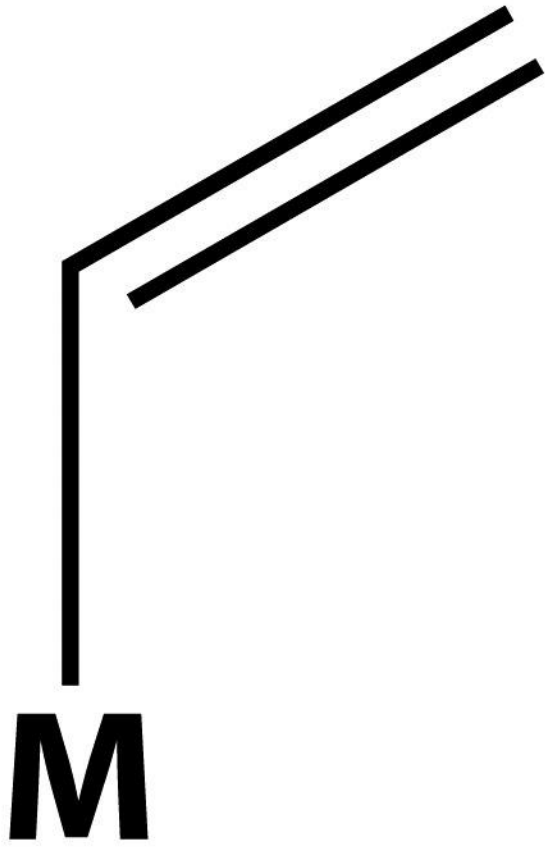
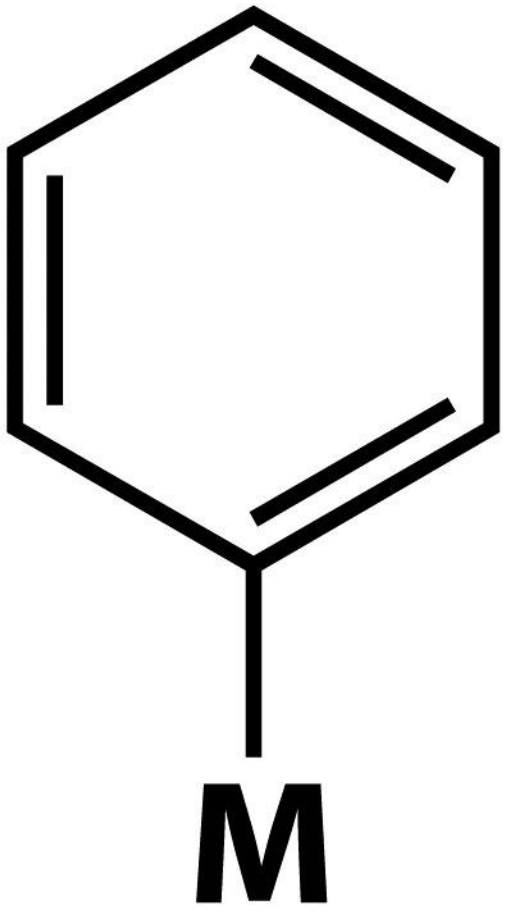


