

Organometallic Chemistry and Homogeneous Catalysis

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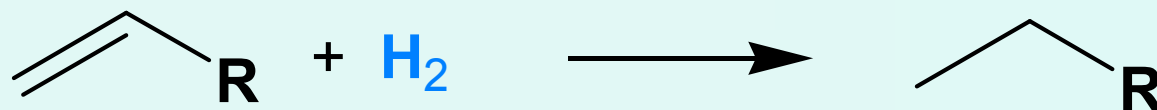
Lecture N11



Kashiwa Campus, January 15, 2010

Hydrogenation

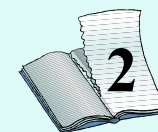
The hydrogenation of olefins, impossible without catalyst, can be catalyzed by numerous transition-metal complexes.



1939, Iguchi – hydrogenation of organic compounds using Rh(III)

Further the results reporting about application of nearly all d-elements in hydrogenation were published

Most active appeared to be complexes of Co, Rh and Ir



1) Wilkinson catalyst $\text{RhCl}(\text{PPh}_3)_3$ (WC)

In 1956 two independent research groups reported about homogeneous catalytic hydrogenation of alkenes and alkynes with $\text{RhCl}(\text{PPh}_3)_3$ in a mild conditions: $T = 25^\circ\text{C}$, $P_{\text{H}_2} = 1\text{atm}$, solvents: benzene, benzene/ethanol, THF, acetone, methanol



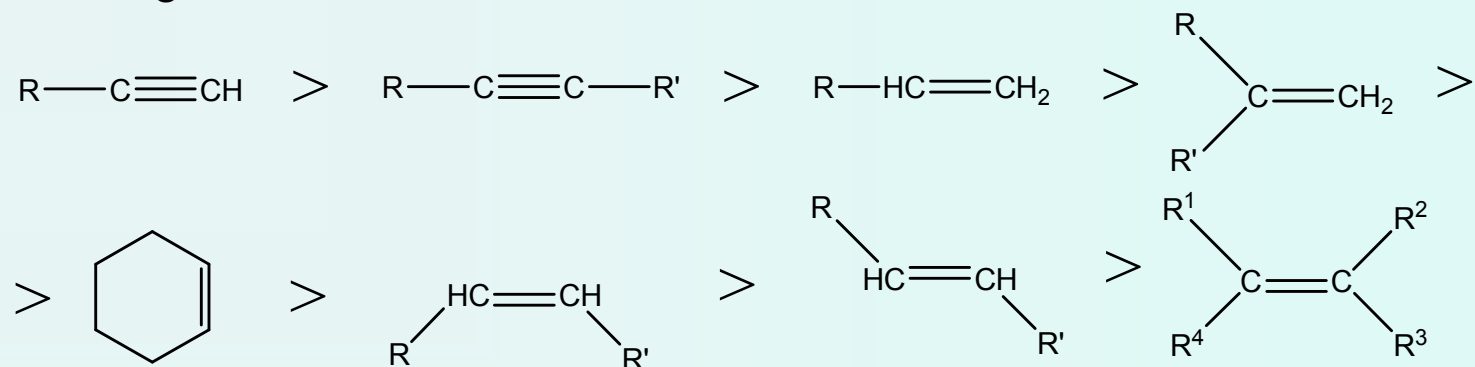
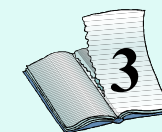
Hydrogenation takes place very selective – other groups as $>\text{C}=\text{O}$, $-\text{C}\equiv\text{N}$, $-\text{NO}_2$, $-\text{COOH}$, aryl do not undergo hydrogenation

$\text{RhCl}(\text{PPh}_3)_3$ was the first highly active homogeneous hydrogenation catalyst and was discovered by Geoffrey Wilkinson (Nobel prize winner for ferrocene).

It was very simply prepared by reacting $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with excess PPh_3 in EtOH:

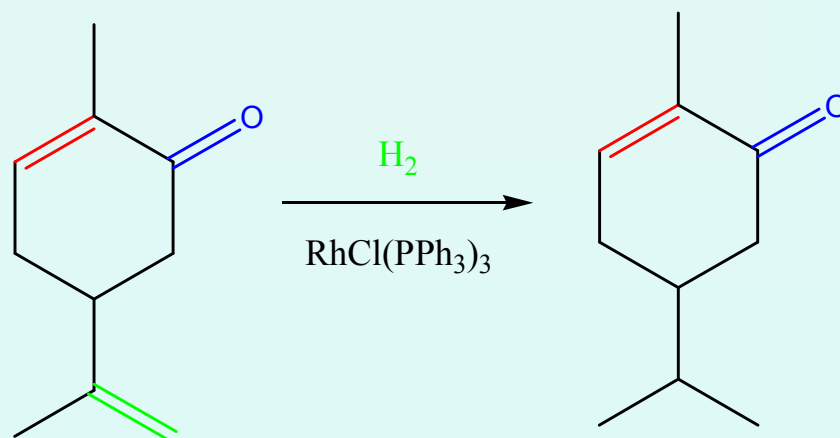


Depending on the nature of substrate the rate of the reaction decreases in the following order:



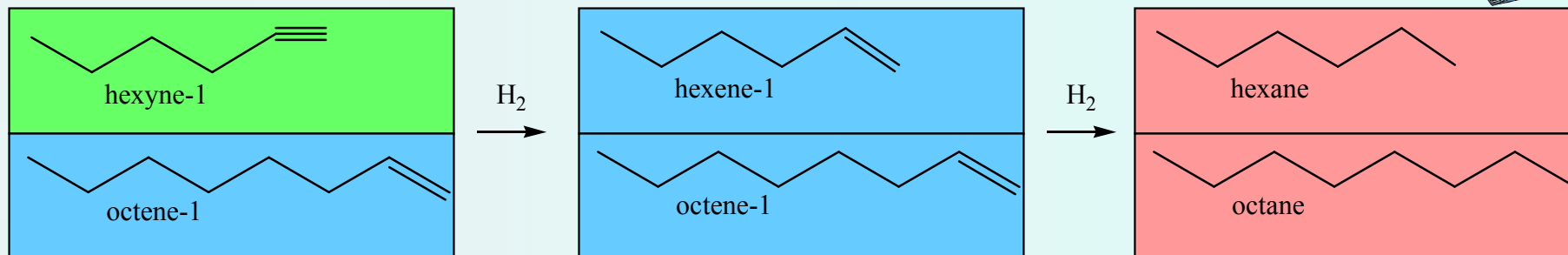
The rates of hydrogenation of alkenes by Wilkinson's catalyst mirror their relative binding affinity to the metal center. Differences in rate between the alkenes is about 50X. Alkenes that bind very tightly (i.e., ethylene) give slow hydrogenation rates, though.

Example 1:



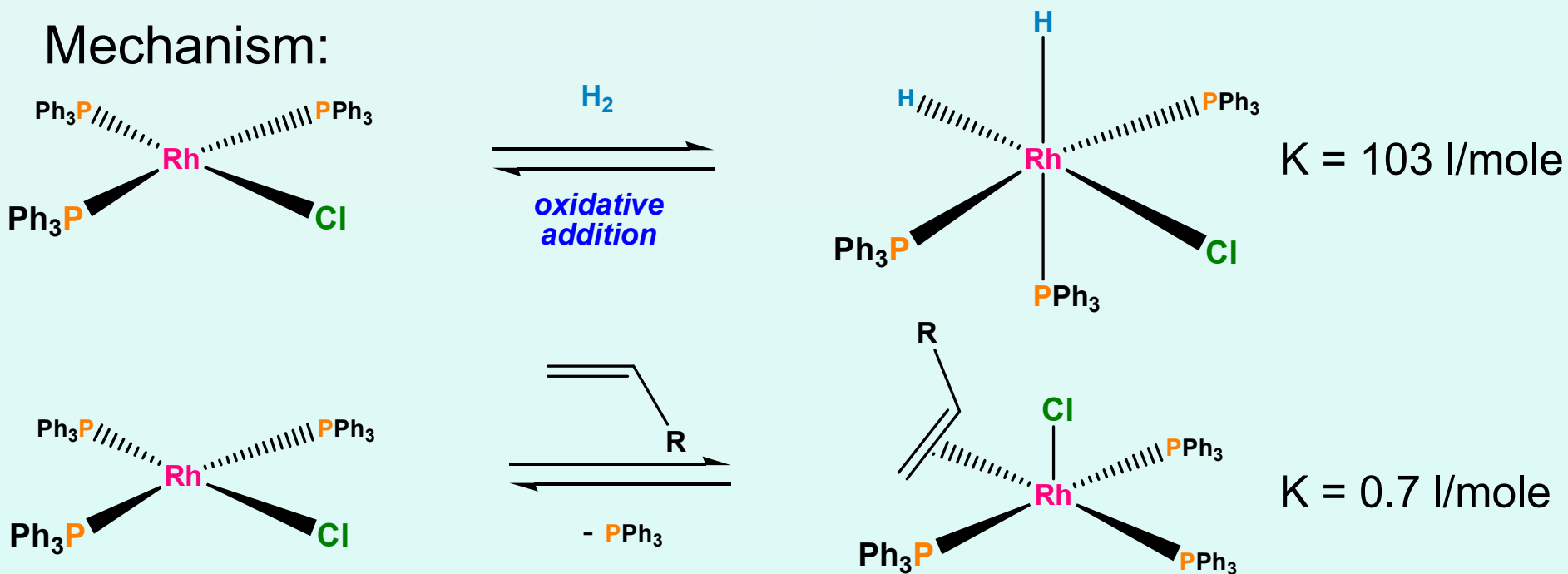
>C=O bond is completely inactive; C=C bond inside the cycle is more hindered than C=C bond out of the cycle, so it is hydrogenated with a 99% selectivity

Example 2:



When both **hexyne-1** and **octene-1** are present in the hydrogenation with $RhCl(PPh_3)_3$, only **hexyne-1** will undergo the hydrogenation. Only when all **hexyne-1** is hydrogenated to **hexene-1** the mixture of **hexene-1** and **octene-1** starts to react with H_2

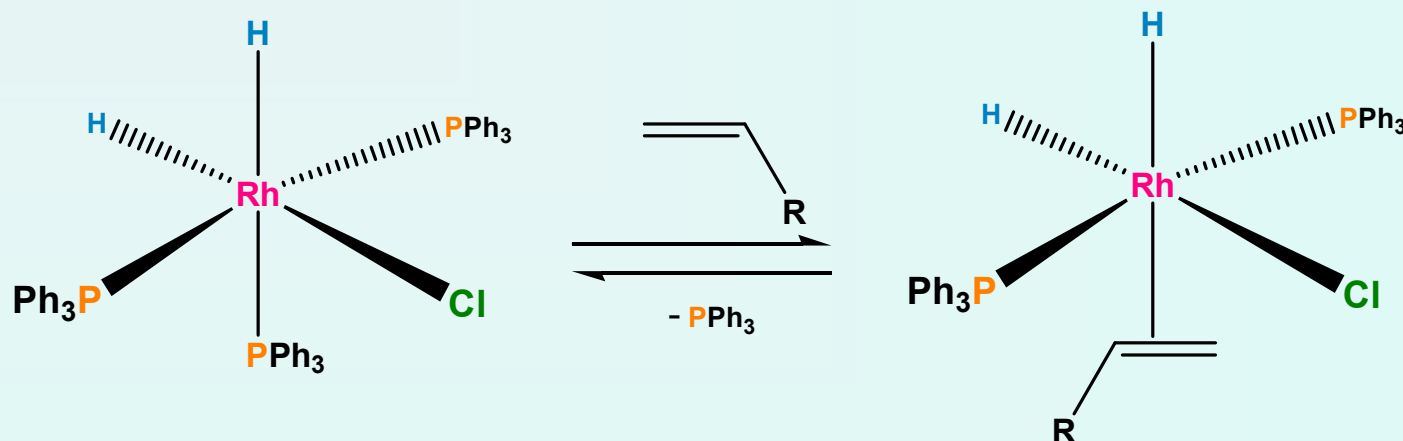
Mechanism:



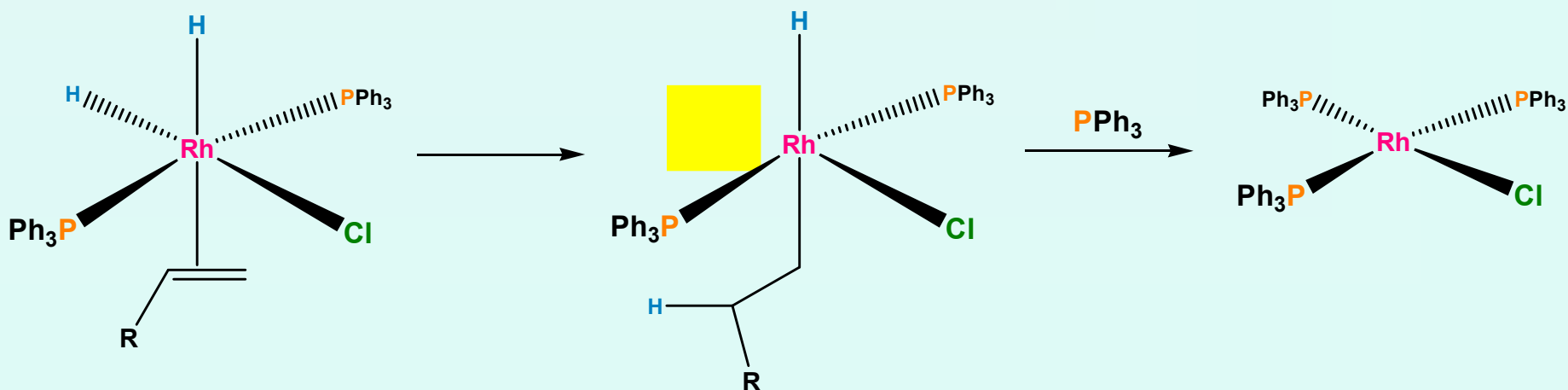
Because of more than 1000-fold difference in the equilibrium constants we can take into account only first equilibrium



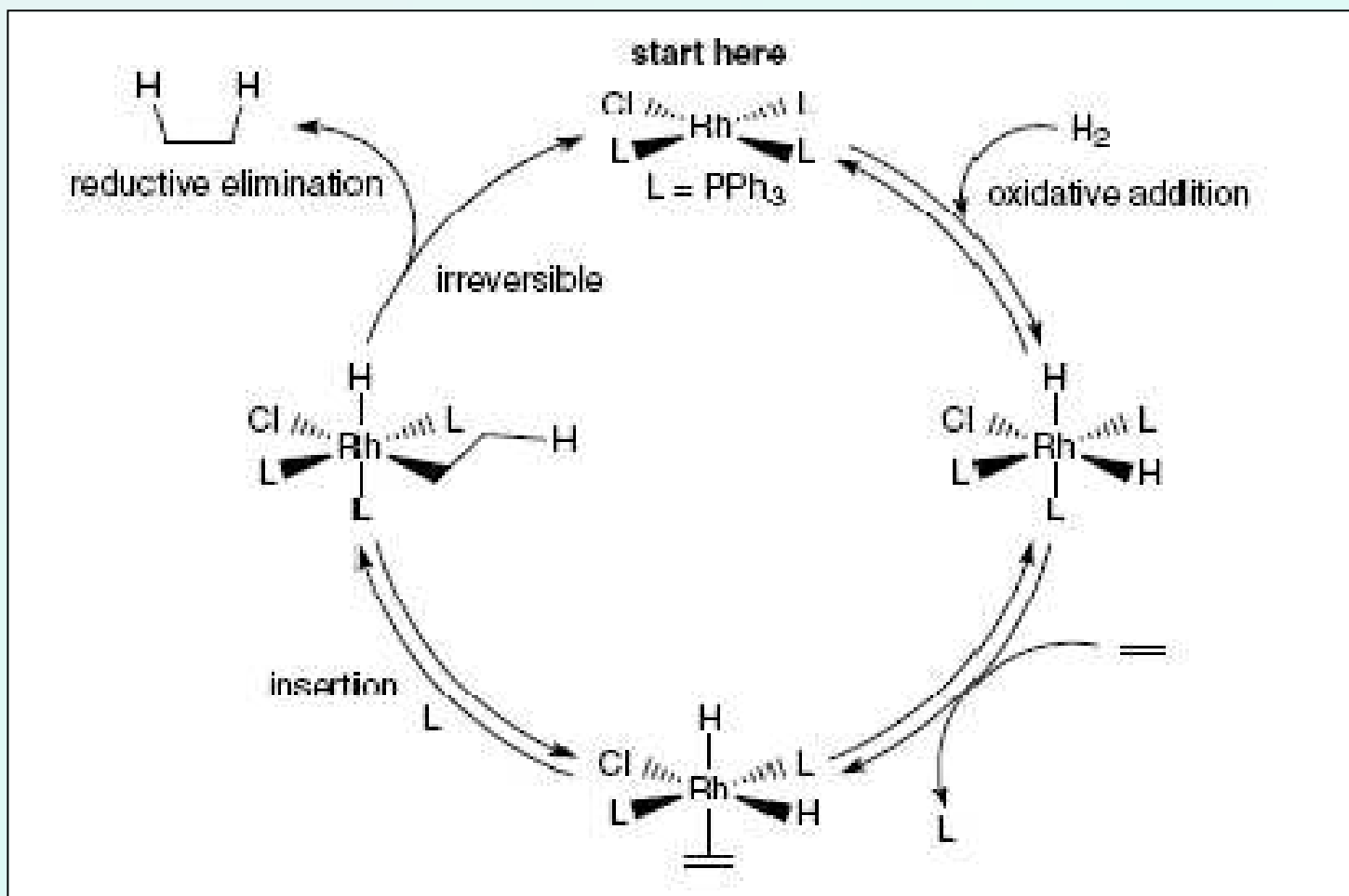
In a new complex PPh_3 ligand is trans to hydride ligand, so due to the trans-effect it can more easily be changed to the other (alkene) ligand:

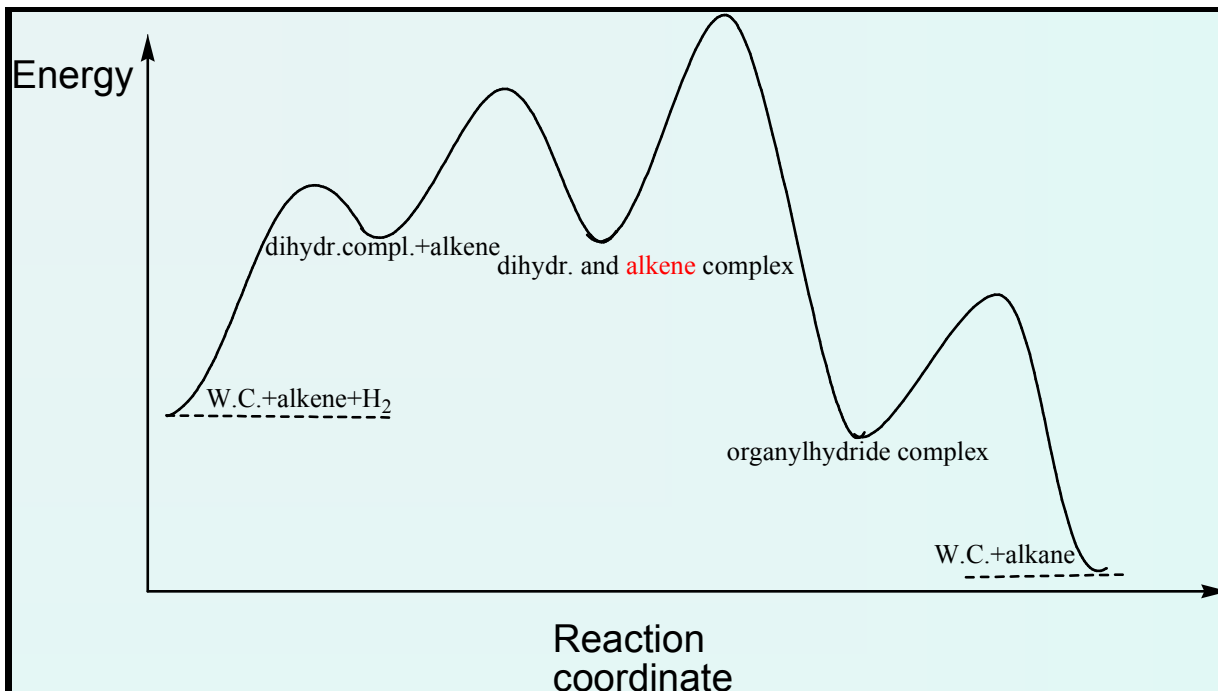


Then insertion (limitation step) and reductive elimination takes place:

