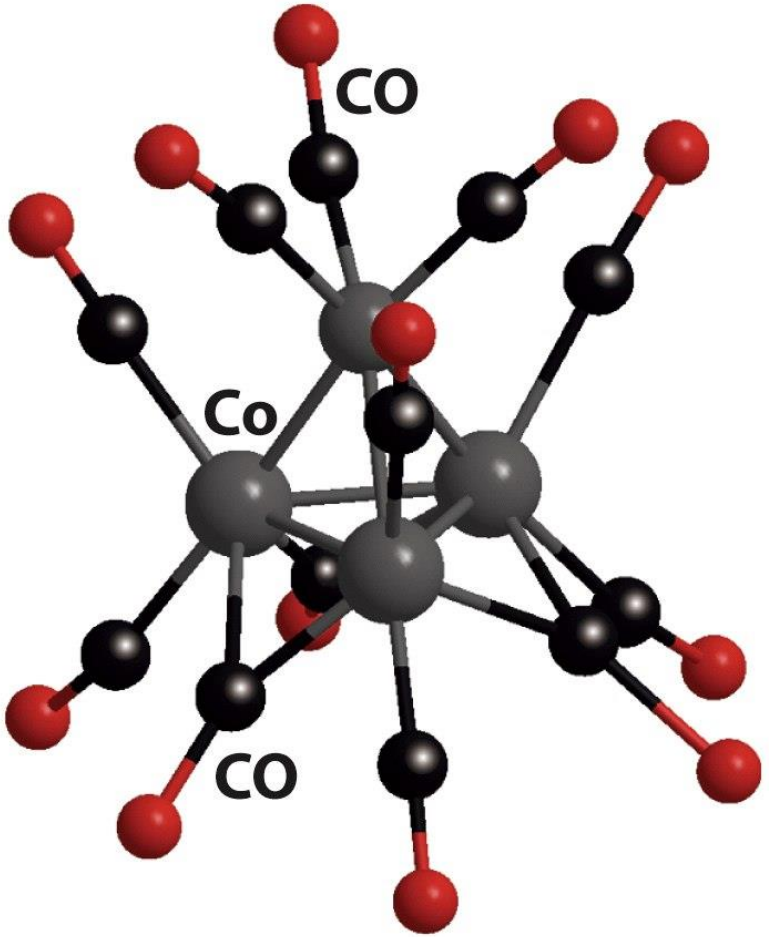
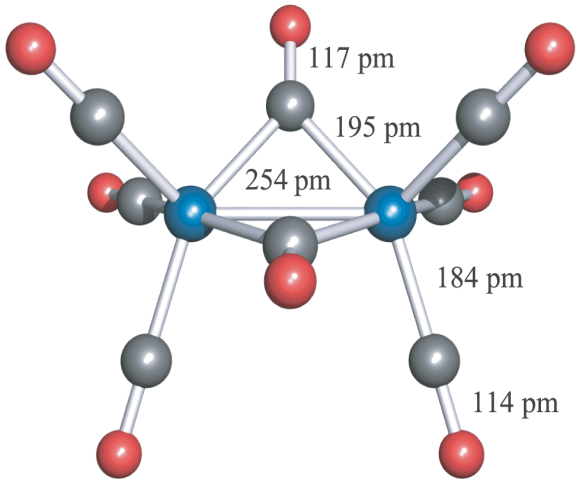
Cluster carbonilico

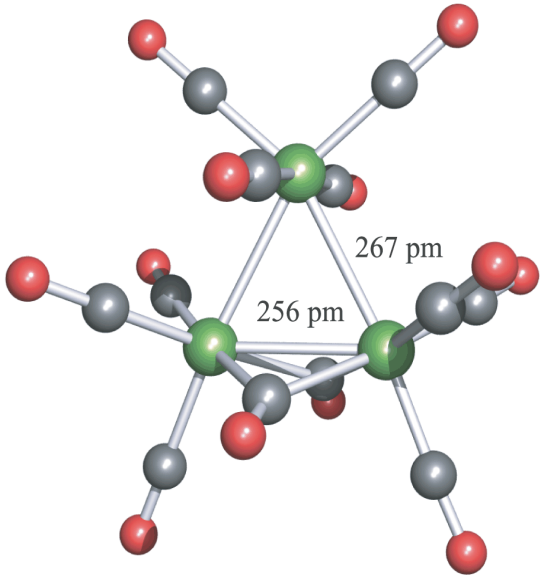


$[Co_4(CO)_{12}]$



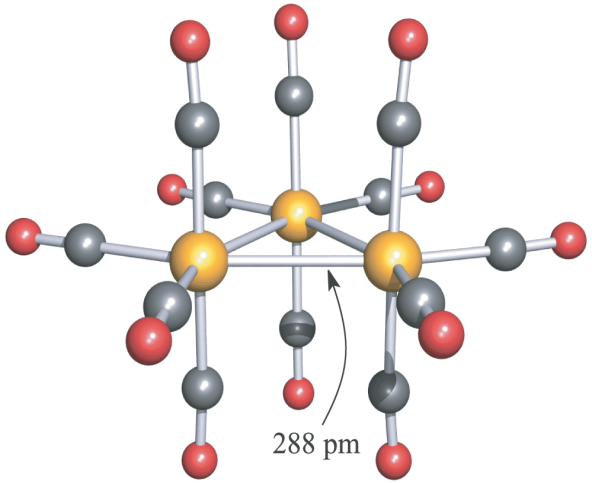
(d)

$Co_2(CO)_8$



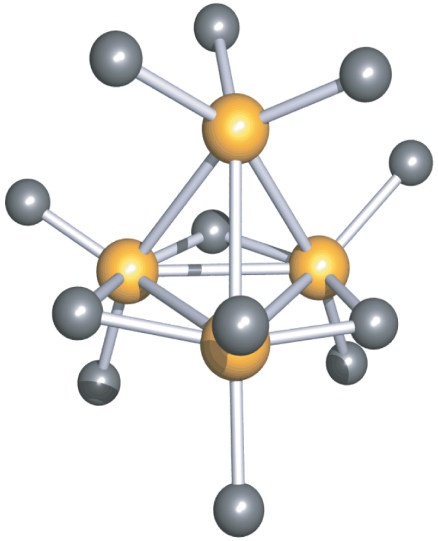
(e)

$Fe_3(CO)_{12}$



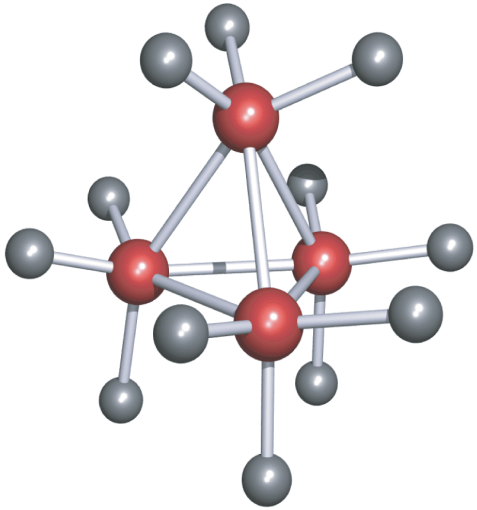
(f)

$Os_3(CO)_{12}$



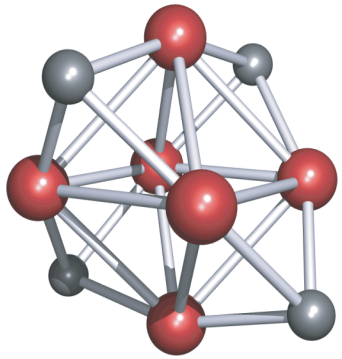
(a)

$Rh_4(CO)_{12}$



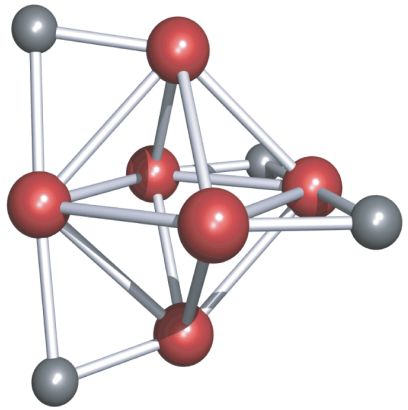
(b)

$Ir_4(CO)_{12}$



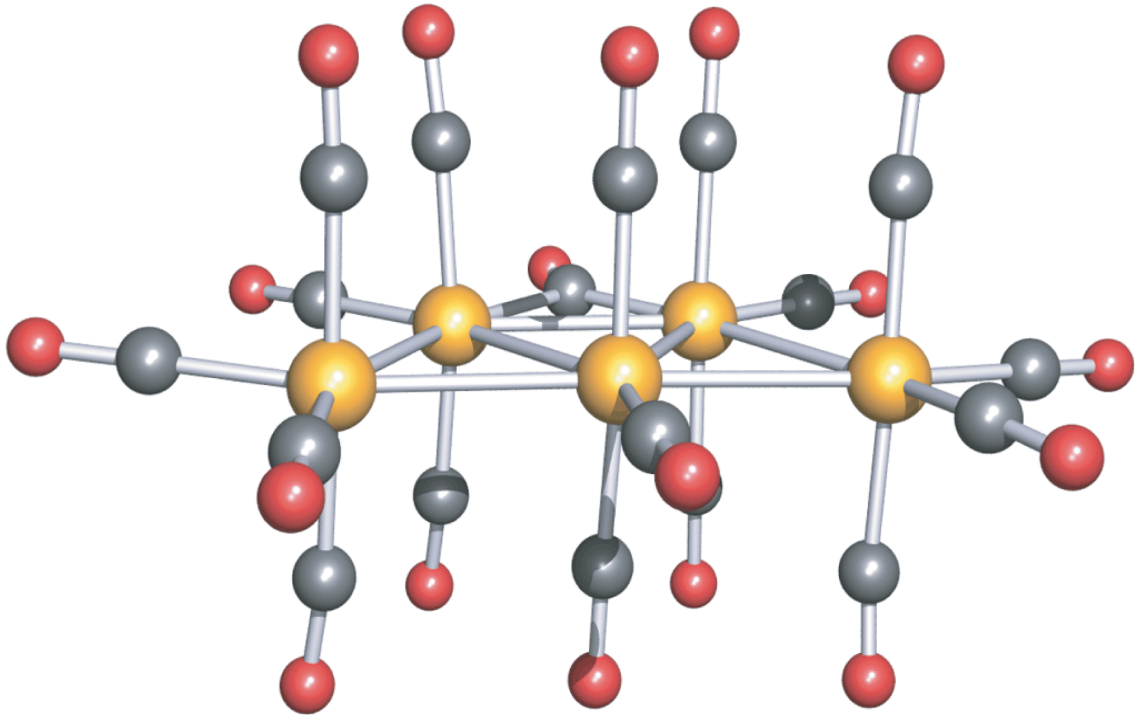
(c)