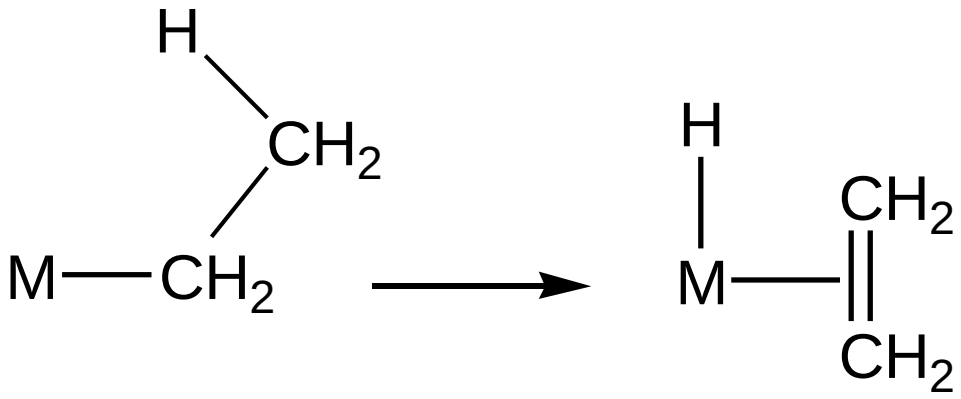
η^1-alchenile

η^1-alchinile



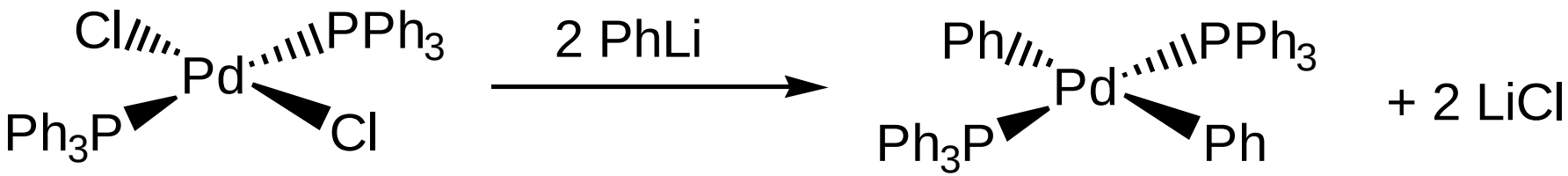
η^1-arile

β-eliminazione di idruro

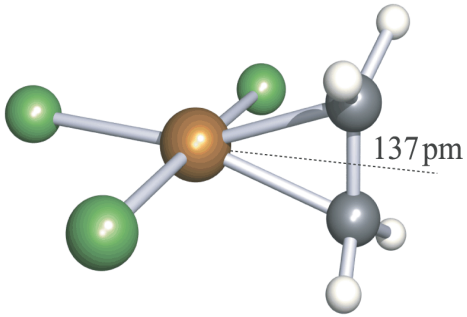


Gruppi stabili:
metile, benzile ($CH_2C_6H_5$), neopentile (CH_2CMe_3), e trimetilsililmetile (CH_2SiMe_3)

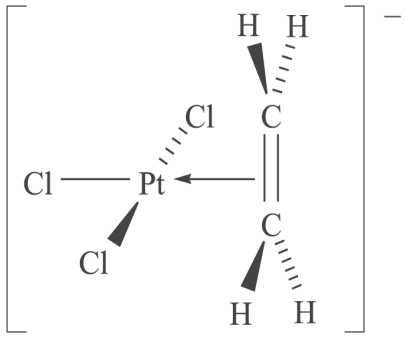
Tipico processo di sintesi



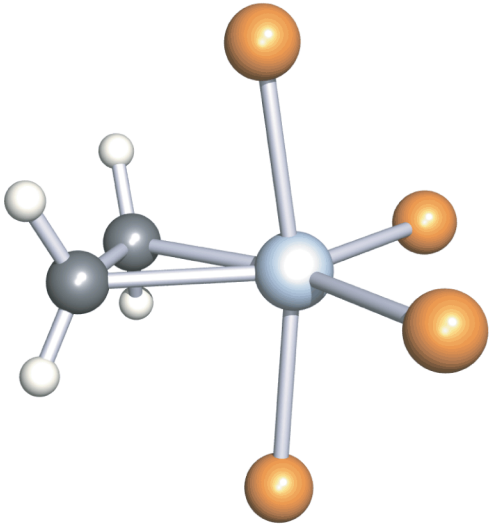
In alternativa si usano reattivi di Grignard



