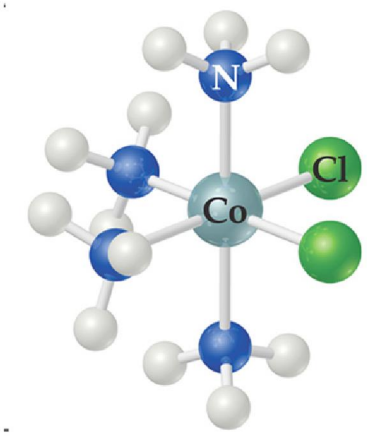


Homogeneous catalysis

Ligand Substitution Reactions

$$ML_n + xP \rightleftharpoons ML_{n-x}P_x + xL$$

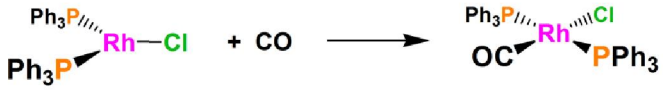
The mechanism of this substitution will almost always depend on whether the parent ML_n complex is coordinatively saturated or not!

Saturated Complex: Dissociative Pathway!

Unsaturated Complex: Associative Pathway (usually)
Dissociative pathway (sometimes)

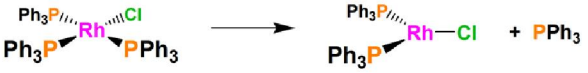
Most of the substitutions we will study will involve 2e- pathways. Odd e- or radical pathways are known, but less common.

Ligand Addition (association): this is when an incoming ligand coordinates to a metal center that has one or more empty orbitals available.

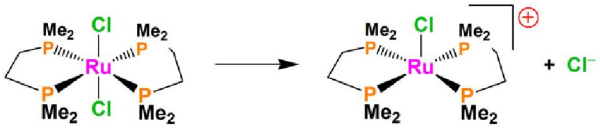


This Rh(+1) complex is d^8 and only 14e-. Adding a ligand takes one to the more stable 16e- square-planar complex.

Ligand Dissociation: this is when a ligand coordinated to a metal dissociates (falls off). The probability of a specific ligand dissociating depends on how strongly or weakly it is coordinated to the metal center and steric effects.

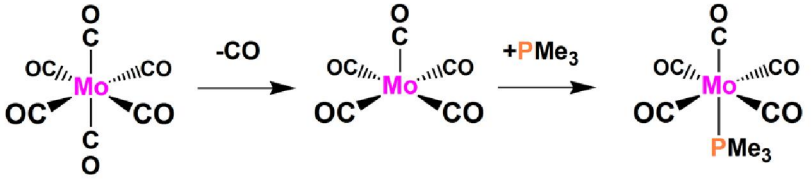


The steric hindrence of the three bulky PPh_3 ligands favors dissociation of one to form the 14e- $RhCl(PPh_3)_2$ complex. The moderate electron-donating ability of the PPh_3 ligand (not a strongly coordinating ligand) makes this fairly facile.



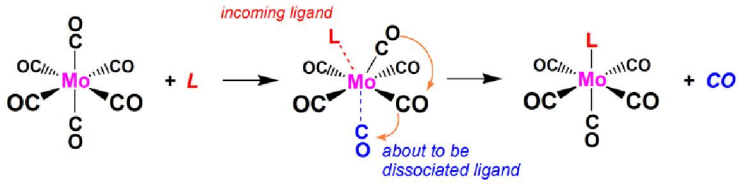
The strongly donating ability of the dmpe ligands combined with their strong chelate effect makes it difficult to dissociate one of the PMe_2 arms. In this case the Cl- anion is the one that dissociates, leaving a cationic complex behind. The two dmpe ligands donate enough electron-density to the Ru center to make it reasonable to dissociate a Cl-.

A **ligand substitution** can occur either by an ***associative*** or ***dissociative*** route. The exact mechanism depends in large part on the electron-count of the metal complex undergoing the ligand substitution. The simplest case is when one is dealing with an **18e-** metal complex. In this case one almost always has a ***dissociative substitution***.



18e- saturated complex | *16e- unsaturated complex* | *18e- saturated complex*

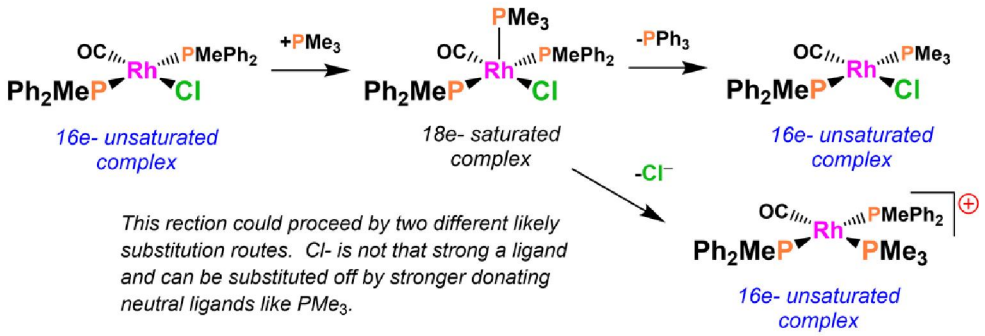
Almost NO evidence for this type of reaction:



18e- complex | ***20e- transition state with added ligand*** | ***18e- complex***

Associative Substitutions

These occur first by a **ligand addition** to the metal complex followed by the **dissociation** of one of the original ligands.



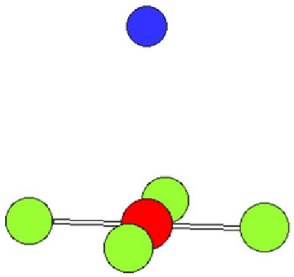
This rection could proceed by two different likely substitution routes. Cl- is not that strong a ligand and can be substituted off by stronger donating neutral ligands like PMe_3.

The filled axial Pt d_{z^2} orbital partially blocks coordination of ligands via the empty axial p_z orbital. This limits, but does not stop ligand association, which is quite common for Rh(I) and Pd(II).

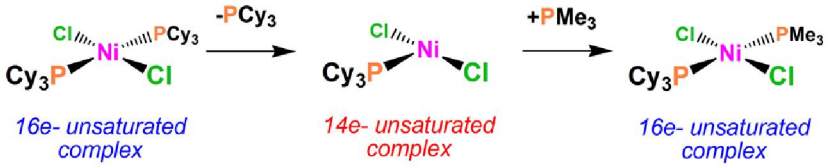
Associative Substitutions

These occur first by a **ligand addition** to the metal complex followed by the **dissociation** of one of the original ligands.

Berry psuedorotation
Formation of a trigonal bipyramid intermediate

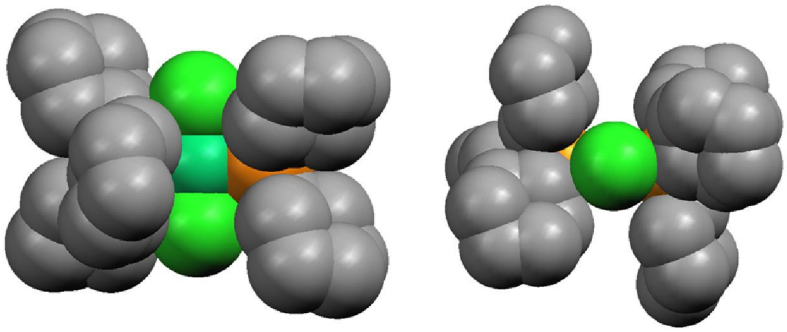


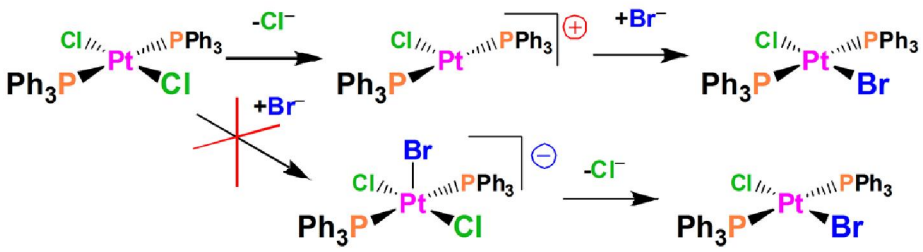
Dissociative substitution can also occur in 16e- (or in very unusual cases, lower electron count systems) complexes. These cases either involve sterically bulky ligands that block the open coordination site, or third row square planar d^8 complexes like Pt(+2) where there are strong electronic factors that limit the coordination of an additional ligand to the empty axial site.



16e- unsaturated complex — *14e- unsaturated complex* — *16e- unsaturated complex*

The large PCy_3 ligands sterically block access to the empty axial p_z orbital





The spatially extended filled axial Pt d_{z^2} orbital partially blocks coordination of ligands via the empty axial p_z orbital. This limits ligand association, although it can occur.

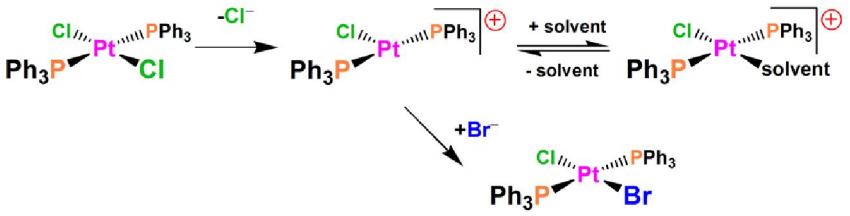
Problem: The rate of substitution reactions on square planar d^8 complexes goes in the order: Ni > Pd >> Pt. Explain why.

Steric Factors

$$Ni(PR_3)_4 \underset{25^oC}{\overset{K_D}{\rightleftharpoons}} Ni(PR_3)_3 + PR_3$$

Ligand:	$P(OEt)_3$	$P(O\text{-}p\text{-tolyl})_3$	$P(O\text{-}i\text{-Pr})_3$	$P(O\text{-}o\text{-tolyl})_3$	PPh_3
Cone angle:	109°	128°	130°	141°	145°
K_D :	$< 10^{-10}$	6×10^{-10}	2.7×10^{-5}	4×10^{-2}	> 1000

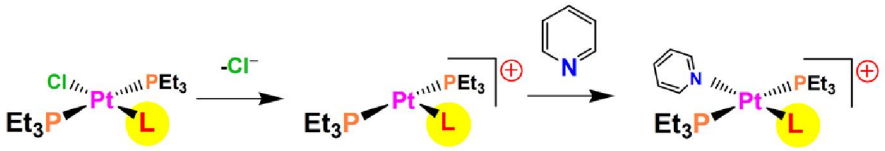
Solvent Effects



acetone	THF (tetrahydrofuran)	DMSO (dimethylsulfoxide) bp = 189°C mp = 18°C
methanol	ethanol	acetonitrile
DMF (dimethylformamide) bp = 153°C mp = -61°C	DME (dimethoxyethane)	water (rarely used)

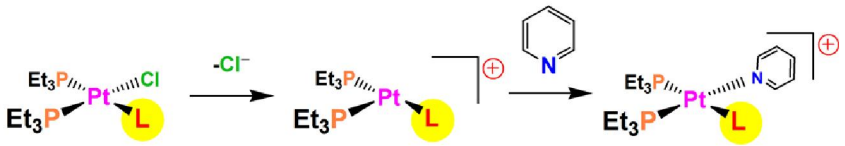
Trans Effect

The ***trans effect*** concerns the electronic effect of one ligand on another ligand when they are ***trans*** (opposite) to one another. The classical *trans* effect involves two σ-donating ligands *trans* to one another.



Relative rate of substitution based on *trans* ligand ● :
$Cl^- = 1$, $Ph^- = 100$, $CH_3^- = 10^3$, $H^- = 10^4$

There is a *cis* effect, but it is much weaker and basically ignored:



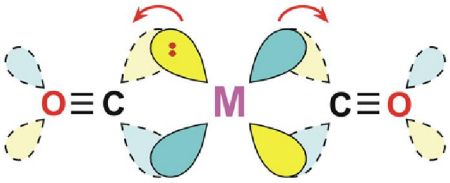
Relative rate of substitution based on *cis* ligand ● :
$Cl^- = 1$, $Ph^- = 2$, $CH_3^- = 4$, $H^- = 4$

Note that when most chemists talk about the *trans* effect they are referring to the σ-σ type of *trans* effect, where a strong σ-donor weakens the σ-donating ligand *trans* to it.

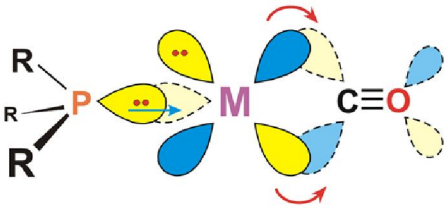
Do NOT overestimate the importance of the *trans*-effect. There are other forms that have different effects.

π-Acceptor *Trans* Effects

Trans effects that involve π-backbonding ligands. CO ligands represent the most common type.



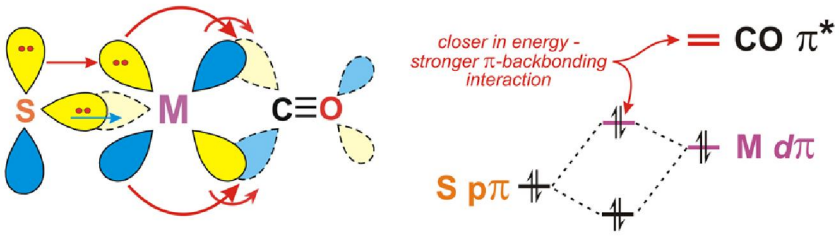
π-backbonding to a metal is ***weakened*** when it is *trans* to another good π-backbonding ligand



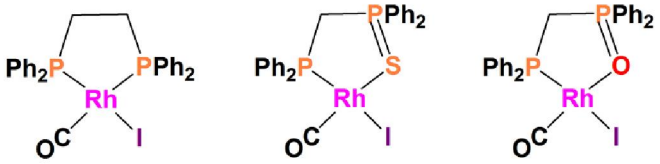
π-backbonding to a metal is ***strengthened*** when it is *trans* to a good σ-donating ligand that can't π-backbond

π-Pushing Effect

There is a further strengthening of M-CO π-backbonding when the *trans* ligand has π-donation properties that can push up the energy of the filled *d* orbitals and, in turn, make them better π-donors to the CO. This can occur even when the ligand is not an especially strong donor.

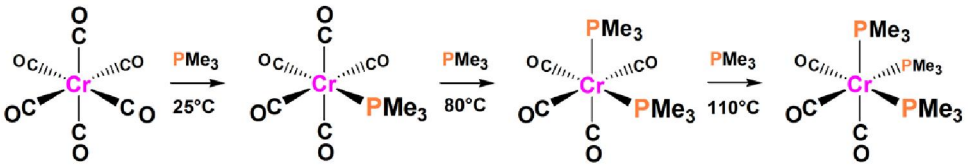


An example of this can be seen in the following three complexes and their *"anomalous"* νCO stretching frequencies:



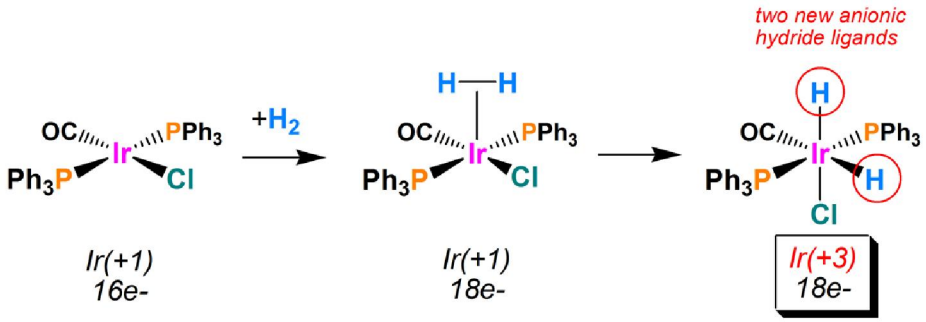
νCO = 2011 cm^{-1} νCO = 1987 cm^{-1} νCO = 1983 cm^{-1}

Problem: Consider the following series of substitution reactions.



As one replaces each CO ligand with a PMe_3, the next CO substitution is progressively more and more difficult requiring higher temperatures and longer times. Once one forms $Cr(CO)_3(PMe_3)_3$, it is extremely difficult to replace another carbonyl ligand. Why? Give all the major reasons?

