Transition metal alkene and alkyne complexes

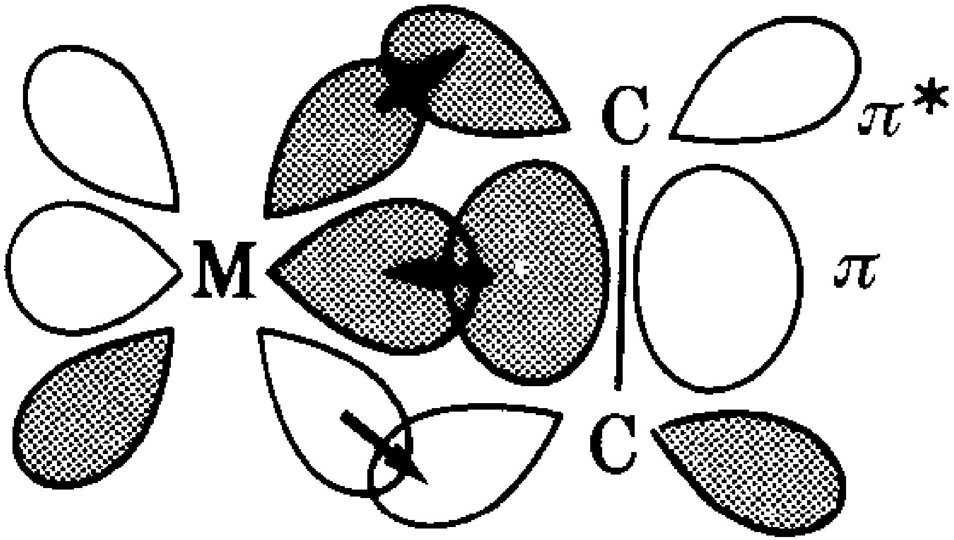
Great number and variety of unsaturated organic molecules, which are <u>stable, economical and available on a very large scale</u>. The multiple C-C bond can be easily transformed into other functional groups, cyclized or (co)polymerized.

Lower cost of ethylene and other olefins as building blocks (derived from petroleum), with respect to acetylene (derived from carbon). However, the interest in alkyne transformations has increased lately, due to the success of some key reaction that employ them as reagents, such as Sonogashira couplings, A^3 (Aldehyde-Alkyne-Amine) coupling, cycloadditions, metathesis, hydrofunctionalizations…

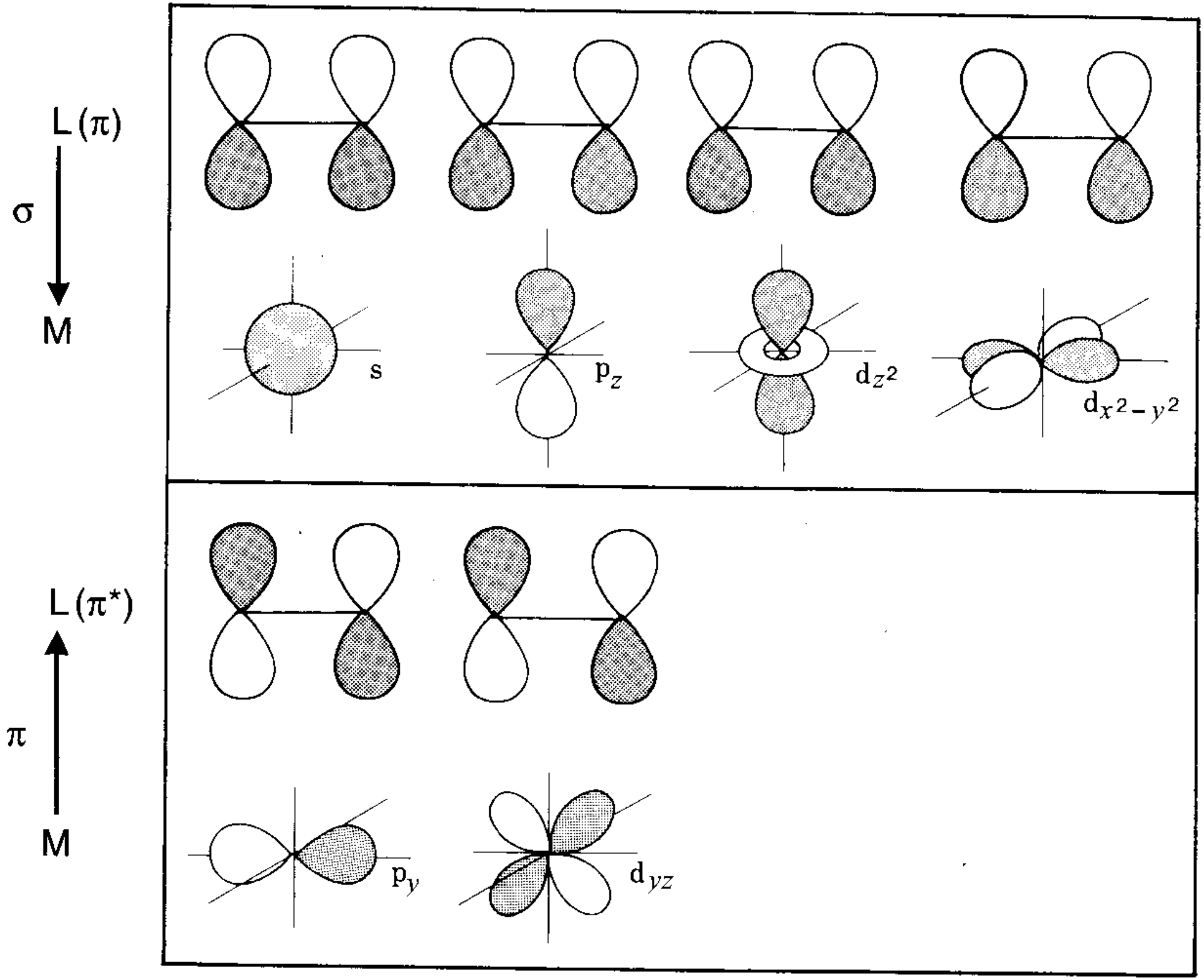
First example of carbon ligands which act as donor towards metal centres with <u>filled molecular orbitals distributed over more than one donor carbon atom and having π symmetry</u>.

Metal-C2 interaction

The interaction between a transition metal center and an unsaturated C2 system can be interpreted in terms of donor-acceptor synergism, through the so-called **Dewar-Chatt-Duncanson (DCD)** model, which involves σ donation to the metal from a filled π bonding orbital of the organic molecule and π back-donation from a filled d metal orbital to a π* antibonding orbital of the organic molecule.

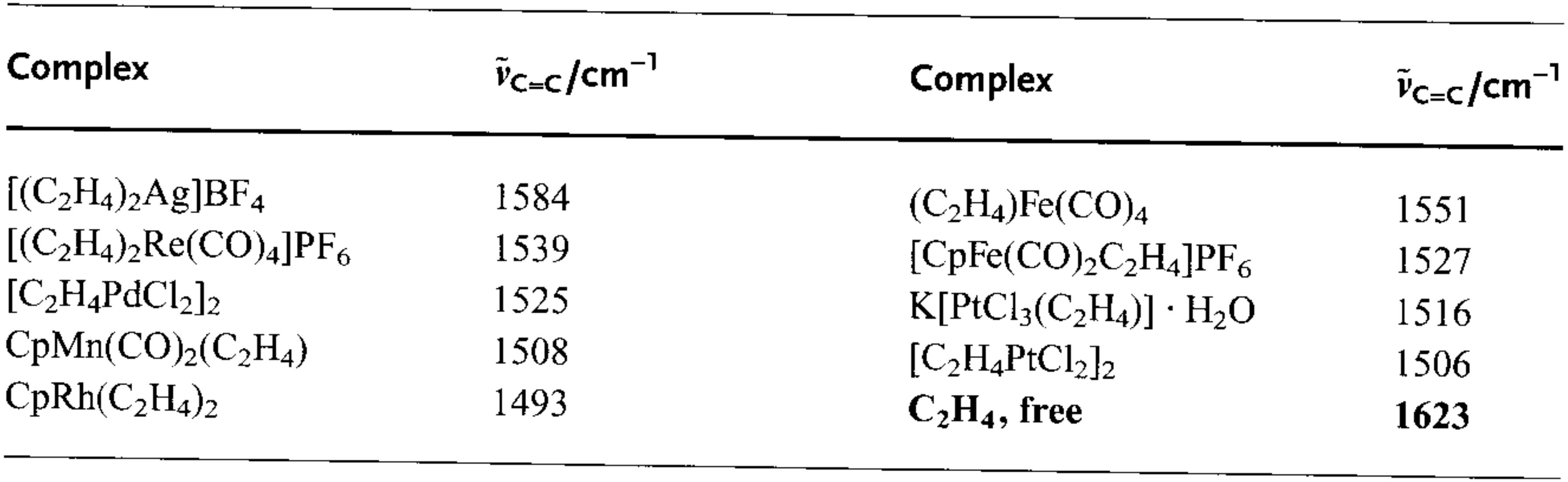


Metal-C2 interaction



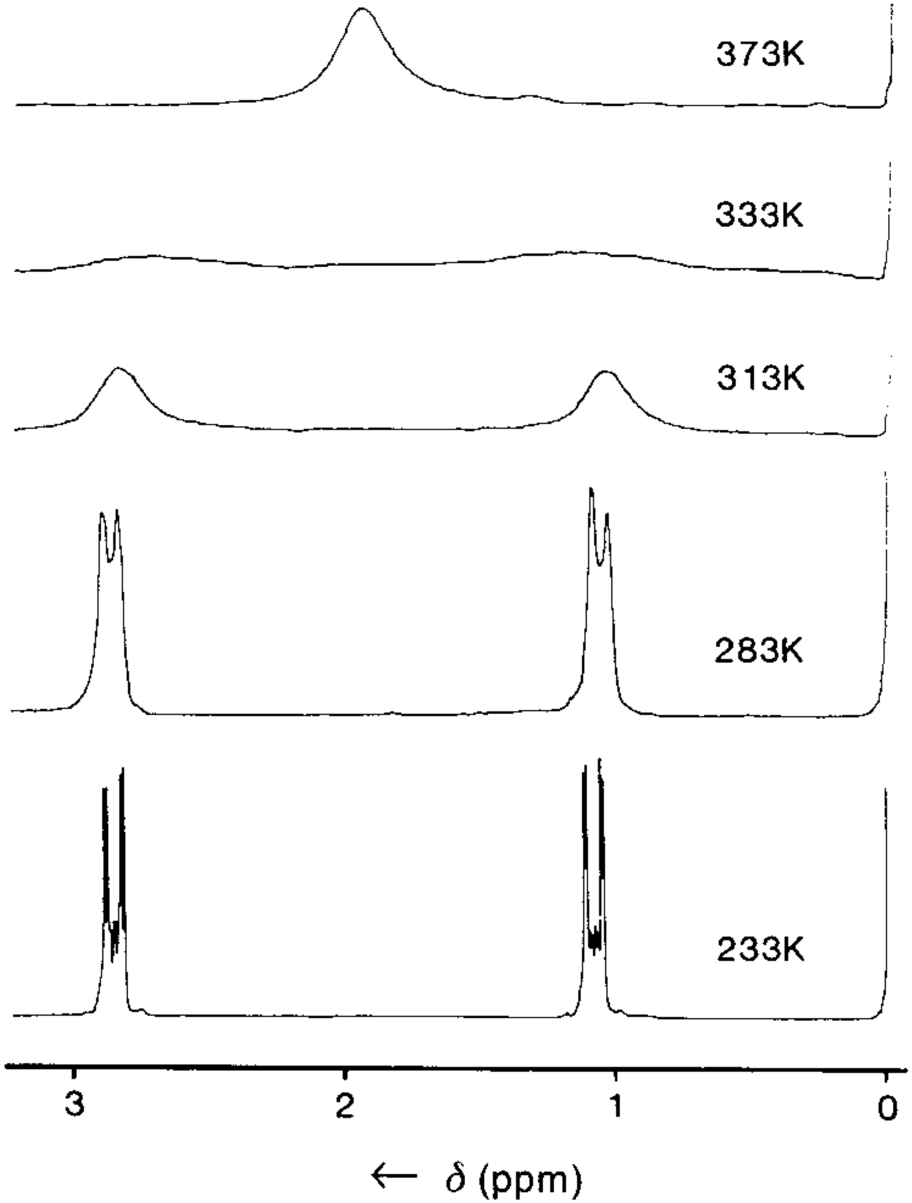
Metal alkene(alkyne) complexes

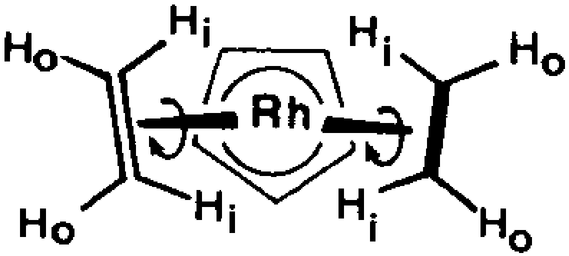
Similarly to metal carbonyls, the energy of a metal-alkene interaction is dominated by the back-donation contribution. However, in this case both donation and back-donation weaken the C=C double bond, which consequently will be invariably weaker compared to the free alkene, as apparent by e.g. IR.



Complex	$\tilde{\nu}_{C=C}/cm^{-1}$	Complex	$\tilde{\nu}_{C=C}/cm^{-1}$
$[(C_2H_4)_2Ag]BF_4$	1584	$(C_2H_4)Fe(CO)_4$	1551
$[(C_2H_4)_2Re(CO)_4]PF_6$	1539	$[CpFe(CO)_2C_2H_4]PF_6$	1527
$[C_2H_4PdCl_2]_2$	1525	$K[PtCl_3(C_2H_4)] \cdot H_2O$	1516
$CpMn(CO)_2(C_2H_4)$	1508	$[C_2H_4PtCl_2]_2$	1506
$CpRh(C_2H_4)_2$	1493	**C_2H_4, free**	**1623**

Metal alkene(alkyne) complexes

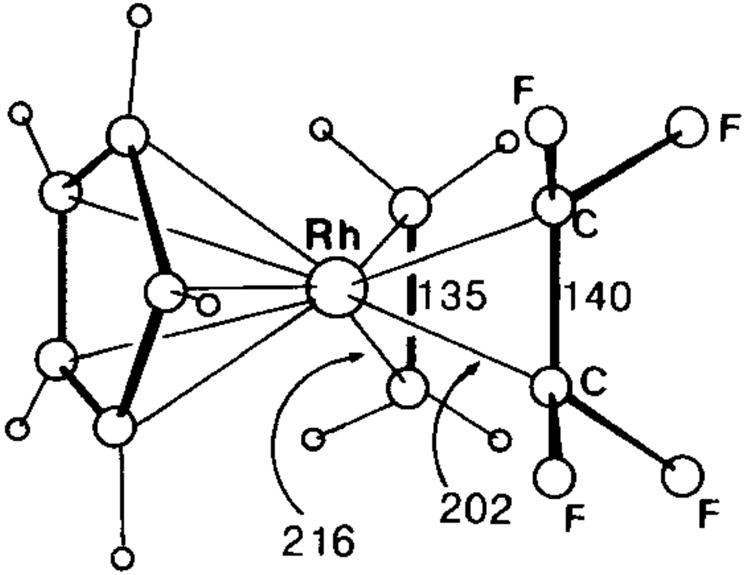




The back-donation contribution (π simmetry with respect to the metal-alkene bond axis) can be evaluated also by determining the energy barriers for the rotation around the metal alkene bond. This estimation can however be complicated by steric and electronic factors, such as the availability of orthogonal orbitals on the metal for back-donation.

Metal alkene(alkyne) complexes

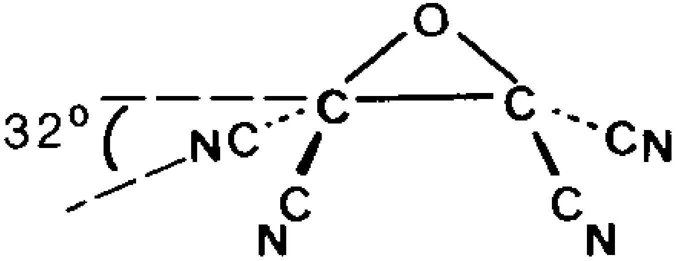
The onset of the donor-acceptor equilibrium also implies a distortion of the coordinated alkene from planarity, the degree of which correlates with the extent of back-donation.



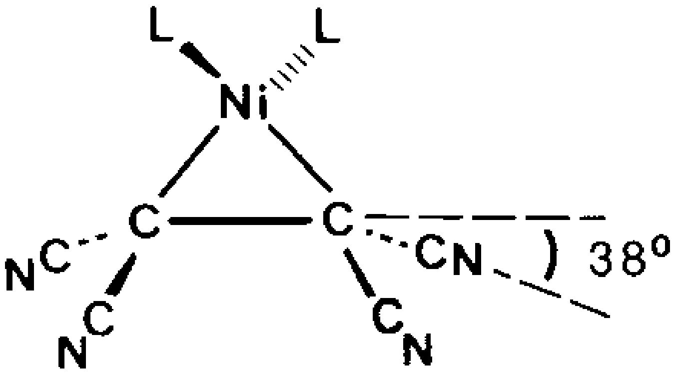
Structure (X-ray diffraction) of **(Cp)Rh(C_2H_4)(C_2F_4)**. The C atoms of C_2F_4 are closer to the metal than the C atoms of C_2H_4. The angle between the two CH_2 planes in C_2H_4 is 138°; in contrast the CF_2 planes in C_2F_4 are at 106° to each other (*Guggenberger*, 1972).

Metal alkene(alkyne) complexes

In compounds in which back-donation predominates, the geometry of the resulting complex is strongly analogous to that of a cyclopropane or an epoxide of the considered alkene.

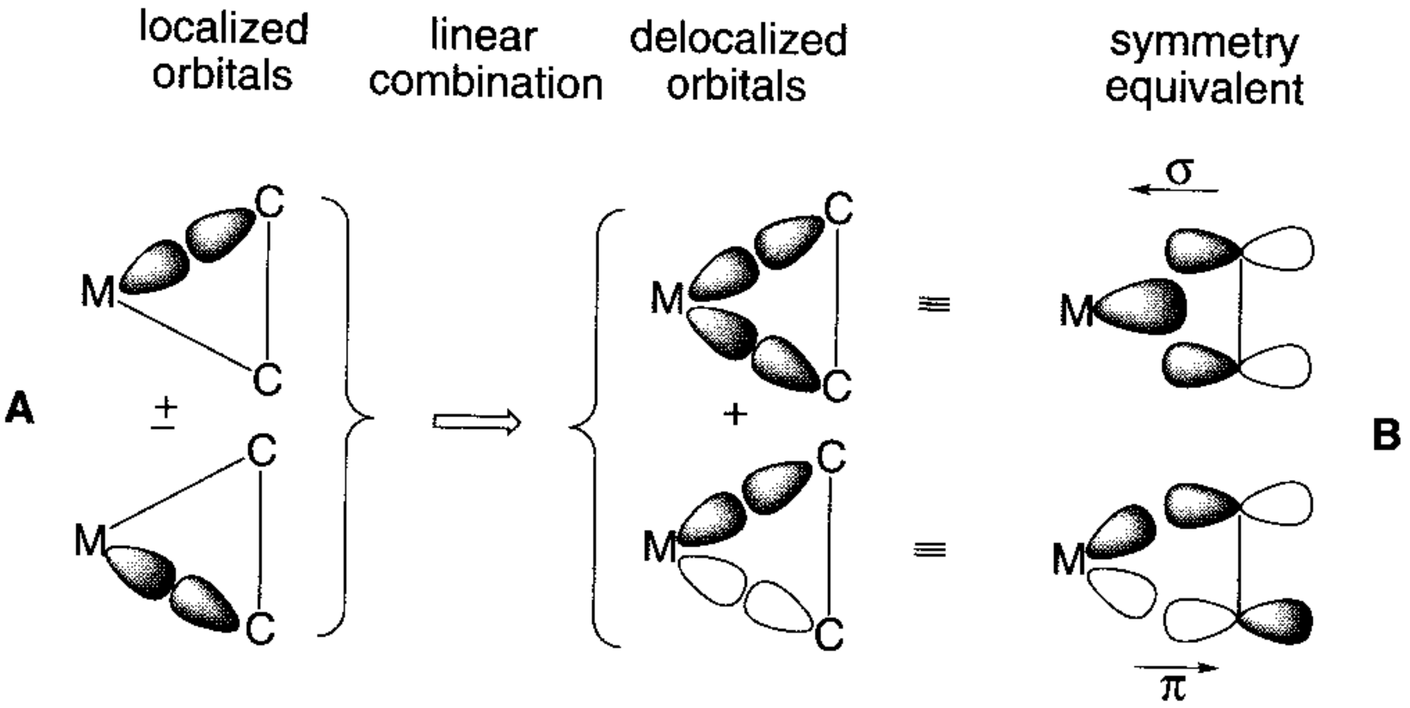


epoxide



(η^2- tetracyanoethylene)Ni complex
(nickelacyclopropane)

Metal-C2 interaction



Metallacyclopropane description:
two localized 2 e2 c MC σ bonds,
alkene acts as a diradical bidentate ligand
(nonplanar)
covalent picture

Dewar–Chatt–Duncanson model:
one delocalized 2 e3 c MC_2 σ bond,
one delocalized 2 e3 c MC_2 π bond,
alkene acts as a “monodentate” ligand (planar)
donor–acceptor picture

Limit representations of the interaction, similar to those employed for Schrock/Fischer carbenes!

Metal alkene(alkyne) complexes

Factor that determine a strong back-donation contribution:

- Electron-rich metal center (low formal oxidation state, absence of π -accepting ligands);

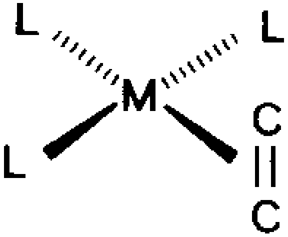
- Electron-withdrawing substituents on the alkene;

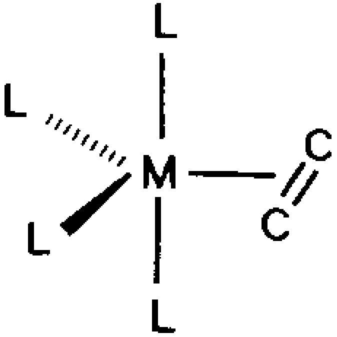
- Ring strain on the (cyclic) alkene, that can be released upon distortion from planarity;

Under these conditions, the more pertinent description of the metal alkene interaction is the metallacyclopropane. Consequently, the olefin should be considered an X_2 ligand and the metal oxidized by two units (oxidative addition of the alkene). Nevertheless all alkene ligands are conventionally considered L ligands, as CO and carbenes…

Metal alkene(alkyne) complexes

The preferred conformation of the alkene relative to the metal alkene bond axis will depend on steric and electronic factors, comprising the coordination number of the metal, the nature and steric bulk of the other ligands and the number of electrons surrounding the metal centre.

