Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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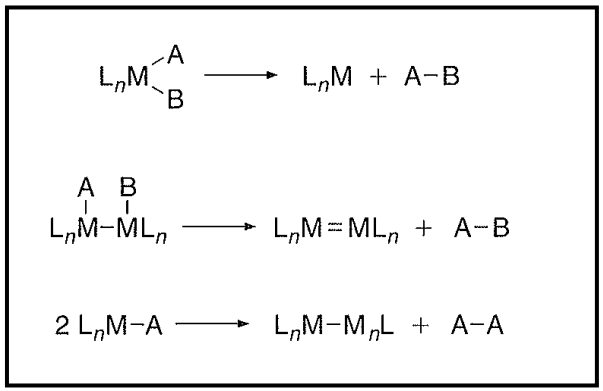
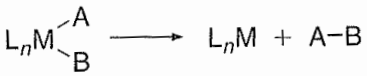
Übersicht

- Reduktive Eliminierung
  - Bildung einer C-H Bindung
  - Bildung einer C-C Bindung
  - Bildung einer C-X Bindung
- Einschubreaktionen
  - 1,1-Insertion
  - CO Insertion
  - 1,2-Insertion
- β-Eliminierung
- α-Eliminierung

Reduktive Eliminierung





For M: •First row complexes react faster than second row complexes, which react faster than third row complexes.
•More electron-poor complexes react faster than more electron-rich complexes.

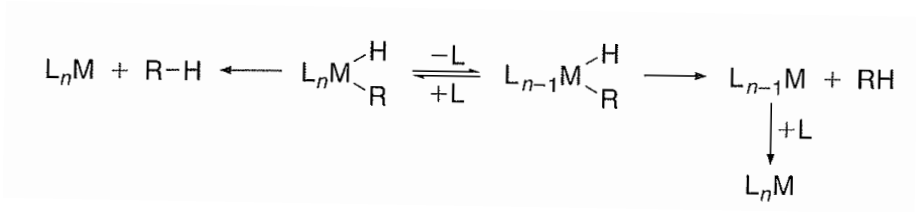
For L: •More sterically hindered complexes react faster than less sterically hindered complexes.

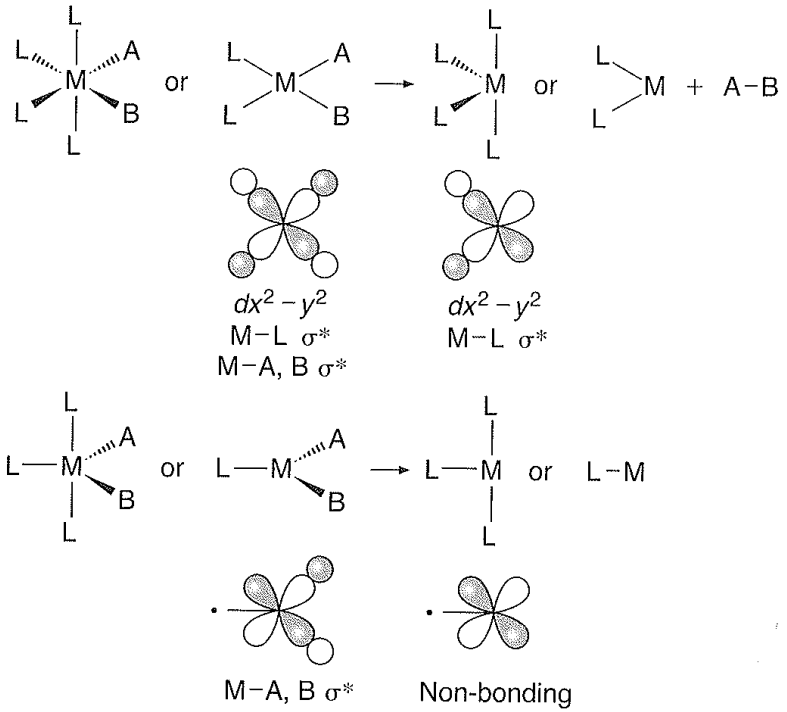
For A and B: H reacts faster than R.

For *n*: complexes in which $n = 1$ or 3 react faster than complexes in which $n = 2$ or 4.

Reduktive Eliminierung: 3 vs 4 Coordinate

The origin of the relative rates for reductive elimination from complexes with odd and even coordination numbers.



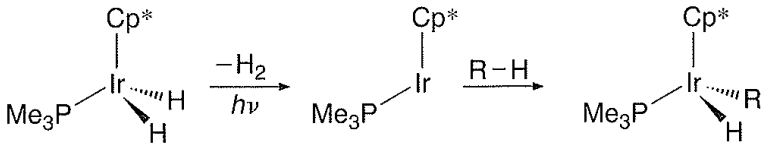


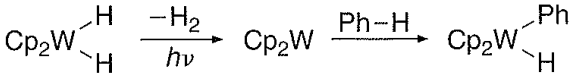
cis vs *trans:*

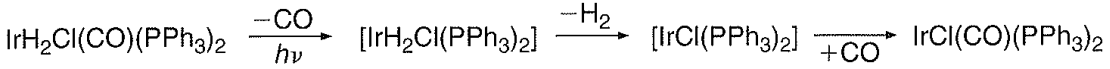
cis $L_nM(A)(B)$	$\longrightarrow$ $L_nM + A–B$	Concerted or stepwise
trans $A–M(L_n)_2–B$	$\longrightarrow$ $L_nM + A–B$	Must be stepwise

•Less structural reorganization $\Longrightarrow$ Faster rates

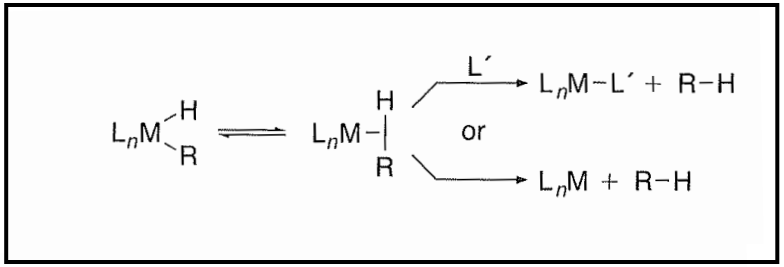
Reduktive Eliminierung: Lichtinduziert

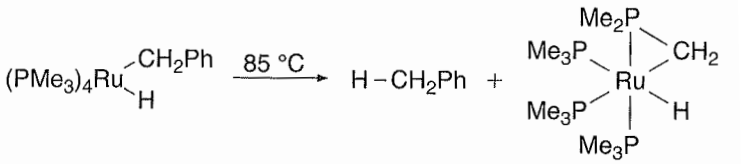


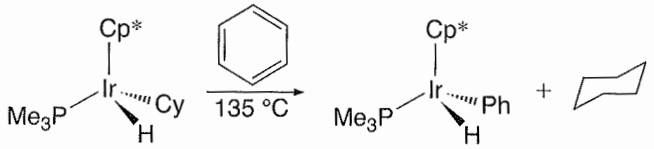


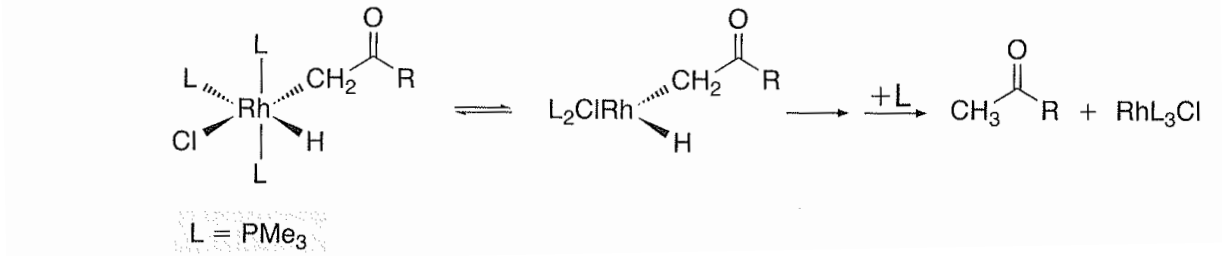


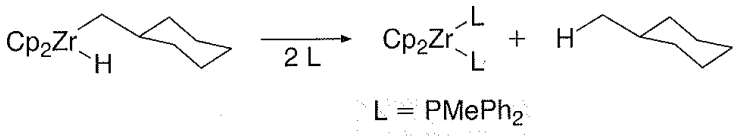
Reduktive Eliminierung -> C-H Bindung



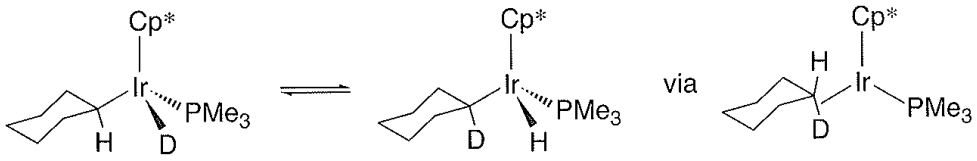




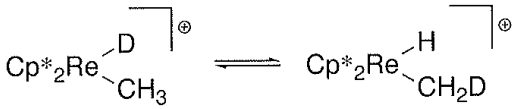


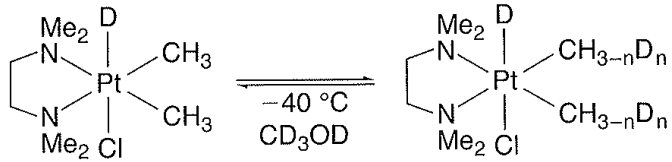


Reduktive Eliminierung: σ-Komplexintermediat



Cp´ = C_5H_5 or C_5Me_5





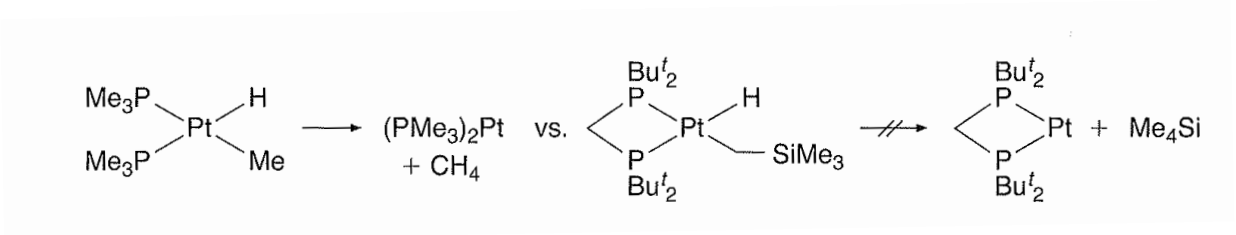
Reduktive Eliminierung: Zusätzliche Liganden

Table 8.1. The effect of ancillary ligand electronic effects on the rate of reductive elimination of benzene from $Cp^*Rh(PR_3)(Ph)(H)$.