C−C = 137 pm *vs* 134 pm nell'etene



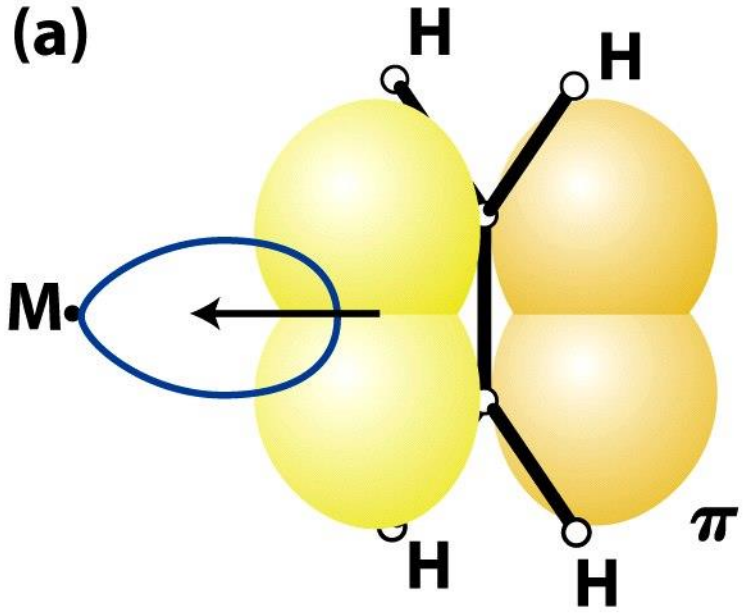
η^2-alchene coordinazione *side-on*



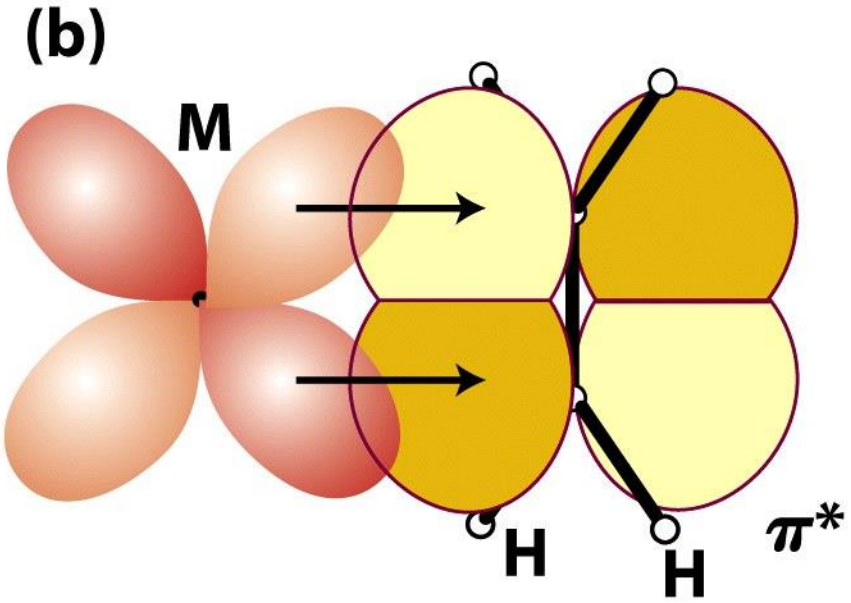
metallaciclopropano

Struttura ai raggi-X di $Ru(\eta^2\text{-}C_2H_4)(PMe_3)_4$

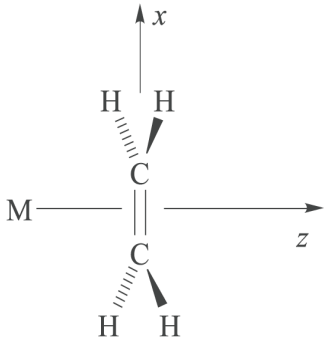
C−C = 144 pm *vs* 134 pm nell'etene

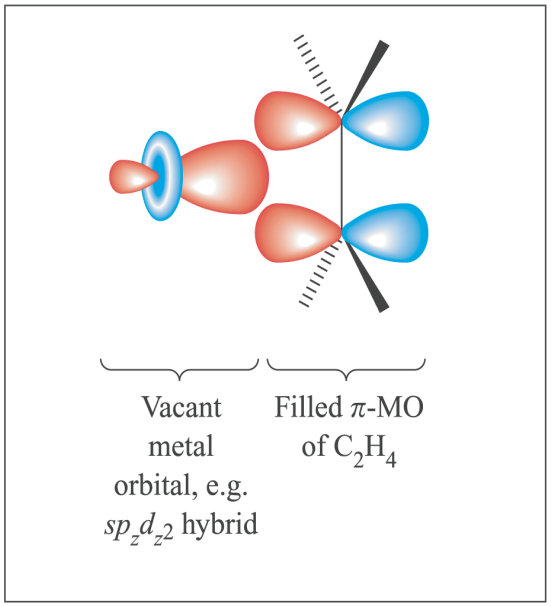


Orbitale di simmetria π per l'etene isolato, ma di simmetria σ quando l'etene è coordinato η^2, cioè *side-on*