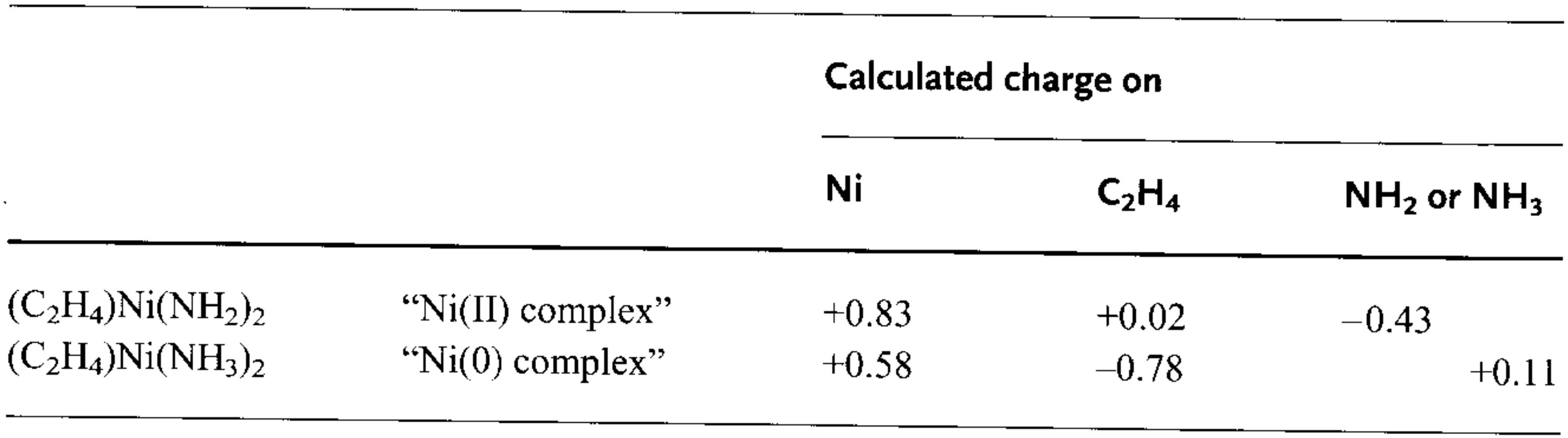




	C.N. 3, 16 VE	C.N. 4, 16 VE	C.N. 5, 18 VE
	L_2M (alkene) L_2M (alkyne)	L_3M (alkene)	L_4M (alkene)
Examples:	$(PPh_3)_2NiC_2H_4$ $Pt(C_2H_4)_3$	$K[PtCl_3(C_2H_4)]$	$(PPh_3)_2IrBr(CO)TCNE$ TCNE = tetracyanoethylene

Metal alkene(alkyne) complexes

It is important to remark that through the metal-alkene(alkyne) interaction a charge variation on the metal can be distributed on the whole complex (and also on the alkene), leaving the electron density on the metal almost unchanged. This is of the utmost importance for the activation of the coordinated alkene in selected reactions.



		Calculated charge on		
		Ni	C_2H_4	NH_2 or NH_3
$(C_2H_4)Ni(NH_2)_2$	“Ni(II) complex”	+0.83	+0.02	–0.43
$(C_2H_4)Ni(NH_3)_2$	“Ni(0) complex”	+0.58	–0.78	+0.11

Synthesis of TM alkene and alkyne complexes

Given the abundance and stability of these ligands, their complexes with transition metals can be prepared by simple addition/substitution reactions.

Transition metal alkene complexes can also form:

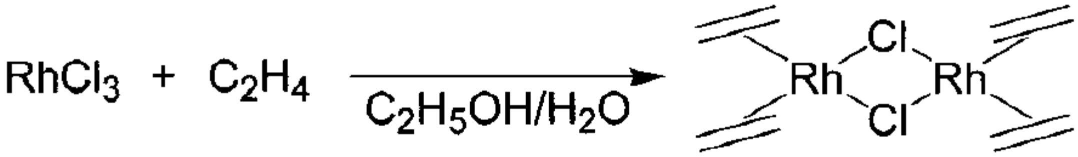
- from alkyl complexes, upon β-elimination or (more rarely) β-removal of a hydride;
- from carbene complexes, upon base-catalyzed tautomerization of the carbene ligand;
- from η^3 allyl complexes, upon nucleophilic attack to the coordinated allyl;
- from transition metal salts, upon reduction in the presence of alkene/alkyne;
- from transition metals upon metal/ligand vapour cocondensation with the alkene/alkyne.

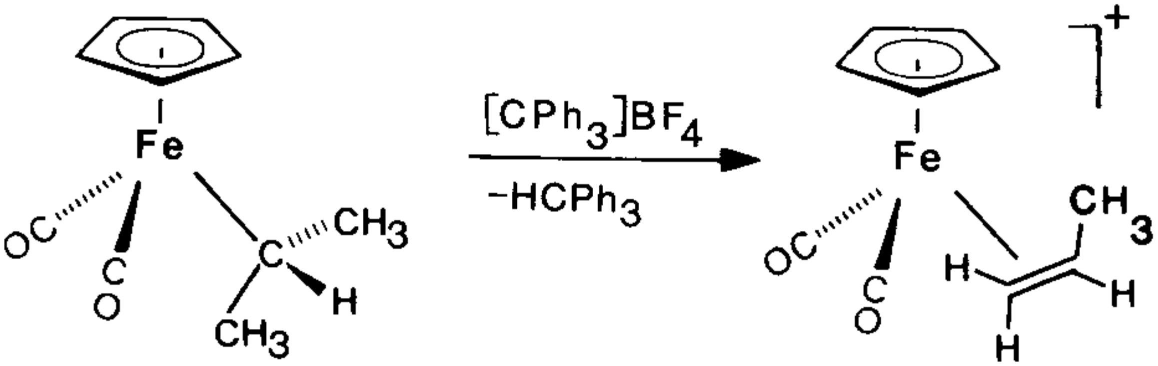
Metal alkyne complexes

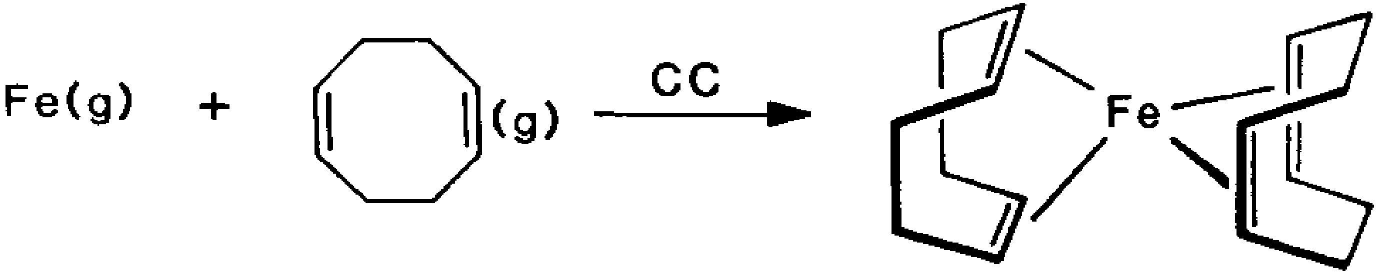
An alkyne as ligand is generally more electron-withdrawing than an alkene (C sp instead of sp^2); consequently, more extensive back-donation is expected compared to an alkene, giving rise to stronger M-alkyne interactions with metal centres capable of back-donating electrons, in which the description of the bond in terms of metallocyclopropene will increase in importance.

Furthermore, it is important to remark that an alkyne has **two** filled and mutually orthogonal π orbitals, hence it can behave as neutral 4-electron donor ligand L_2 towards two different metal centers or even towards the same metal.

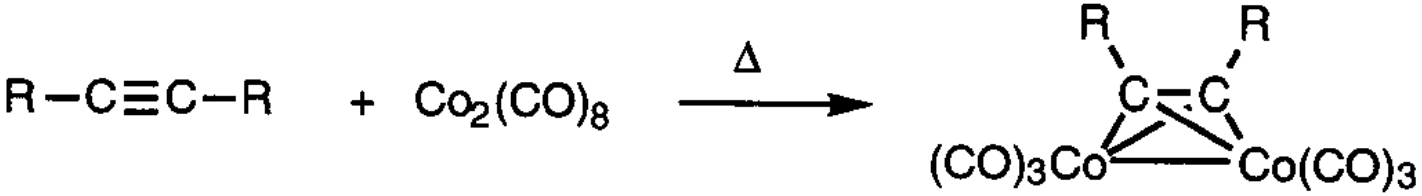
Synthesis of TM alkene and alkyne complexes

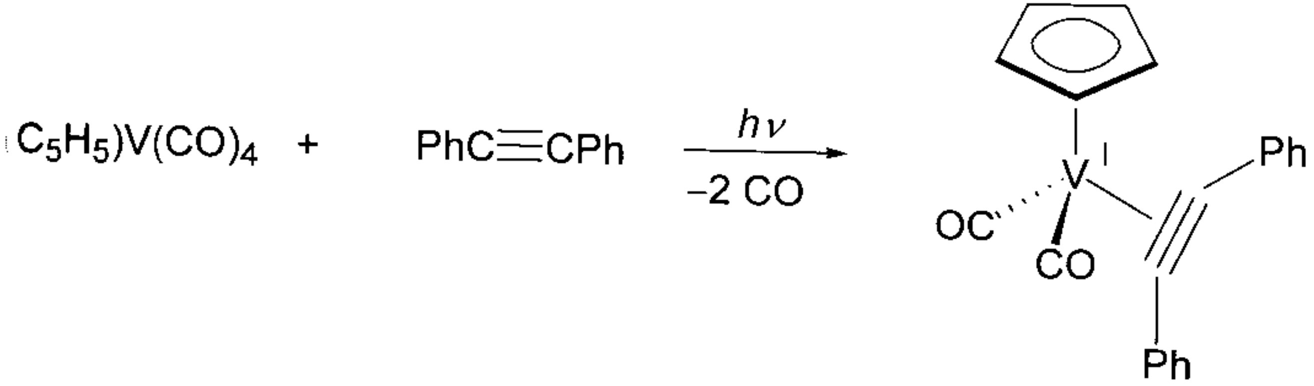


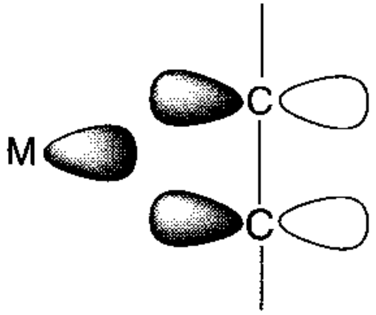




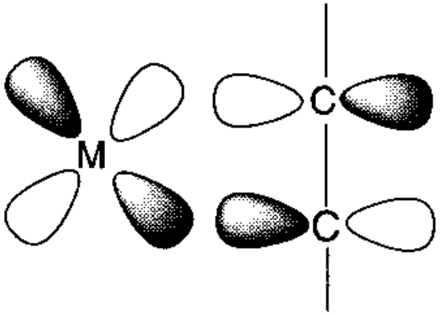
Metal alkyne complexes



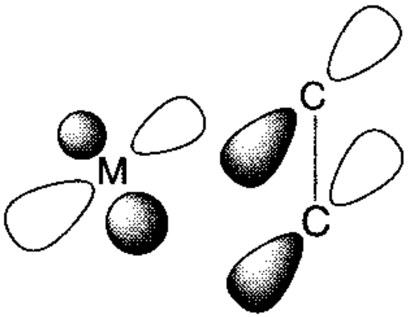




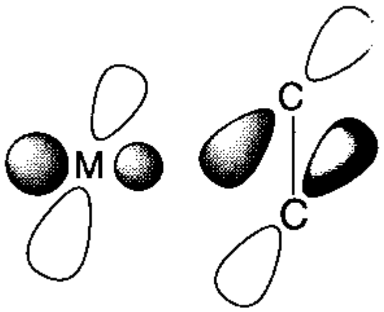
$M \xleftarrow{\sigma} L(\pi_{\|})$



$M \xrightarrow{\pi} L(\pi^{*}_{\|})$



$M \xleftarrow{\pi} L(\pi_{\perp})$



$M \xrightarrow{\delta} L(\pi^{*}_{\perp})$

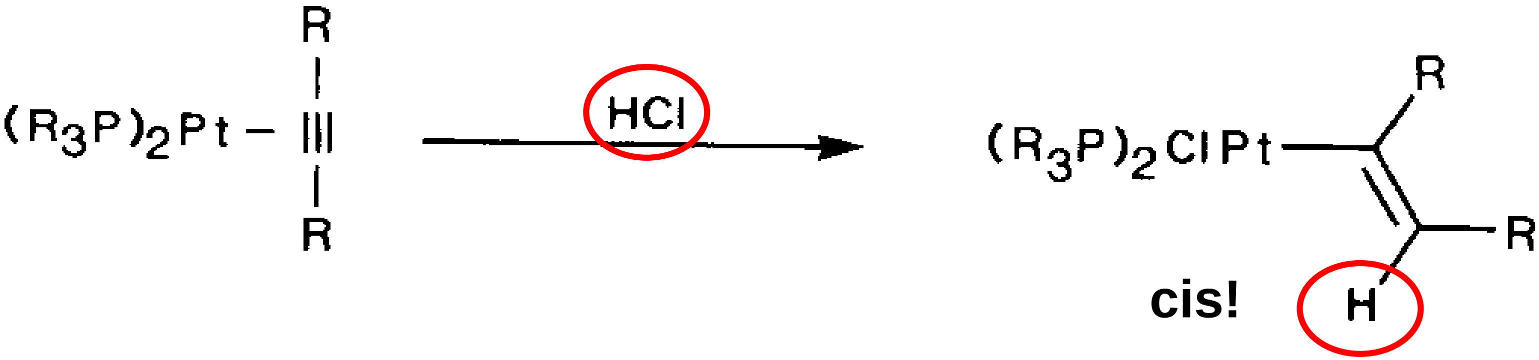
Applications of TM alkene and alkyne complexes

Coordinated alkenes (and, to a much lesser extent, alkynes) are employed as supporting (ancillary, spectator) ligands for transition metal centers in low oxidation state. They are able to stabilize the metal centre and occasionally also to impart chirality to the complex.
In general, though, these ligands can be removed with relative ease, hence their complexes are often employed as reagents or intermediates for the preparation of other complexes or of catalytically active species.
Examples: dibenzylidenacetone (dba), norbornadiene (nbd), cyclooctadiene (cod), cyclooctatetraene (cot)…

The main application of transition metal alkene or alkyne complexes remains their use as **reagents or more often intermediates in processes which convert the unsaturated compound into other products**.

Reactivity of metal alkene/alkyne complexes

Depending on the nature of the metal centre, the net result of alkene/alkyne coordination can be an increase or a decrease in electron density on the ligand, with the related consequences on its reactivity towards nucleophiles/electrophiles. In the majority of cases, though, coordination suppresses the reactivity of the ligands towards external electrophiles. Consequently, metal complexes can be employed in the protection of multiple C-C bonds from electrophilic attack. In some instances, though, electrophilic attack can however take place on the metal, with an involvement of the unsaturated compound in a second stage.



Reactions of metal alkene/alkyne complexes

- **Isomerization**;
- **Hydrogenation/hydroformylation;**
- **Addition of HY (protic, hydridic…) to the double/triple bond;**
- **(Oxidative) functionalization (alkene→functional alkene)**;
- Cycloaddition to metallocarbenes (metathesis etc.);
- Cyclopropanation (no formation of a metal alkene complex!)
- **(reductive) cyclooligomerization**;
- **Oligo- and (co)polymerization**.

Reactions involving formal oxidation of the C-C multiple bond (epoxydation, aziridination, dihydroxylation) will not be covered in this course, since **the mechanisms of these reactions do not involve organometallic compounds**, but rather external attack of the olefin to the metal-coordinated oxidant. Other oxidative reactions involve instead the intermediacy of radicals and are not covered here for reasons of time.

Alkene isomerization

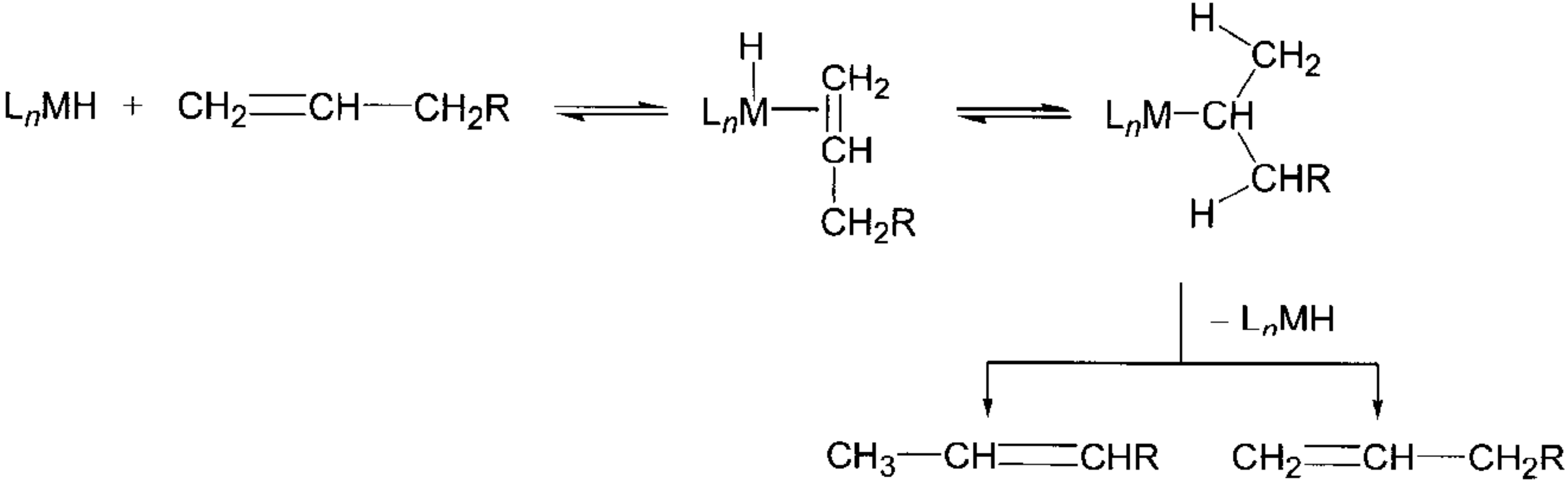
Numerous metal complexes are able to catalyze alkene isomerization reactions. Usually these reactions are under thermodynamic control, so that the reaction tends to produce the most stable alkene (internal alkenes from terminal ones, conjugated alkenes from nonconjugated ones).

However, isomerizations are equilibrium reactions; consequently, if consecutive reaction arise which exclusively consume a terminal alkene without touching the internal ones, the isomerization equilibrium can be completely shifted towards the former.

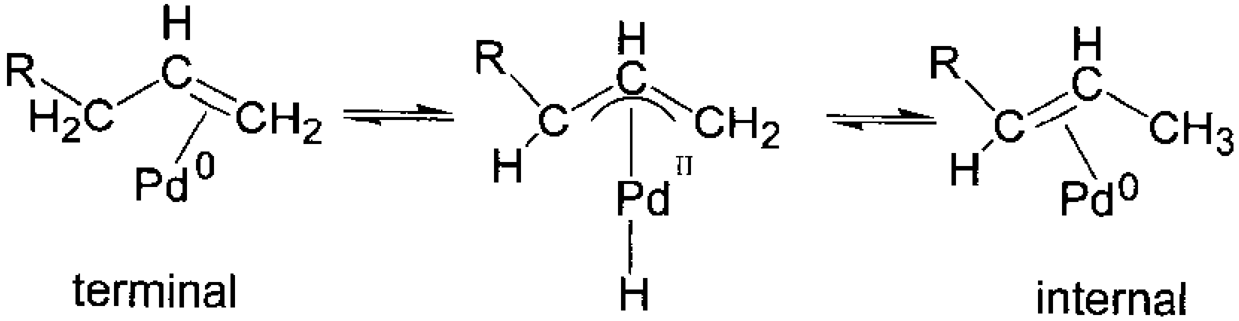
Two metal-catalyzed isomerization mechanisms can be distinguished, depending on the presence or absence of a metal-hydride bond in the catalytically competent species.

Alkene isomerization - Mechanisms

a) Presence of an M-H bond: alkene insertion/β-elimination;



a) Absence of M-H bonds (and M electron-rich): allylic C-H activation;



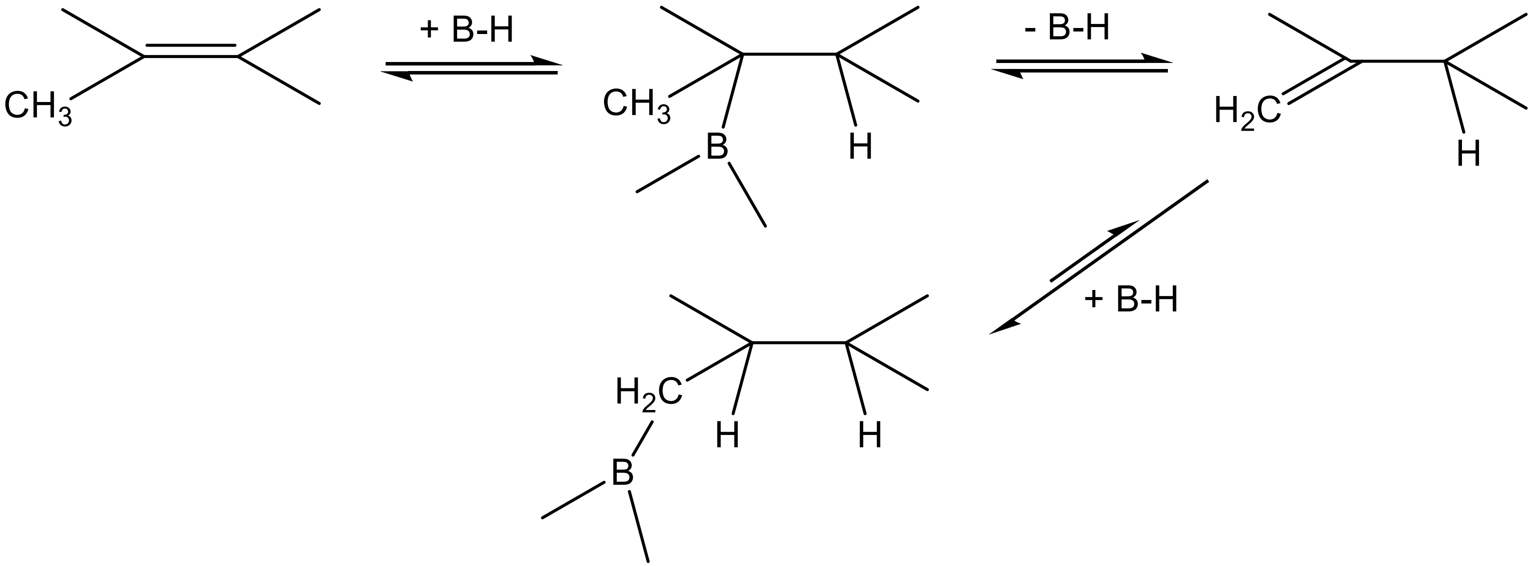
Alkene isomerization

The use of metal catalysts to promote alkene isomerization reactions can appear superfluous, as this reaction can be also catalyzed by simpler, cheaper, easier to remove compounds (e.g. mineral acids). However:

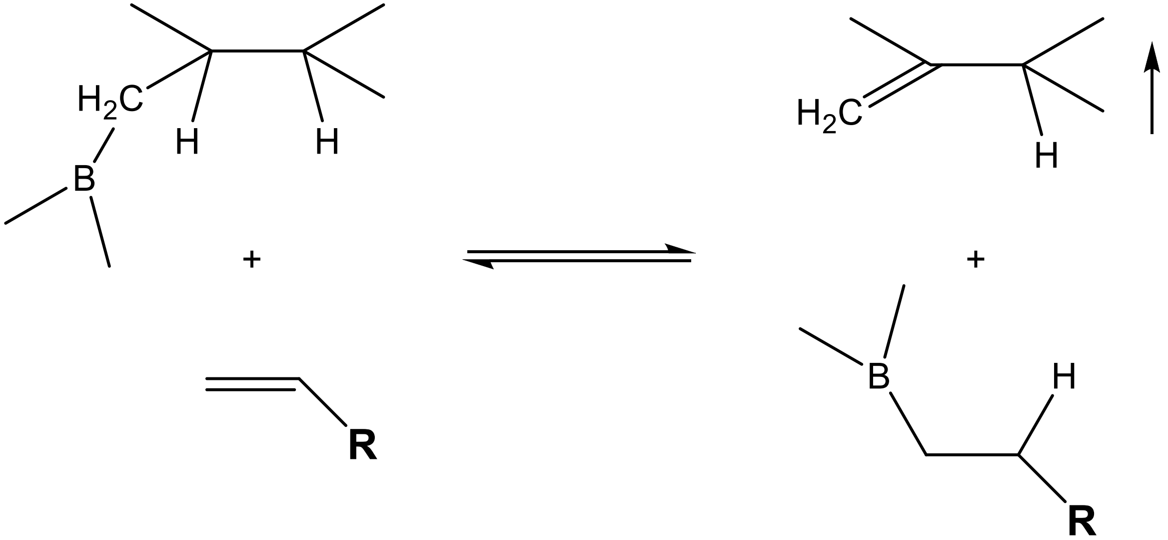
1)In the case of isomerizations with a reaction mechanism based on M-H insertion, it is possible to develop a counterthermodynamic isomerization in cases in which the insertion/β-elimination equilibrium is shifted towards the coordinated alkyl rather than towards the alkene;

2) Isomerization reactions with chiral metal catalysts can be performed in a highly enantioselective way.