$Ir_6(CO)_{16}$
rosso



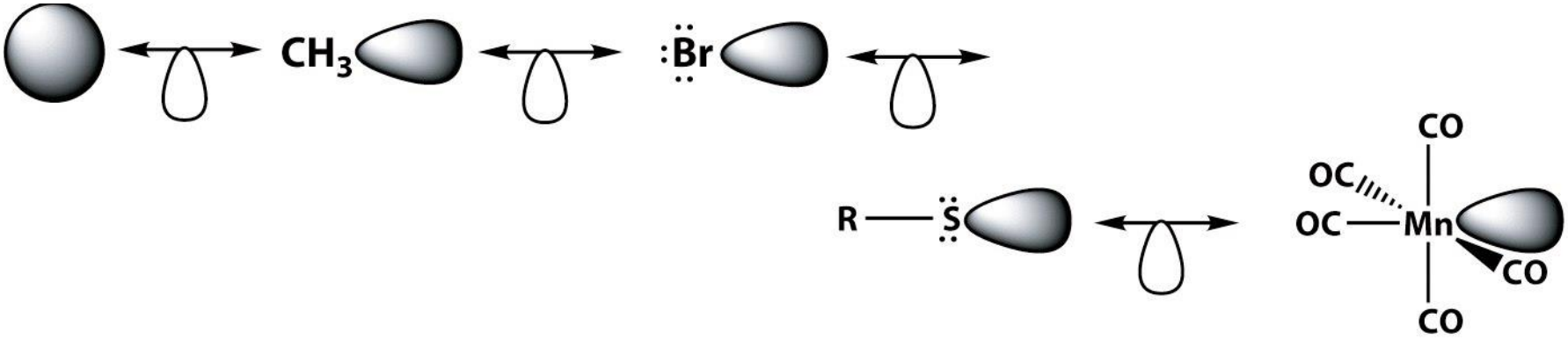
(d)

$Ir_6(CO)_{16}$
nero



$Os_5(CO)_{18}$

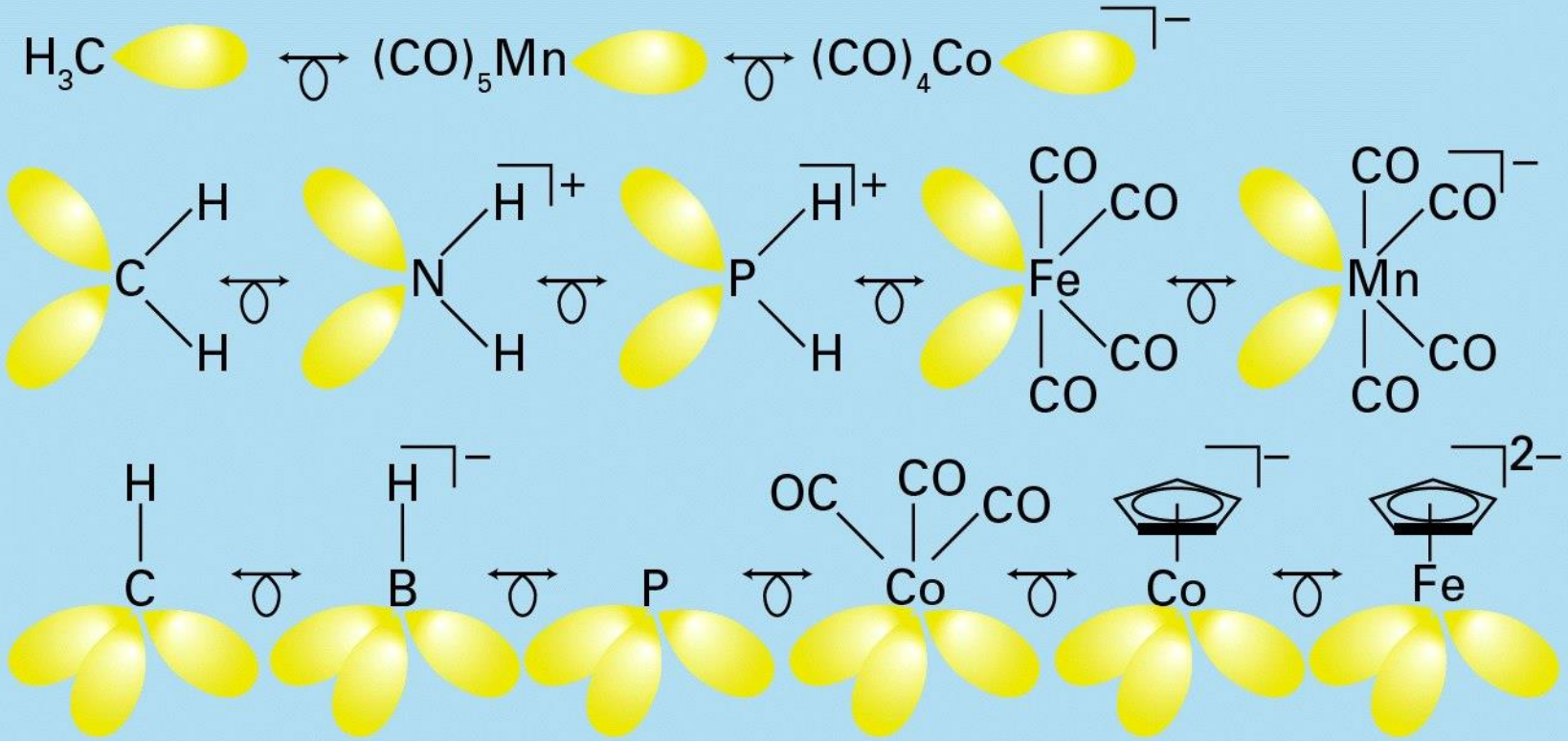
Serie di frammenti isolobali



Gli **orbitali di frontiera** dei frammenti isolobali hanno:

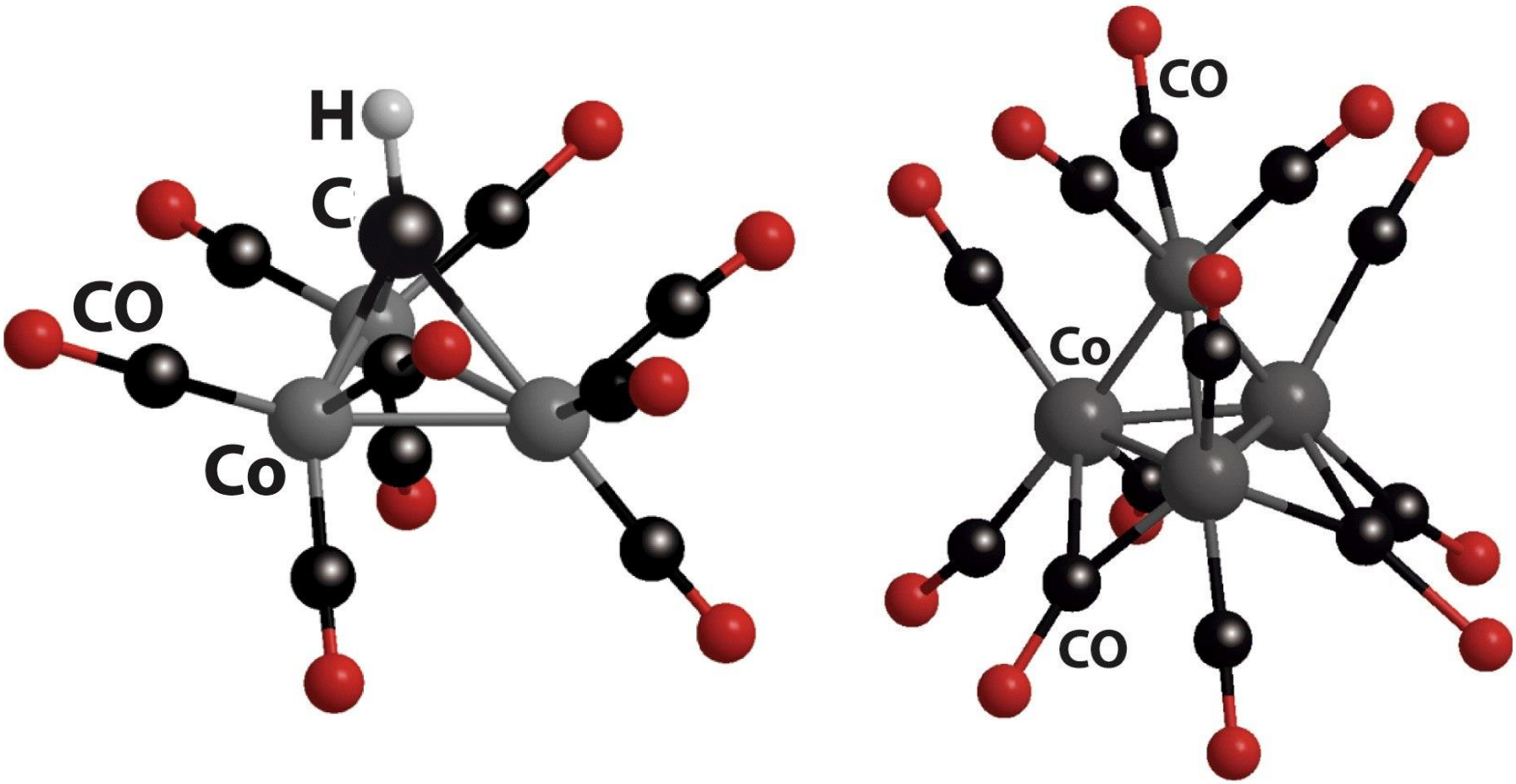
- stessa simmetria
- energie simili
- stessa occupazione elettronica