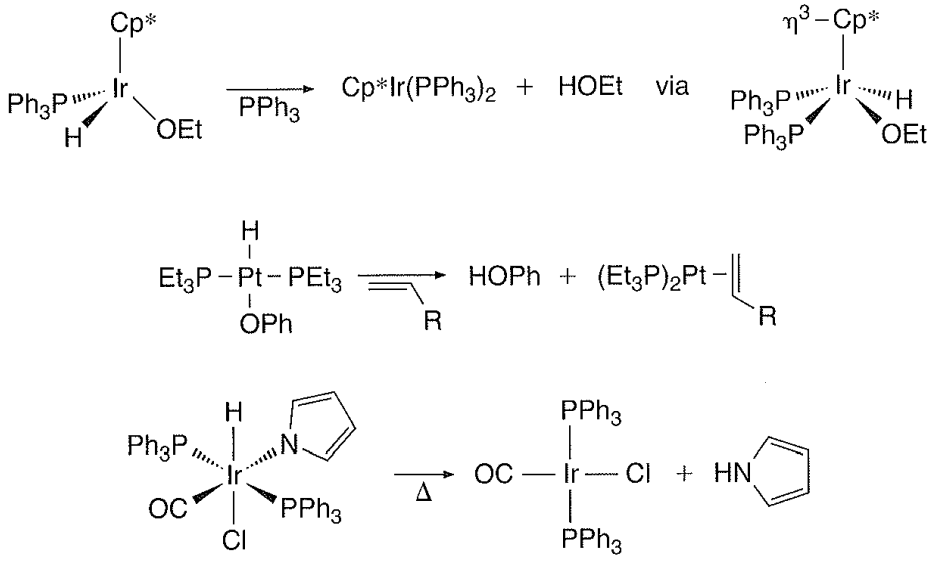
Entry	PR_3	Cone angle (deg)	T (°C)	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
1	PMe_3	118	23	$3.35(17) \times 10^{-7}$	26.1
2	PMe_2Ph	122	23	$1.08(5) \times 10^{-6}$	25.4
3	PMe_2Bu^t	139	24.5	6.6×10^{-5}	24.5
4	$PMePh_2$	136	24.5	$1.11(6) \times 10^{-5}$	24.2

Table 8.2. The effect of ancillary ligand steric properties on the rate of reductive elimination of benzene from $Cp^*Rh(PR_3)(Ph)(H)$.

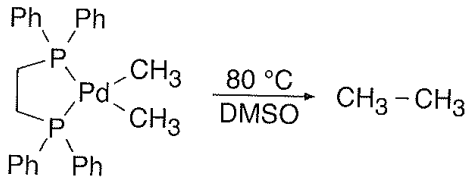
Entry	PR_3	Cone angle (deg)	T (°C)	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
1	PMe_3	118	23	$3.4(2) \times 10^{-7}$	26.1
2	$P(n\text{-}Bu)_3$	132	24.5	$2.4(1) \times 10^{-6}$	25.1
3	PMe_2Bu^t	139	24.5	6.6×10^{-5}	24.5

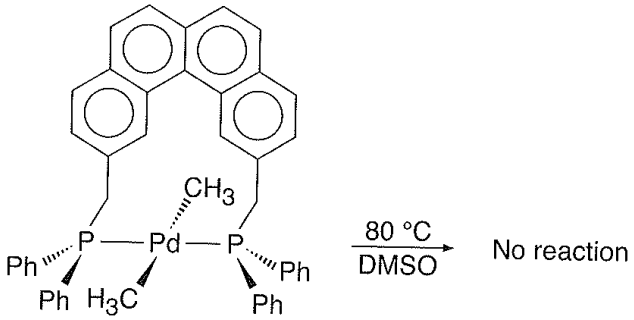


Reduktive Eliminierung -> X-H Bindung

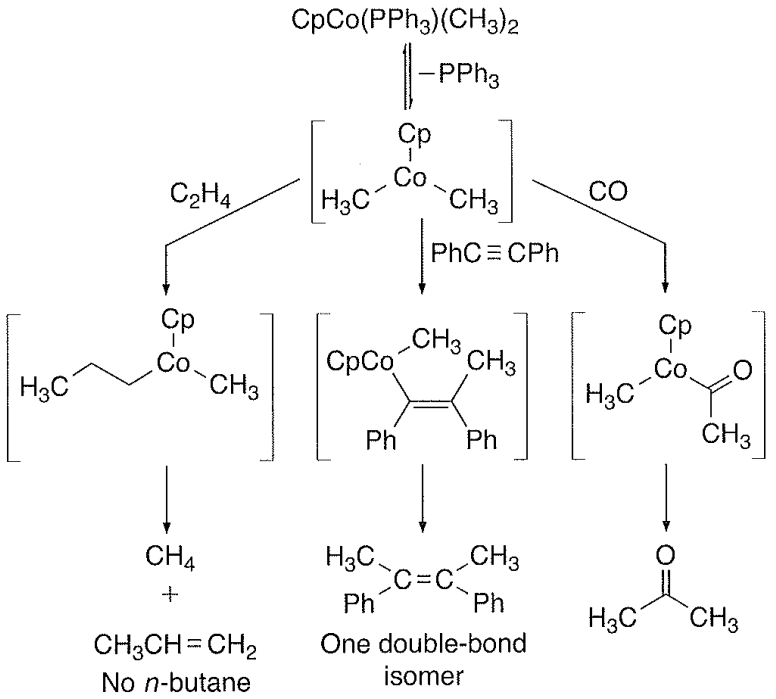


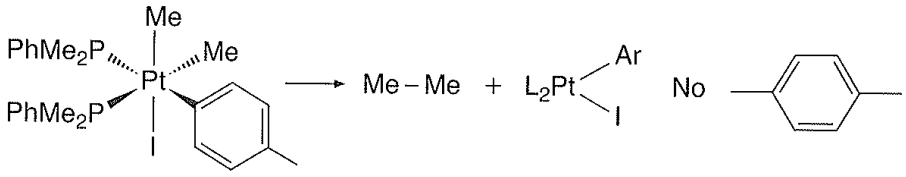
Reduktive Eliminierung -> C-C Bindung



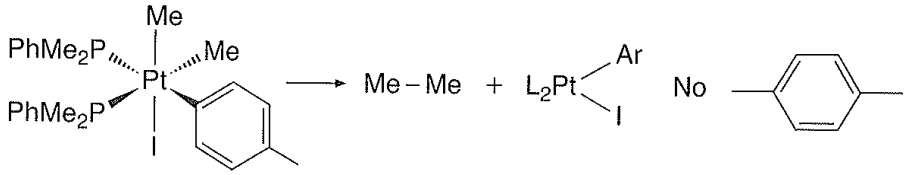


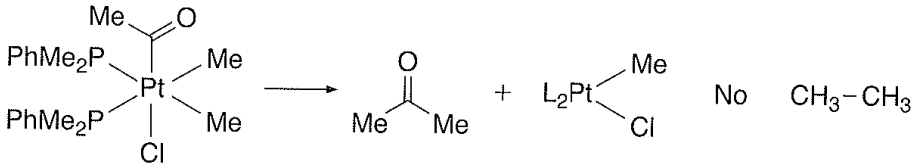
Reduktive Eliminierung: -> C-C Bindung



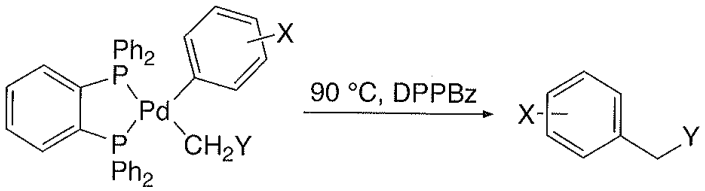


Reduktive Eliminierung: -> C-C Bindung



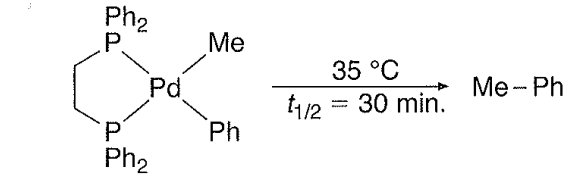


Elektronenarme Aryl + elektronenreiche Alkygruppe



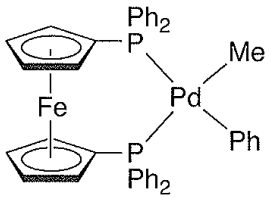
Relative rates:
X = *p*-CN > *p*-CF_3 > *p*-H > *p*-Me > *p*-OMe
Y = H > Ph > C(O)R > CF_3 > CN

Reduktive Eliminierung: Bite Angle



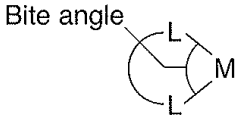
35 °C
$t_{1/2}$ = 30 min.

