Transition metals allyl, polyene and polyenyl complexes

Broad class of compounds, in which transition metals are bound to unsaturated ligands through their π-system, and this is extended over three or more carbon atoms.

Neutral ligands L_n (polyenes, arenes) or anionic L_nX (allyls, polyenyls); in the first case the ligands are in general **stable neutral molecules**, in the second case **formal carbanions**, which however once bound to metal centres display a superior stability with respect to carbanions bound through simple σ bonds.

Similar nature of the TM-ligand interaction and variable but comparable reactivity between the different ligands. Coordinated allyls, polyenes and polyenyls do easily convert one into another, which justifies a unified treatment. Employed both as reactive or as supporting ligands.

Metal-ligand interaction

The interaction is established between atomic orbitals on the metal and molecular orbitals of the ligand, which originate from the combination of the 2p orbitals of the C atoms taking part in the ligand π system.

High energy, occupied molecular orbitals donate electron density towards the metal centre, wheres low energy, unoccupied molecular orbitals accept electron density back-donated by the metal. Generally, more than two molecular orbitals are involved!

Depending on the extension of the involved π system and on its simmetry, the quali- and quantitative description of the interaction can become quite complicated and can be exactly defined only upon using computational methods. Intuitively, though, more extended π systems will involve more electrons in the interaction, hence give rise to more stable compounds.

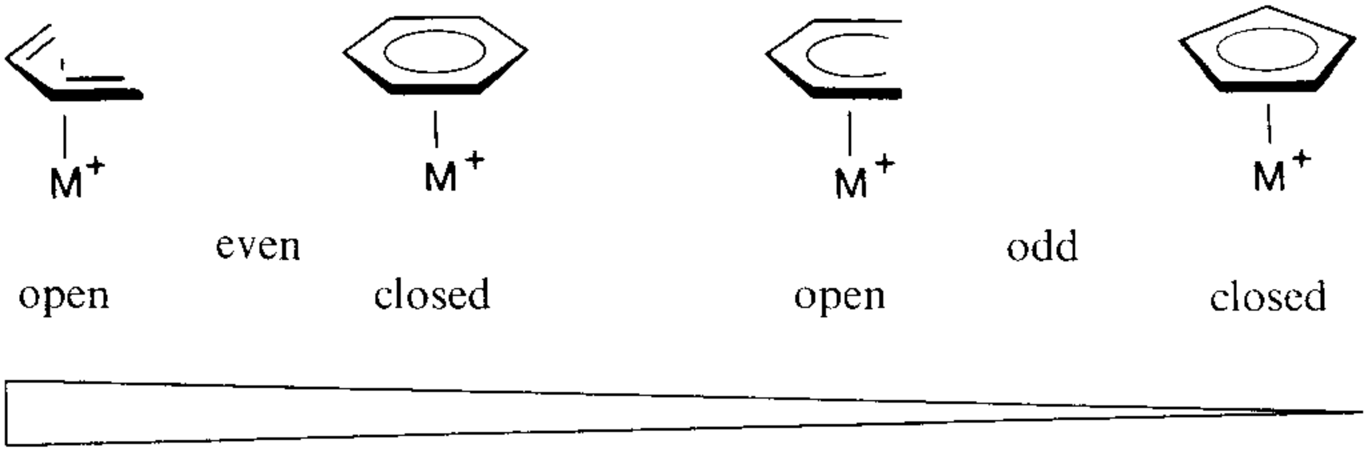
Reactivity of the complexes

The reactivity of complexes of this kind obviously depends on the electron density present on the ligand, hence on the metal-ligand and intraligand redistribution of electron density taking place upon coordination.

For example, cyclopentadienyl, a ligand which is formally anionic and «closed» (= cyclic, aromatic) maintains a significant electron density even when coordinated, hence it reacts mainly with electrophiles. On the other hand, neutral, open chain ligands bound to metal cations react mainly with nucleophiles.

Such a behaviour can be rationalised in terms of the **Green-Davies-Mingos (DGM) rules**, which determine the kinetic preference for nucleophilic attack to a particular ligand of this kind in an 18 electrons cationic complex.

The Davies – Green – Mingos (DGM) rules



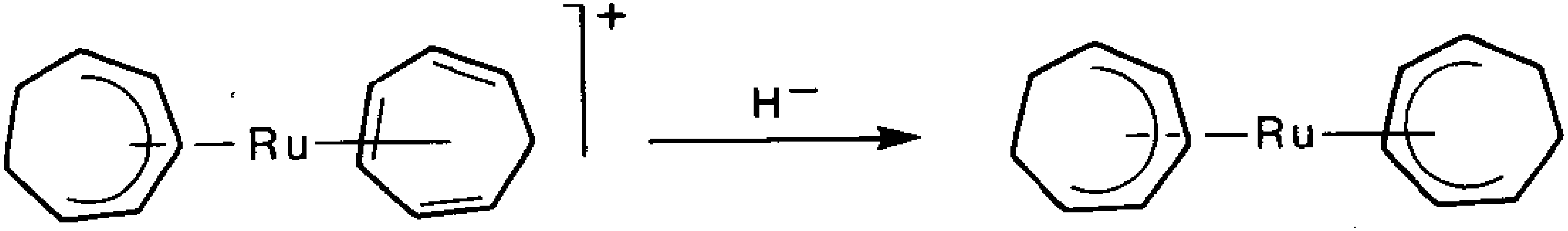
① Nucleophilic attack occurs preferentially at **even** coordinated polyenes.

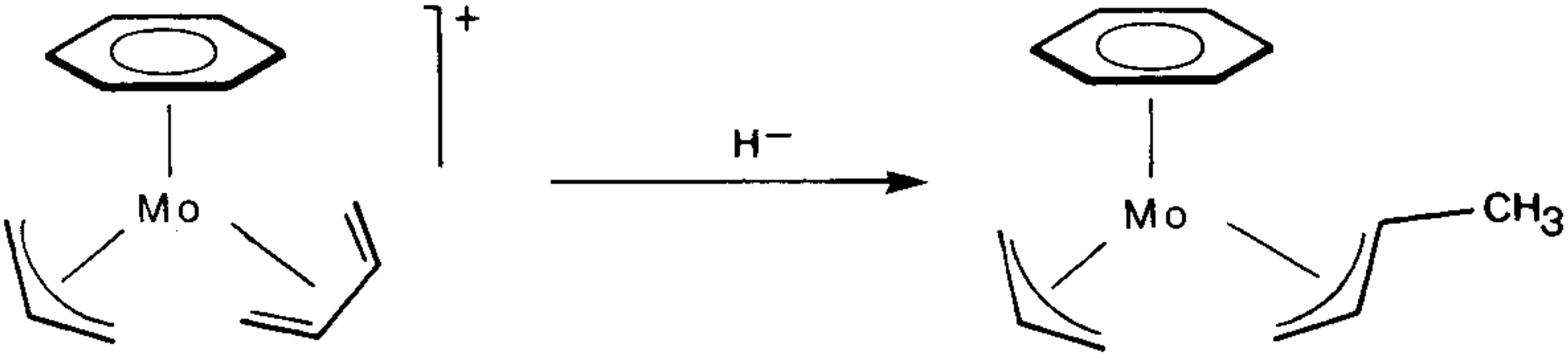
② Nucleophilic addition to **open** coordinated polyenes is preferred over addition to closed polyene ligands.

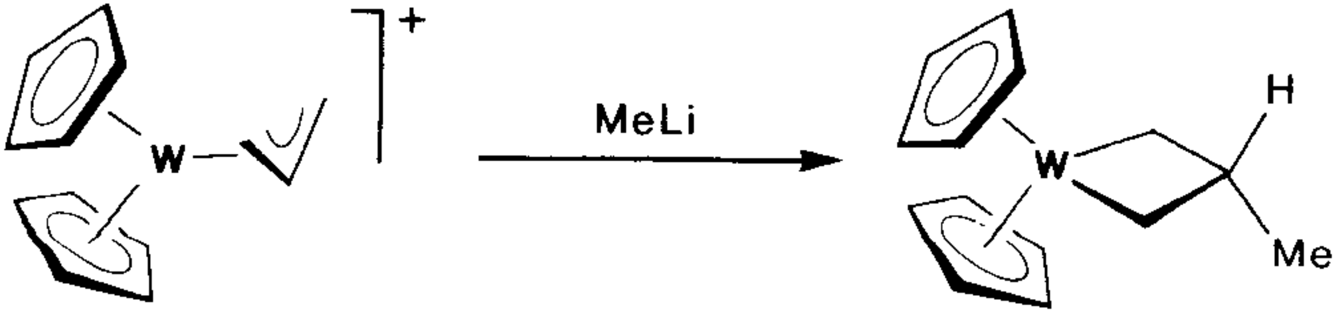
③ In the case of even open polyenes, nucleophilic attack always occurs at the **terminal carbon atom**; for odd open polyenyls, attack at the terminal carbon atom occurs only if ML_n^+ is a strongly electron-withdrawing fragment.

The Davies–Green–Mingos (DGM) rules must be applied in the sequence ① ② ③.

Application of the DGM rules





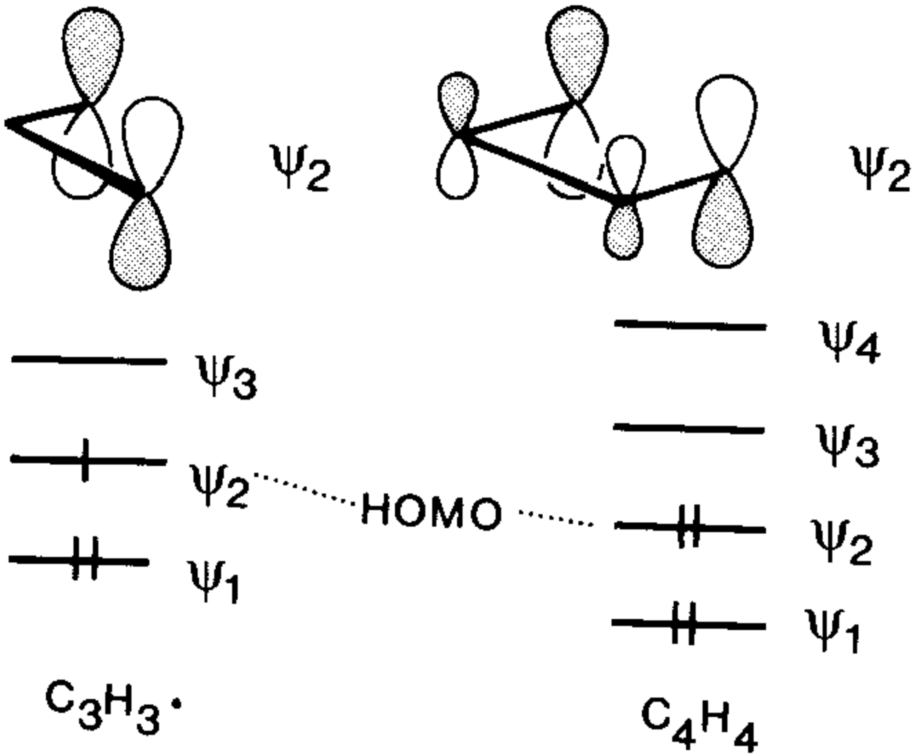


Explanation of the DGM rules

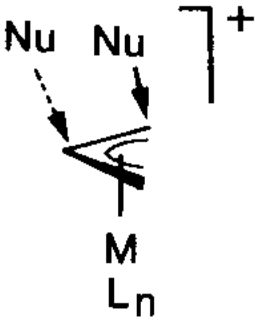
Rule 1: ligands with an odd number of C atoms (allyls, polyenyls) are formally anionic, hence strongly electron-withdrawing metal centres will be needed in order to decrease electron density on them to the point that they are amenable to nucleophilic attack, whereas this process will be much easier with neutral ligands (polyenes, arenes).

Rule 2: «closed» ligands (cyclic, aromatic) exhibit more symmetric molecular orbitals compared with open chain, non aromatic ligands. Consequently, the shift in electron density upon ligand coordination will affect in a more similar way ALL the C atoms, whereas with less symmetric ligands some C atoms (e.g. the terminal ones, see Rule 3) will experience a stronger variation in electron density compared to others.

Explanation of the DGM rules – Rule 3



As suggested by the diagram, removal of charge dominates at the **terminal** carbon atoms, which consequently attain higher partial charges δ^+ and which, therefore, are the preferred sites for nucleophilic attack (rule ③).

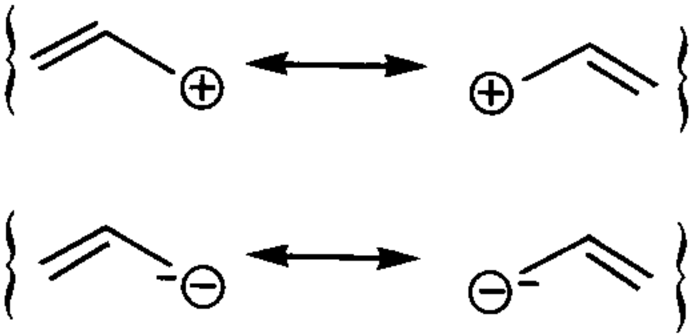


L_nM^+ is a strong electron acceptor

(η^3-C_3H_5) reacts like $C_3H_5^+$

L_nM^+ is a weak electron acceptor

(η^3-C_3H_5) reacts like $C_3H_5^-$



Synthesis of the complexes

Complexes with formally **anionic** allyl and polyenyl ligands can be prepared using the same methodologies employed for complexes containing simple σ M-C bonds; the coordinated η^1 ligand can subsequently rearrange to η^n occupying additional coordination sites.

Complexes with **neutral** polyene or arene ligands can be instead prepared starting from the free ligands through the same methodologies employed for metal alkene and alkyne complexes. Exceptions are the (very few) ligands which are unstable in the free state (e.g. cyclobutadiene), which can be prepared e.g. by cyclodimerisation of coordinated alkynes.

Further to this, neutral and anionic ligands of this family can be interconverted one into the other, as it will be apparent in the following…

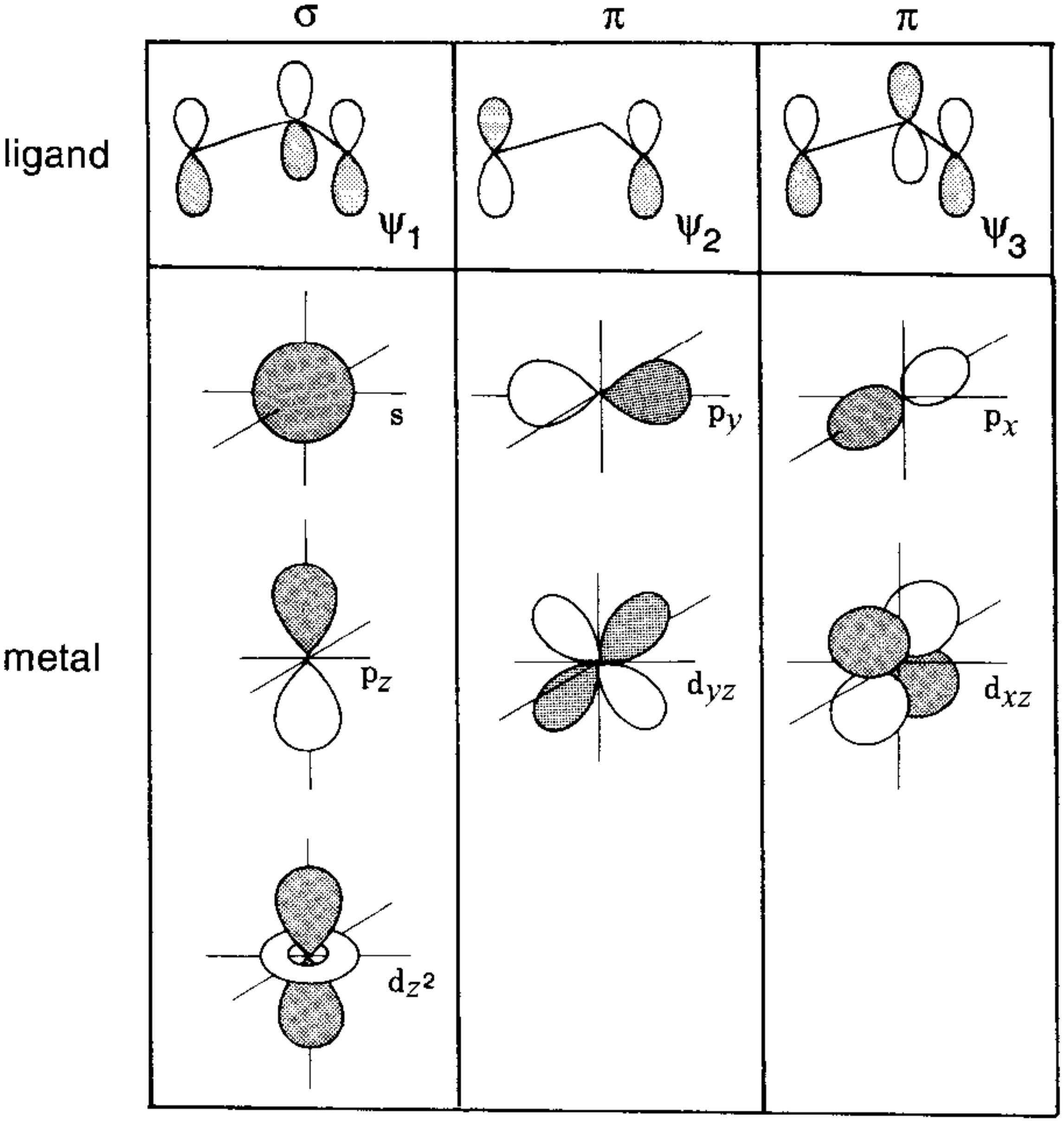
Metal-allyl and polyenyl complexes

The allyl group is the simplest ligand coordinating through an extended π system (three C atoms), and also the most reactive. Homoleptic allyl complexes are generally unstable and decompose by reductive elimination of hexadiene.

Such reactivity has been put to advantage in numerous processes that make use of allyl complexes as intermediates. Such processes are characterised by a high efficiency and generality, by a well understood reaction mechanism and by the possibility to run the reaction with a high degree of selectivity (chemo-, regio-, stereo-).

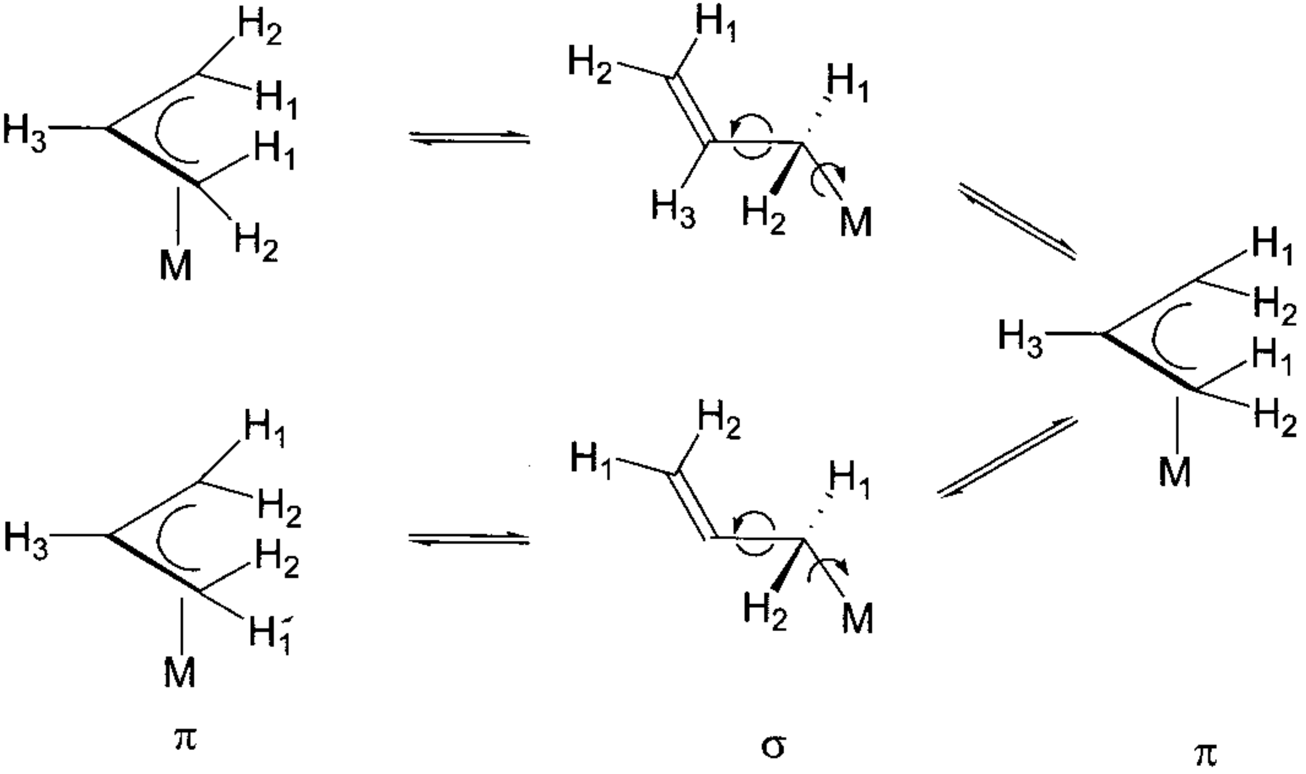
Higher polyenyl are generally less reactive when coordinated. They are employed as supporting ligands (e.g. cyclopendacienyl, see further) or as reagents in stoichiometric reactions.