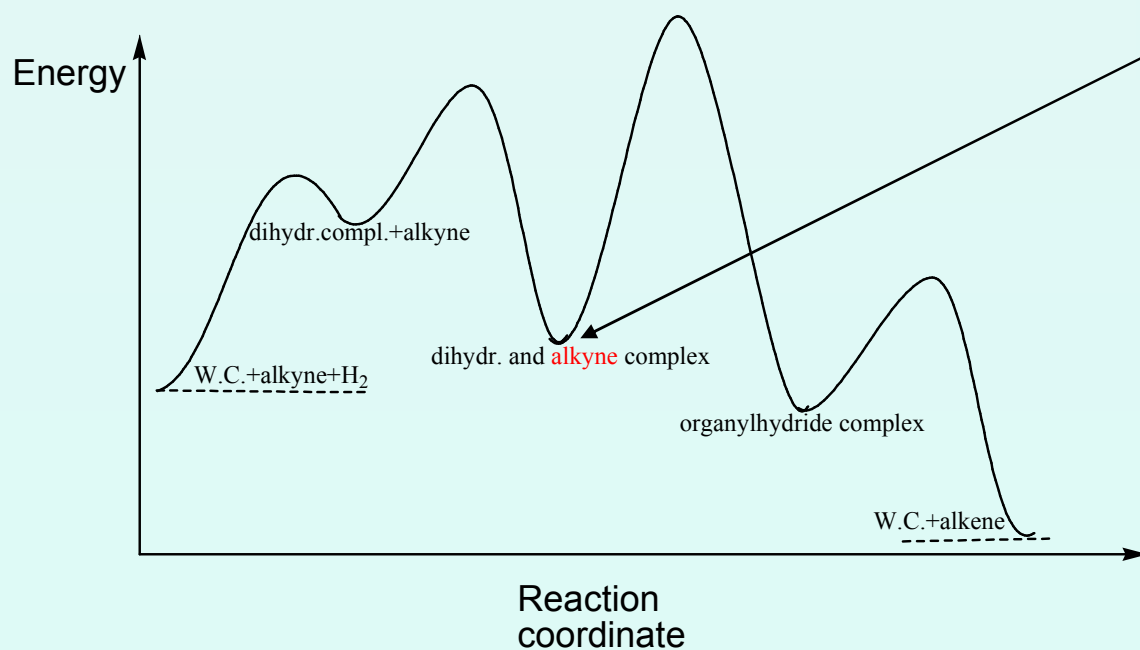


The mechanism involves three reversible steps: oxidative addition of H_2 , substitution by the olefin of PPh_3 that is labilized in *trans* position vs. the hydride ligand (*trans* effect), insertion of the olefin to Rh-H bond. The last step, reductive elimination of the alkyl and hydride ligands to yield the alkane, is totally irreversible, and has allowed to successfully use this system for asymmetric catalysis

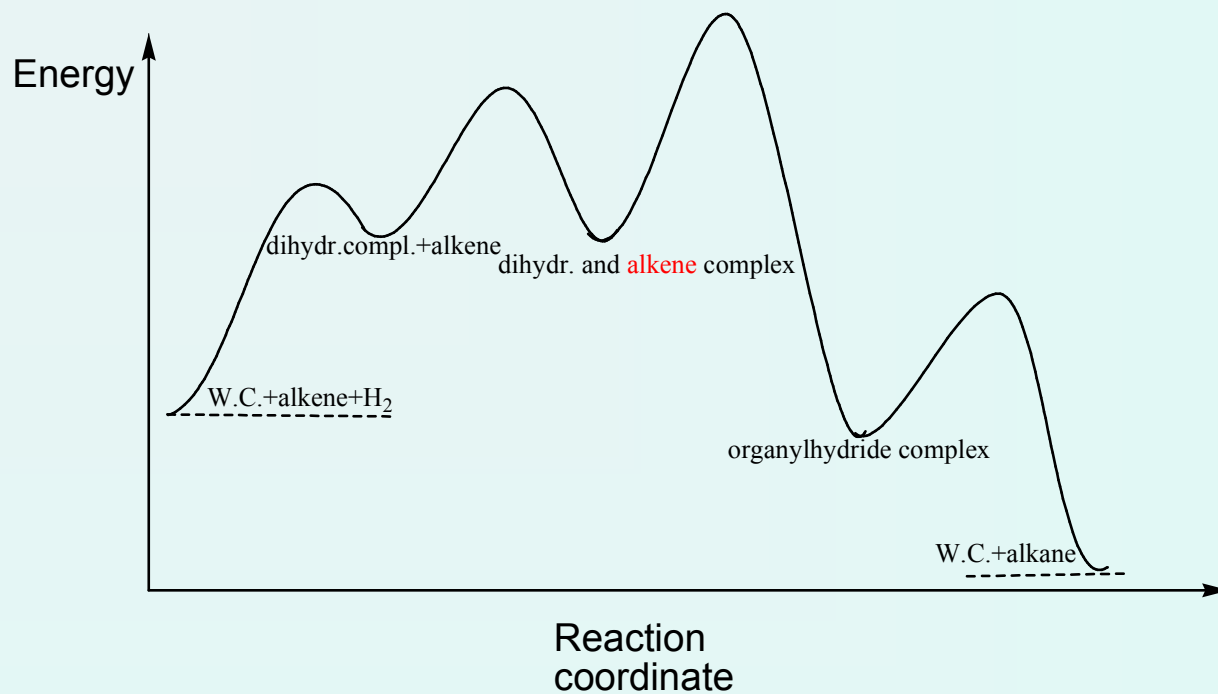




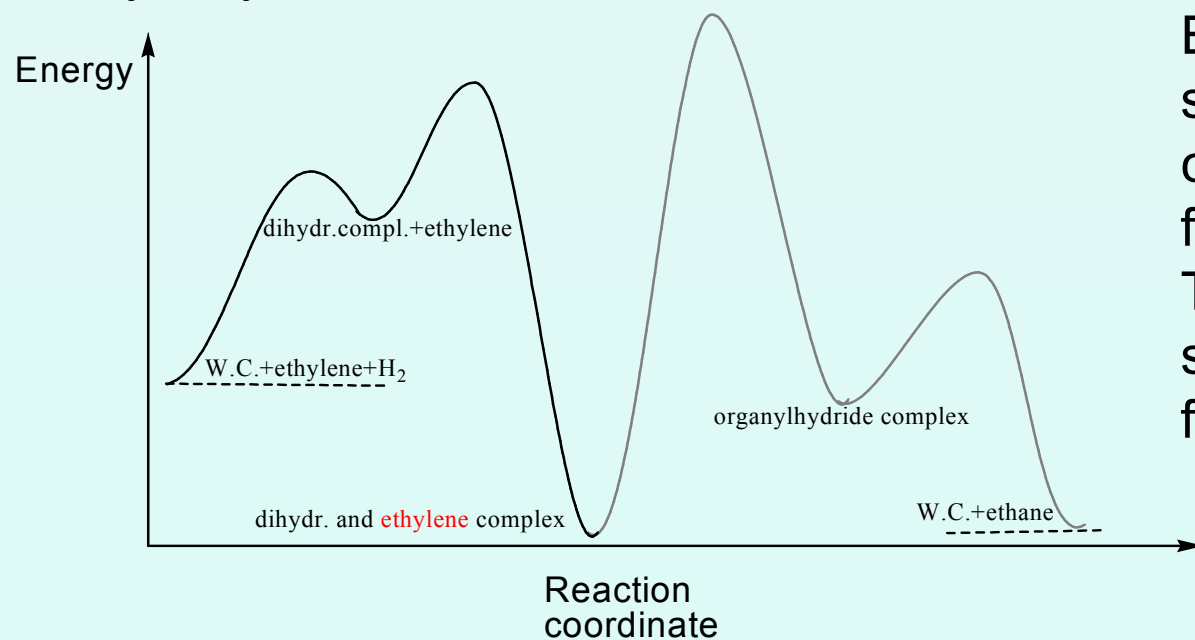
Why alkynes are more active than alkenes?



Alkynes form more stable π -complexes with Rh, so the reaction should take place slowly. But the formation of more stable complex shifts the equilibrium to the right and equilibrium concentration also increases, so the rate of the reaction increases



Why ethylene is not active?

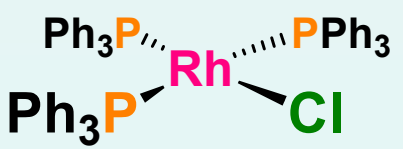
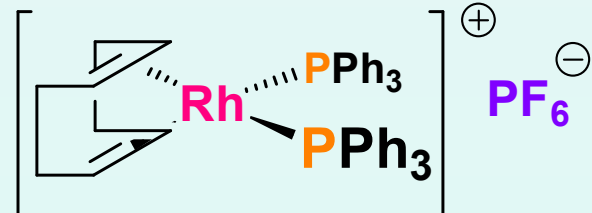
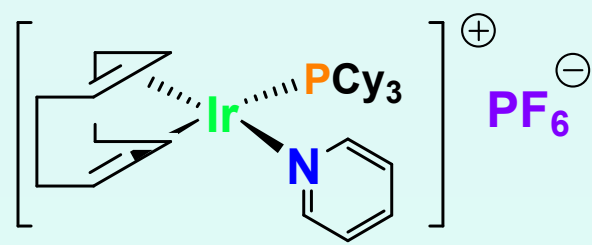


Ethylene does not have any steric hindrance when coordinates with Rh and forms extra-stable π -complex. That means that the reaction stops on the stage of the formation of π -complex

Other catalysts (analogues of WC):

Crabtree *Acc. Chem. Res.* **1979**, *12*, 331

TOF

Catalyst	1-Butene	Cyclohexene	1-Methylcyclohexene	2,3-Dimethyl-2-butene
 <i>Wilkinson's catalyst</i>	650	700	13	---
 <i>Schrock-Osborn catalyst</i>	4000	10	---	---
 <i>Crabtree's catalyst</i>	6400	4500	3800	4000

A ligand effect for the hydrogenation of **cyclohexene** with WC:



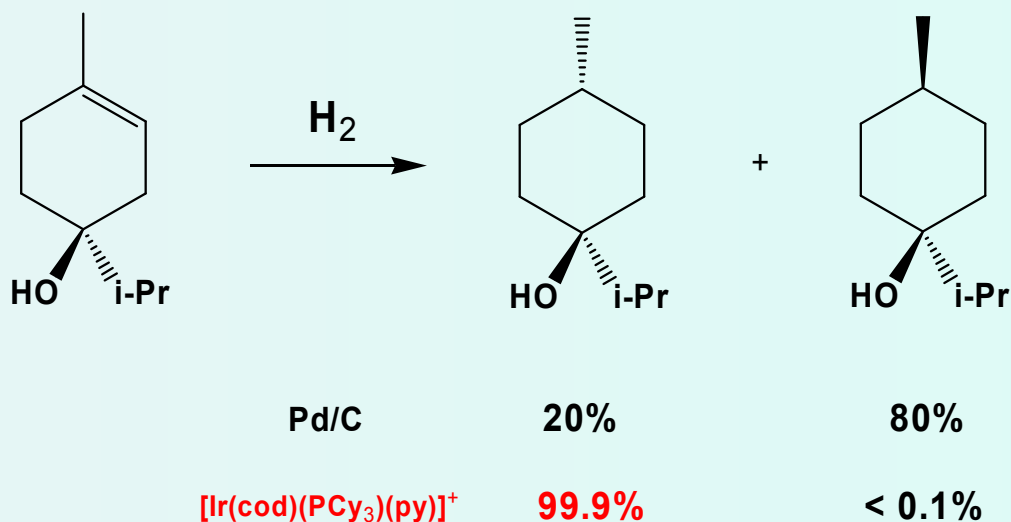
Ligand:	Relative reactivity:
$(4\text{-ClC}_6\text{H}_4)_3\text{P}$	1.7
Ph_3P	41
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	86
$(4\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$	100

The catalytic efficiency of other catalysts similar to WC (TOF - the *turn over frequency*)

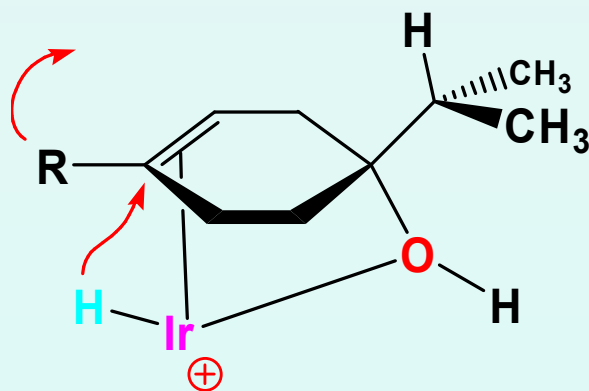
Catalyst	Temp °C	Solvent	TOF (hr ⁻¹)		
			1-hexene	cyclohexene	Me ₂ C=CMe ₂
$[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]^+$	0	CH ₂ Cl ₂	6,400	4,500	4,000
$[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]^+$	0	CH ₂ Cl ₂	5,100	3,800	50
$[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]^+$	0	acetone	10	0	0
$[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$	25	CH ₂ Cl ₂	4,000	10	0
HRuCl(PPh ₃) ₃	25	C ₆ H ₆	9,000	7	0
RhCl(PPh ₃) ₃	25	C ₆ H ₆ /EtOH	650	700	0
RhCl(PPh ₃) ₃	0	C ₆ H ₆ /EtOH	60	70	0

Directing Effects

Crabtree has demonstrated some very interesting substrate directing effects in hydrogenation:



The weak ligand bonding of the OH group on the substrate directs one specific side of the alkene to coordinate to the metal center in order to form an alkene-OH chelate to the Ir.



positive charge on Ir is important to attract the partial negatively charged OH group. One also needs the presence of an empty orbital

Group binding affinities: amide > OH > OR > ester ~ ketone

Amine groups bind too strongly and inhibit catalysis. Rigid structures with stronger chelates, like the norbornene ligand shown to the right, are also poor substrates.

2) Pentacyanocobaltat $\text{Co}(\text{CN})_5^{3-}$



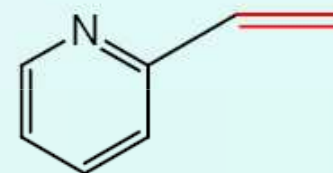
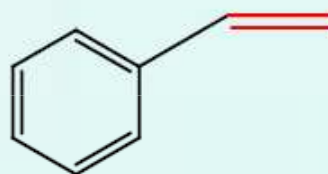
1942, Iguchi. Solvent: water solution of HCl

This catalyst is completely inactive towards unconjugated bonds (ordinary alkenes do not undergo hydrogenation). Only C=C bonds conjugated with C=C, C=O, C≡N, Ph etc. undergo hydrogenation

Substrates: $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

$\text{CH}_2=\text{CH}-\text{COOH}$

$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$



Note: only **C=C** bond undergoes hydrogenation

Reaction conditions: $T=25^\circ\text{C}$, $P=1\text{ atm}$

Disadvantage: most of substrates are insoluble in water (aq. HCl). Using of similar catalysts soluble in organic media requires more severe conditions ($T>100^\circ\text{C}$, $P_{\text{H}_2}=30\text{ atm}$)

Mechanism:

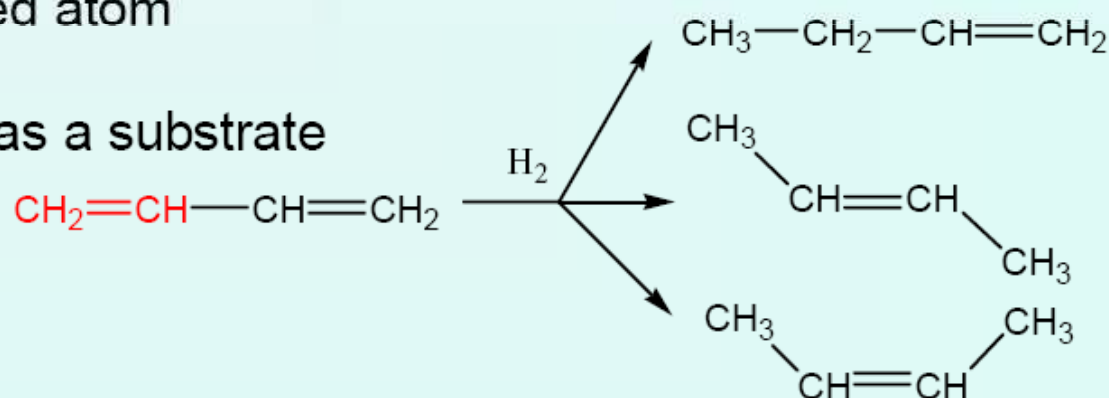


The reaction starts with homolytic cleavage of H-H bond:



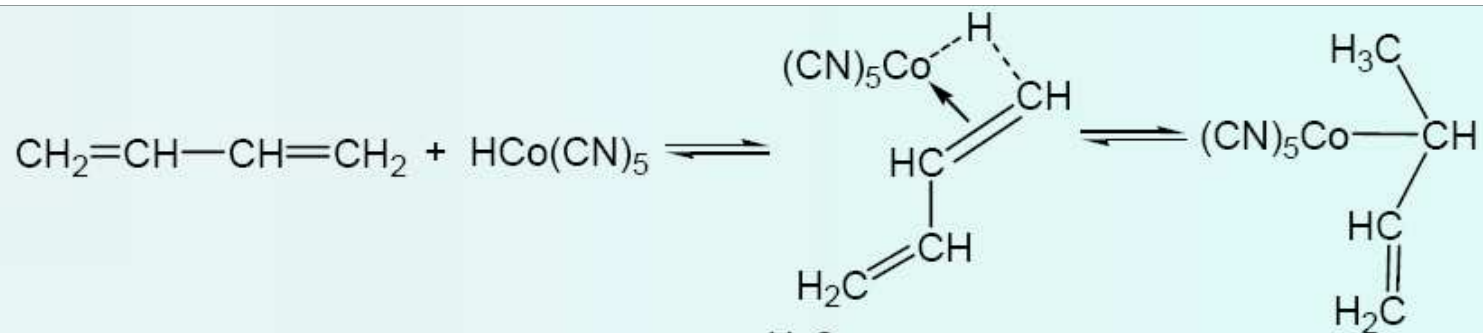
Usually we regard hydrogen as a hydride ligand H^- , so the oxidation state of cobalt should be increased from +2 to +3. But it was shown in polarographic experiments that oxidation state of cobalt is +2. It means that hydrogen exists not as an ion but as stabilized atom

Let's choose 1,3-butadiene as a substrate

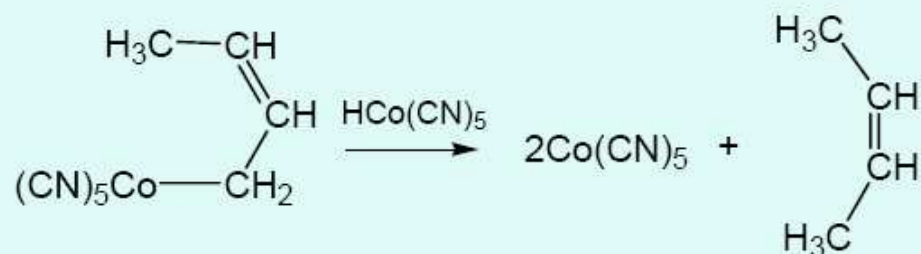
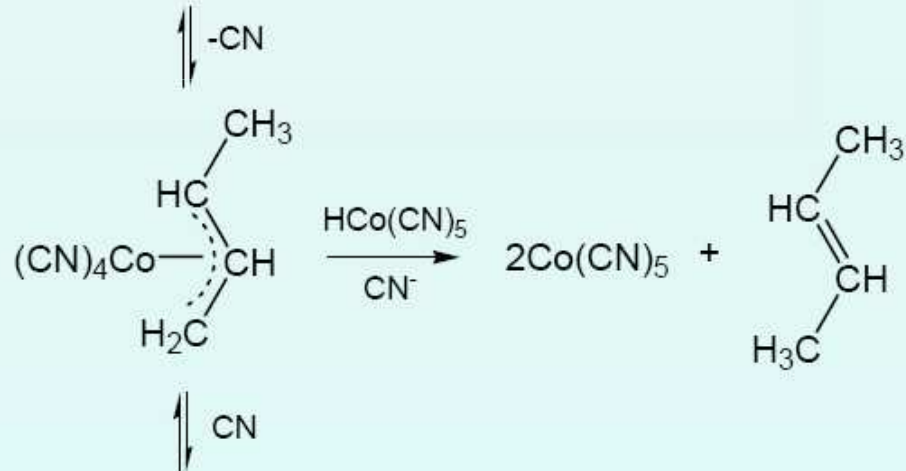
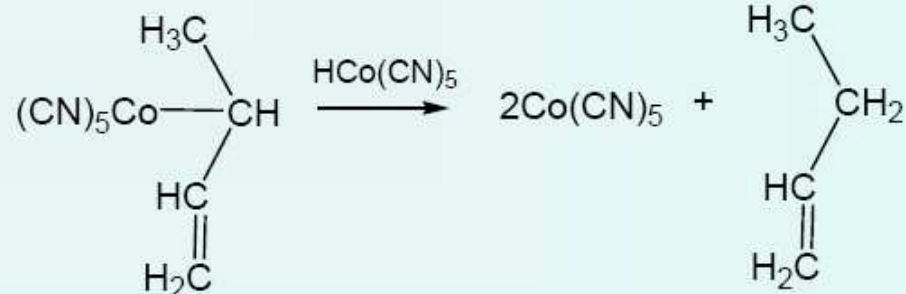