Me – Ph



0 °C
Rapid

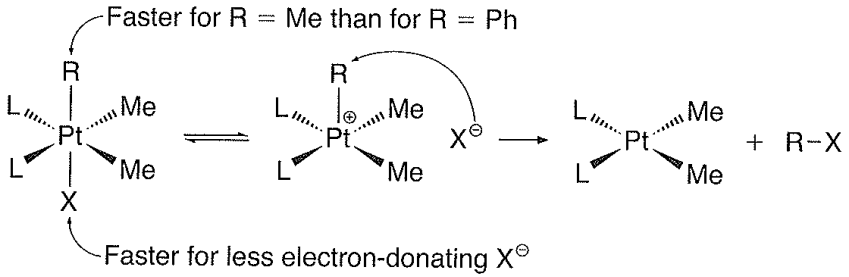
Me – Ph



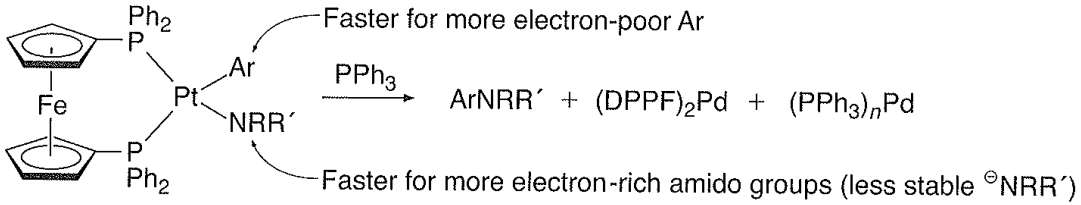
Ligand	"Bite angle"
DPPE	90.6[a]
DPPF	99.1[b]

Reduktive Eliminierung: -> C-X Bindung

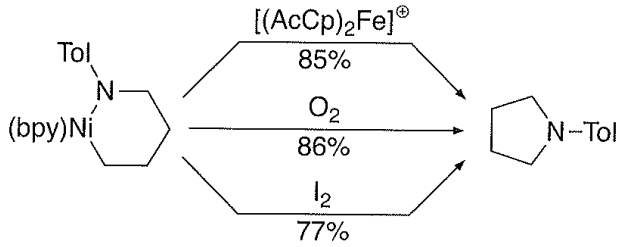
Pt(IV)

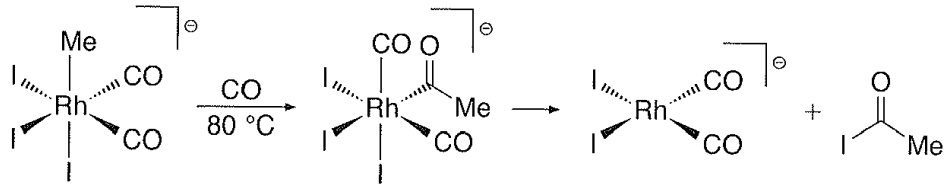


Pt(II)

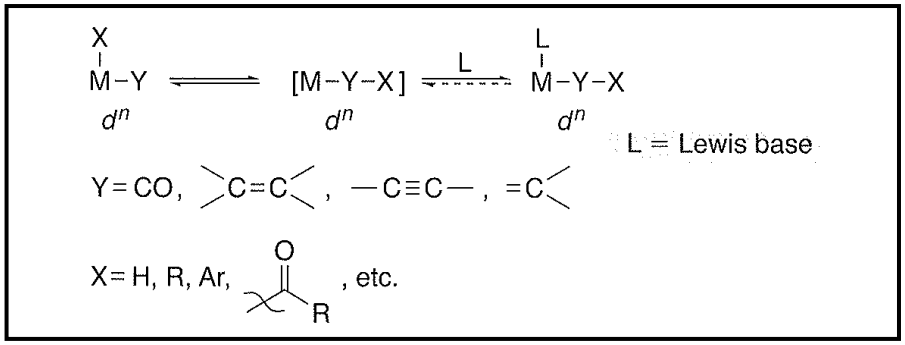


Reduktive Eliminierung: -> C-X Bindung



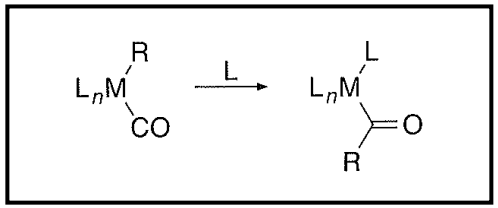


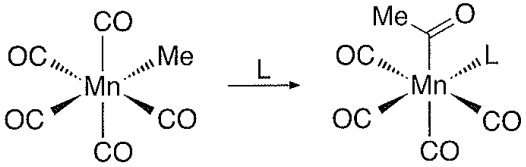
Insertionsreaktionen



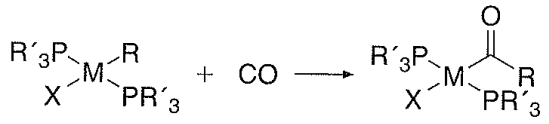
1. Migratory insertion does not lead to a change in formal oxidation state, unless the inserting ligand Y is an alkylidene, alkylidyne, or isoelectronic ligand bound by a metal–ligand multiple bond.
2. The groups undergoing the migratory insertion process must be coordinated cis to each other within the coordination sphere of the metal.
3. A vacant coordination site is created during the forward insertion reaction of Equation 9.1, and a vacant coordination site must be present for the reverse reaction to occur. This mechanism makes it necessary for coordinatively saturated (18-electron) metal–alkyl complexes to dissociate a ligand prior to β-hydrogen and β-hydrocarbyl elimination reactions.
4. Migratory insertion occurs by a concerted process and, therefore, proceeds with retention of configuration at the α-carbon of a migrating alkyl group.
5. Ligand X can migrate onto Y, creating an open site on the metal at the original position of ligand X, or the unsaturated group Y can insert into the M–X bond, creating an open site on the metal at the original position of group Y.
6. The position of the insertion equilibrium depends upon the strengths of the M–X, M–Y, M–(YX) bonds and M(Y–X) bonds.
7. One-electron oxidation, coordination of Lewis acids, and attack by Lewis bases can accelerate the insertion processes.