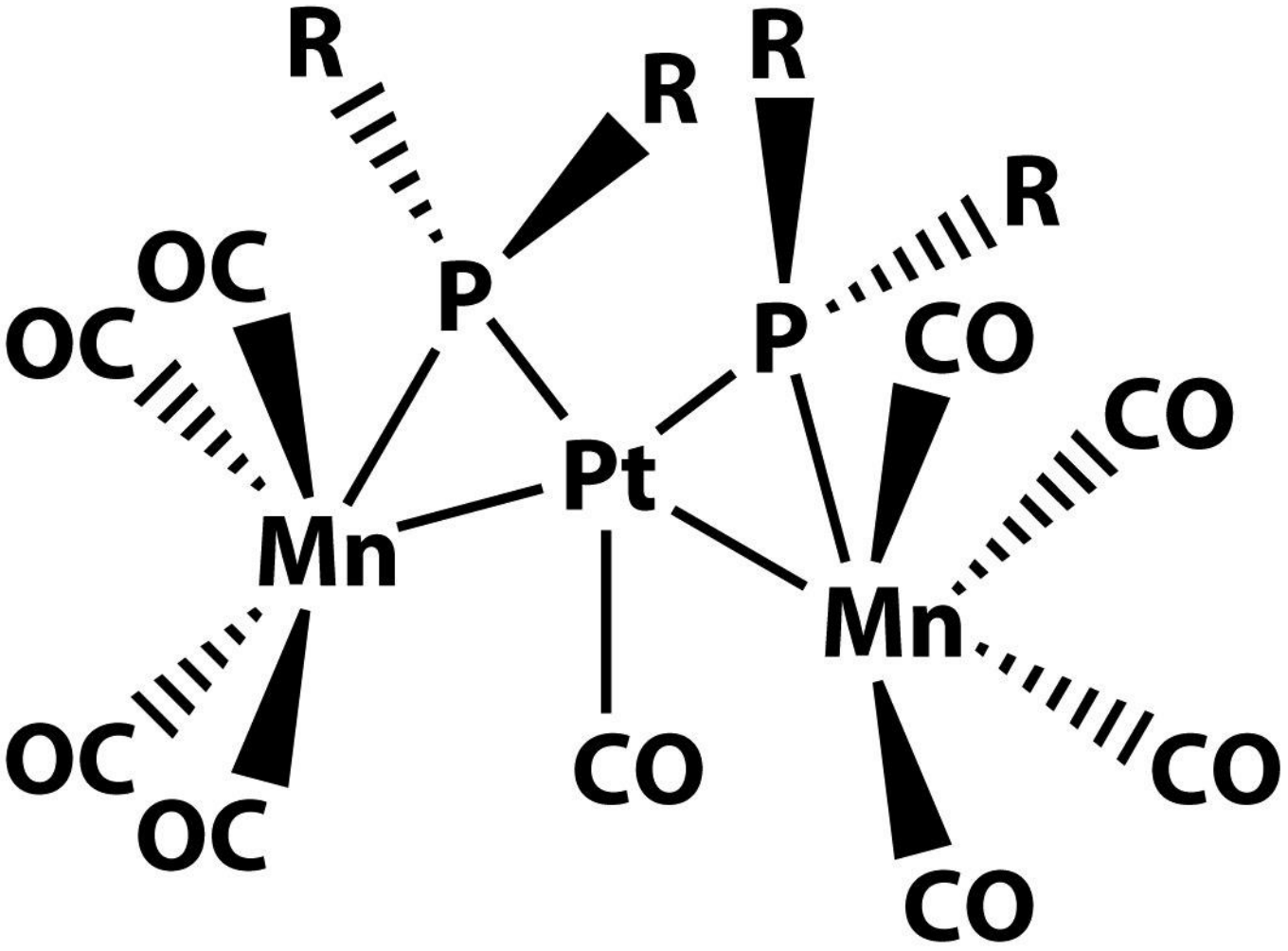
Table 21.10 Selected isolobal fragments

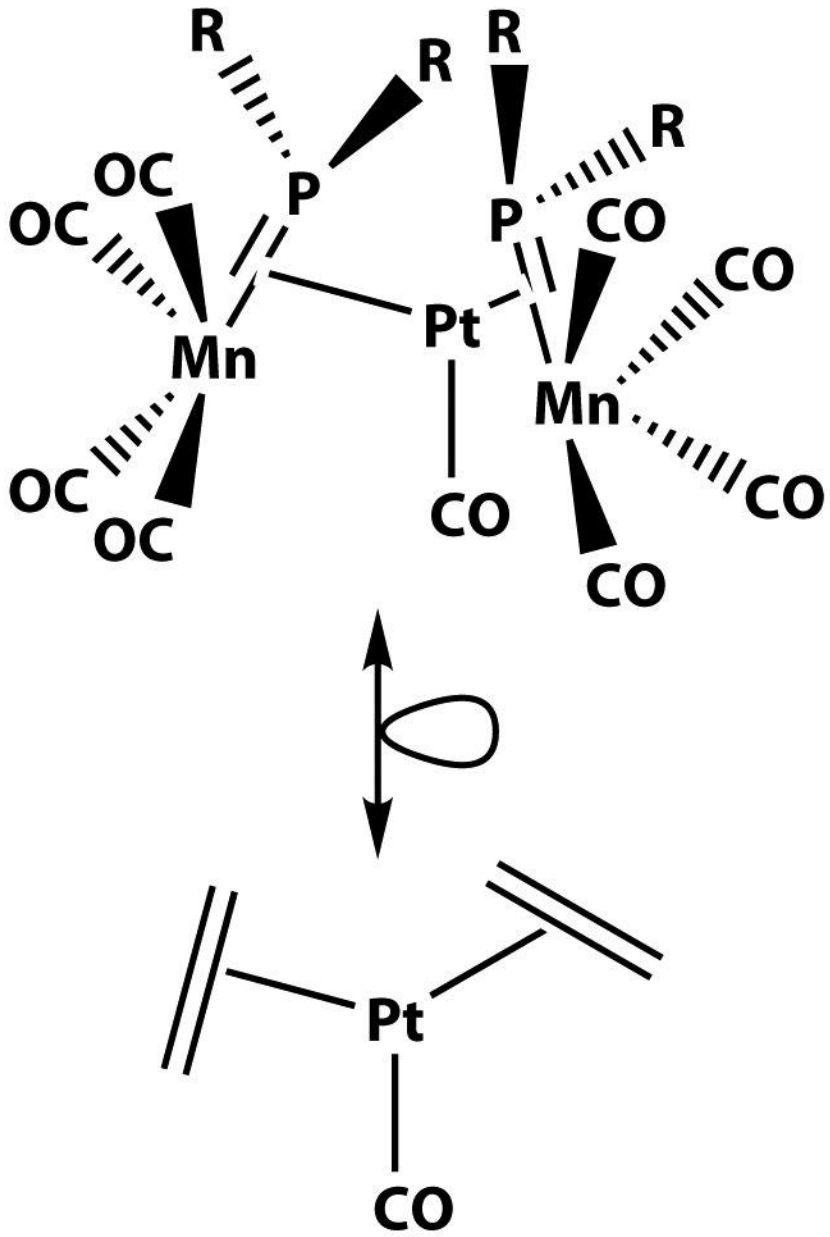


Note that electrons can be added to or subtracted from each member of the isolobal group and still maintain isolobality. For example, $CH_3^+ \leftrightarrow Mn(CO)_5^+ \leftrightarrow Co(CO)_4$.