Depending on the $\text{CN}^-/\text{Co}^{2+}$ ratio different products can be formed:

- 1) $\text{CN}^-/\text{Co}^{2+} \geq 5:1$ main product is 1-butene (~90%)
- 2) $\text{CN}^-/\text{Co}^{2+} < 5:1$ main product is *trans*-2-butene (~85%)
in both cases only small (~5%) amount of *cis*-2-butene forms



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Rate of the reaction \sim
 $\sim [\text{HCo}(\text{CN})_5]^2[\text{Diene}]$

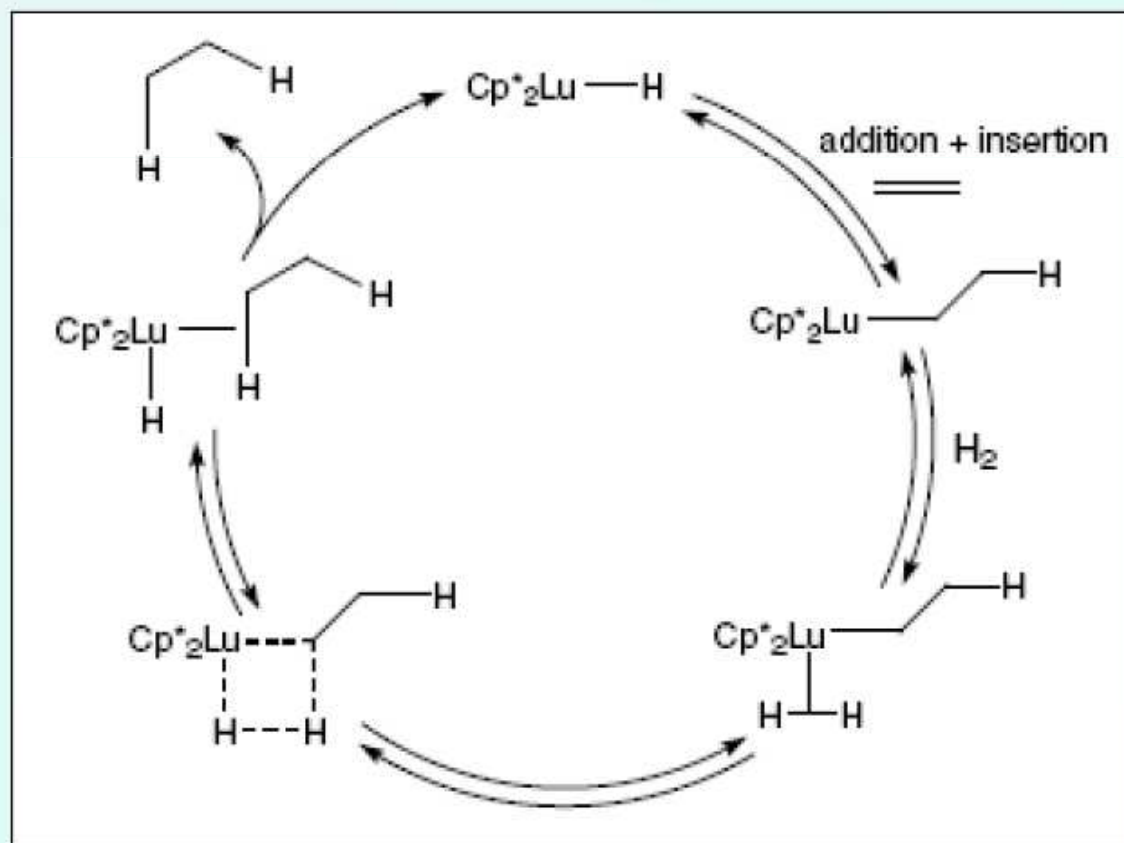


3) Lanthanide Hydrogenation Catalysts

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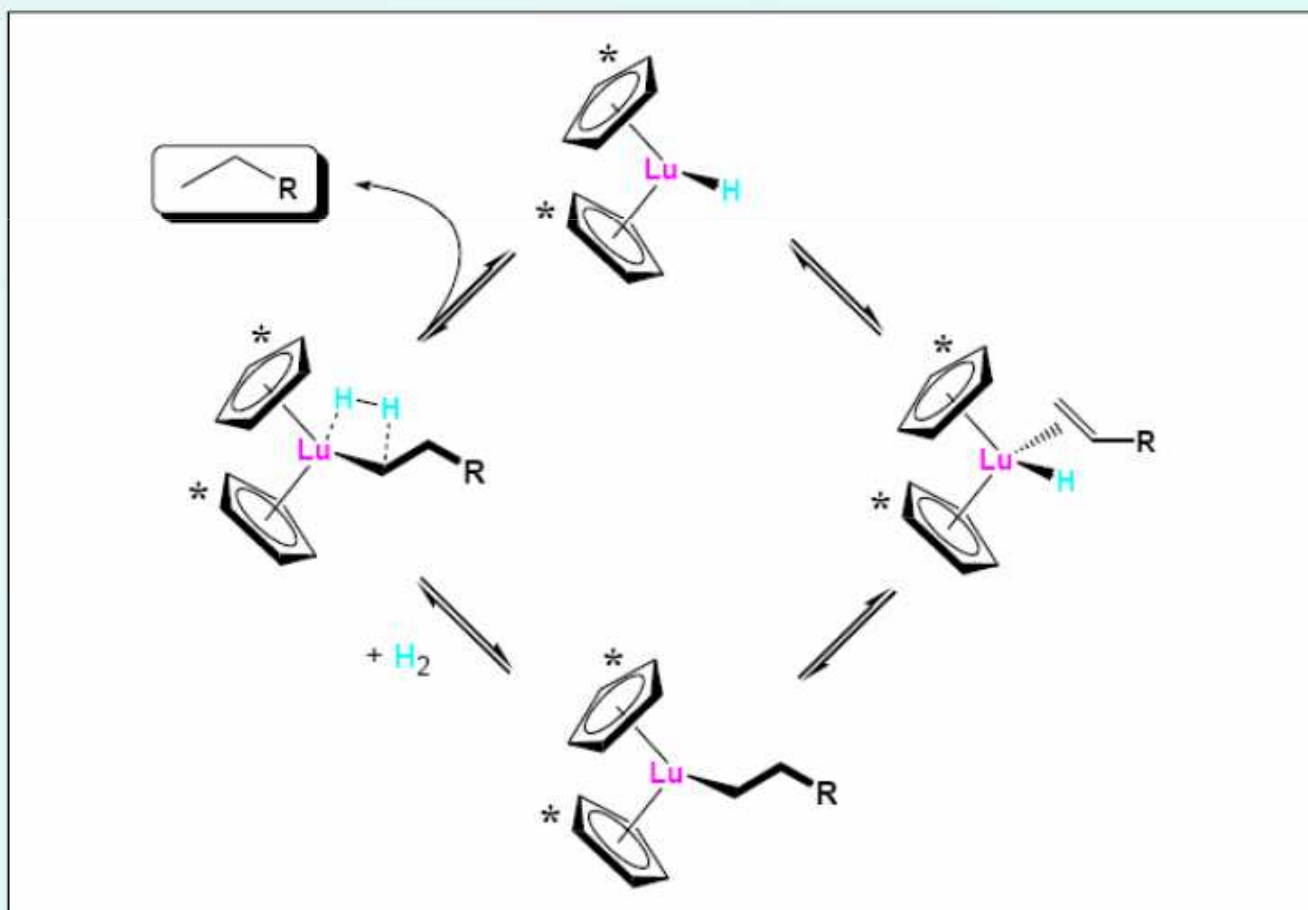
MECHANISM INVOLVING σ -BOND METATHESIS

Tobin Marks reported the extraordinary activity of $(\text{Cp}^*_2\text{LuH})_2$ for the hydrogenation of alkenes and alkynes. The monometallic complex catalyzes the hydrogenation of 1-hexene with a TOF = $120,000 \text{ h}^{-1}$ at 1 atm H_2 , 25°C !! This is one of the most active hydrogenation catalysts known.



Lanthanide complexes such as $[\text{LuCp}^*_2(\text{H})]$ are extremely active catalysts for the hydrogenation of terminal olefins. **First**, the olefin coordinates onto the metal center, then insert into the Lu-H bond to give a Lu-alkyl intermediate. **Then**, the reversible addition of H_2 onto the d^0 -metal center gives a transitory dihydrogen complex that cannot undergo oxidative addition of H_2 in the absence of d -electrons on Lu. Thus, this formation of the Lu- H_2 species is followed by σ -bond metathesis irreversibly giving the alkane and a Lu-H species.

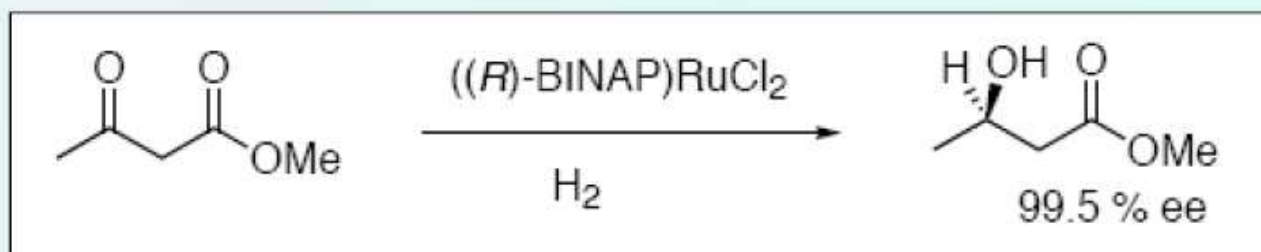
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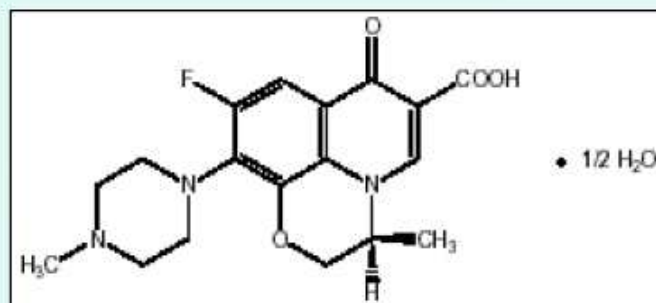
4) Ionic Hydrogenation



Ryori Noyori was a recipient of the 2001 Nobel Prize for his development and application of the BINAP ligand. Using Ru(II) in place of Rh(I) resulted in a more general catalyst that could hydrogenate ketones and imines as well as alkenes.

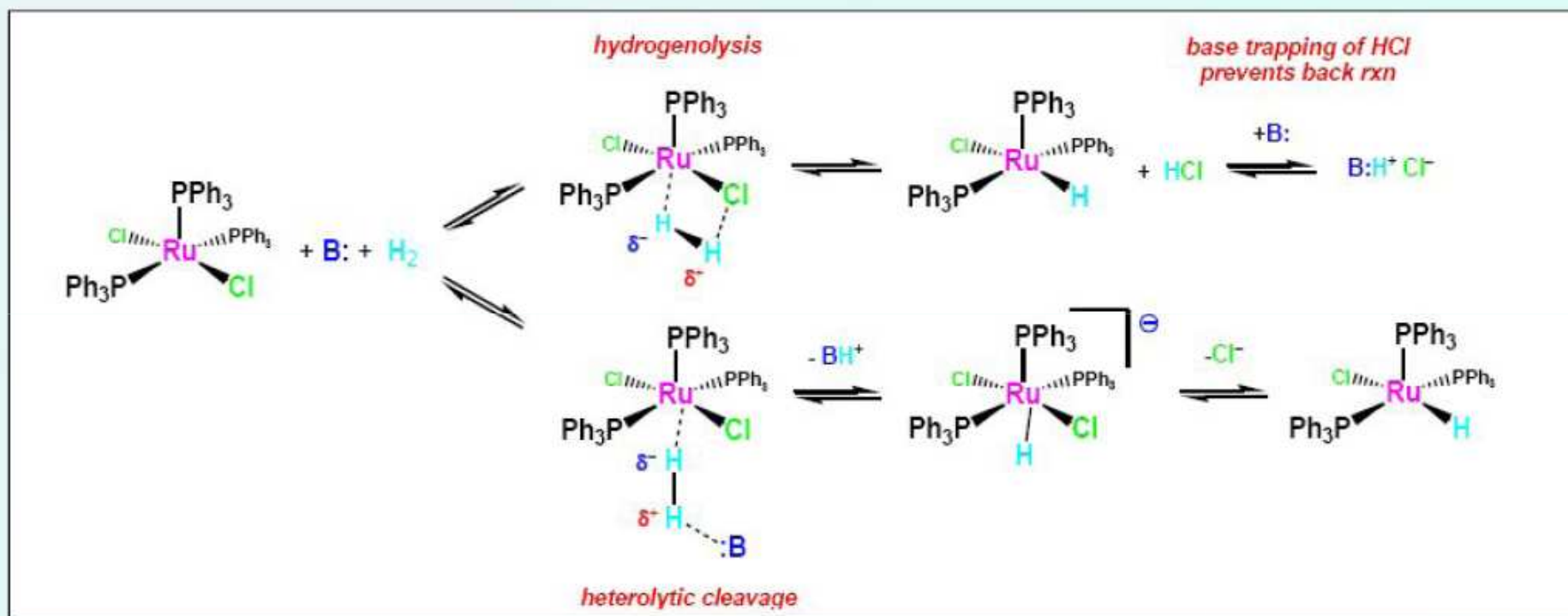


This catalyst system has been commercialized for the synthesis of (*R*)-1,2-propanediol, which is used as a precursor for the synthesis of the antibiotic [levofloxacin](#).

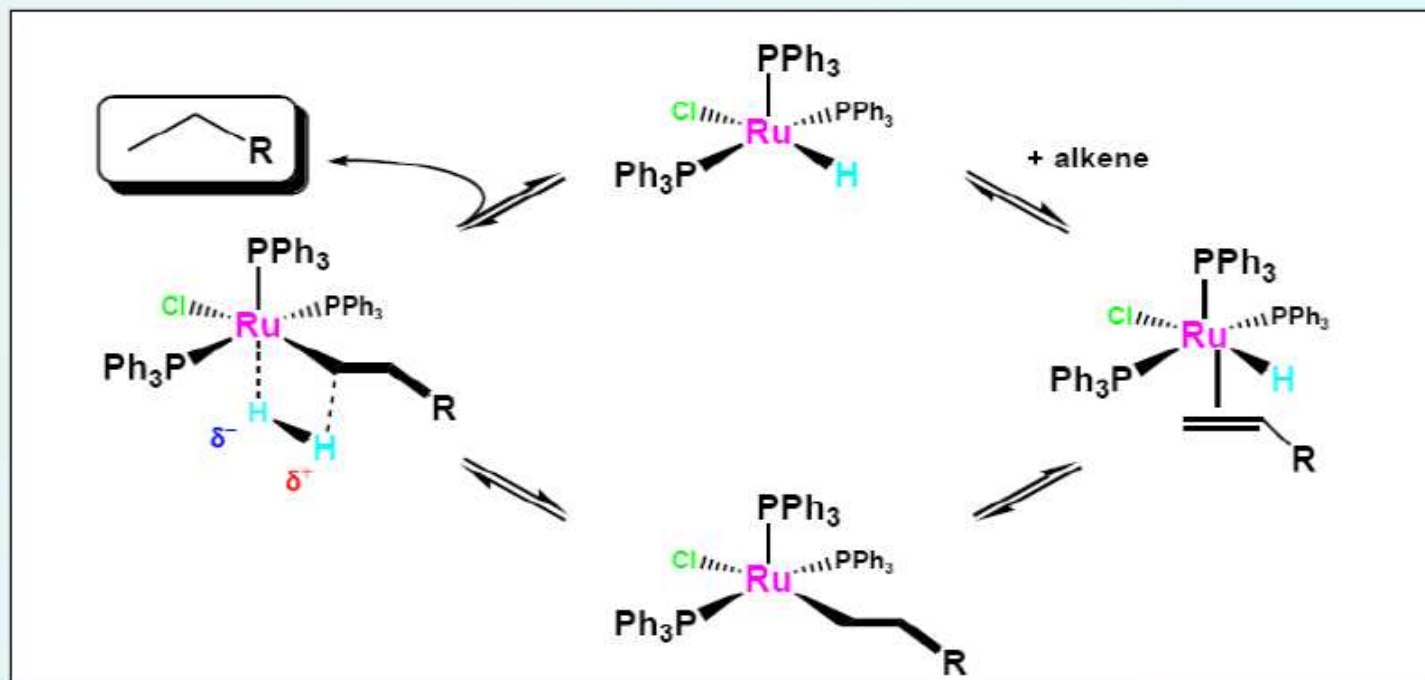


The Noyori catalyst is believed to follow ionic mechanism in the reduction of carbonyls and imines. In an ionic mechanism H₂ is added as H⁺ and H⁻, rather than by a migratory insertion process. This mechanism is particularly prevalent in the reduction of ketones and imines that can serve as proton acceptors.