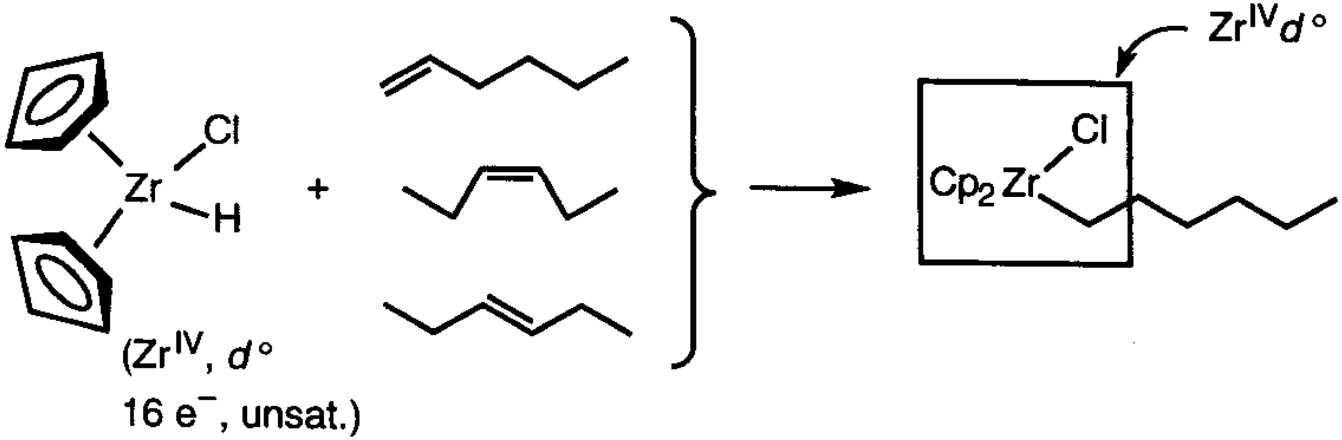
Alkene isomerization through hydroboration

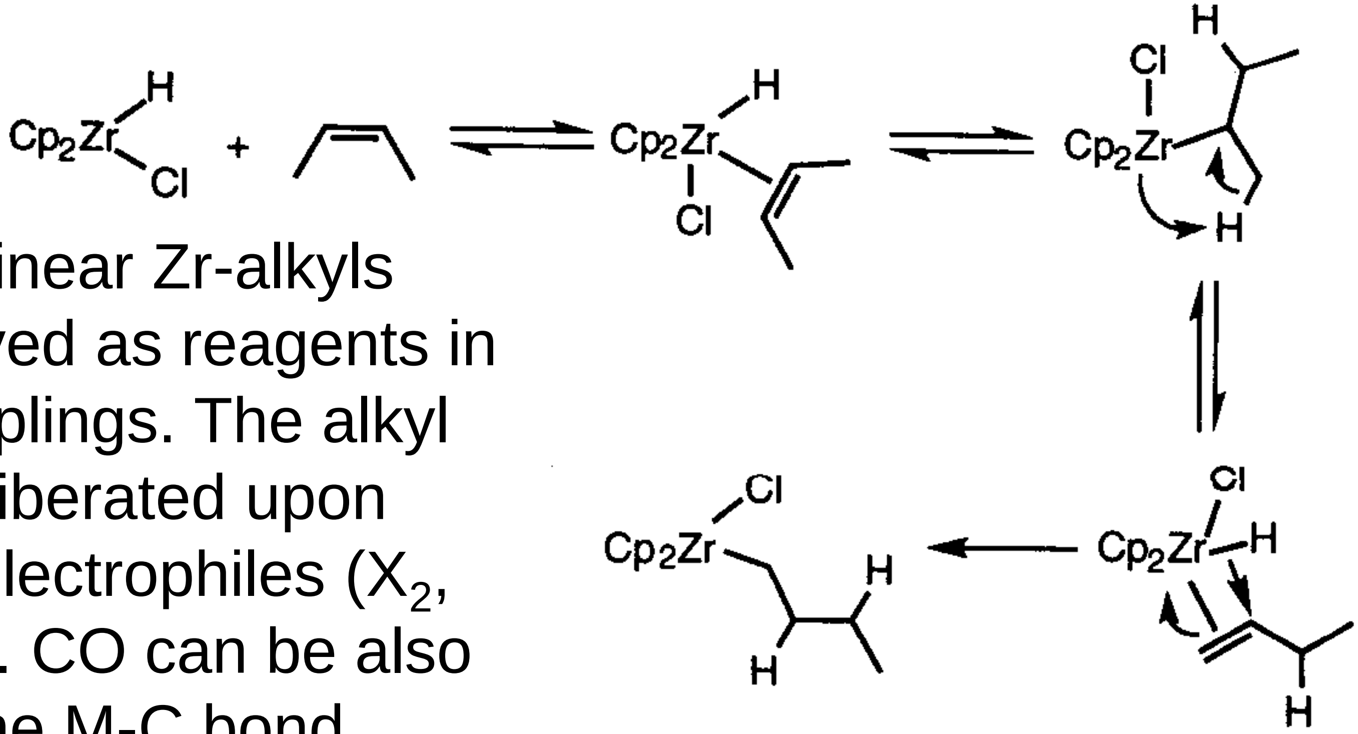


- By adding a terminal alkene with a higher boiling point, the isomerized terminal alkene can be separated.



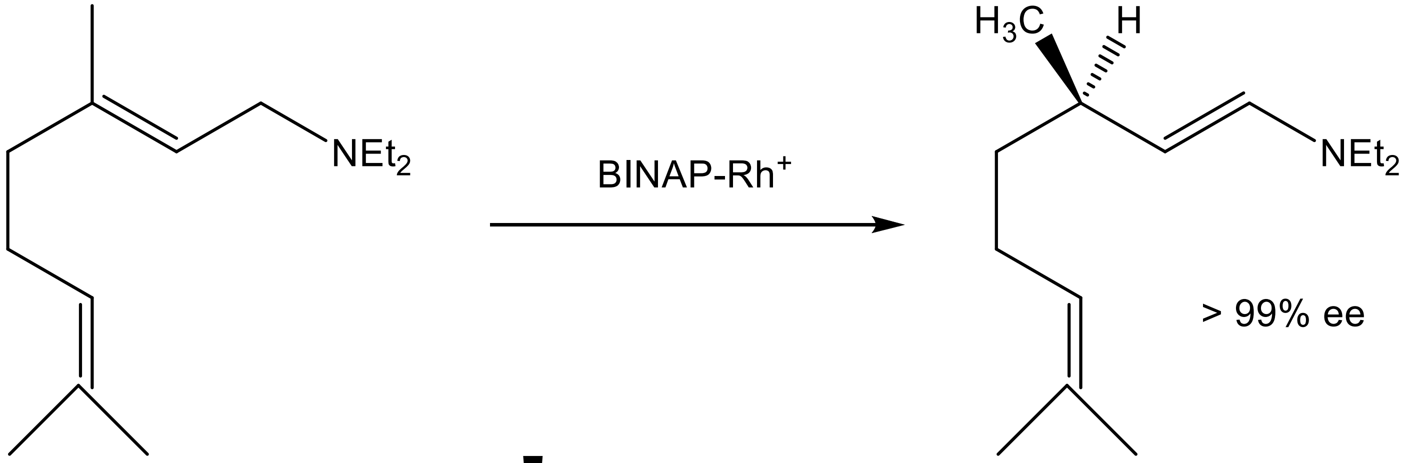
Isomerization with the Schwartz reagent





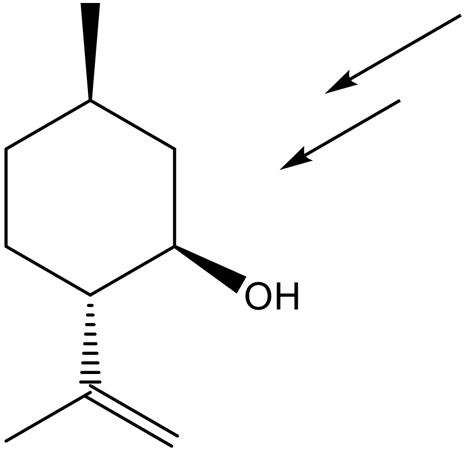
The resulting linear Zr-alkyls can be employed as reagents in e.g. cross-couplings. The alkyl group can be liberated upon reaction with electrophiles (X_2, H^+, peroxides). CO can be also inserted into the M-C bond.

Asymmetric isomerization
Takasago process (6000 t/year)

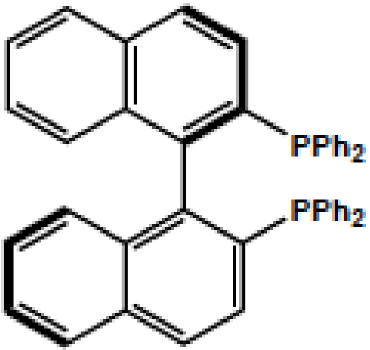


BINAP-Rh$^+$

> 99% ee



(-) - menthol



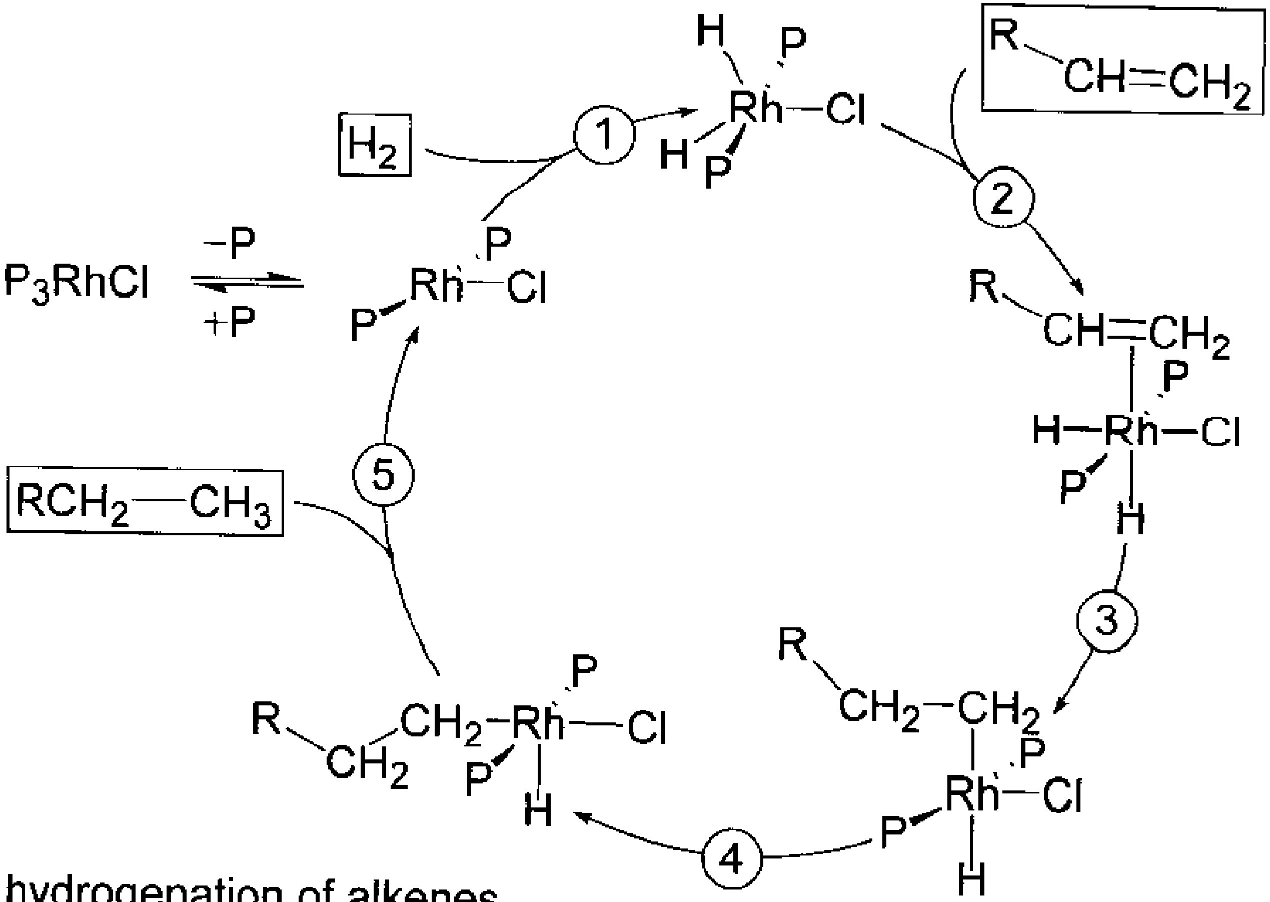
BINAP

Addition to the C=C bond - Hydrogenation

Hydrogenation with metal complexes has been extensively studied from the 1960s. Academic interest for these reactions has quickly turned into technological relevance, in particular due to the possibility of performing asymmetric hydrogenations.

The best performing metals for reactions of this kind belong essentially to the triad Rh, Ir, Ru, even if complexes of several other metals are capable of promoting hydrogenation. The reaction mechanism is quite similar for all the metal centers, and generally involves the activation of dihydrogen by oxidative addition, with formation of a metal hydride in which the unsaturated compound inserts.

Hydrogenation - mechanism



hydrogenation of alkenes

Alkene hydroformylation

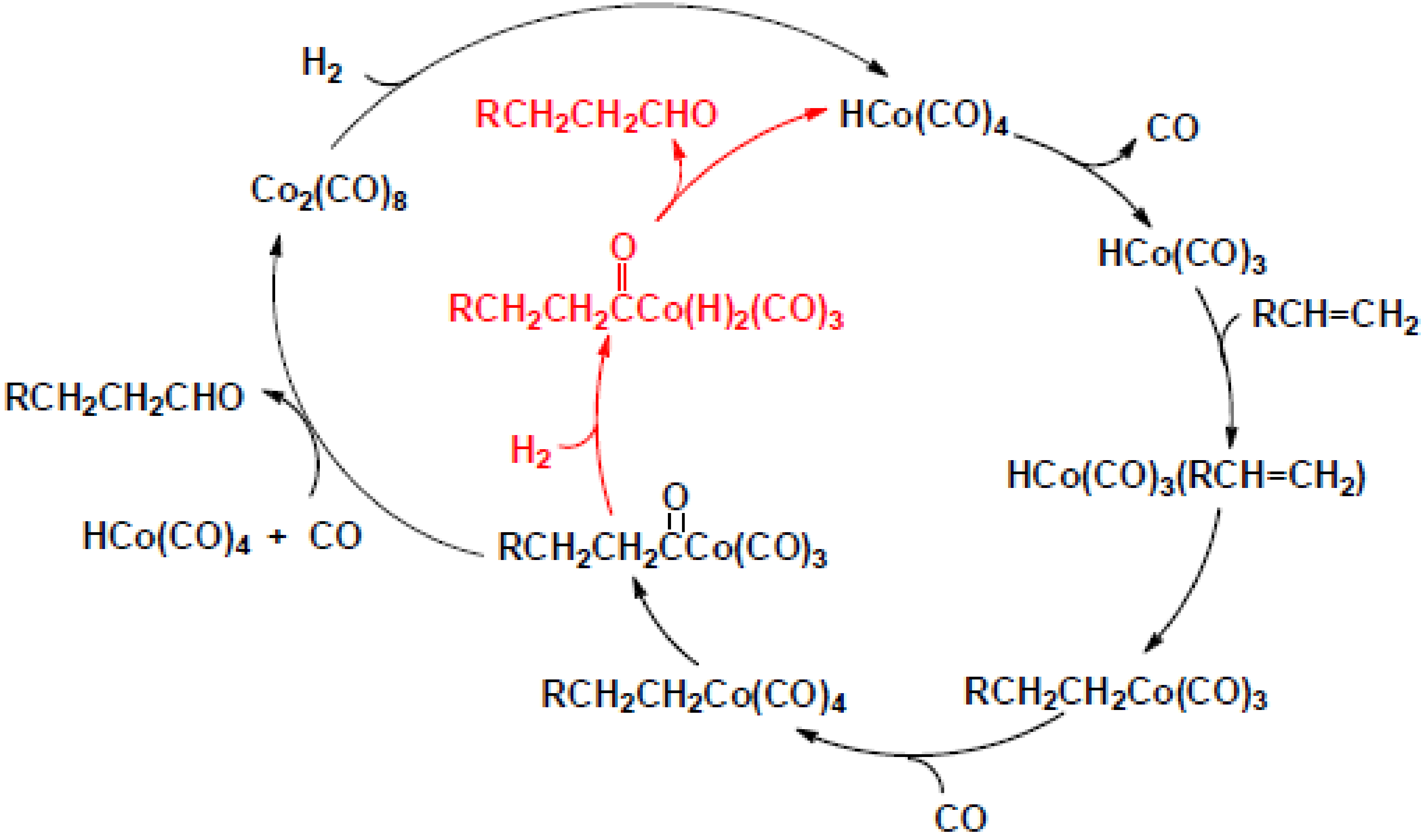
By running the hydrogenation of primary alkenes in the presence of CO, it is possible to intercept the metal alkyl intermediate inserting CO and subsequently reductively eliminating the intermediate acyl as an aldehyde:

$$C_nH_{2n} + H_2 + CO \xrightarrow{[cat]} C_nH_{2n+1}CHO$$

Hydroformylation is the technologically most important synthetic process among those exploiting homogeneous metal catalysts. The best performing complexes for this reaction are undoubtedly those based on Co or Rh.

The regiochemistry of the reaction with simple alkenes is generally *anti*-Markovnikov (H on internal C, formyl in terminal position). With vinylarenes or olefins substituted with electron-withdrawing groups, the regioselectivity can however be inverted, which paves the way to the development of asymmetric hydroformylation.

Alkene hydroformylation with Co



Alkene hydroformylation

Hydroformylation proceeds efficiently only with terminal alkenes. However, hydroformylation catalysts are also able to perform alkene isomerization, so that internal alkenes can be isomerized to terminal ones (even if the isomerization equilibrium favours internal alkenes), which subsequently undergo hydroformylation selectively.

Catalytic systems based on Co are more economical from the point of view of the metal, but also less active, less selective for the linear product (generally the desired one) and less stable (high CO pressures are needed to stabilize the catalyst). On the other hand, Rh catalysts are more costly but also more active and selective.

Addition of HY - Hydrofunctionalization

The hydroformylation reaction is (formally) a first example of hydrofunctionalization, reaction in which hydrogen and a functional group are added across a CC multiple bond.

Several of these reaction take place with alkenes spontaneously (hydroboration, hydroalogenation…) or under acid catalysis (hydration, hydroalkoxylation…). Use of metal catalysts, though, **accelerates** the reaction under **mild conditions** and renders it **regio-**, **stereo-** and often also **enantioselective**. Furthermore, metal catalysis is generally required with **alkynes**.

The nature of the H-Y bond adds to the CC multiple bond can range from «hydridic» (B-H, Si-H) to «protic» (O-H, S-H, X-H) through more or less «neutral» (C-H, N-H, P-H).

Addition of HY - Hydrofunctionalization

Given the widely different nature of HY, the underlying reaction mechanism can be quite different as well!

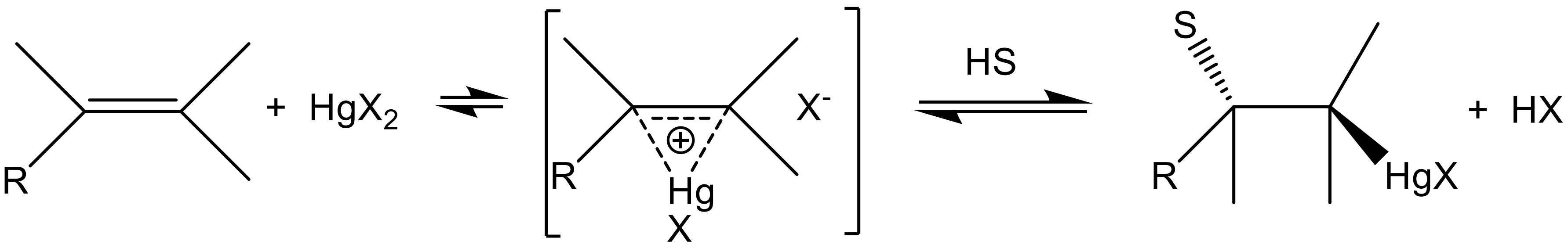
External nucleophilic attack of HY to the coordinated CC bond, followed by proton transfer/protonolysis;

Precoordination (and in some cases deprotonation) of HY to the metal, followed by insertion of the CC bond and proton transfer/protonolysis;

Oxidative addition of HY, followed by coordination of the CC bond, insertion and reductive elimination.