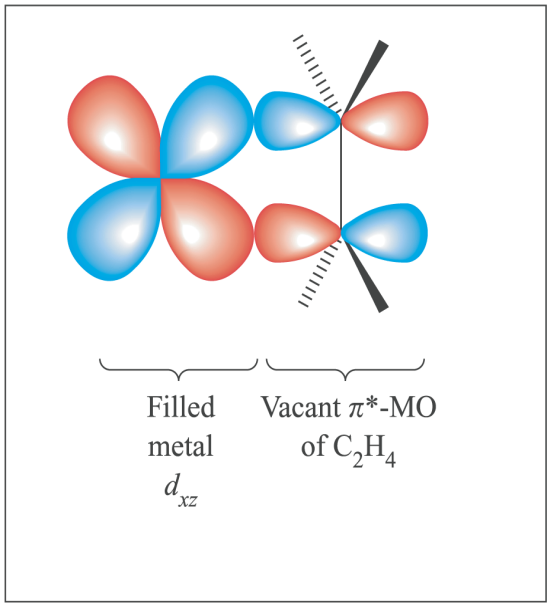


modello di Dewar – Chatt – Duncanson





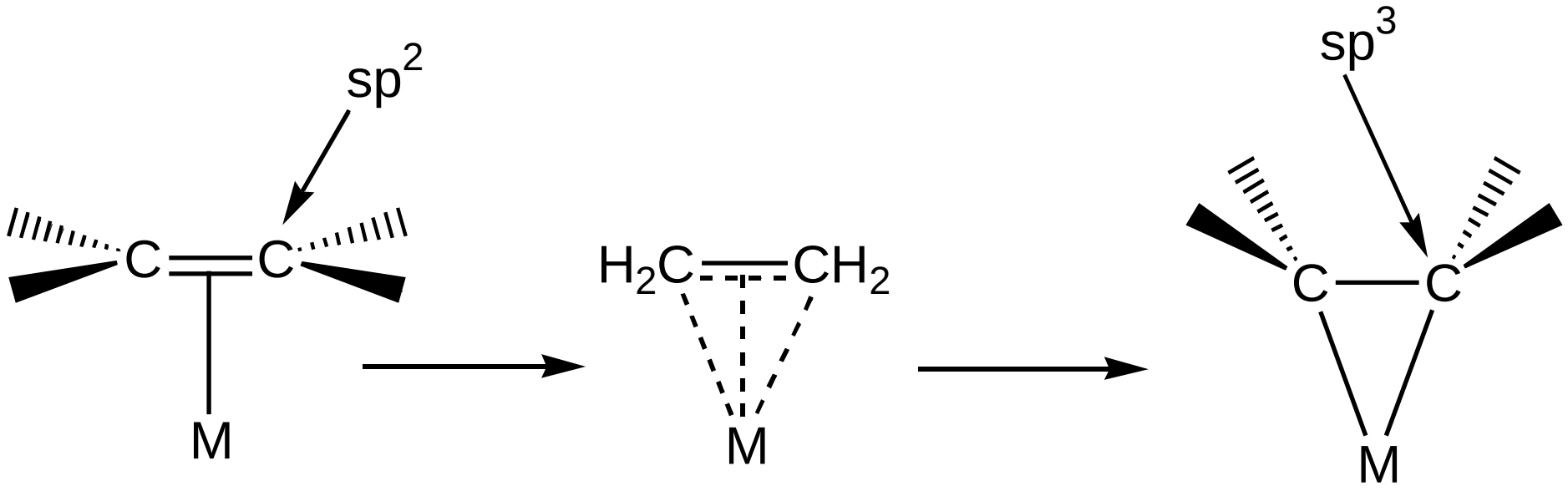
Alkene-to-M donation
(a)



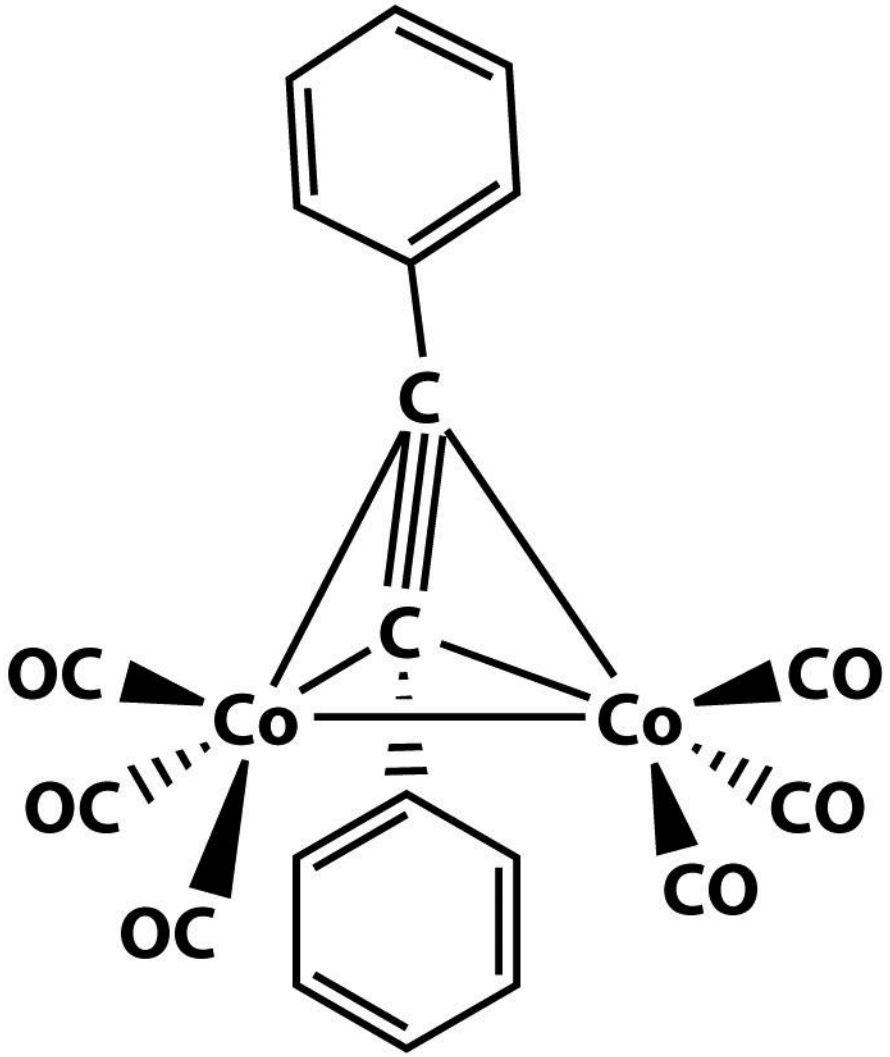
M-to-alkene back-donation
(b)