Insertionsreaktionen: CO

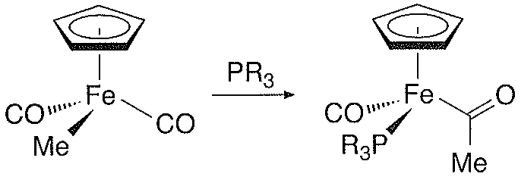


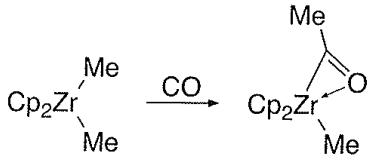


L = NH_2,Cy or PPh_3

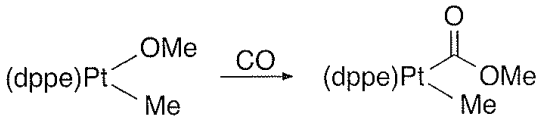


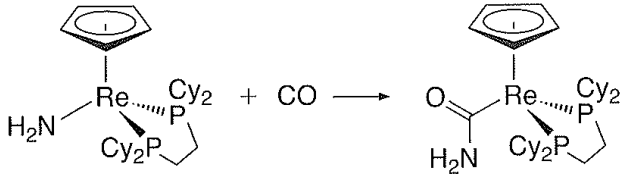
M = Pd or Pt
X = Cl, Br, I

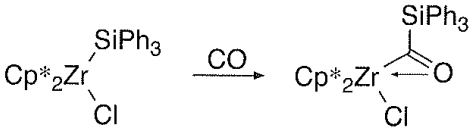


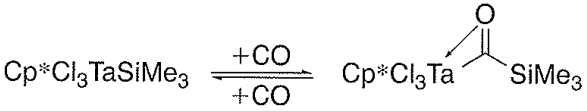


Insertionsreaktionen: CO in M-X

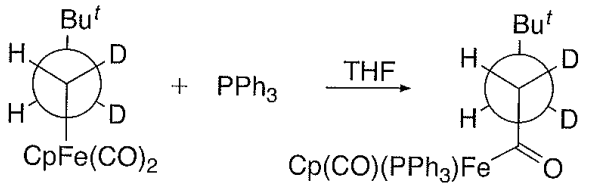




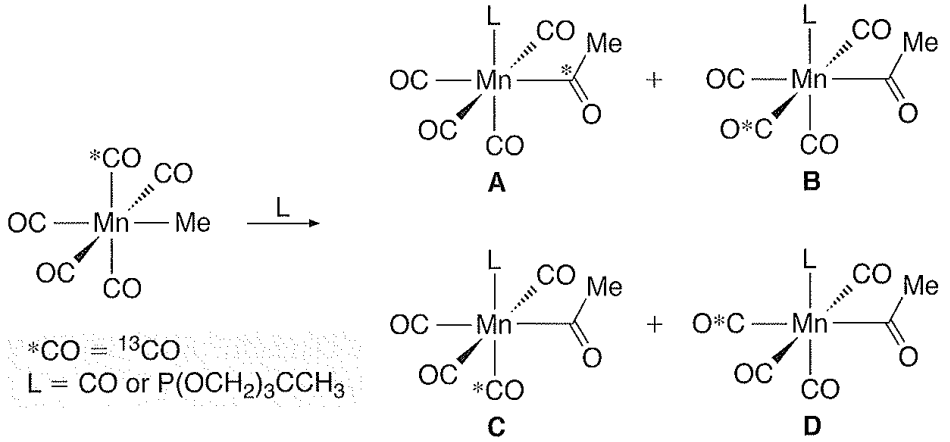




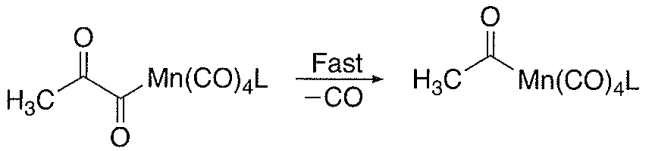
CO-Insertionsreaktionen: Stereochemie

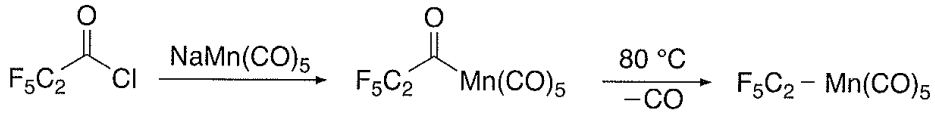


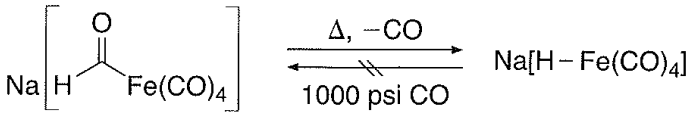
Me wandert: kein **C**
CO wandert: kein **D**



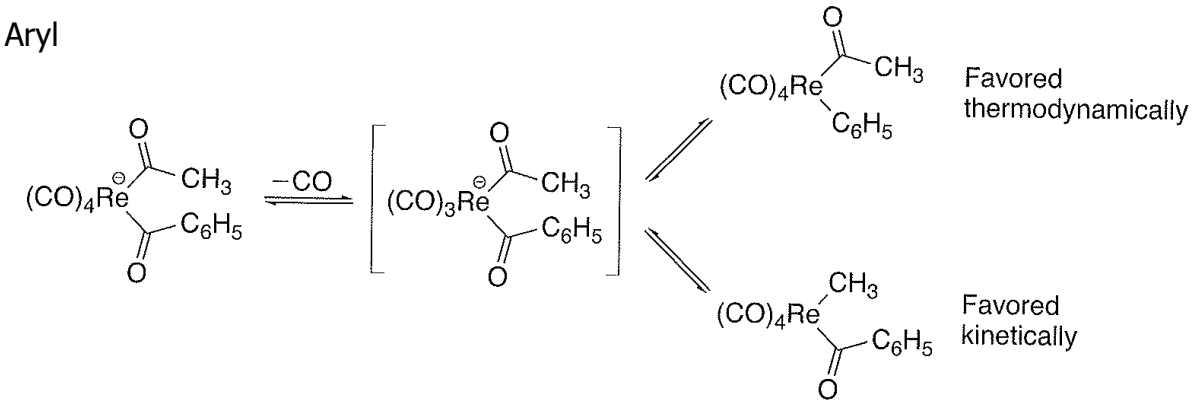
CO-Insertionsreaktionen: Thermodynamik





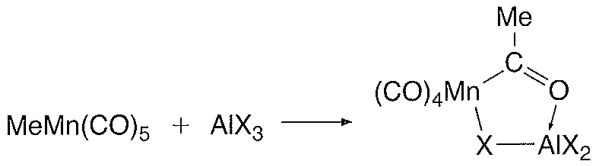


Alkyl wandert schneller als Aryl

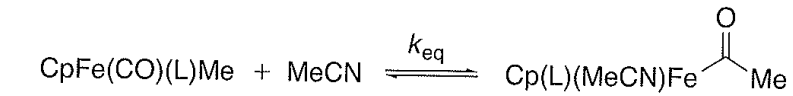


CO-Insertionsreaktionen: Katalyse

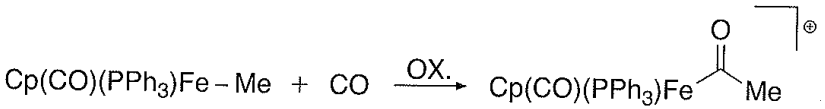
Lewis Säure



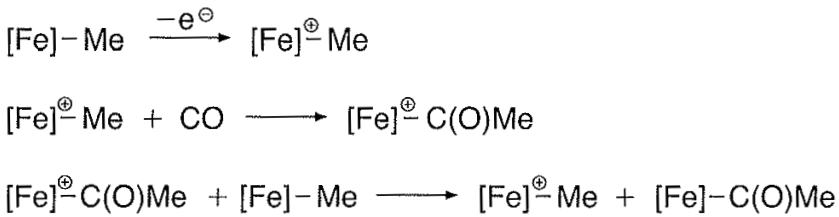
Oxidation



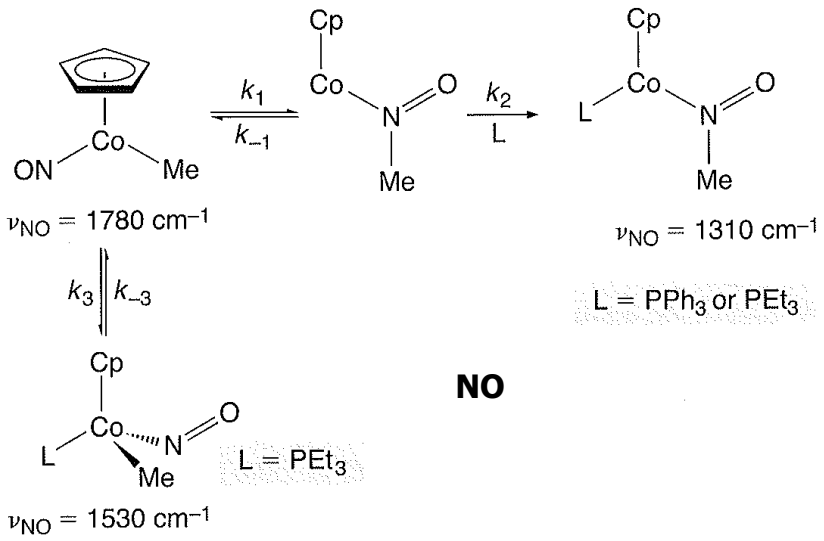
L = CO or PPh_3



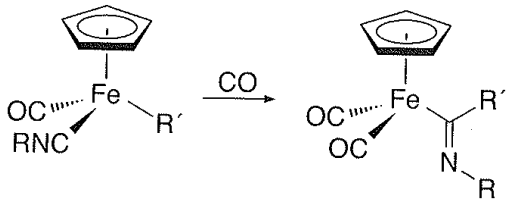
OX. = $Ag^{\oplus}$ or $Cp_2Fe^{\oplus}$



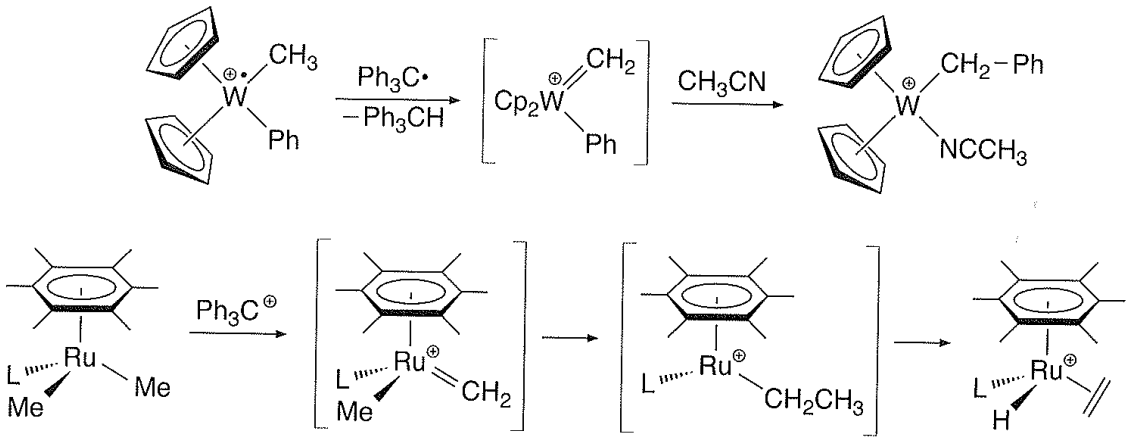
Insertionsreaktionen: Andere 1,1-Insertionen