Other mechanisms involving more extensive transformations of HY or of the unsaturated substrate in the coordination sphere of the metal before addition are also possible.

Solvomercuration

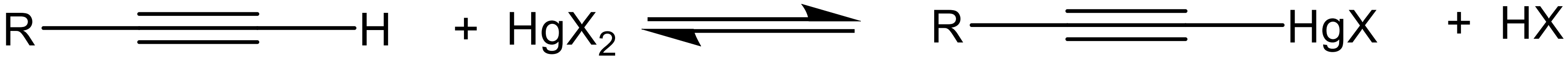


Interaction with HgX^+ forms a highly reactive intermediate which triggers external nucleophilic attack (Umpolung). The nucleophile is usually the solvent (HS), hence the reaction name: the reaction is highly **stereoselective** (*trans*) and **regioselective** (the nucleophile attacks the more substituted carbon).

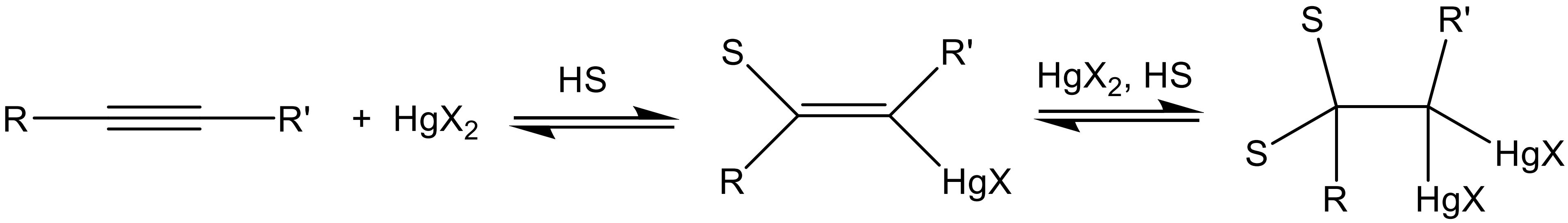
The reaction is reversible, hence it is operated in the presence of a (non nucleophilic) base, which neutralises the produced acid; this role can be also played by the mercury counteranion X^- . Consequently, protonolysis cannot take place!

Alkyne solvomercuration

Solvomercuration can take place also with alkynes, but not with terminal alkynes, since in this case mercuration is generally preferred:

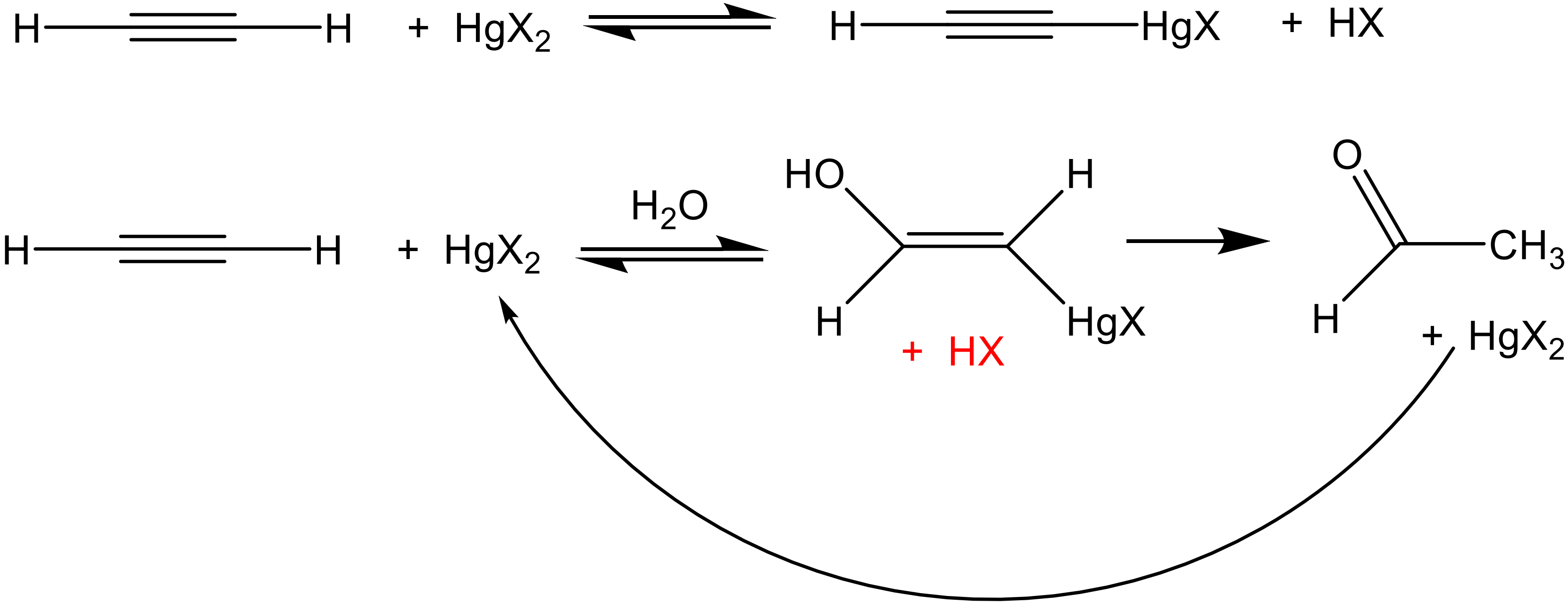


The reaction with internal alkynes is still stereoselective, whereas the regioselectivity depends on steric effects of the substituents of the triple bond. Furthermore, the obtained vinylmercury compound can undergo a second solvomercuration reaction.



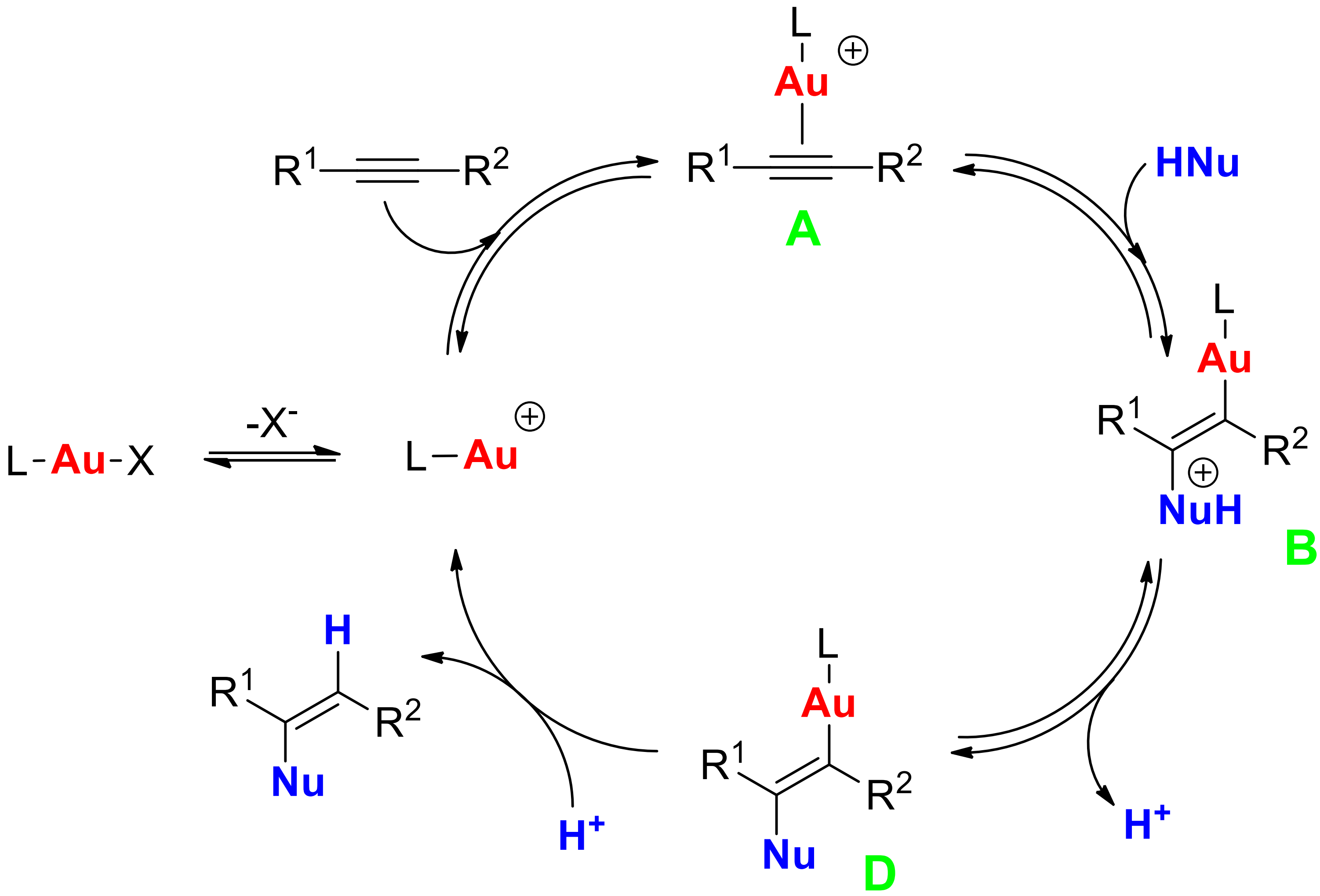
Solvomercuration - applications

The most important application of this reaction regards the **hydration of acetylene** (Kucherov, **1881**):



Acetylene undergoes prevalent metallation, but the reversibility of this process allows quantitative hydration. The mercury(II) salt serves as catalyst for the reaction.

Au(I) catalyzed **alkyne** hydrofunctionalizations



L= phosphine, N-heterocyclic carbene...

HNu= water, alcohols, carboxylic acids, amines, (hetero)arenes…

Hydrofunctionalizations – nucleophilic HY

Alkyne hydrofunctionalizations with **nucleophilic** HY can proceed upon external nucleophilic attack by the nucleophile to a precoordinated alkyne or by precoordination/deprotonation of HY.

Electronegative, carbophilic, cationic metal centres, such as Au(I), Au(III), Pd(II), Pt(II), Pt(IV), Rh(III) are generally required in the former case in order to impart electrophilicity to the alkyne.

Alternative mechanisms are operative for some HY with metal centres that easily form alkylidenes from terminal alkynes, as well as with early transition metals.

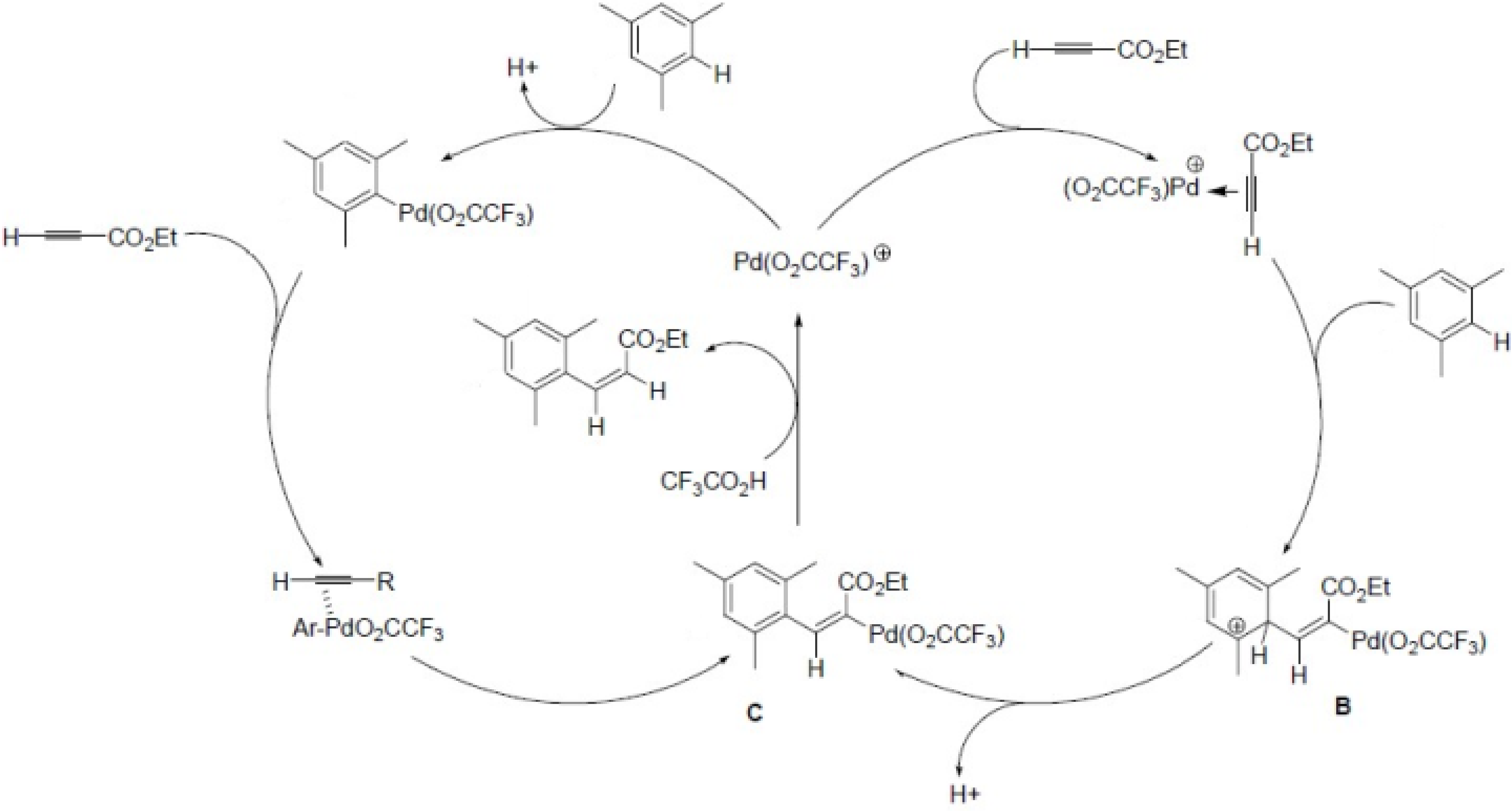
Nucleophilic HY react also with coordinated **alkenes**, which are generally more electrophilic compared to alkynes. However, the evolution of the resulting intermediate is often different, since β-elimination is generally faster than protonolysis (see below).

Alkyne hydroarylation

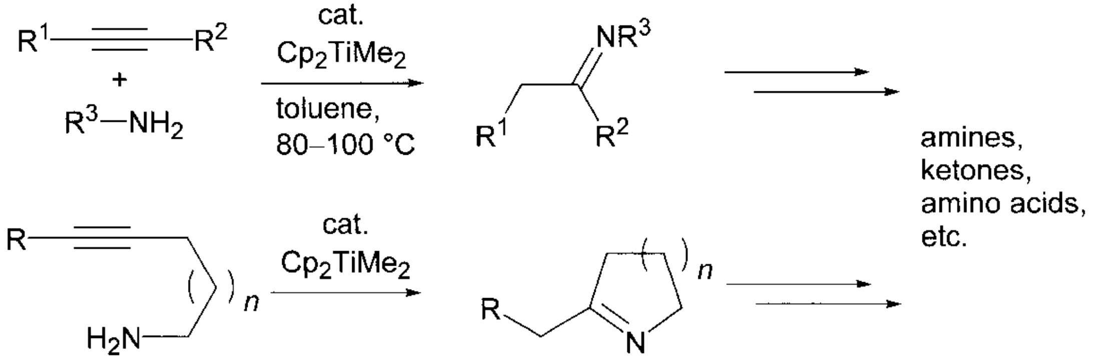
Ar-H + HCC-COOEt → Ar-HC=CHCOOEt

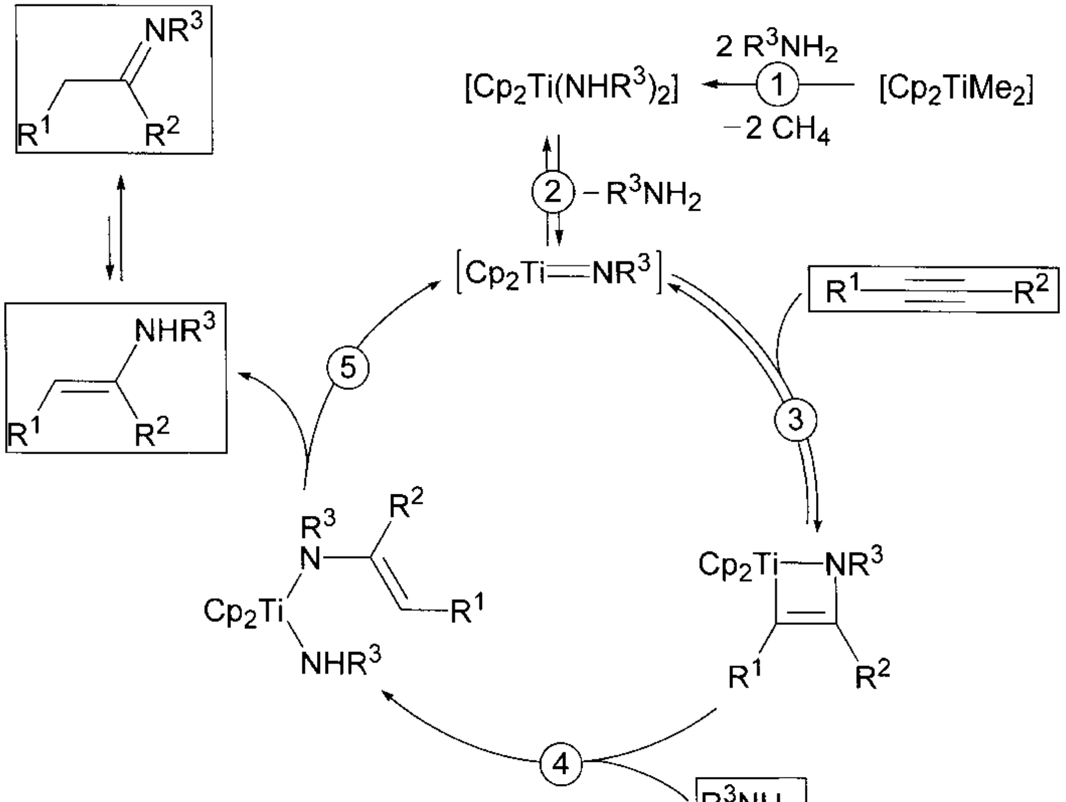
HY Precoordination (and deprotonation)

External nucleophilic attack (Friedel-Crafts)



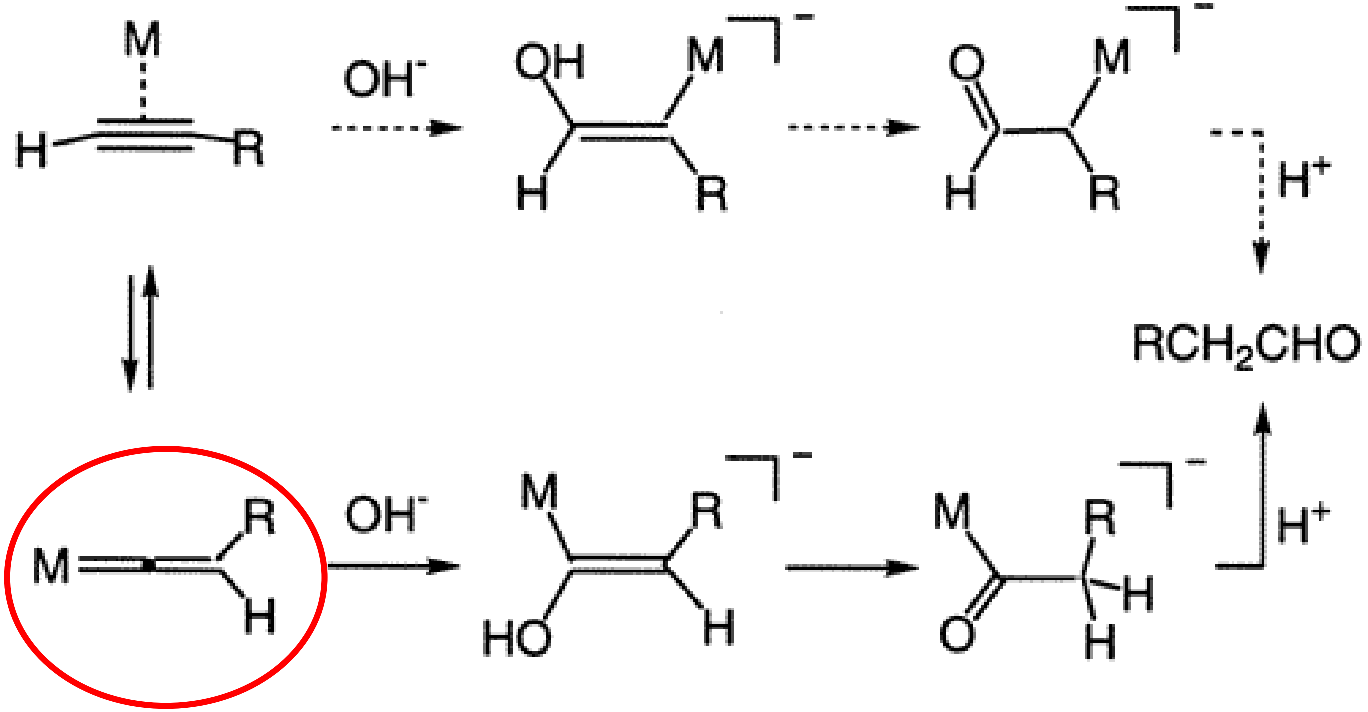
Alkyne hydroamination with early TM





hydroamination

Alkyne hydration through alkylidines (Ru)



The occurrence of this mechanism is limited to terminal alkynes. The regioselectivity of water addition is in this case **opposite** with respect to the mechanism based on external nucleophilic attack (Markovnikov vs. *anti*-Markovnikov)

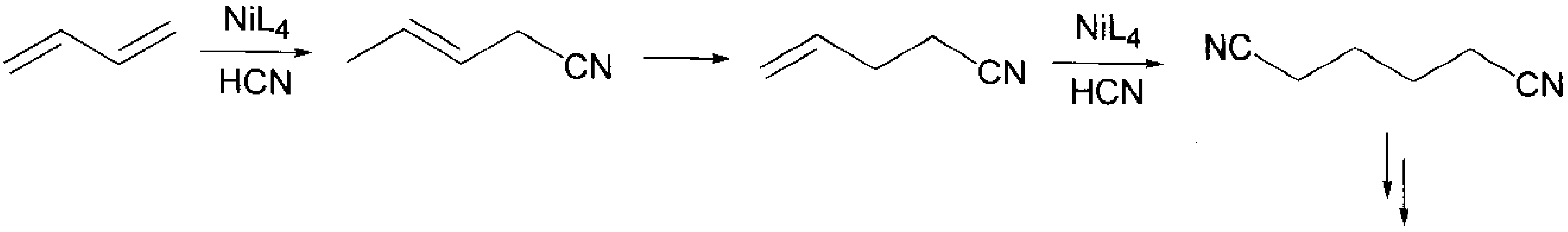
Hydrofunctionalizations via oxidative addition

Hydrofunctionalizations with non-nucleophilic HY having hydridic or weakly acidic character generally proceed via <u>oxidative addition of HY</u>, followed by insertion of the unsaturated compounds and reductive elmination.