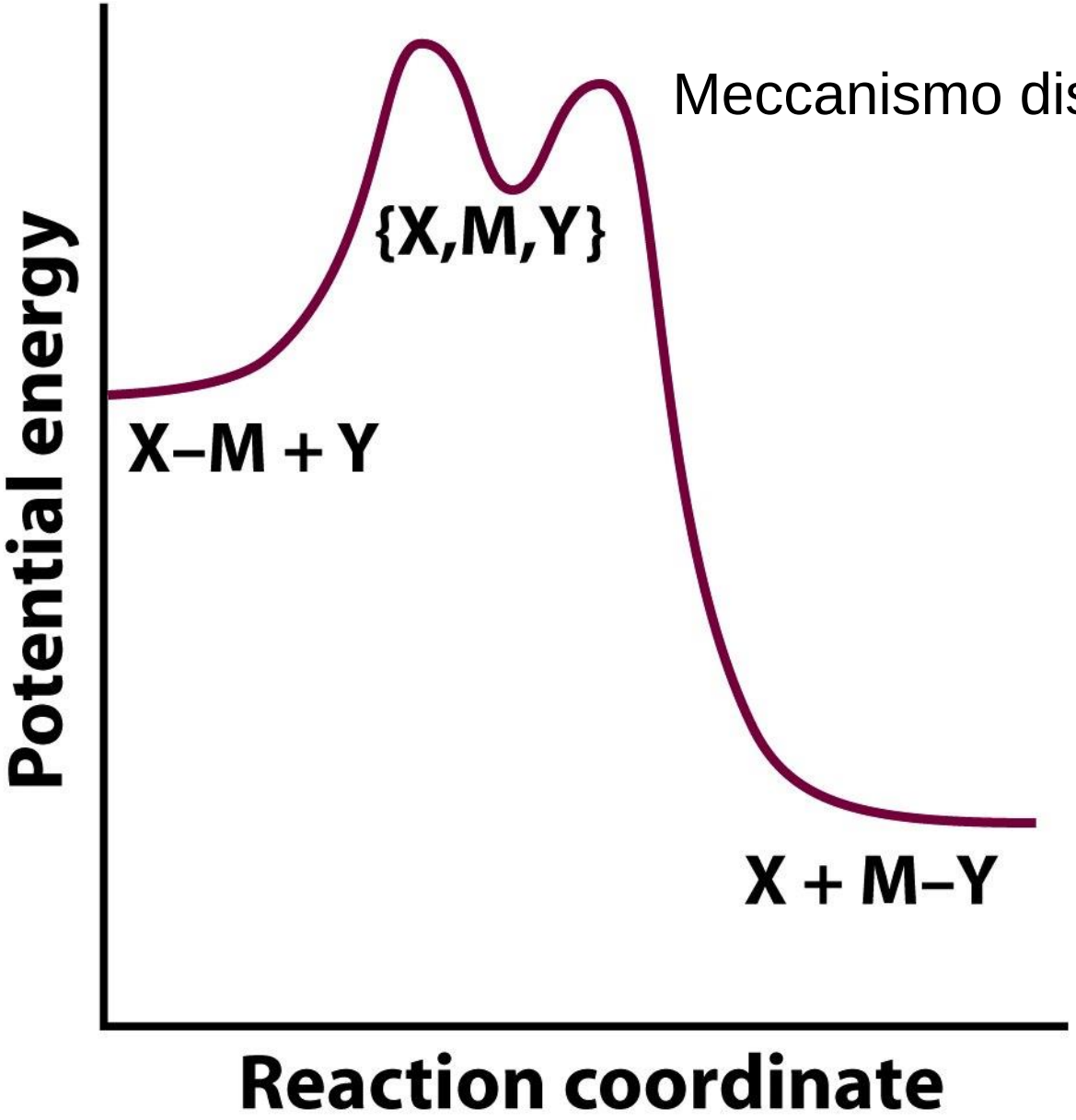
$[Co_3(CH)(CO)_9]$ vs $[Co_4(CO)_{12}]$



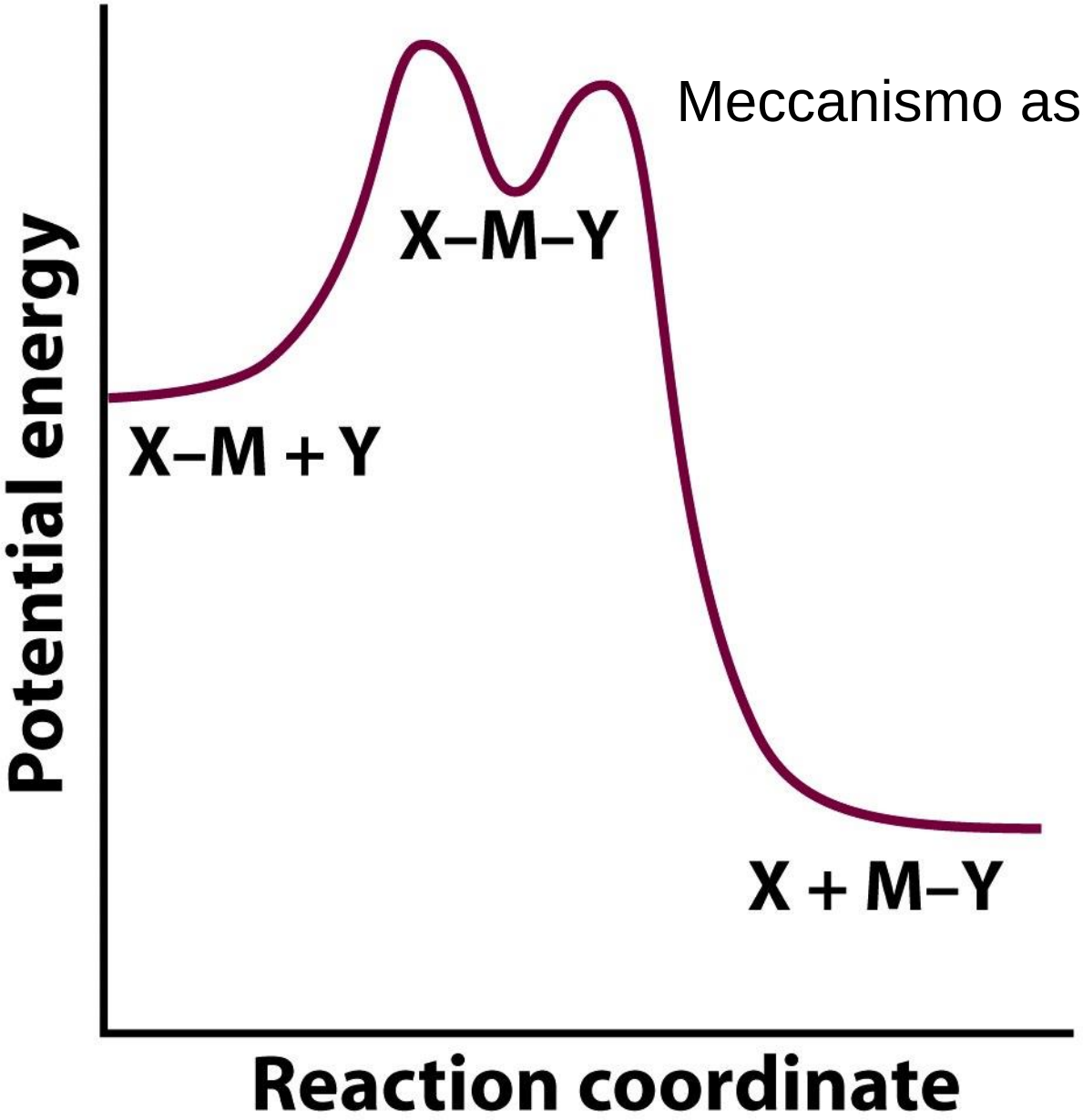

R
R
R
R
P
P
OC
OC
CO
CO
Pt
Mn
Mn
OC
OC
CO
CO
CO

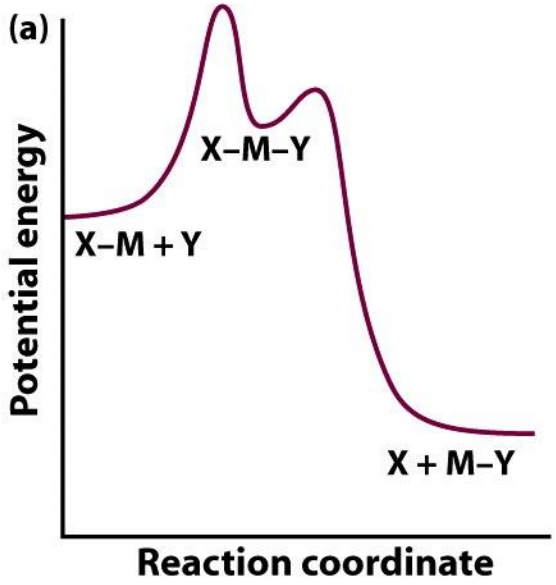

R
R
R
R
P
P
OC
OC
CO
CO
Mn
Pt
Mn
OC
OC
CO
CO
CO
Pt
CO

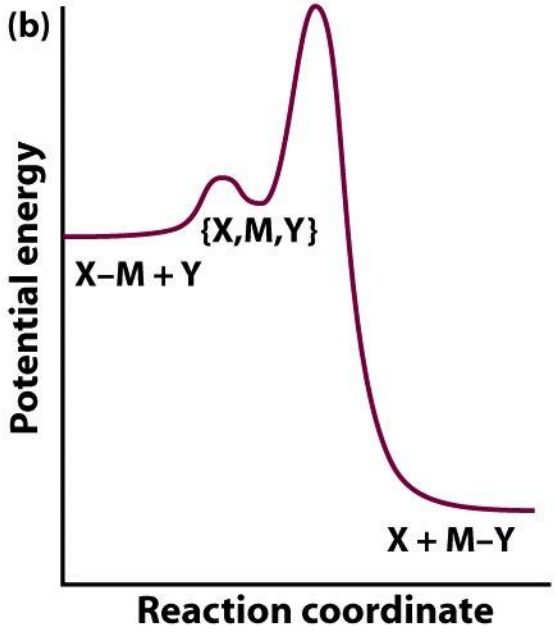
Meccanismo dissociativo



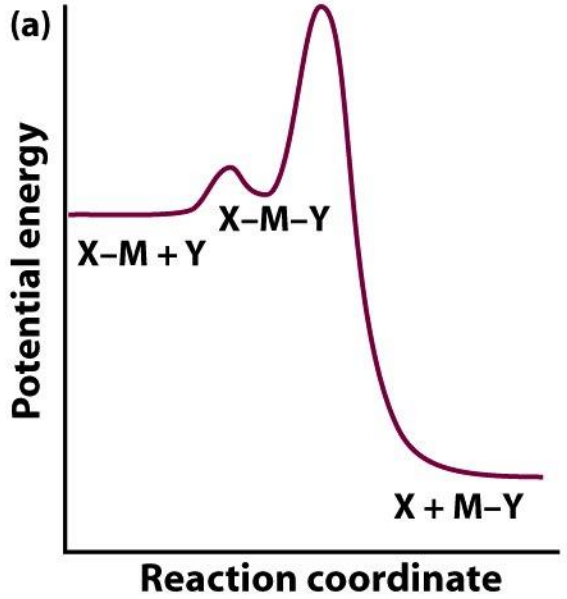
Meccanismo associativo

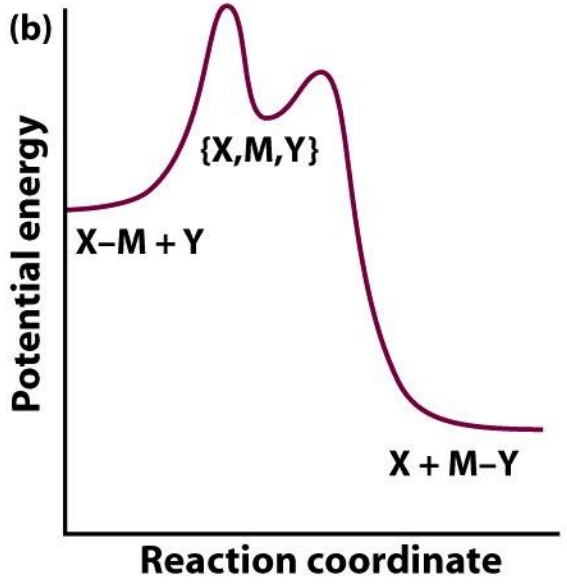






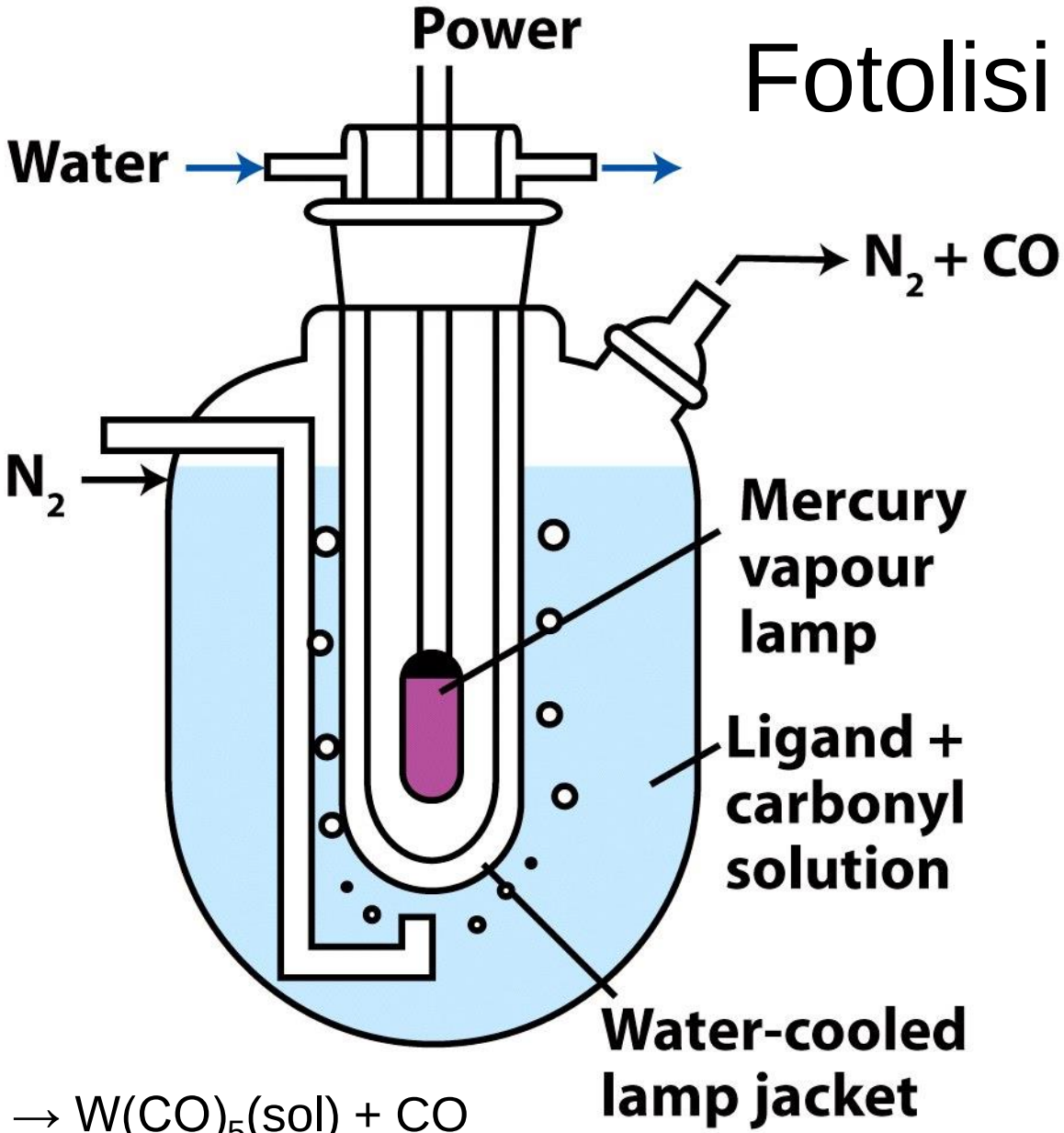
Attivazione di tipo associativo





Attivazione di tipo dissociativo

Fotolisi

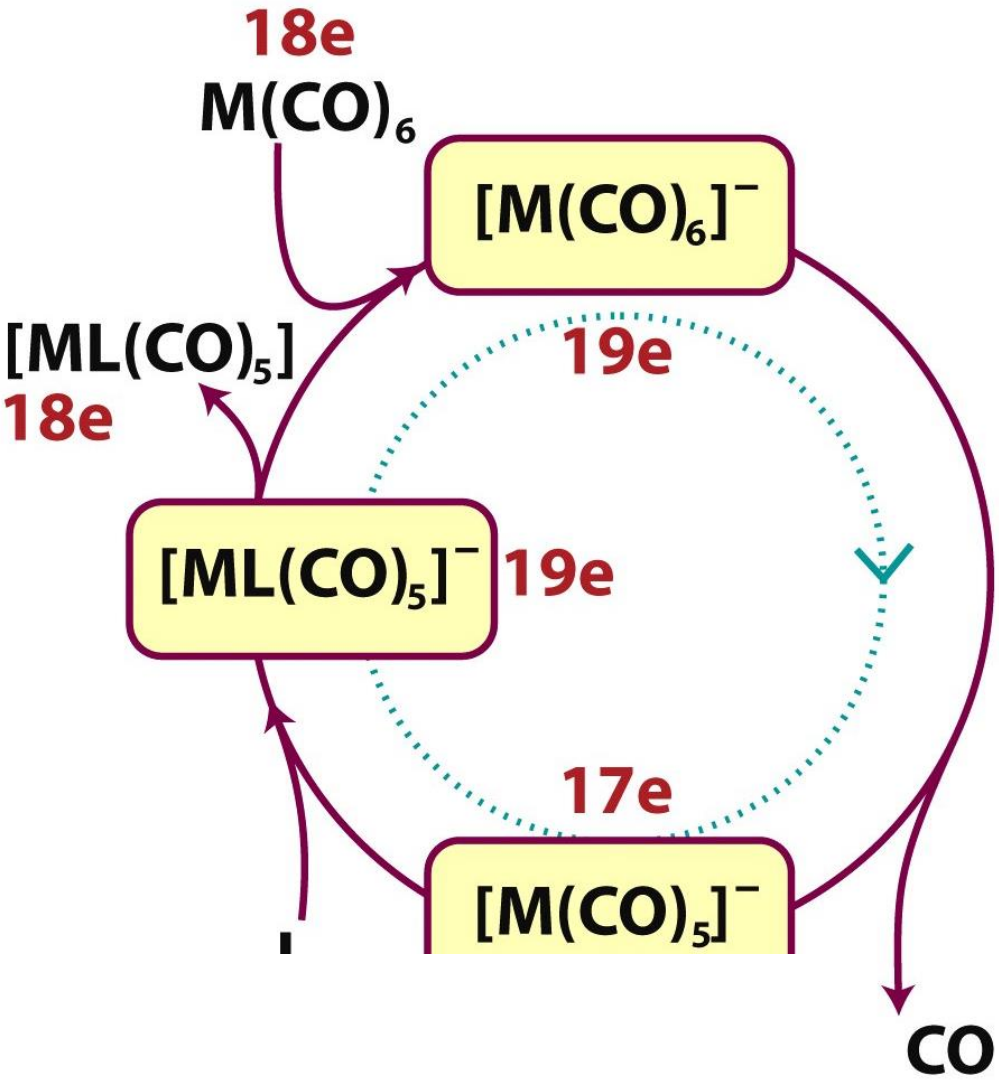