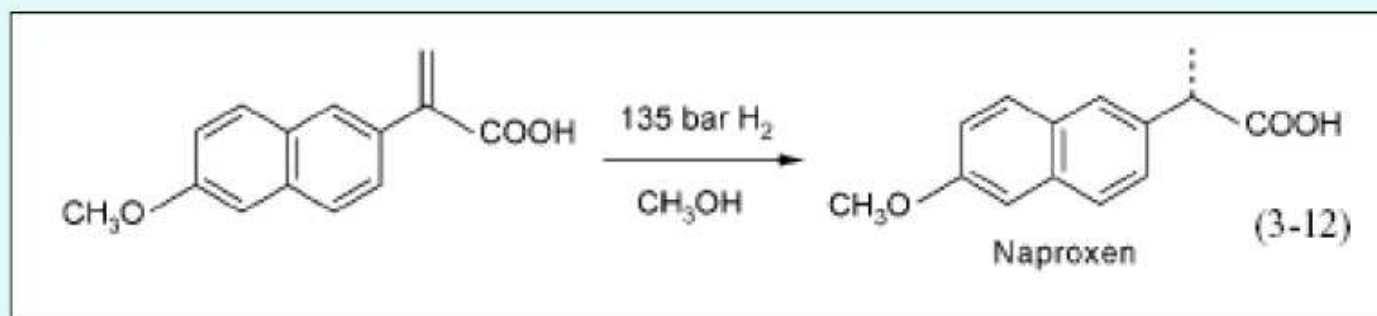
Ru has a strong tendency to perform a heterolytic activation of H_2 instead of oxidative addition to make a metal dihydride. This can occur either via hydrogenolysis or heterolytic cleavage mechanisms, giving the same net result:



Shown below is a proposed catalytic cycle for $Ru(+2)$ catalyzed hydrogenation (Note that there is no change in oxidation state of the $Ru(+2)$):



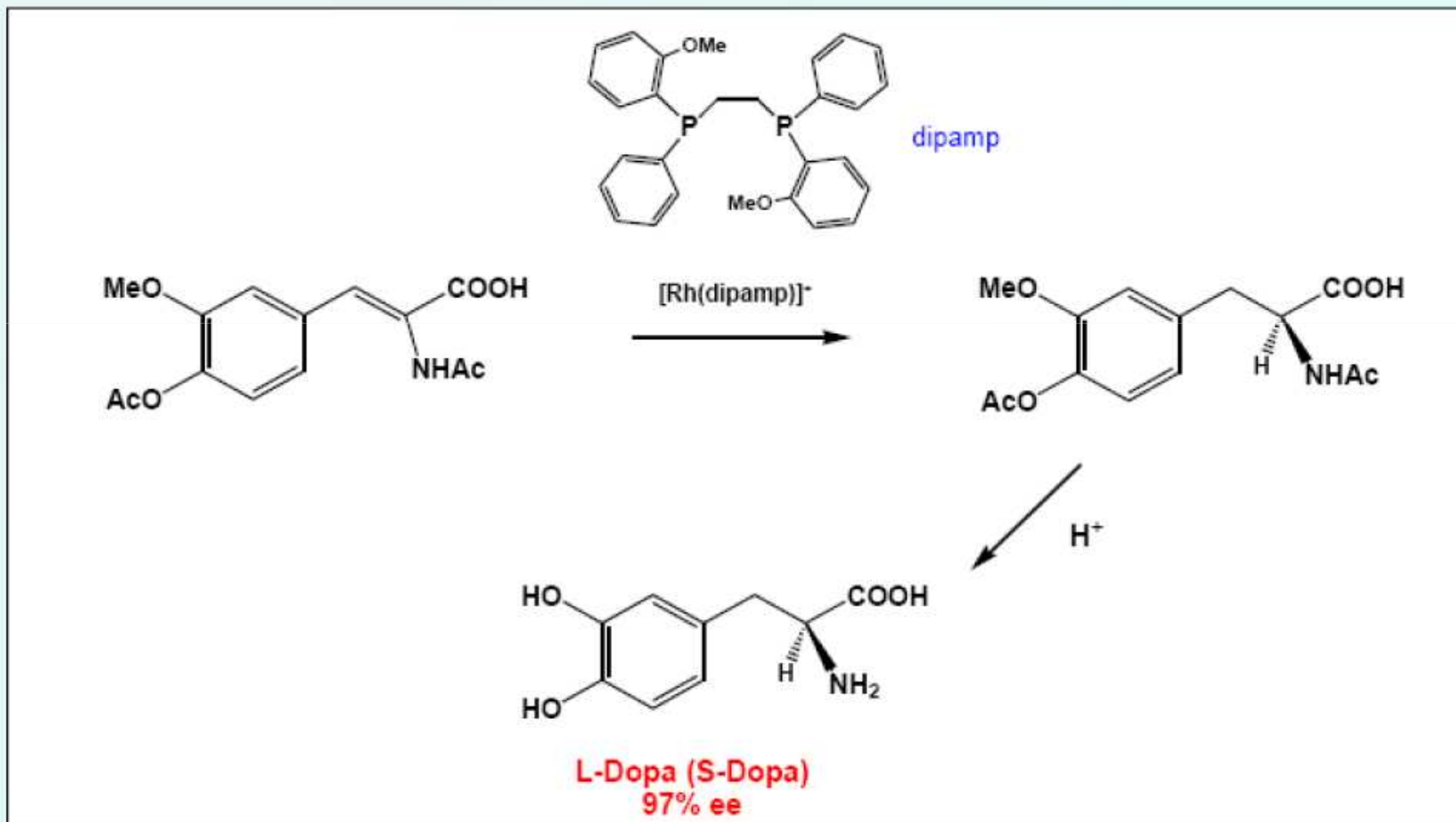
The drug **naproxen** is a member of the class of 2-arylpropionic acids. (*S*)-naproxen, is one of the world's largest-selling prescription drugs. It is sold as the pure (*S*)-isomer because the (*R*)-isomer is a liver toxin. Catalyst: (*S*)-BINAP Ru(II) chloride. The optical yields of 96–98%:



Asymmetric Hydrogenation

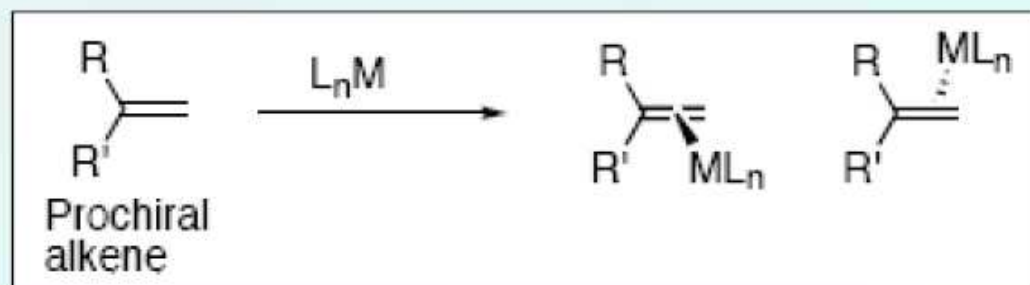
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The first example of this was reported in 1968 by Bill Knowles and coworkers at Monsanto for the asymmetric hydrogenation of α -acetamidocinnamic acid to produce L-Dopa, an important pharmaceutical for the treatment of Parkinson's disease.

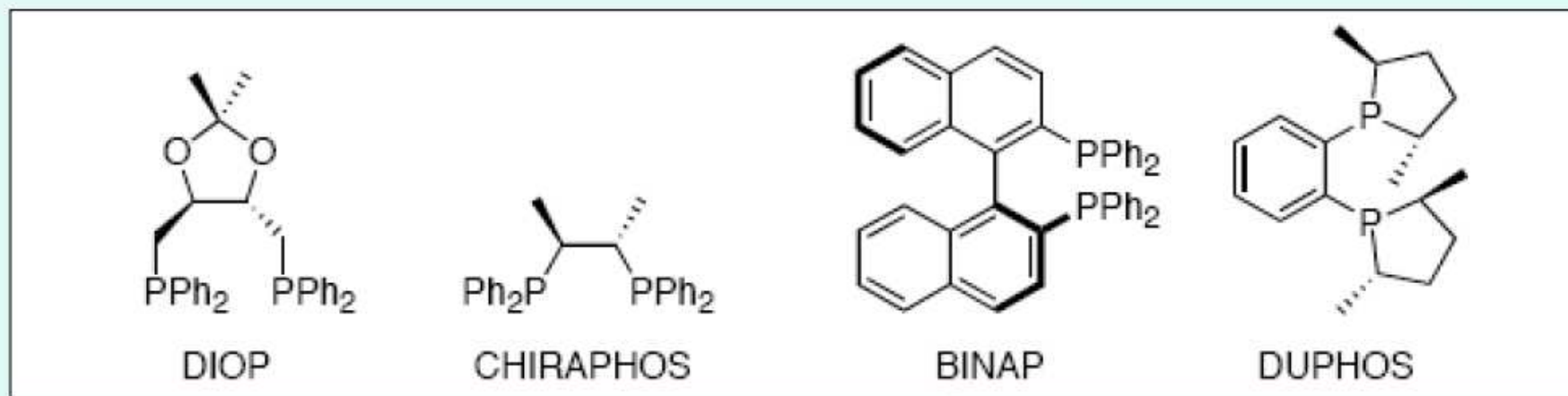


This seminal work by William Knowles was recognized with the Nobel prize in 2001.

Coordination of a prochiral alkene to a transition metal center produces a pair of enantiomeric alkene complexes that are converted to enantiomeric hydrogenation products. If the starting organometallic complex is chiral, though, the alkene complexes are diastereomers of each other.

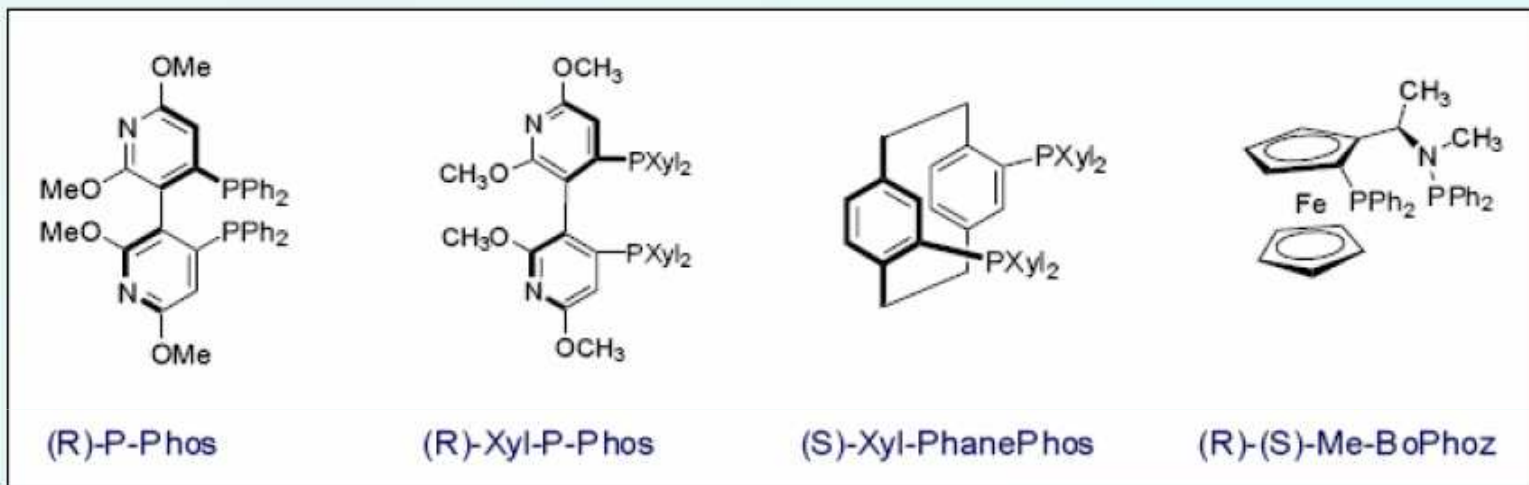


DIPAMP is chiral at phosphorous. Other ligands, which have chiral backbones have become more popular because of their ease of synthesis from optically pure organic precursors:

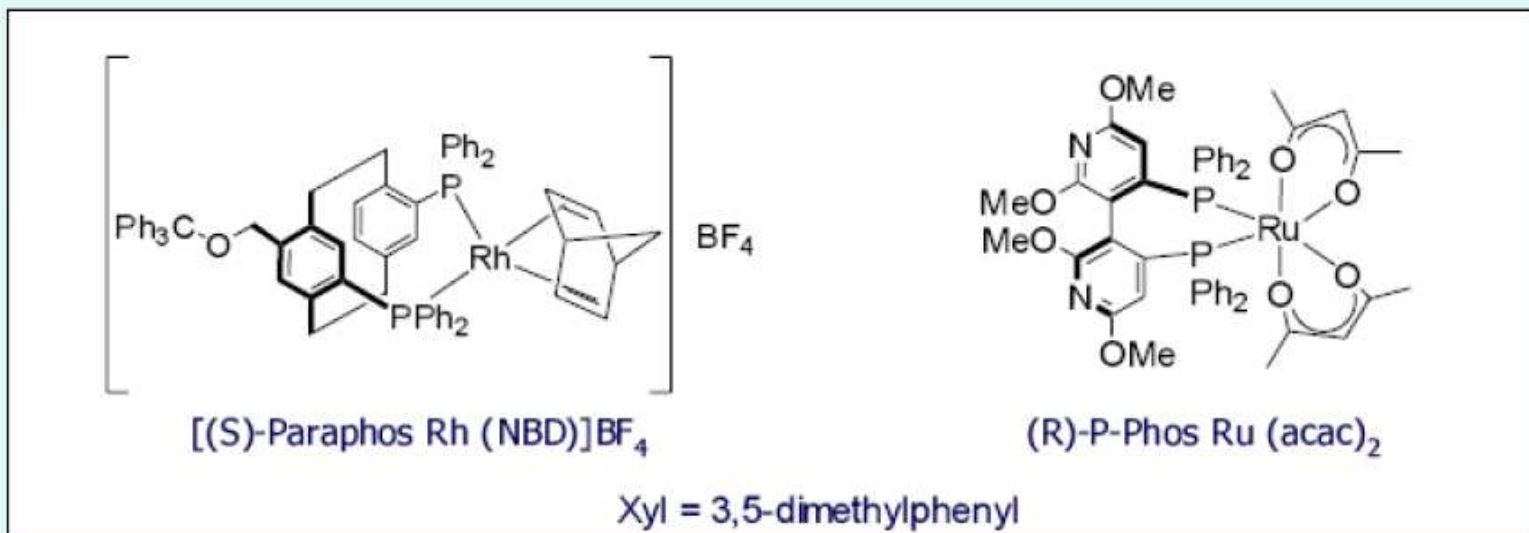


Asymmetric Hydrogenation Ligand/Catalyst Kit

Ligands:

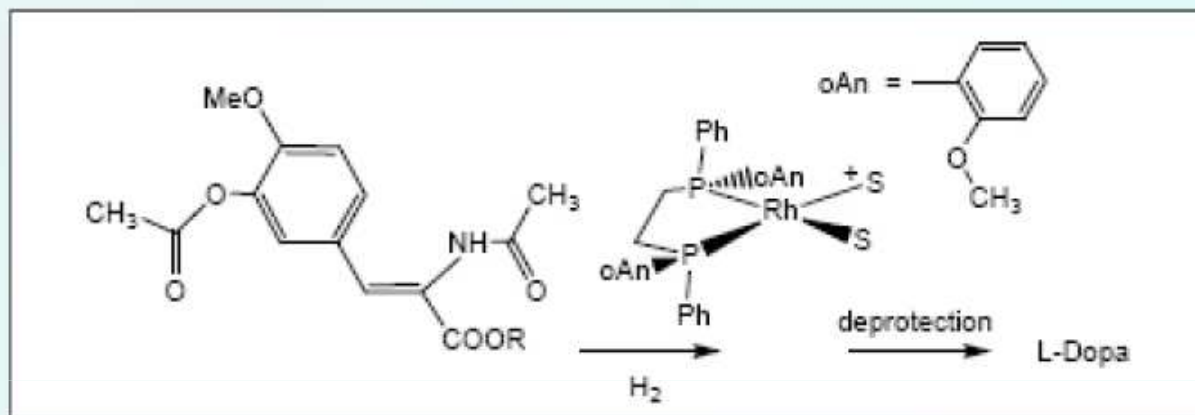


Catalysts:

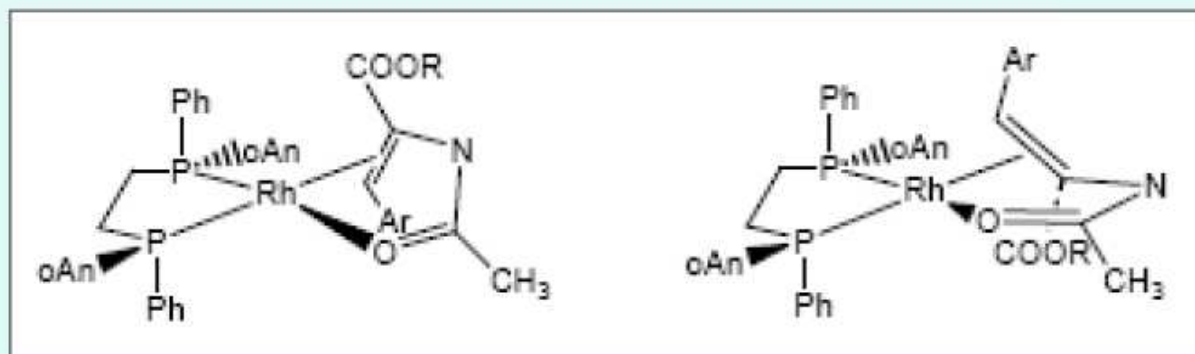


Synthesis of L-Dopa

The hydrogenation reaction is carried out with a substituted cinnamic acid. The acetamido group is of particular importance because it functions as a secondary complexation function in addition to the alkene functionality.

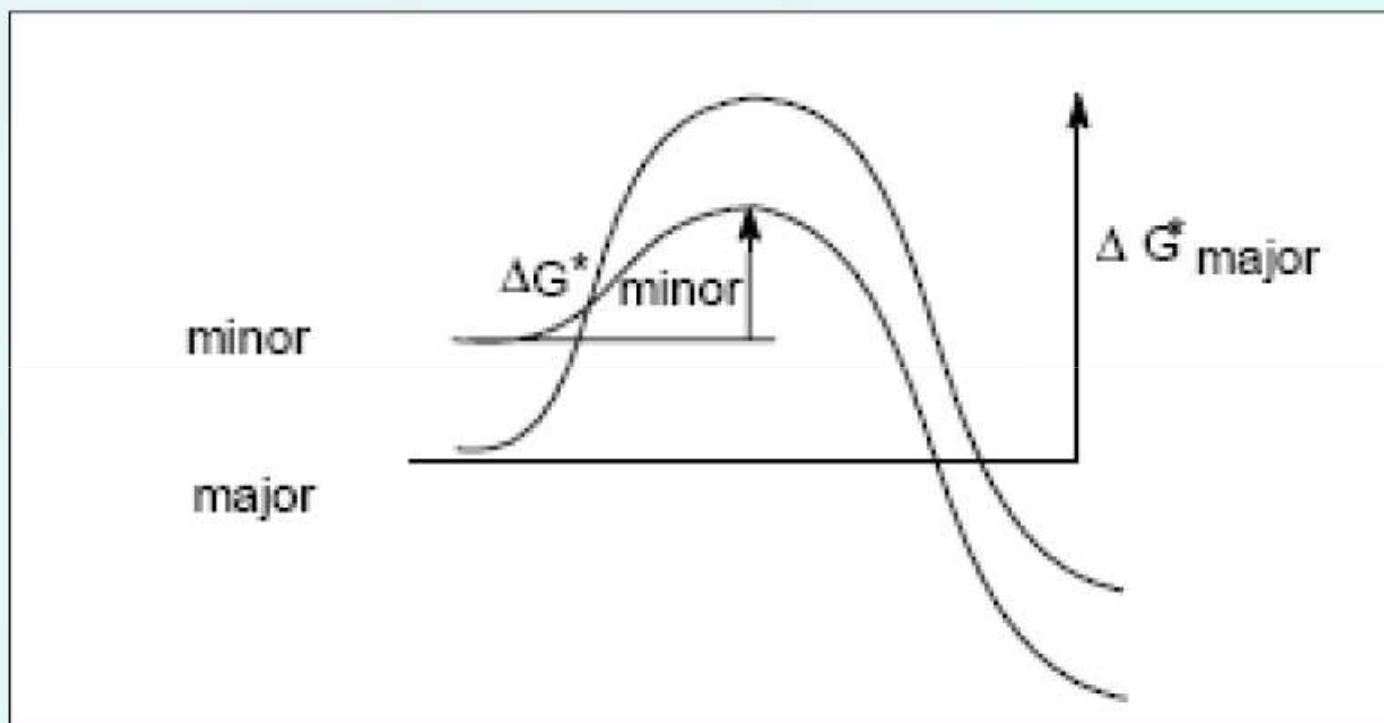


In the first step the alkene co-ordinates to the cationic rhodium species (containing an enantiopure phosphine DIPAMP with the chirality at phosphorus carrying three different substituents, Ph, o-An, CH₂)