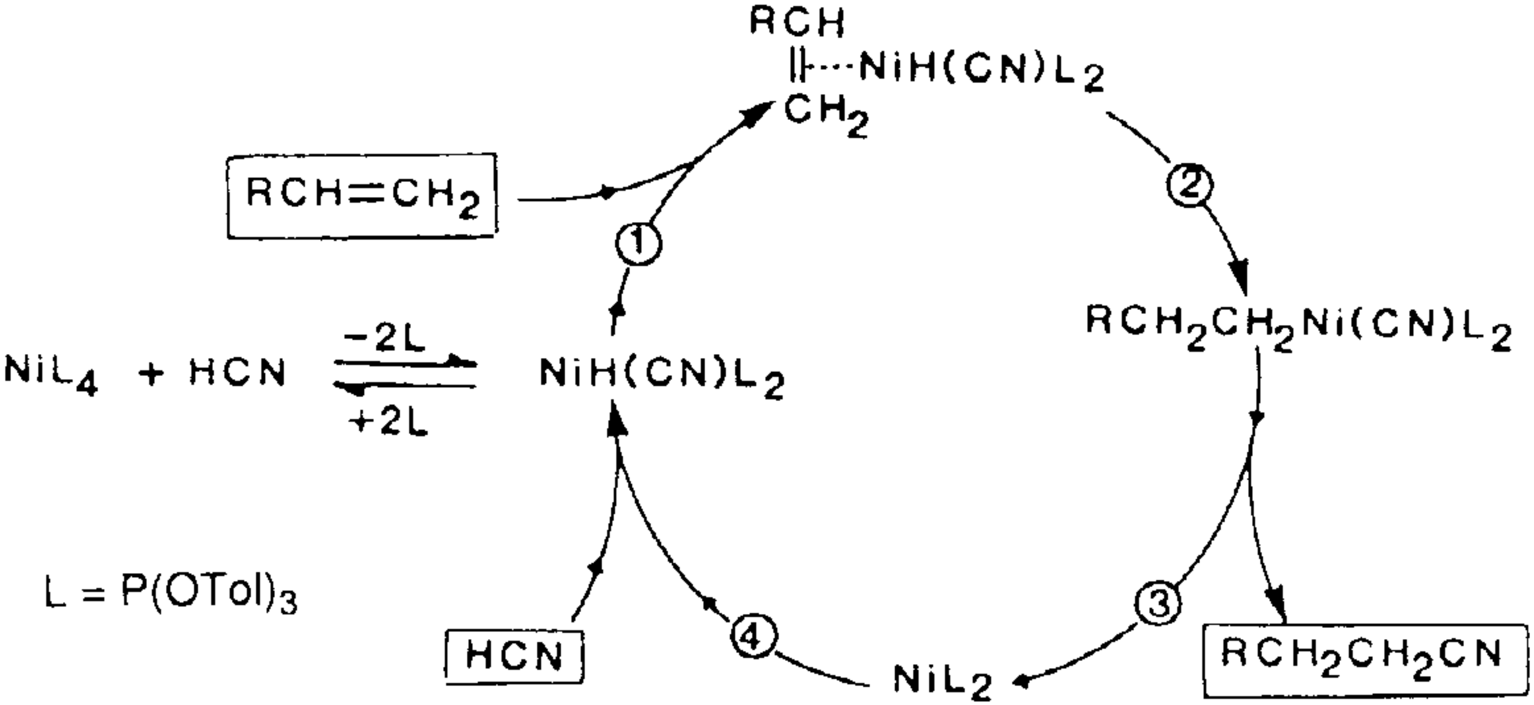
Consequently, electron-rich, coordinatively unsaturated metal centres are needed as catalysts.

O-H and N-H bond do not easily undergo oxidative addition to metal centres. However, oxidative addition of an acid cocatalyst (via protonation of the metal centre) can trigger interesting reactions involving water/alcohols and CO...

Alkene hydrocyanation



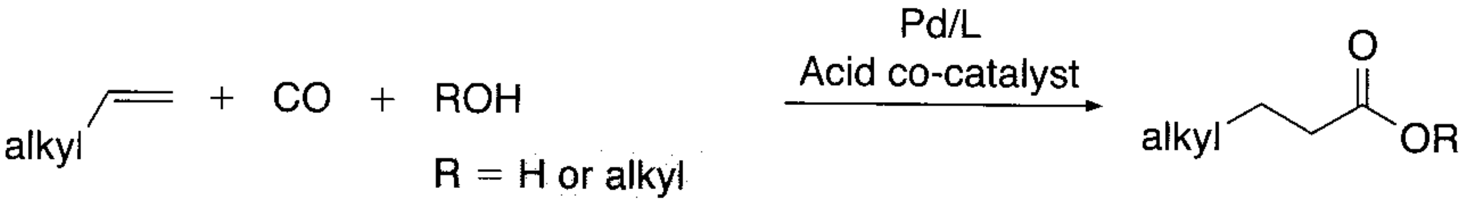
nylon 66

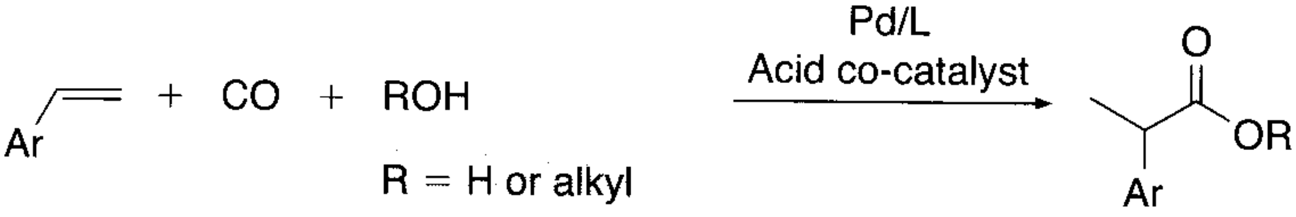


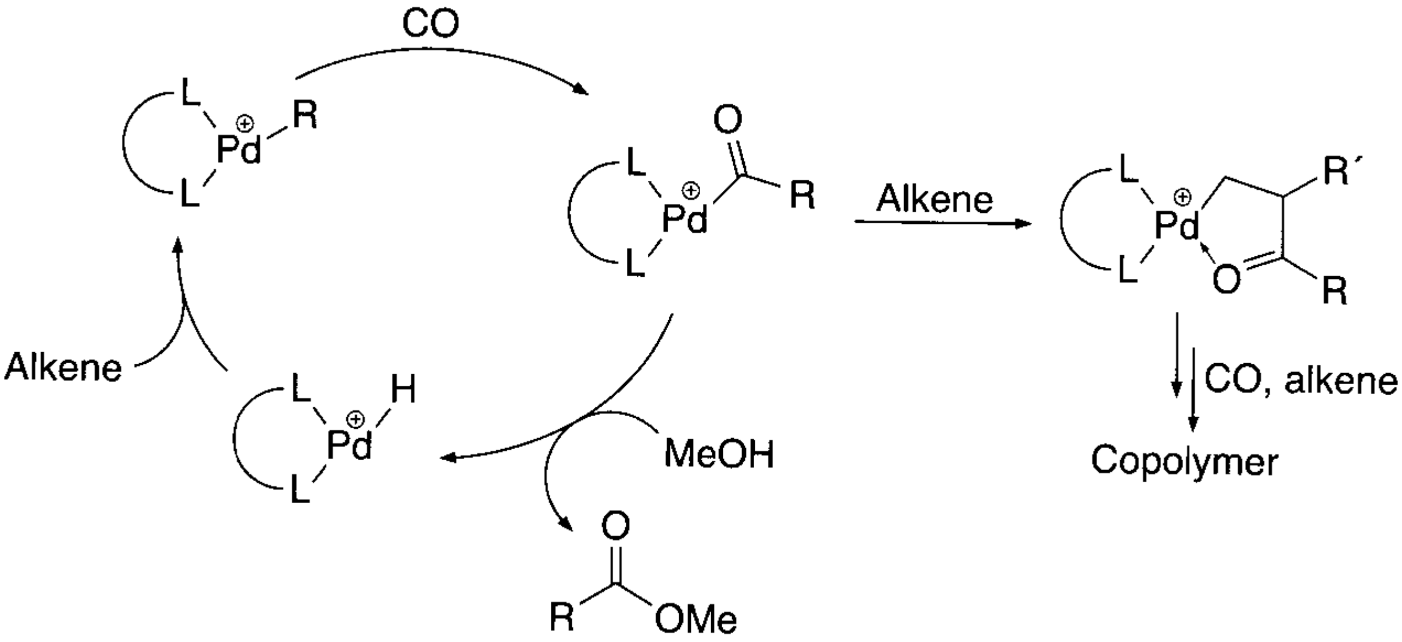
L = $P(OTol)_3$

hydrocyanation

Hydrocarboxylation and hydroesterification

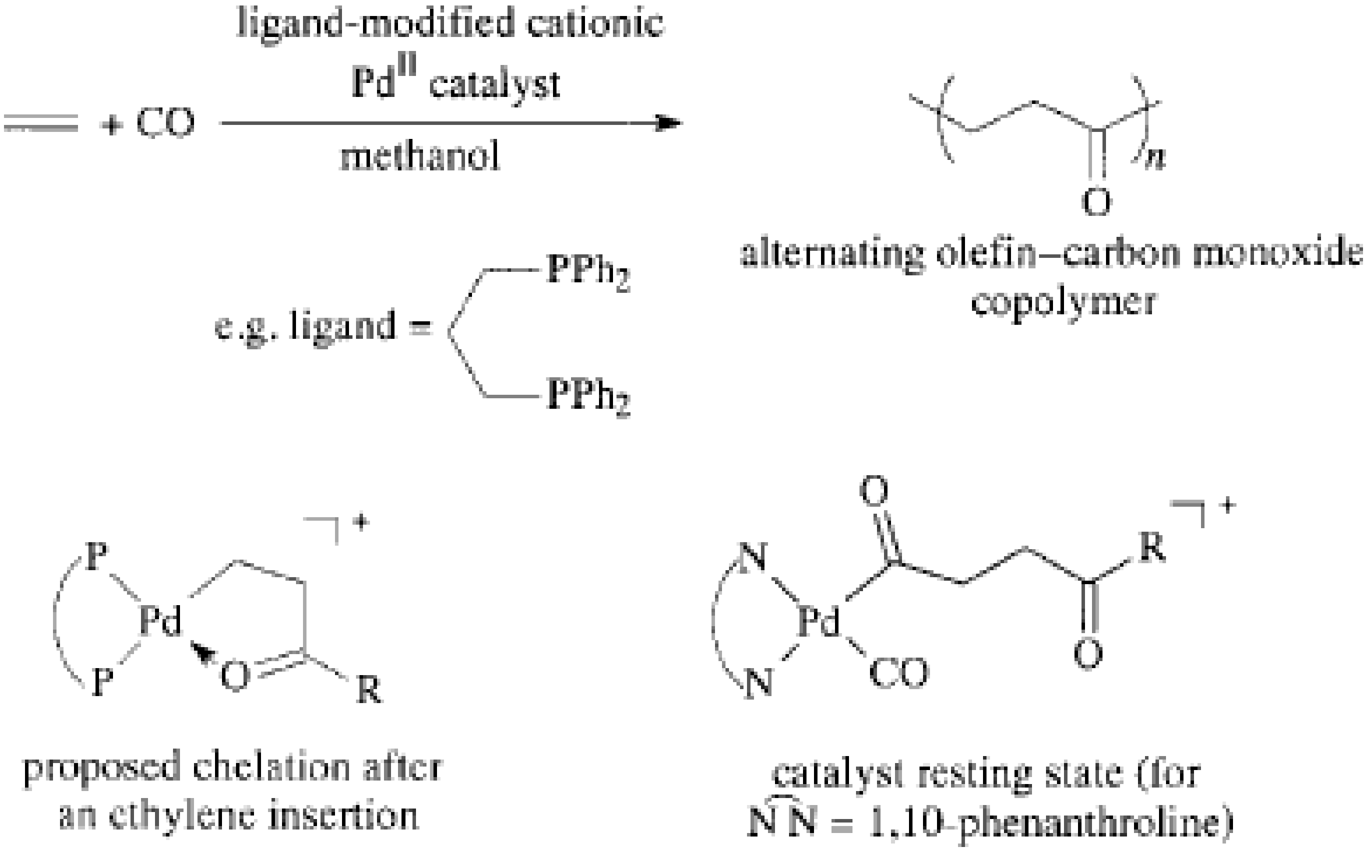






Copolymerization CO - alkenes

WIth cationic Pd(II) complexes containining a bidentate chelating ligand, it is possible to perform a strictly alternating copolymerization of CO and ethylene (or other terminal alkenes).

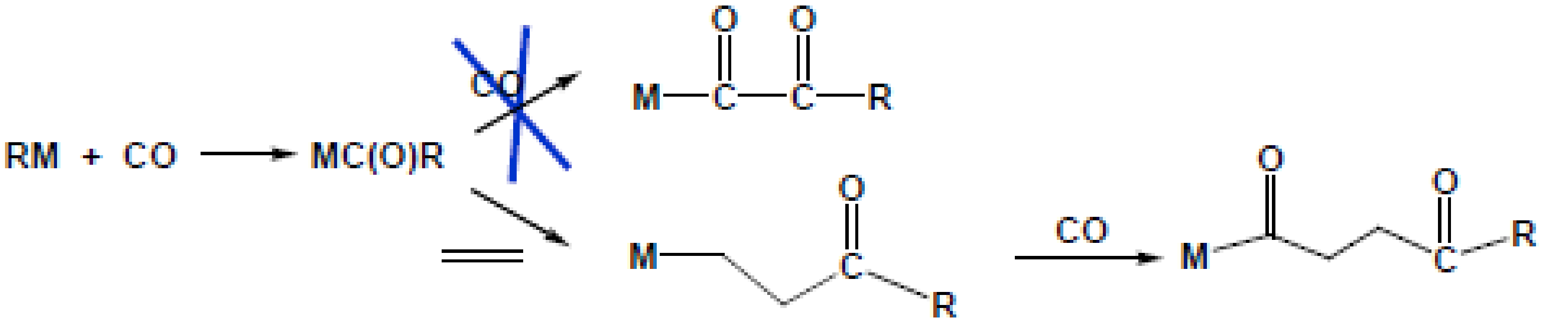


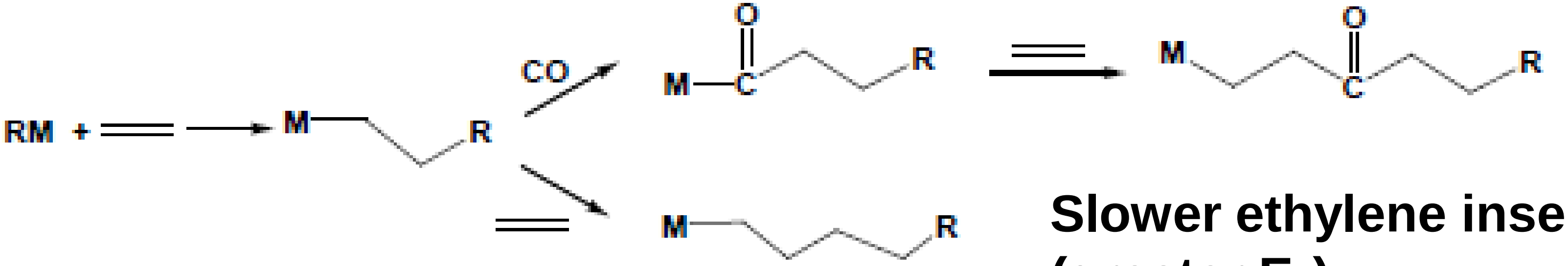
alternating olefin–carbon monoxide copolymer

proposed chelation after an ethylene insertion

catalyst resting state (for N͡N = 1,10-phenanthroline)

Copolymerization CO - alkenes



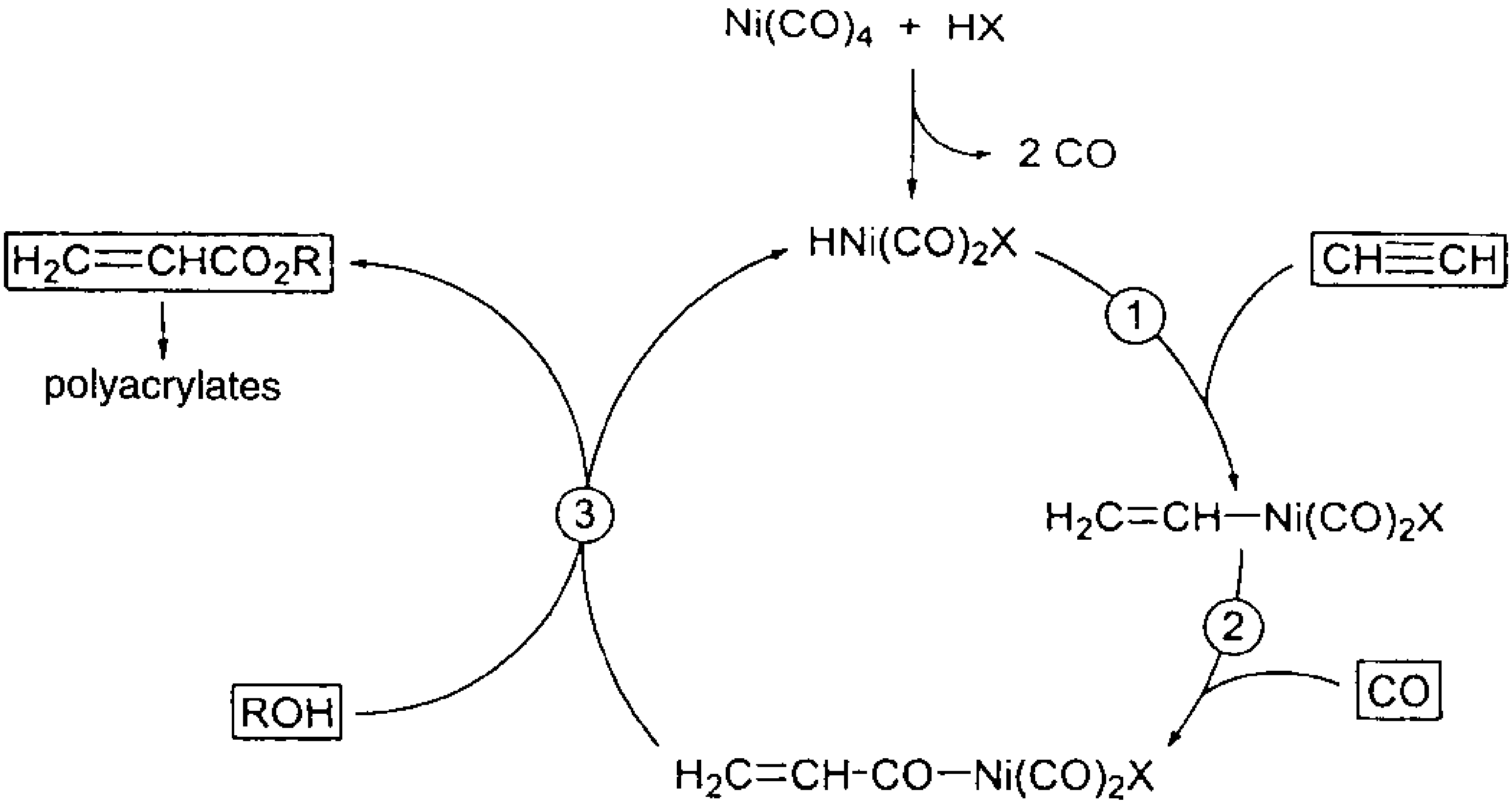


Slower ethylene insertion (greater E_a)

The alternating insertion of the monomers is explained with the different reactivity of CO and ethylene towards insertion into M-alkyl and M-acyl bonds. The M-alkyl intermediate is also not prone to β-elimination (cationic character of the complex, cyclic intermediate with unavailability of free coordination sites).

Alkyne hydrocarboxylation (Reppe synthesis)

$$\mathrm{HCCH} + \mathrm{CO} + \mathrm{HO\text{-}R} \rightarrow \mathrm{H_2C{=}CHCOOR}$$



hydrocarboxylation

Alkene (oxidative) functionalization

In an oxidative functionalization reaction, an external nucleophile Nu^- attacks a metal coordinated (terminal) olefin to form a metal-bound alkyl; a β-elimination generally follows to yield the reaction product (formally oxidized, H-Nu exchange). The metal complex then reductively eliminates HX.

The main limitation of these reaction is the need to reoxidize the catalyst to close the catalytic cycle, which is often a slow and inefficient process compared to catalyst deactivation, e.g. upon metal aggregation. In order to prevent deactivation, the oxidant and the ligands at metal need to be optimized.

The reaction is generally regioselective with Nu attack at the more substituted alkene carbon.

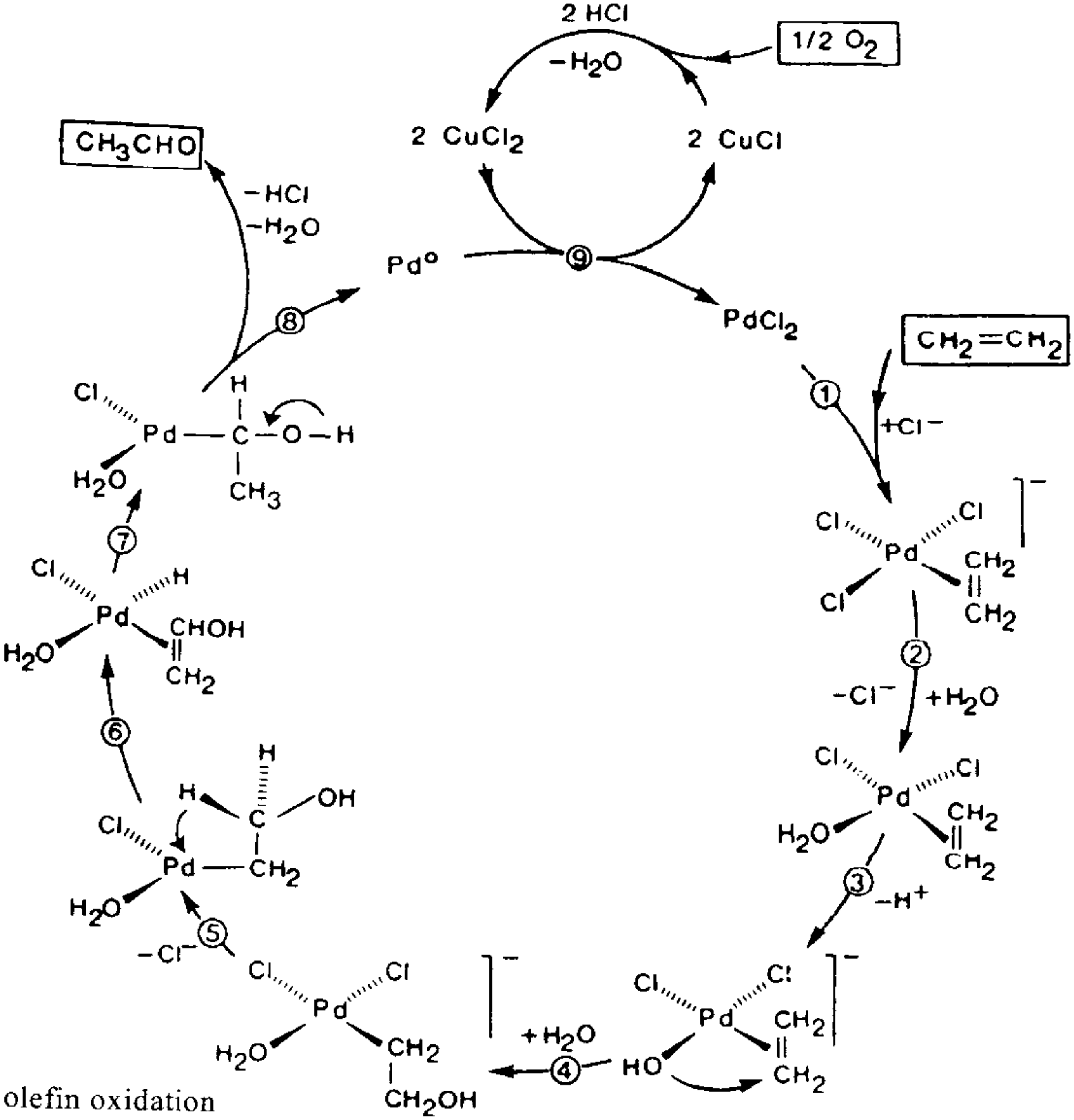
The metal center most widely employed for reactions of this kind is **palladium(II)**.