$W(CO)_6$ + sol → $W(CO)_5$(sol) + CO

$W(CO)_5$(sol) + L → $W(CO)_5$L + sol

Sostituzione indotta da un processo redox

aggiunta di quantità catalitica di un riducente monoelettronico

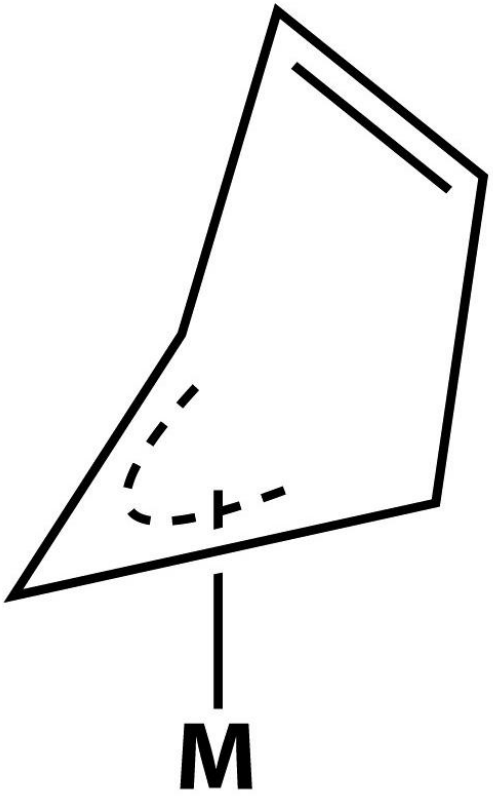


16e: meccanismo associativo

$$[Ir(CO)Cl(PPh_3)_2] + PEt_3 \rightarrow [Ir(CO)Cl(PPh_3)_2(PEt_3)] \rightarrow$$

$$[Ir(CO)Cl(PPh_3)(PEt_3)] + PPh_3$$

Sostituzioni con meccanismo associativo in complessi con 18 elettroni



$[V(CO)_5(NO)] + PPh_3 \rightarrow [V(CO)_4(NO)(PPh_3)] + CO$

$[Re(\eta^5\text{-}Cp)(CO)_3] + PPh_3 \rightarrow [Re(\eta^5\text{-}Cp)(CO)_2(PPh_3)] + CO$