NO

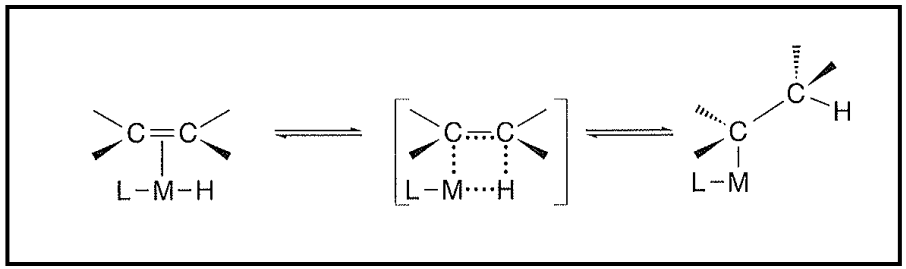


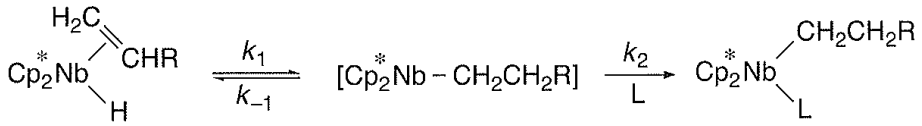
Isonitrile

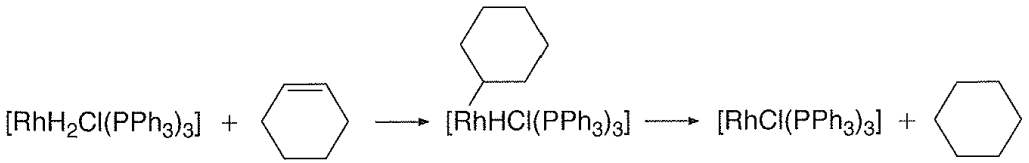


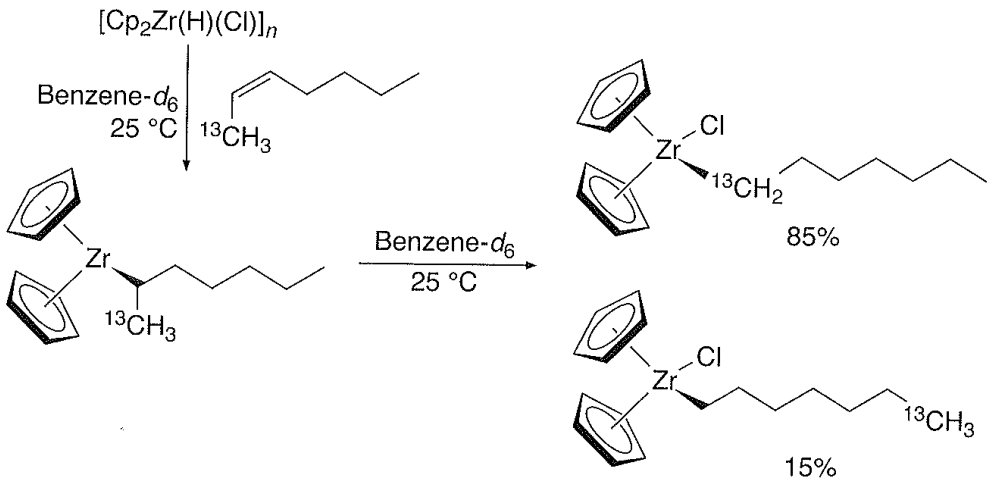
Carbene

1,2-Insertionsreaktionen: Olefine

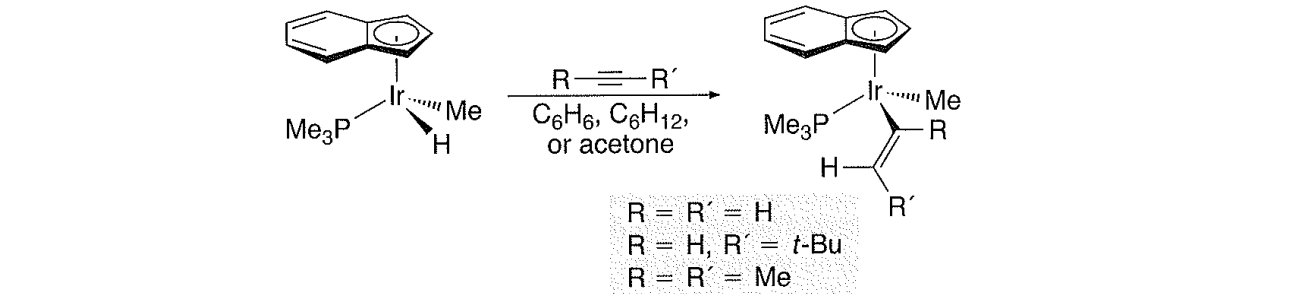


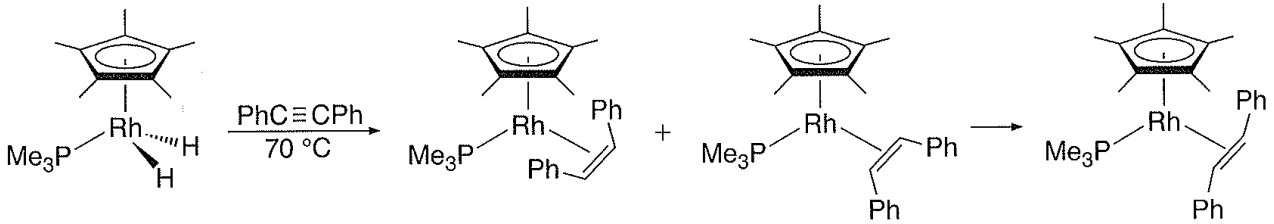


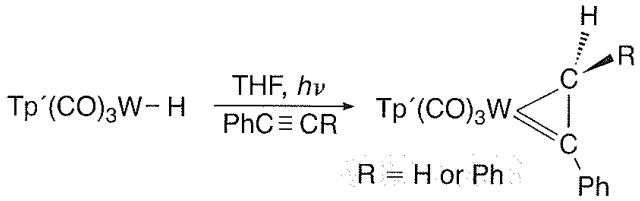


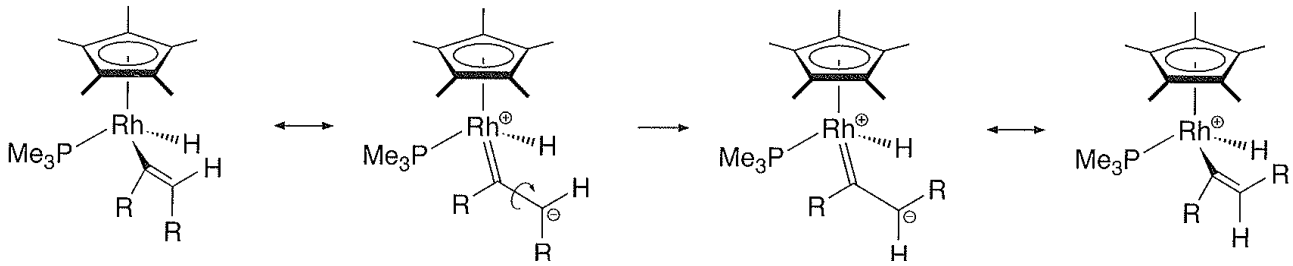


1,2-Insertionsreaktionen: Alkine

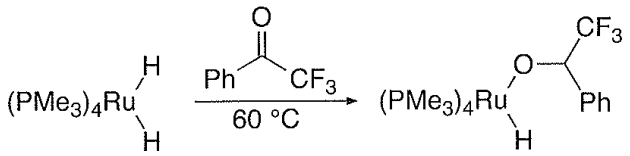


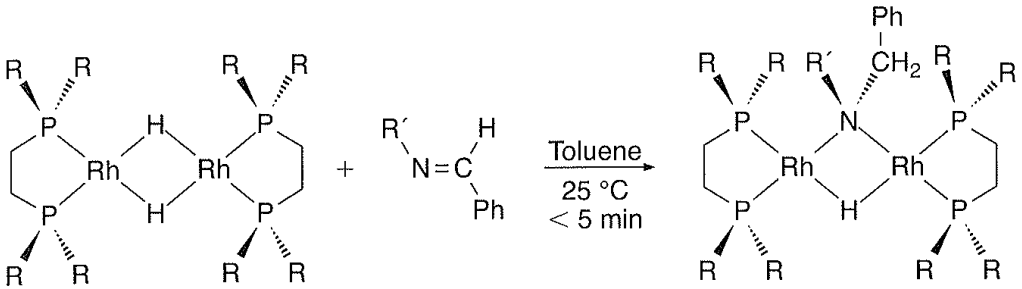






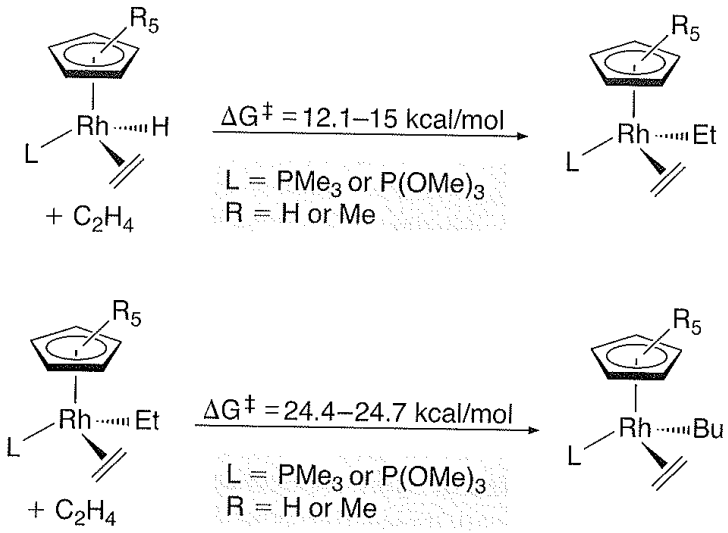
1,2-Insertionsreaktionen: Ketone, Imine