The Wacker process

The so called Wacker process is the most popular and best studied example of formal oxidative functionalization of alkenes (ethylene), also given its past technological significance. The classic Wacker process produces acetaldehyde upon nucleophilic attack of water on coordinated ethylene. The metal is then reoxidized by dioxygen using a copper(I) salt as mediator.

$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$
$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$
$2CuCl + 2HCl + 1/2O_2 \rightarrow 2CuCl_2 + H_2O$

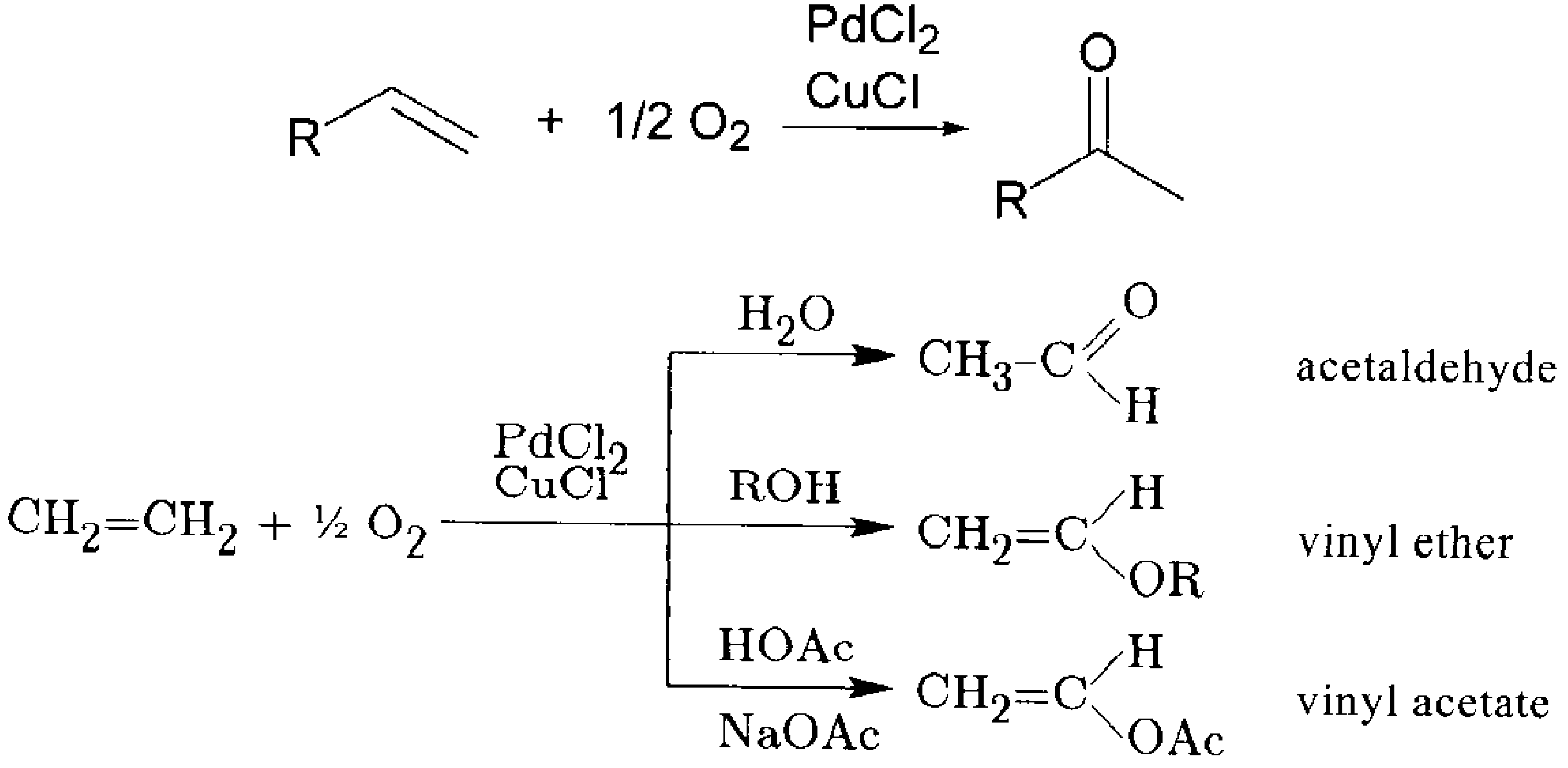
Depending on the reaction conditions, the mechanism can involve a proper external nucleophilic attack or a formal insertion of the olefin in a Pd-OH bond…



olefin oxidation

Variants of the Wacker process

With terminal alkenes instead of ethylene, methylketones are generally produced (attack at the most substituted C). Wth nucleophiles different from water other products can be obtained:



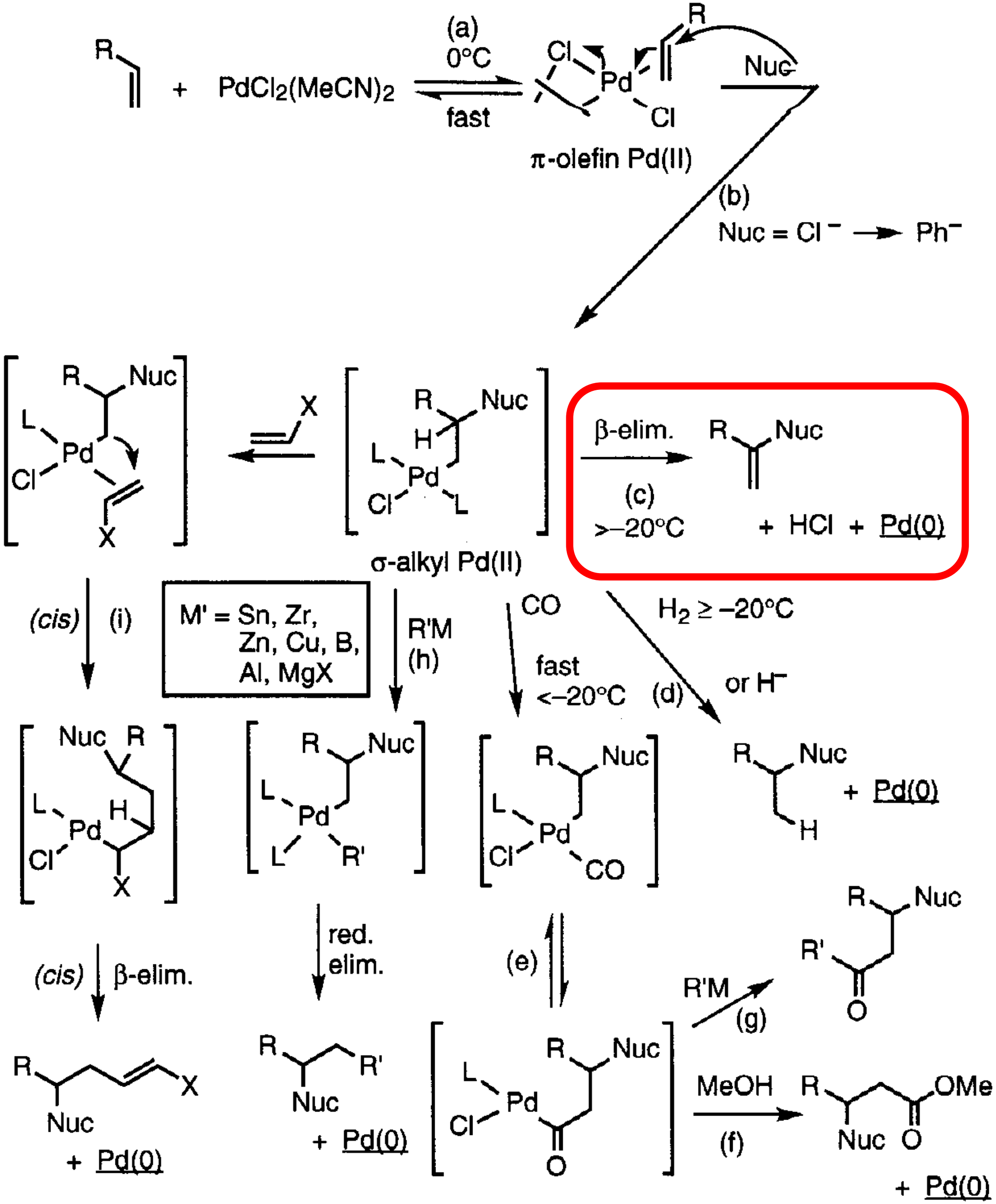
Alkene (oxidative) functionalization

The reaction works well with oxygen-containing nucleophiles (water, alcohols, carboxylates);

Nitrogen-containing nucleophiles often compete with the alkene for coordination to the metal center, and may also easily reduce it, so that only the less coordinating nitrogen nucleophiles (e.g. aromatic amines) work well;

Nucleophiles at carbon generally cannot be employed as they easily reduce the metal center;

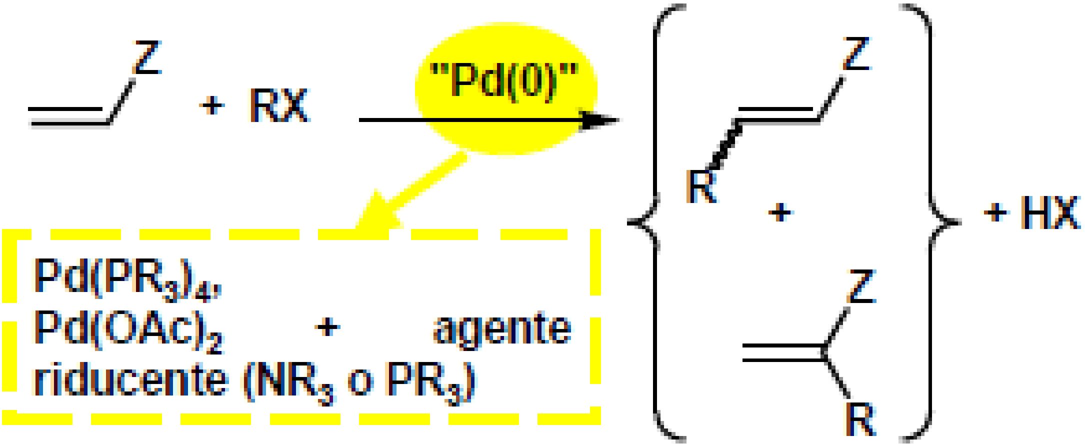
Intramolecular oxidative functionalization reactions are generally cleaner and more efficient than intermolecular ones. Consequently, numerous examples of cyclizations are known based on this reaction.



X = H, Ph, R, CO_2R, CN, COR, OAc, NHAc

The Heck reaction

The Heck reaction is related to an oxidative functionalization reaction but also to a standard cross-coupling reaction. In this reaction, the use of RX as source of the “nucleophile” allows to close the catalytic cycle without the need for external oxidants.



$Pd(PR_3)_4$, $Pd(OAc)_2$ + agente riducente (NR_3 o PR_3)

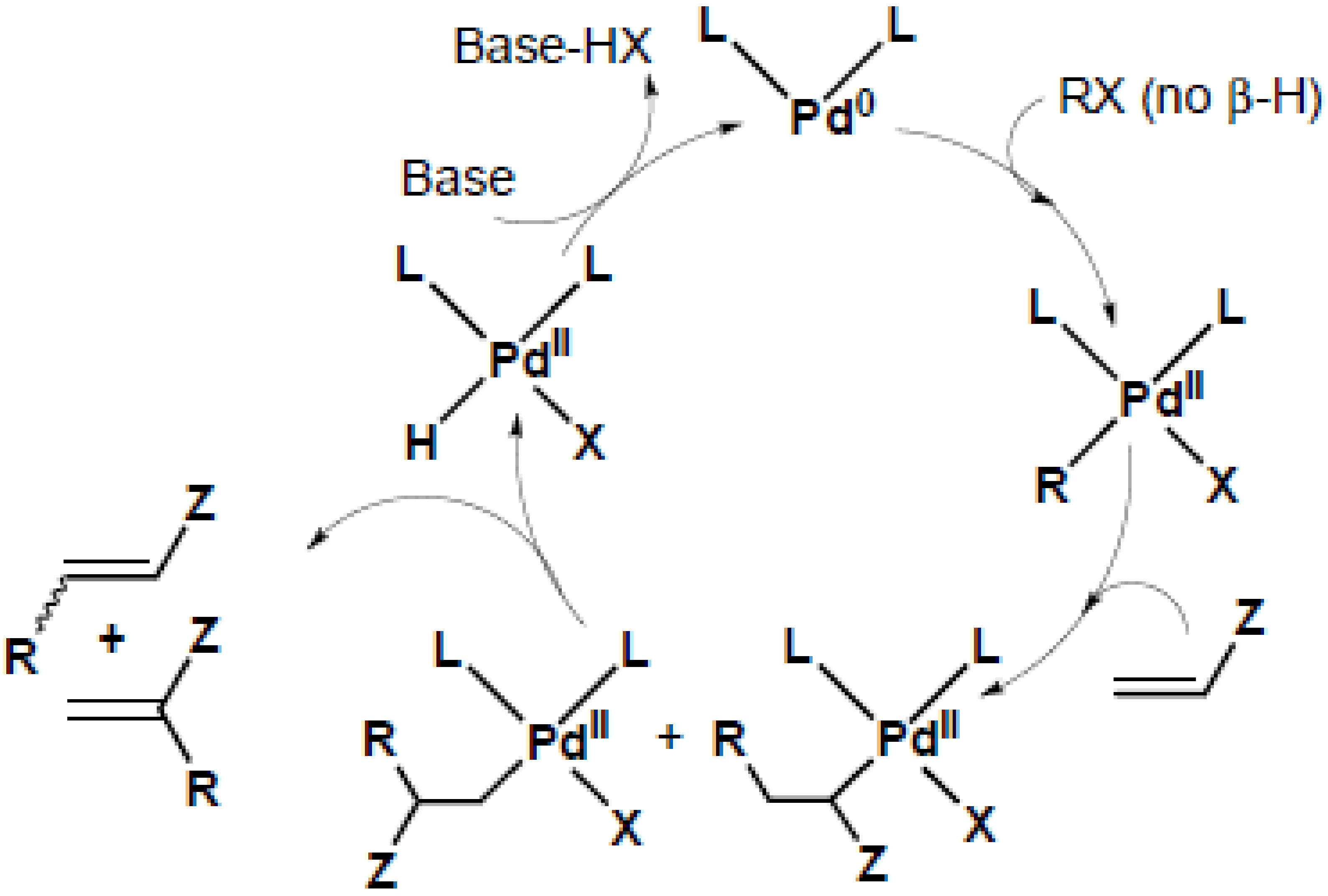
R = arile, vinile

X = I, Br, COCl, OTf

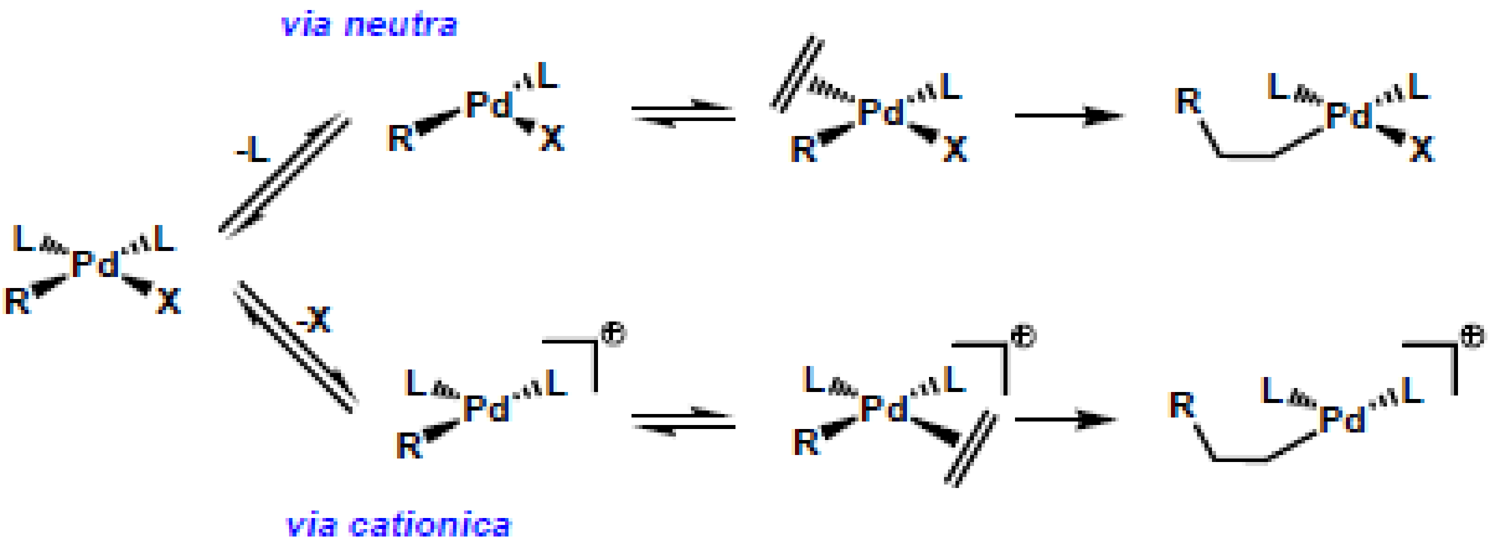
Z = H, R, Ph, CN, CO_2R, OMe, OAc, NHAc

The Heck reaction

L generalmente fosfine (mono o bidentate) o 1,10-fenantroline

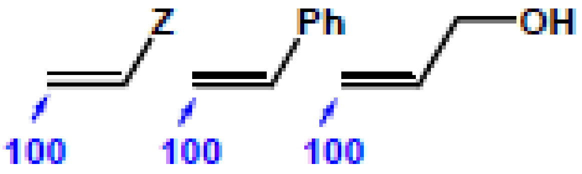


The Heck reaction



Prodotti di arilazione tipici

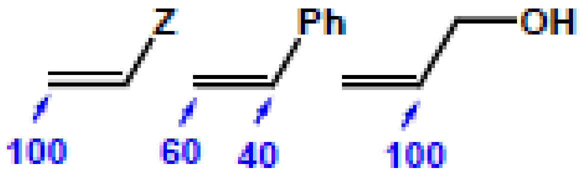
via neutra



Z = COOR, CONH$_2$, CN

Migrazione di R sempre sul carbonio meno sostituito; prevalgono gli effetti sterici e si formano prodotti lineari

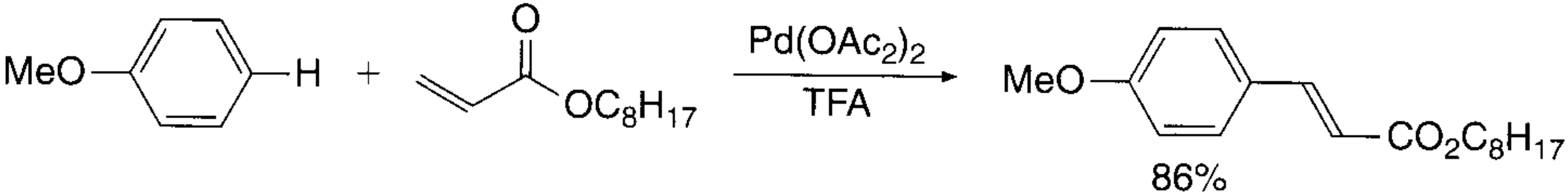
via cationica



Importanti effetti elettronici; migrazione di R (formalmente anione) sul carbonio con minore densità elettronica

The Fujiwara – Moritani reaction

The Fujiwara-Moritani reaction (which has been reported earlier than the Heck reaction!) is a variant of the Heck reaction in which the intermediate Pd-(hetero)aryl is formed upon C-H functionalization of a (hetero)arene. Clearly, in this case it is necessary to add an oxidant in order to oxidize back the Pd to the oxidation state +II and close the catalytic cycle



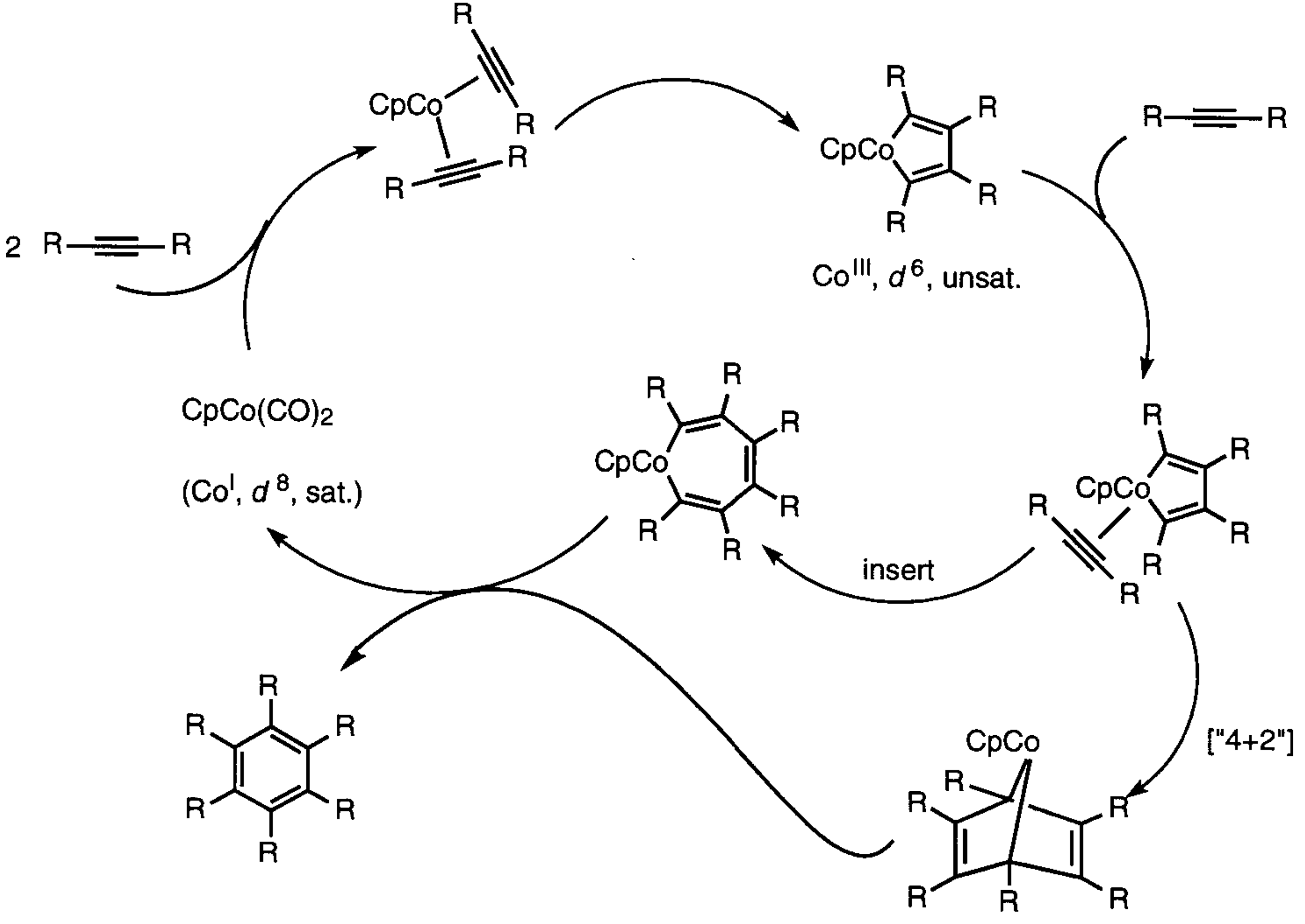
Alkyne (reductive) cyclooligomerization

Cyclooligomerizations are reaction in which <u>two multiple CC bonds coordinated to a metal center dimerize in the coordination sphere of the metal leading to metallaycles</u>, which can then further react adding more unsaturated molecules via insertion reactions.