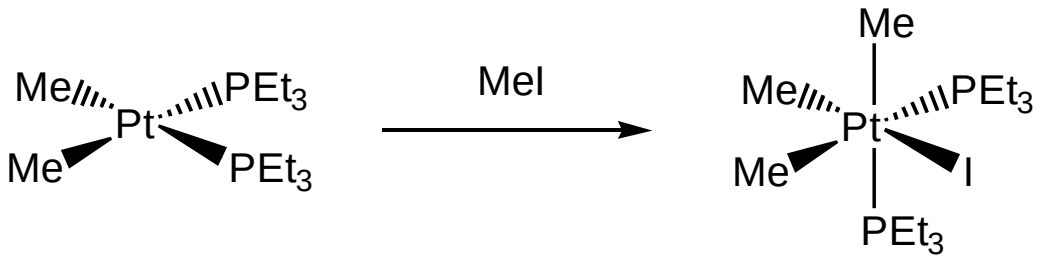
Sostituzione dei leganti in un cluster

$$3[Fe_3(CO)_{12}] + 6PPh_3 \rightarrow$$

$$[Fe_3(CO)_{11}(PPh_3)] + [Fe_3(CO)_{10}(PPh_3)_2] + [Fe(CO)_5] + [Fe(CO)_4(PPh_3)] + [Fe(CO)_3(PPh_3)_2] + 3CO$$

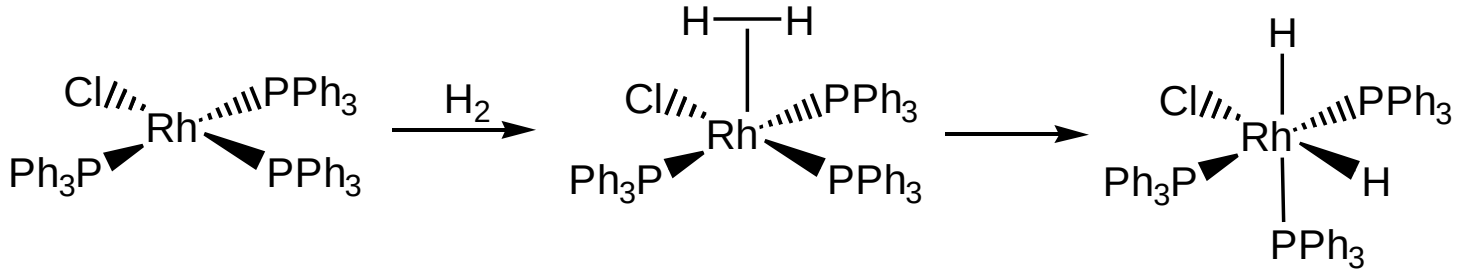
La stabilità dei legami metallo-metallo, e quindi dei cluster, aumenta scendendo in un gruppo.

Addizione ossidativa



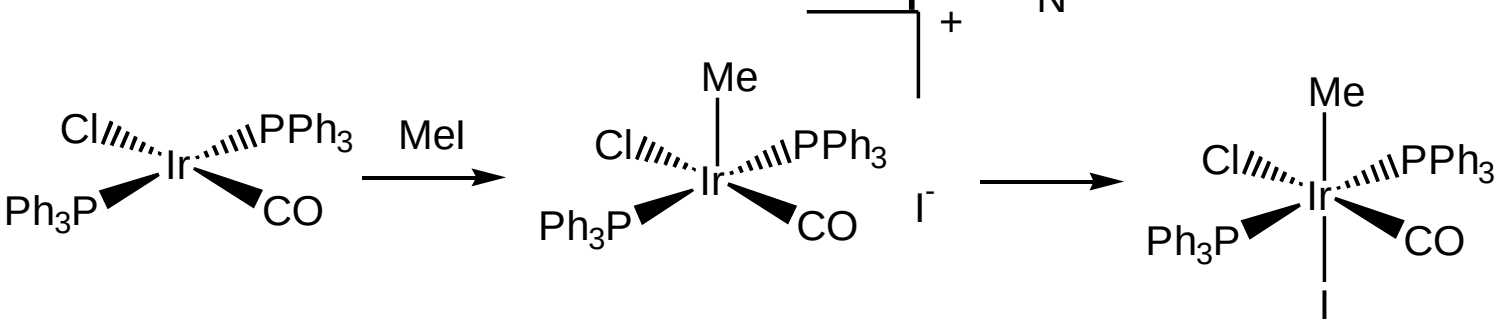
16e Pt(II) 18e Pt(IV)

Meccanismo concertato



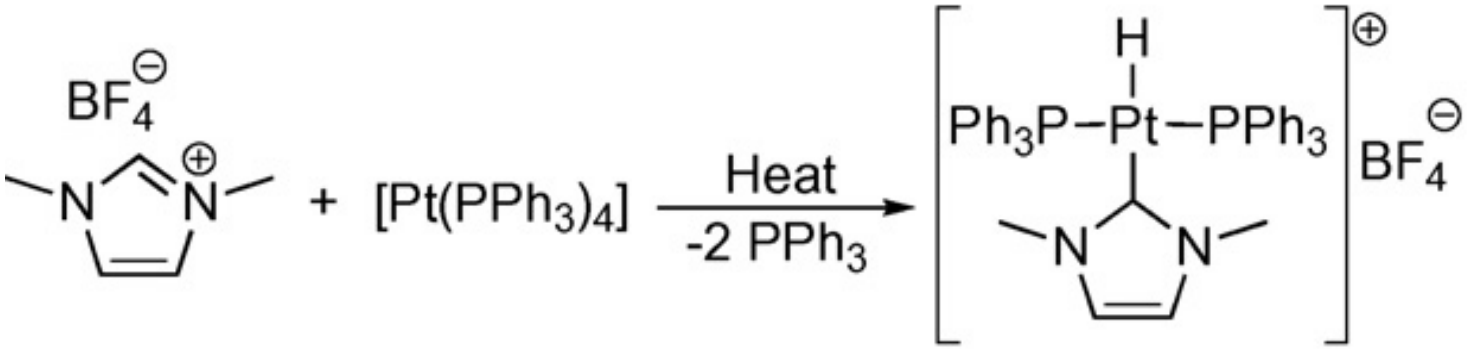
16e Rh(I) 18e Rh(I) 18e Rh(III)