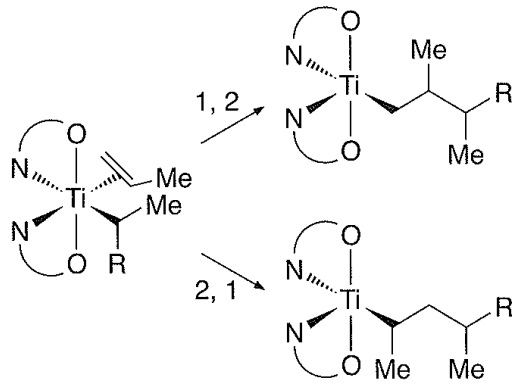




R´	R
C_6H_5	Pr^i
C_6H_5	OPr^i
CH_3	Pr^i
CH_3	OPr^i
CH_2Ph	Pr^i
CH_2Ph	OPr^i

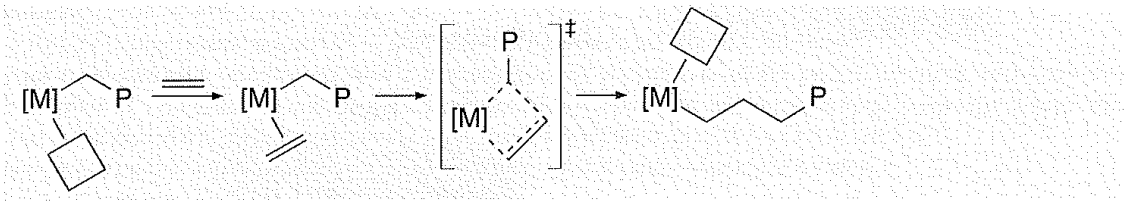
1,2-Insertionsreaktion in M-C Bindung



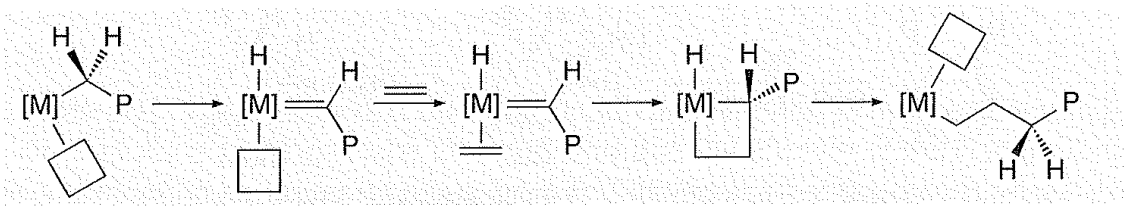


1,2-Insertionsreaktion: Ziegler Natta

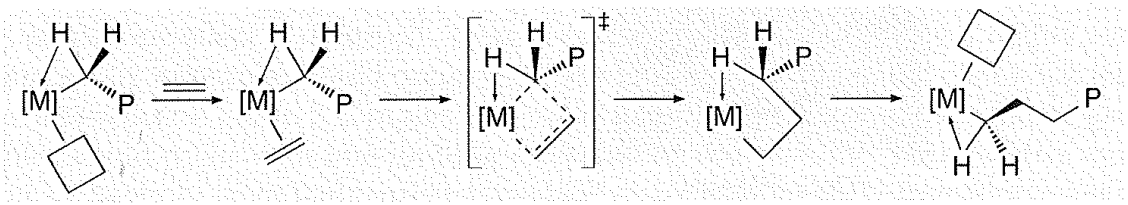
Cossee–Arlman mechanism (direct insertion)



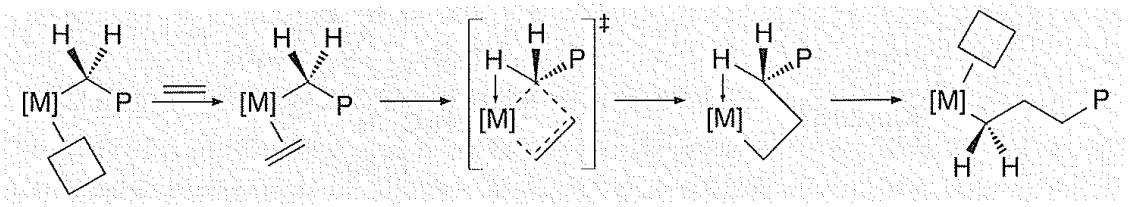
Green–Rooney mechanism (hydrise shift)



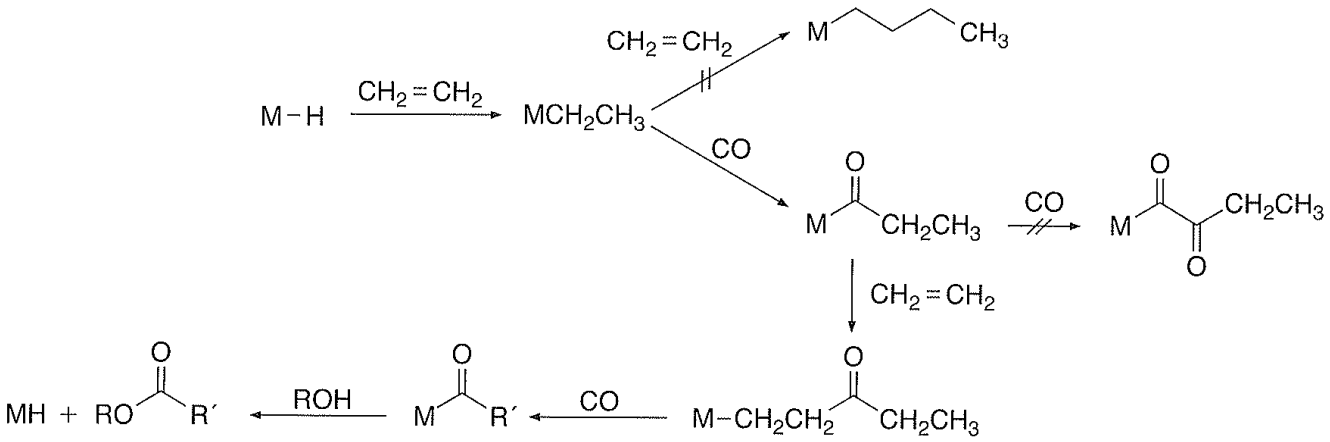
Modified Green–Rooney mechanism (ground and transition state α-agostic interaction)