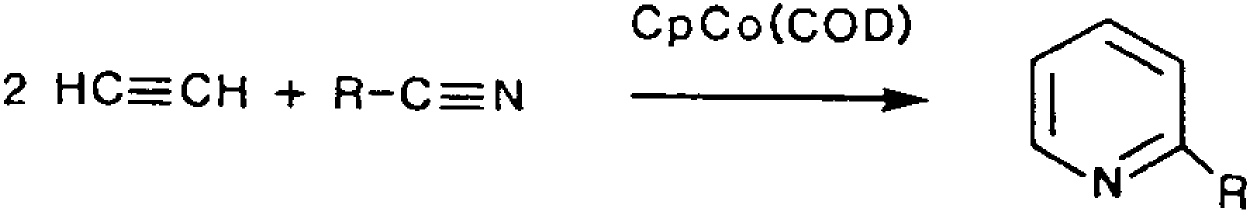
These reactions are feasible when back-donation from the metal to the unsaturated compound is extensive. Consequently, <u>they are also much easier with alkynes (more electron-withdrawing) rather than with alkenes</u>. Reaction between two alkynes leads to metallacyclopentadienes, whereas reaction between one alkyne and an alkene leads to metallacyclopentenes.

When the cyclooligomerization reaction is effected with two different reagents, it generally gives rise to complex product mixtures. In peculiar cases, this can however be avoided.

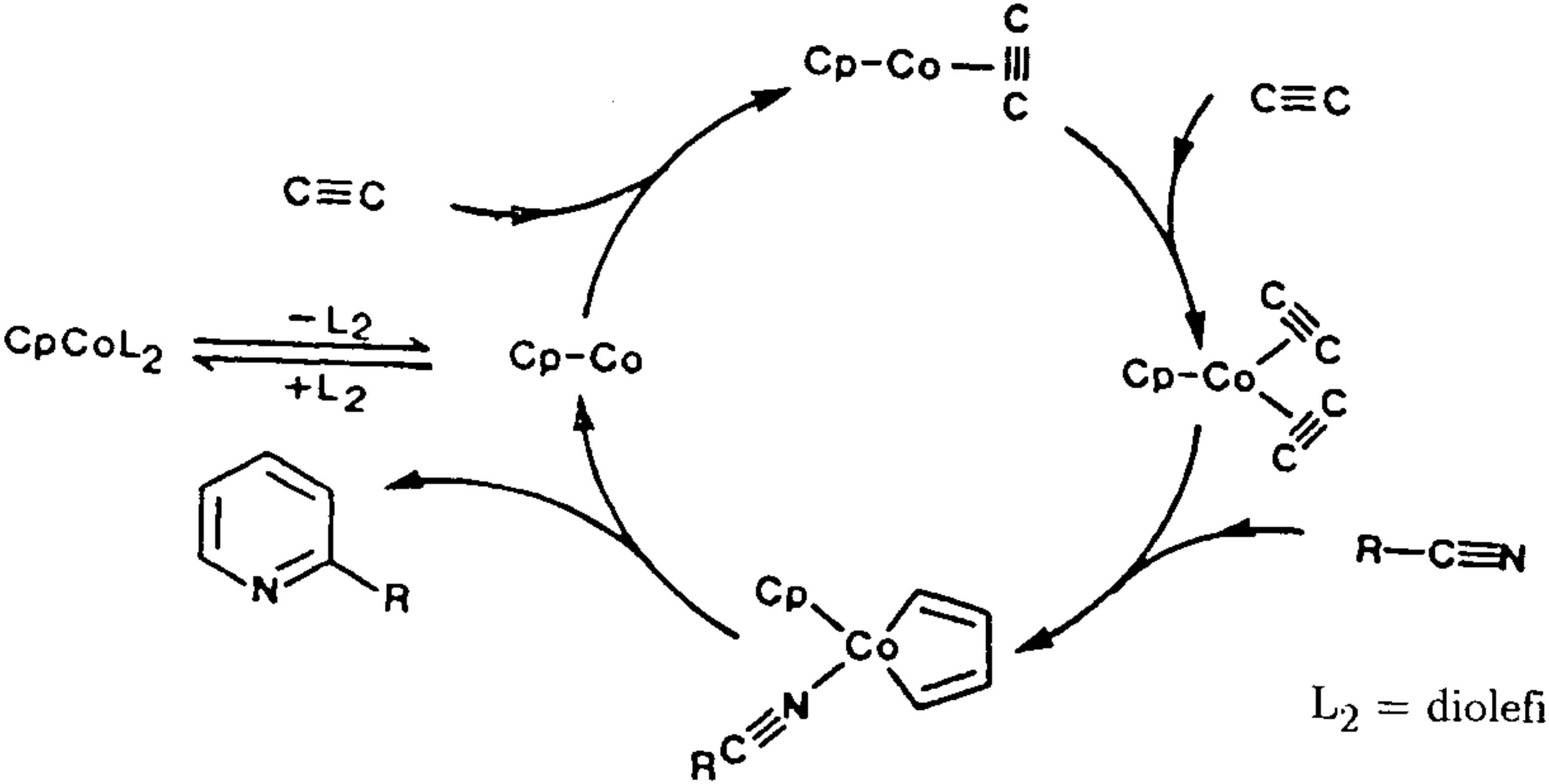
Alkyne (reductive) cyclooligomerization



The Bönnemann reaction



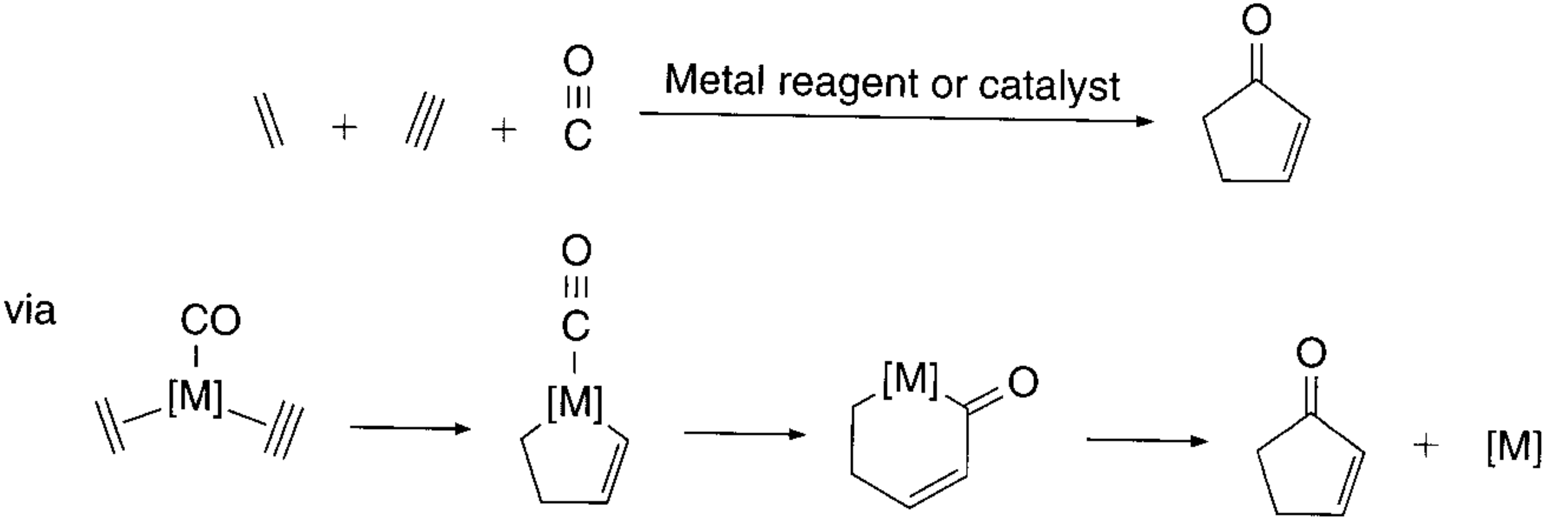
COD =
1,5−cyclooctadiene



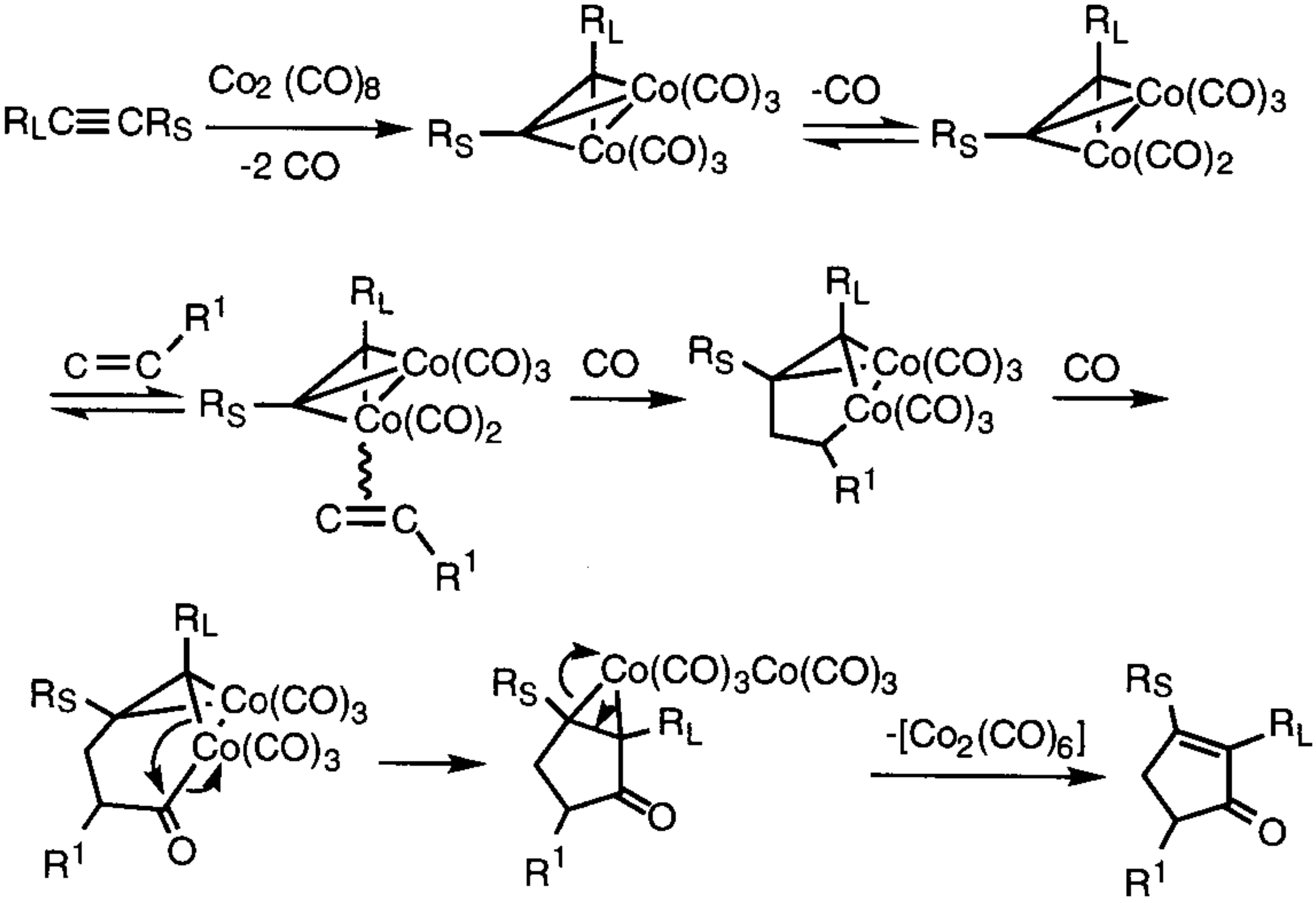
L_2 = diolefin

The Pauson – Khand reaction

The Pauson-Khand reaction is an intermolecular reductive cyclodimerization reaction between an alkene and an alkyne, in which a CO molecule is also involved to yield cyclopentenones. The reaction, initially discovered as a stoichiometric process, was later developed into catalytic and even enantioselective versions.

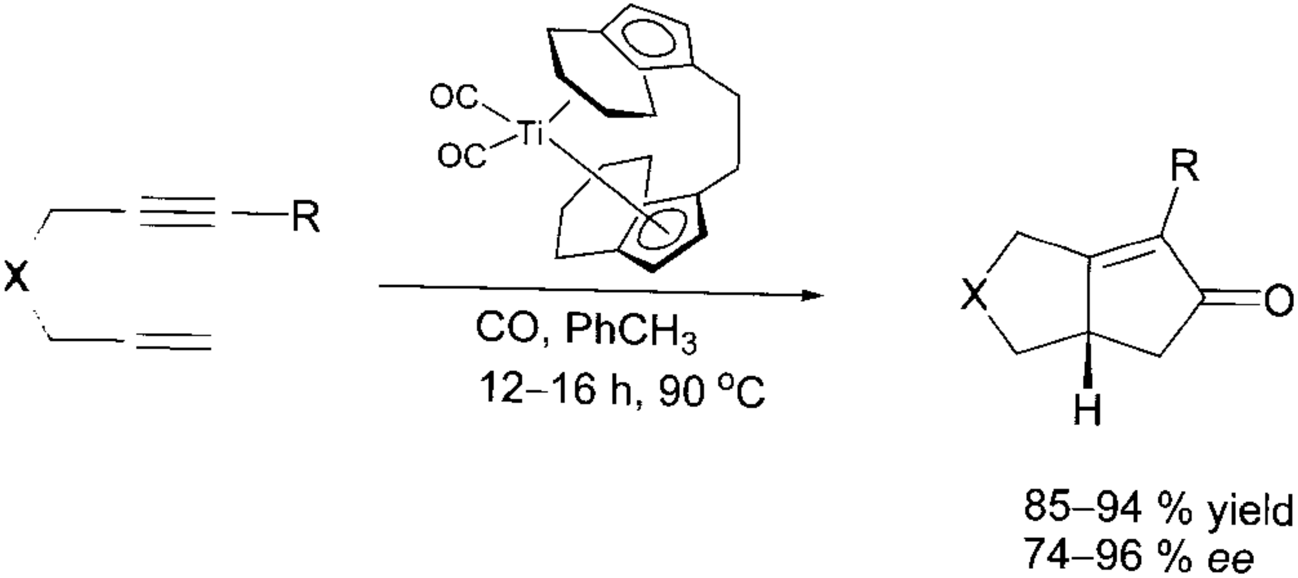


The Pauson – Khand reaction: mechanism

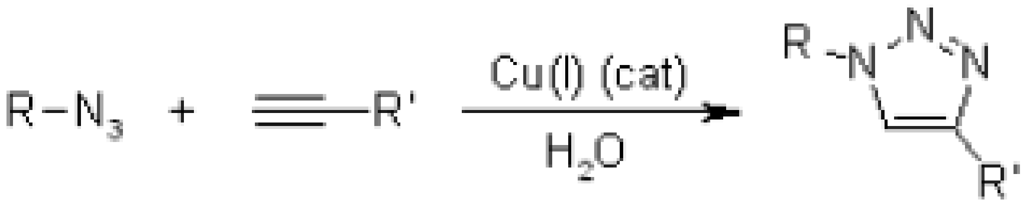


Enentioselective Pauson-Khand reaction

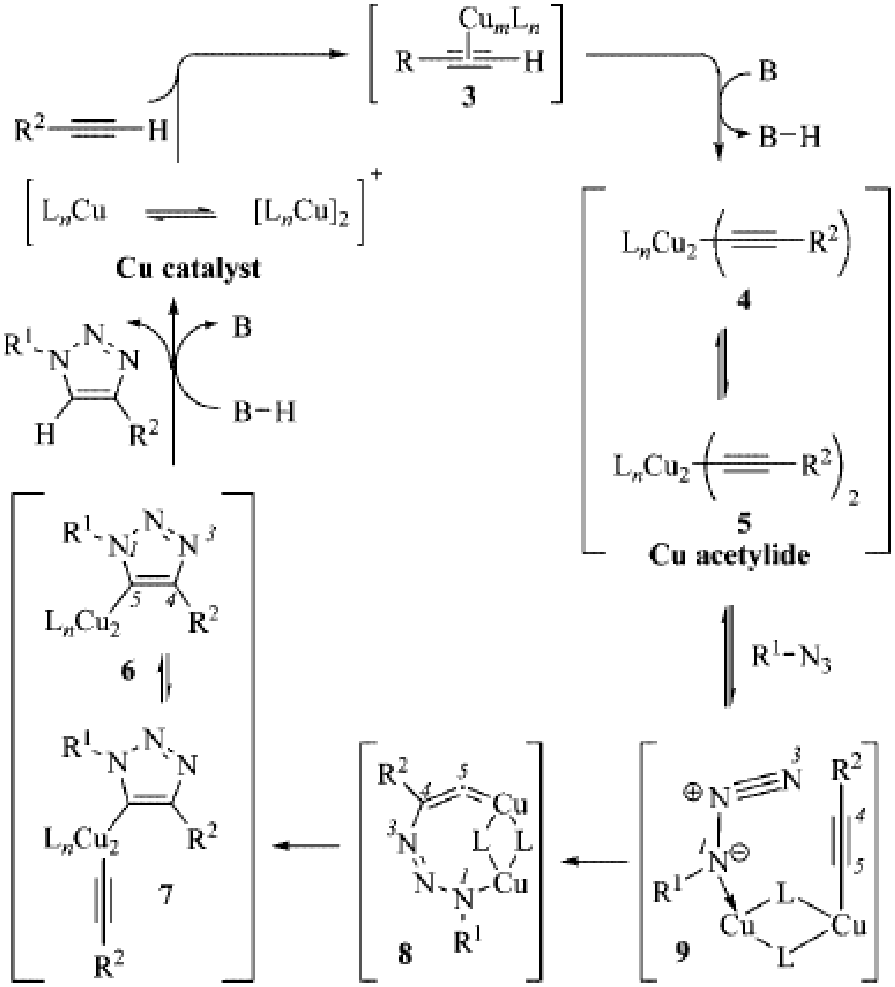
The reaction (intramolecular) is very efficiently run with metallocene complexes of Ti(II).



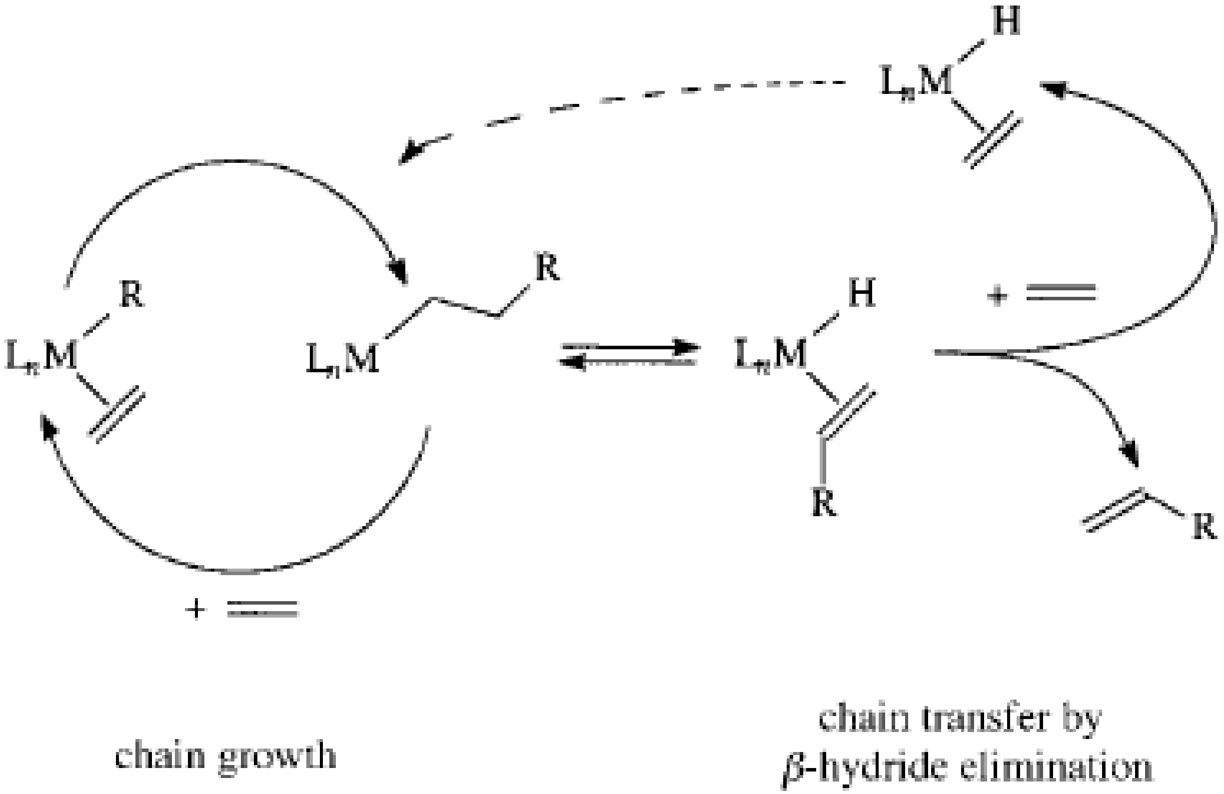
Azide-alkyne cycloaddition (Huisgen)



Paradigmatic example of “click chemistry”: modular reactions, general, which form bonds between reagent molecules in an efficient, complete and clean way under mild reaction conditions and in the absence of special precautions, so that no product purification is needed.



