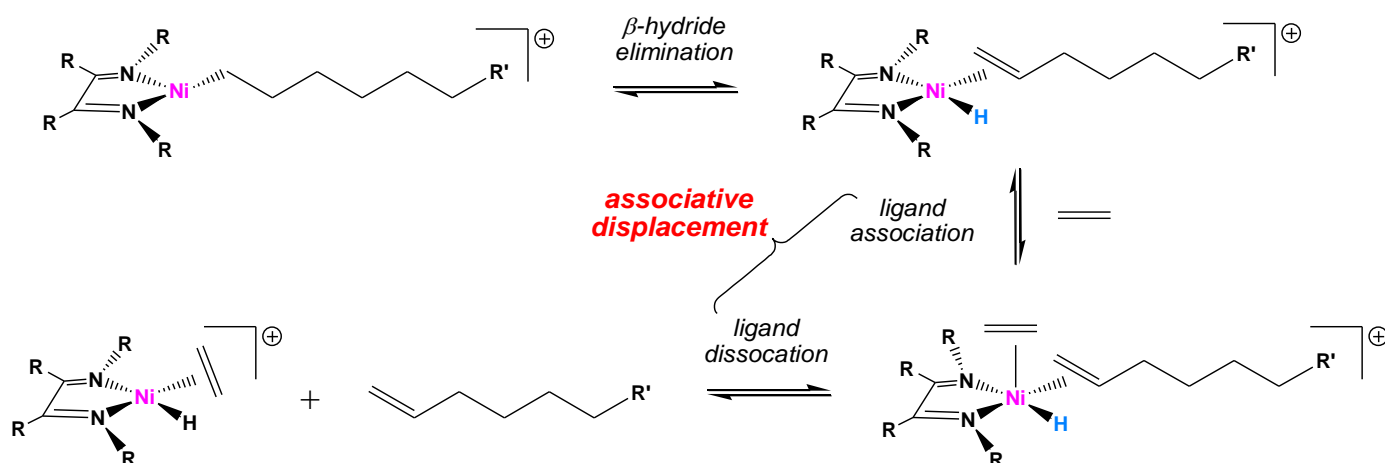
“An accident in our laboratory in 1976 brought about equimolecular amounts of water into the system compared to the trimethylaluminum, and, surprisingly, an unusual high polymerization activity of ethylene was observed.”

Kaminsky and Sinn suspected that the water and AlEt_3 reacted to form methylaluminumoxane (MAO), and they subsequently discovered that MAO-activated *homogeneous* metallocene catalysts were capable of polymerizing propene and higher olefins. This seminal discovery by Kaminsky and Sinn started the search for **single-site** catalysts.

Late Transition Metal Polymerization Catalysts

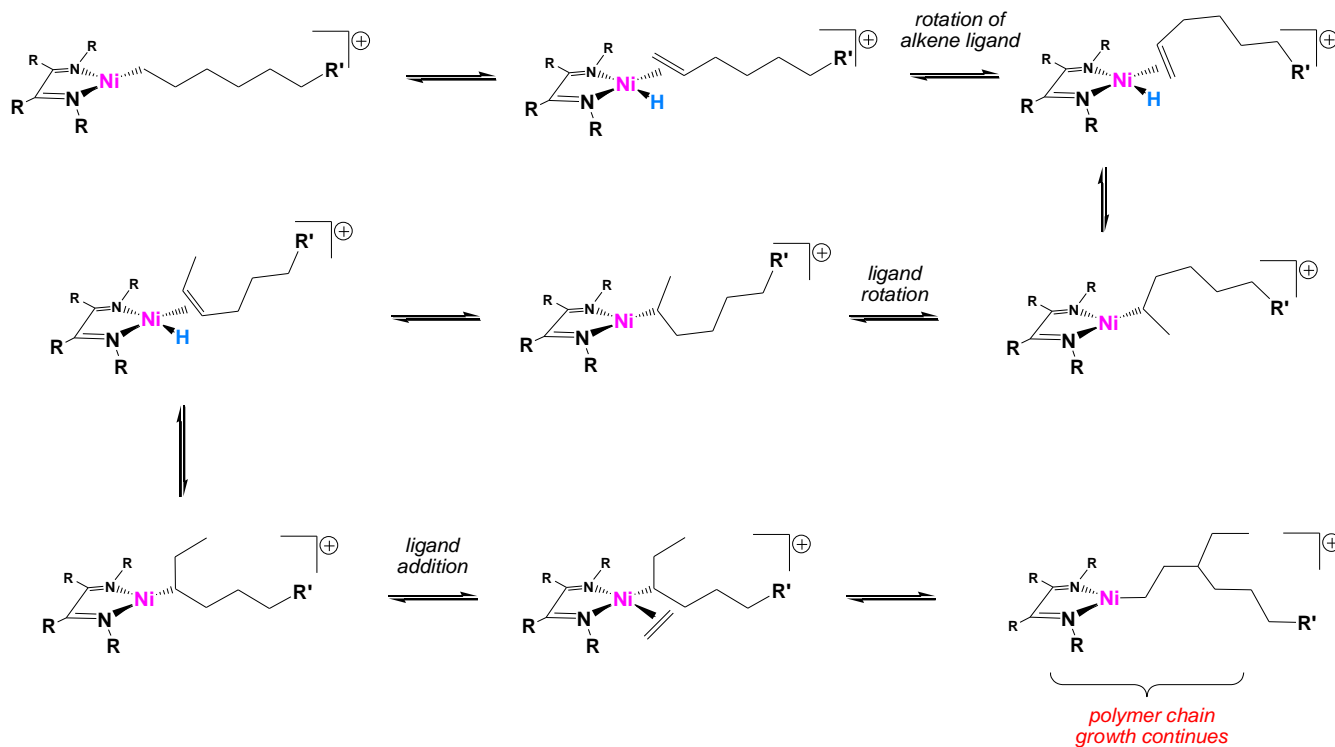
Well characterized Group 8 polymerization catalysts were reported by Brookhart in 1998 (*J. Am. Chem. Soc.* **1998**, *120*, 4050) and Gibson in 1999 (*J. Am. Chem. Soc.* **1999**, *121*, 8728.). These catalysts operate via the simple Cossee alkene addition and migratory insertion mechanism.