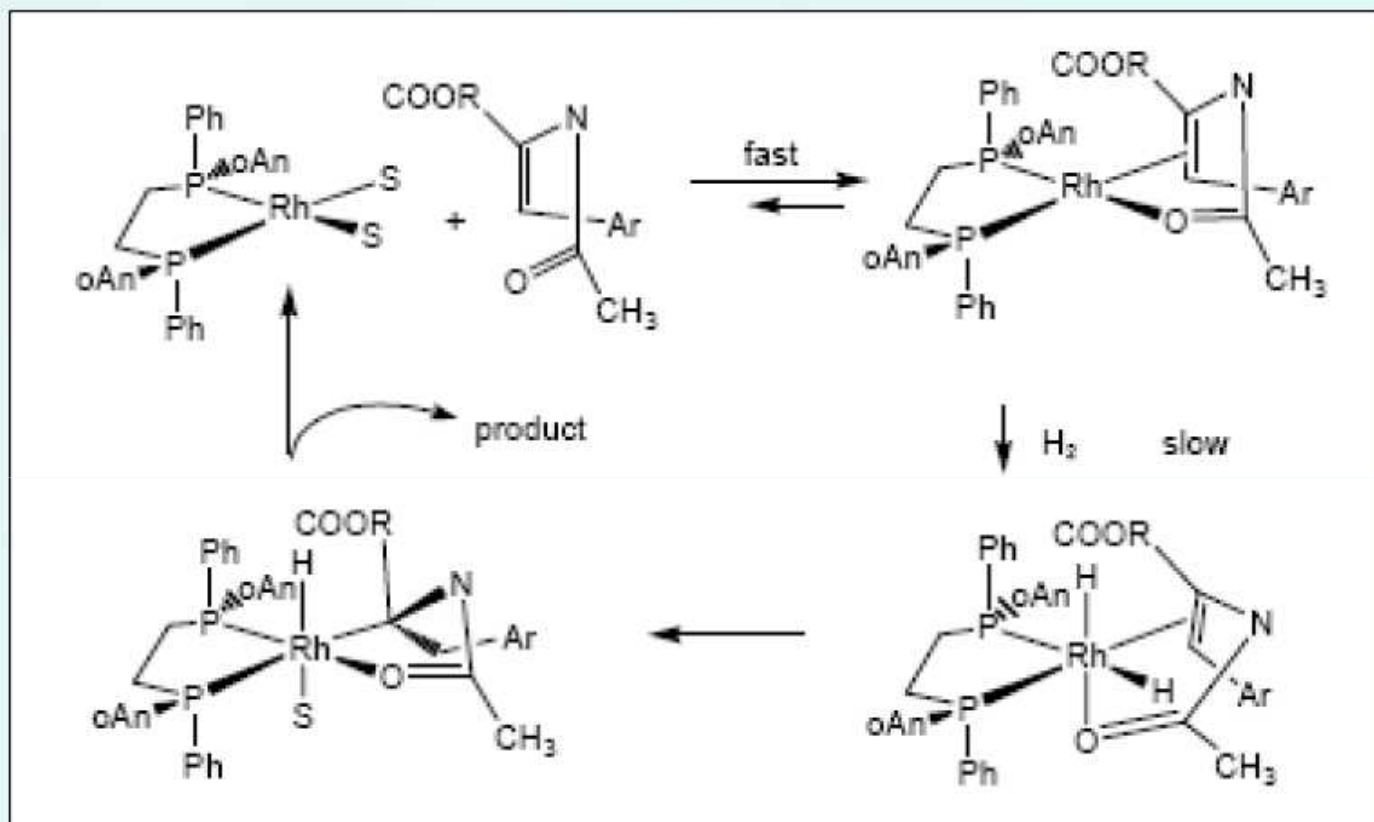
Kinetic studies

Detailed studies (Halpern and Brown) have revealed that the most stable intermediate of the two alkene adducts is not the one that leads to the major observed enantiomeric product:



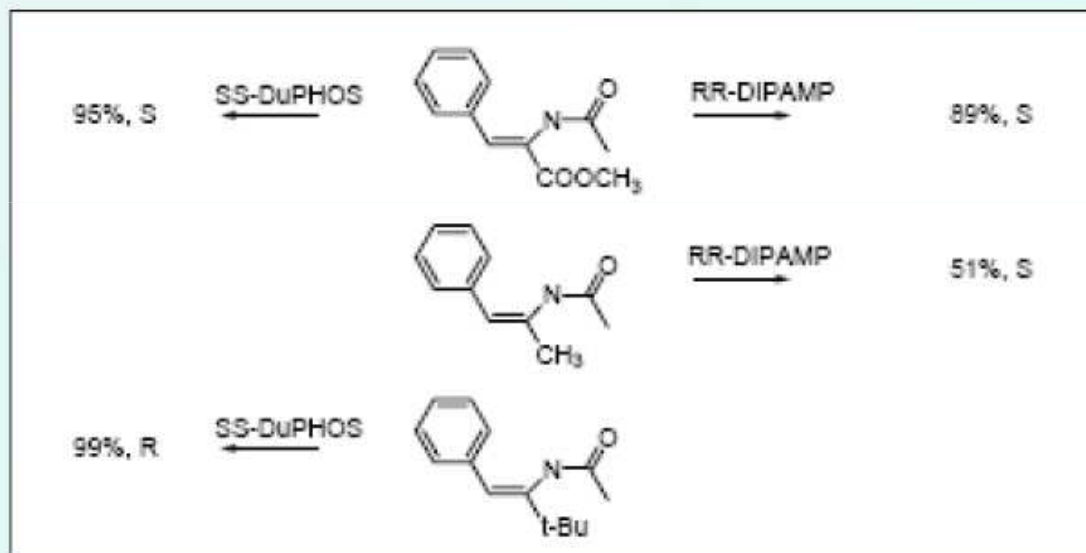
This means that the less stable intermediate alkene complex reacts faster in the subsequent reactions. The next step in the hydrogenation sequence involves the oxidative addition of dihydrogen to the alkene complex.

The oxidative addition of H_2 is irreversible, and provided that no dissociation of the alkene occurs, this step determines the enantioselectivity:



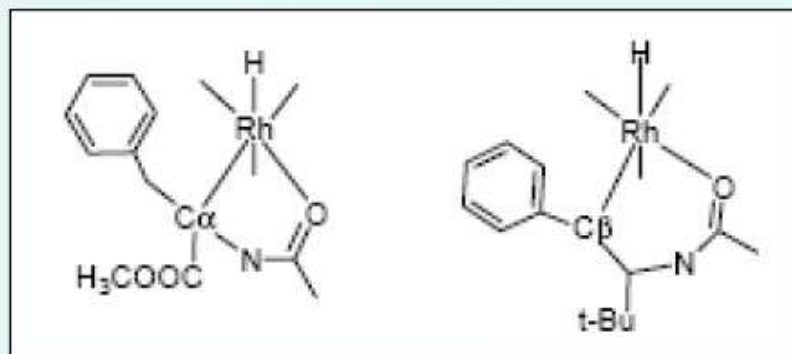
In the examples studied, neither the dihydride intermediates nor the alkyl intermediates have been observed and therefore it seems reasonable to assume that addition of H_2 is also the rate-determining step. The minor diastereomer reacts with H_2 ca. 1000 times faster than the major diastereomer.

The enantioselectivity depends not only on the phosphine structure, but also on the structure of the enamide substrate, especially the α -substituent, as was already reported by Knowles. In a few substrates the enantioselectivity even reverses! These exceptions to the general rule have found explanation in electronic effects. Knowles reported that an electron withdrawing substituent at the α -position was important in order to obtain a high enantioselectivity:



When the α -substituent is an ester and (SS)-DuPHOS is used one obtained the S-enantiomer of the amide. An electron releasing group (t-butyl) in this instance completely reverses the chirality!

The explanation is that for electron-withdrawing α -substituents rhodium forms an α -alkyl bond, while for electron releasing α -substituents rhodium forms a β -alkyl benzylic bond:



It should be noted that not the final stabilities, but rather the intermediates and transition states determine which isomer is formed. In the precursor alkene complex calculations show that already the respective α and β carbon atoms occupy the positions closest to the plane of coordination and that the respective barriers in both cases are indeed the lowest in the model studied.

Polymerization



The two largest production:

Polyethylene

Polypropylene

Mainly by heterogeneous process until the early 1990 (use of homogeneous metallocene catalysts)

Polymers and oligomers:

Typical "polymer properties" appear at » 1000 monomer units

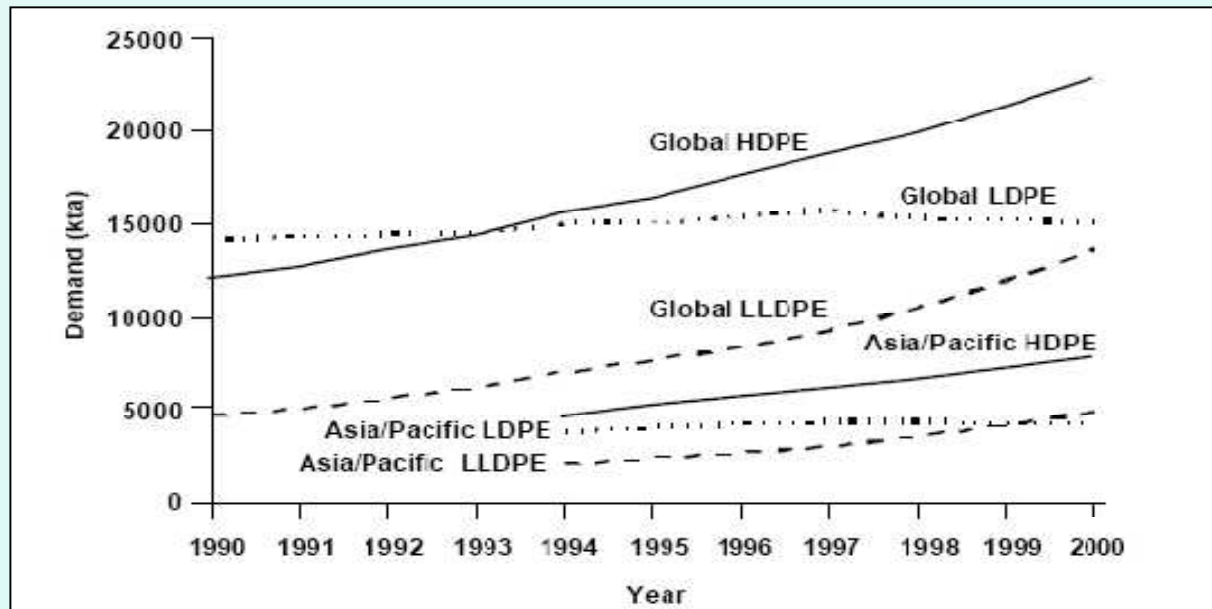
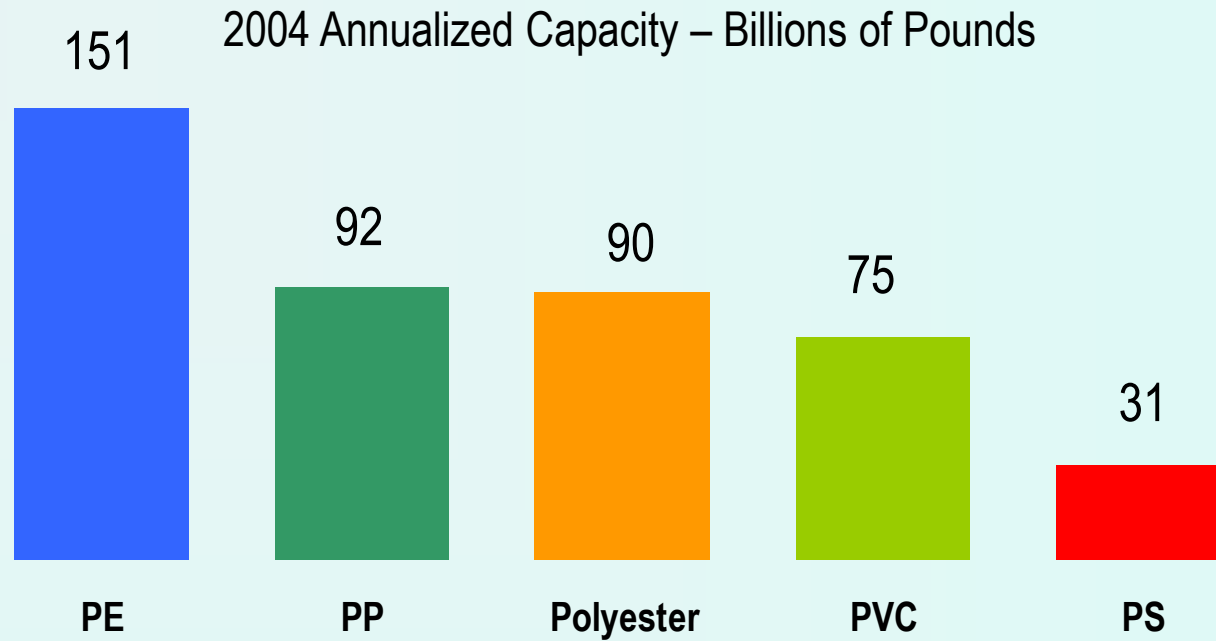
* more for small apolar monomers (polyethene)

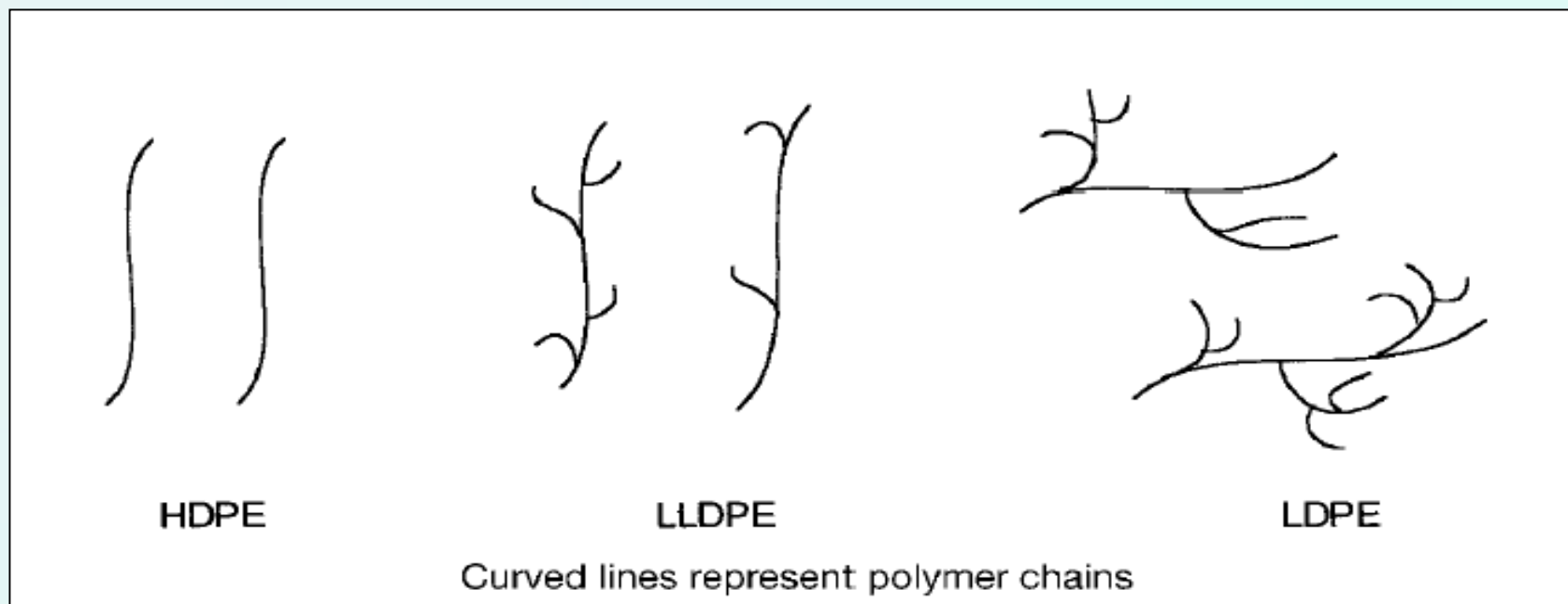
* less for large polar monomers (polyester)

"Oligomers" consist of 5-50 units. This is the region where separation of individual components is difficult.

Oligomers are mostly used as "performance chemicals" (synthetic detergents, fuel additives)

1. Polyethylene (discovered in 1933 by ICI lab)

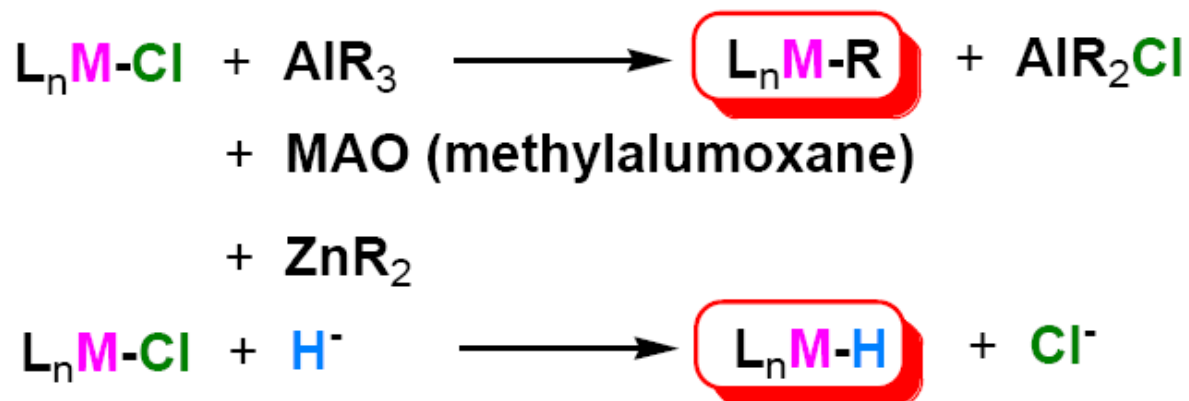




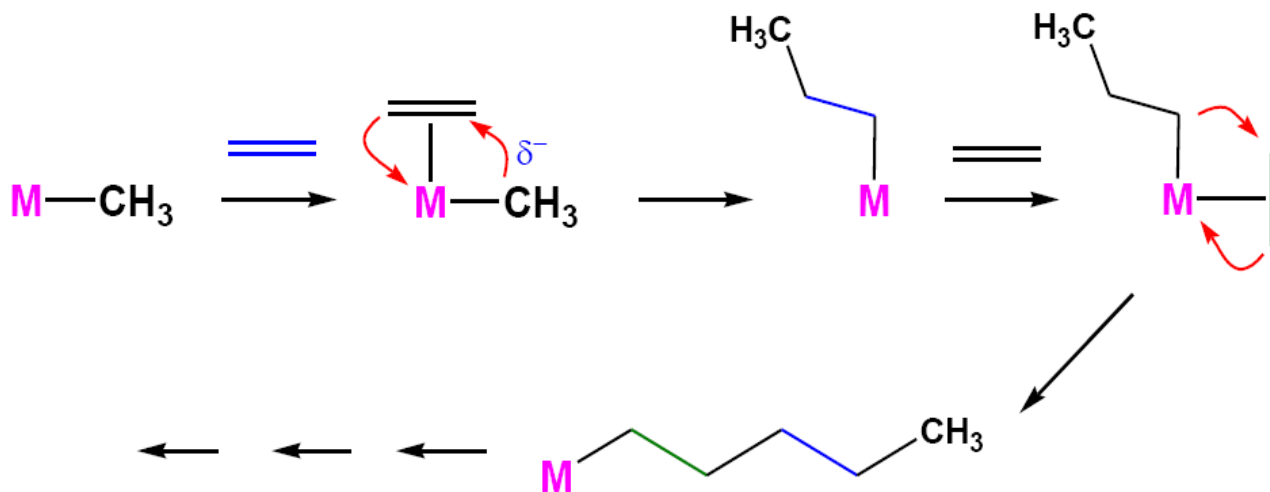
1. HDPE: ← Coordination polymerization
With low temp and pressure (0.96 g/cm^3)
2. LDPE: ← Free radical polymerization
With high temp and pressure (0.92 g/cm^3)
3. LLDPE ←
With low temp and pressure (0.92 g/cm^3) – higher tensile strength and higher impact and puncture resistance

Mechanism of metal-catalyzed polymerization:

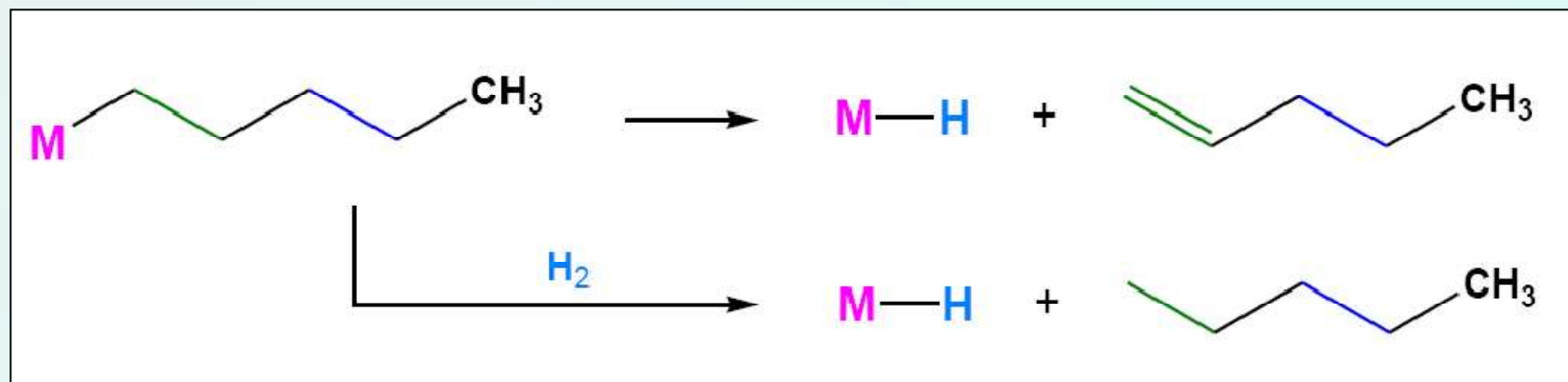
Initiation: generating the active catalyst from a less active catalyst precursor



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



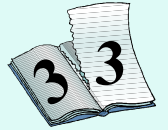
Termination: a reaction step that stops the polymer chain growth



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

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

Molecular weight distribution



M_i = mol wt of polymer i

N_i = number of molecules of this polymer

- Number-average: M_n is the simple average of total mass of the chains divided by the number of chains:

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

- Weight-average: 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.