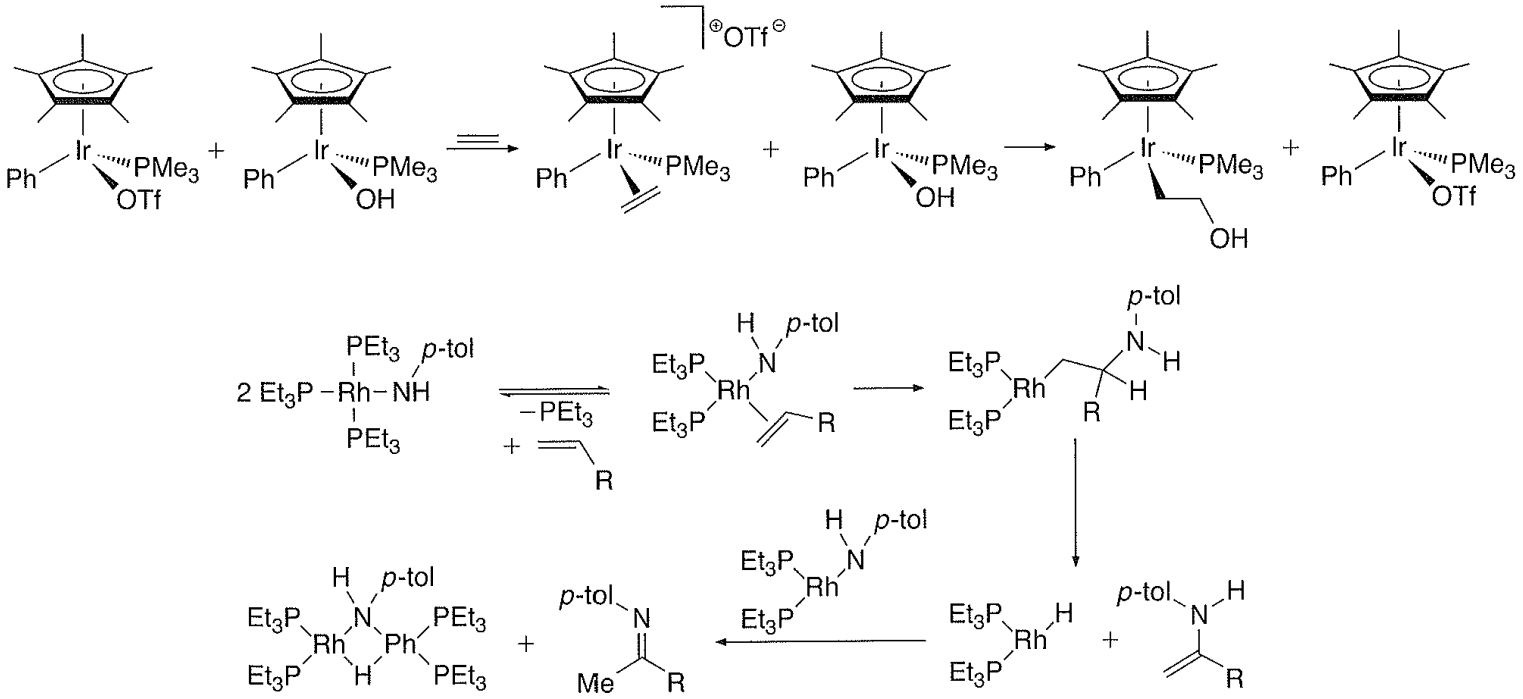
Transition state α-agostic mechanism



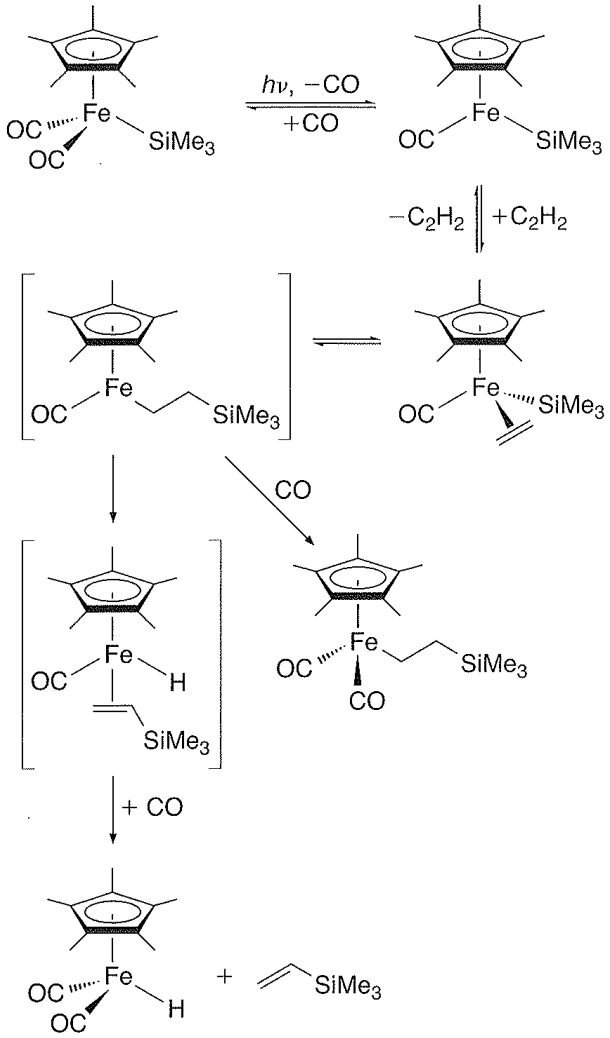
Konsekutive 1,1- und 1,2-Insertionsreaktion

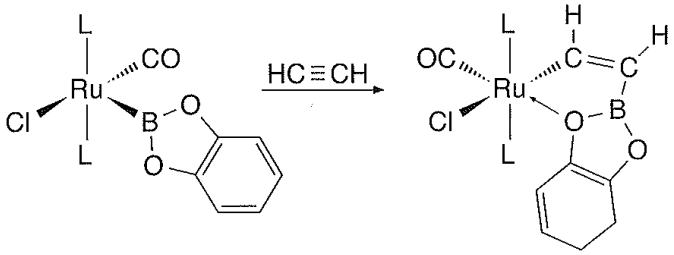


1,2-Insertionsreaktion in M-X Bindung



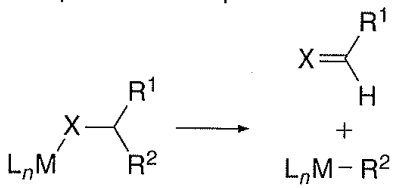
1,2-Insertionsreaktion in M-E Bindung





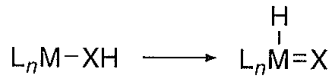
Eliminierung

β-Elimination processes

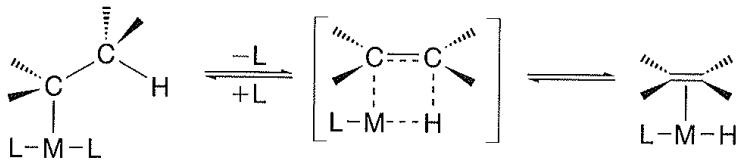


Relative rates: $R^2 = H > R^2 =$ alkyl or aryl
For X = CH_2, studied for $R^2 =$ H, alkyl, Ar, OR and Cl
For X = O or NR, studied for $R^2 =$ H and aryl

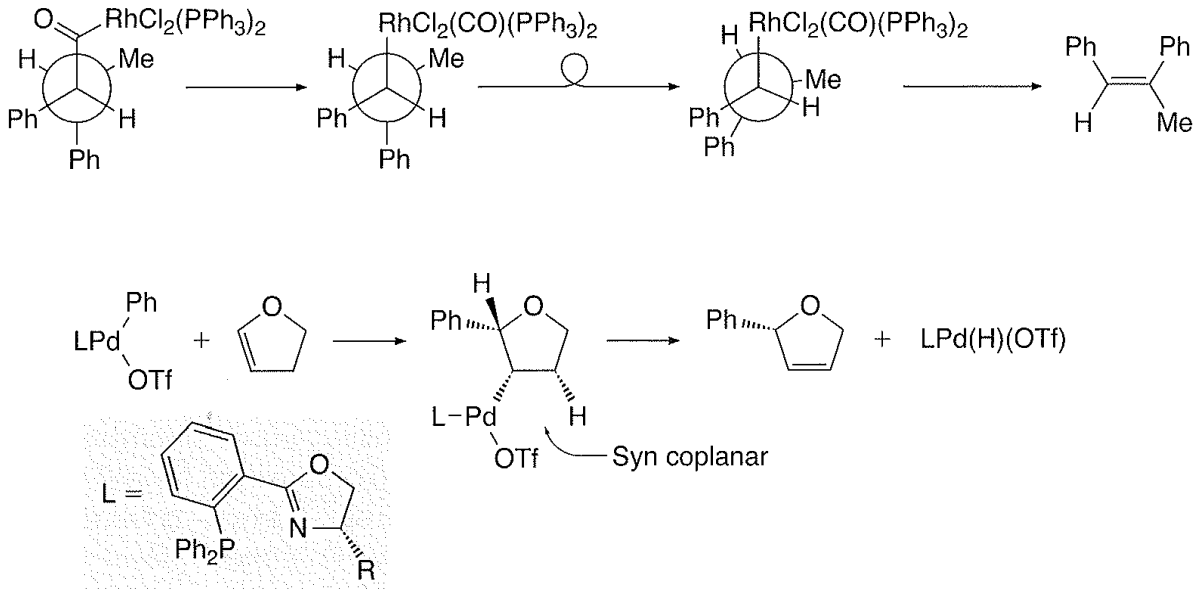
α-Elimination processes



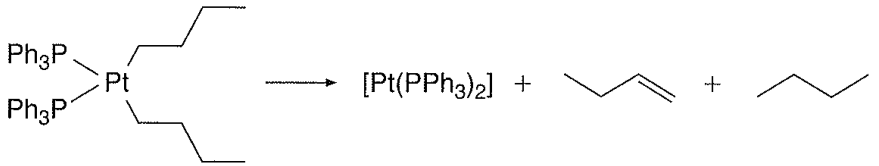
X = O, NR or CR_2



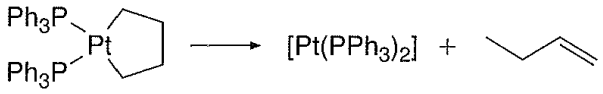
β-Hydrideliminierung



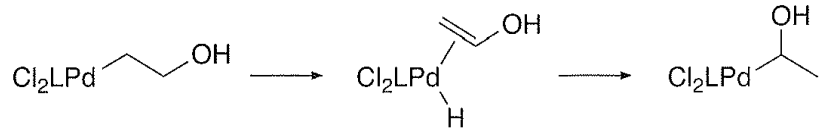
β-Hydrideliminierung: Sterik und Elektronik