modello di Dewar – Chatt – Duncanson

Retrodonazione π

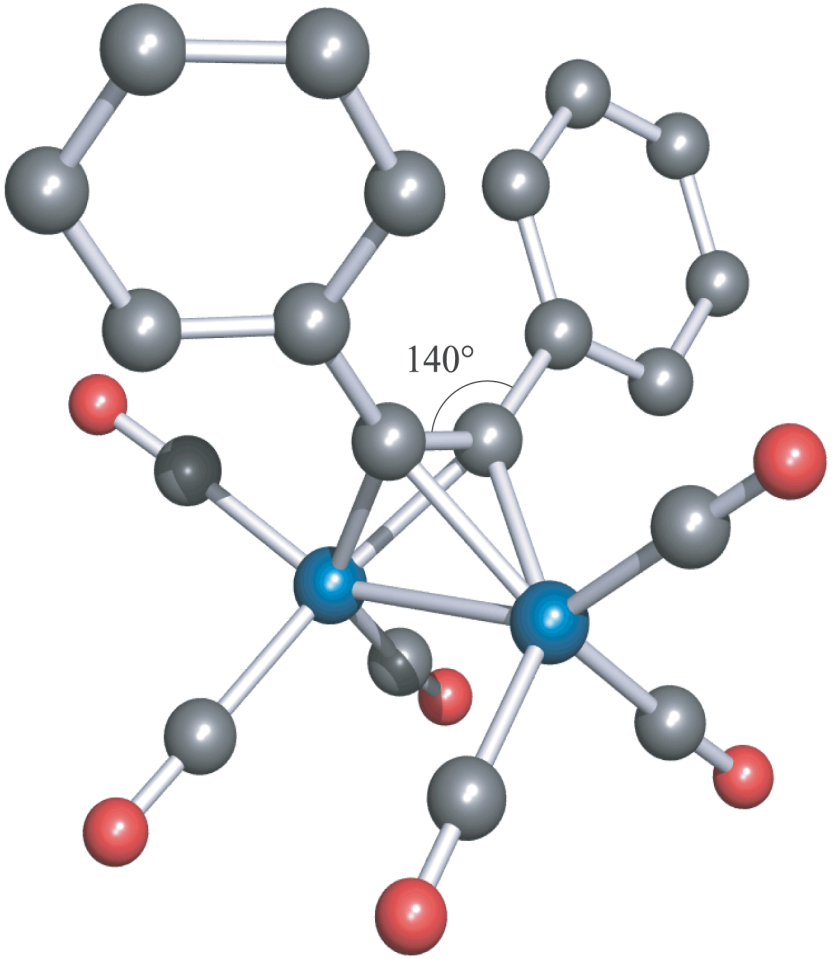


metallociclopropano



$[Co_2(PhC{\equiv}CPh)(CO)_6]$