A key in preparing an efficient polymerization catalyst was the realization that the facile β -hydride eliminations occurring on Group 8 metals (especially Ni and Pd) lead to an **associative displacement problem** that short circuited the chain growth pathway. When a growing polymer alkyl chain does a β -hydride elimination from a 3-coordinated catalyst species, a 4-coordinate hydride-alkene is formed.



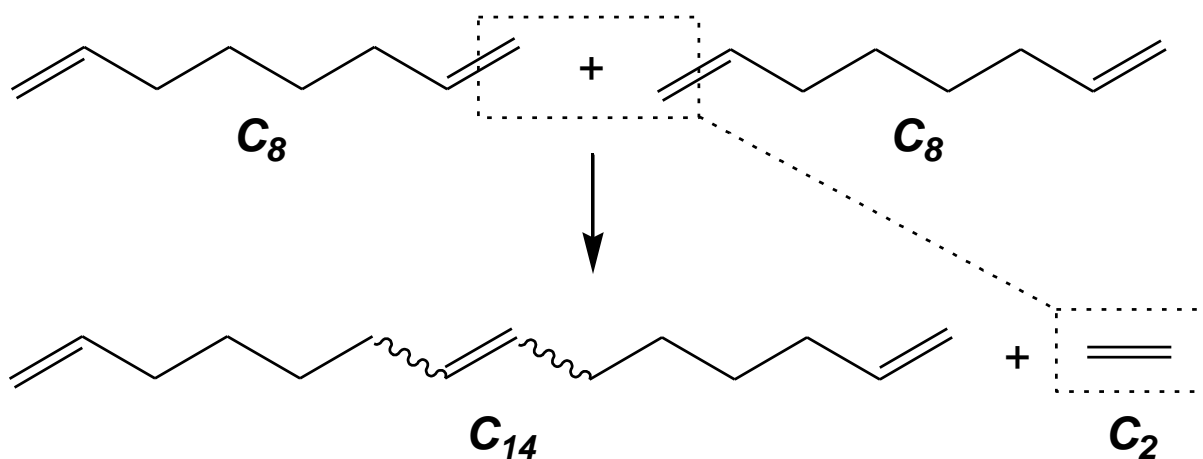
A small ethylene can easily coordinate to the axial metal site leading to a less stable 5-coordinate complex. This promotes loss of the longer alkene chain leading to termination of the chain growth. By placing extremely bulky R-groups on the diimine ligand, Brookhart was able to effectively block both axial coordination sites while still allowing equatorial alkene coordination.

An unusual aspect of Brookhart's Ni and Pd polymerization catalysts was that they could produce highly branched polyethylene, with the amount of branching controlled in large part by the ethylene pressure. Mechanistic studies indicated that facile β -hydride eliminations on these catalysts under lower ethylene pressures enabled a "**chain-walking**" isomerization process shown below. This leads to branching (sometimes extensive) of the growing polymer chain. Under higher ethylene pressures, the empty coordination site needed for β -hydride elimination is more rapidly filled by an ethylene leading to more linear chain growth.