Metal-allyl interaction



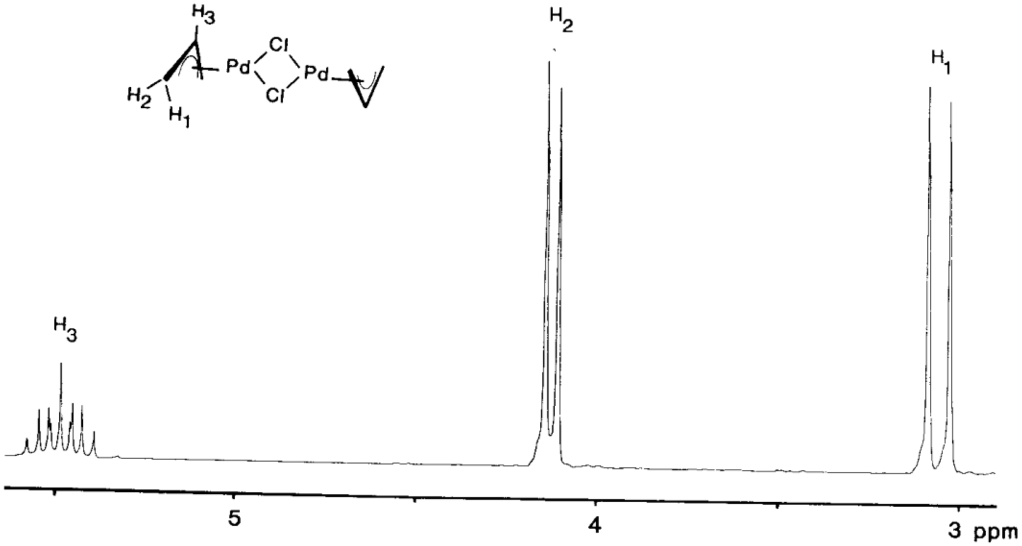
Structure of metal-allyl complexes

TM allyl compounds display a fast equilibrium between η^3 and η^1 coordinated allyl. Such equilibrium can be easily evidenced by ^{1}H NMR; it racemizes the complex in the case of prochiral acylclic allyls (bearing different terminal substituents) and is consequently of notable importance in enantioselective processes.

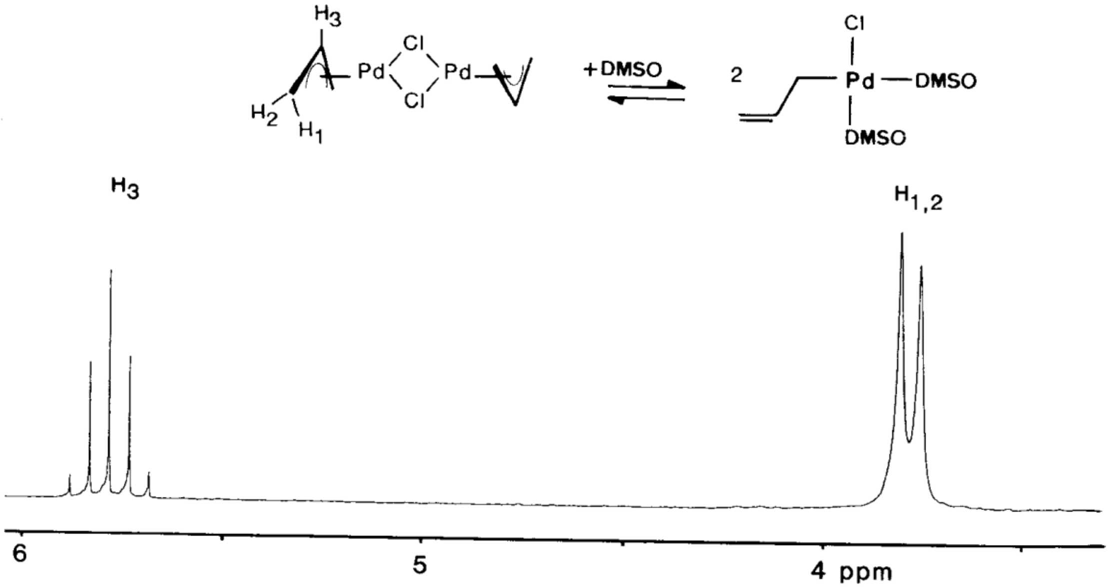


Structure of metal-allyl complexes

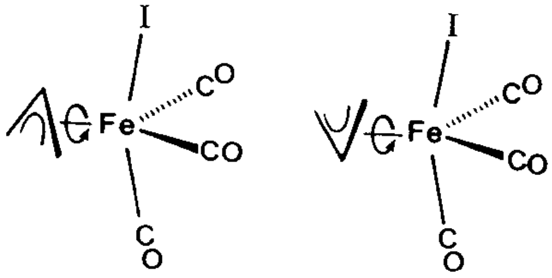
^{1}H NMR spectrum of $[C_3H_5PdCl]_2$ (**$CDCl_3$**, 25 °C, 200 MHz):



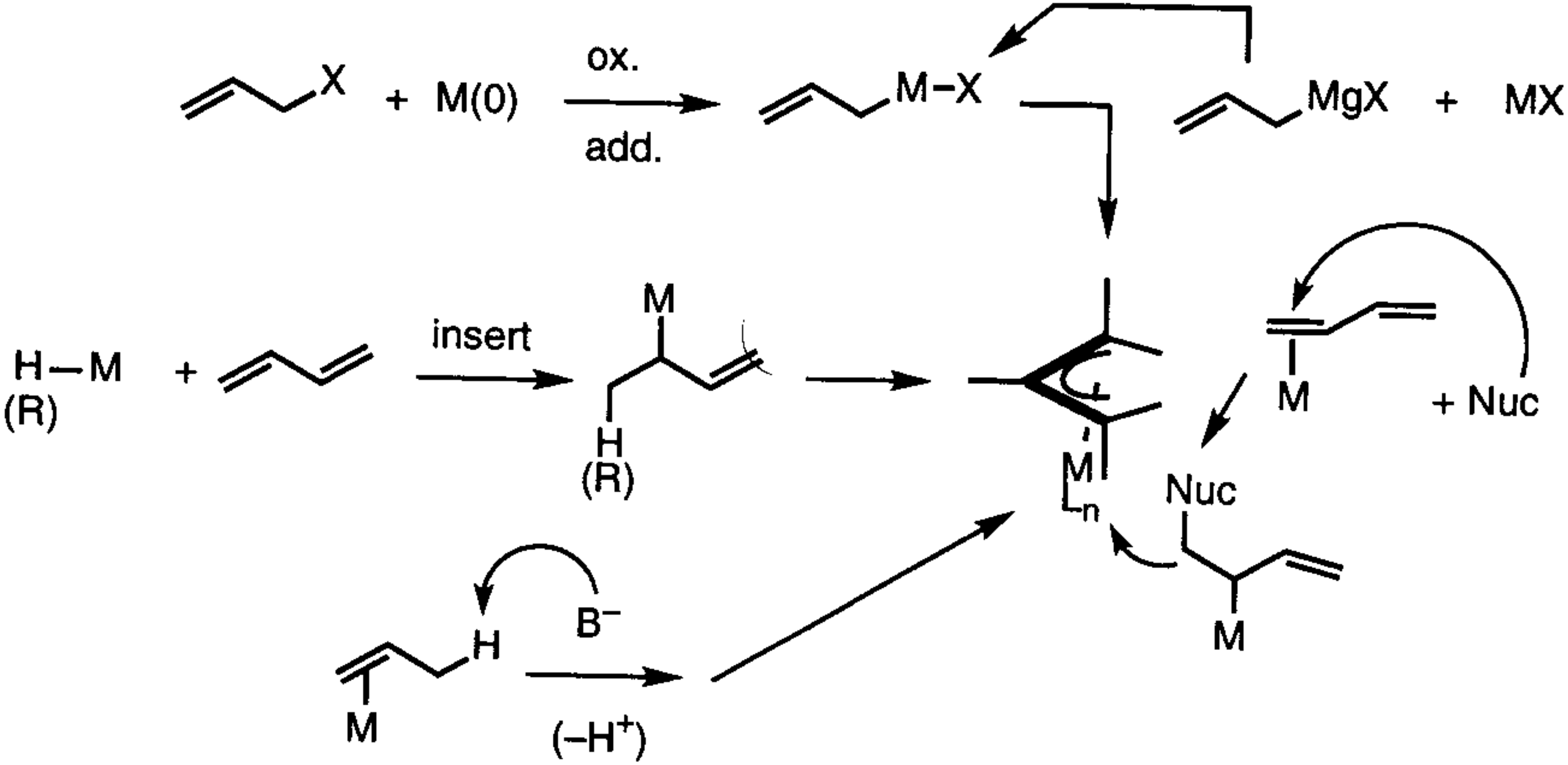
^{1}H NMR spectrum of $[C_3H_5PdCl]_2$ ($[D_6]$DMSO, 140 °C, 200 MHz):



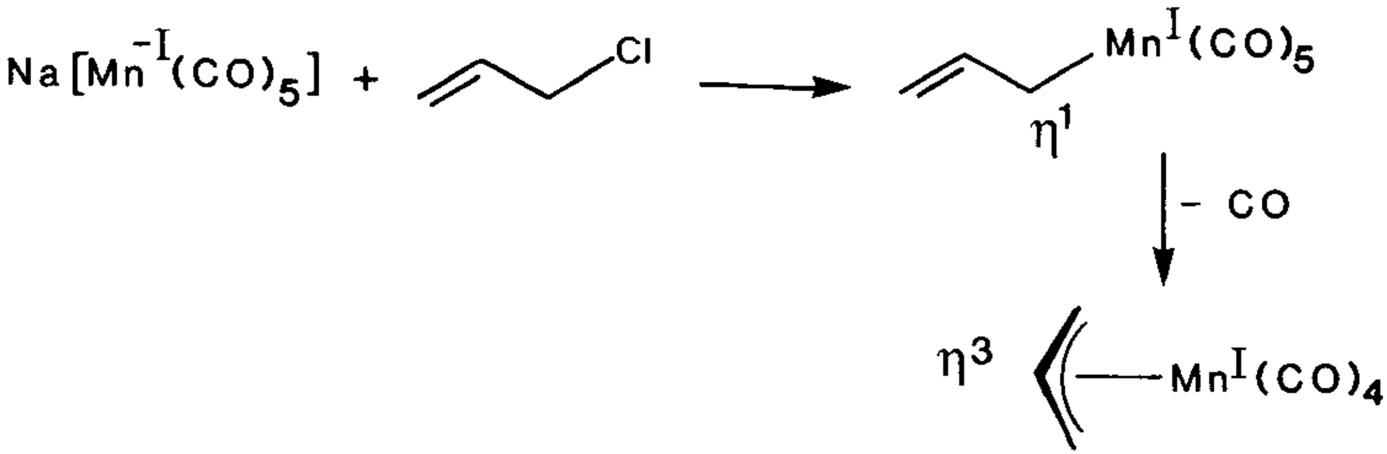
Rotation around the M-allyl bond axis also contributes to mediate the chemical environment around the H atoms