Oxidative Addition



There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:

- Non-Electrophillic
- Non-Electrophillic "Intact"
- Electrophillic

Non-electrophillic: these molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. These molecules usually require the presence of an **empty orbital** on the metal in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.

H_2, C-H bonds, Si-H bonds, S-H bonds,
B-H bonds, N-H bonds, S-S bonds, C-C bonds, etc.

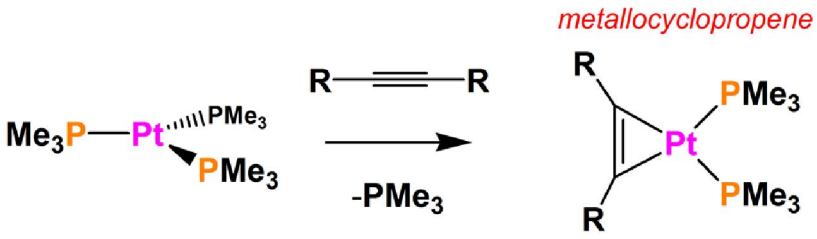
H_2 is by far the most important for catalytic applications, followed by Si-H bonds, B-H, N-H, and S-H bonds.

C-H bond activation and functionalization is very important, but still not practical.

Non-electrophillic "Intact": these molecules may or may not contain electronegative atoms, but they do need to have a **double** or **triple bond** present. One also needs a metal center with an **empty orbital** (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

Typical "intact" ligands that can perform an oxidation addition without fragmenting apart are (O_2 can also act as an **electrophillic** substrate):

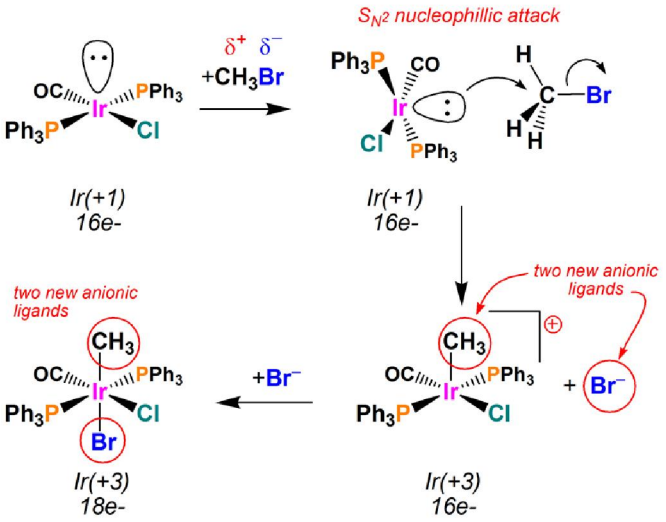
alkenes, alkynes, and O_2



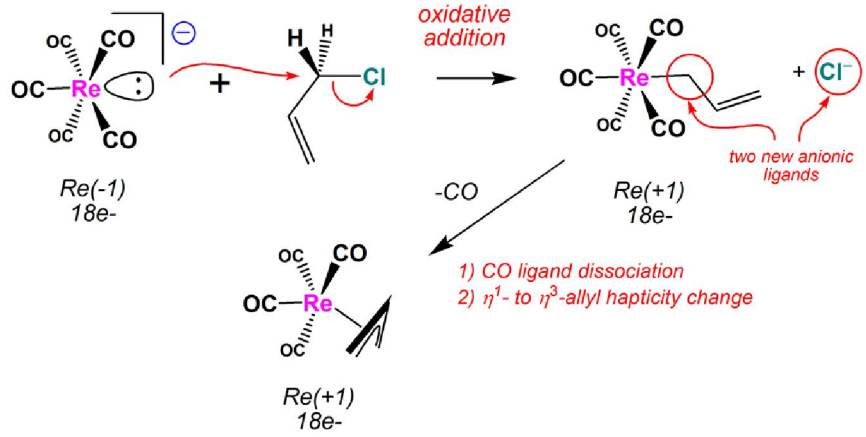
Electrophillic: these molecules ***do*** contain electronegative atoms and are good oxidizing agents. They are often considered to be *"reactive"* substrates.

These molecules do ***NOT*** require the presence of an **empty orbital** (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

X_2 (X = Cl, Br, I), R-X, Ar-X, H-X, O_2, etc.



In the case of a starting **18e-** complex (shown below) only ***one*** of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.



WARNING:

d^0 metals can ***NOT*** do ***oxidative additions***!!

So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and *d*-electron count!

Kinetic Data for Oxidative Addition Reactions of $MX(CO)(PR_3)_2$

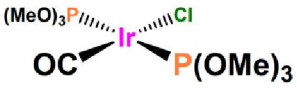
M	X	PR_3	Reactant	Rate Const (M^{-1} sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (J/mol K)
Ir	Cl	PPh_3	H_2	0.67	10.8	–23
	Br			10.5	12.0	–14
	I			> 100		
Ir	Cl	PPh_3	O_2	3.4×10^{-2}	13.1	–21
	Br			7.4×10^{-2}	11.8	–24
	I			30×10^{-2}	10.9	–24
Ir	Cl	PPh_3	CH_3I	3.5×10^{-3}	5.6	–51
	Br			1.6×10^{-3}	7.6	–46
	I			0.9×10^{-3}	8.8	–43
Ir	Cl	$P(p\text{-}C_6H_4\text{-}OMe)_3$	CH_3I	3.5×10^{-2}	8.8	–35
		$P(p\text{-}C_6H_4\text{-}Cl)_3$		3.7×10^{-5}	14.9	–28
Rh	Cl	PPh_3	CH_3I	12.7×10^{-4}	9.1	–44
		$P(p\text{-}C_6H_4\text{-}OMe)_3$		51.5×10^{-4}	10.2	–43

Data adapted from "Principles and Applications of Organotransition Metal Chemistry", Coleman, Hegedus, Norton & Finke, University Press, **1987**; refs: Chock & Halpern, *JACS*, **1966**, *88*, 3511; Ugo, Pasini, Fusi, Cenini, *JACS*, **1972**, *94*, 7364; Douek & Wilkenson, *J. Chem. Soc. (A)*, **1964**, 2604. Rxns generally run in benzene at 25°C.

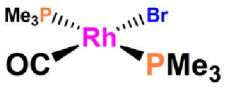
Oxidative additions are easy to identify **IF YOU ELECTRON COUNT** the metal complexes. When an oxidative addition rxn occurs the metal will be oxidized, usually by 2e-. So, if you start with a metal in the 0 oxidation state (d^8), after the oxidative addition the metal will be in the +2 oxidation state (d^6). Once you get used to looking at organometallic rxns you will be able to identify common oxidative additions quite quickly. **H_2, R-X, and H-SiR_3 are three of the most common substrates that perform oxidative addition reactions in catalytic cycles.**

Problem: H_2 will do an oxidative addition most readily to which of the following complexes. Why?

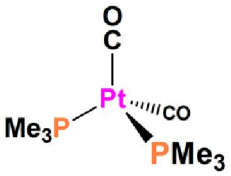
a)



b)

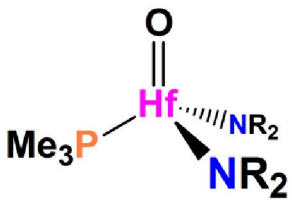


c)

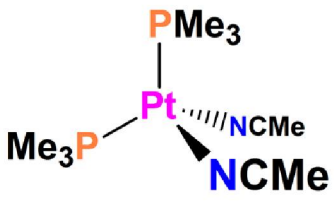


Problem: CH_3Br will do an **oxidative addition** most readily to which of the following complexes. Why?

a)



b)



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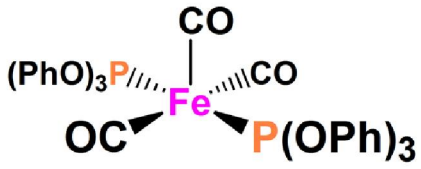
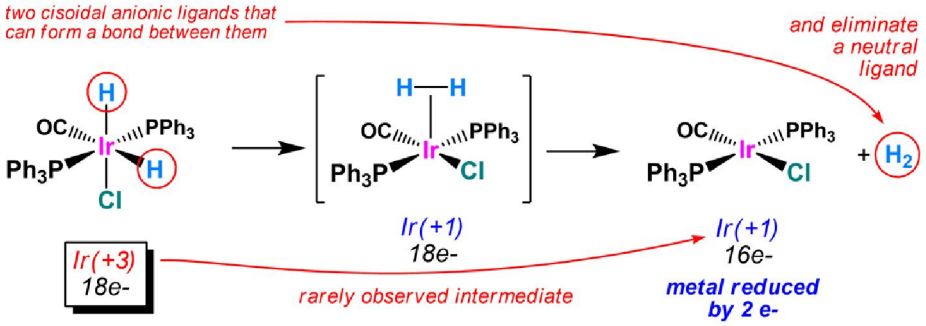
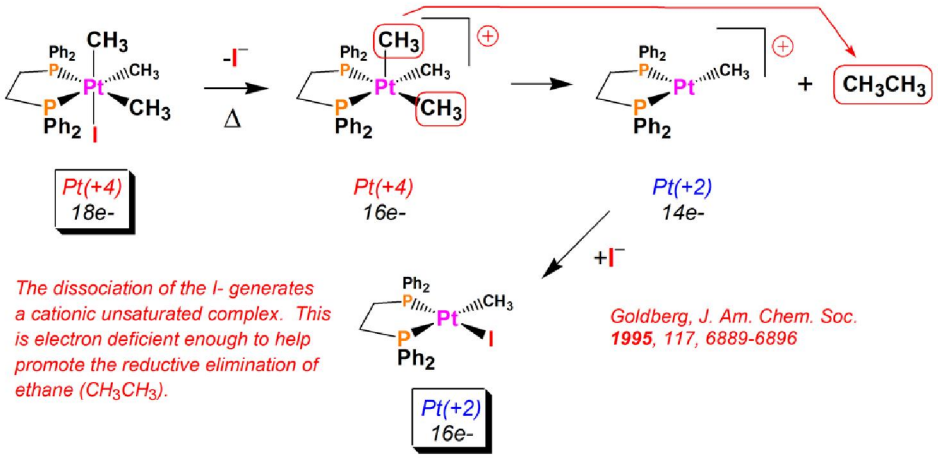


Reductive Elimination

A ***reductive elimination*** reaction is the reverse of an oxidative addition. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by 2e-. The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.



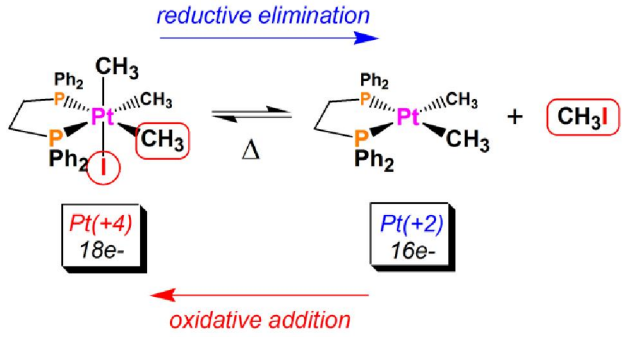
While reductive elimination can occur from saturated 18e- complexes (so long as the two ligands that you want to reductively eliminate are **cisoidal** to one another), it has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.



The dissociation of the I- generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane (CH_3CH_3).

Goldberg, J. Am. Chem. Soc. ***1995****, 117, 6889-6896*

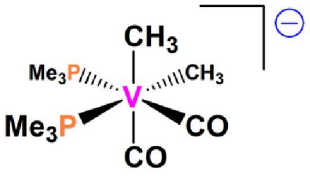
In studying the above system, it was also found that one could have reductive elimination of CH_3I from the starting 18e- complex. This reaction, however, is very reversible due to the high reactivity of CH_3I for doing an oxidative addition back reaction with the electron-rich neutral Pt(+2) complex to make the Pt(+4) octahedral compound.



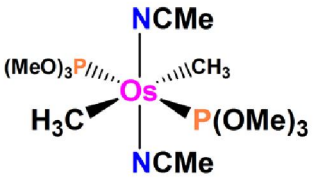
The reductive elimination of the CH_3I is kinetically favored. This is because the orbitals around the iodide anion are spherically symmetric and this makes it much easier to overlap with the alkyl group orbital to perform the reductive elimination. The sp^3 directed orbitals on the two CH_3 groups are more difficult to overlap in order to get the reductive elimination to occur. But the reductive elimination of the CH_3CH_3 is thermodynamically considerably more favorable and the back oxidative addition much more difficult.

Problem: Which of the following compounds will be most likely to do a reductive elimination of ethane (CH_3-CH_3)? Why?

a)



b)



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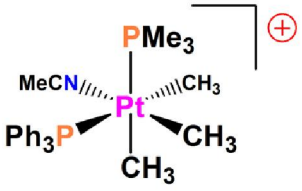
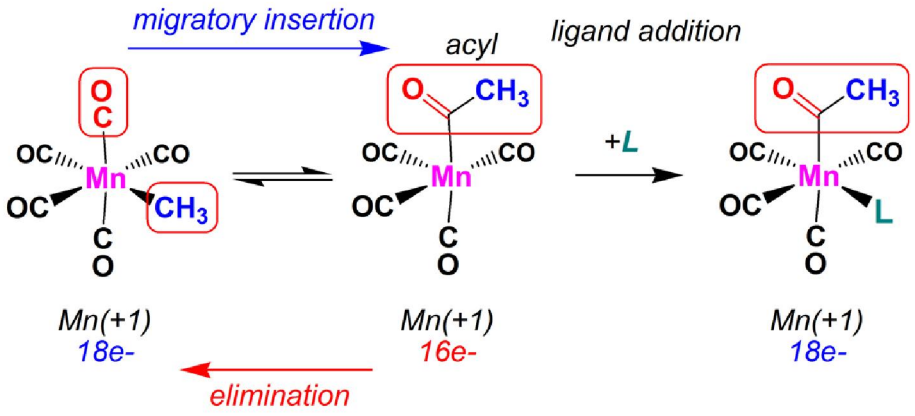


Migratory Insertion & Elimination Reactions

A ***migratory insertion*** reaction is when a **cisoidal anionic and neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. ***There is NO change in the oxidation state or d electron-count of the metal center.***



General Features of Migratory Insertions:

1) **No change in formal oxidation state**
2) **The two groups that react must be cisoidal to one another**
3) **A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., β-hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.**
4) **Migratory insertions are usually favored on more electron-deficient metal centers.**

The following are common **anionic** and **neutral** ligands that can do ***migratory insertion*** reactions with one another:

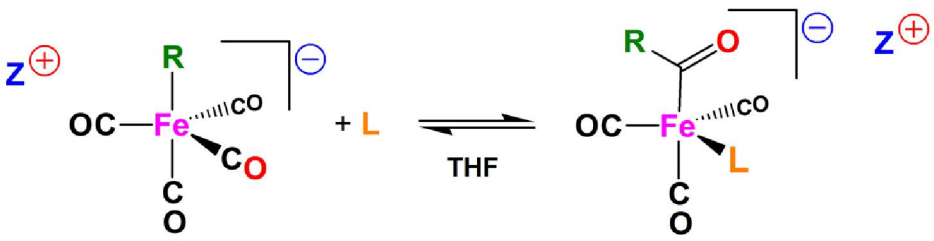
Anionic: H^-, R^- (alkyl), Ar^- (aryl), $acyl^-$, O^{2-} (oxo)

Neutral: CO, alkenes, alkynes, carbenes

CO and alkyl migratory insertions (as shown on previous slide) are extremely important and are often generically referred to as **carbonylation** reactions.

Hydride and CO migratory insertions to produce formyl groups are not common due to the *thermodynamic instability* of the formyl-metal interaction.