Oligo/Polymerization of olefins - mechanism



Polymerization can be promoted by shifting the insertion-β-elimination process towards the alkyl **or** by preventing the subsequent substitution reaction, which effectively terminates the chain growth (chain transfer).

Insertion vs. β-elimination

The position of this equilibrium is influenced by suitably acting on steric and and especially electronic factors. Insertion will be namely favoured by:

- steric bulk of the ligands, high coordination numbers;

- unavailability of orbitals on the metal for back-donation;

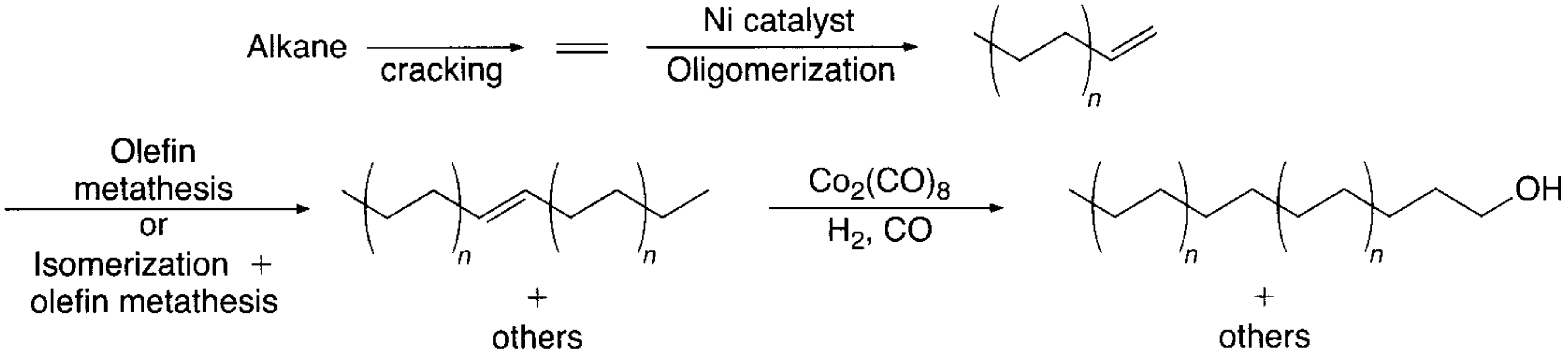
- positive charge on the metal (lowers the energy of d orbitals, making back donation less favourable)

Early TM are favoured! (First two points)

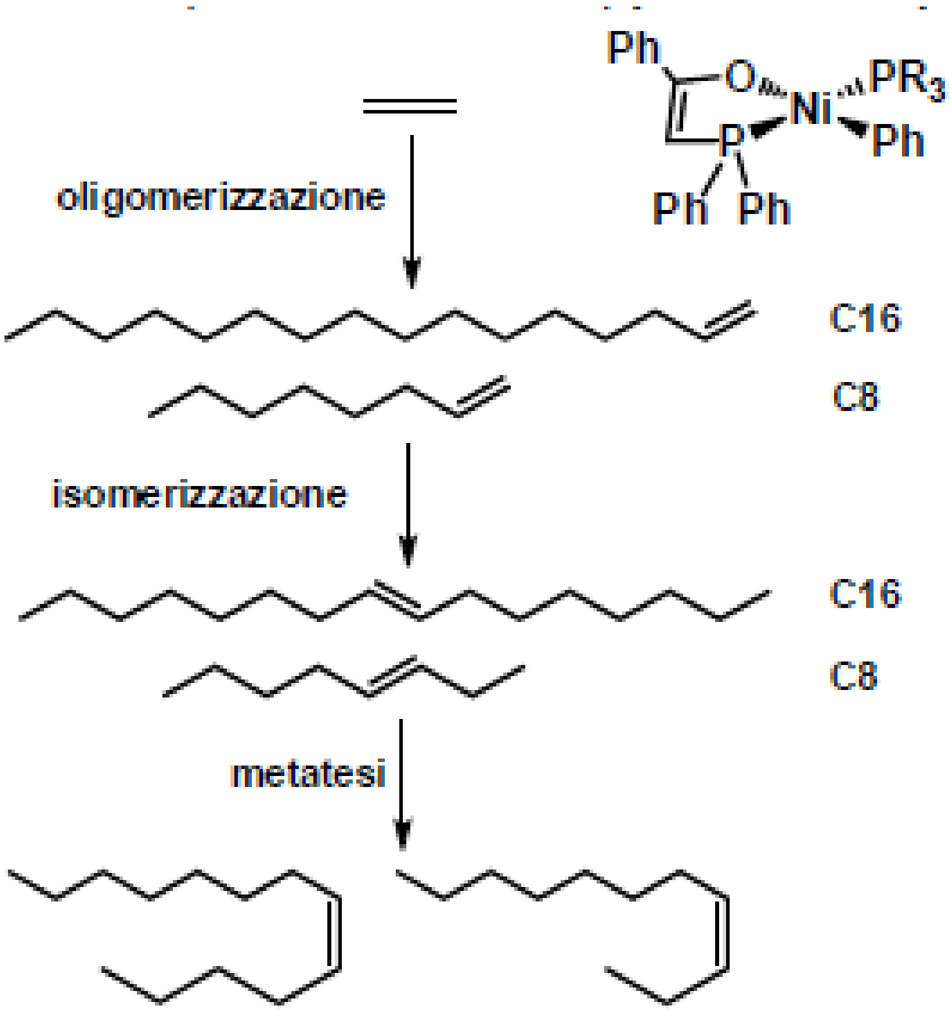
Analogous factors influence also the kinetics of the process. To these, still other factors sum, such as the nature of the metal (e.g. rate of β-elimination: **Ni < Pd >> Pt**)

Ethylene oligomerization: SHOP process (Shell Higher Olefin Process)

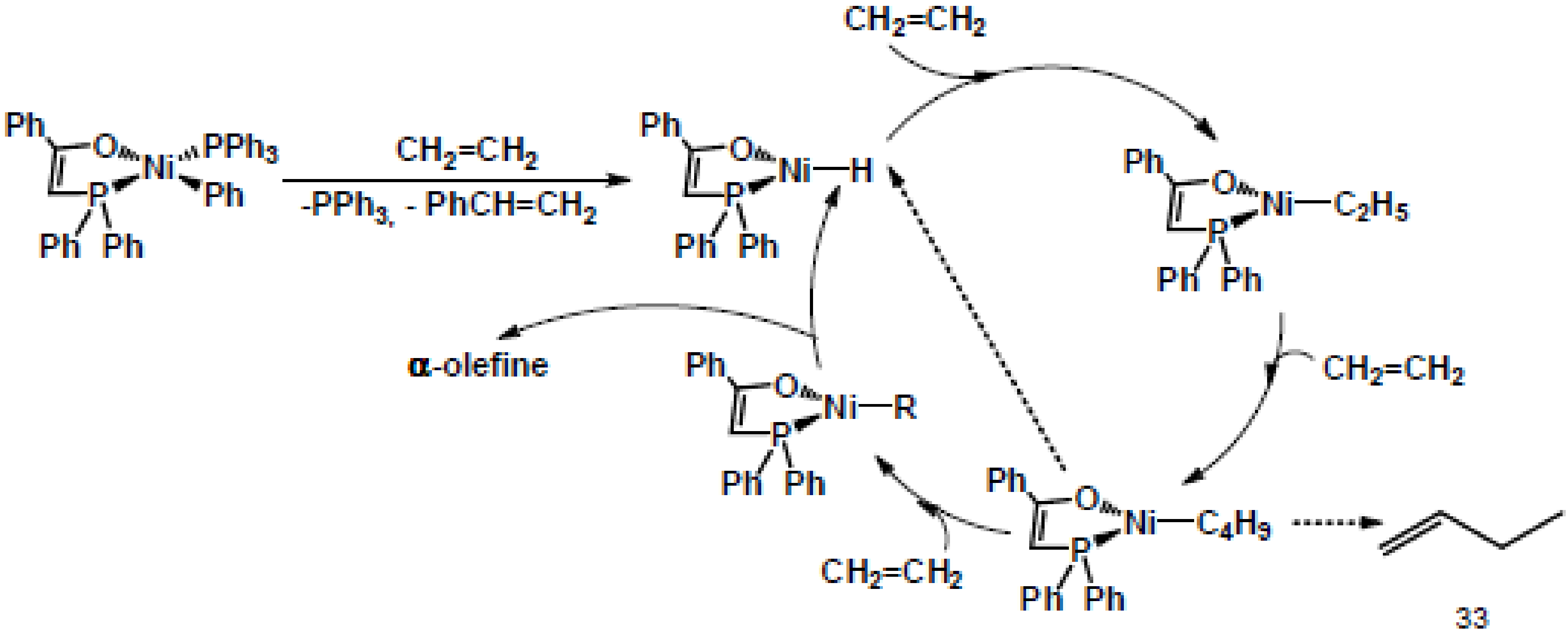
Multistep process, in which to an oligomerization reaction follows a step of isomerization and metathesis with formation of C12 olefins fron C8 and C16 compounds. Subsequently, an isomerization/hydroformylation process of the C12 olefins produces the desired alcohols (aldehydes).



SHOP process



SHOP process - mechanism

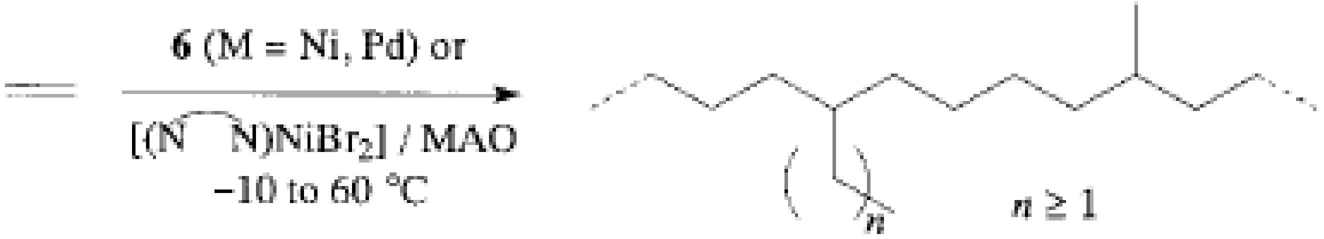


Simple Ni(II) salts promote instead the simple ethylene dimerization (“Ni effect” in the studies by Ziegler). Scavenging the phosphine ligand results instead in polymerization.

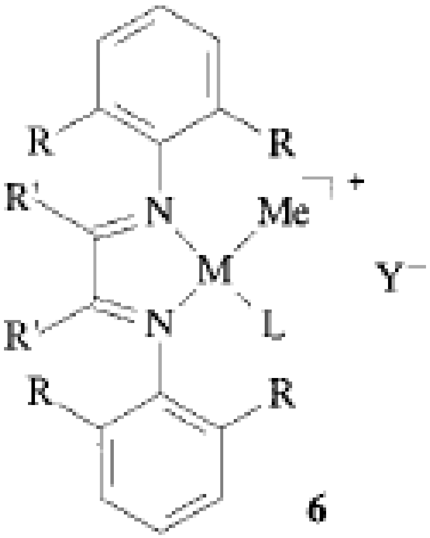
What are the factors that influence the selectivity of the process towards di-, oligo or polymerization?

Olefin polymerization with late TM

In 1995, Brookhart reported on late transition metal catalysts which were extremely active for olefin polymerization. Chains were formed from linear to highly branched and it was possible to introduce polar comonomers (e.g. acrylates).

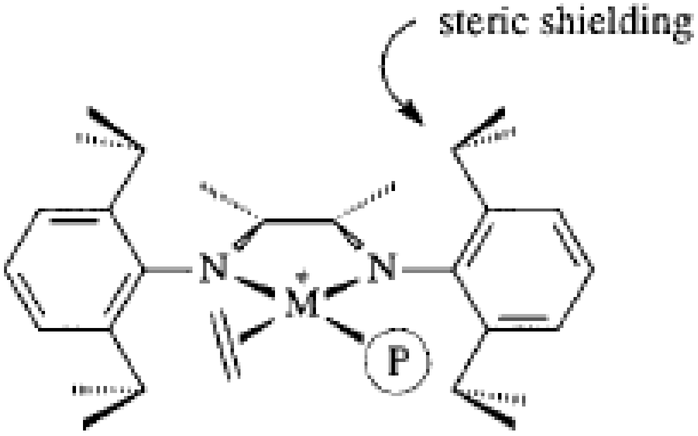


linear to highly branched ethylene homopolymer



6

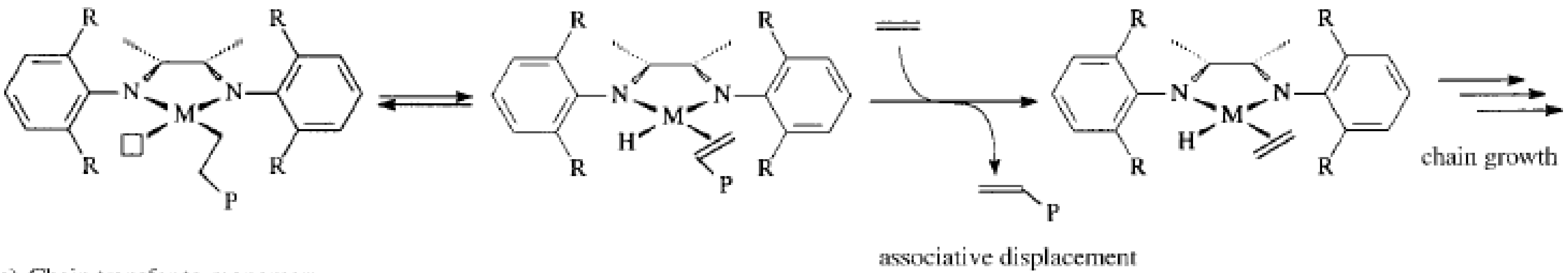
M = Ni, Pd
R' = Me, H, 0.5 naphthalene-1,8-diyl
R = *i*Pr, Me
L = OEt_2, R"CN
$Y^- = BAr^F_4{}^-, SbF_6{}^-$



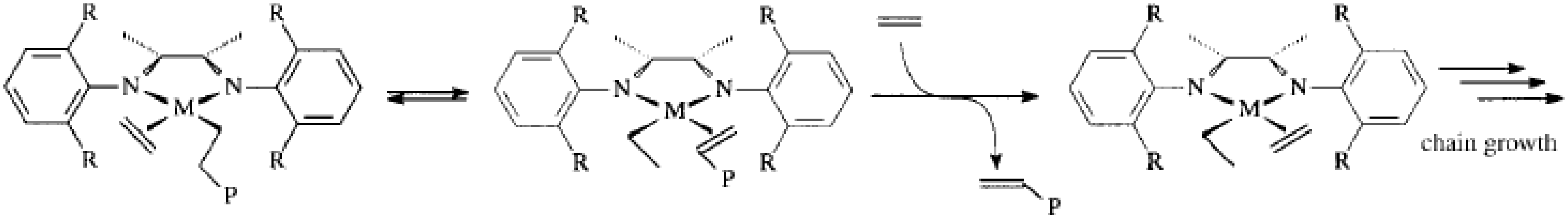
Olefin polymerization with late TM

The reason of the selectivity towards polymerization is the steric bulk of the substituents on the aryl groups, which block the substitution mechanism leading to chain transfer.

a) Chain transfer by associative exchange:

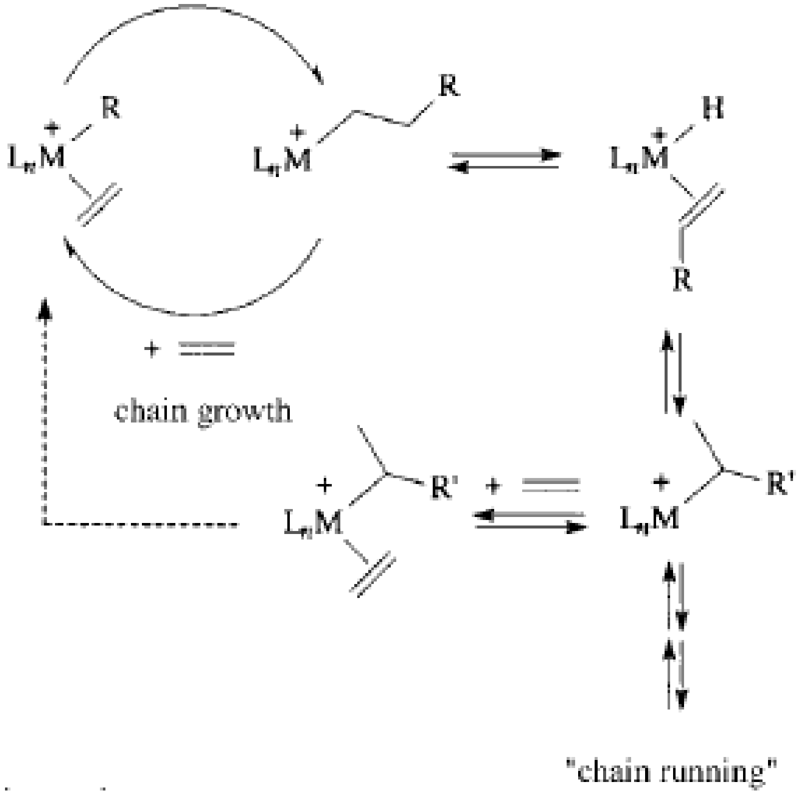


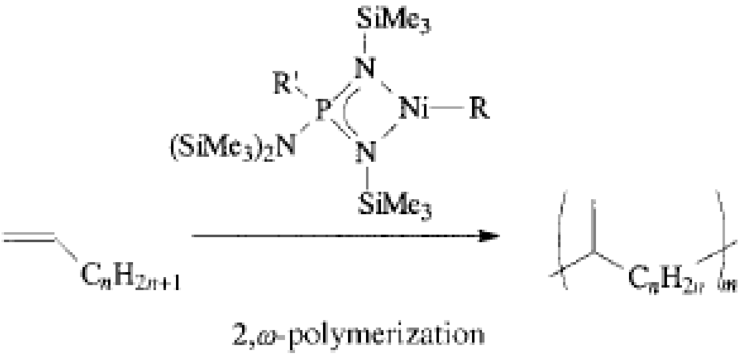
b) Chain transfer to monomer:

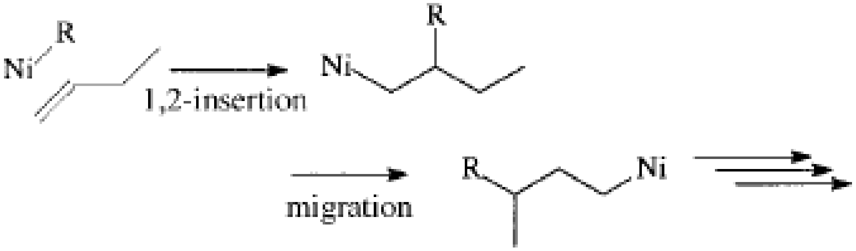


Olefin polymerization with late TM

The ramification that is produced in the polymer, especially in the case of Pd, is originated by insertion- β-elimination processes which lead to “migration” of M along the chain (“chain running” mechanism). This mechanism leads to very peculiar results, for example in the polymerization of terminal aliphatic olefins.

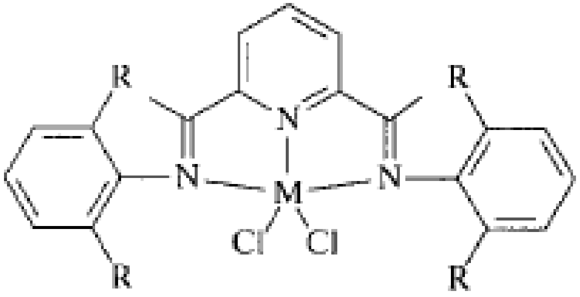






Olefin polymerization with late TM

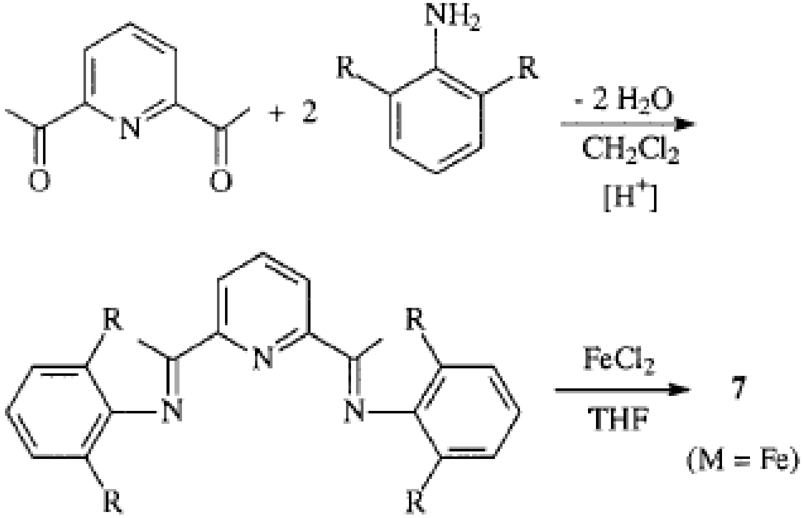
Starting from 1998, analogous Fe-based catalysts have been reported, which show catalytic activities approaching those of the best Ziegler-Natta catalysts and turn out to be stable, cheap and easy to prepare.



7

M = Fe, Co
R = *i*Pr, Me

activation
e.g. by MAO



Olefin polymerization with early TM

The most studied and employed TM catalysts for alkene polymerization remain still today thos based on early TM.

The discovery of Ziegler-Natta catalysts, together with heterogeneous catalysts based on Cr for ethylene polymerization (Philips) has promoted an enormous deal of research activity (academic and especially industrial) on these reactions, aimed at:

1) Maximize the activity of the catalytic system for different olefins;
2) Copolymerize different (functionalized) alkenes;
3) Determine the polymer chain morphology (linear/branched);
4) Control the tacticity of the polymer; this property refers to the configuration of the pseudochiral C atoms present in the chain after the polymerization of terminal alkynes: atactic polymer (random configuration), isotactic (same configuration for all chiral C atoms), sindiotactic (alternating configuration for all chiral C atoms).