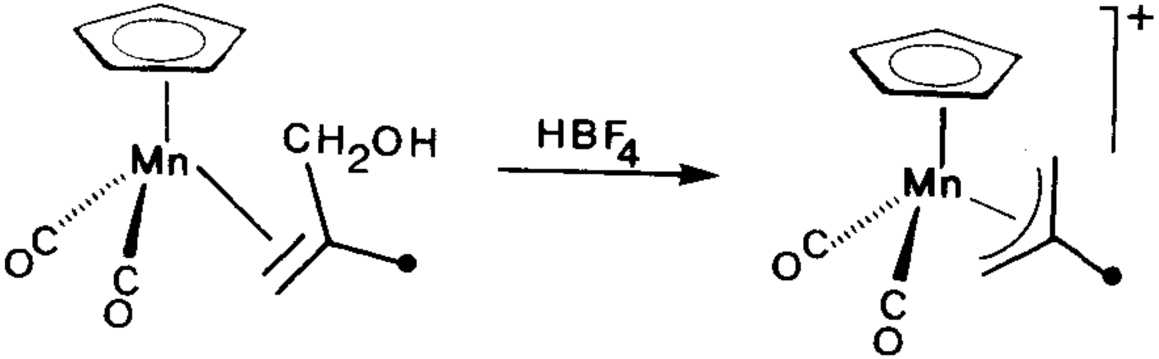


Synthesis of the complexes

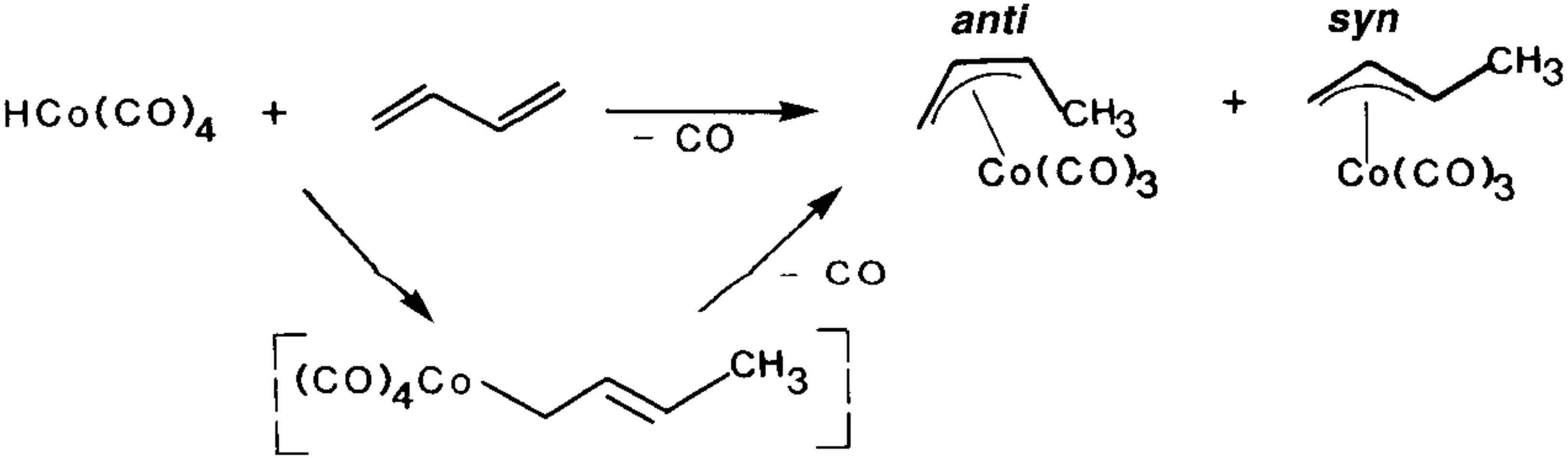


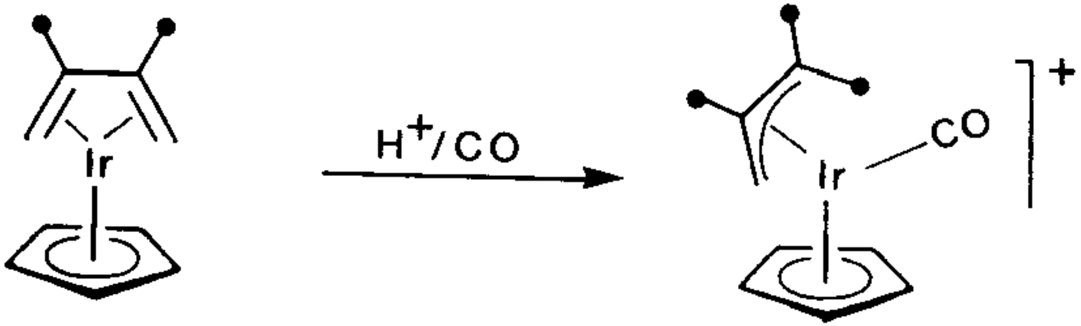
Synthesis of the complexes

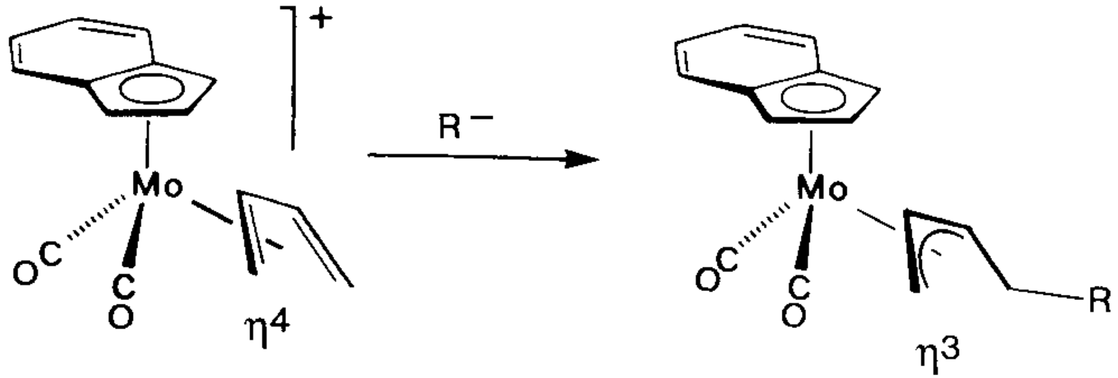




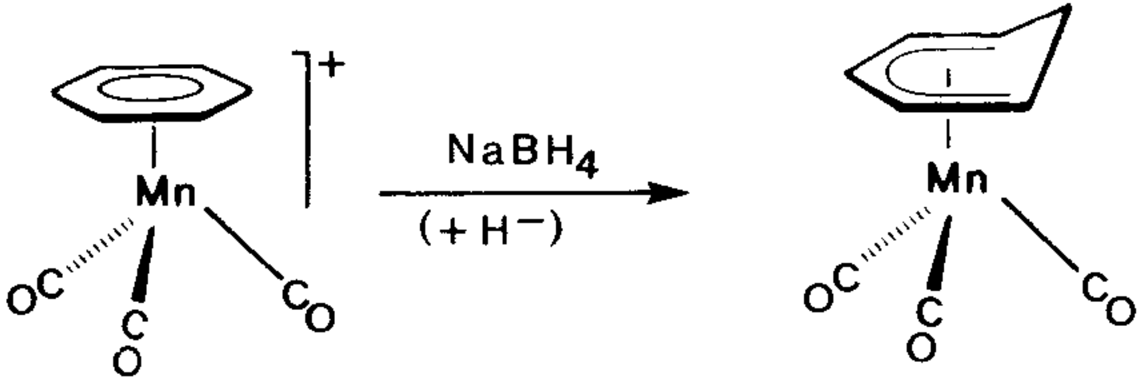
Synthesis of the complexes



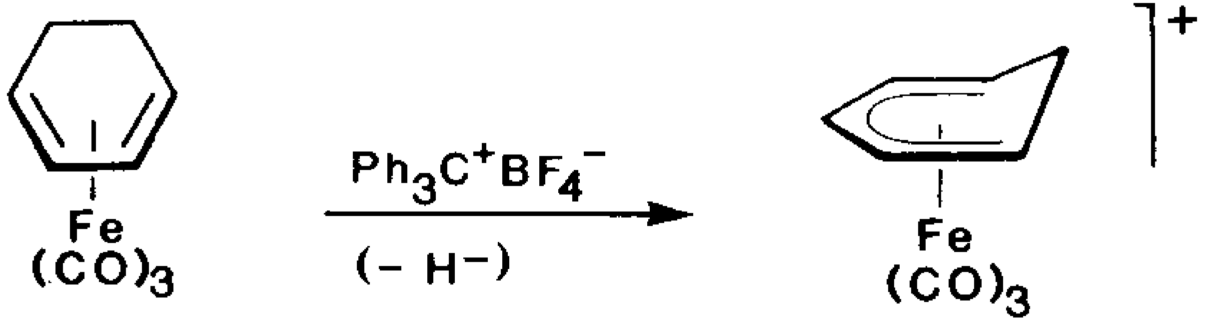




Synthesis of the complexes

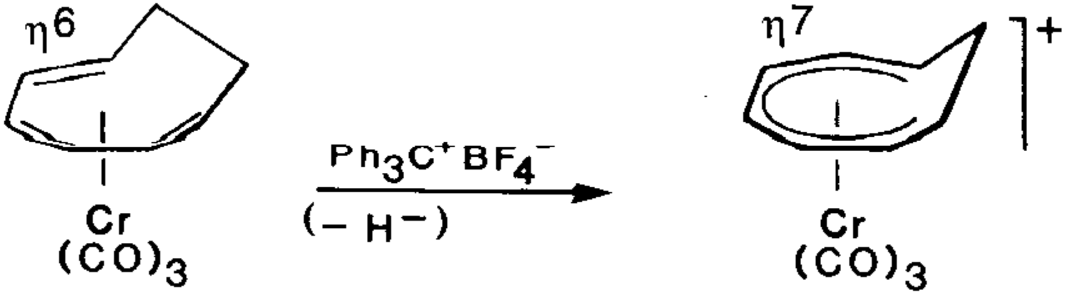


hydride addition

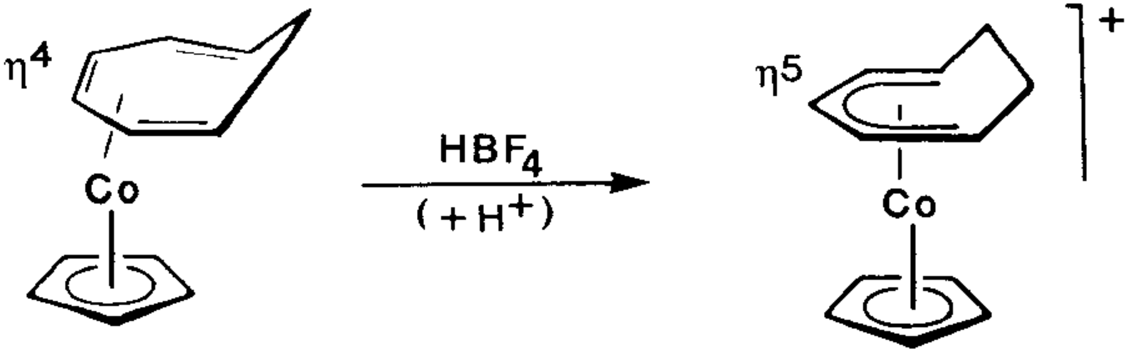


hydride abstraction

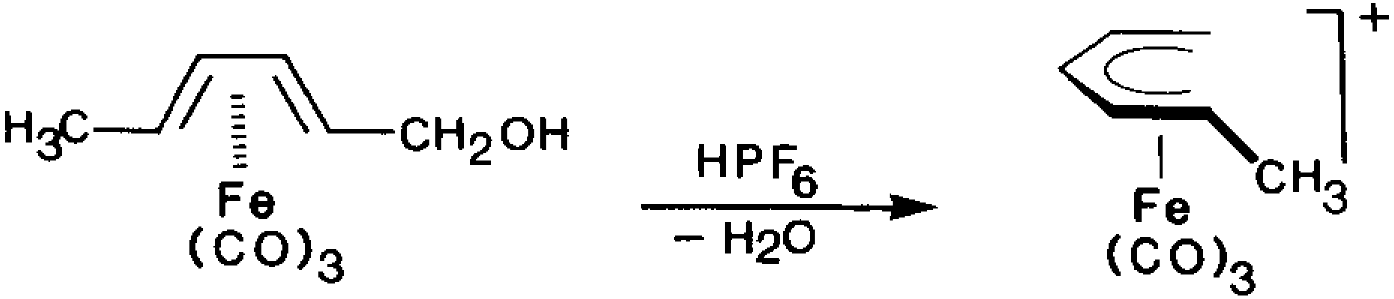
Synthesis of the complexes



a homotropylium complexes



protonation of an uncoordinated double bond



Reactivity of metal-allyl and –polyenyl complexes

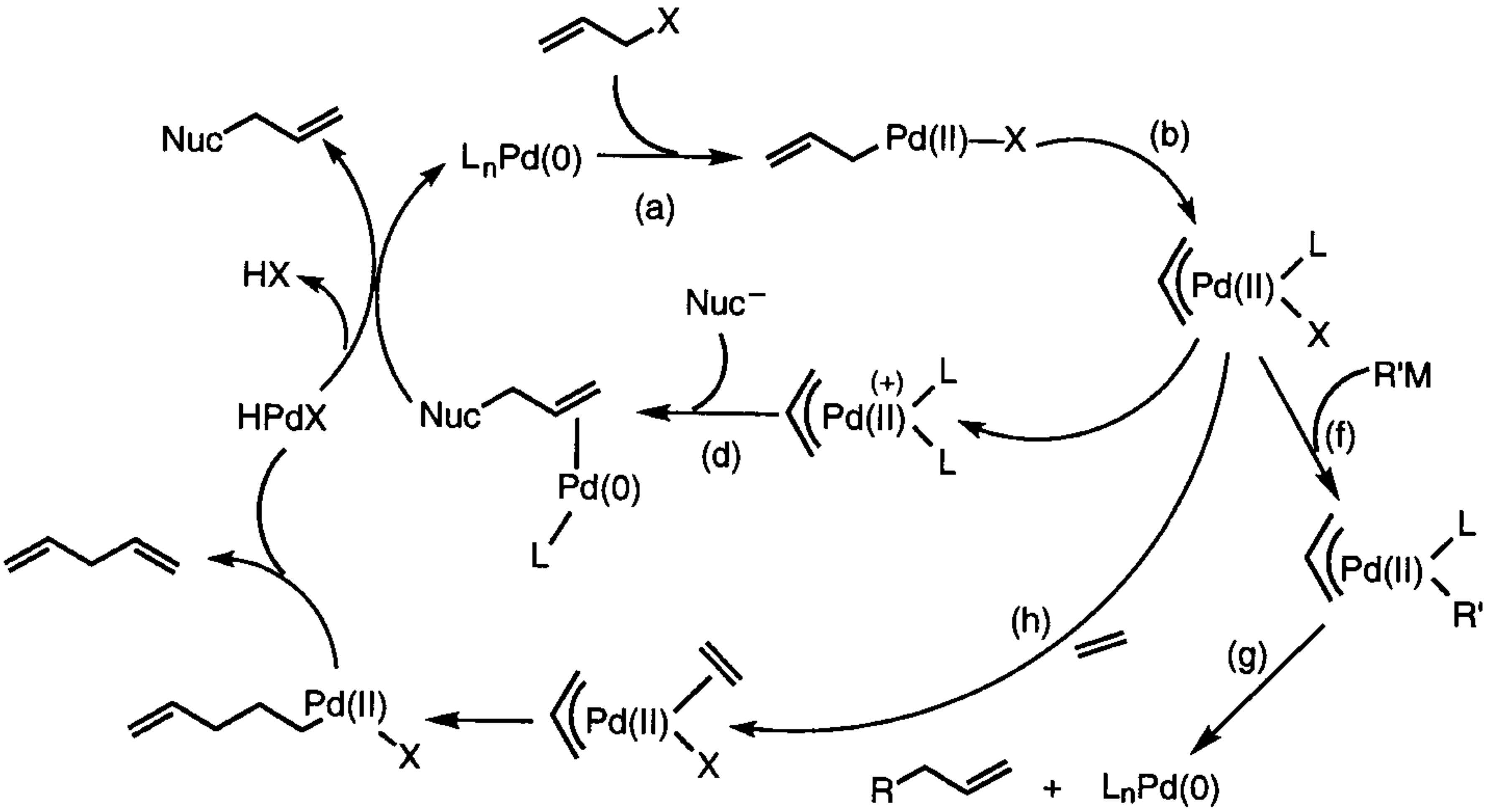
The reactivity of coordinated allyls combines in a way aspects typical of the reactivity of metal alkyls and of metal alkene complexes.

With respect to the former, allyls can undergo **reductive elimination** reactions (e.g. with organic residues σ bound to the metal) or insertion reactions (e.g. with CO, alkenes etc.).

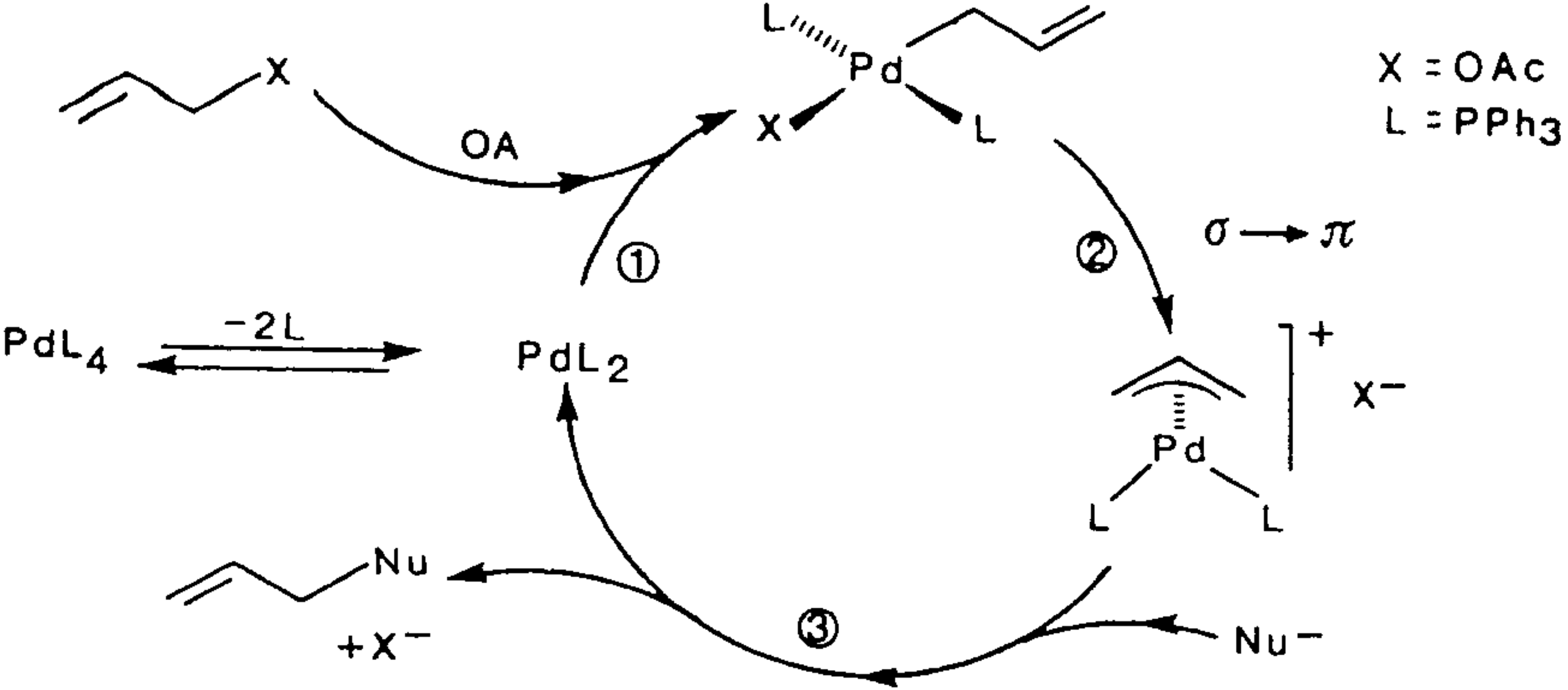
With respect to the latter, they can be subjected to **nucleophilic attack**, external or upon precoordination to the metal centre.

Such processes often lead to the reduction of the metal centre (Pd). If the allyl complex is formed by oxidative addition, it is consequently possible to close a Pd(0)/Pd(II) catalytic cycle.

Reactivity of metal-allyl complexes

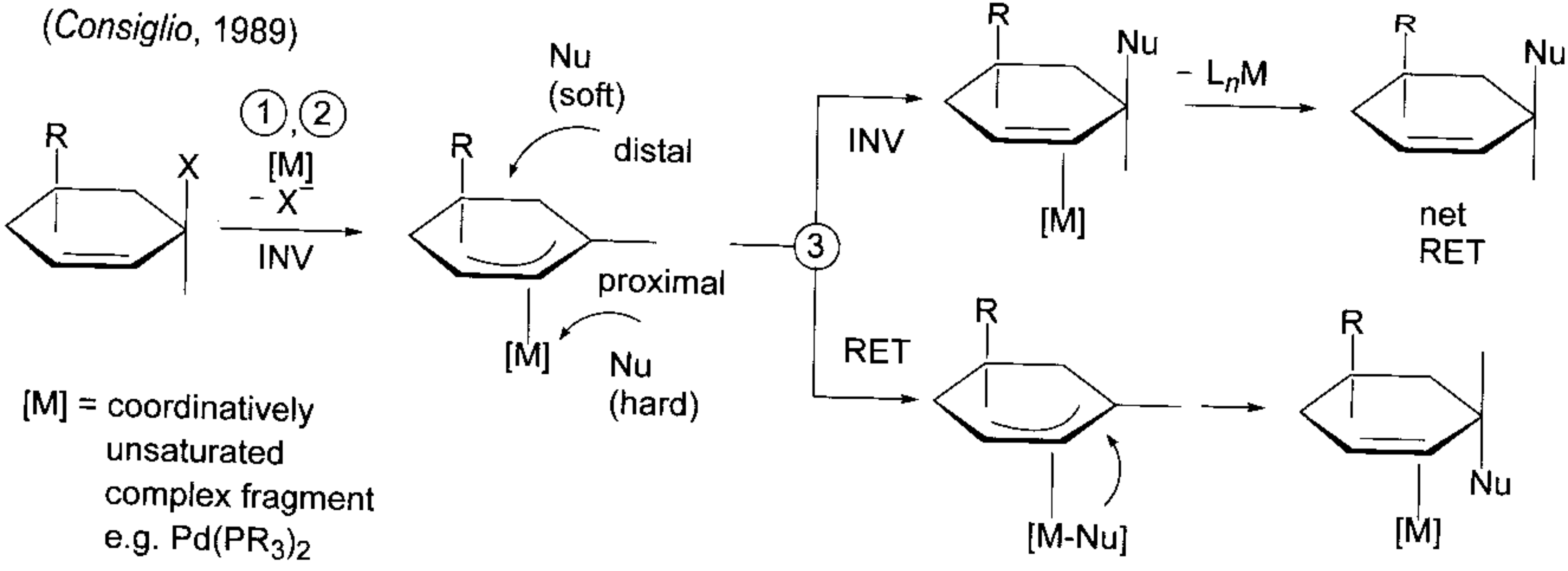


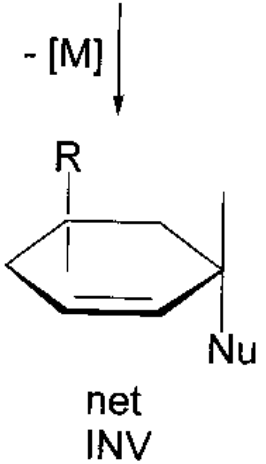
Allylic substitution reaction



Synthetically useful reaction, very well studied, particularly in its asymmetric variant. Reaction dominated by Pd catalysis.

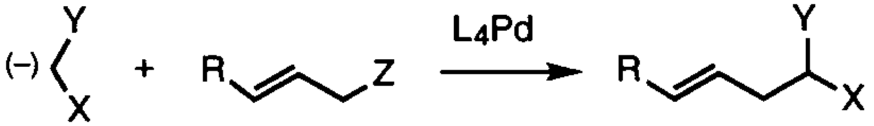
Allylic substitution- stereoselectivity

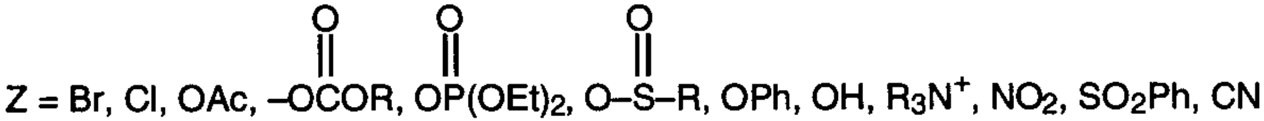




The reaction can proceed with net **inversion** or **retention** of configuration, depending whether the nucleophile precoordinates or not to the metal centre. Clearly, the reaction will be certainly stereoselective only with cyclic alkynes (racemization is prevented) Another issue is the **regioselectivity** of the reaction.

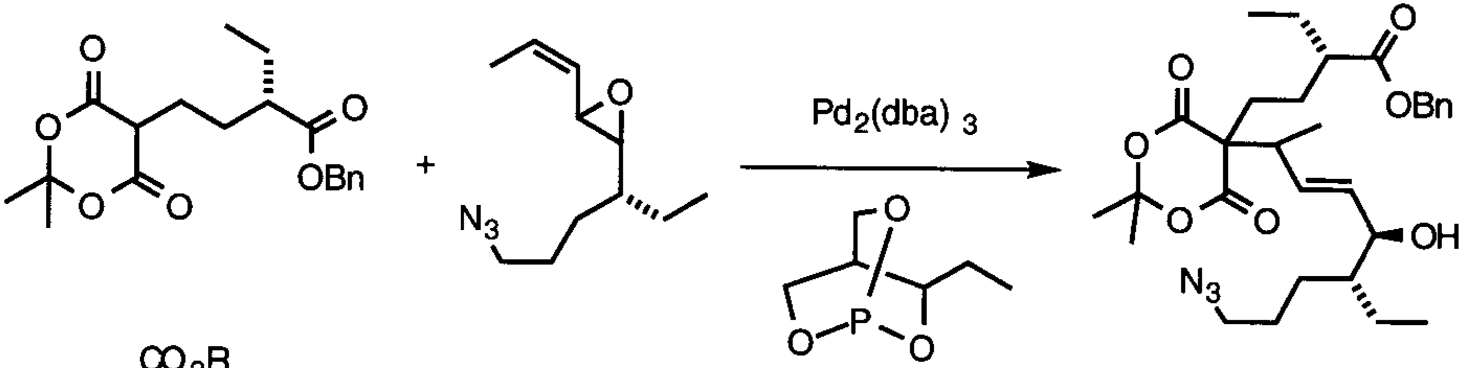
Allylic substitution reaction

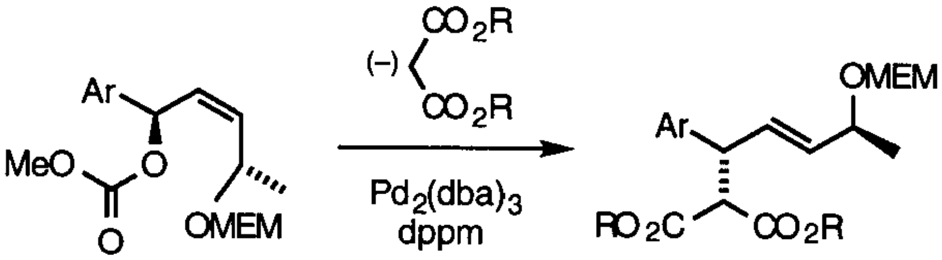




$Z = Br, Cl, OAc, -OCOR, OP(OEt)_2, O-S-R, OPh, OH, R_3N^+, NO_2, SO_2Ph, CN$

$X, Y = CO_2R, COR, SO_2Ph, CN, NO_2$



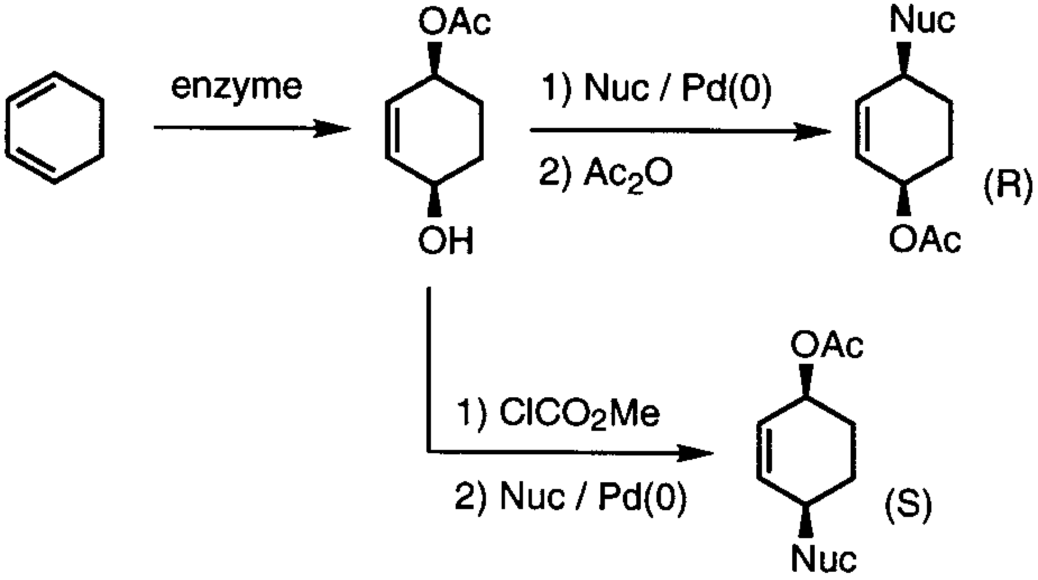


96%

complete chirality transfer

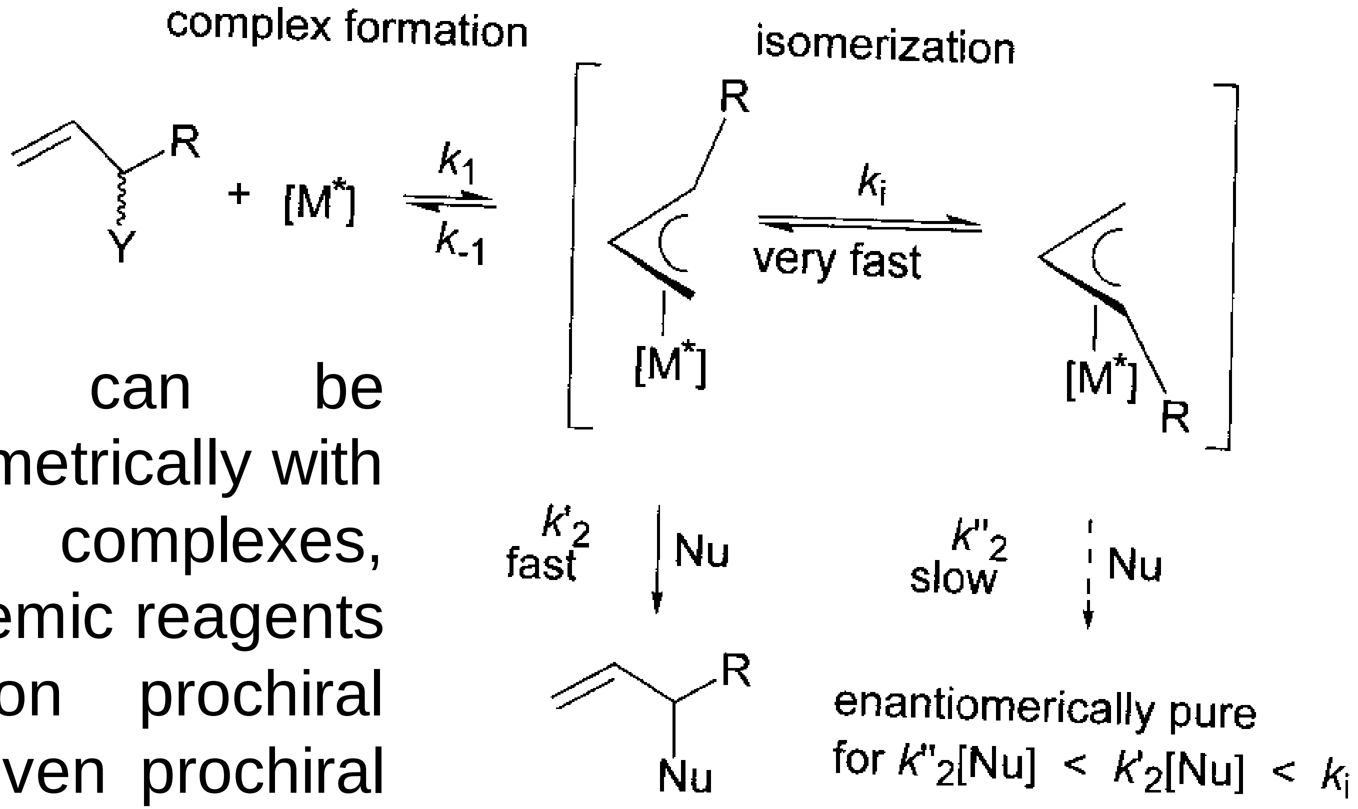
Allylic substitution reaction- regioselectivity