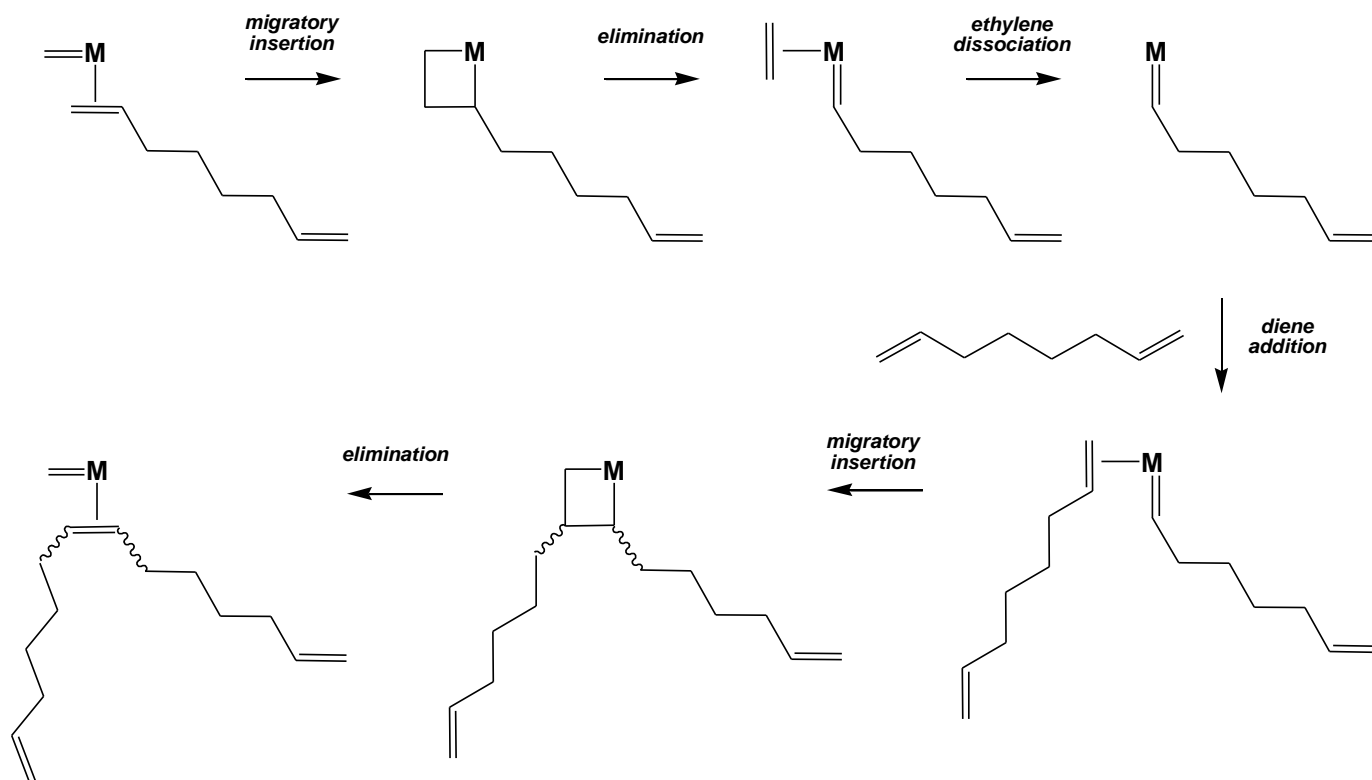


Metathesis

Metathesis catalysis refers to the reaction of two unsaturated substrates (typically alkenes or alkynes) that leads to a switching of the atom groups on each end of the bond with the unsaturation. This is shown below for the reaction of two C_8 dienes.

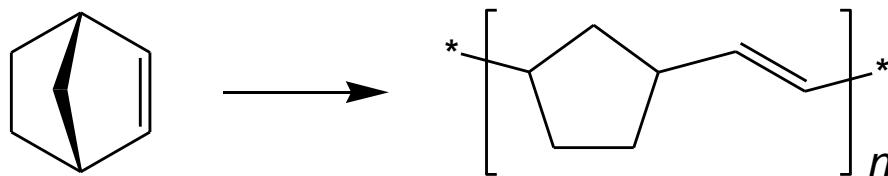


The proposed mechanism for this involves metal-alkylidenes and is shown below:



Carrying this reaction out over and over with the more reactive terminal double bonds leads to **acyclic diene metathesis (ADMET)** polymerization with longer chain α,ω -diene substrates. The general reaction relies on the loss of ethylene from the reaction mixture to drive the reaction to high couplings and molecular weights. The internal double bonds generated are not as reactive as the terminal double bonds for the metathesis reaction.

Ring opening metathesis polymerization, ROMP, (Schrock, R. R., *Acc. Chem. Res.* **1990**, *24*, 158. Grubbs, R. H.; Tumas, W., *Science*, **1989**, *243*, 907) is another mechanism for polymerization related to the Green-Rooney alkylidene pathway that can operate when one deals with cyclic alkenes. The first commercial product using ROMP was prepared by CdF Chimie from norbornene using a heterogeneous catalyst based on MoO_3 supported on alumina.



ROMP works best on cyclic alkenes that have some ring strain to drive the ring opening process and minimize possible ring closing reactions. A proposed mechanism for the ROMP of norbornene using a Cp_2Ti center is shown below. In this mechanism one considers the alkylidene as a dianionic ligand, so the reaction with the alkene is considered a **migratory insertion**. The subsequent elimination reaction can proceed in two ways, backwards (non-productive) and forward, which opens the norbornene ring and extends the polymer chain.