Some Electronic effects



best Lewis acid - can coordinate to electron-rich CO ligands and drain off some e- density

Z^+ = Li^+ > Na^+ > $(Ph_3)_2N^+$

strongest coordinating ligand - best trapping ligand

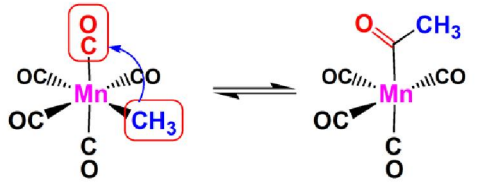
L = PMe_3 > $PPhMe_2$ > PPh_2Me > CO

most electron-rich alkyl group makes the best nucleophile for migrating to the electron-deficient CO

R = n-alkyl$^-$ > $PhCH_2^-$

Migration vs. Insertion

Migration

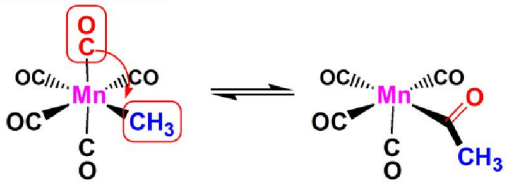


Mn(+1)
18e-

Mn(+1)
16e-

a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion

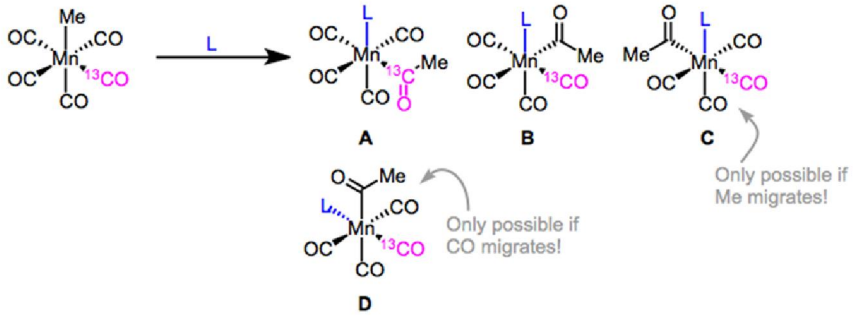


Mn(+1)
18e-

Mn(+1)
16e-

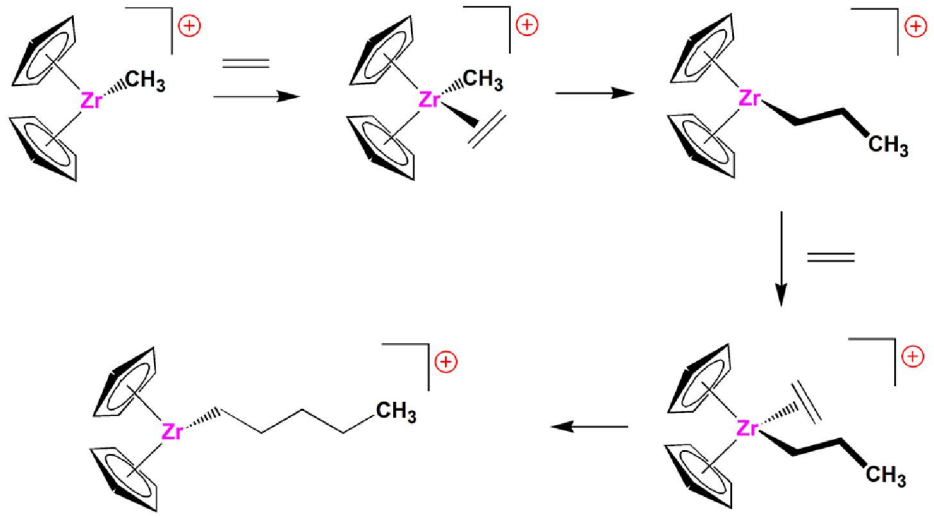
an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

Migration vs. Insertion

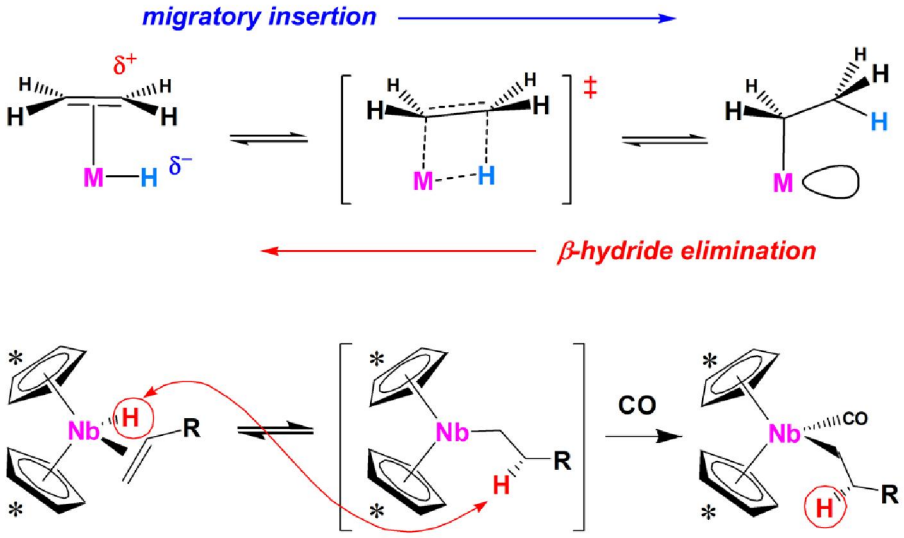


Product D has been NEVER observed!!!!

Alkene Migratory Insertions

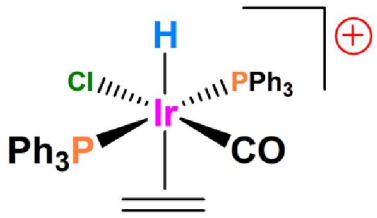


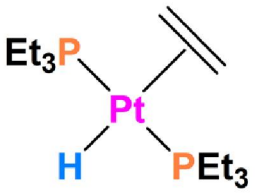
Alkene Migratory Insertion – β-Hydride Elimination



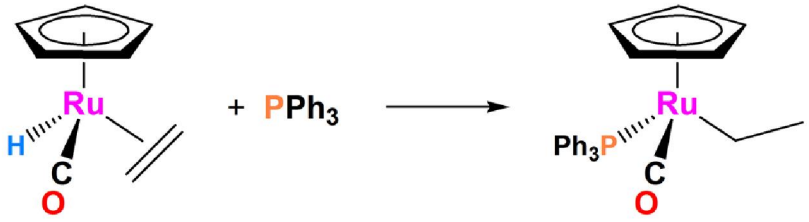
NMR irradiation of the Nb-hydride resonance affects the NMR resonance for the alkyl hydride, demonstrating that they are connected by the migratory insertion mechanism

Problem: Why don't either of the complexes shown below do alkene-hydride migratory insertions at room temperature?

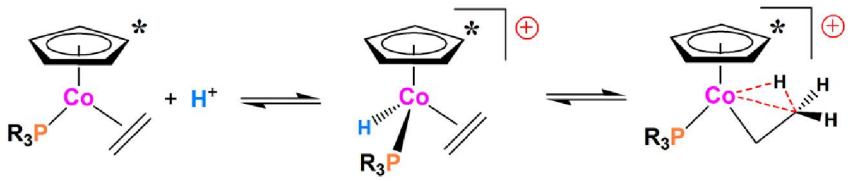




Problem: Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.



Agostic C-H to Metal Interactions – "Frozen Migratory Insertion"

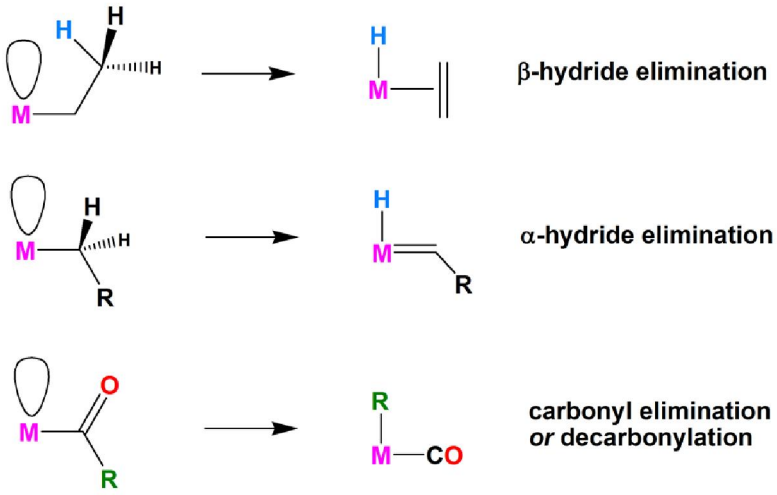


*One of the C-H bonds of the methyl group is within bonding distance to the Co center. This is called an **Agostic** C-H bond interaction.*

Because the C-H bond is sharing some of its σ-bond electron density with the metal, the C-H bond is *weakened*. This produces some relatively clear-cut spectroscopic characteristics:

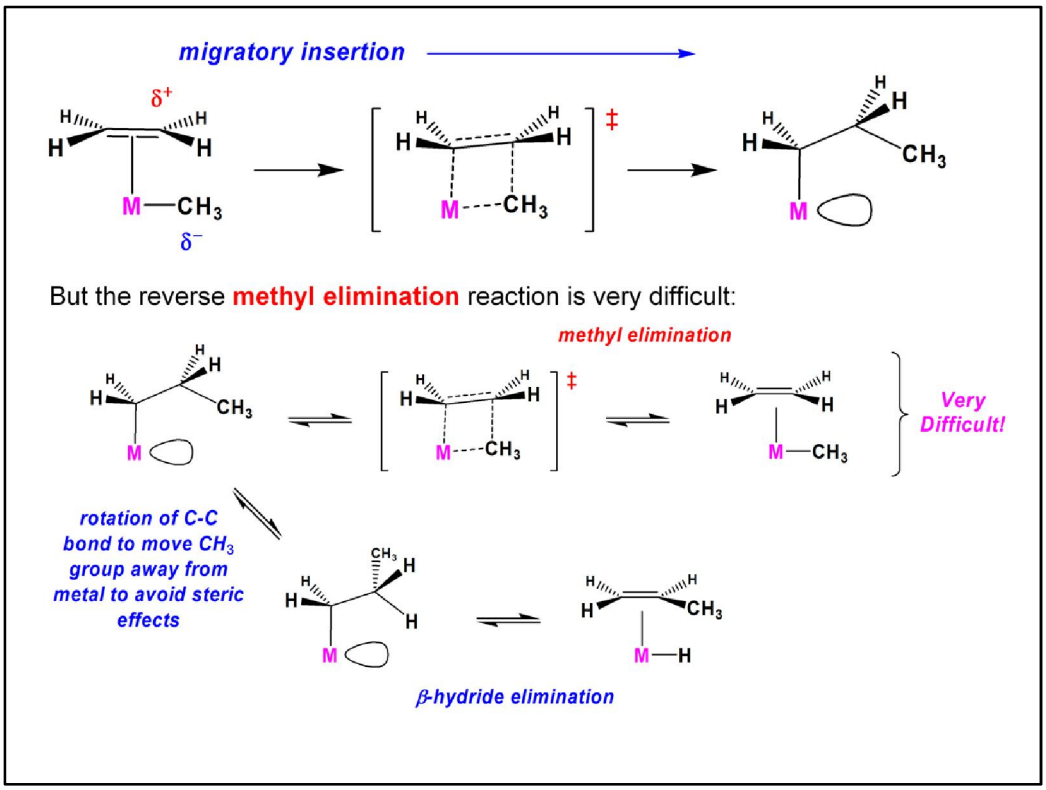
1) $\nu_{C\text{-}H}$ infrared stretching frequency is lowered to the mid-2500 cm^{-1} region from a normal value of 2900-3000 cm^{-1}
2) the $J_{C\text{-}H}$ coupling constant in the ^{13}C NMR is lowered to around 70-90 Hz from a normal value of 150 Hz.
3) the ^{1}H chemical shift of the agostic proton is in the –10 to –15 ppm region, much like a metal-hydride resonance.

Eliminations

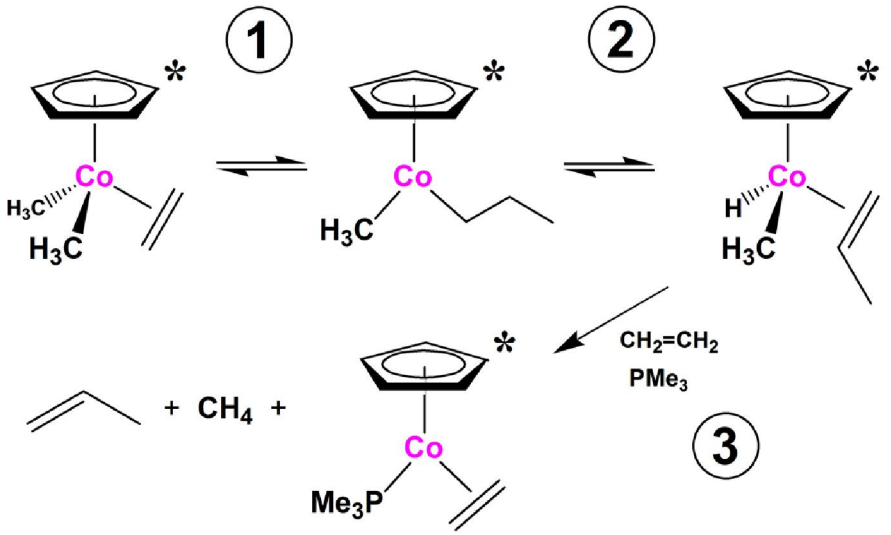


The key points are:

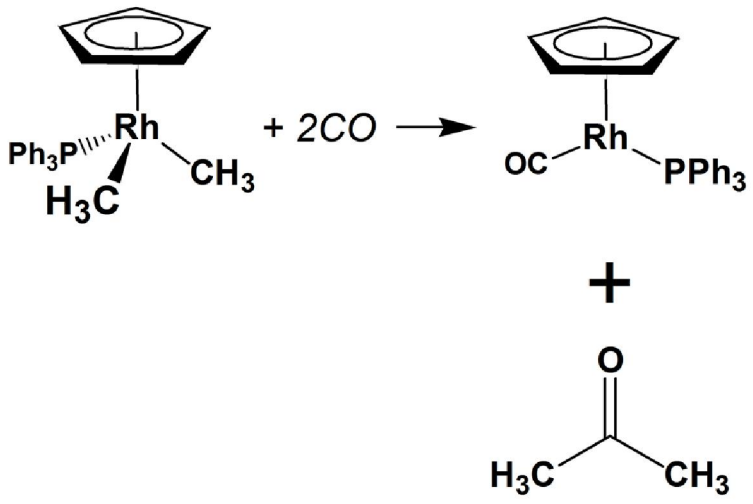
1) **No change in formal oxidation state**
2) **You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.**


migratory insertion
δ+
δ−
M—CH3
M----CH3
‡
CH3
M
But the reverse methyl elimination reaction is very difficult:
methyl elimination
Very Difficult!
rotation of C-C bond to move CH3 group away from metal to avoid steric effects
β-hydride elimination
M—H

Problem: Identify each step in the following mechanism. Some steps may have several things occurring.



Problem: Sketch out a detailed mechanism and label each step for the following overall reaction.



Relevant homogeneous processes

"A mechanism is a theory deduced from the available experimental data. The experimental results are facts; the mechanism is conjecture based on those facts"

Lowry & Richardson

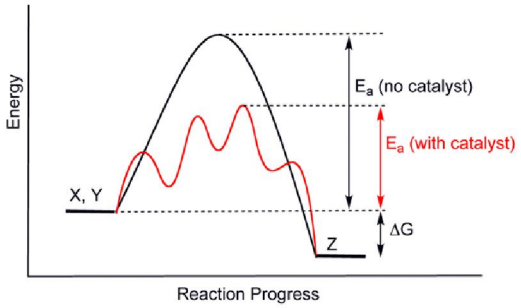
"You can never prove that your mechanism is right - only wrong."

Guy in the audience asking about your proposed mechanism

- **Hydrogenation**
- **Hydroformilation**
- **Monsanto process (carbonylation of methanol)**
- **Polymerization**

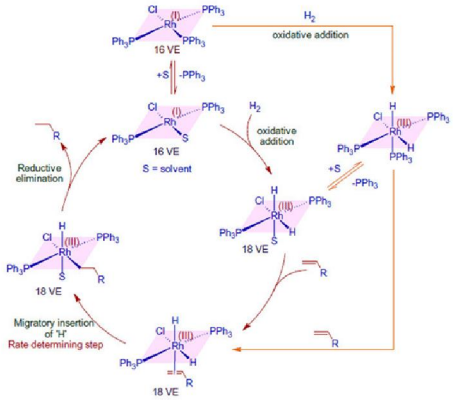
Reaction mechanisms

Sequence of elementary steps that lead to the overall reaction.



Rate Determining Step:
higher E_{att}

Regeneration of the active species



Hydrogenation

- Addition of H_2 across a multiple bond, such as C=C, alkynes or even C=O, constitute an important synthetic procedure both lab and industrial scale.
- It finds increasing use in the production of specialty chemicals and pharmaceuticals.
- Activation energy of uncatalyzed reactions can be as high as 60 kJ/mol.
- Hydrogenation catalysts add molecular hydrogen to the C=C group of an alkene to give an alkane.
- Three general types have been distinguished, according to the way each type activates H_2.