The **regioselectivity** with respect to the formation of two possible allyls can be controlled through the different tendency of functional groups to act as leaving groups (chloride > carbonate > acetate >> hydroxide…)



The **regioselectivity** with respect to the nucleophilic attack is instead more difficult to control. Attack usually takes place at the less substituted, terminal C atom, but electronic effects can count a lot. Often the problem is overcome using **symmetrical allyls**!

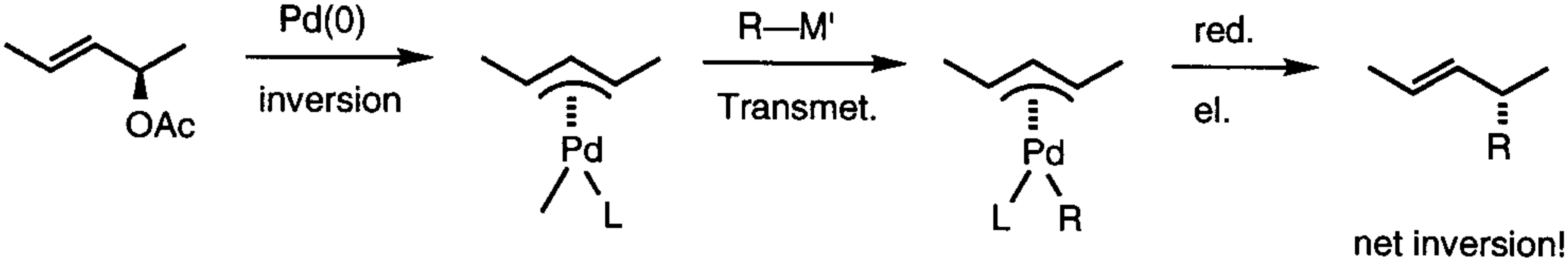
Asymmetric allylic substitution reactions



The reaction can be conducted asymmetrically with chiral Pd(II) complexes, starting from racemic reagents which yield non prochiral (symmetric) or even prochiral allyls. In the latter case, the coordinated allyl must isomerize rapidly and the resulting diastereotopic complexes must react with different reaction rates.

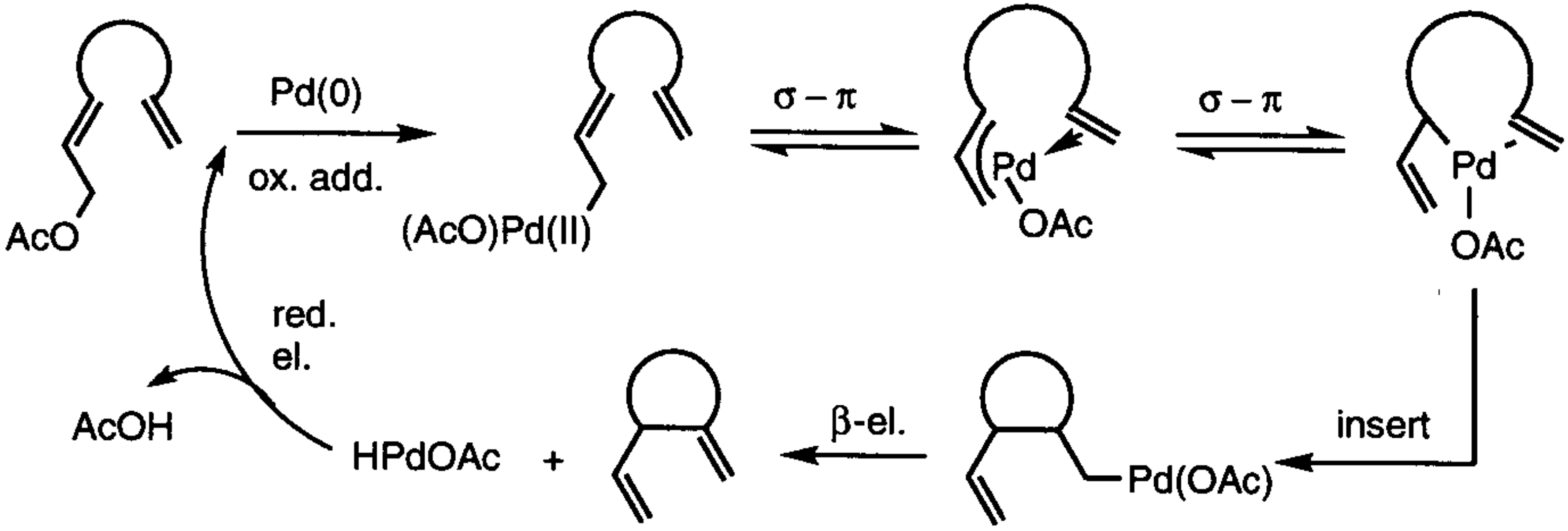
Allylic substitution upon metathesis – reductive elimination

Reaction very similar to a cross-coupling reaction, proceeding with net inversion of configuration. For this purpose, weakly nucleophilic organometallic reagents are employed, for example organotin compounds (Stille-type coupling).

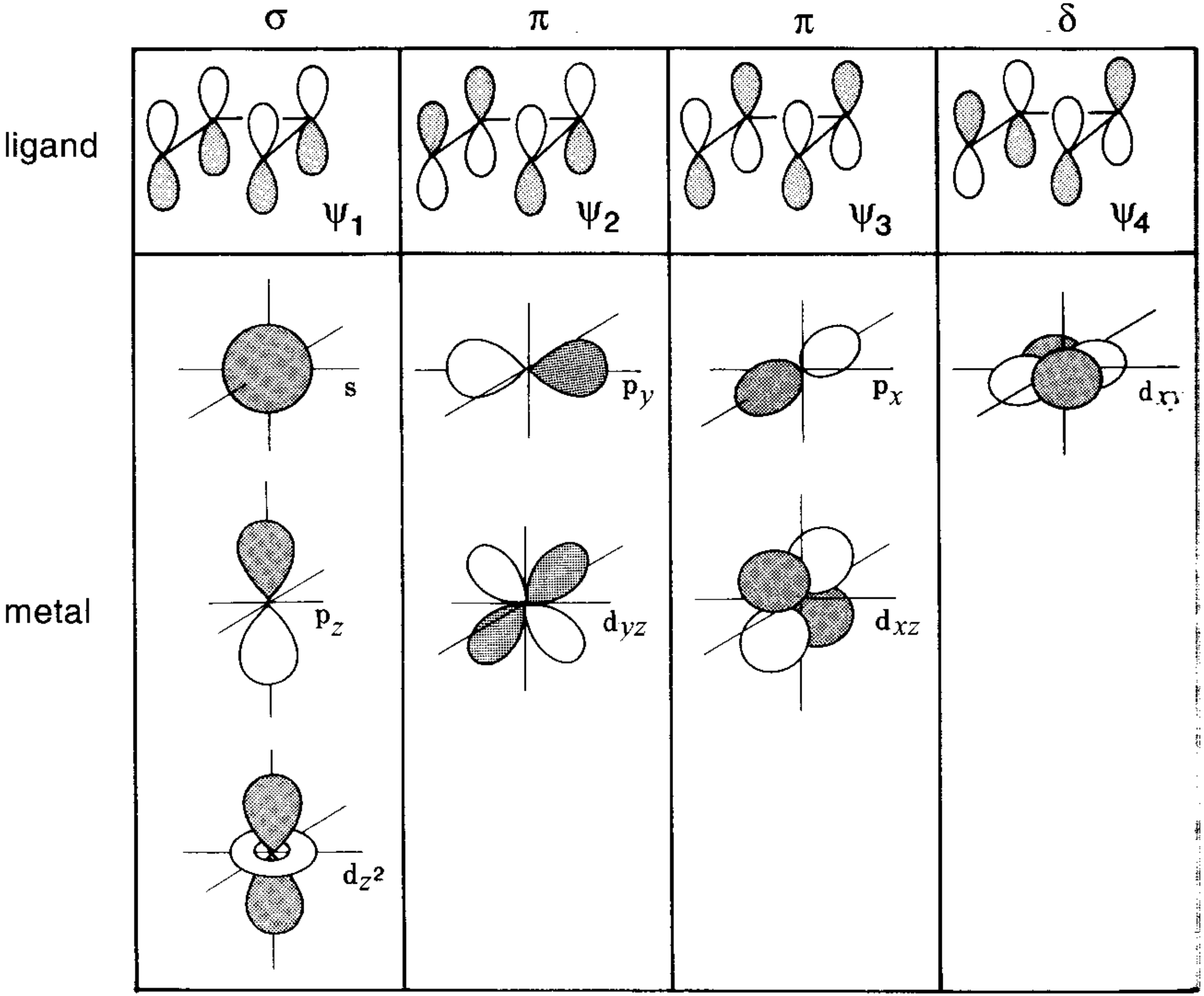


Insertions in the allyl M-C bond

Allyls can be considered as «stabilized alkyls». As such, they react inserting olefins, CO etc. in the M-C bond, giving rise to interesting reactions, particularly intramolecular ones.

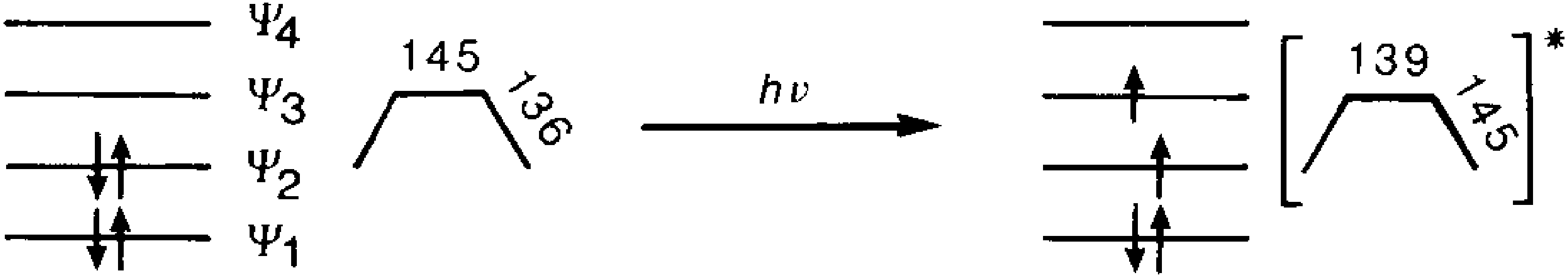


Metal-diene complexes



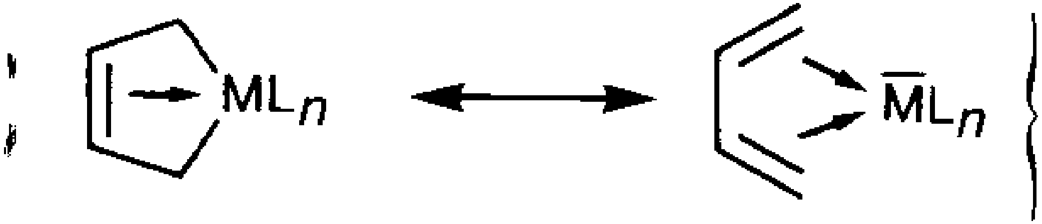
Diene o or metallacyclopentene?

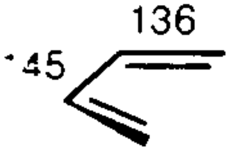
The donor-acceptor synergism reduces the electron density on the HOMO $\psi 2$, (a bonding orbital for the terminal C=C bonds) and populates the LUMO $\psi 3$, (a bonding orbital for the central C-C bond). The net result is a shortening (increased double bond character) of the central bond and a lengthening (increased single bond character) of the terminal bonds. In practice, a transition from diene to metallacyclopentene takes place…..

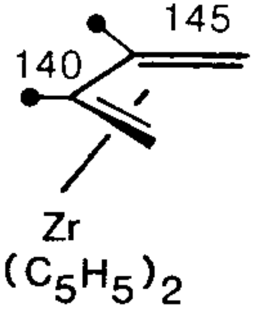


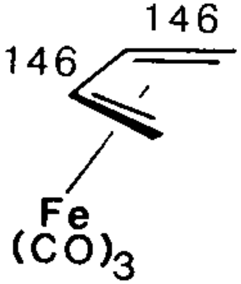
Diene o or metallacyclopentene?

The higher or lower appropriateness of either limiting formula is correlated as usual to the back-donating capacity of the metal. The higher the back-donation, the higher the weight of the metallacyclopentane form.





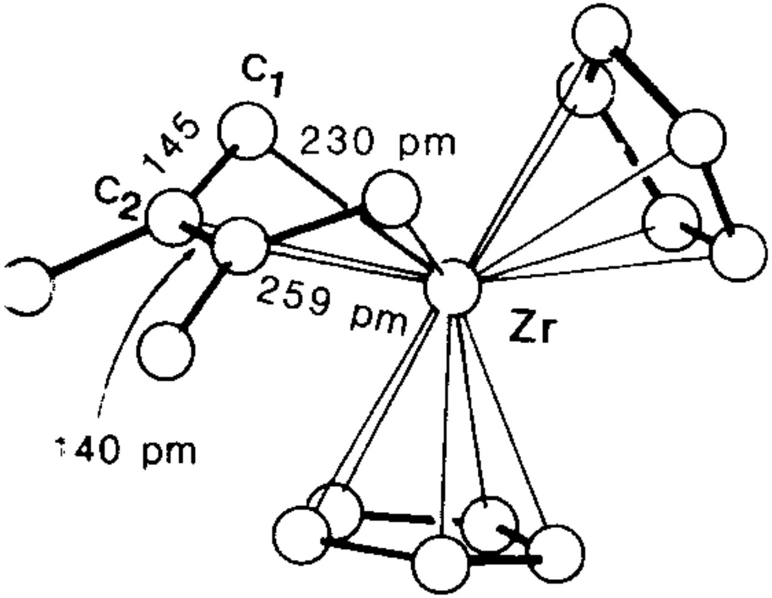


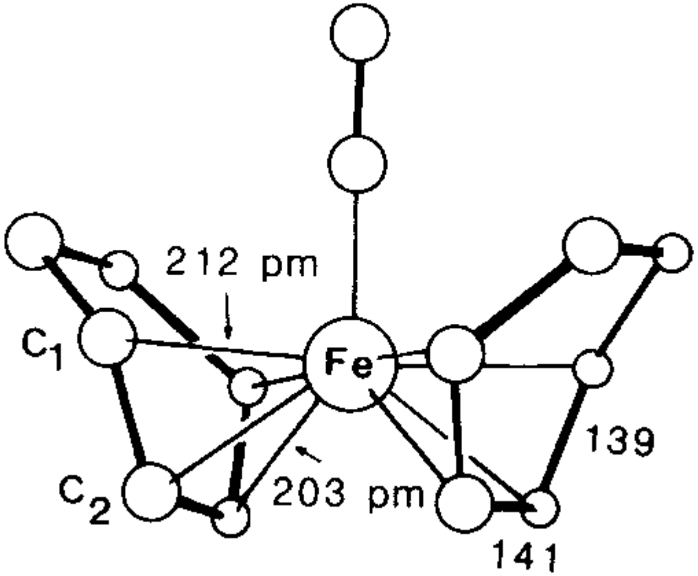


Metal-diene complexes

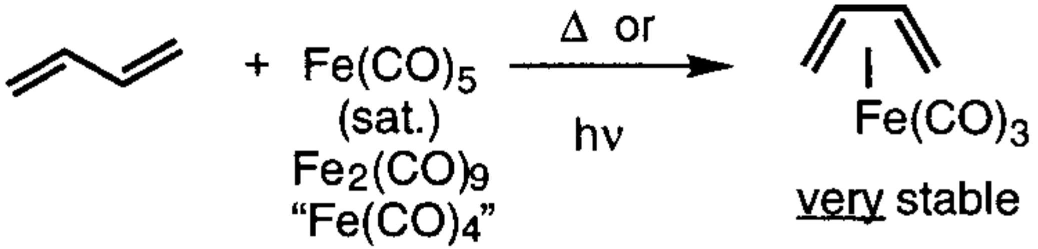
“metallacyclopentene”
(η^4-dimethylbutadiene)ZrCp$_2$
M–C$_1$ (terminal) = short
M–C$_2$ (internal) = long

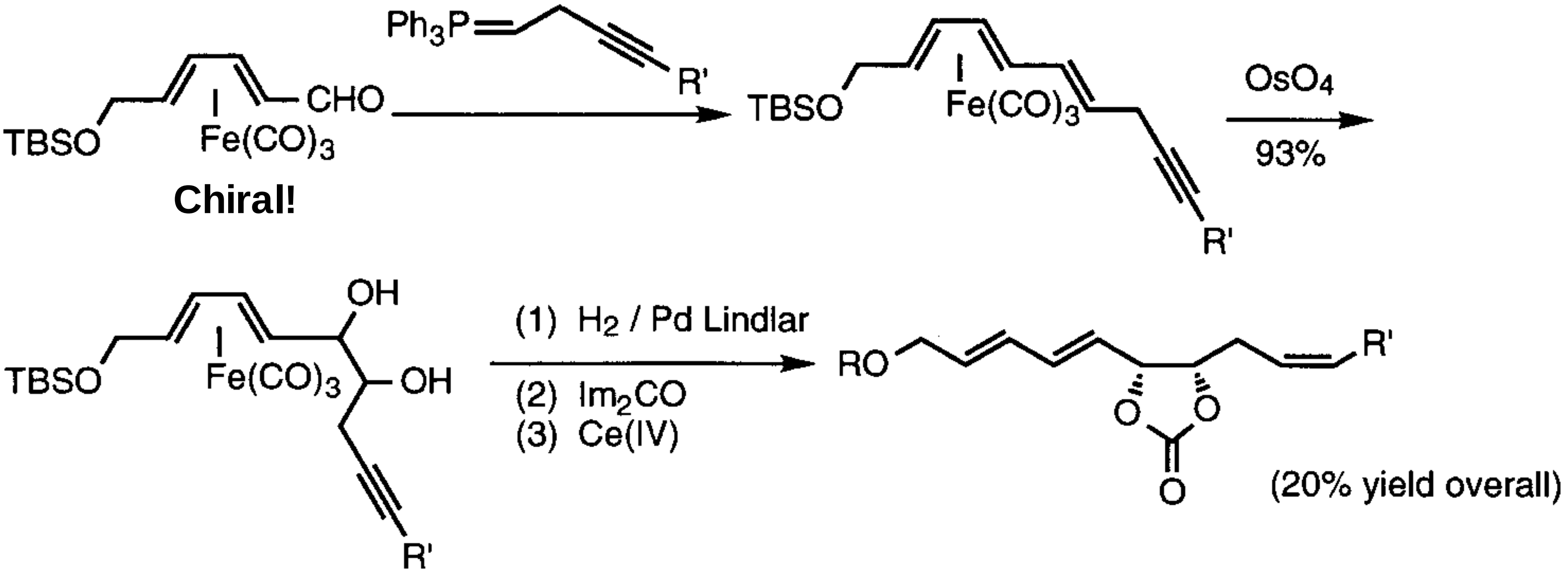
“π-complex”
(η^4-cyclohexadiene)$_2$Fe(CO)
M–C$_1$ (terminal) = long
M–C$_2$ (internal) = short