Meccanismo di tipo S_N2

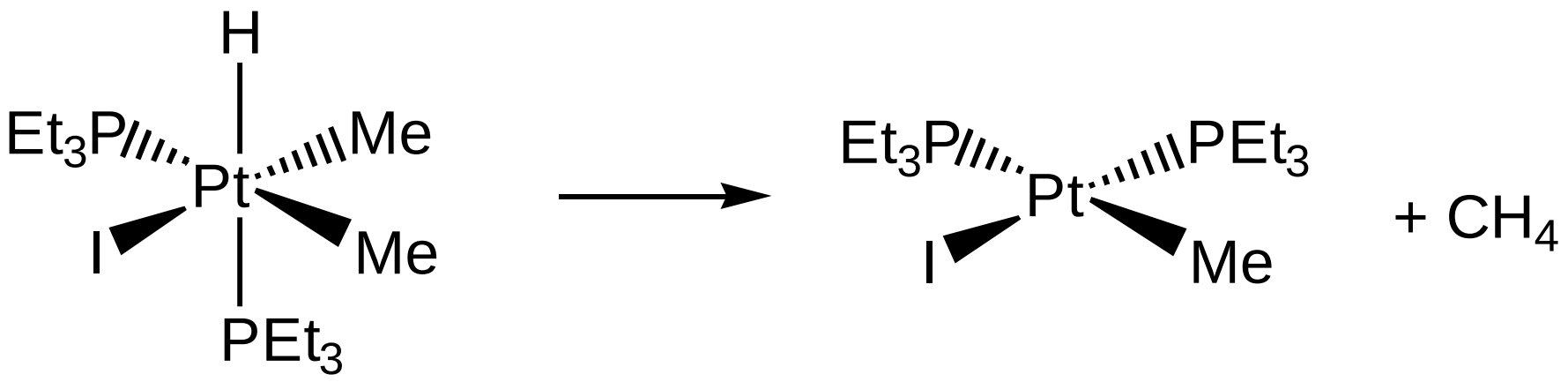


Caso anomalo di addizione ossidativa

addizione ossidativa di sali di imidazolio su precursori zerovalenti



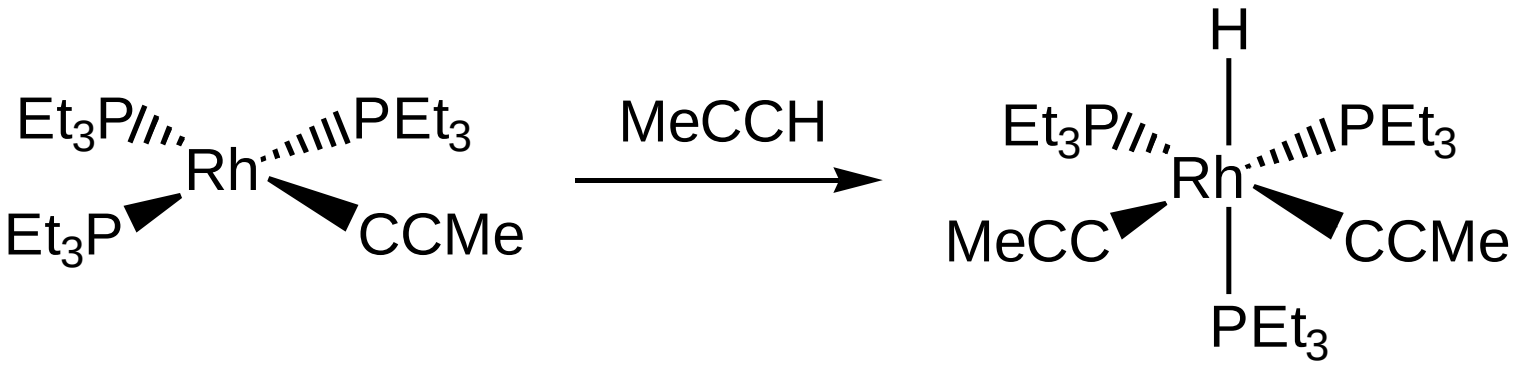
Eliminazione riduttiva

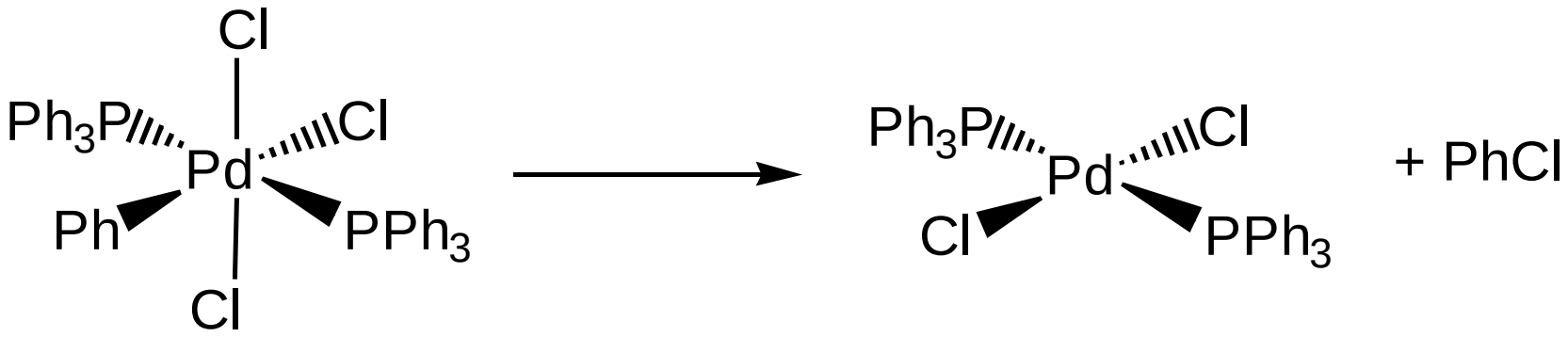


18e Pt(IV)

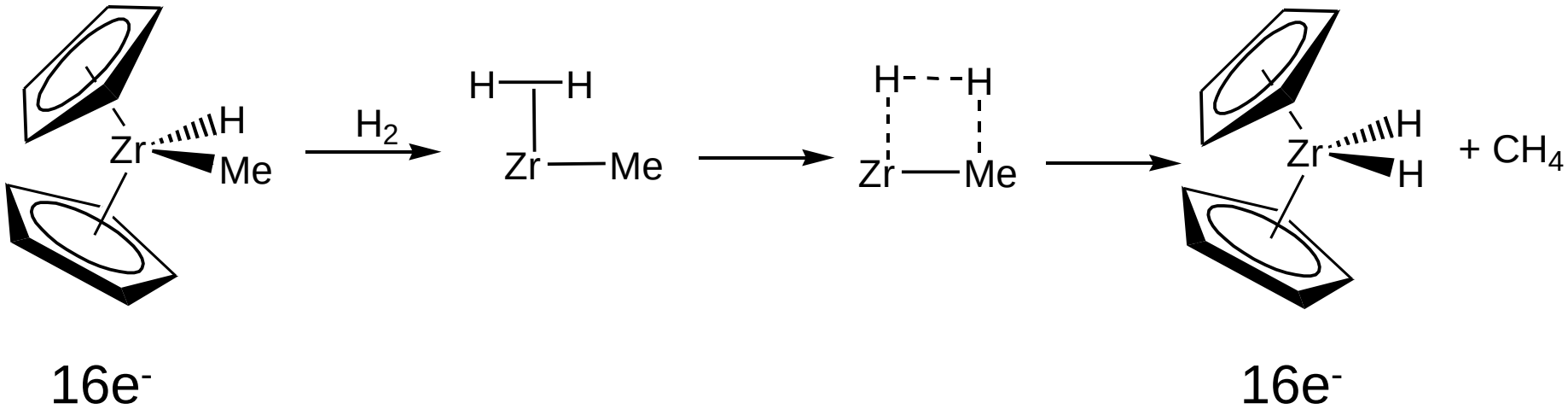
16e Pt(II)