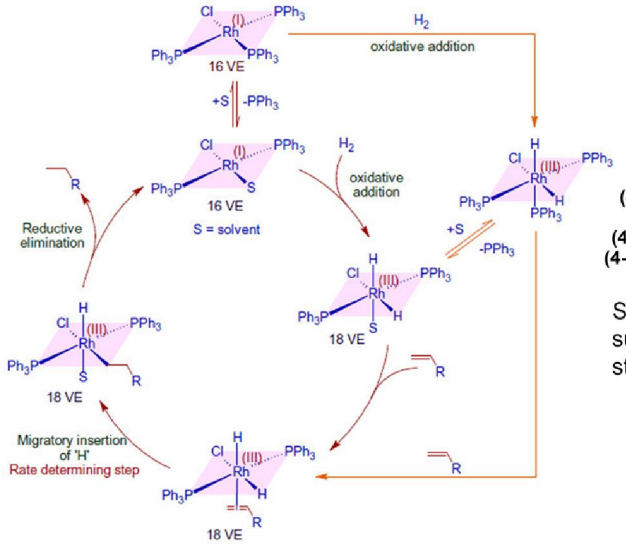
1. oxidative addition
2. heterolytic activation
3. homolytic activation

Hydrogenation – Wilkinson catalysts

Oxidative addition

$Rh(PPh_3)_3Cl$

Sir G. Wilkinson



Ligand:	Relative rates for hydrogenation of cyclohexene:
$(4\text{-}ClC_6H_4)_3P$	1.7
PPh_3	41
$(4\text{-}CH_3C_6H_4)_3P$	86
$(4\text{-}CH_3OC_6H_4)_3P$	100

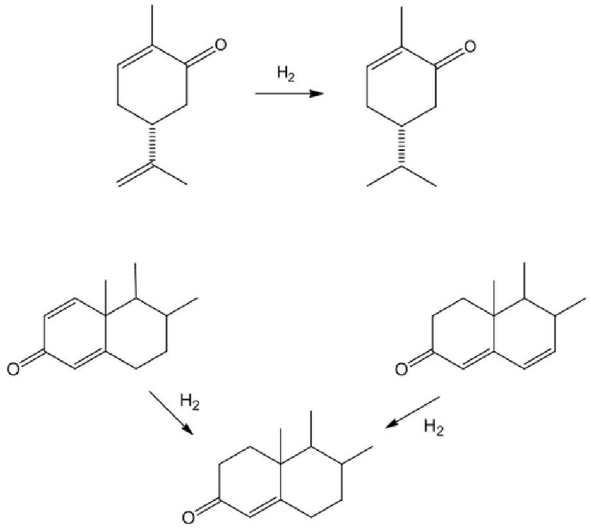
Simplistically, the relative rates suggest that the rate-determining step is OA of H_2.

Hydrogenation – Wilkinson catalysts

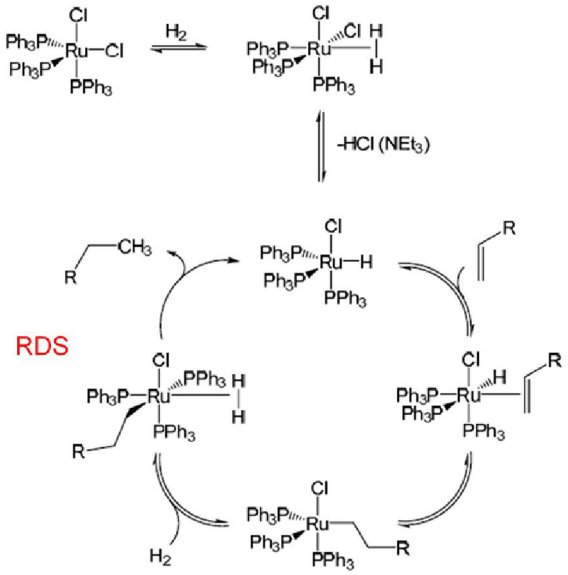
$Rh(PPh_3)_3Cl$

Sir G. Wilkinson

Highly selective catalyst!!!

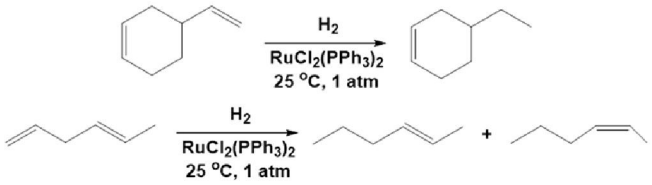


Hydrogenation – Heterolytic H_2 activation

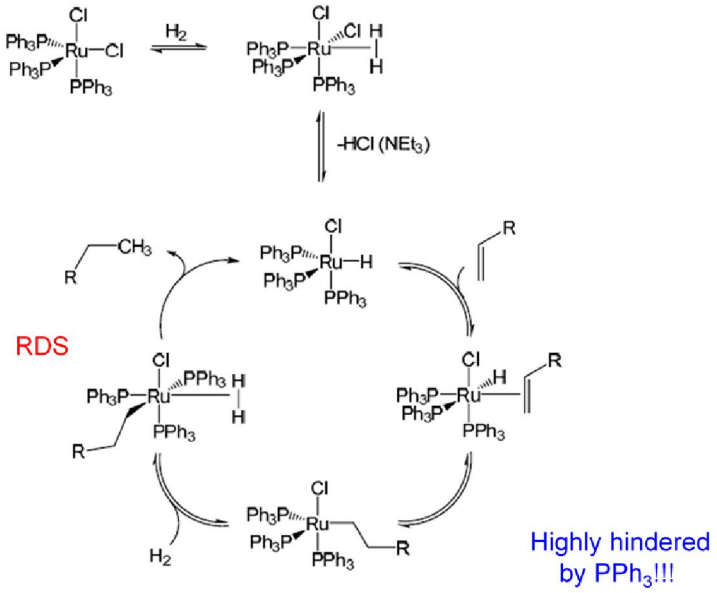


Hydrogenation – Heterolytic H_2 activation

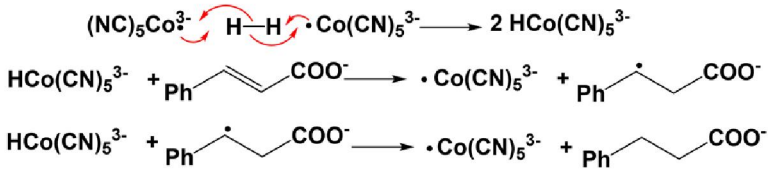
$RuCl_2(PPh_3)_2$ hydrogenates selectively terminal double bonds over internal double bonds:



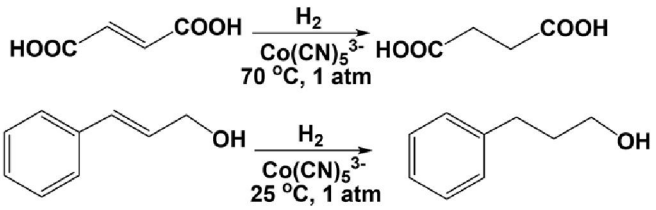
Hydrogenation – Heterolytic H_2 activation



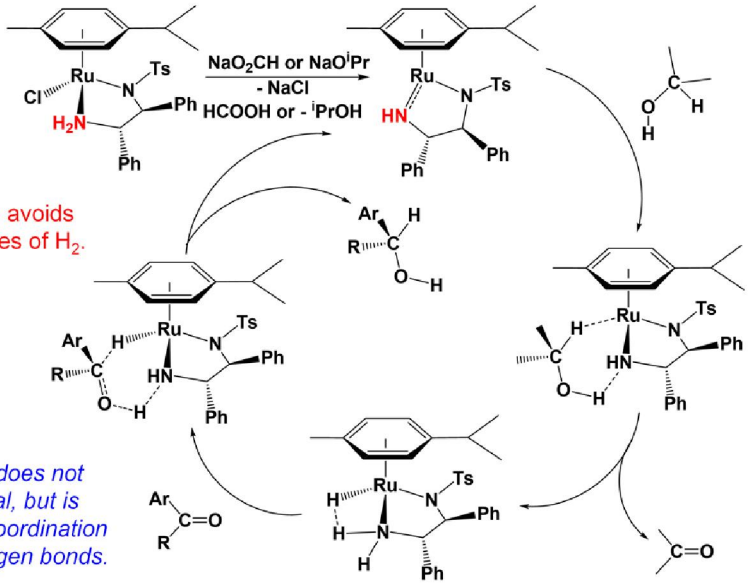
Hydrogenation – Homolytic H_2 activation



The resulting organic radical needs to be moderately stable: only "activated" alkenes will be hydrogenated (formation of a conjugated radical).



Hydrogenation – H-transfer reaction



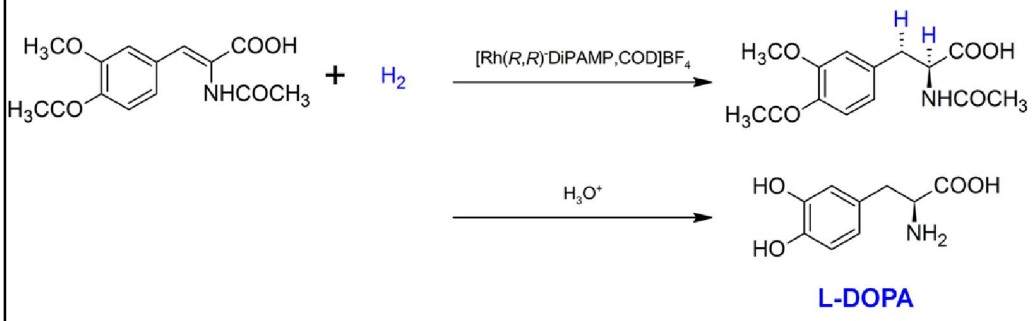
Transfer hydrogenation avoids the use of high pressures of H_2.

The ketone substrate does not coordinate to the metal, but is oriented in the second-coordination sphere by forming hydrogen bonds.

Morris, R. H. et al. *Coord. Chem. Rev.* 2004, *248*, 2201

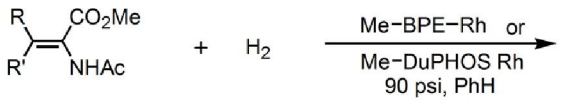
Hydrogenation – Asymmetric catalysis

Knowles
Noyori
Sharpless
Noble Prize 2011



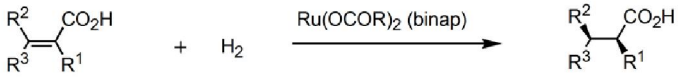
L-DOPA

Hydrogenation – Asymmetric catalysis



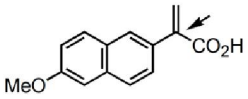
96-99% *ee*

Knowles

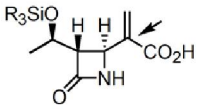


96-99% *ee*

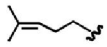
Noyori



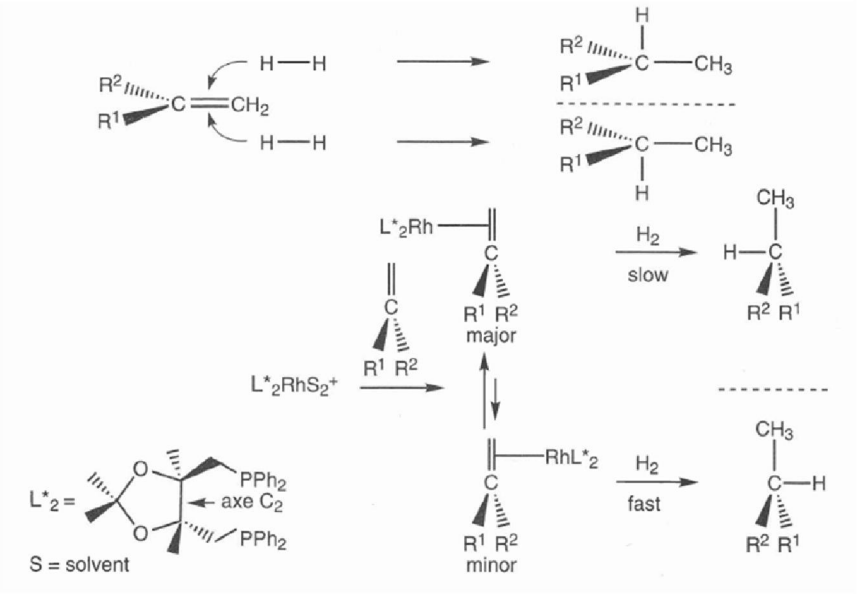
97% ee (Naproxen)



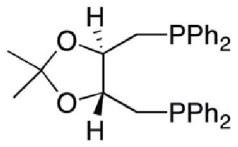
74% ee (Thienamycin)

R^1	R^2	R^3	ee
Me	Me	H	91
H		Me	87
H	Me	Ph	85
Ph	H	H	92
H	$HOCH_2$	Me	93
H	CH_3	$COOCH_2CMe$	95

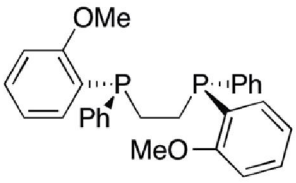
Hydrogenation – Asymmetric catalysis



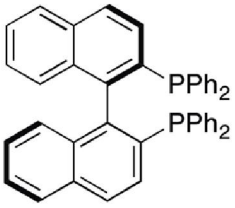
Hydrogenation – Asymmetric catalysis



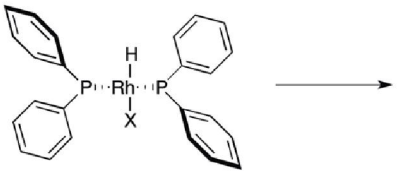
(*R*,*R*)-DIOP

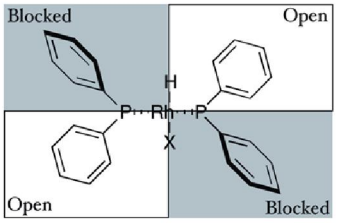


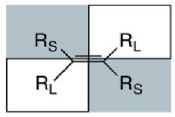
(*R*,*R*)-DIPAMP



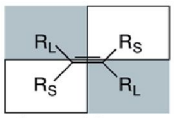
(*R*)-BINAP







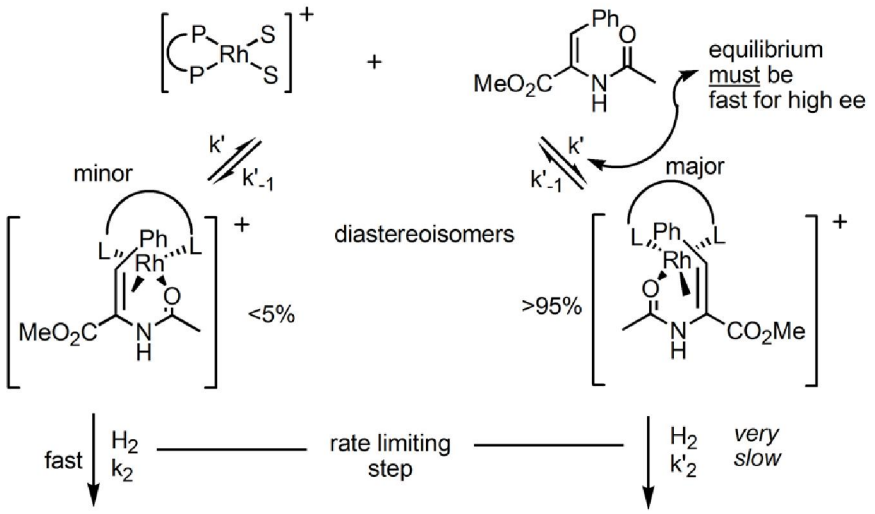
Favoured Orientation



Disfavoured Orientation

Hydrogenation – Asymmetric catalysis

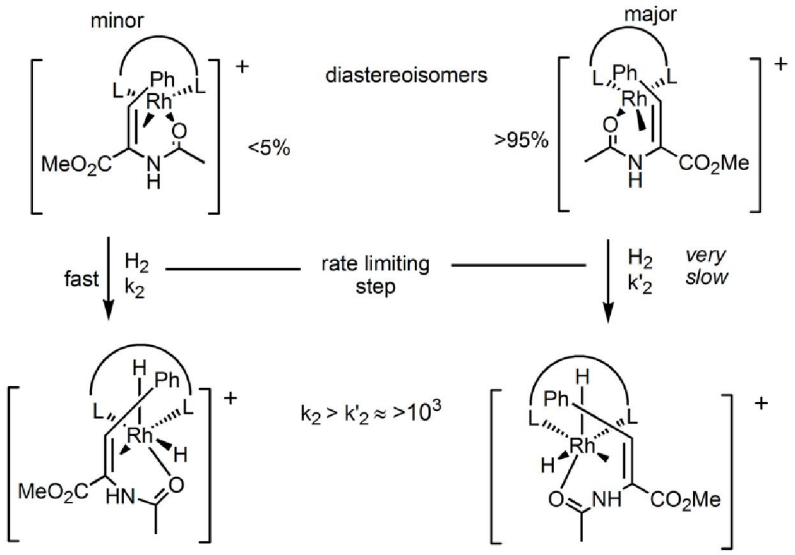
Knowles



Halpern, J. *Science* **1982**, *217*, 401-407.