Metal-diene complexes as protective groups

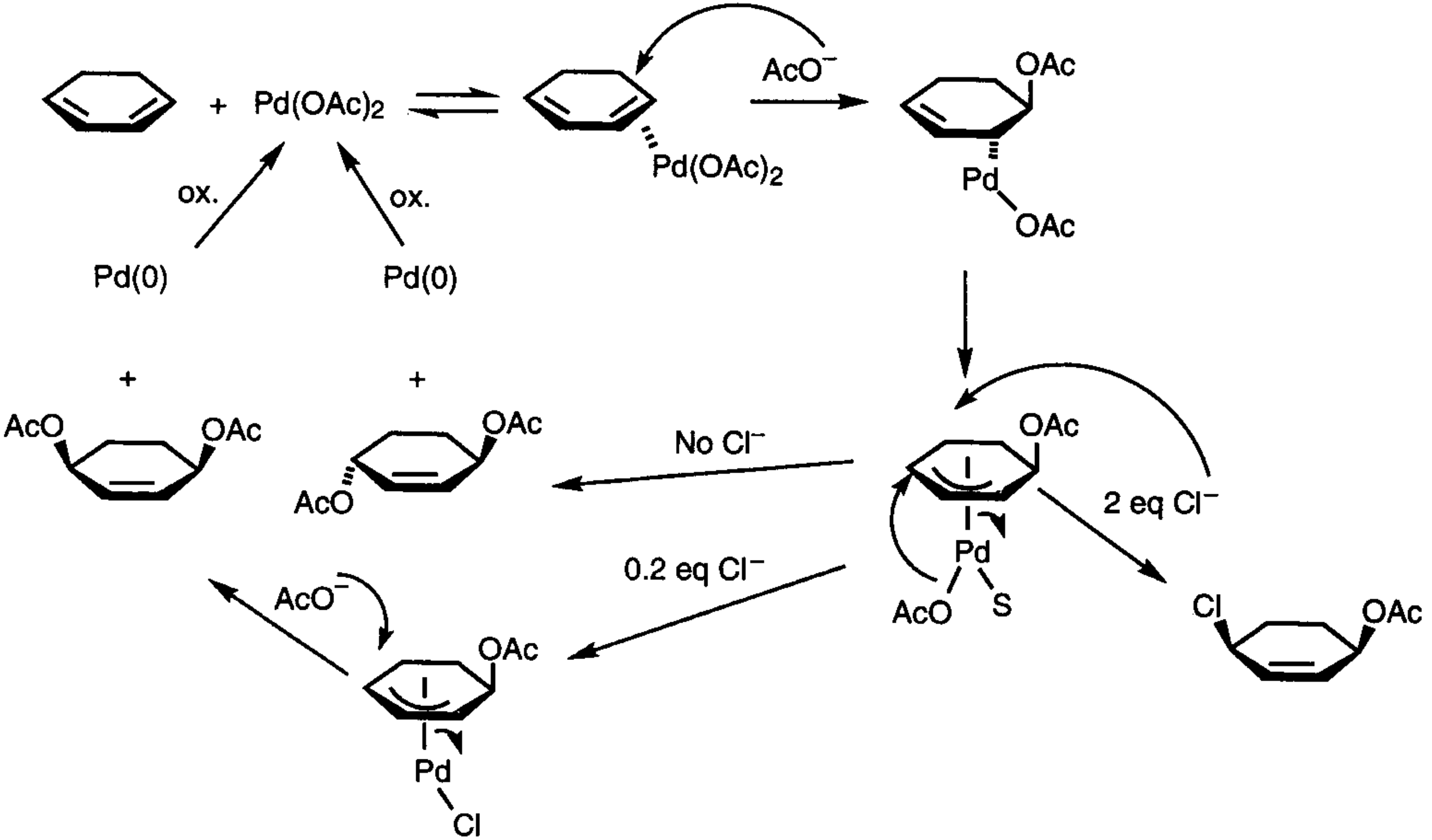




Chiral!

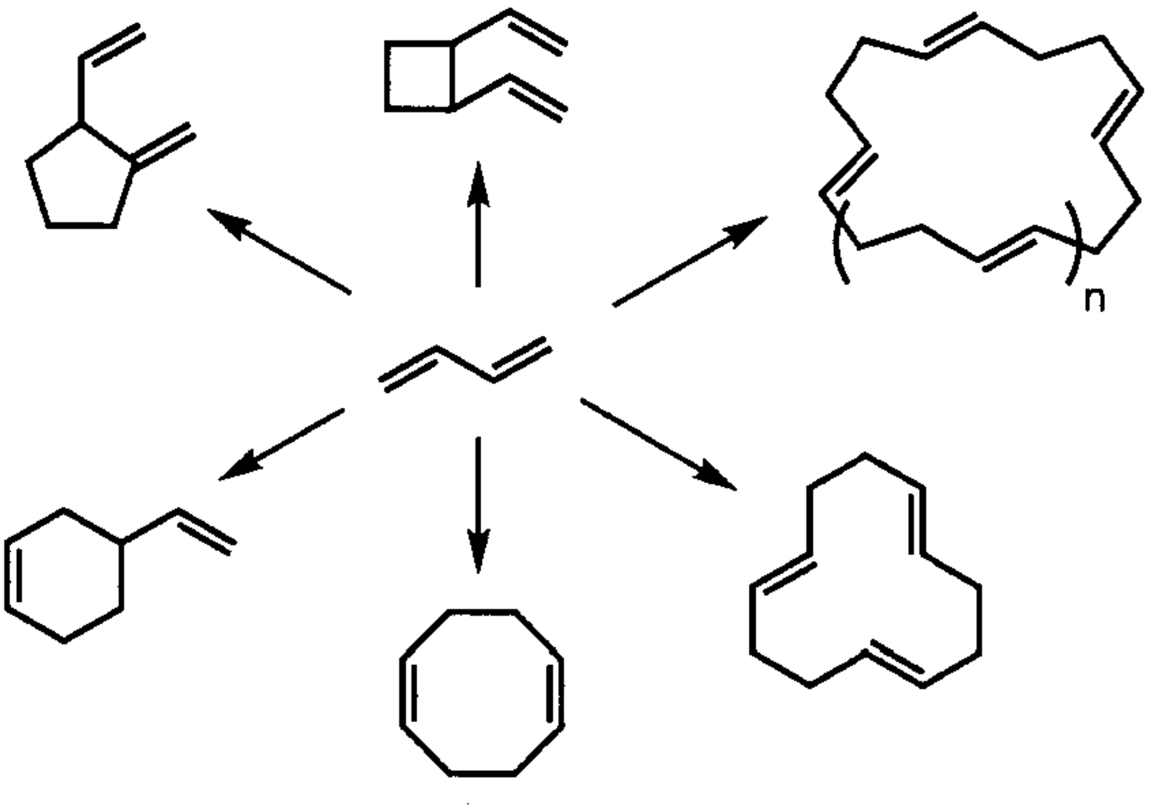
Nucleophilic attack to coordinated dienes

The reaction produces a coordinated allyl, which can undergo further additional nucleophilic attack, external or via preccordination to the metal centre.

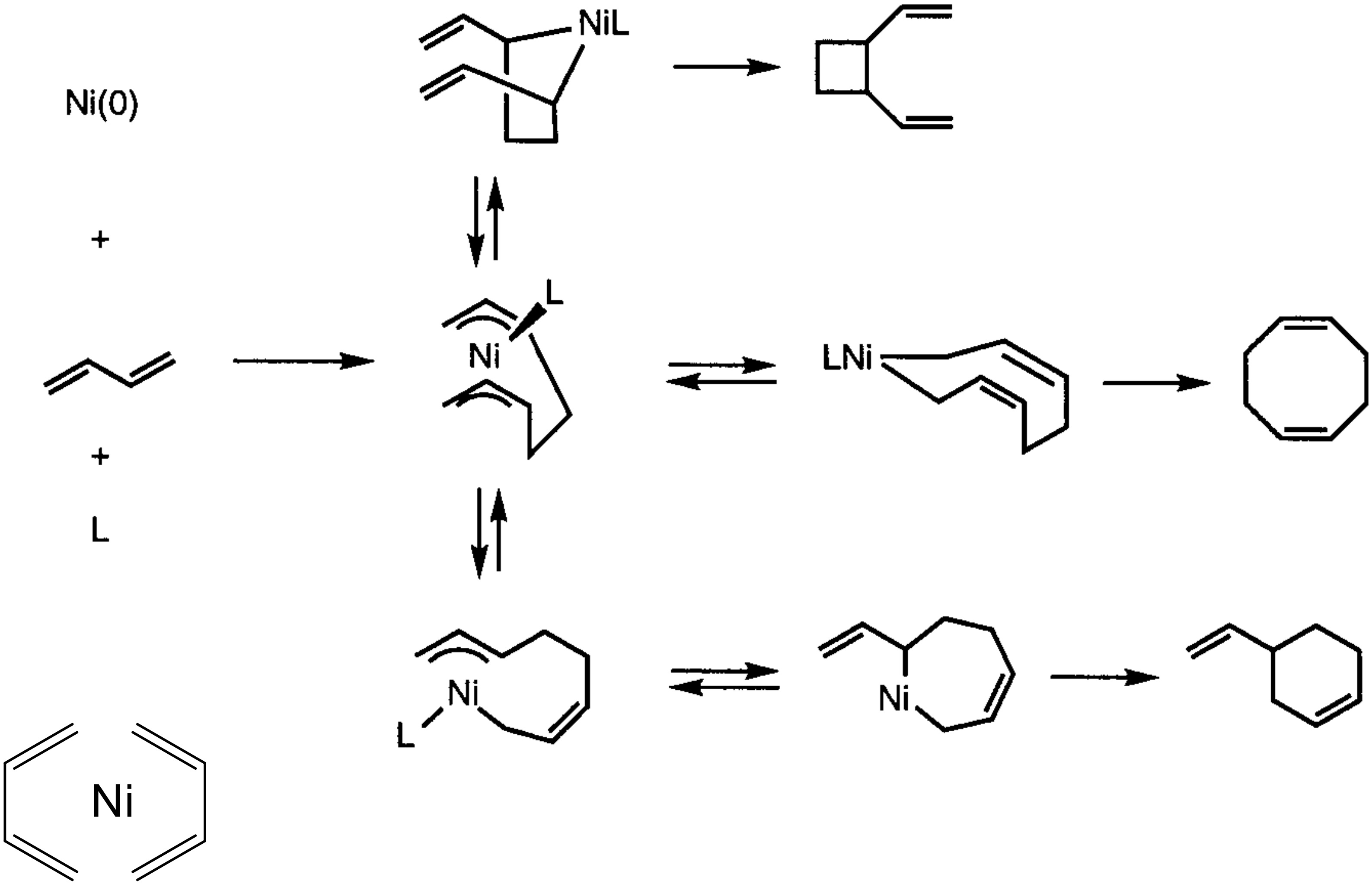


Butadiene cyclooligomerization

Reaction promoted by Ni(0). The chemoselectivity of the reaction can be controlled by adding suitable ligands for Ni.

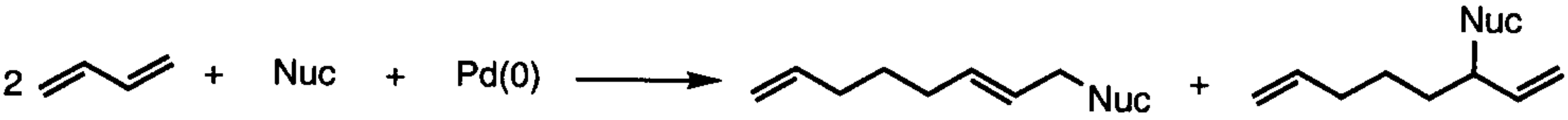


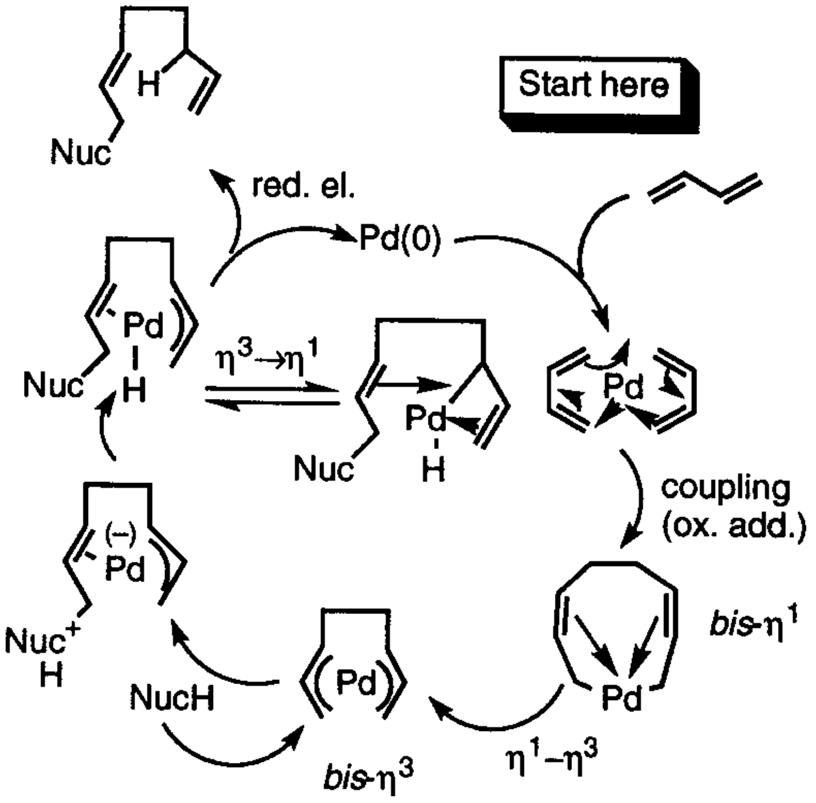
Butadiene cyclooligomerization



Butadiene “telomerization”

Telomer: product of oligomerization + addition of HNu

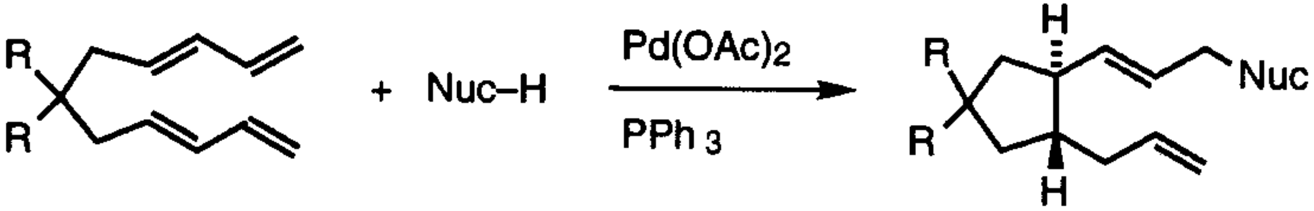




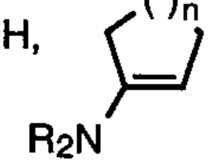
NucH = AcOH, H_2O, ROH, RNH_2,  where X, Y = CO_2Et, CN, NO_2, COR

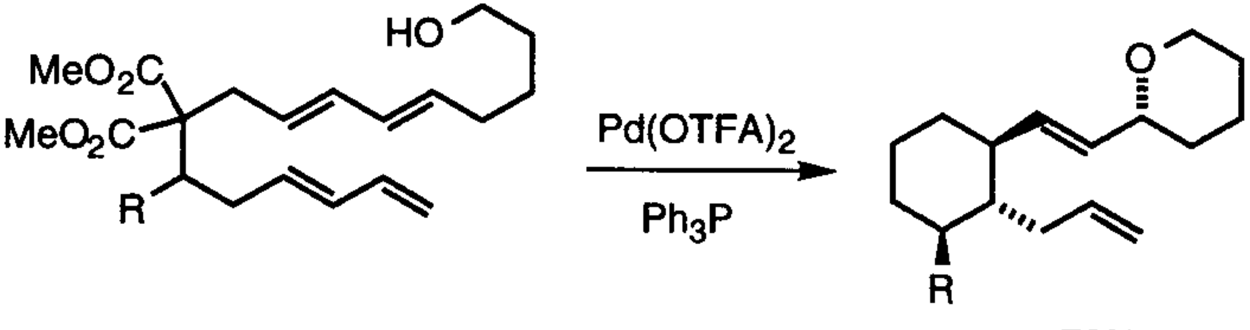
Intramolecular "telomerization"

Telomer: product of oligomerization + addition of HNu



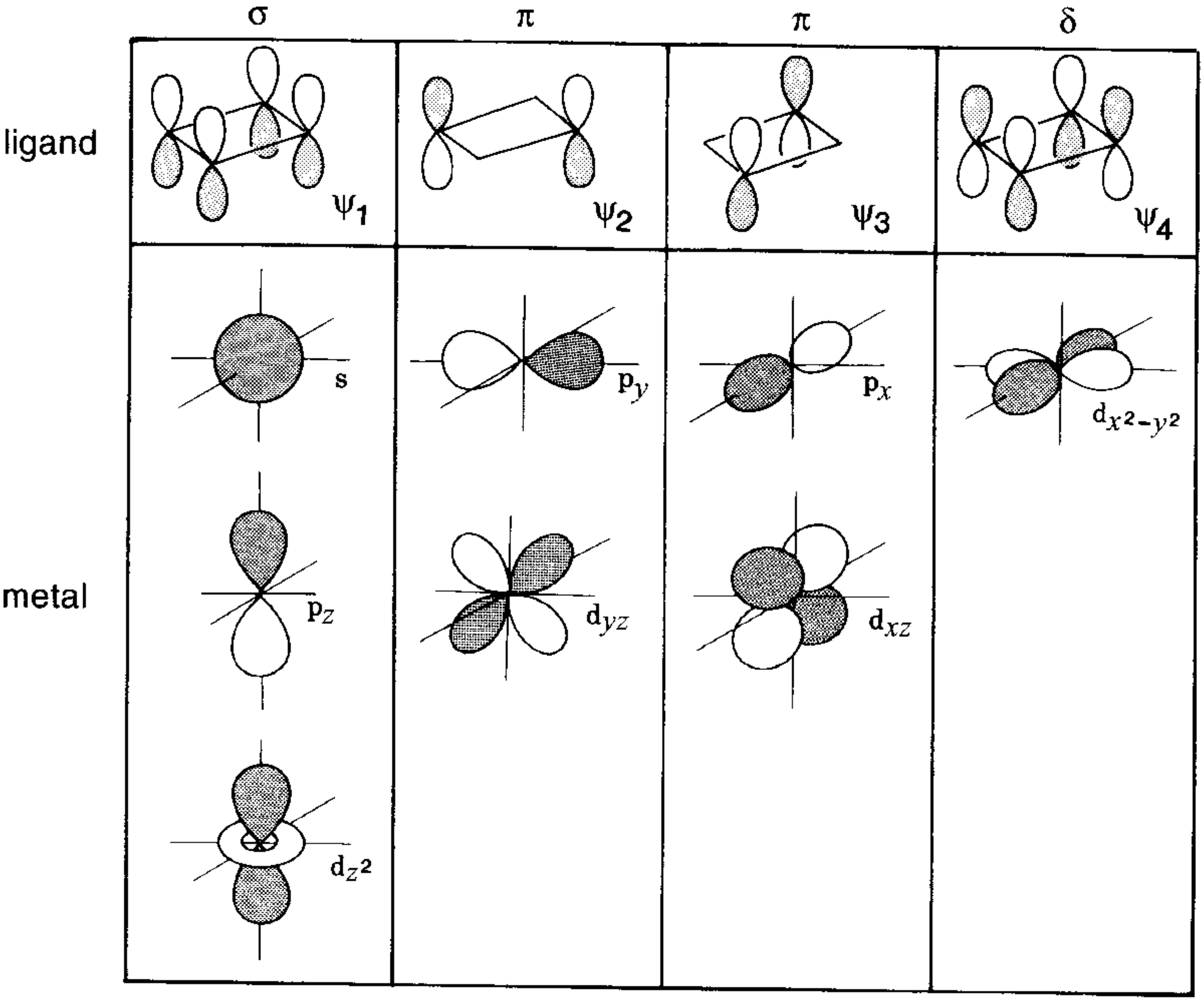
NucH = $PhCH_2OH$, PhOH, Et_2NH, *p* TsOH, CH_3NO_2, $CH_2(CO_2Et)_2$, R_3SiH,