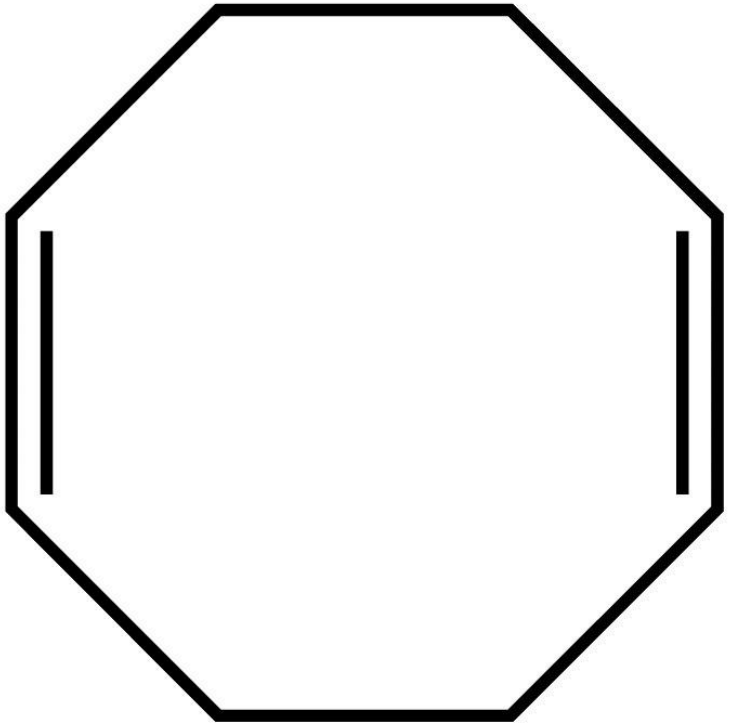
4-electron donor



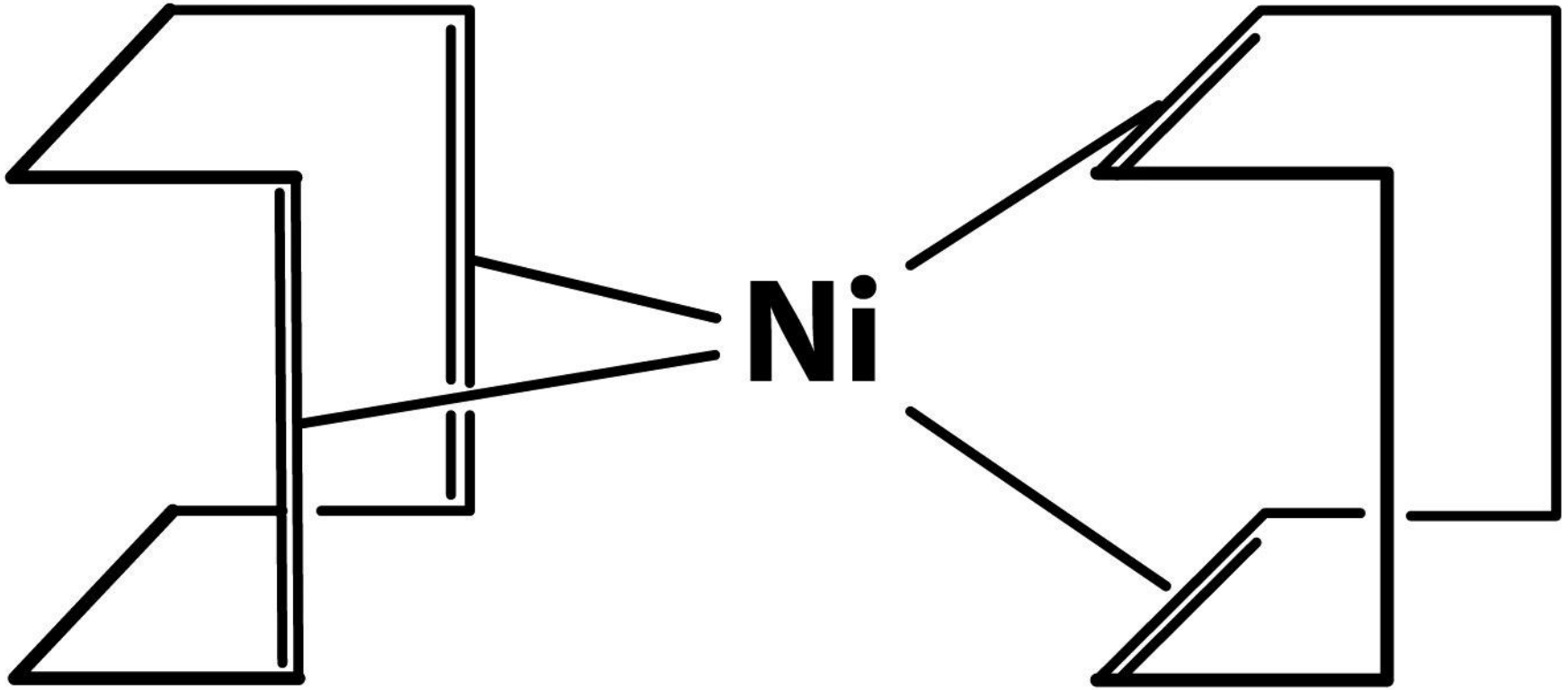
C—C in Co_2C_2-unit = 136 pm *vs* 120 pm in C_2Ph_2