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

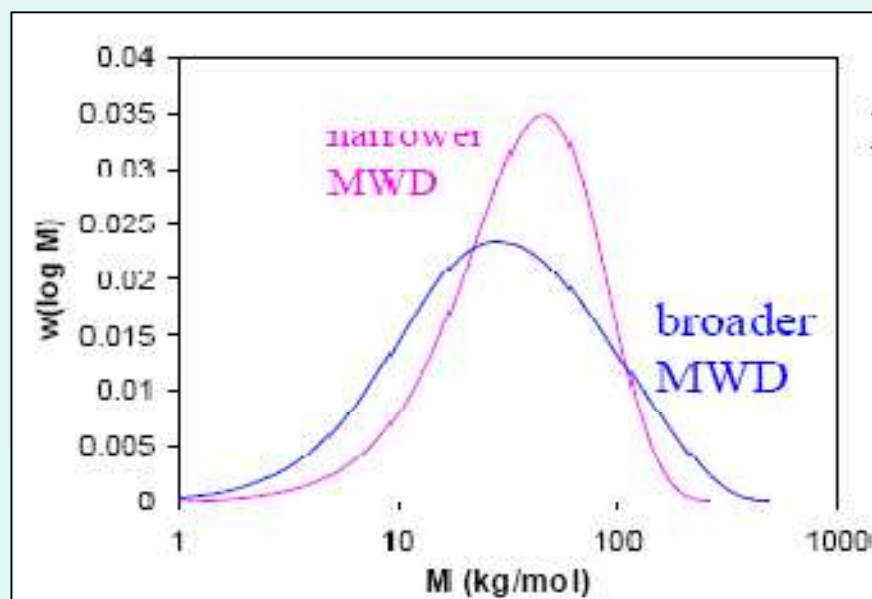
In M_w more “weight” is provided to the higher molecular weight polymers, while M_n treats all of them the same. The basis for M_w is that the larger molecules contribute more to the properties of the polymer so they should have more importance. M_w is always greater than M_n and the narrower the distribution, 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 polydispersity:

$$Q = \frac{\overline{M}_w}{\overline{M}_n}$$

Polydispersity depends on the process and the operating conditions, the catalyst, but is often independent of molecular weight.

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) statistical M_w/M_n polymer distribution is equal to 2.0.

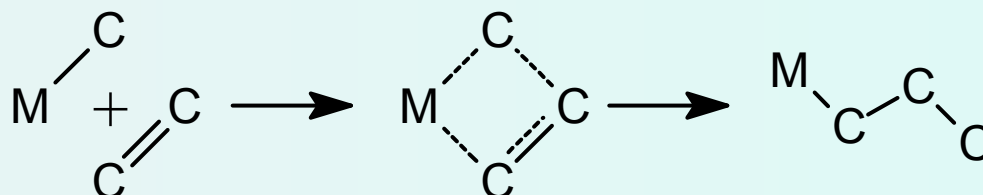


These two materials have the same weight average molecular weight but different breadths of MWD

Metal-centered olefin polymerization



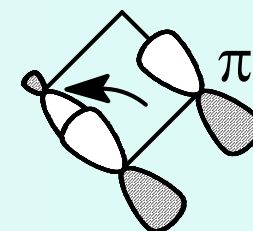
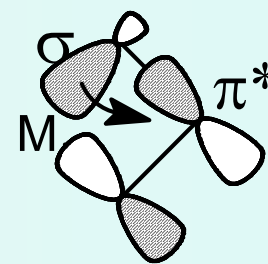
Basic mechanism:



2+2 addition is normally "forbidden".

"Allowed" here because of asymmetry in M-C bond:

- Empty acceptor orbitals at M
- Polarity $M^{\delta+}-C^{\delta-}$ bond
- d -orbitals at M \Rightarrow easier to form small CMC angles



Requirements for an active catalyst

- M-C or M-H bond (can be formed *in situ*)
- Empty site or labile ligand (anion)
- Highly electrophilic metal center
- No easily accessible side reactions
- For stereoregular polymerization: fairly rigid metal environment

CATALYSTS FOR POLYETHYLENE and POLYPROPYLENE

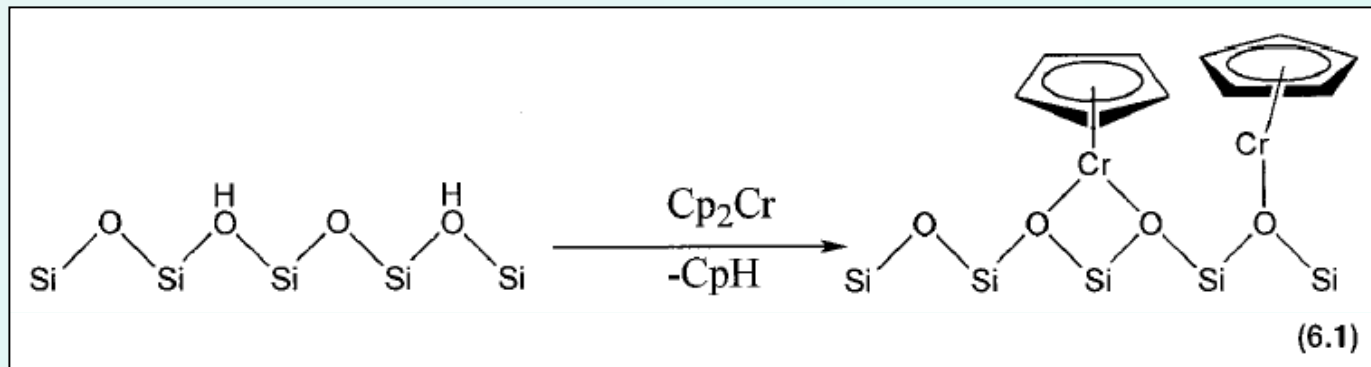


Heterogeneous catalysts

1. Phillips Catalyst (CrO_3 on silica)

2. Union Carbide Catalyst

Silica + chromocene \rightarrow silica supported catalyst



3. Ziegler Catalyst

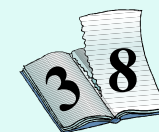
A. TiCl_4 + trialkylaluminum compound in organic solvent

(colloidal \rightarrow heterogeneous)

B. TiCl_3 on solid support

For both chromium- and titanium-based catalysts, choice and pretreatment of the supported catalyst as well as other process parameters determine the molecular weights, distribution of the molecular weights, and the extent of branching of the polymer chains \rightarrow Physical properties

Three generations of catalysts



1. TiCl_4 /organoaluminum compound

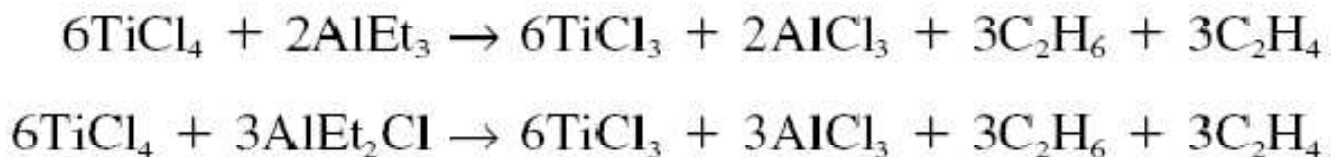
TiCl_3 from the reduction of TiCl_4 by the organoaluminum compound

TiCl_3 exists in 4 crystalline forms: α , β , γ , δ (polymorphs)

β form (purple) has a chain structure, the others (brown) are layers.

α , γ , δ give high tacticity, β does not.

Reduction of TiCl_4 by organoaluminum compound:



2. TiCl_4 /organoaluminum/promoter

Monoethyl reagent, AlEtCl_2 , poisons the catalyst by blocking the coordination site.

Promoters such as ethers, esters, etc. are added to destroy AlEtCl_2 and to prevent its formation by reactions:

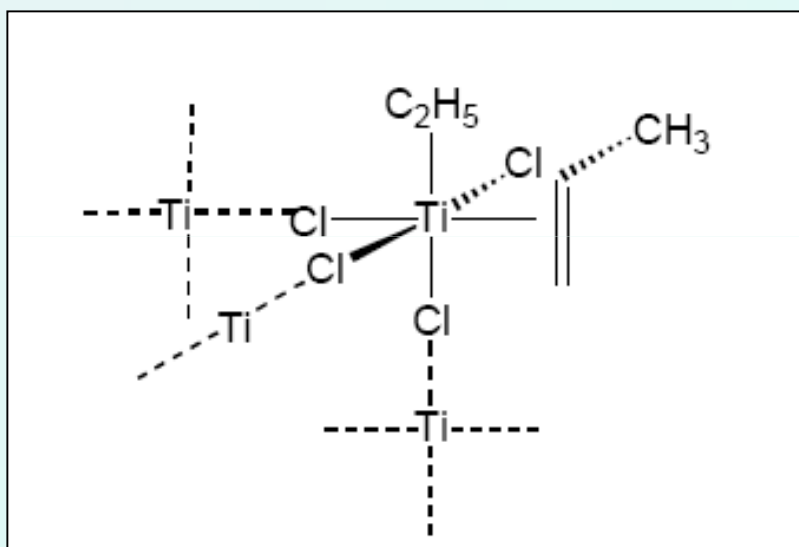


3. TiCl_3 supported on MgCl_2 /organoaluminum/promoter

Highly effective: 30,000 g of polypropylene per gram of catalyst per hour could be achieved with an isotacticity index of 96–99%.

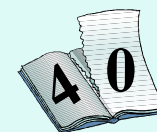
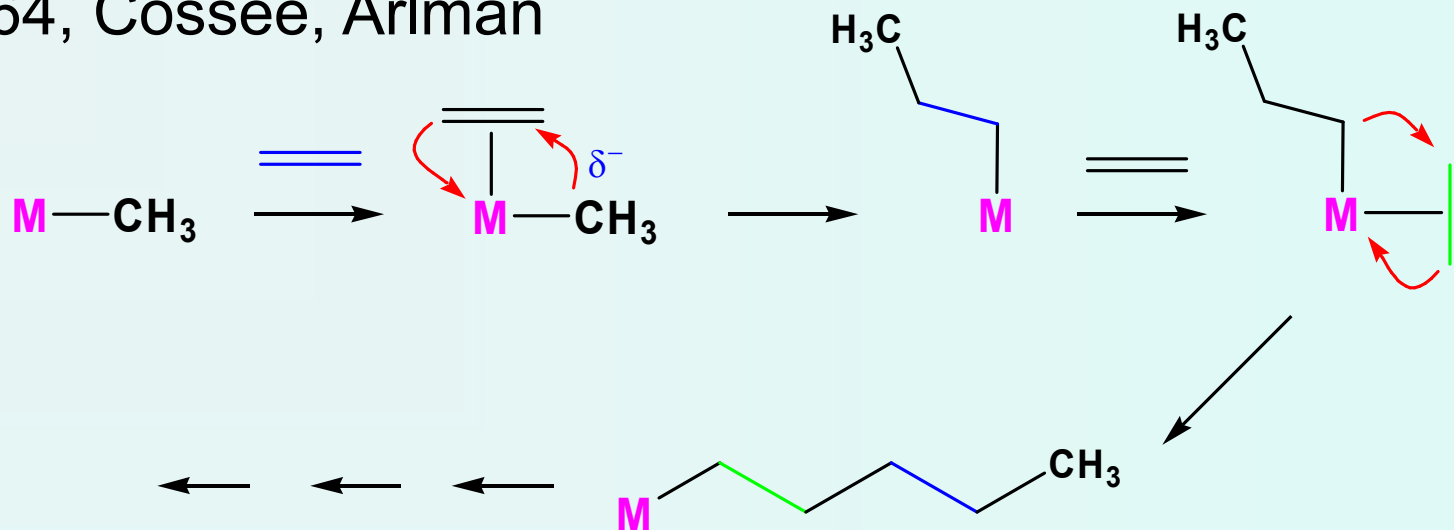


The mechanism proposed for the polymerisation on solid titanium chloride catalysts is essentially the same for all catalysts and it is usually referred to as the **Cossée-Arlman mechanism**



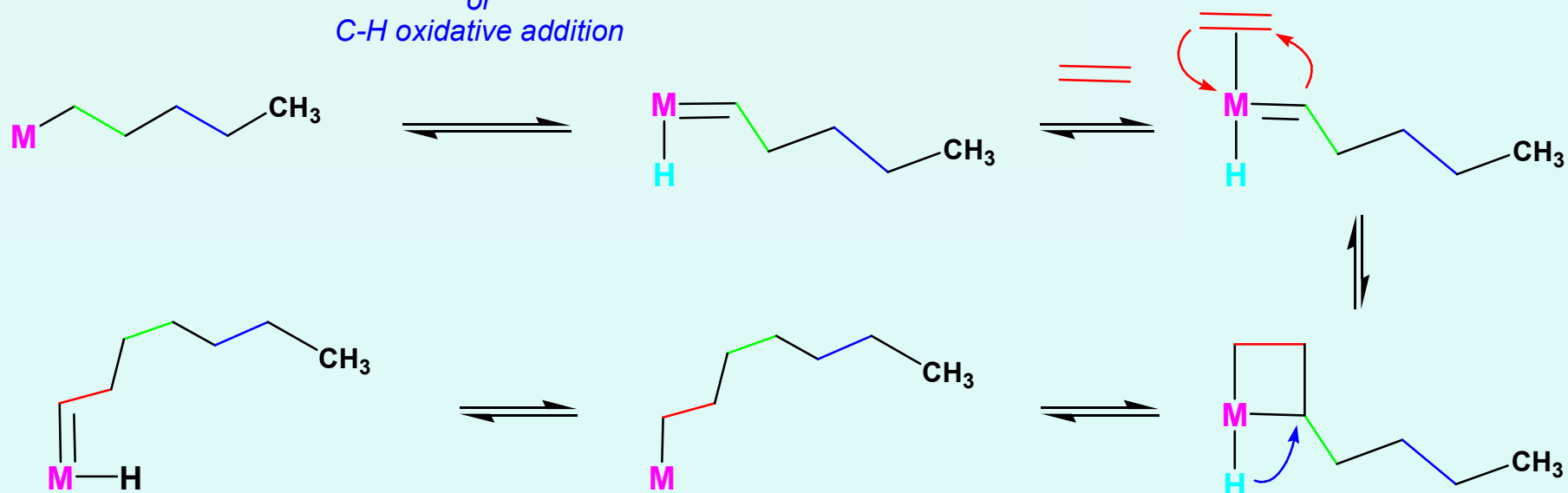
Titanium is hexa-coordinated in the TiCl_3 (or supported catalysts) by three bridging chloride anions (indicated by dashed Ti atoms), one terminal chloride anion, and one terminal chloride that is replaced by an alkyl group by the alkylating agent (Et_2AlCl or Et_3Al), and a vacancy that is available for propene co-ordination

1964, Cossee, Arlman

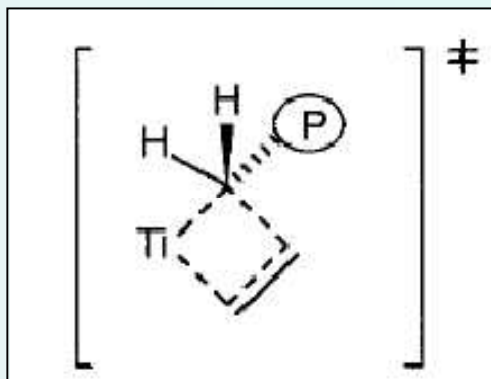


1978, Green, Rooney

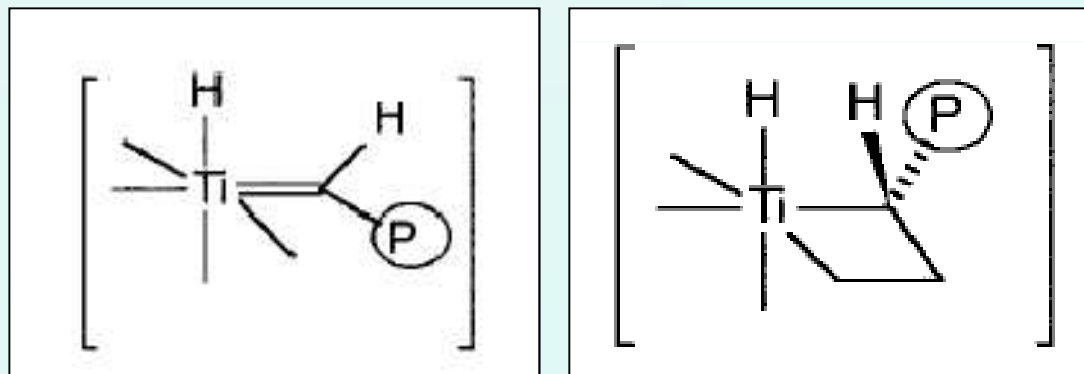
*α -hydride elimination
or
C-H oxidative addition*



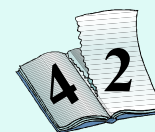
The *transition state* for the **Cossee–Arlman** mechanism:



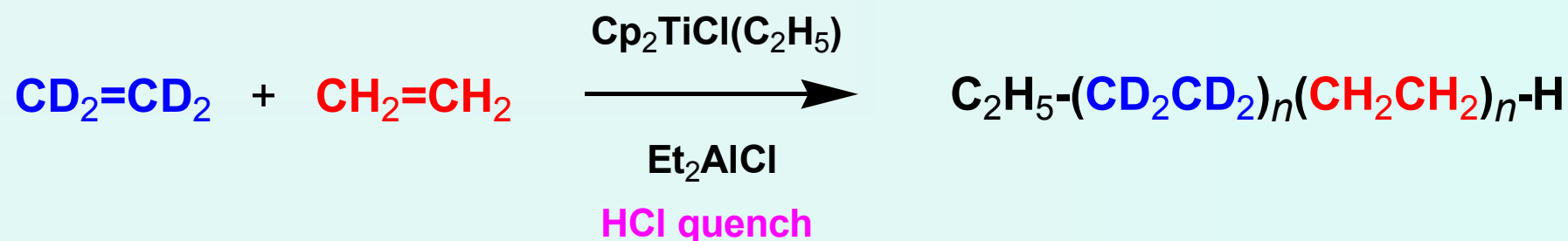
The two *intermediates* for the **Green-Rooney** mechanism:



It is difficult to determine the transition state or intermediates in heterogeneous Ziegler-Natta catalysis \Rightarrow difficult to decide what mechanism (mechanism Cossee-Arlman or Green-Rooney Mechanism) is the true mechanism.

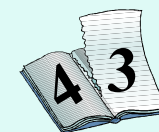


If the migratory insertion mechanism was working, one should *NOT* get any scrambling of the deuteriums and hydrogens in the polyethylene chain (easily confirmed by ^1H and ^2H NMR). However, if the polymerization was working by the Green-Rooney metallacycle mechanism, the α -hydride elimination and 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

Summary about commercial Ziegler-Natta catalysts:

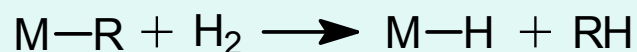


- High-surface TiCl_3 formed *in situ* from TiCl_4 and Al alkyl
- TiCl_3 on support (e.g. MgCl_2), prepared in a complicated process starting e.g. from TiCl_4 and $\text{Mg}(\text{OAr})_2$.

Nature of active site not very clear.