Hydrogenation – Asymmetric catalysis

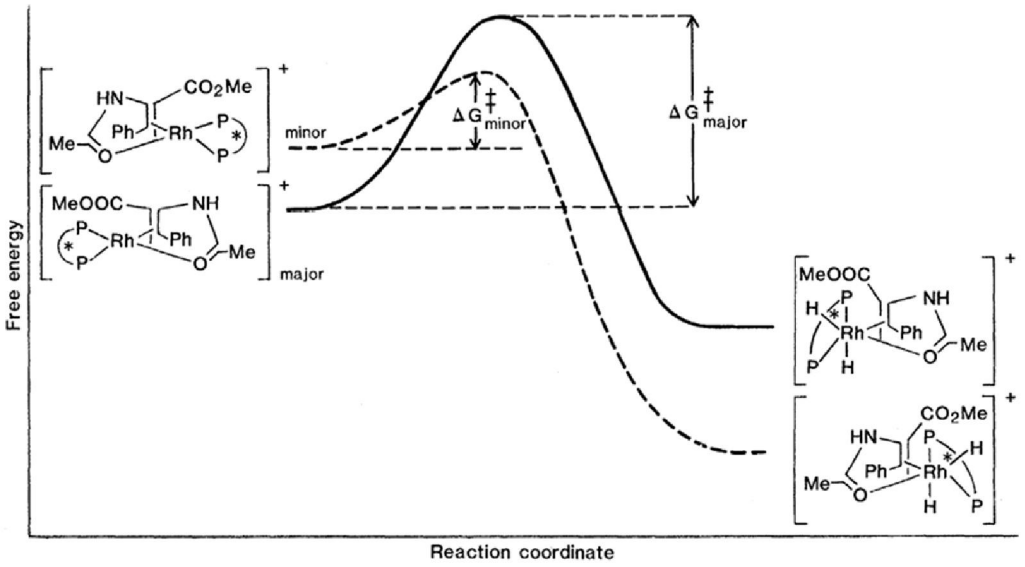
Knowles



Halpern, J. *Science* **1982**, *217*, 401-407.

Hydrogenation – Asymmetric catalysis

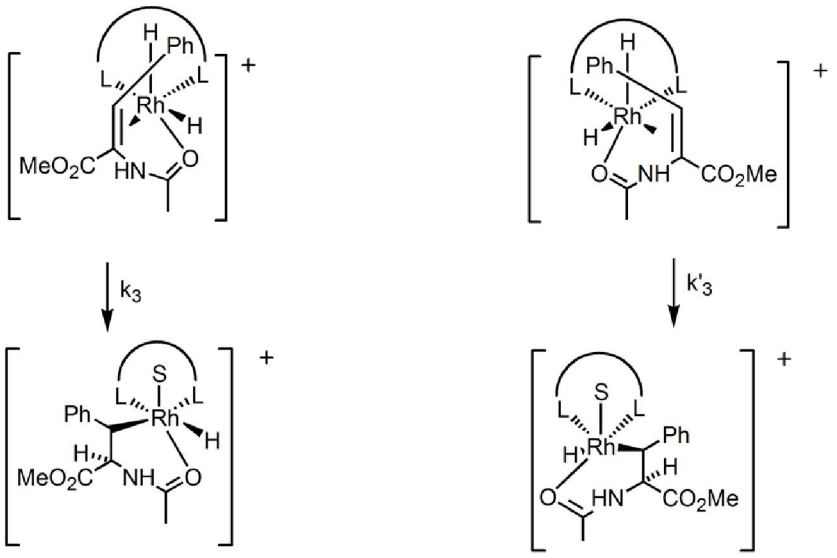
Knowles



Halpern, J. *Science* **1982**, *217*, 401-407.

Hydrogenation – Asymmetric catalysis

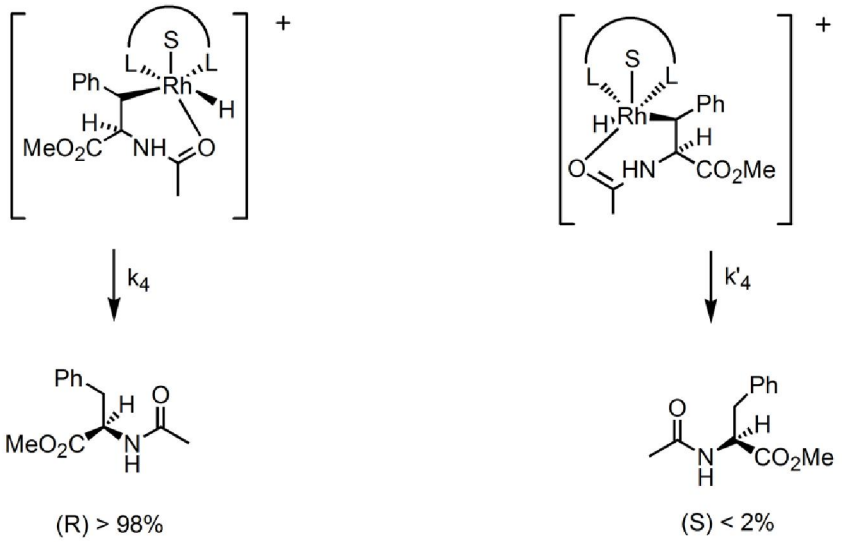
Knowles



Halpern, J. *Science* **1982**, *217*, 401-407.

Hydrogenation – Asymmetric catalysis

Knowles



Halpern, J. *Science* **1982**, *217*, 401-407.

Hydrogenation – Asymmetric catalysis

Knowles

Relazione fra e.e. prodotto e $\Delta\Delta G^{\ddagger}$ calcolato a 25°C

k_R/k_S	$\Delta\Delta G^{\ddagger}$ (kcal/mole)	e.e. prodotto	
RACEMO 1	0	0	50 - 50
3	0.648	50	75 - 25
10	1.358	82	91 - 9
100	2.717	98	99 - 1
1000	4.076	99.8	99.9 - 0.1

Conclusione: bastano piccole differenze nelle Ea‡ per ottenere e.e. elevati

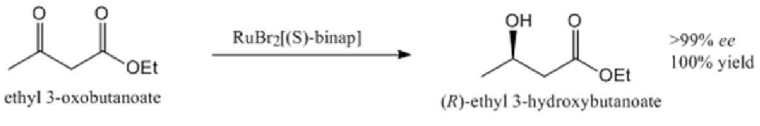
Può sembrare facile discriminare i 2 cammini. Nella pratica non è affatto facile.
L'obiettivo è ottenere $\Delta\Delta G^{\ddagger}$ di 4 kcal/mol (almeno per i farmaci).

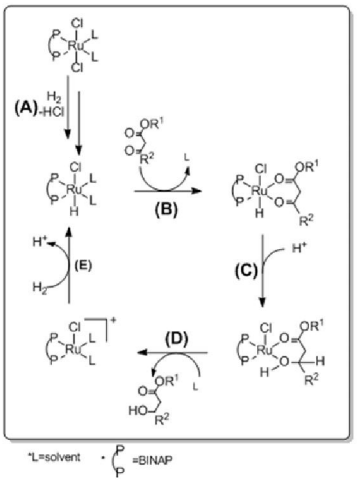
Per riuscire ad ottenere e.e. così elevati si deve procedere per via sperimentale, modificando i leganti non partecipativi.

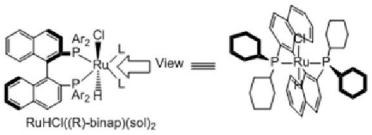
Halpern, J. *Science* **1982**, *217*, 401-407.

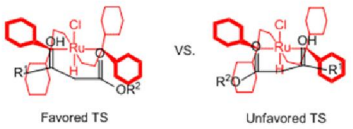
Hydrogenation – Asymmetric catalysis

Noyori

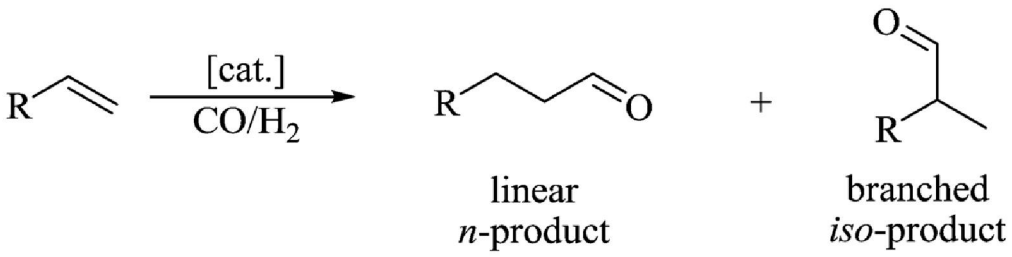




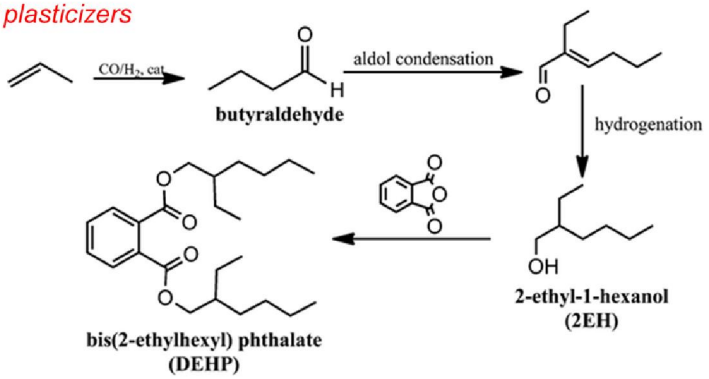




Hydroformylation

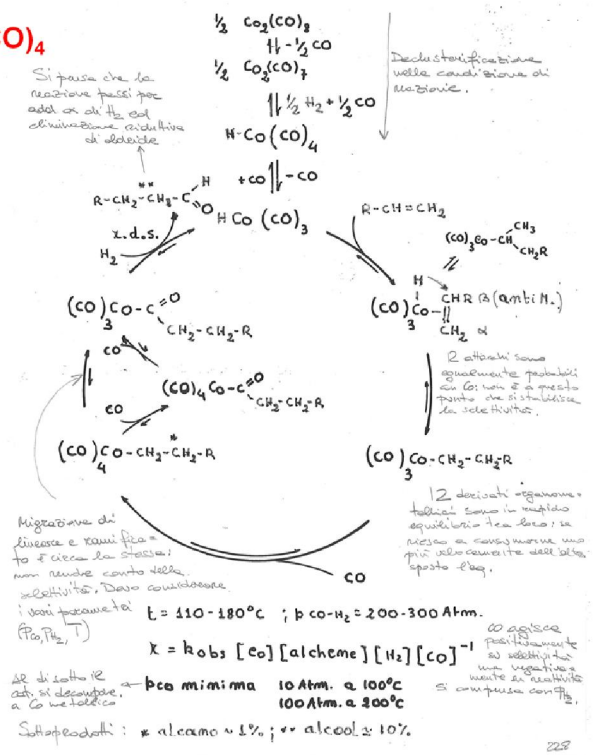


Synthesis of plasticizers



Hydroformylation – $HCo(CO)_4$

$HCo(CO)_4$ dissocia un CO per generale la specie attiva



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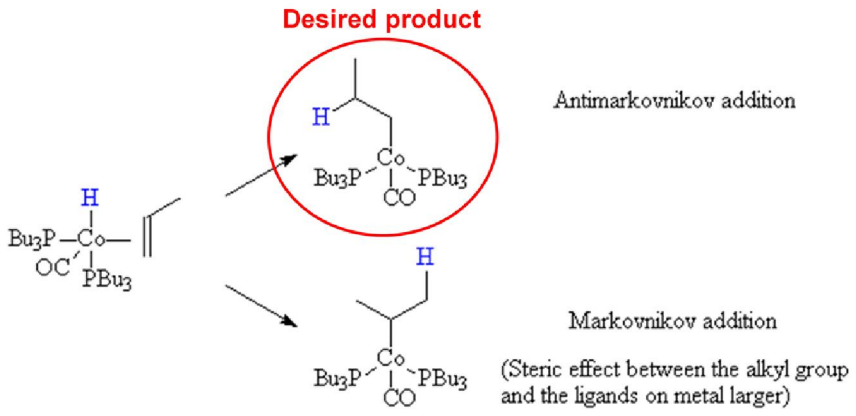

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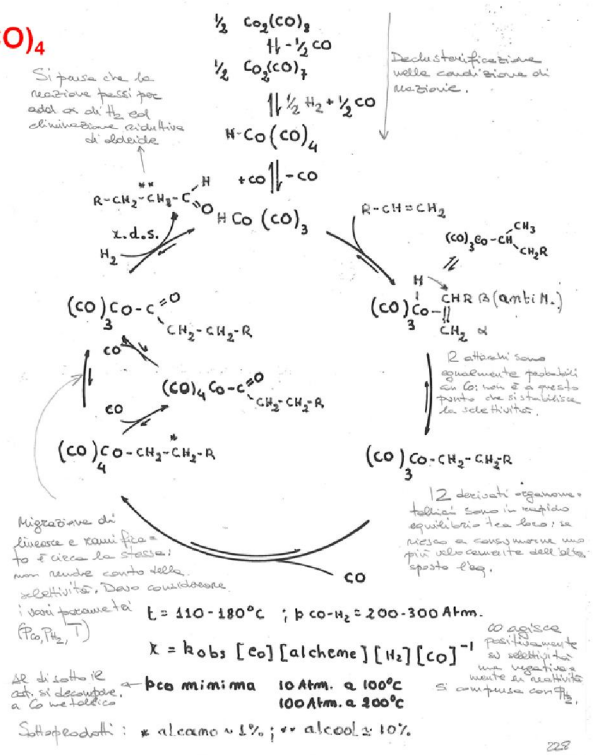
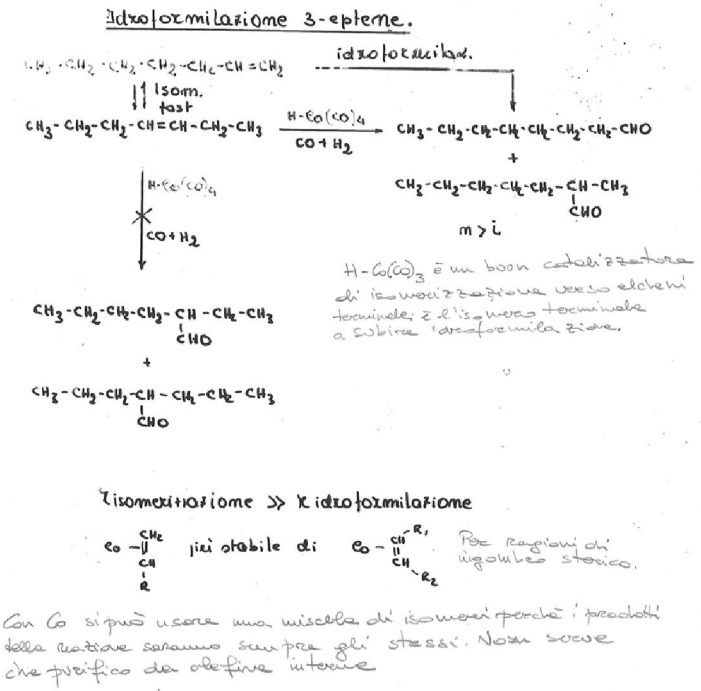


Hydroformylation – $HCo(CO)_4$



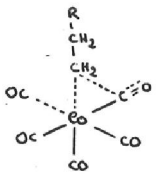
Hydroformylation – $HCo(CO)_4$

Idroformilazione [oleme:
cat: $H\text{-}Co(CO)_4$

Andamento del rapporto n/i con la p_{CO}; p_{H_2}; temperatura

		n/i
Δp_{CO}	(2,5 → 80 Atm.) (a 100°C)	1.6 → 4.4 (61.5% → 81.5% n) → limite della selettività
Δp_{H_2}		[rat. ind.
Δt		u

con Co: $\Delta(\Delta G^{\neq})$ ≥ 1 kcal/mol

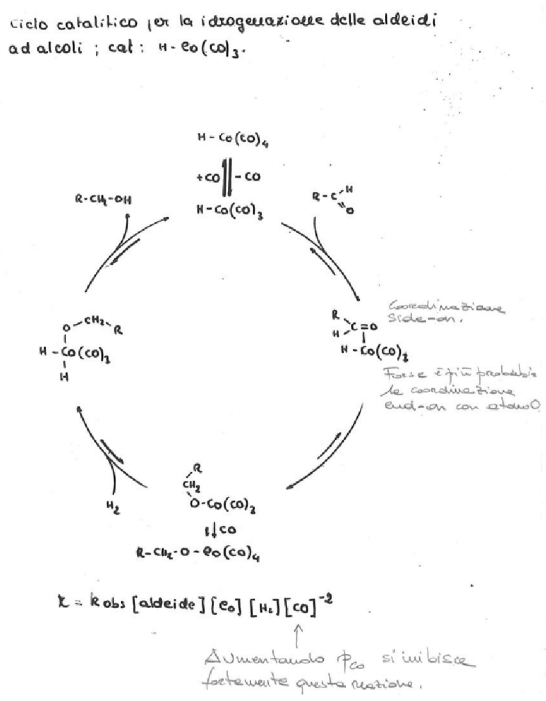


Mentre sta avvenendo la migrazione di R su CO coordinato, entra la nuova molecola di CO. L'ingresso di questa crea un ingombro sterico tale da favorire la migrazione dell'aldeide lineare rispetto a quello ramificato.

stato di transizione
responsabile della selettività;
meccanismo concertato:
l'acile lineare è favorito rispetto a quello ramificato.