I due piani C_2Co, cioè i due legami η^2, sono circa ortogonali

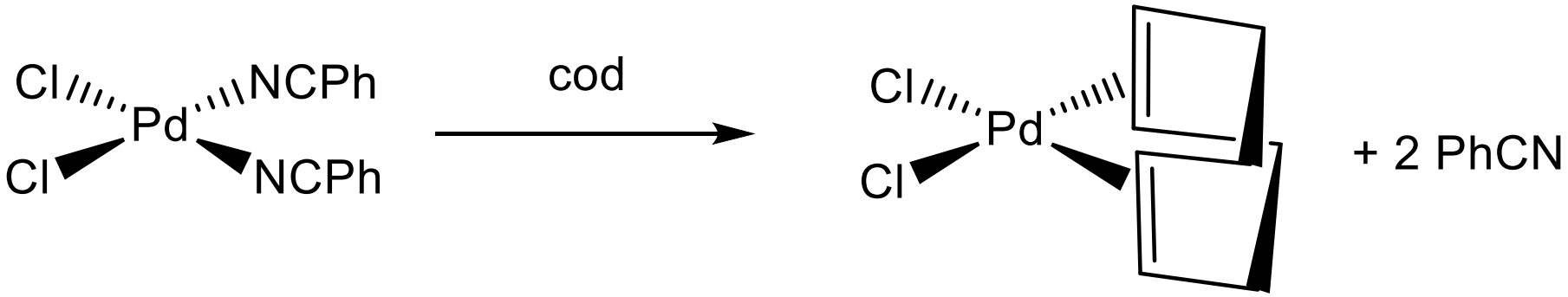
Dieni non-coniugati



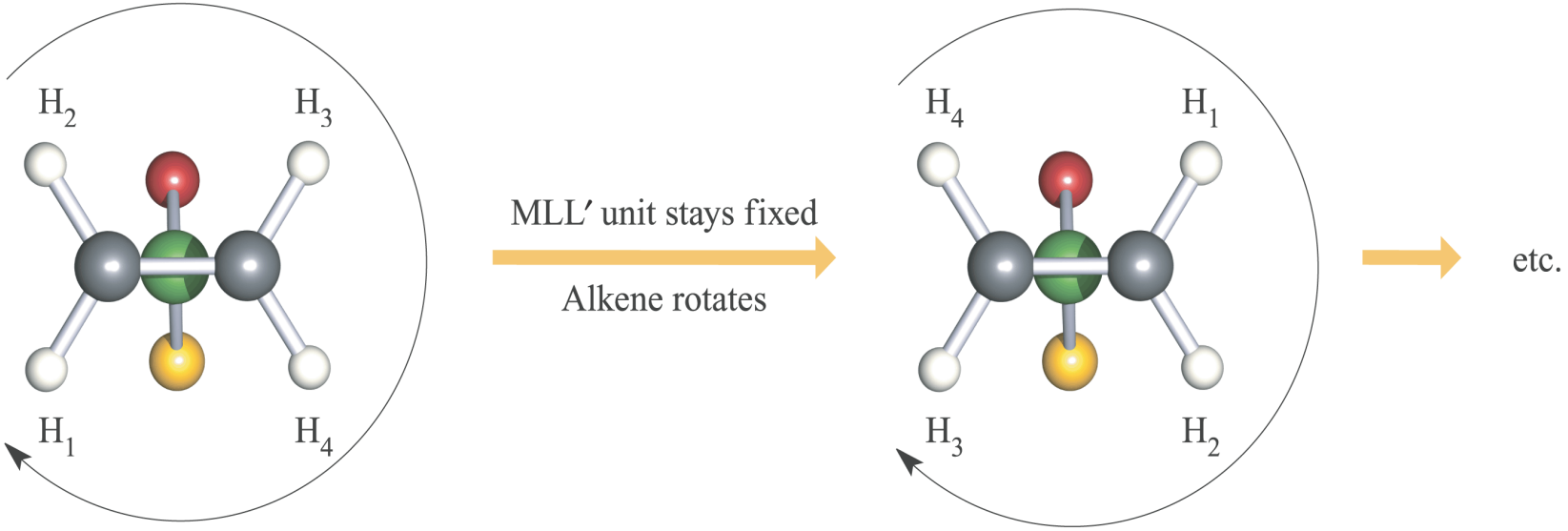
Cycloocta-1,5-diene, cod



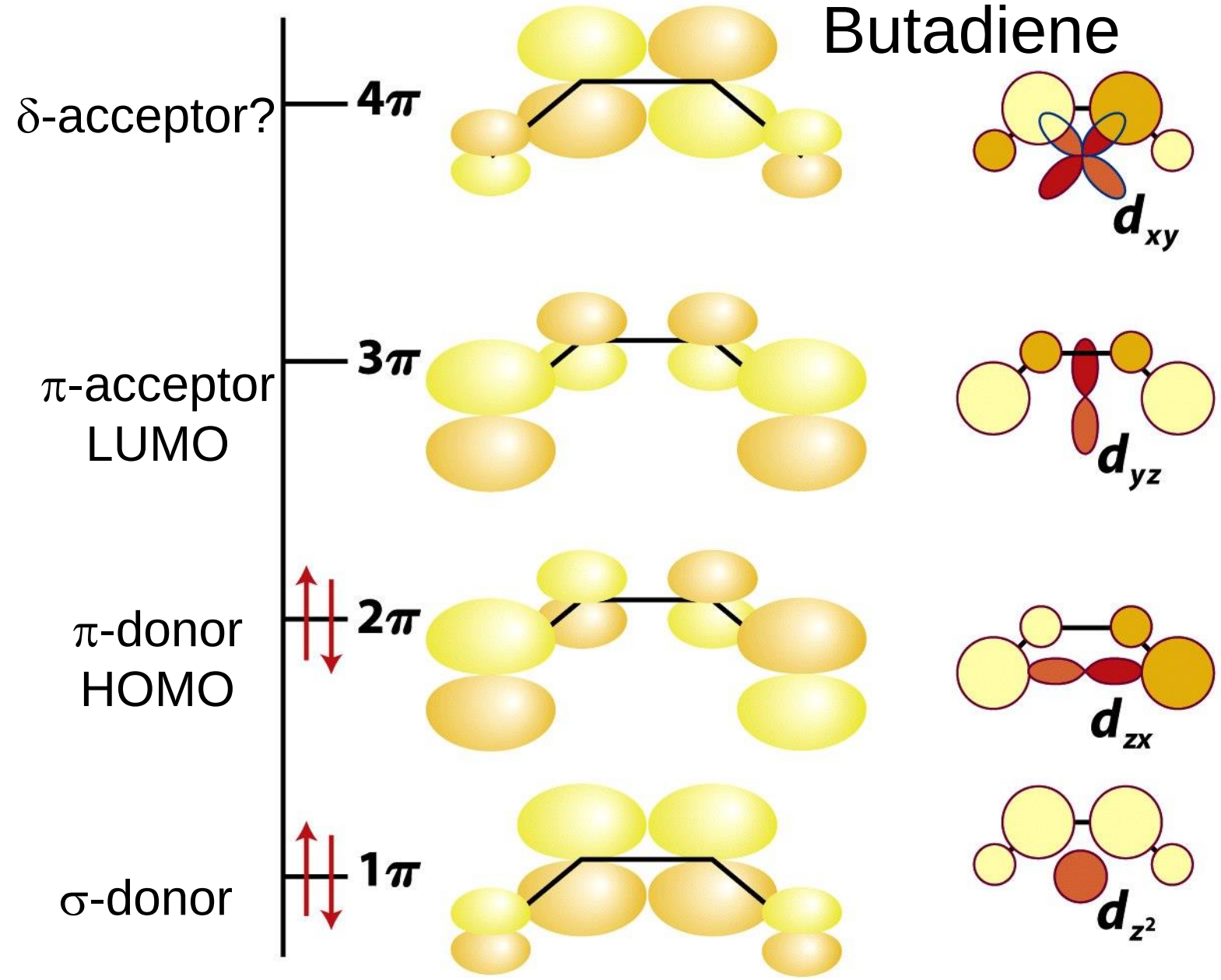
$Ni(cod)_2$


Cl
Pd
NCPh
Cl
NCPh
cod
Cl
Pd
Cl
+ 2 PhCN