Esempi


Et3P
PEt3
Rh
Et3P
CCMe
MeCCH
H
Et3P
PEt3
Rh
MeCC
CCMe
PEt3


Cl
Ph3P
Cl
Pd
Ph
PPh3
Cl
Ph3P
Cl
Pd
Cl
PPh3
+ PhCl

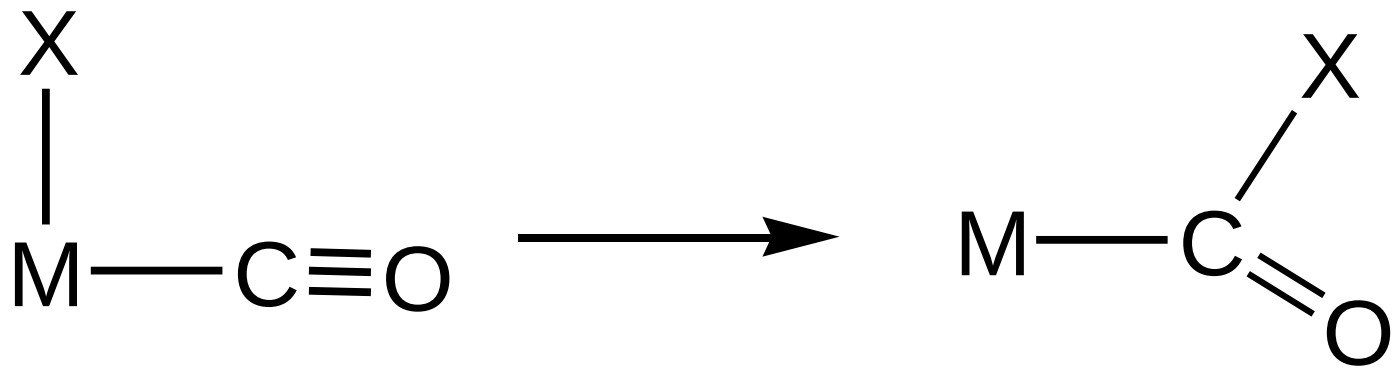
Metatesi di legame σ



16e-

16e-

Inserzione migratoria 1,1

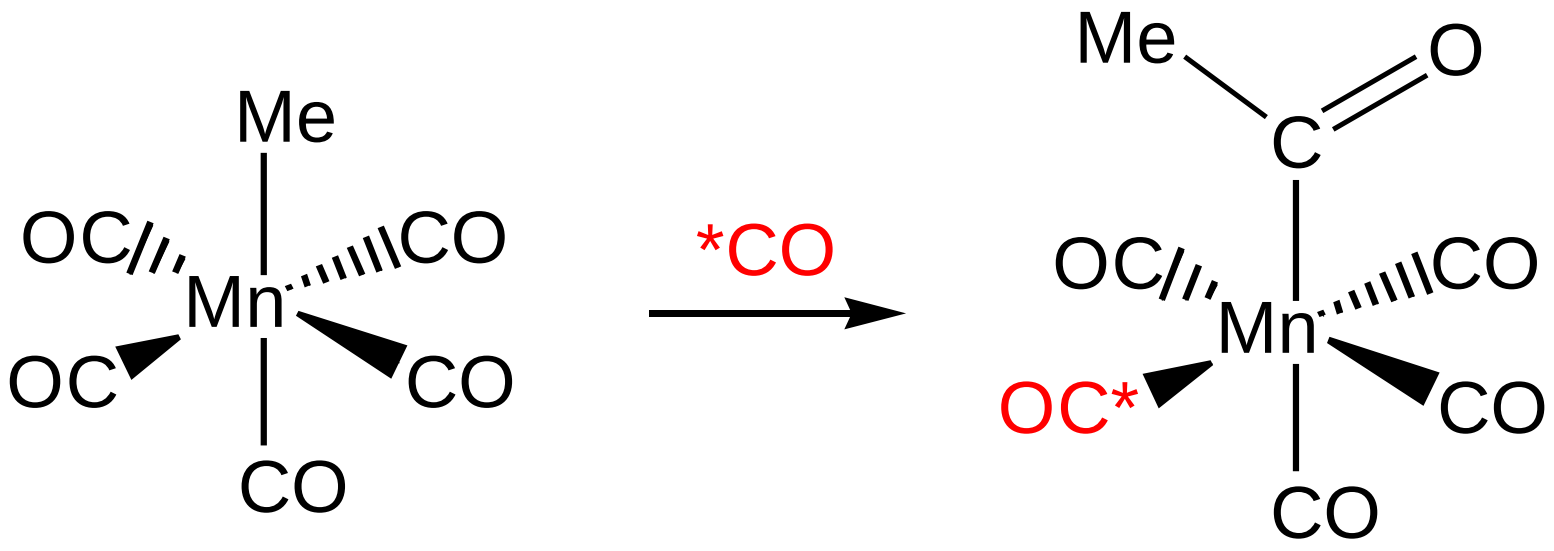


X = H, R, Ar

$[Mn(CH_3)(CO)_5] + PPh_3 \rightarrow [Mn(CH_3CO)(CO)_4(PPh_3)]$

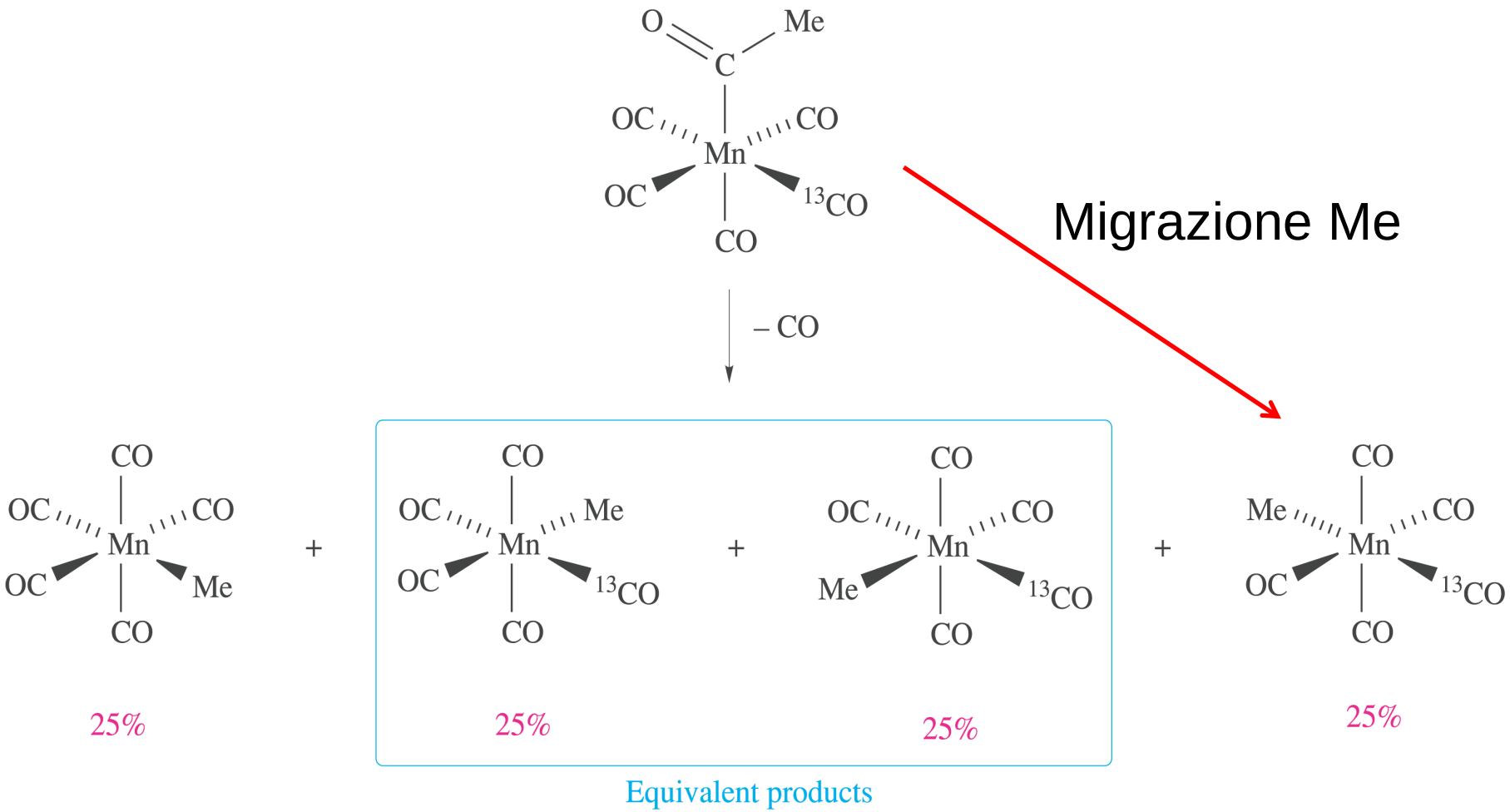
Migrazione di X su C o inserzione di CO nel legame M–X?

Meccanismo dell'inserzione migratoria 1,1



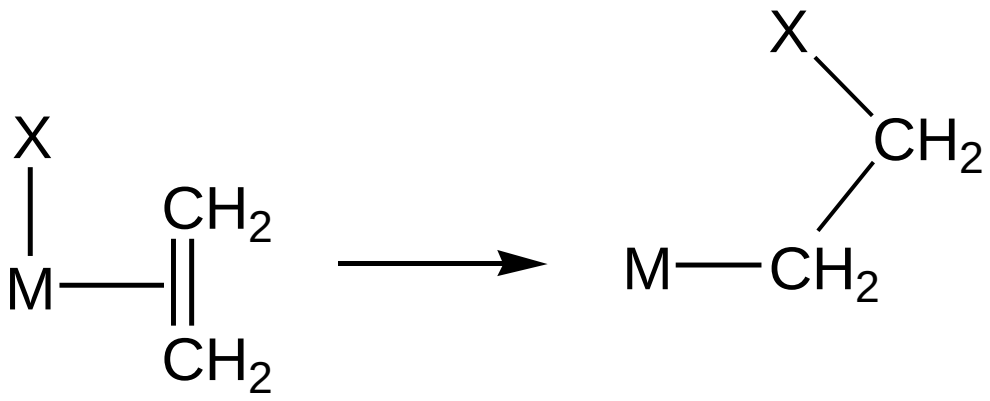
Reazione inversa

cis-[Mn(CH_3CO)$(CO)_4$($^*CO$)] → [Mn(CH_3)$(CO)_5$] + $^*CO$

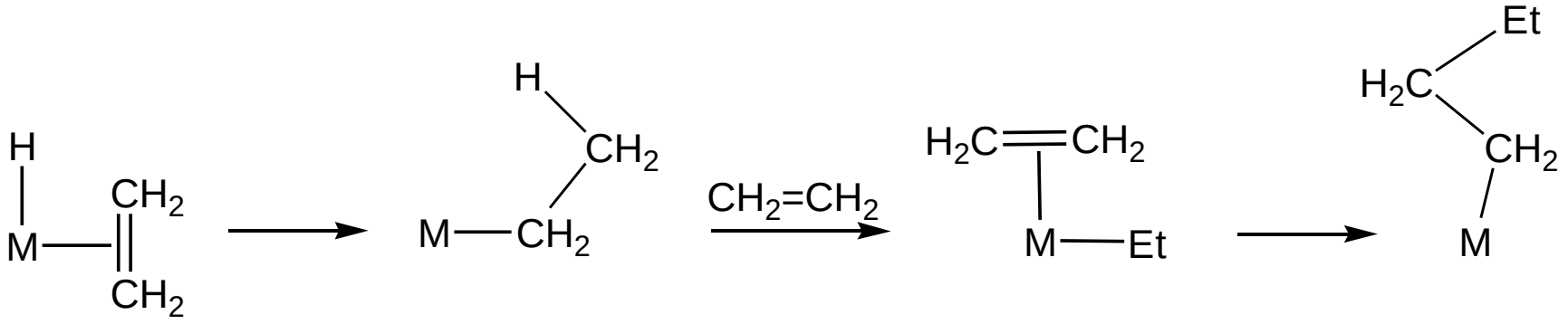

O
Me
C
OC
CO
Mn
OC
13CO
CO
– CO
Migrazione Me
CO
OC
CO
Mn
OC
Me
CO
25%
+
CO
OC
Me
Mn
OC
13CO
CO
25%
+
CO
OC
CO
Mn
Me
13CO
CO
25%
+
CO
Me
CO
Mn
OC
13CO
CO
25%
Equivalent products

Inserzione 1,2

con leganti coordinati η^2

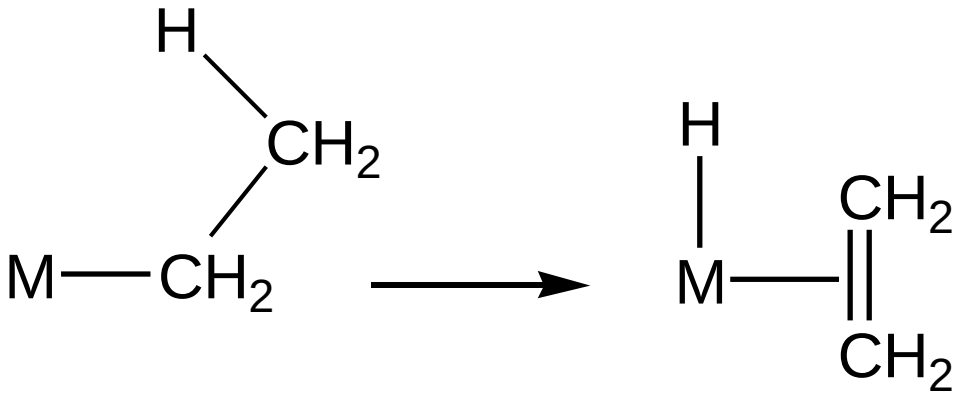


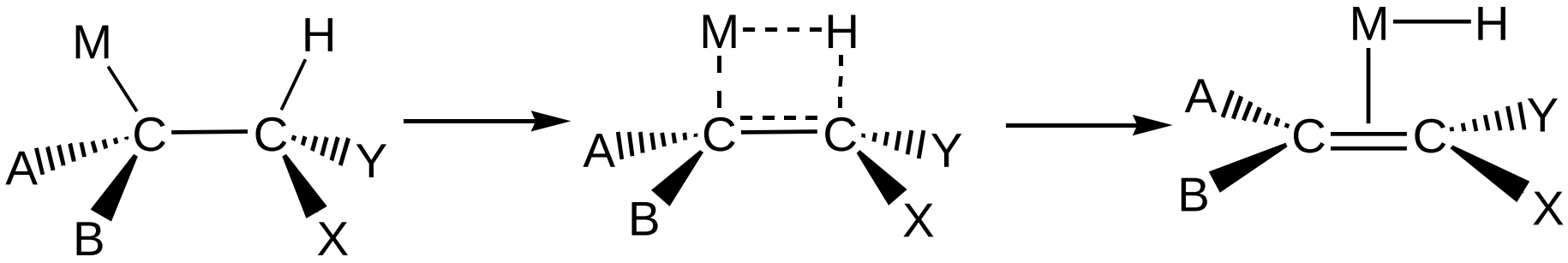
X = H, R, Ar



Formazione di polietilene

β-eliminazione di idruro





Intermedio *syn*

Isomerizzazione di alcheni