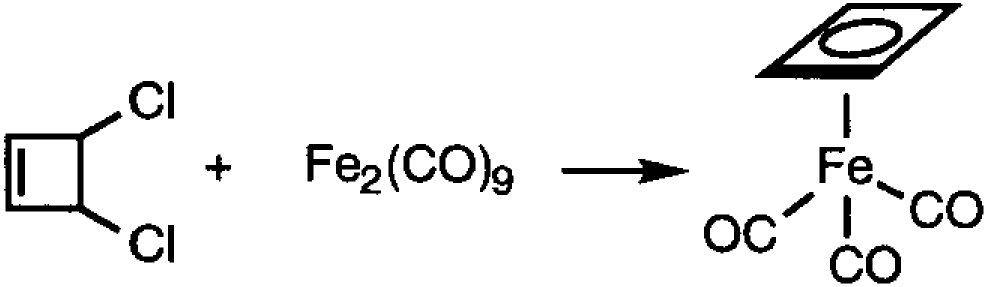


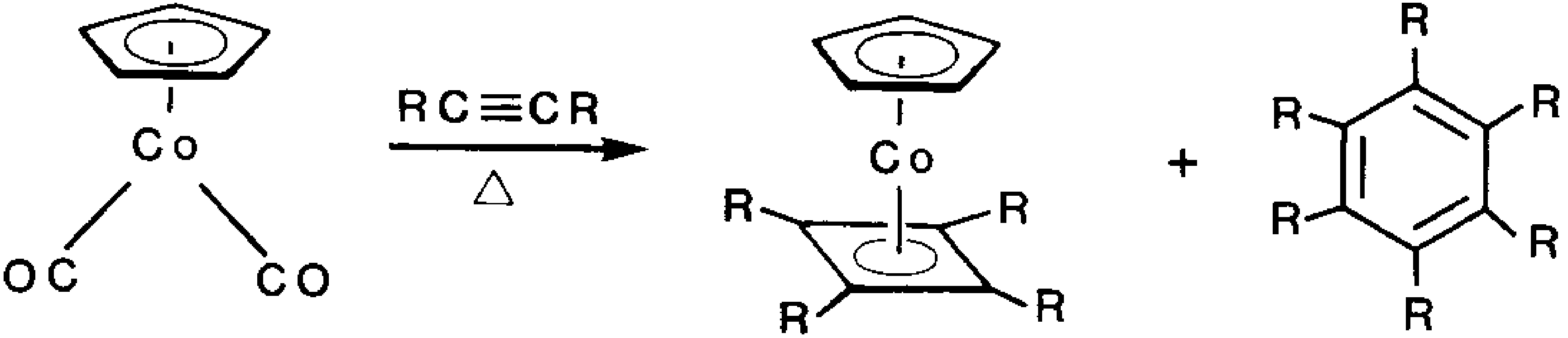
73%

Cyclobutadiene metal complexes



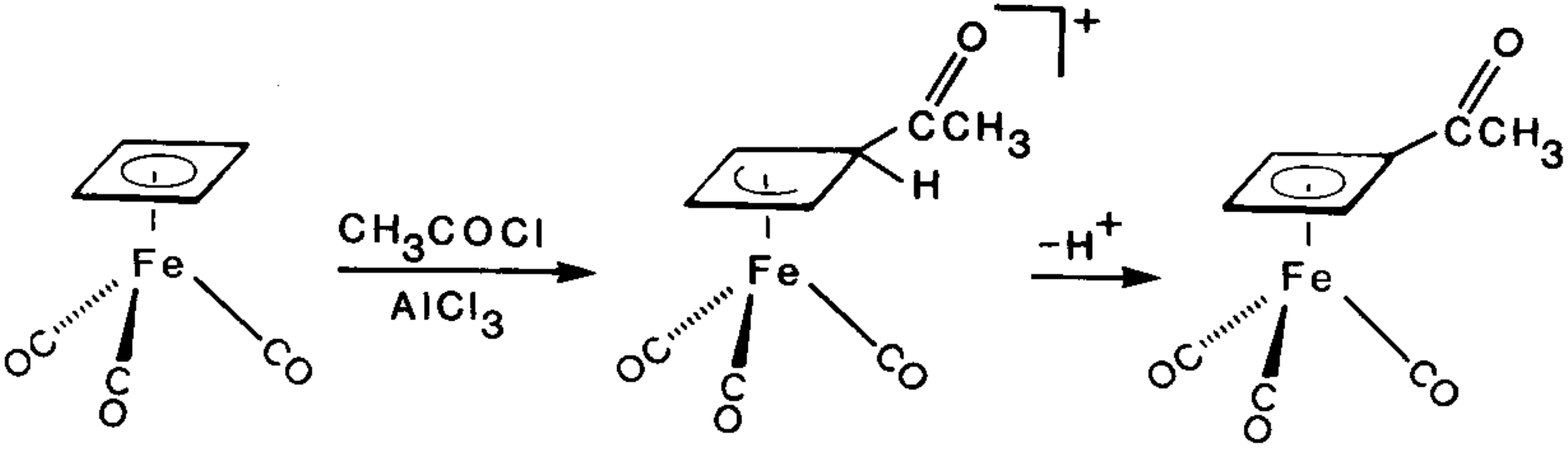
Cyclobutadiene metal complexes: preparation



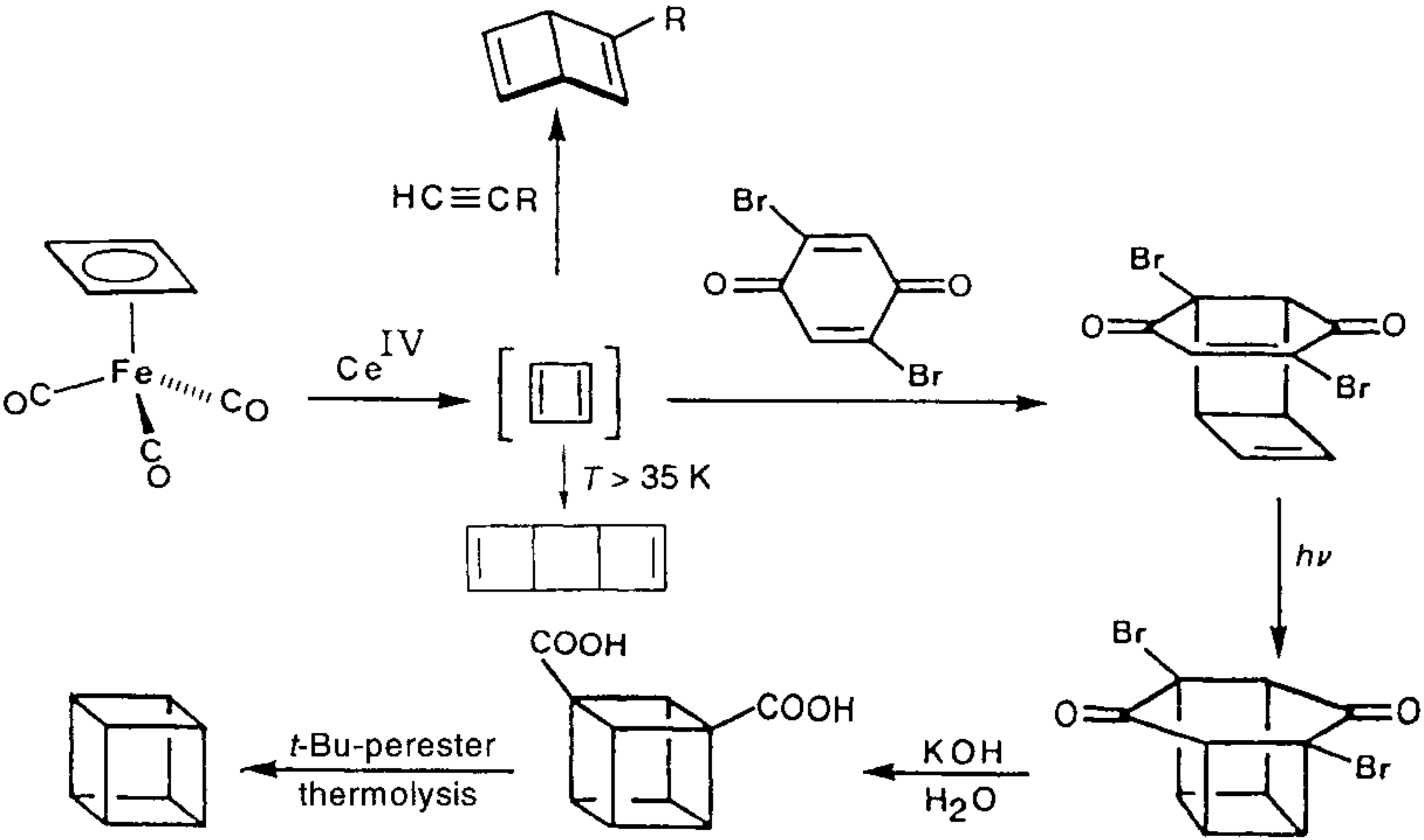


Cyclobutadiene metal complexes

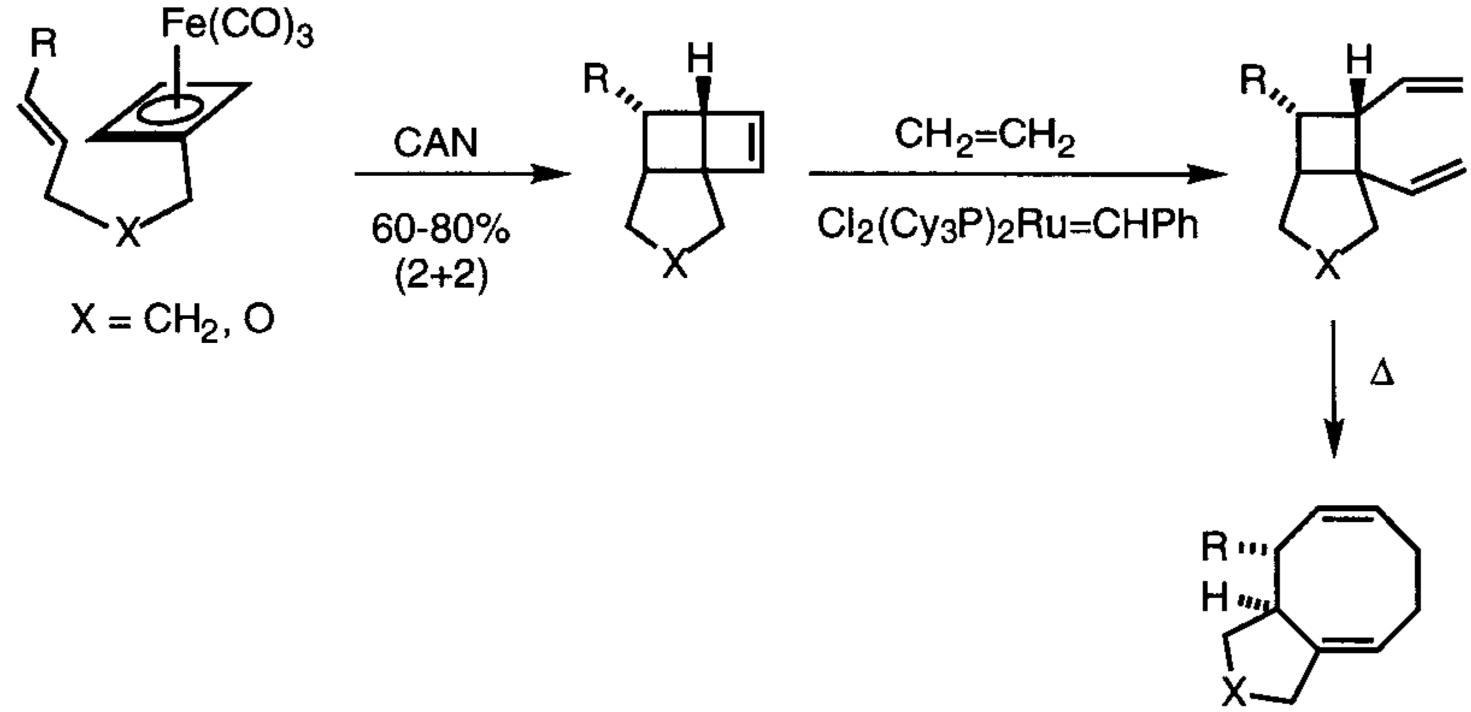
Cyclobutadiene features free low energy orbitals, and electron donation for the metal stabilizes the ligand (increase in aromatic character). Consequently, coordinated cyclobutadiene will be electron-rich and will typically react with electrophiles, in a manner analog to a «normal» aromatic compound.



Cyclobutadiene metal complexes

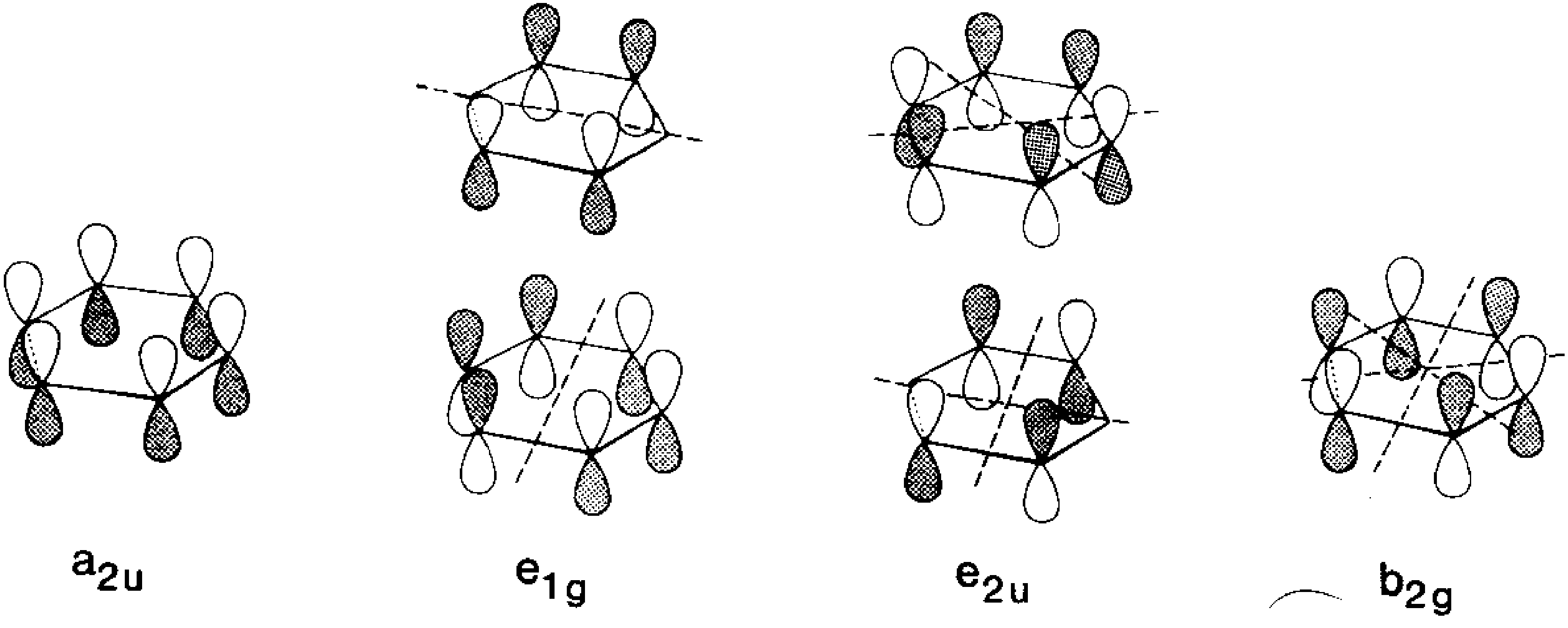


Cyclobutadiene metal complexes



Metal-arene complexes

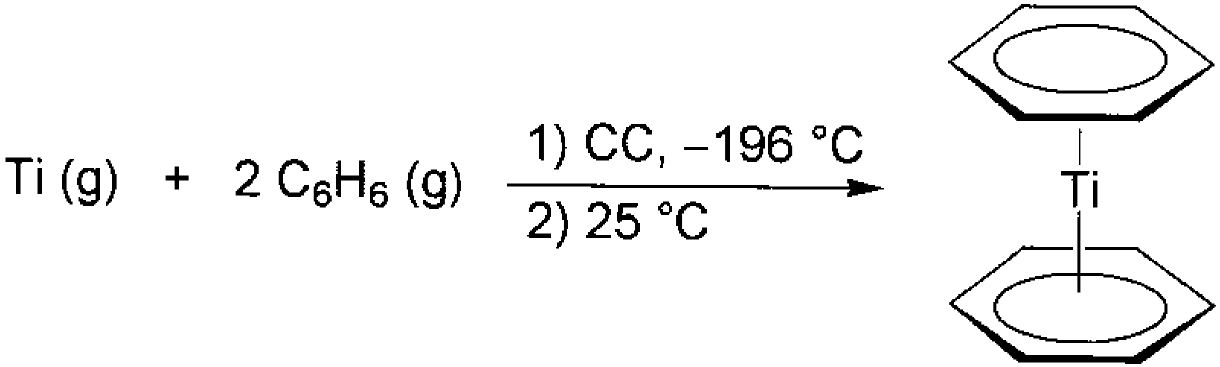
Common ligands in organometallic chemistry, often employed as supporting ligands; however, complexes with **electron-withdrawing metal centres** and with **electron-neutral or electron-rich arenes** have been extensively studied as stoichiometric reagents, given their peculiar reactivity.



Metal-arene complexes: synthesis

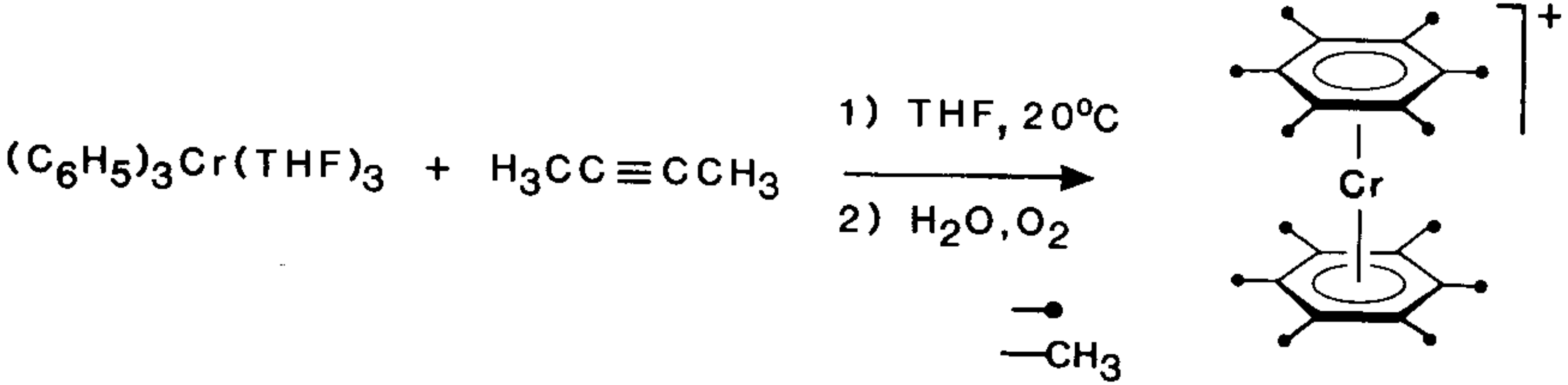
Metal-arene complexes can be prepared upon addition/substitution reactions like those employed for the preparation of complexes with other unsaturated molecules as ligands (alkenes, alkynes). Since however an η^6 coordinated arenes occupies three coordination sites, such reactions can be problematic, especially if the preparation of homoleptic complexes is envisaged. The latter can be prepared through alternative methods:

- metal-ligand cocondensation:



Metal-arene complexes: synthesis

- Alkyne cyclotrimerization:



- Reduction of metal salts (Fischer – Hafner):

$$\begin{tikzcd}
3\,\mathrm{CrCl_3} + 2\,\mathrm{Al} + 6\,\mathrm{arene} \arrow[r, "1.\ \mathrm{AlCl_3}", "2.\ \mathrm{H_2O}"'] & 3\,[(\mathrm{arene})_2\mathrm{Cr}]^+ + 2\,\mathrm{Al^{III}} \arrow[d, "\mathrm{Na_2S_2O_4}\ \mathrm{KOH}"] \\
& (\eta^6\text{-arene})_2\mathrm{Cr}
\end{tikzcd}$$

Scope:

V	Cr	–	Fe	Co	Ni
–	Mo	Tc	Ru	Rh	–
–	W	Re	Os	Ir	–

Metal-arene complexes: synthesis

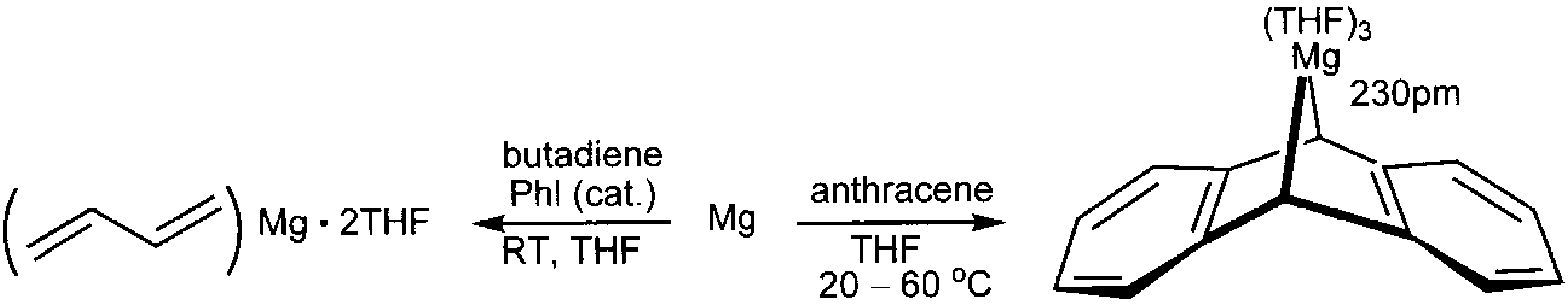
- “reductive complexation”: reaction of metal salts or complexes with arenes prereduced upon reaction with group 1 or group 2 metals:

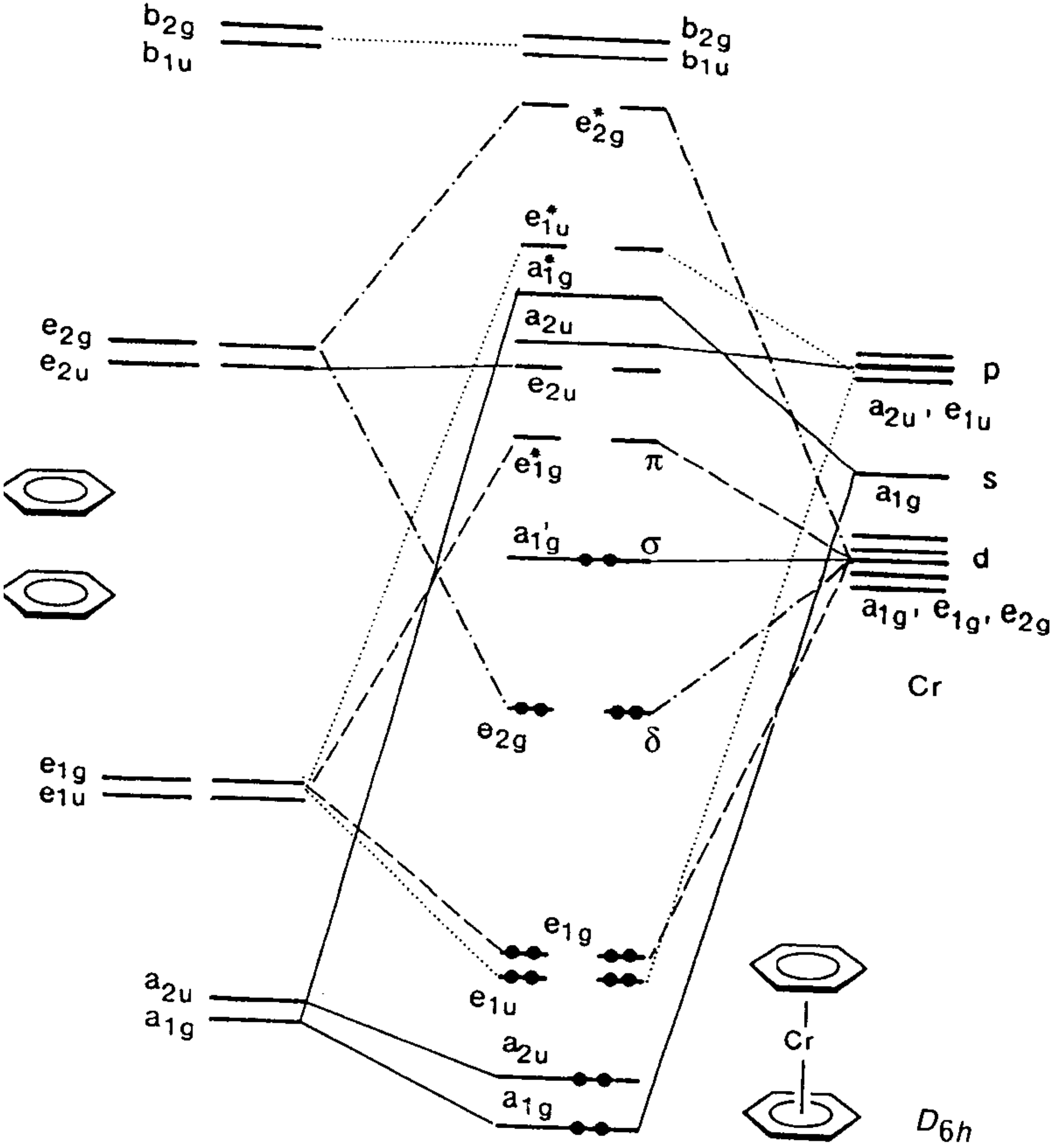
$$\mathrm{MCl}_n(\mathrm{THF})_{6-n} + n\,\mathrm{LiC}_{10}\mathrm{H}_8 \longrightarrow (\eta^6\text{-}\mathrm{C}_{10}\mathrm{H}_8)_2\mathrm{M} + n\,\mathrm{LiCl}$$

$\mathrm{C}_{10}\mathrm{H}_8$ = napththalene

$\mathrm{M} = \mathrm{Cr}, \mathrm{Mo} \quad n = 3$

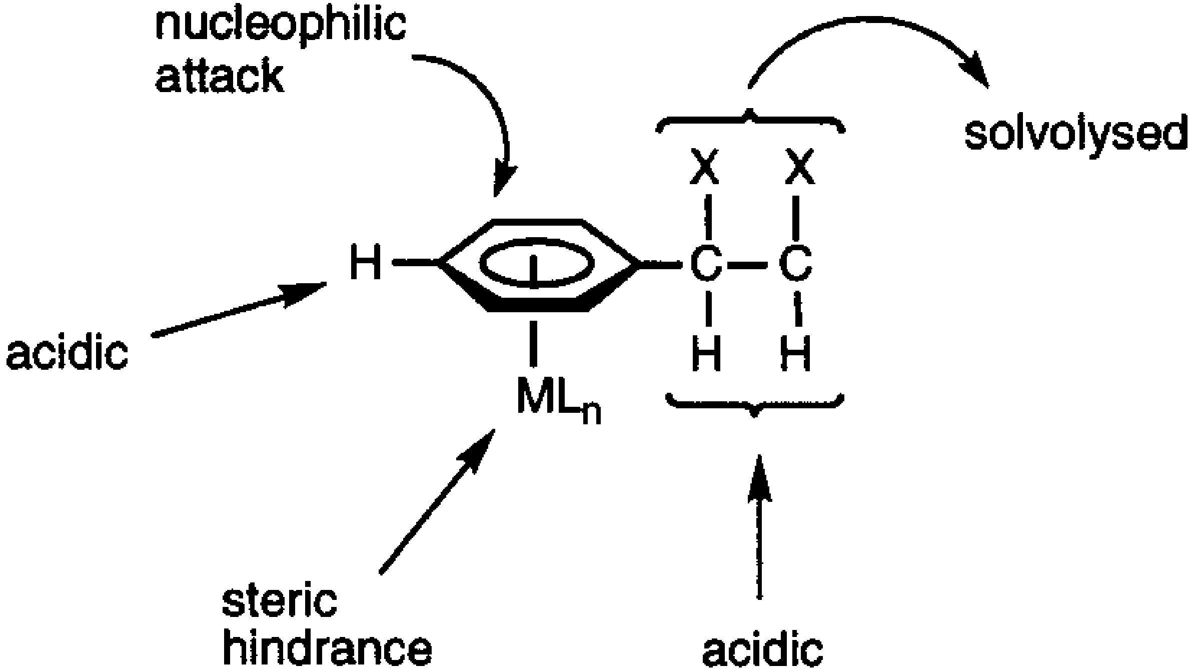
$\mathrm{M} = \mathrm{V} \quad n = 4$



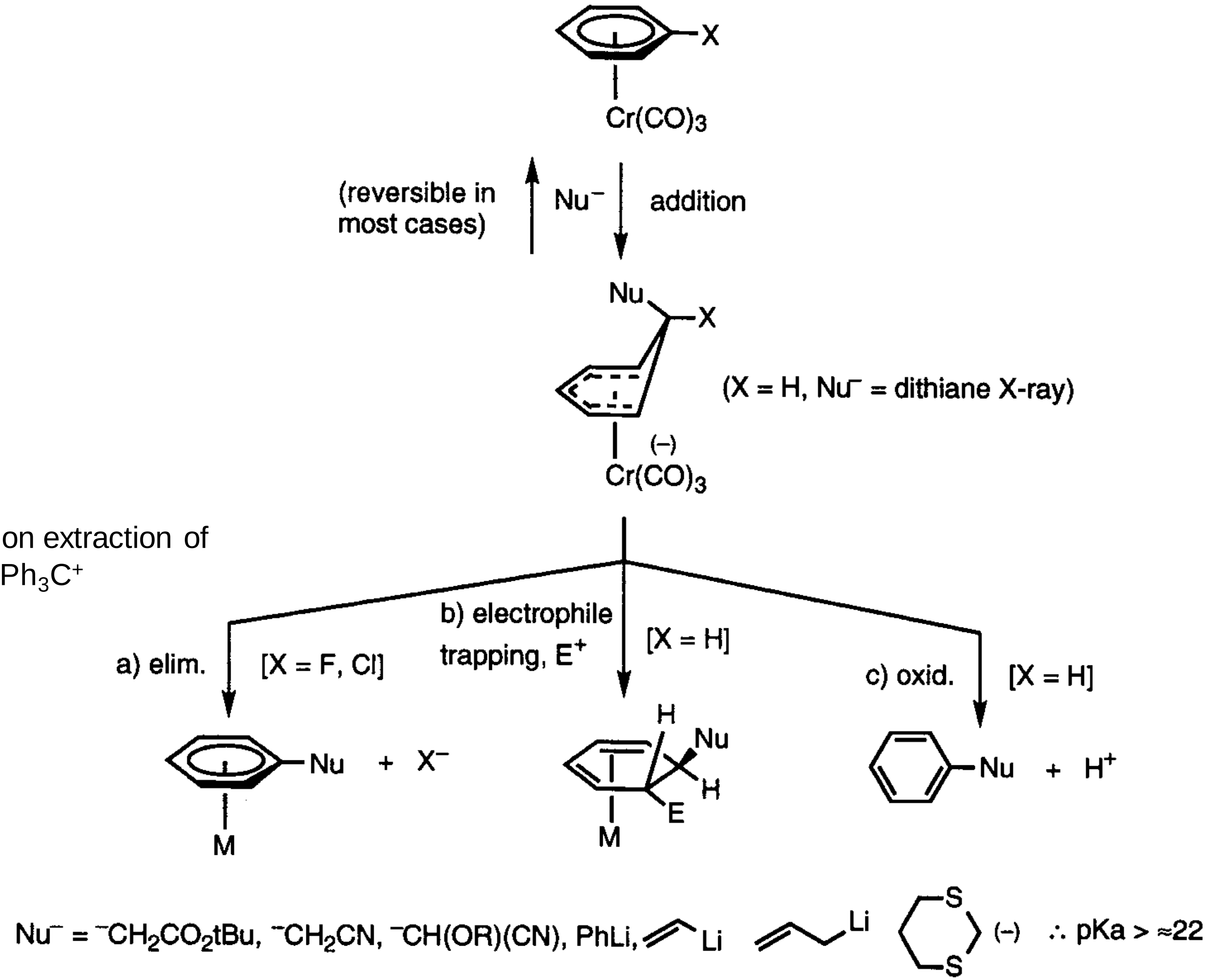

b2g
b1u
b2g
b1u
e*2g
e*1u
a*1g
a2u
e2g
e2u
e2u
p
a2u , e1u
e*1g
π
s
a1g
a′1g
σ
d
a1g , e1g , e2g
Cr
e2g
δ
e1g
e1u
e1g
e1u
a2u
a1g
a2u
a1g
Cr
D6h

Reactivity of coordinated arenes

The reactivity of an arene η^6 coordinated to an electron-withdrawing metal centre (es. $Co(CO)_3$) is comparable to that of nitrobenzene (similar loss of electron density); the reactivity with electrophiles is depressed whereas the one with nucleophiles is promoted. Furthermore, ring deprotonation is promoted, as well as chage buildup on the α o β carbons.