Chain transfer is slow \Rightarrow high MW

H_2 or temperature used to control MW:



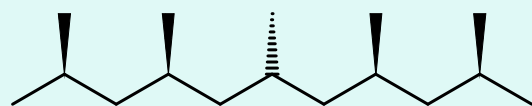
Distribution of different sites on surface

\Rightarrow broad MWD ($Q = 5-30$)

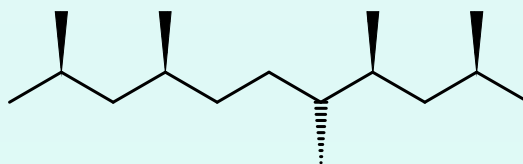
Catalyst productivity $> 10^6$ g/g Ti/hr

\Rightarrow catalyst residue removal not needed.

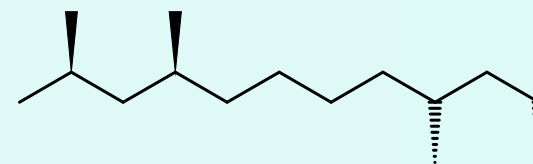
Errors in Ziegler-Natta catalysts:



Stereo-errors

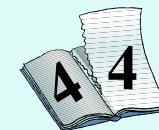


Regio-errors



"1,3-insertion"

Metallocene Catalyst

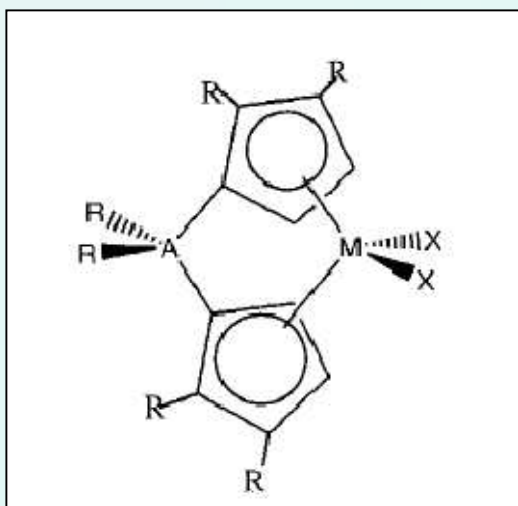


Background

Homogeneous catalysts discovered in 1980s

\$5 billions investment + 1500 patent

0.5 mln tones of polypropylene a year in 2003



M = Ti(IV), Zr(IV)

A = C(IV), Si(IV)

R = H, CH₃, etc.

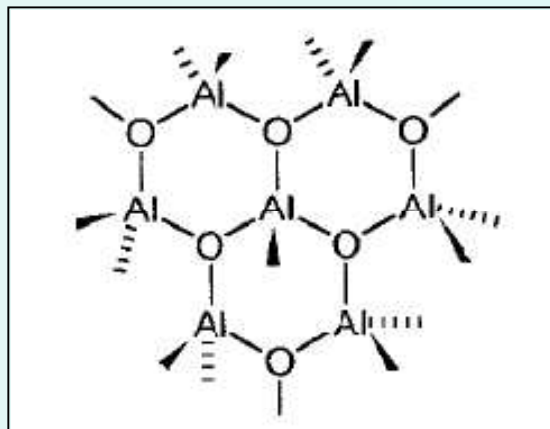
X = Cl, Alk

The development of the new family of homogeneous catalysts based on biscyclopentadienyl Group 4 metal complexes for the stereoselective polymerisation of alkenes is mainly due to [Kaminsky, Ewen and Brintzinger](#).

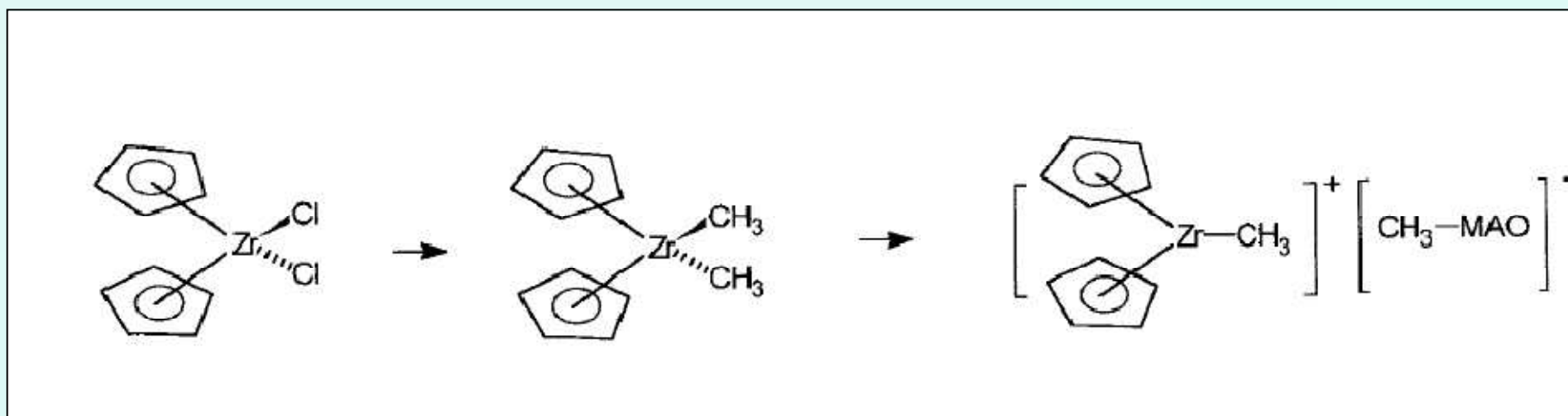
In 1980 Kaminsky reported on an extremely fast homogeneous catalyst for the polymerisation of ethene formed from the interaction of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ and $(\text{CH}_3\text{AlO})_n$

MAO

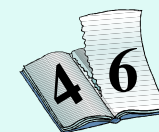
The general formula of MAO is given by $\text{Me}_2\text{Al}[\text{O-AiMe}]_n\text{-OAlMe}_2$, where n is between 5 and 20.



MAO to generate coordinatively unsaturated intermediates:

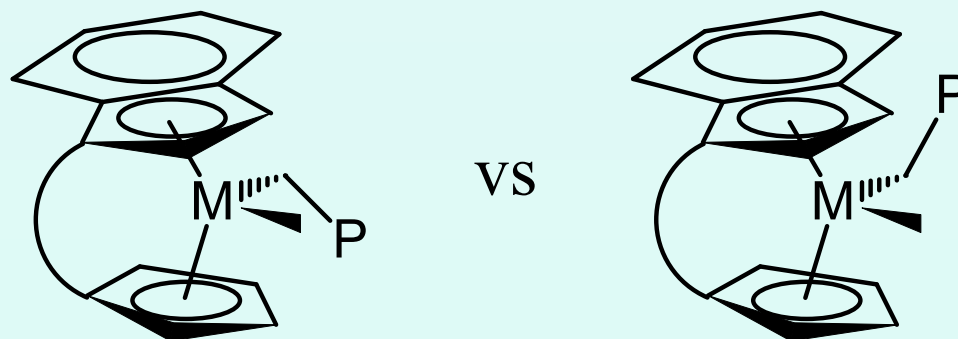


Advantages of Metallocene catalysts over Ziegler-Natta catalysts

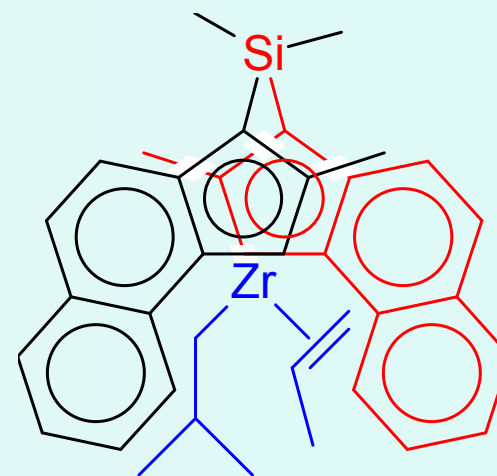
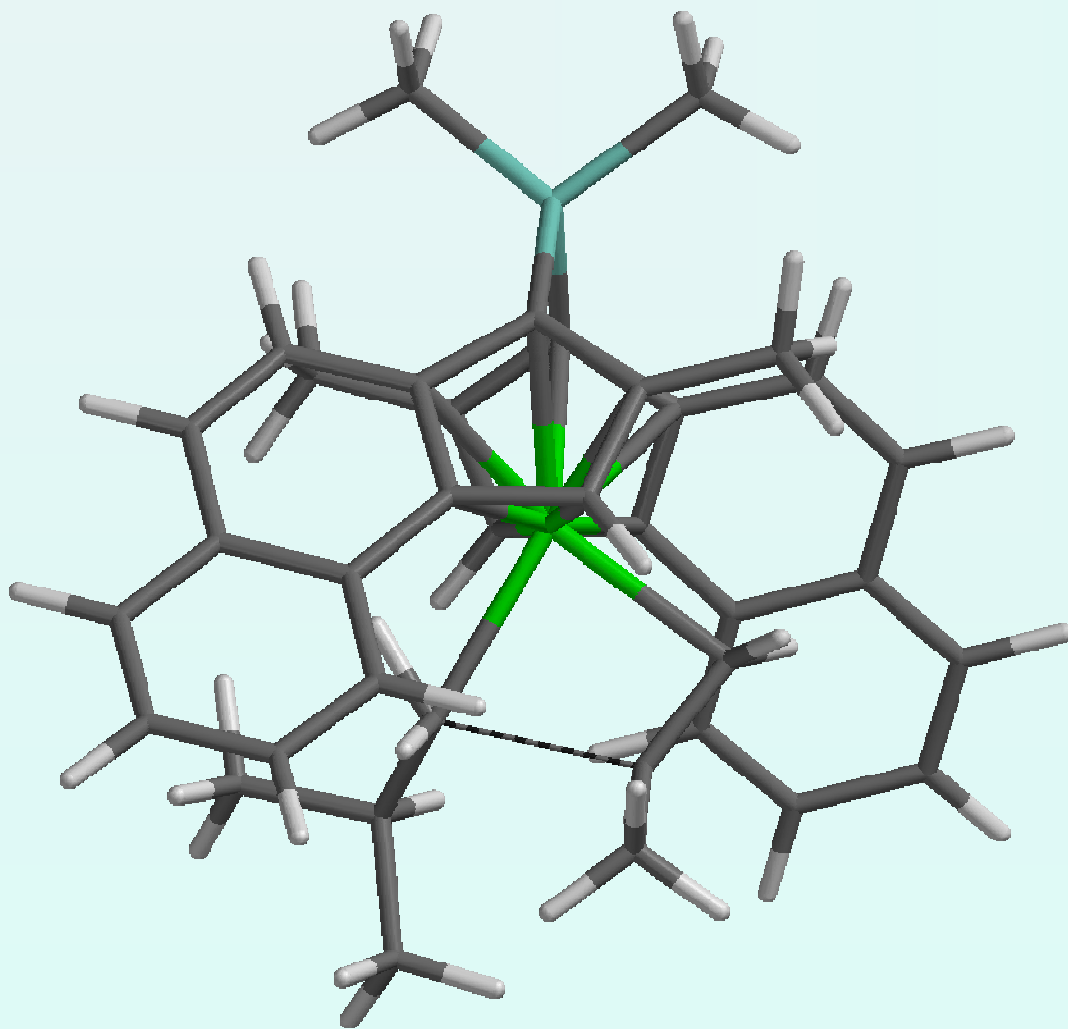


1. Polymerize a very wide variety of vinyl monomers irrespective of their molecular weights and steric features.
2. Produce extremely uniform homopolymers and co-polymers (Ziegler–Natta catalyst, with nonidentical coordination environments around the catalytically active metal centers, give polymers with broad molecular-weight distributions.)
3. The predominant mechanism for chain termination is by β -hydride elimination. This produces a vinyl double bond at the end of each polymer chain.
4. The most important feature of the metallocene catalysts is their ability to produce highly stereoregular polymers \rightarrow choices of ligands

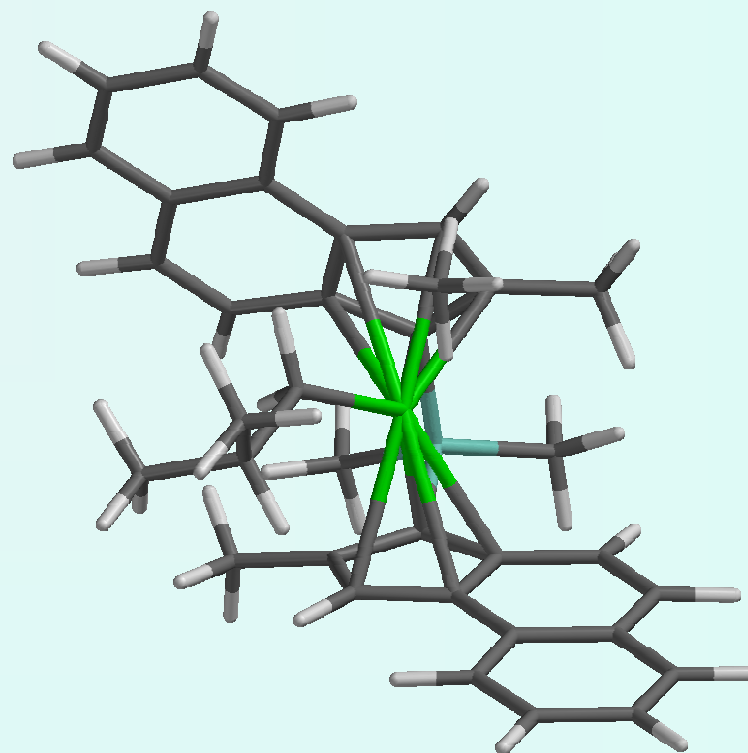
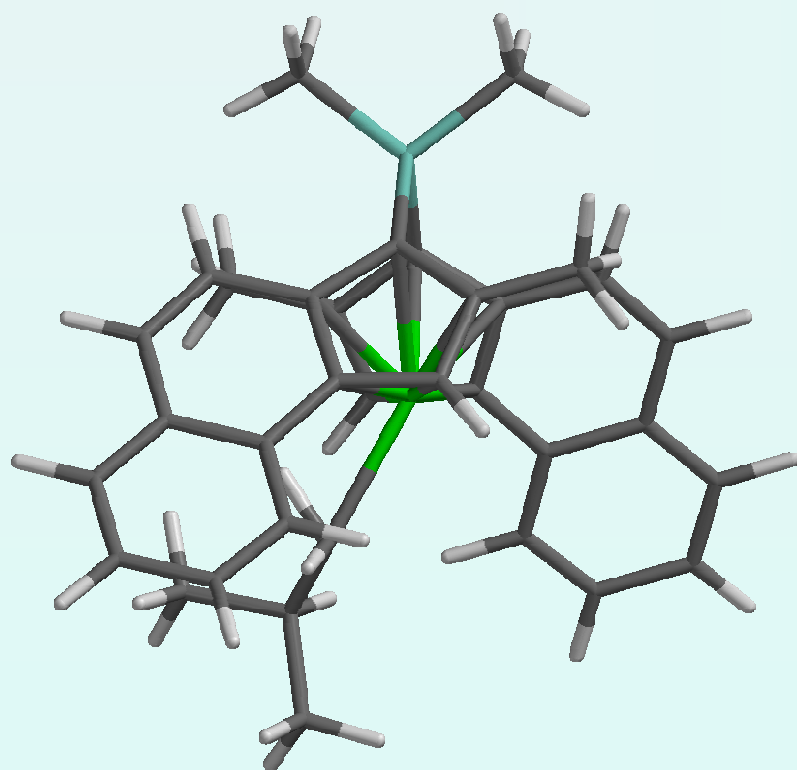
The "trick" of metallocenes - discrimination between chain positions ("site control")



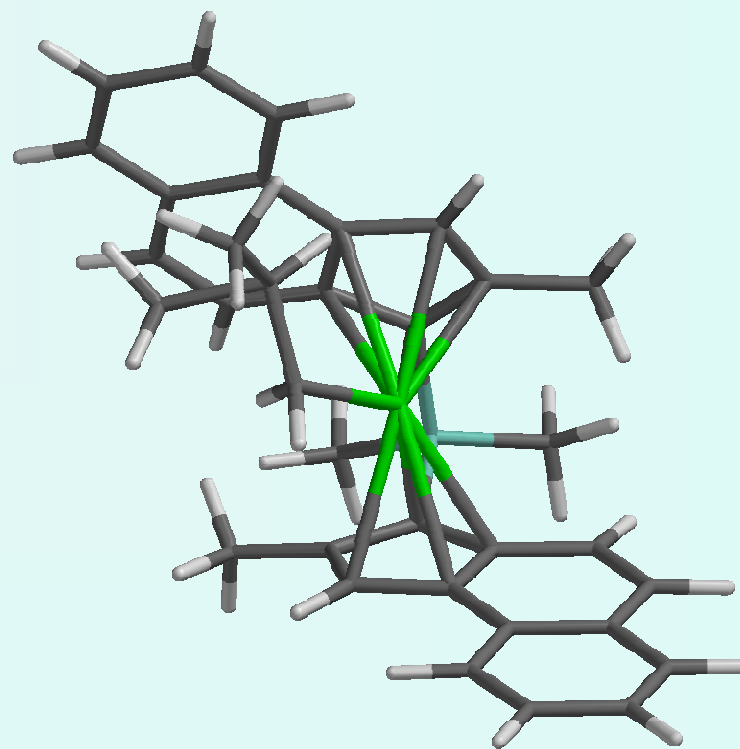
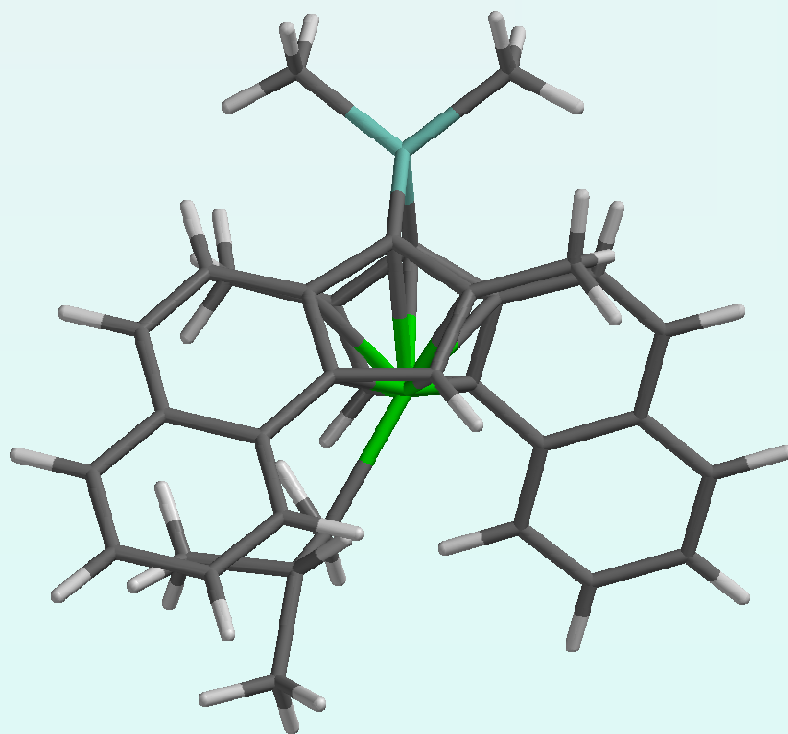
One "real" catalyst