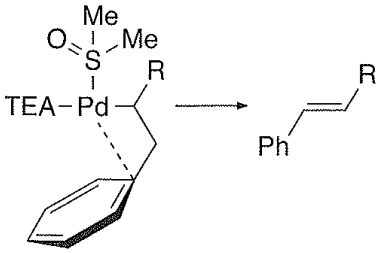


schnell



sehr langsam

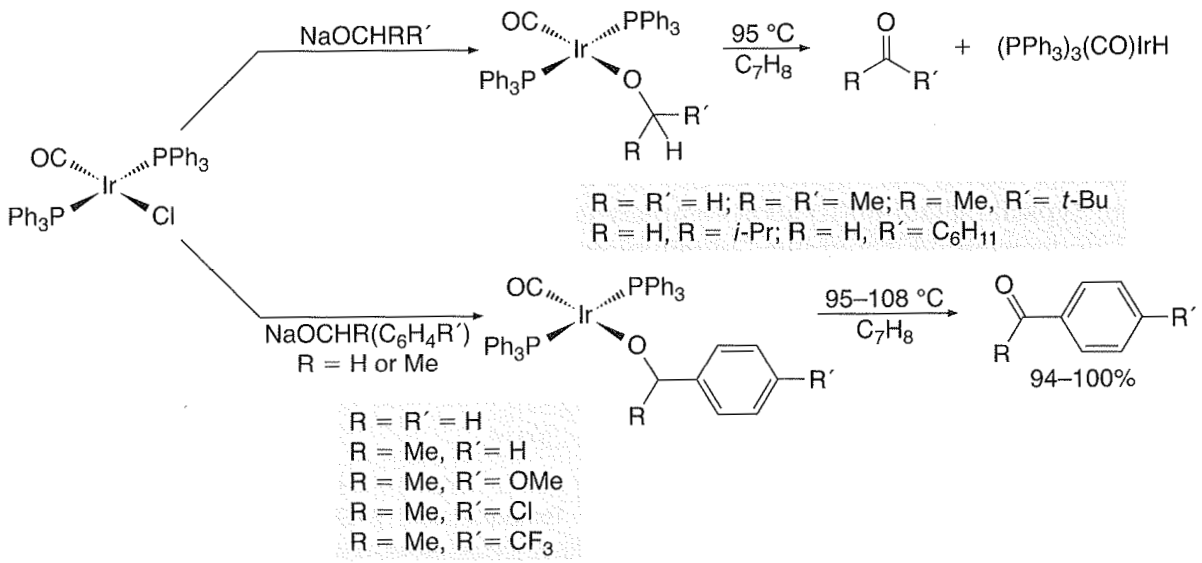


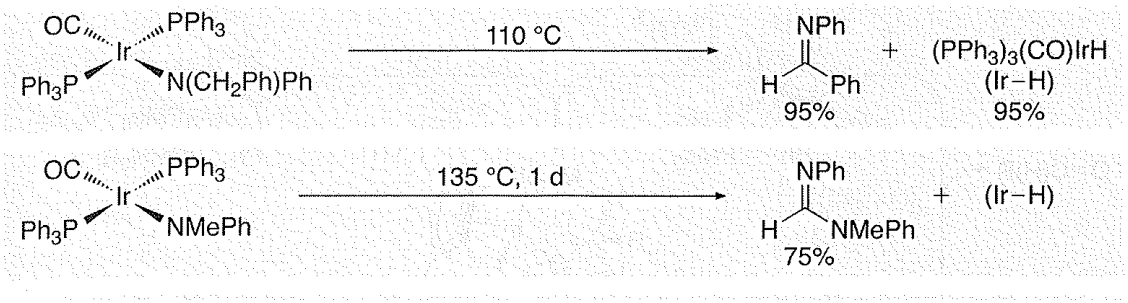


R	Temperature	$t_{1/2}$ for β-elimination
Ph	−20 °C	< 15 min
$CO_2{}^tBu$	20 °C	< 6 min
CN	23 °C	25 h

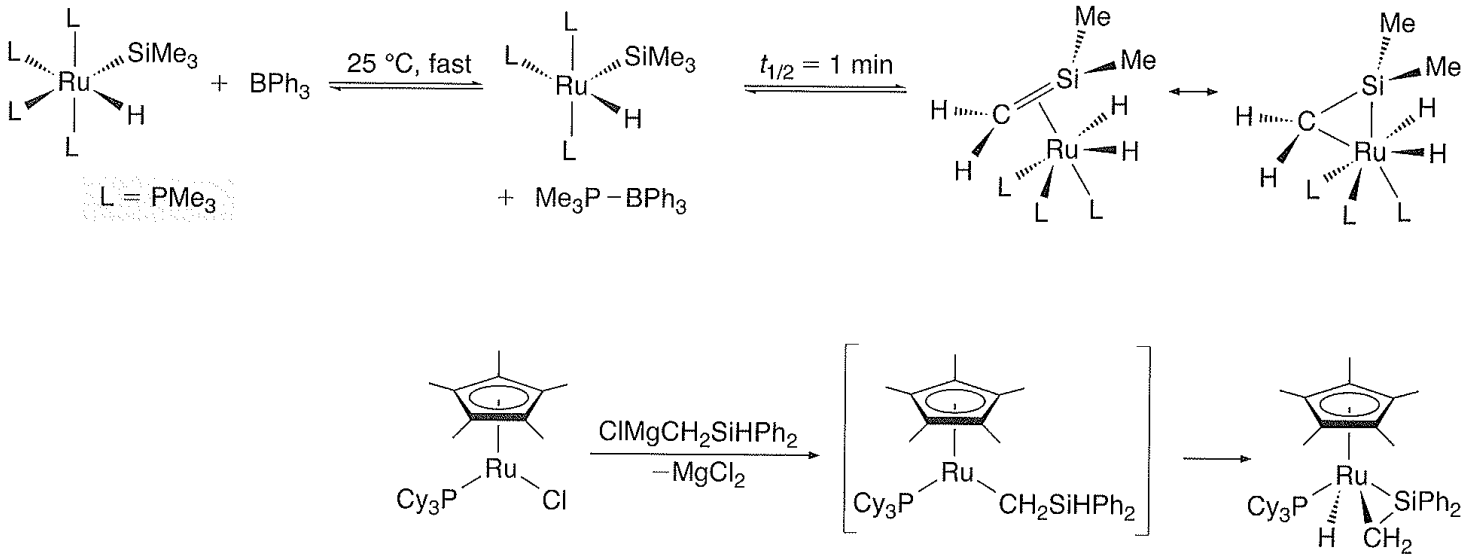
Other ligands: Steric hindrance decreases, while electron donation increases rate of ß-elimination

β-Hydrideliminierung von Alkoxiden und Amiden

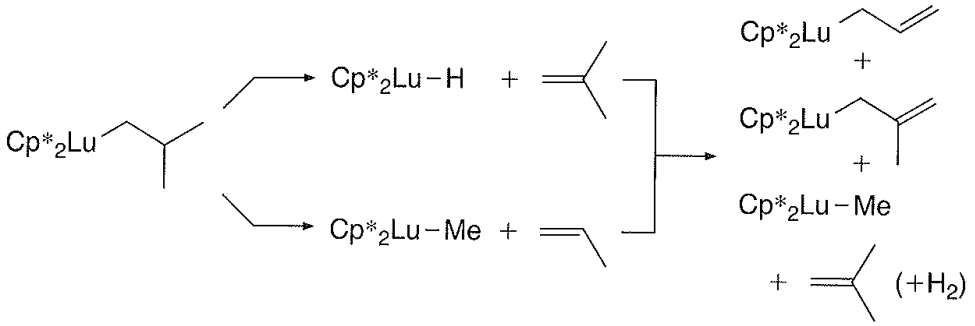


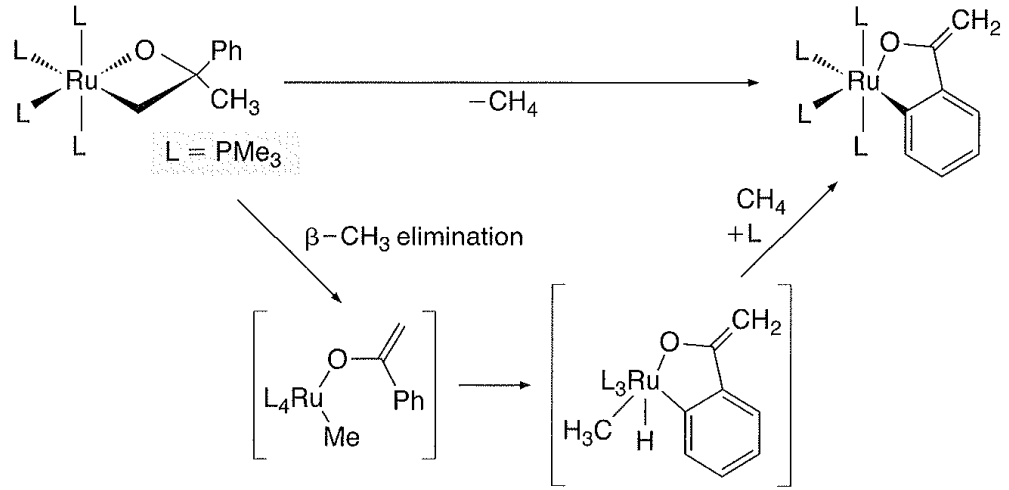


β-Hydrideliminierung von Silylkomplexen

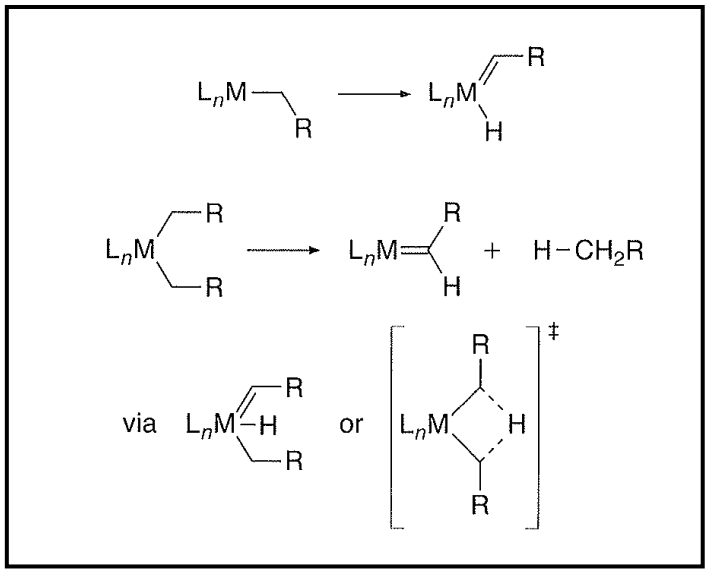


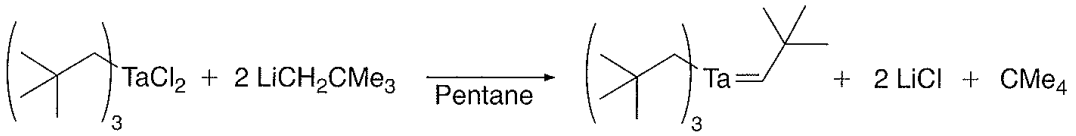
β-Alkyleliminierung

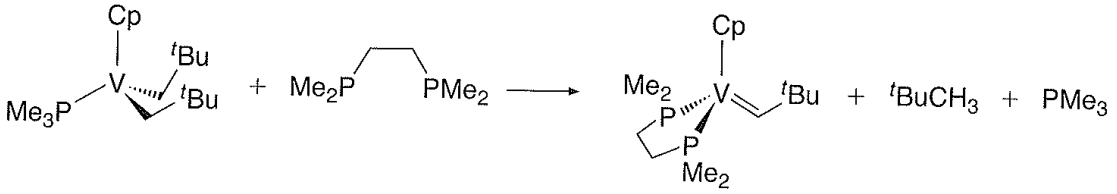




α-Eliminierung







α-Eliminierung