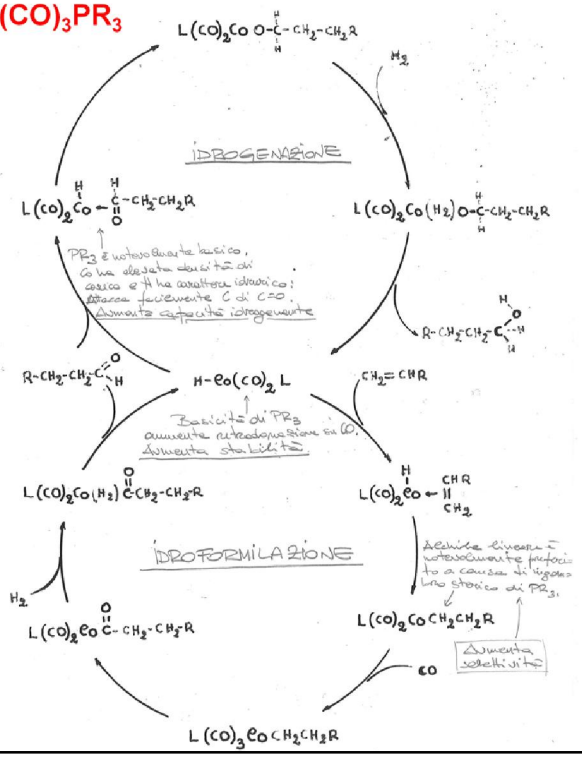
$\Delta(\Delta G^{\neq})$ è molto piccolo: l'influenza sulla selettività è scarsa.

Hydroformylation – $HCo(CO)_4$

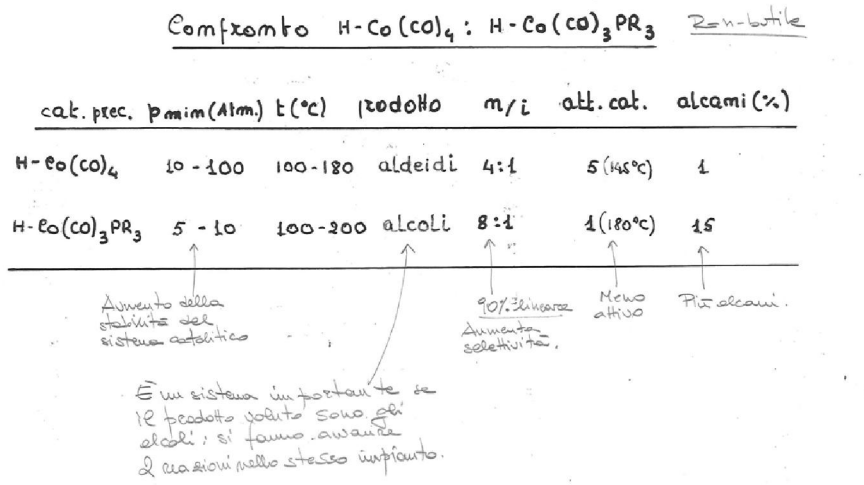


Hydroformylation – $HCo(CO)_3PR_3$

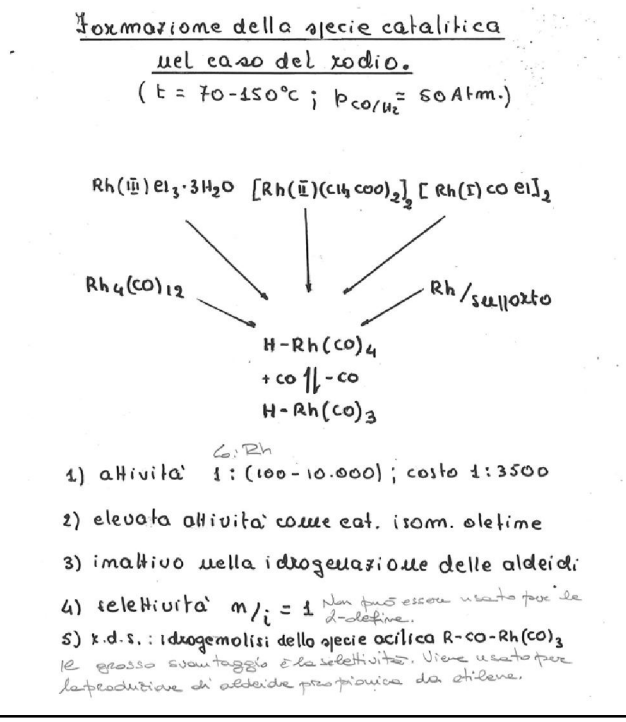
$HCo(CO)_3PR_3$ dissocia un CO per generale la specie attiva



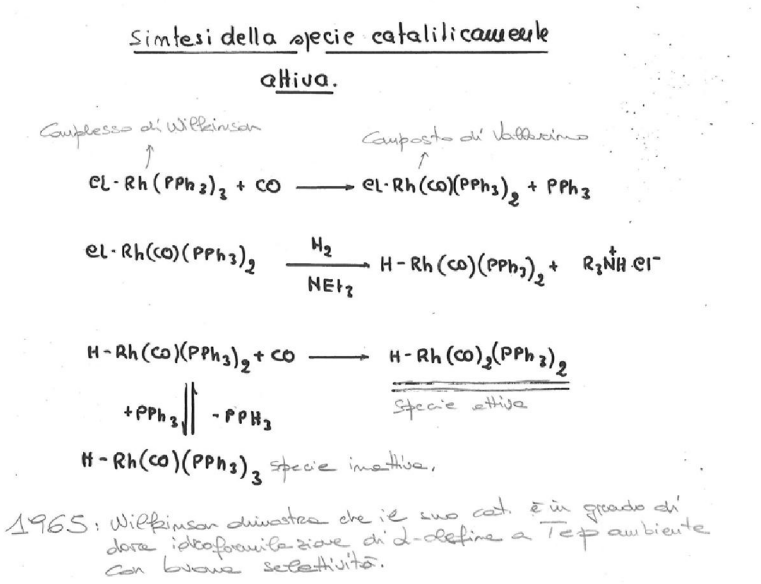
Hydroformylation – $HCo(CO)_4$ vs $HCo(CO)_3PR_3$



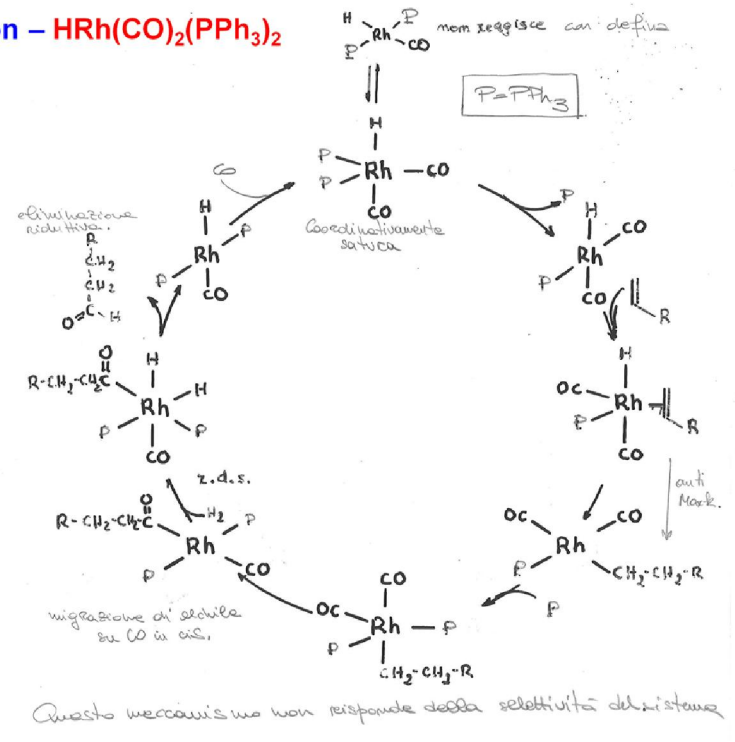
Hydroformylation – $HRh(CO)_4$



Hydroformylation – $HRh(CO)_2(PPh_3)_2$

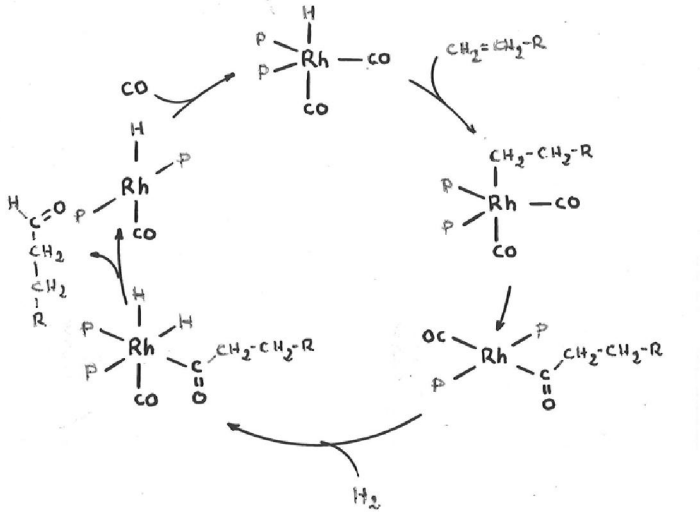


Hydroformylation – $HRh(CO)_2(PPh_3)_2$



Hydroformylation – $HRh(CO)_2(PPh_3)_2$

Questo meccanismo è stato proposto per giustificare la selettività. Si ammette che penta coordinato interagisca con olefina per dare l'alchile derivato. Si ipotizza un meccanismo concertato. È necessario avere 2 molecole di PPh_3 per avere ingombro sterico sufficiente da dare alta selettività n/i.



Hydroformylation – $HRh(CO)_2(PPh_3)_2$

Idroformilazione del propene: andamenti della selettività e attività.

cat.: $H-Rh\,CO(PPh_3)_3$

t (°C)	p (Atm)	P/Rh	n/i	$\bar{r}$ (g./min./m.)
100	30	3	1:1 (50% n)	
100	30	13	2:1 (66.7% n)	
125	12.5	603	15.3:1 (94% n)	
100	35	5		13
100	35	50		2.5

Per ottenere buona selettività si deve sacrificare l'attività.

$RhH(CO)(PPh_3)_3$ inattivo $\overset{-CO}{\underset{+PPh_3}{\rightleftharpoons}}$ $RhH(CO)_2(PPh_3)_2$ attivo e selettivo $\overset{-CO}{\underset{+PPh_3}{\rightleftharpoons}}$

$RhH(CO)_2PPh_3$ $\overset{-CO}{\underset{+PPh_3}{\rightleftharpoons}}$ $RhH(CO)_4$ attivo; non selettivo

Per avere alta selettività, devo abbassare P_{CO} e aumentare rapporto P/Rh.

Si lavora in PPh_3 fusa.

A bassi P/Rh tende a formarsi: $RhH(CO)_4$: attivo ma non selettivo.

Aumentando P/Rh produco la specie selettiva ma anche quella inattiva: perdo in attività.

Hydroformylation – Co vs Rh

Confronto Cobalto - Rodio.

Verrà probabilmente sostituito da cat. con leghe solfonate: ci ha guadagno in selettività (97%) e più facile recupero del catalizzatore

	$H-Co(CO)_4$	$H-Co(CO)_3PR_3$	$H-Rh(CO)_2(PPh_3)_2$
temp. (°C)	140 - 180	160 - 200	80 - 120 } impianto meno costoso.
p (Atm.)	250 - 350	50 - 100	15 - 25 }
M%/ol.	0.1 - 1	0.5 - 1	$10^{-2} - 10^{-3}$
n/i	3-4 : 1 (80% lim.)	6-8 : 1 (88% lim)	10-14 : 1 (93.3% lim.)
aldeidi %	~ 80	–	~ 96
alcoli %	~ 10	~ 80	–
alcani %	~ 1	~ 15	~ 2 ⊛
altri prod.	~ 9	~ 5	~ 2

⊛ La idrogenazione degli alchemi viene inibita sia dal CO che dalla PPh_3.

2) $H-Rh(CO)_2(PPh_3)_2$ è un ottimo cat. di idrogenazione degli alchemi.

Rh ha vari vantaggi: impianto meno costoso (lavora a condizioni più blande) e dà selettività più alta.

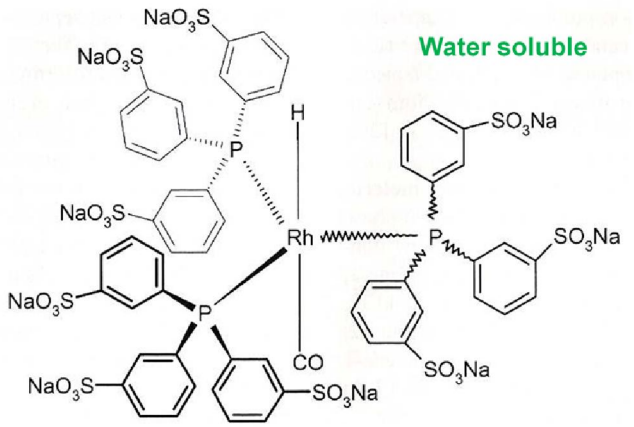
L'inconveniente è l'altissimo costo del metallo.

Hydroformylation – Co vs Rh

Table 3. Comparison of industrial hydroformylation processes of different companies [5, 11]

Process parameters	RuhrChemie	Shell	UCC
Catalyst	$HCo(CO)_4$	$Co(CO)_3PR_3$	$HRh(CO)(PPh_3)_3$
Pressure, MPa	20–30	4–8	1.5–2.0
Temperature, °C	140–180	160–200	85–115
Propylene conversion, %			85–89
n-Butanal/*iso*-butanal selectivity	80/20	88/12	92/8
Expenses for catalyst separation	High	High	High

Hydroformylation – Modified Rh catalysts



The process is limited to short alkenes that have an appreciable solubility in water.
Reaction is slower because of low alkenes concentration.