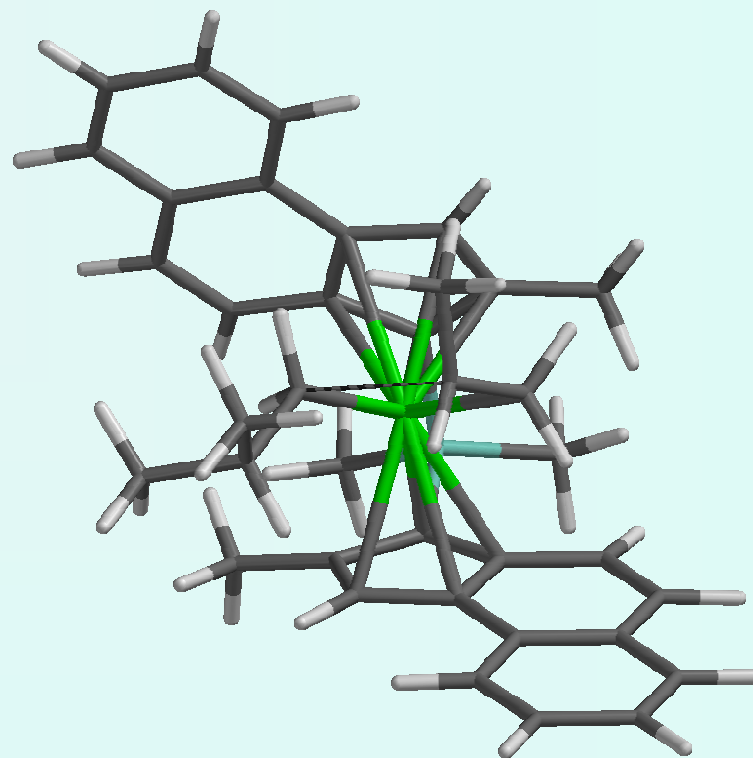
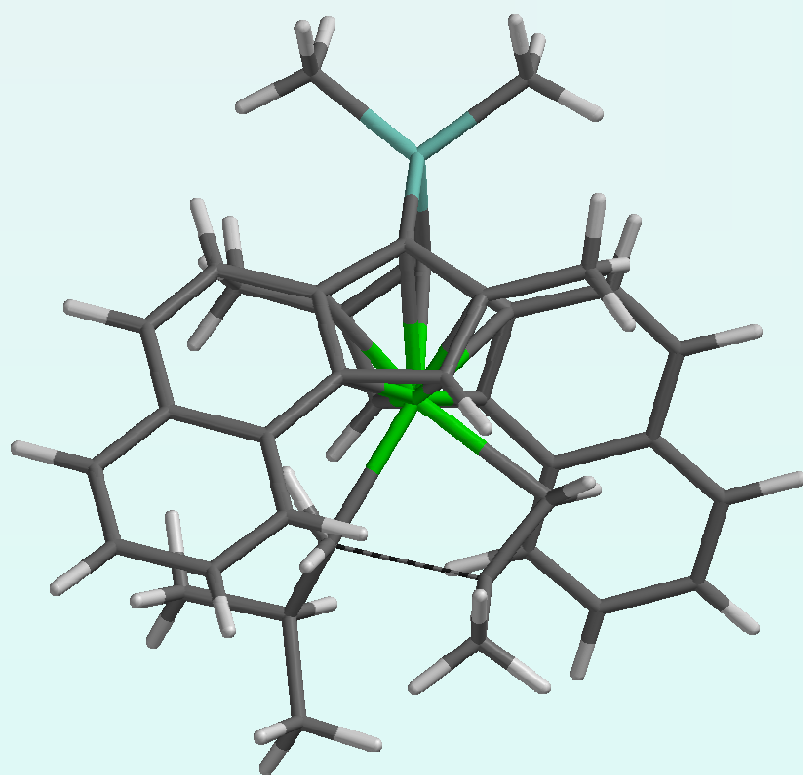
Preferred alkyl chain orientation



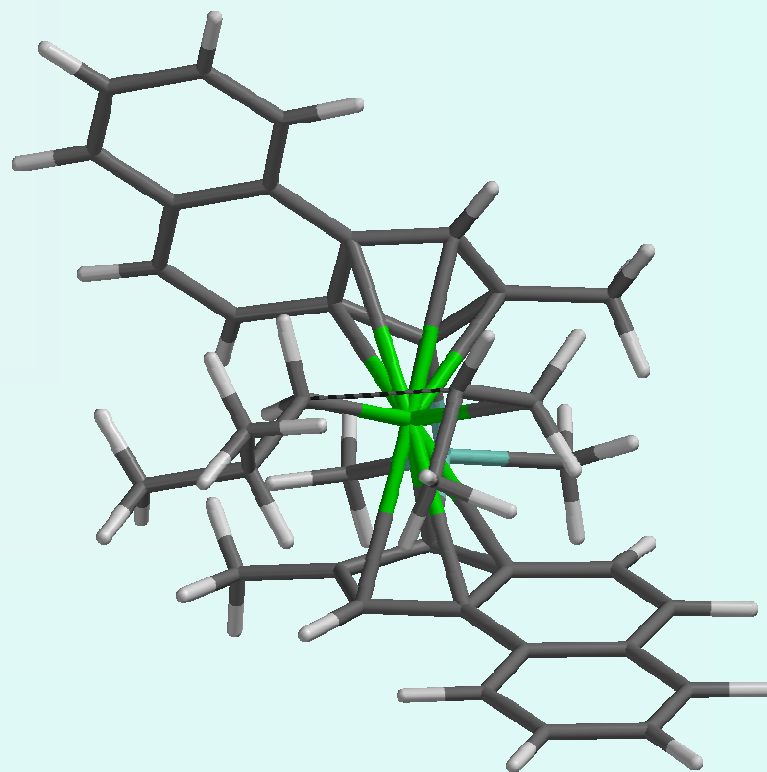
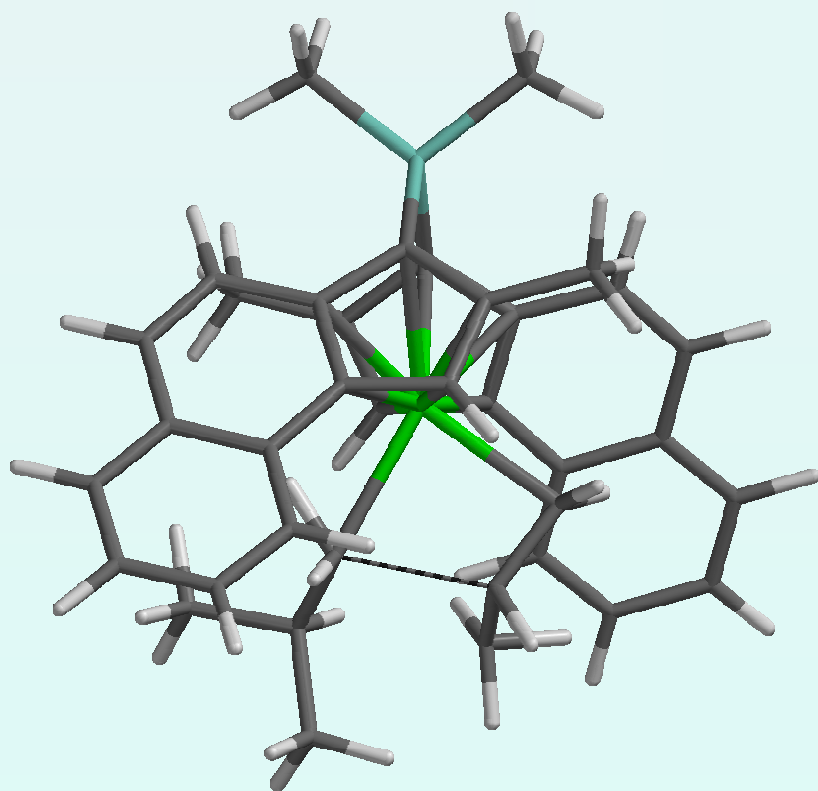
"Wrong" chain orientation



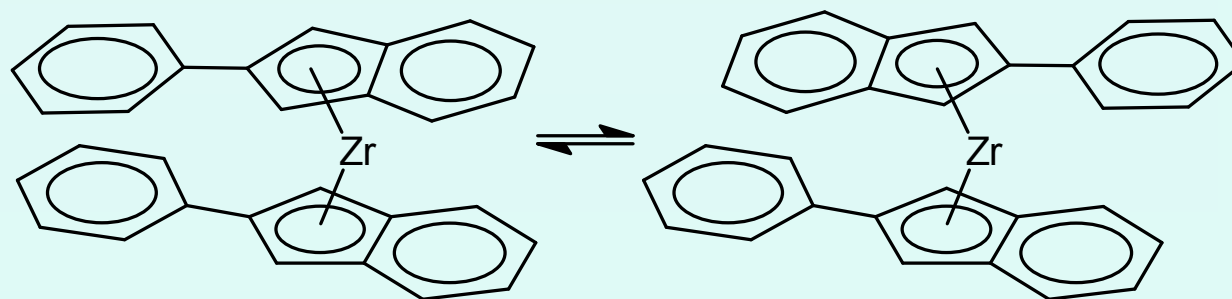
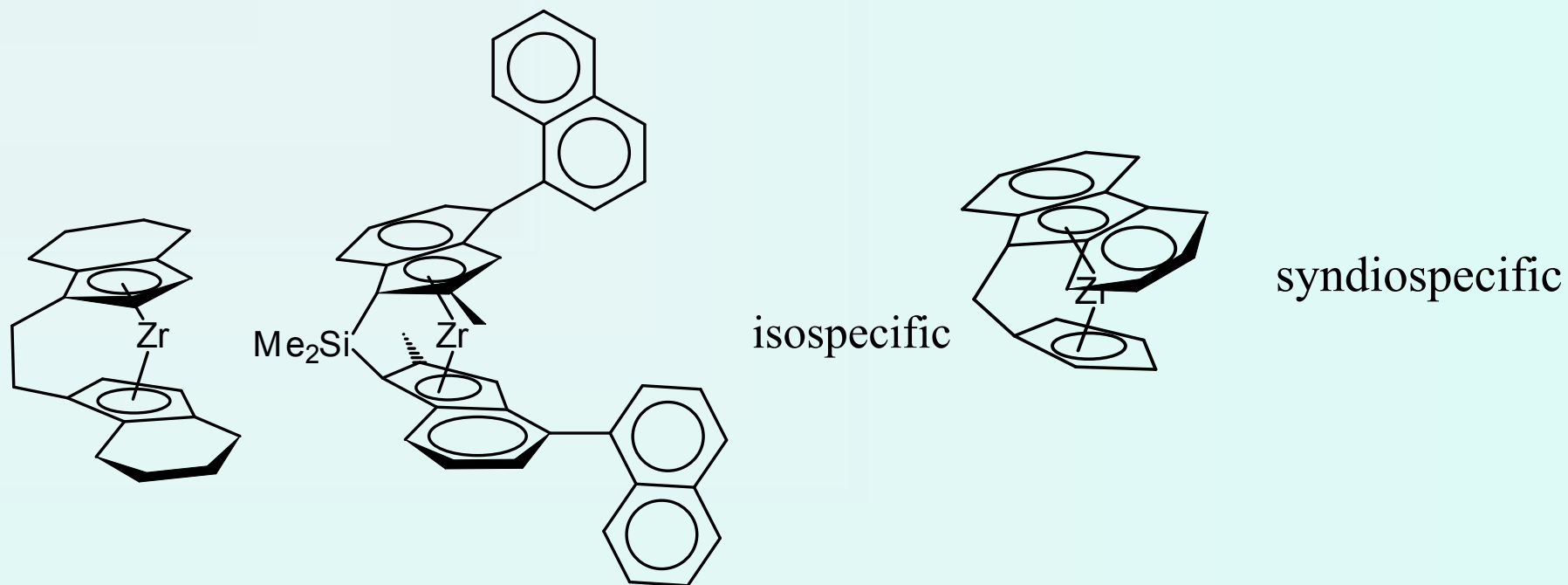
Preferred olefin orientation



"Wrong" olefin orientation



Typical metallocenes

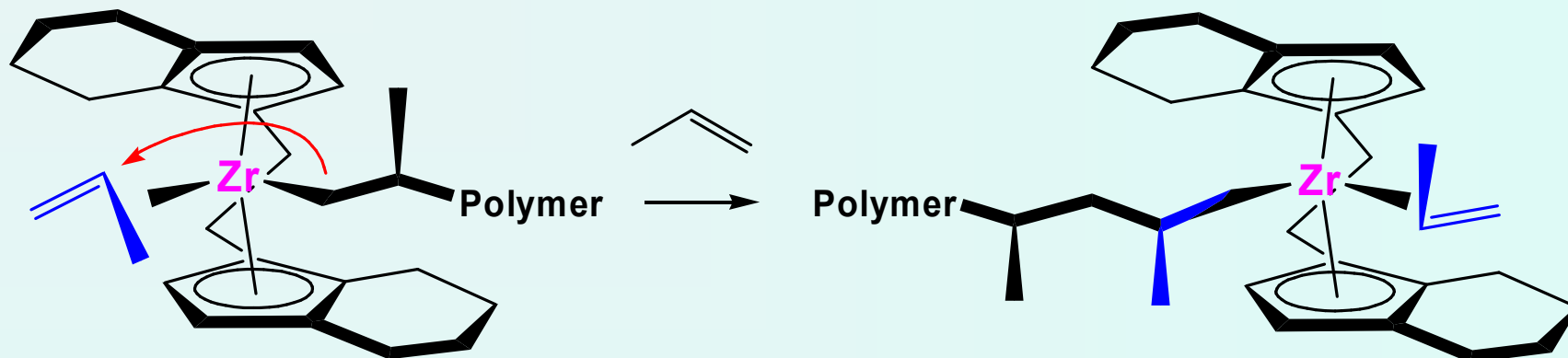


block-isotactic

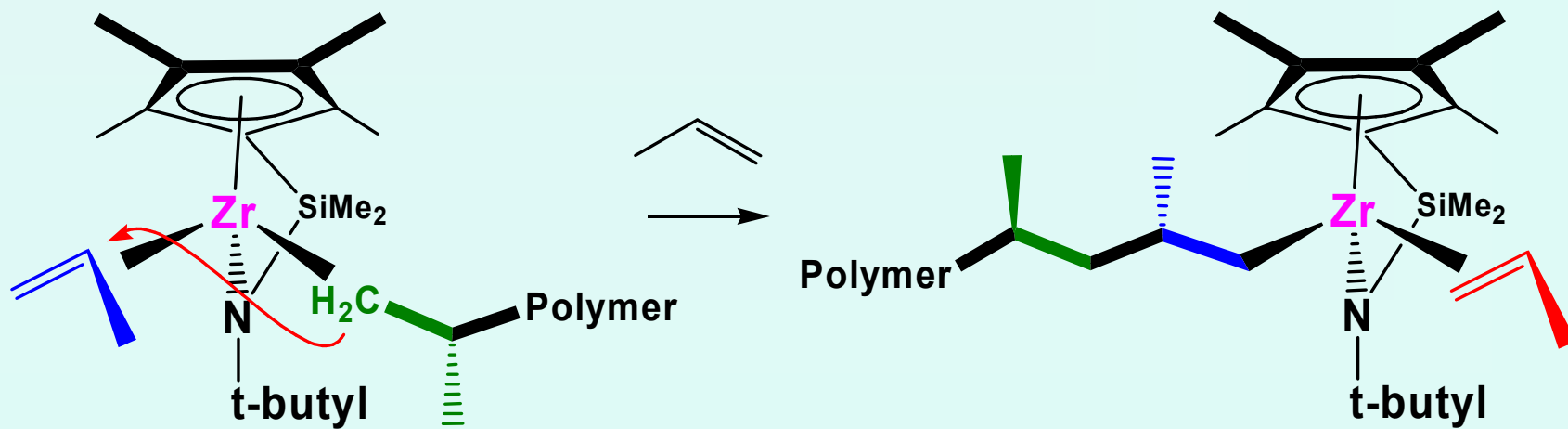
A catalyst with small ligands that offer little steric directing effect, like Cp_2TiCl_2 , will generate **atactic** polypropylene



C_2 symmetry (chiral) - Isotactic polymer



Bulky-Small Catalyst environment - Syndiotactic polymer



After every insertion, the chain moves to the other site at Zr

- Chain preferences the same (i.e. related by 2-fold axis)
⇒ isospecific polymerization
- Chain preferences opposite (i.e. related by mirror plane)
⇒ syndiospecific polymerization
- One site with a strong preference, the other without preference
⇒ hemi-isotactic polymerization

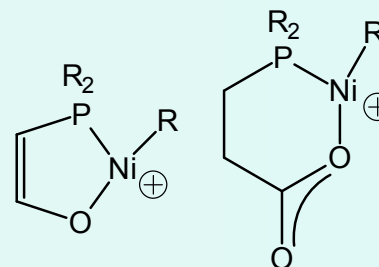
Summary about metallocene catalysts:

- Difficult to get MW as high as Ziegler-Natta catalysts
- H₂ has same effects as in Ziegler-Natta catalysis
- Narrow MWD ($Q \approx 2$)
- Rates can be extremely high ($> 10^7$ g/g Zr/hr)

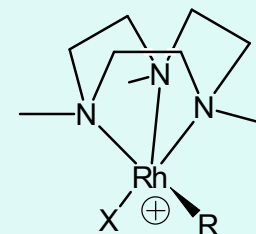
Polymerization at LTM centers



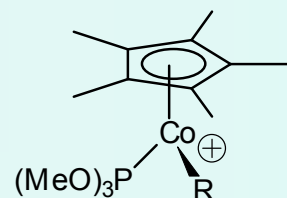
- Mostly low MW,
but with "hard" donors MW can be higher.
- Isomerization ("chain running").
- Lower sensitivity to functionalized olefins.



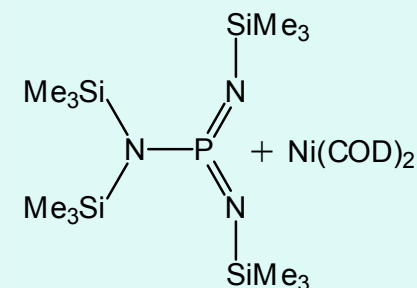
SHOP (Keim)



Flood



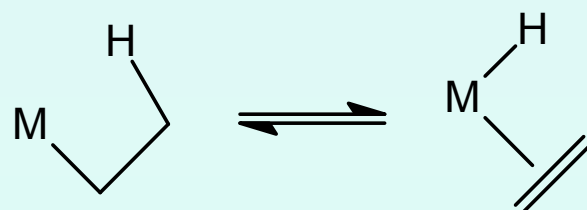
Brookhart



Fink

Problem:

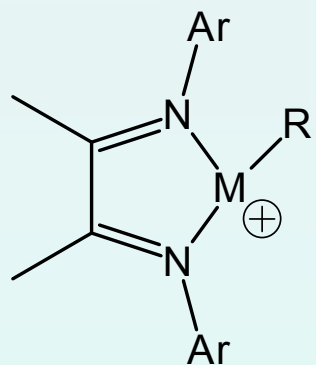
- Easy chain transfer by β -elimination because M-H bond stable (relative to M-C bond).



- Low MW (dimers or oligomers instead of polymers)

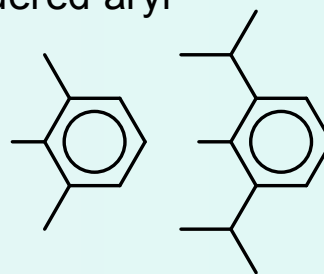
Good example: Brookhart system (1995)

These catalysts operate via the simple Cossee alkene addition and migratory insertion mechanism.

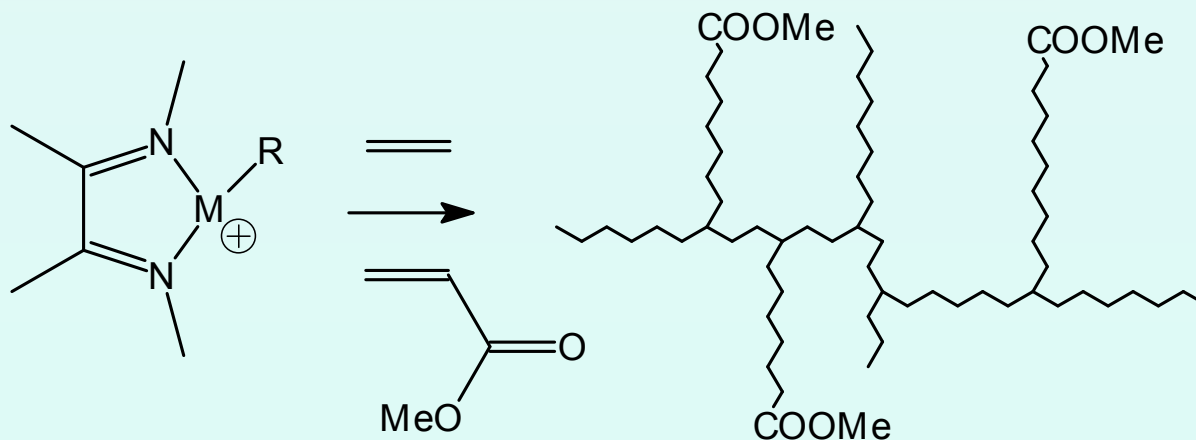


M = Ni or Pd

Ar = hindered aryl



More compatible with functionalized olefins(!)



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.