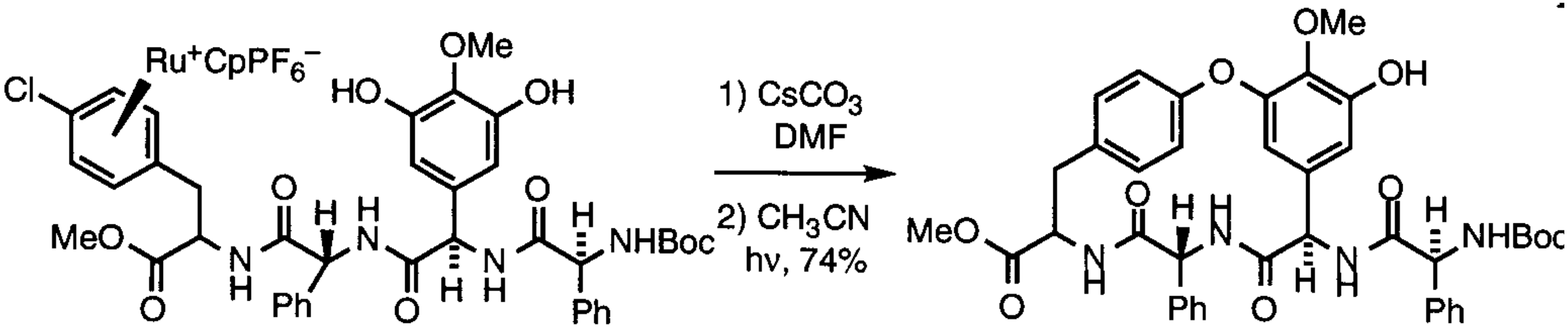


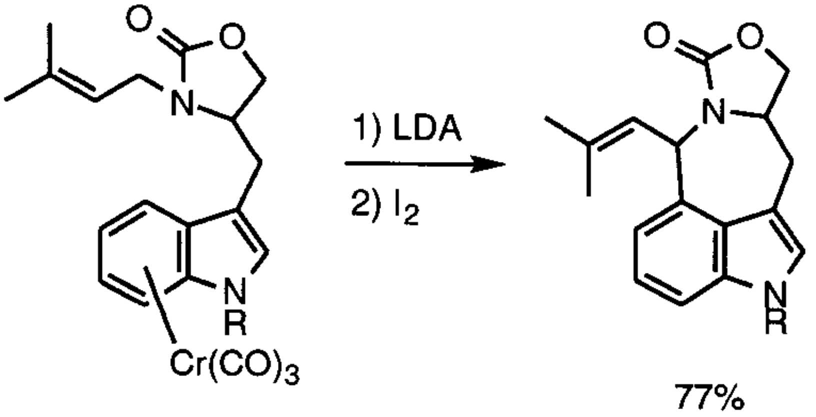
Reactivity of coordinated arenes

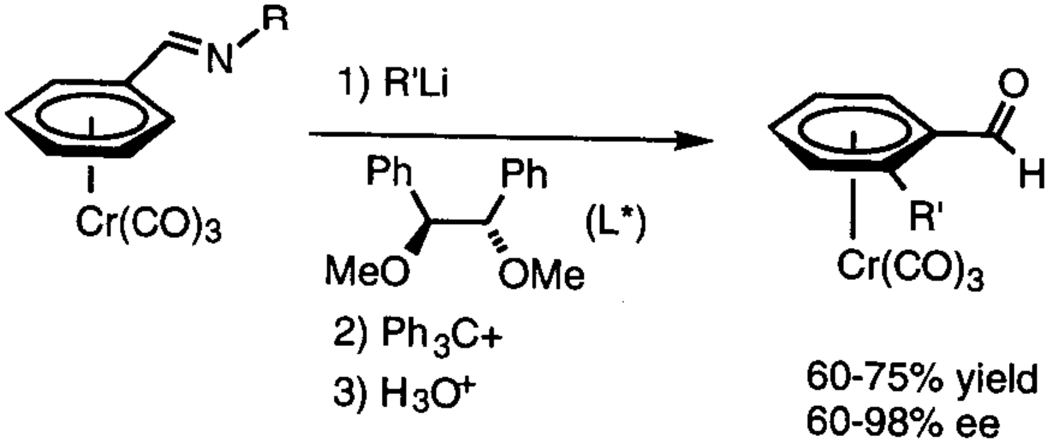


Also upon extraction of H^- with Ph_3C^+

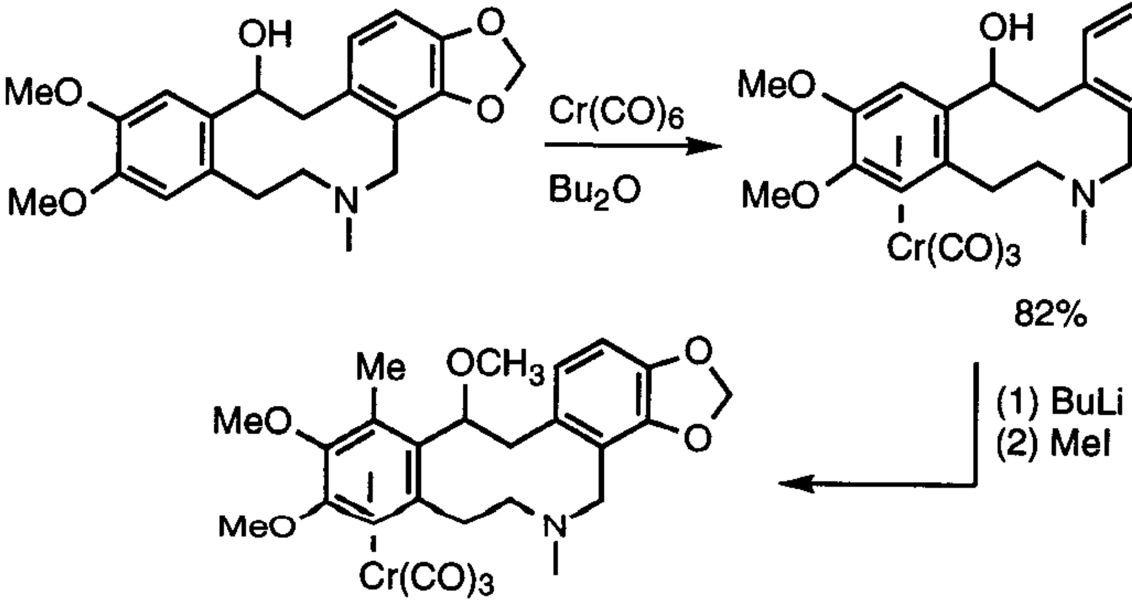
Reactivity of coordinated arenes



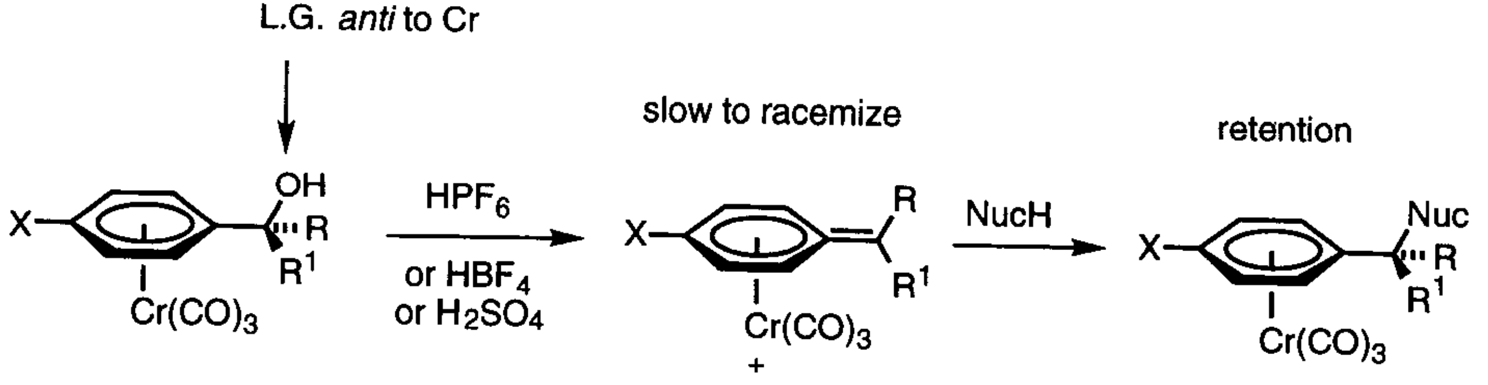




Reactivity of coordinated arenes



Eq. 10.36



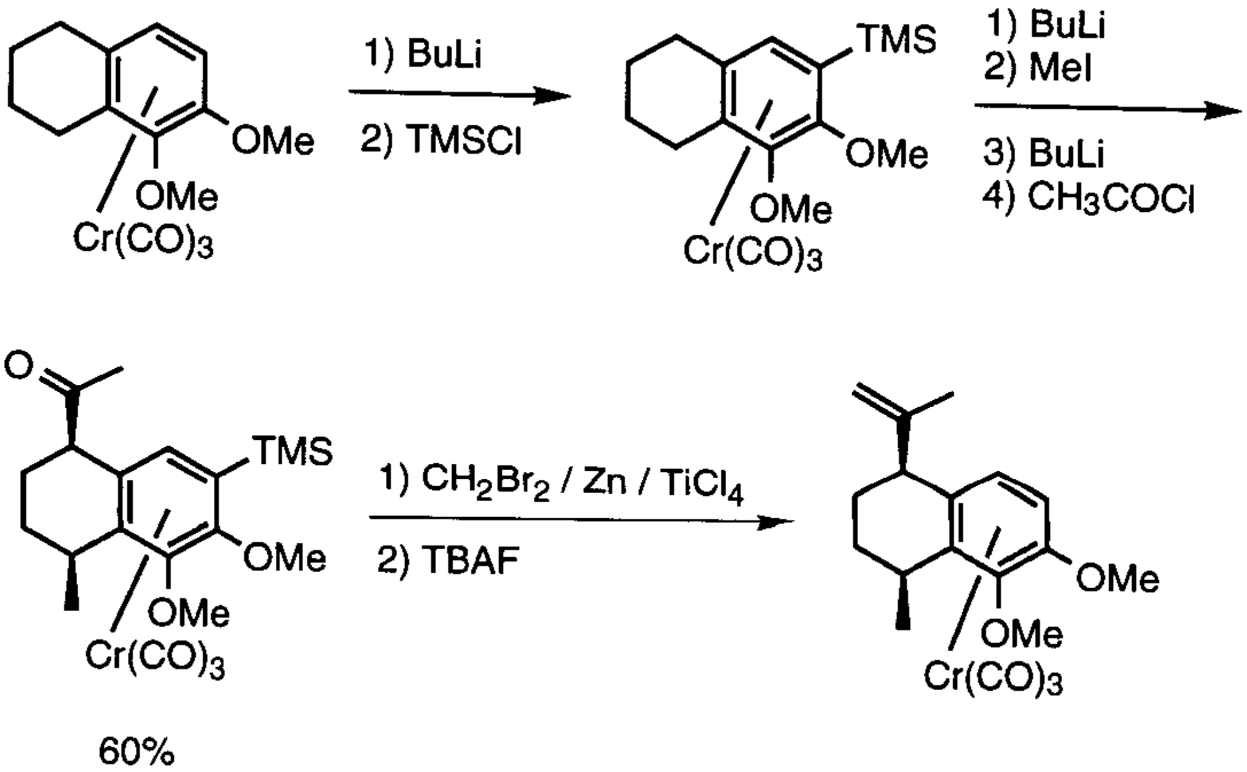
X = H, OMe

R = H, Me; R^1 = H, Me, Ph

23-92%

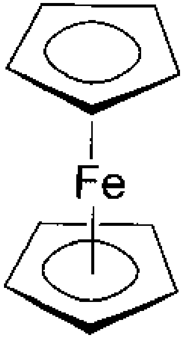
NucH = MeOH, EtOH, NH_3, $MeNH_2$, Me_2NH, EtSH, BuMgBr

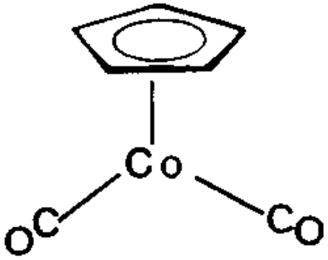
Reactivity of coordinated arenes

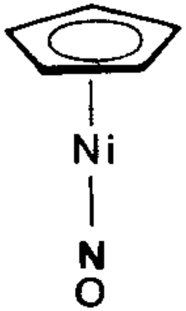


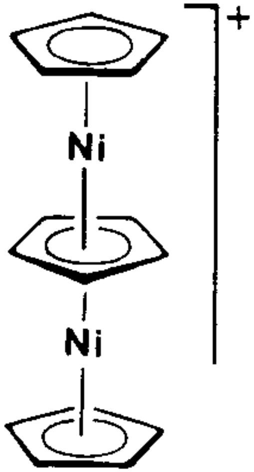
Metal-cyclopentadienyl (Cp) complexes

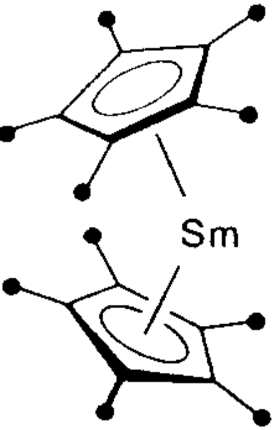
Great variety of compounds. Homoleptic complexes are often unstable to air (exception: ferrocene); heteroleptic complexes are more stable. Cp is a common supporting ligand for complexes/catalysts of group 4-9 metals.

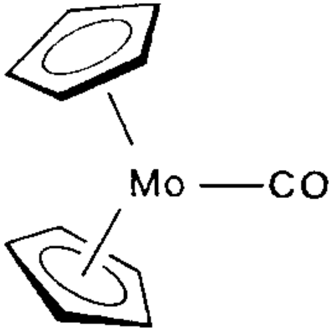


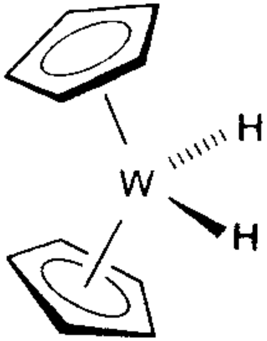












Metal-Cp complexes: synthesis

In contrast to other allyls and polyenyls, Cp is a carbanion stabilized by ring aromaticity. This increases its stability and greatly facilitates the syntyhesis of its metal complexes.

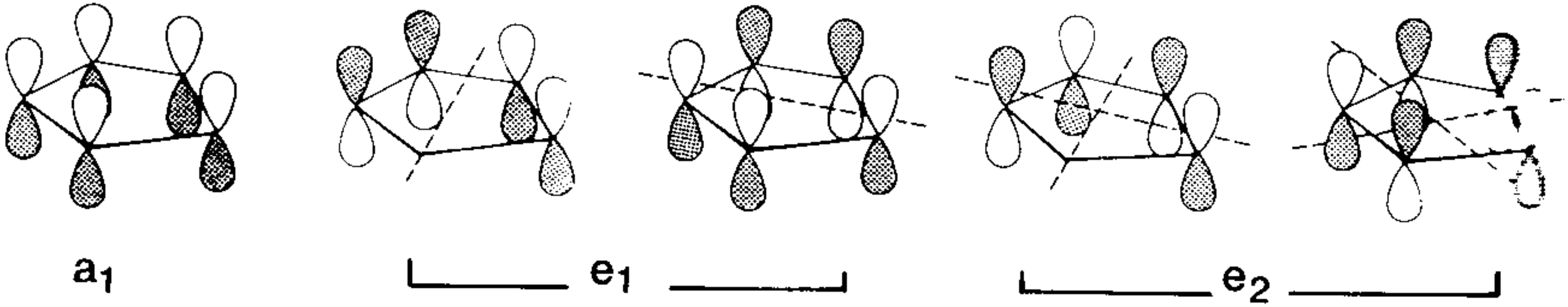
Monomeric cyclopentadiene is initially prepared upon cracking of commercial dicyclopentadiene (retro-Diels-Alder) and then deprotonated with a strong base forming the reagent MCp (M= Na, Tl); in the final steo, Cp is then transferred to the metal centre upon metathesis.

The process can also take place in «one pot», by mixing cyclopentadiene and a trtansition metal complex bearing a basic ligand, or upon deliberate addition of bases.

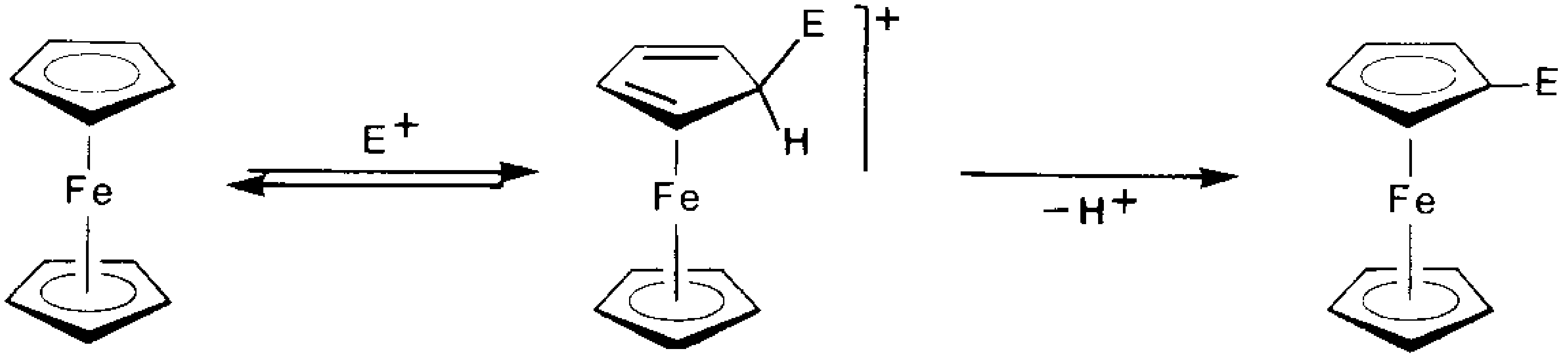
In a limited number of cases, it is possible to perform a «direct syntyhesis» upon mixing metal and cyclopentadiene:

$M + 2C_5H_6 \rightarrow M(C_5H_5)_2 + H_2$ at high temperature

Metal-Cp complexes: synthesis

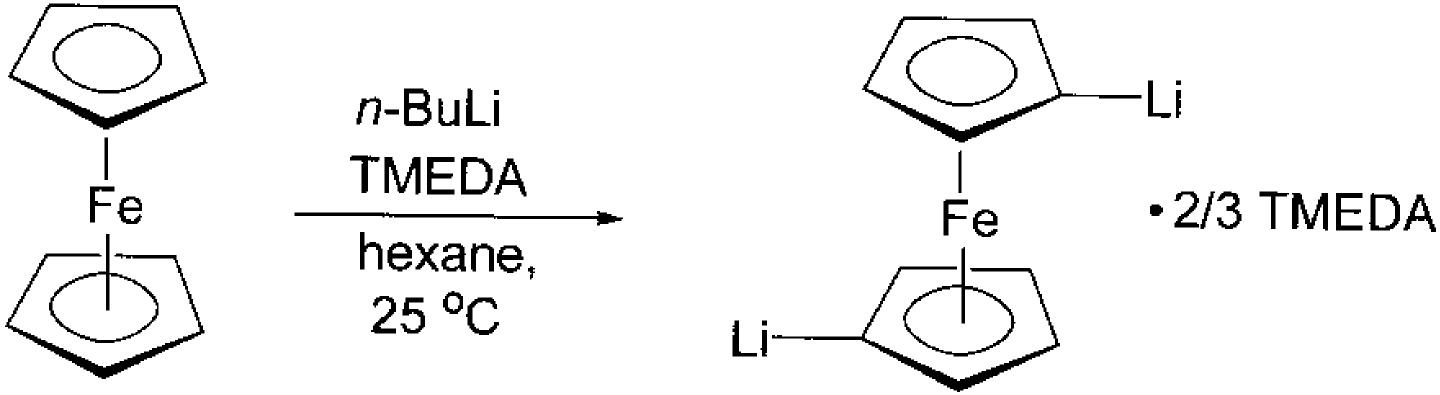


The anionic character and the closed structure render coordinated Cp less susceptible of nucleophilic attack. The coordinated ligand reacts with electrophiles instead, as it is common with aromatic compounds.

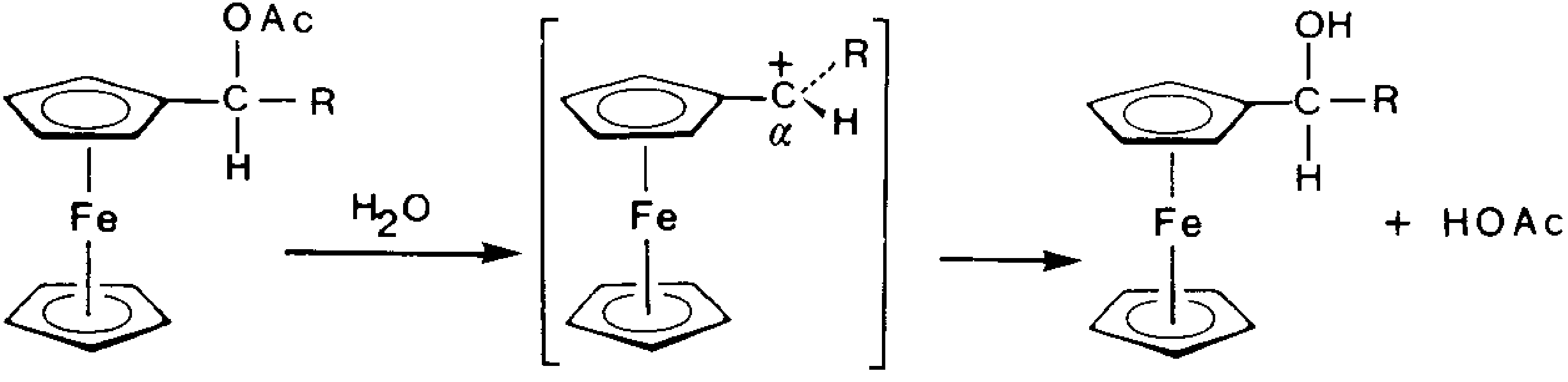


Metal-Cp complexes: reactions

- Deprotonation of a coordinated ligand:



- Stabilization of carbocations in position α to the ring:



Applications of metal-Cp complexes

Metal-Cp complexes find a myriad of applications:

-Cp as **supporting ligands** in catalytic processes (metallocenes etc.);

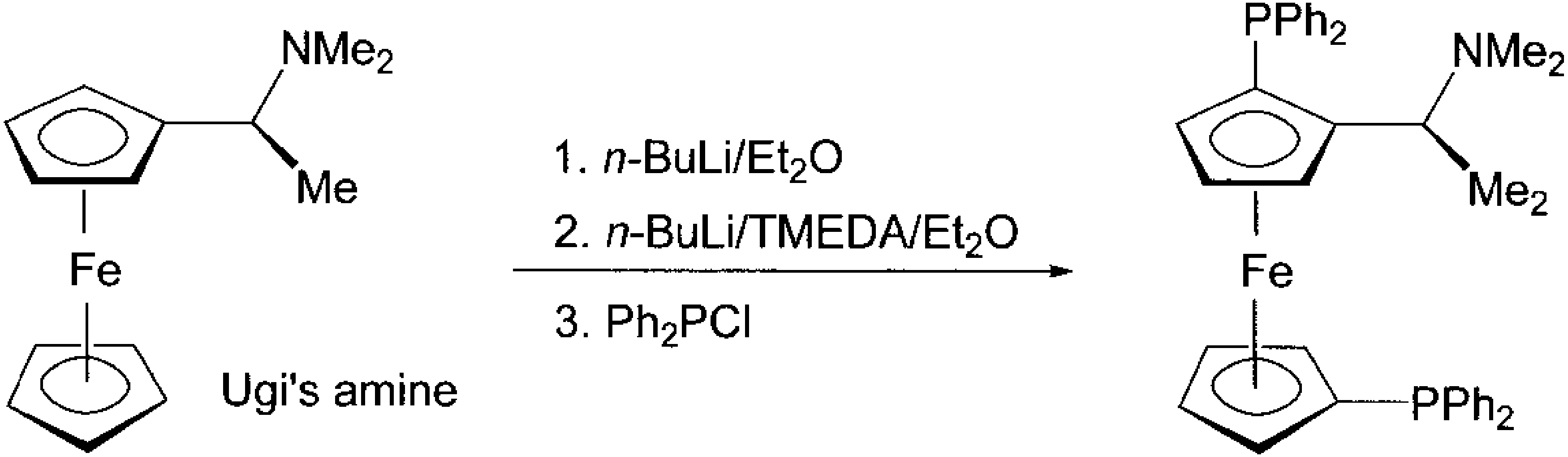
- Metal-Cp complexes (in particular ferrocene) as materials for **nonlinear optics (NLO)**;

- Metal-Cp complexes(Ru complexes) as **antitumor agents**;

- Use of ferrocene as standard/reagent in **electrochemical processes** (ferrocene/ferricinium couple);

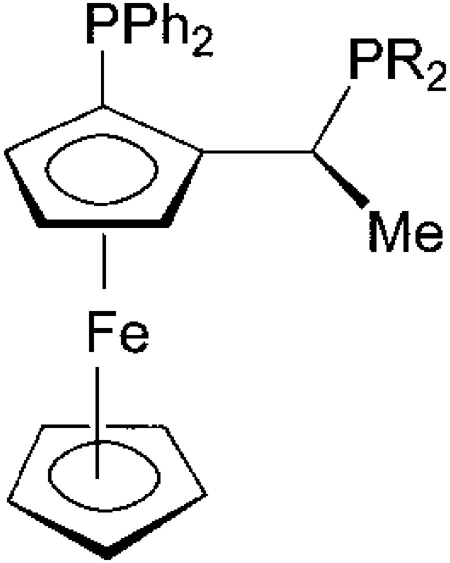
- Use of ferrocene as **ligand scaffold** (strongly electron-donating, <u>flexible</u>, <u>chiral</u>)

Chiral ligands based on M-Cp complexes



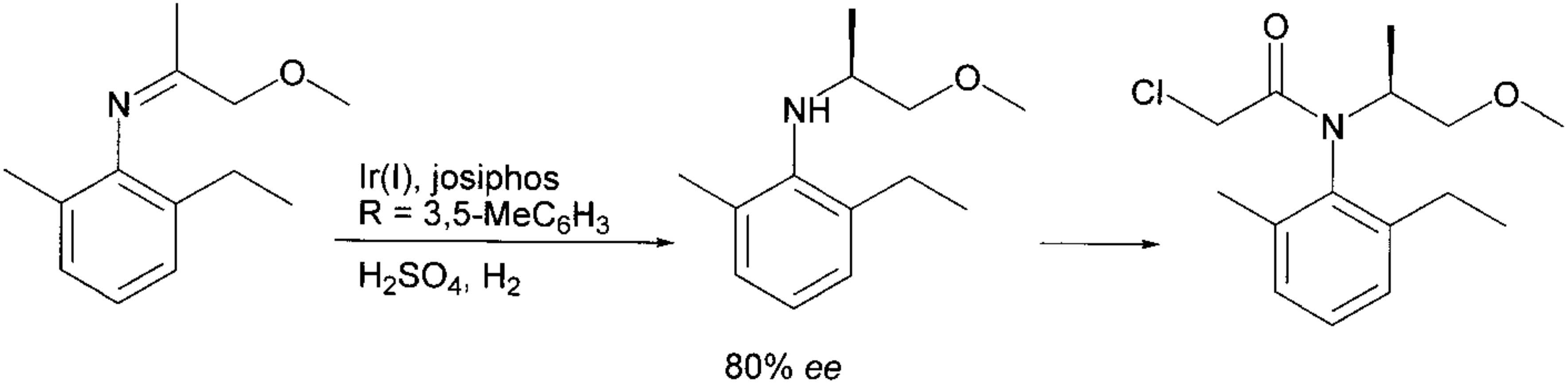
Ugi's amine

(*S*, *R*) - BPPFA

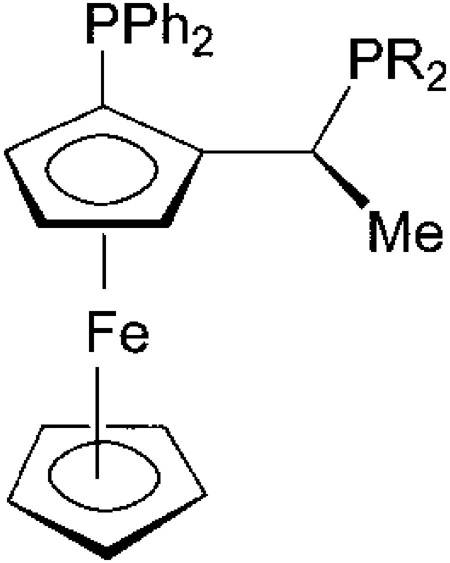


Example:
(*S*, *R*)-josiphos
(*Togni*, 1994)

Chiral ligands based on M-Cp complexes



Production of *S*-Metolachlor (10000 t/year); cat. 0.001 mol%



Example:
(*S*, *R*)-josiphos
(*Togni*, 1994)