Hydroformylation – Co vs Rh

Table 3. Comparison of industrial hydroformylation processes of different companies [5, 11]

Process parameters	RuhrChemie	Shell	UCC	RuhrChemie/Rhone-Poulenc
Catalyst	$HCo(CO)_4$	$Co(CO)_3PR_3$	$HRh(CO)(PPh_3)_3$	$HRh(CO)(TPPTS)_3$
Pressure, MPa	20–30	4–8	1.5–2.0	4–6
Temperature, °C	140–180	160–200	85–115	110–130
Propylene conversion, %			85–89	85–99
n-Butanal/*iso*-butanal selectivity	80/20	88/12	92/8	94/6
Expenses for catalyst separation	High	High	High	Low

Wacker process: synthesis of acetaldehyde

$$C_2H_4 + ½\ O_2 \rightarrow CH_3CHO$$

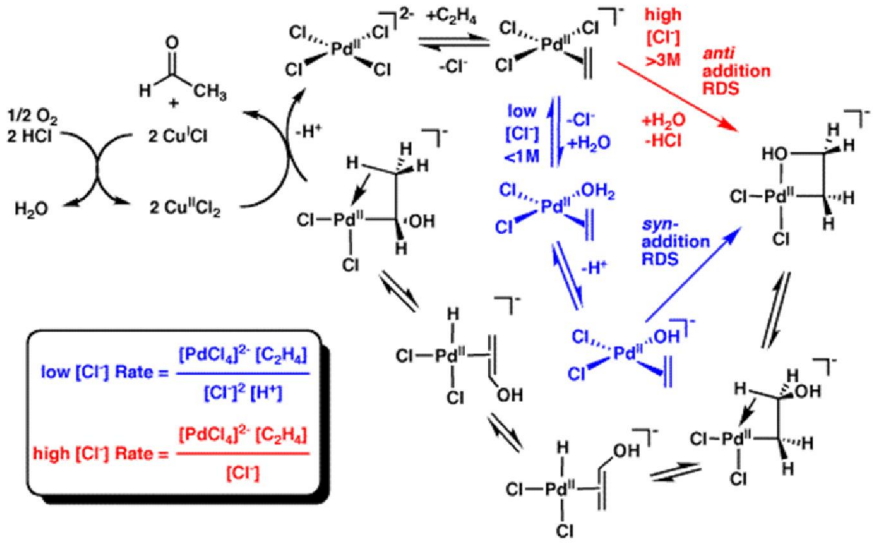
It is a multi-step process:

$$[PdCl_4]^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2\ HCl + 2\ Cl^-$$

$$Pd + 2\ CuCl_2 + 2\ Cl^- \rightarrow [PdCl_4]^{2-} + 2\ CuCl$$

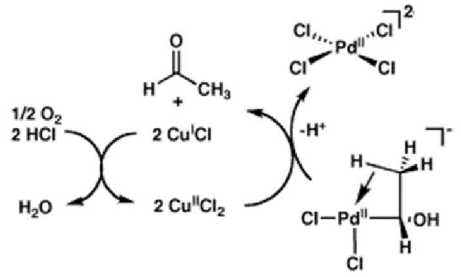
$$2\ CuCl + ½\ O_2 + 2\ HCl \rightarrow 2\ CuCl_2 + H_2O$$

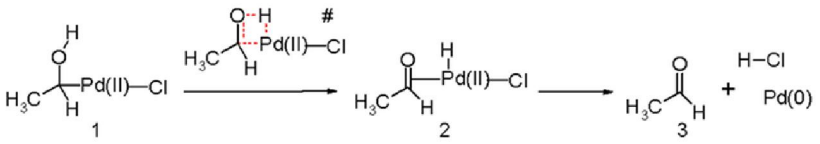
Wacker process: synthesis of acetaldehyde



Wacker process: synthesis of acetaldehyde

$[PdCl_4]^{2-} + C_2H_4 + D_2O \rightarrow CH_3CHO + Pd + 2\ DCl + 2\ Cl^-$





Carbonylation

1. **Methanol to acetic acid**

   $CH_3OH + CO \rightarrow CH_3COOH \qquad \Delta H = -136\ 6\ kJ\ mol^{-1}$

   (BASF $[Co(CO)_4]^-$, BP-Monsanto$[RhI_2(CO)_2]^-$, BP (The Cativa Process, Ir + Ru)

2. **Propyne to methylmethacrylate**

   $CH_3C{\equiv}CH + CO + CH_3OH \rightarrow CH_3C(=CH_2)\text{-}COOCH_3$

   (Shell, a Pd complex)

3. **Carbonylation of appropriate secondary alcohol** in the synthesis of Ibuprofen (Hoechst, Pd catalyst)

Methanol to acetic acid

1. BASF Process based on $Co(CO)_4$ complex
1. Monsanto-BP Process based Rh carbonyl complex
2. BP-Cativa process based on Ir carbonyl complex

More than 60% of the world acetic acid production employs the Methanol Carbonylation route

Acetic acid Processes

Options	Catalyst	Reaction conditions	Yield	By-product
Methanol Carbonylation	Rh complex	180-220°C 30-40 atm	MeOH:99% CO:85%	none
Acetaldehyde Oxidation	Mn acetate or Co acetate	50-60°C atm.press	CH_3CHO: 95%	none
Direct oxidation Of Ethylene	Pd/heteropoly acid/metal	150-160°C 80 atm	ethylene: 87%	CH_3CHO CO_2
Hydrocarbon Oxidation (n-butane, Naphtha)	Co acetate or Mn acetate	150-230°C 50-60 atm	nC_4: 50% naphtha: 40%	Formic acid propionic acid, etc.

Catalyst Systems For Methanol Carbonylation

Company/Technology	Central Catalyst Atom	Cocatalyst (Promoter)
Monsanto/BP	Rhodium	CH_3I/HI
Celanese AO Plus	Rhodium	LiI/CH_3I
BP Cativa	Iridium	CH_3I/Re or Ru
Chiyoda Acetica	Rhodium	CH_3I/Immobilized Complex on solid support

BASF Process - Formation of active Co catalyst

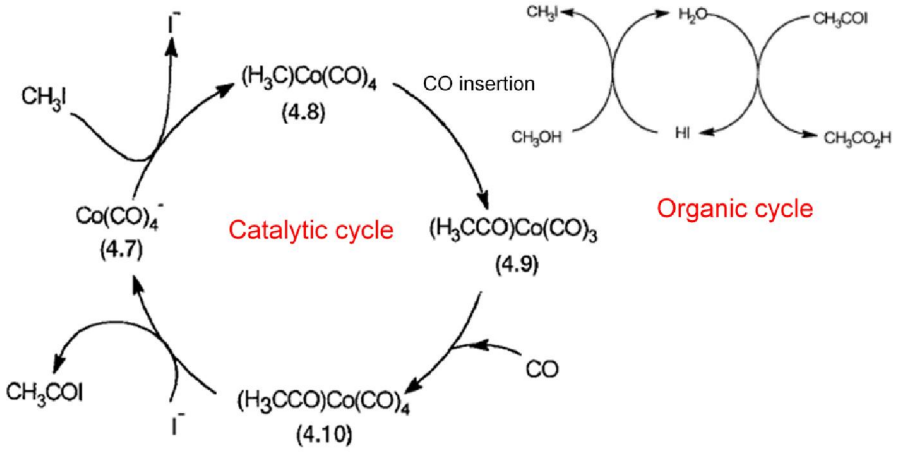
$2CoI_2 + 2H_2O + 10CO \leftrightharpoons Co_2(CO)_8 + 4HI + 2CO_2$

$Co_2(CO)_8 + H_2O + CO \leftrightharpoons \mathbf{2HCo(CO_4)} + CO_2$

$3\ Co_2(CO)_8 + 2nMeOH \leftrightharpoons 2[Co(MeOH)_n]^{2+} + \mathbf{4[Co(CO)_4]^-} + 8\ CO$

- HCo(CO)4 produced in these reactions catalyze FT type reactions and lead to the formation of by products
- The rate of Co catalyzed carbonylation is strongly dependent on both CO and MeOH concentrations and pressure.
- The complex $Co(CO)_4^-$ is an 18 e^- nucleophile.
- The attack on CH_3I is a comparatively slow step.
- High temperatures are therefore required with the Co catalyst.
- This in turn necessitates high pressure of CO to stabilize the $Co(CO)_4^-$ at high temperatures.

The BASF Process: The Catalytic & Organic cycles



The organic chemical cycle:

$CH_3OH + HI \leftrightharpoons CH_3I + H_2O$

$CH_3COI + H_2O \rightarrow CH_3COOH + HI$

1. Nucleophilic attack by $Co(CO)_4^-$ on CH_3I
2. Carbonyl insertion into a metal-alkyl bond
3. Another CO group adds to the 16 e^- species
4. Reaction with I^- to eliminate acetyl iodide

Methanol to Acetic acid by Carbonylation- Process

	BASF(1955)	BP-Monsanto (1970)
Metal concentration	10^{-1}mole per liter of **Co**	10^{-3} mole per liter of **Rh**
Temperature, °C	230	180 – 190
Pressure, bar	500 – 700	30 – 40
Selectivity (%) based on		
a) methanol	90	> 99
b) CO	70	90
By-Products	CH_4, glycil acetate other oxygenated HCs	CO_2, H_2
Effect of H_2	Amount of by-products increases	No effect
Promoter, CH_3I	Essential	Essential

BP-Monsanto Process with Rh- Methanol to acetic acid

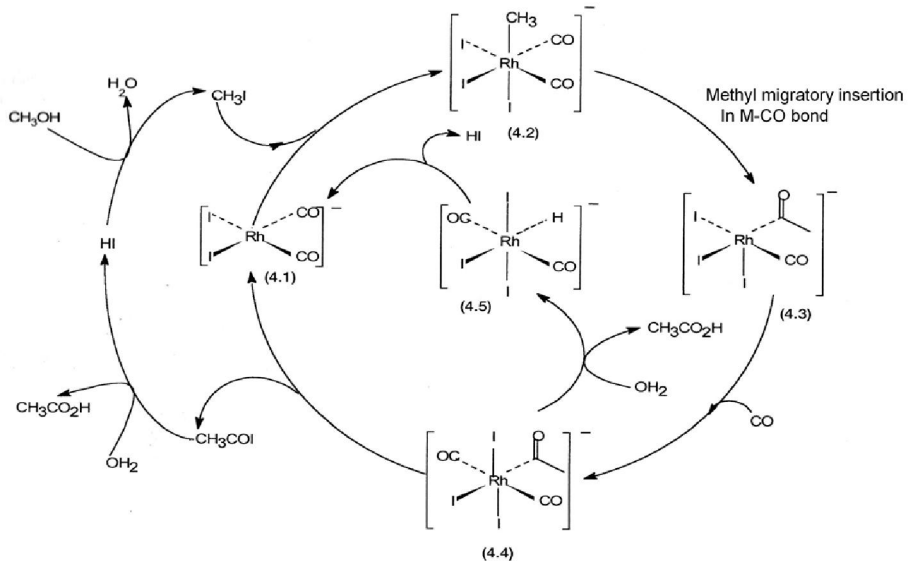


Figure 4.2 Monsanto process: The organic and organometallic cycles are combined. The inner cycle shows an additional pathway for product formation.

The Cativa (Ir) Process

- Operate at reduced water levels (< 8 wt%)
- Price of Rh (US$ 500 per oz) vs Ir (US$ 60 per oz) was the motivation when research started, now Ir price is at US$ 450 per oz!
- Mechanism:
  - Oxidative additon of MeI to the Ir center is about 150 times faster than the equivalent reaction with Rh
  - MeI addition is therefore not the rate-determining step
  - The slowest step is the insertion of CO to form Ir-acetyl species, involves the elimination of ionic iodide and coordination of additional CO ligand.

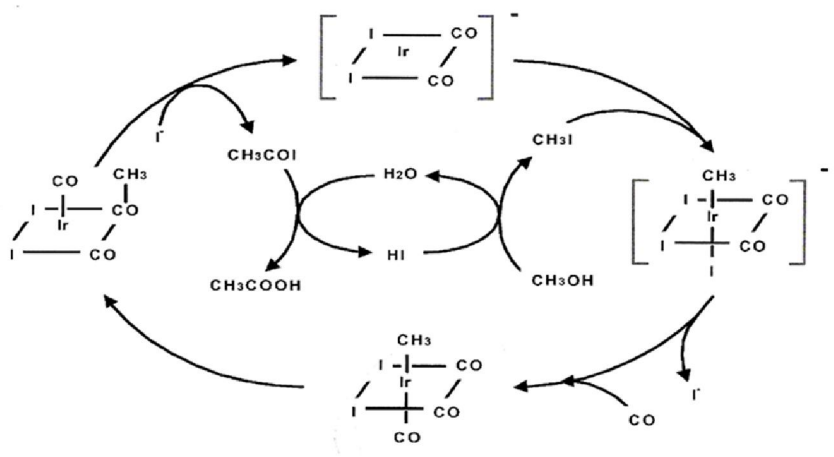
  Hence,

  $$\text{rate} \propto [\text{catalyst}] \quad [CO] / [I^-]$$

- High rates should be achieved by operating at low iodide concentration.
- Inclusion of species capable of assisting in the abstraction of iodide should promote the rate-determining step.
- The patent suggests that Ru or Re are the preferred promoters
- A proprietary blend of promoters has been found to increase the reaction rate

No addition of Li iodide!

Methanol carbonylation on Ir complex



- Rate is about 25 % faster than the Monsanto Rh catalysts.
- Acetic acid selectivity of >99% based on CH_3OH.
- The oxidative addition is no longer rate-determining and migration of the methyl group to the coordinated carbon monoxide is rate-determining.

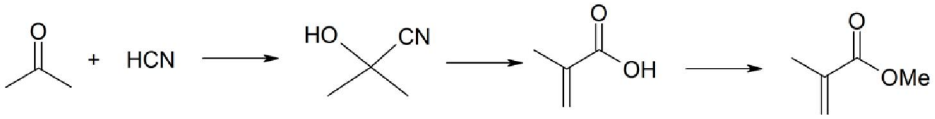
Methanol Me oAc carbonylation Processes

Table 1. Catalyst systems for carbonylations of methanol and methyl acetate.

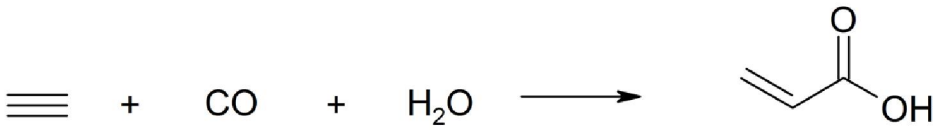
Company	Product	Central atom	Complex	Co-catalyst
Monsanto	AcOH	Rh	$[Rh(CO)_2I_2]^-H^+$	MeI/HI
HCC	AcOH	Rh	$[Rh(CO)_2I_2]^-Li^+$	MeI/LiI
Eastman	Ac_2O	Rh	$[Rh(CO)_2I_2]^-Li^+$	MeI/LiI
Hoechst	Ac_2O	Rh	$[Rh(CO)_2I_2]^-P(R)_4^+$	MeI/P salts
BP	Ac_2O/AcOH	Rh	$[Rh(CO)_2I_2]^-N(R)_4^+$	MeI/N salts (Zr compound)
BP	AcOH	Ir	$[Ir(CO)_2I_2]H^+$	MeI/iodide salts, metal carbonyls (i. e., Ru iodide carbonyls

Carbonylation of alkynes: Methyl methacrylate (MMA)

- The conventional method: A large amount of solid wastes



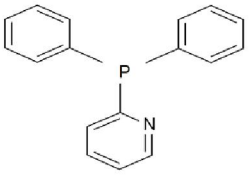
- Pd catalyzed homogeneous reaction by **Shell**
- A Pd complex catalyzes the reaction between propyne, methanol and CO

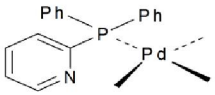


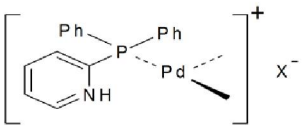
Regioselectivity as high as 99.95%

Shell Process for MMA

- Milder conditions, 60ºC & 10-60 bar pressure.
- Methanol as a solvent as well as a reactant
- The pre catalyst is $Pd(OAc)_2$ mixed with an excess of phosphine ligand to generate the active catalytic intermediate in situ.
- HX as a co-catalyst.

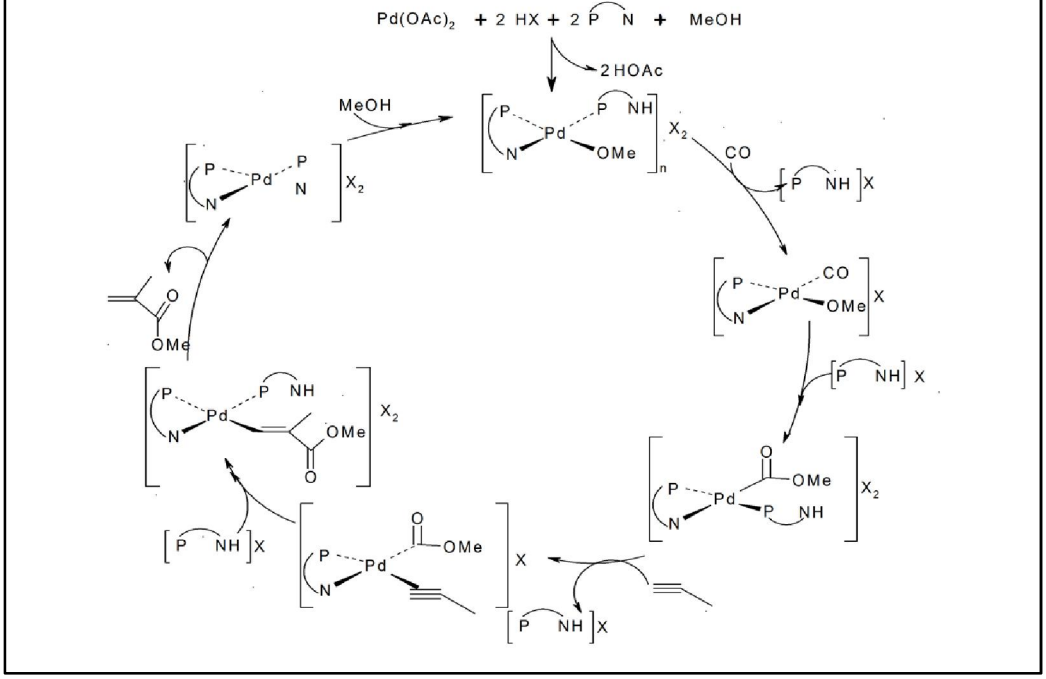






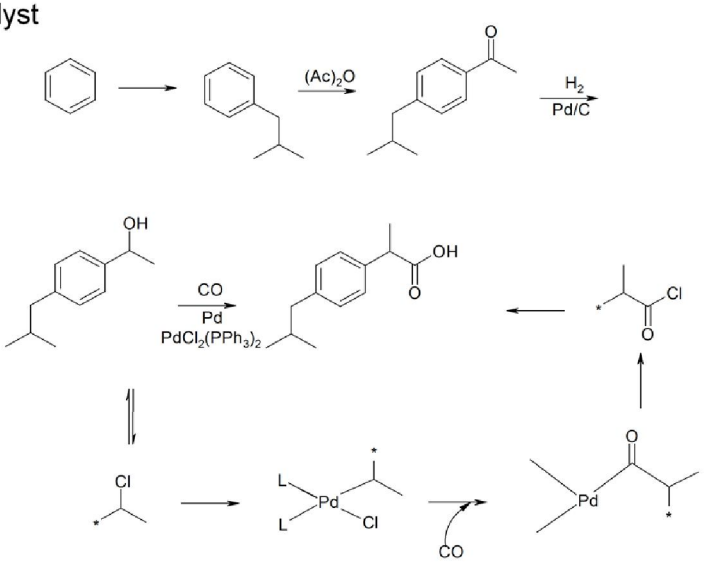
Pd can chelate with P and N. The fourth coordination may be a solvent molecule. In the protonated form, the ligand acts as a labile, weakly coordinating ligand and easily displaced by reactants, such as CO, methylacetylene, etc.

Carbonylation of propyne in methanol to MMA-Shell process



Ibuprofen synthesis - Hoechst

Carbonylation of appropriate secondary alcohol with a Pd catalyst



[organic solvent + HCl : 50 bar : 130 °c]

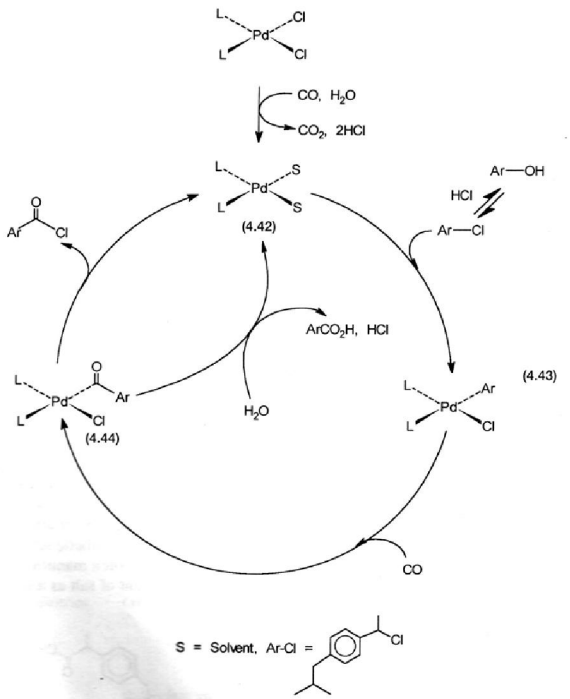


Figure 4.12 Hypothetical cycle for Hoechst–Celanase ibuprofen process. For all the proposed intermediates *cis* geometry is assumed.

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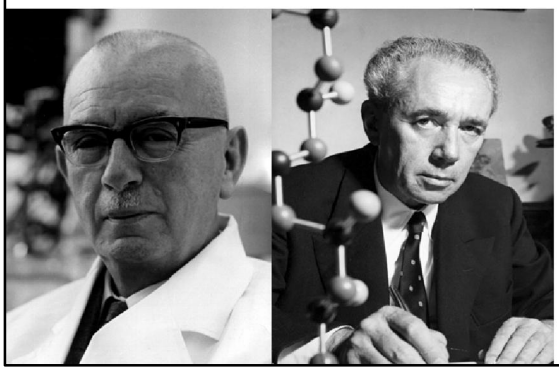
KNOWLEDGE & BEYOND

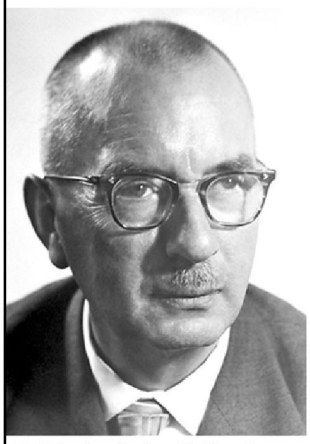
ZIEGLER-NATTA CATALYST



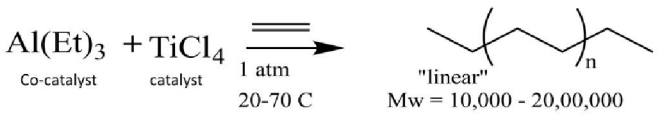
History

- Karl Ziegler in 1953 polymerized ethylene catalytically to polyethylene.
- Giulio Natta utilized Ziegler's catalyst to produce polypropylene in 1954.
- In 1963, both Karl Ziegler and Giulio Natta were awarded the Nobel Prize for their discoveries.
- In 1973 the 2nd generation Ziegler-Natta catalysts were introduced with β-$TiCl_3$ at lower temperatures.
- In 1980 3rd generation catalysts supported on $MgCl_2$ were commercialized by many companies.
- In 1991 4th generation Ziegler-Natta catalysts based on aluminoxane activated metallocene complexes were used.
- Two broad classes:
    - ❖ Heterogeneous Catalyst: Based on Ti compounds
    - ❖ Homogeneous Catalyst: Based on complexes of Ti, Zr and Hf

Ziegler's Discovery (Germany,1953)

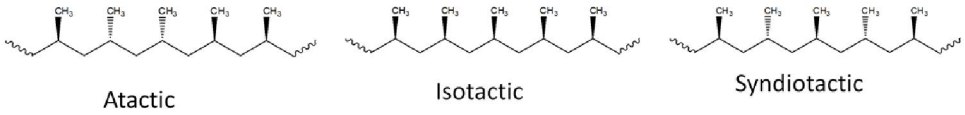


Karl Ziegler-the last Al-Chemist
"...because he turned aluminium into gold."

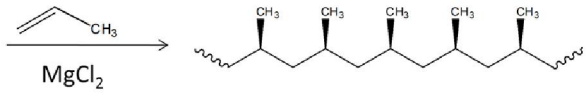


Using propylene

- Propene can polymerize in three ways:



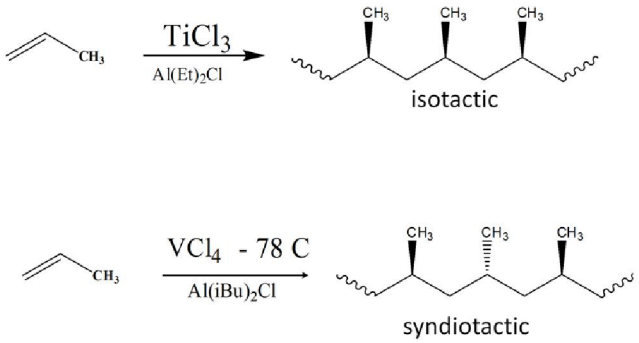
Atactic Isotactic Syndiotactic

- $TiCl_4 + Al(C_2H_5)_3$ 

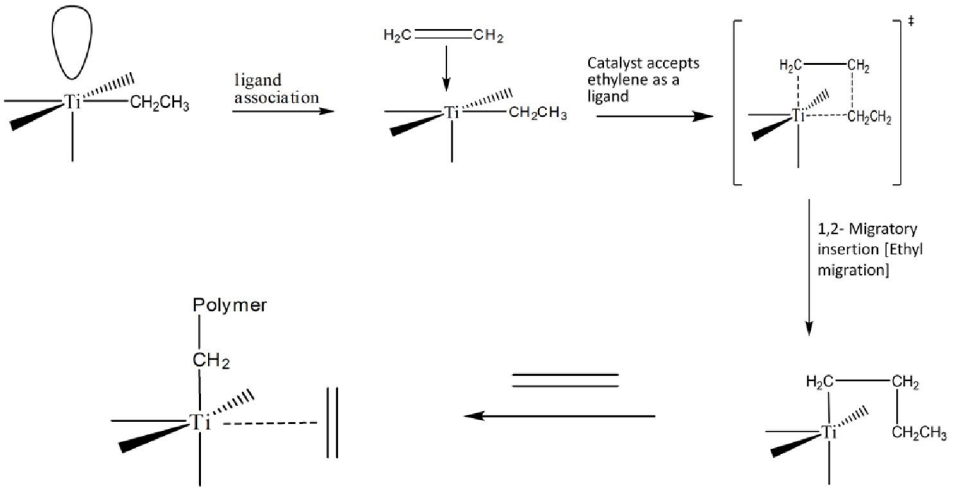
❑Highly selective towards isotactic product

❑Highly stable product

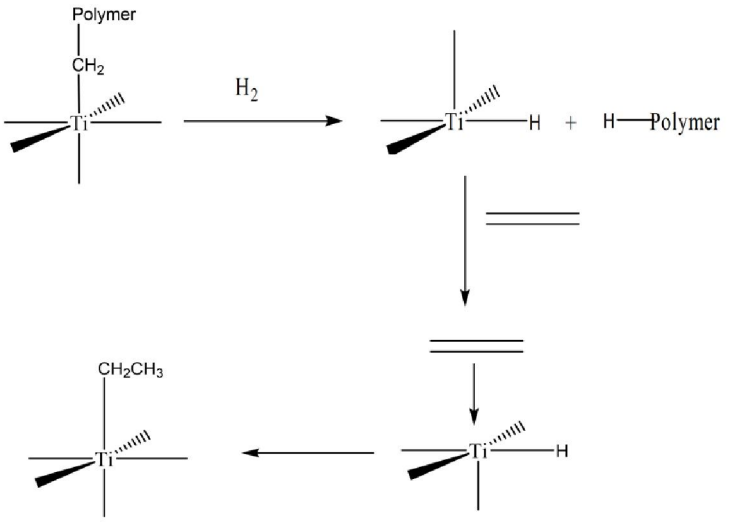
Natta's Discovery (Italy,1954)



Mechanism of Ziegler-Natta Polymerization: The Cossee Mechanism

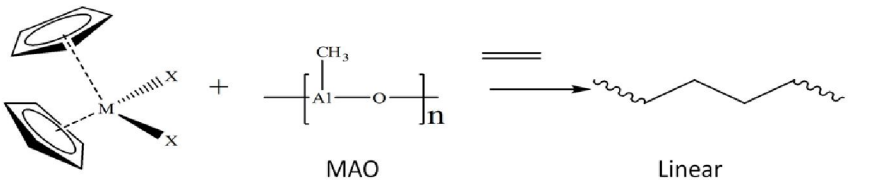


Termination Step: Chain Transfer



Kaminsky Catalyst System

Homogeneous Ziegler Natta Catalyst

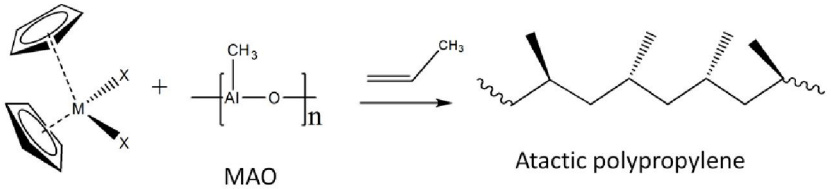


MAO

Linear

M = Ti, Zr, Hf

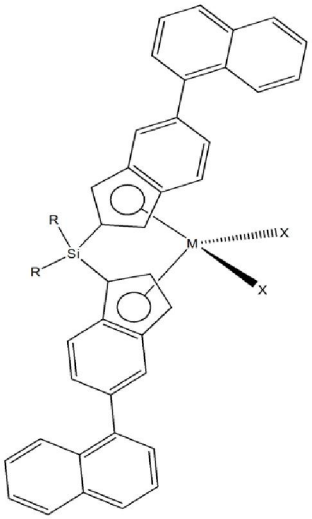
MAO=methylaluminoxane



MAO

Atactic polypropylene

Brintzinger System



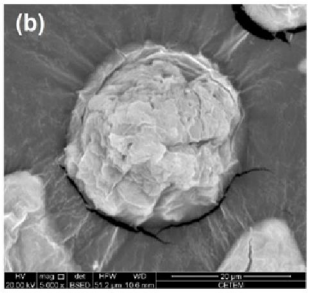
ansa-metallocene

R= CH_3, C_2H_5
X= Cl, Br, CH_3
M= Ti, Zr

Brintzinger developed these catalysts which when activated with MAO catalysed the stereoselective polymerizations of propylene with very high activities. Thus for the first time isotactic polyolefins were obtained using homogeneous Ziegler-Natta catalyst

Importance of Ziegler Natta Catalyst

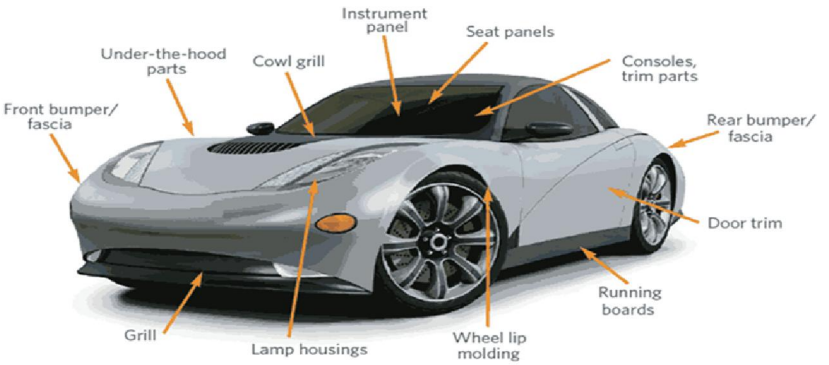
- High Efficiency
- High Stereoregularity (99% tacticity)
- Longer Lifetime
- High concentration of polymer product
- Lower cost in production
- Easy regeneration of catalyst
- Controls growth and formation of polymer product
- Control of polymer particle morphology in spherical shape
- Higher stability



Applications of Ziegler-Natta Catalyst

Production of:

- High density polyethylene (HDPE)
- Linear low density polyethylene (LDPE)
- Ultra-high molecular weight polyethylene (UHMWPE)
- Thermoplastic polyolefins (TPO's)
- Polybutylene (PB)
- Shiny lustrous polyacetylene film which have semiconducting properties
- Crystalline polypropylene
- Carbon nanotubes nanocomposites

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