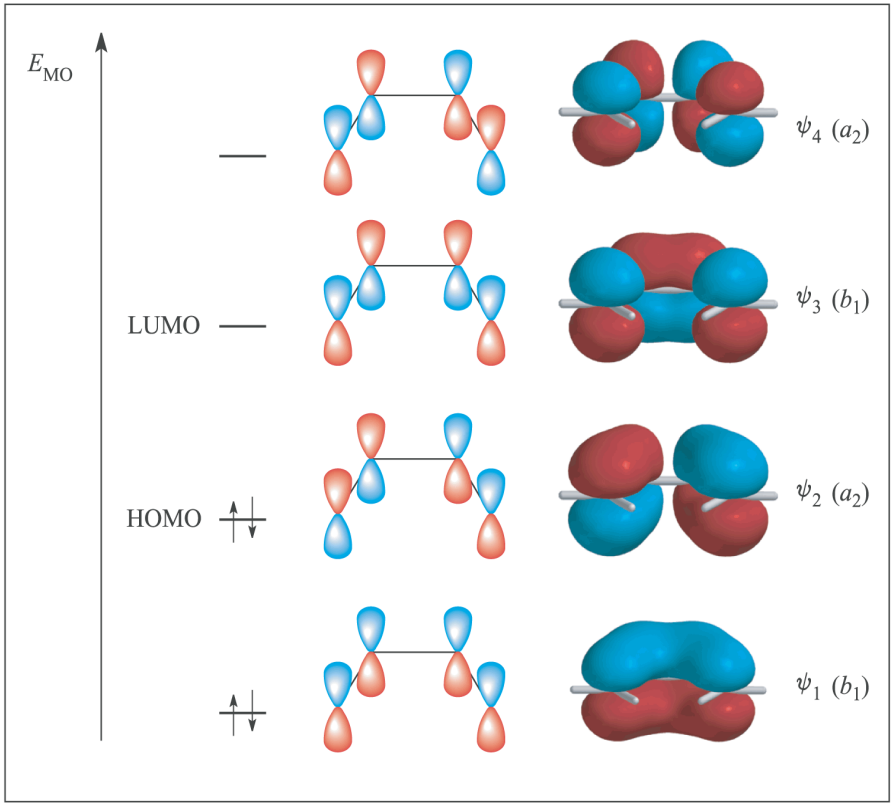
Flussionalità del legame η^2-alchene



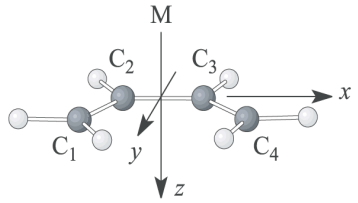
Butadiene

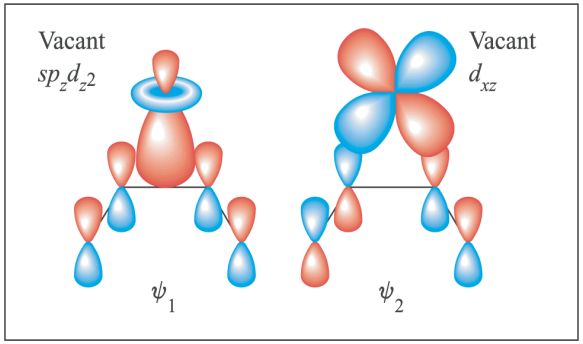


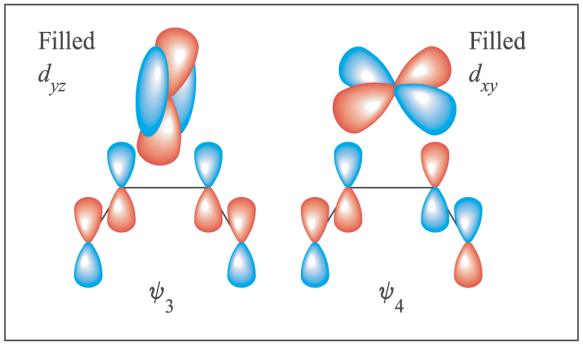
Il butadiene giace nel piano *xy*, sopra al metallo


E_{MO}
LUMO
HOMO
ψ_4 (a_2)
ψ_3 (b_1)
ψ_2 (a_2)
ψ_1 (b_1)

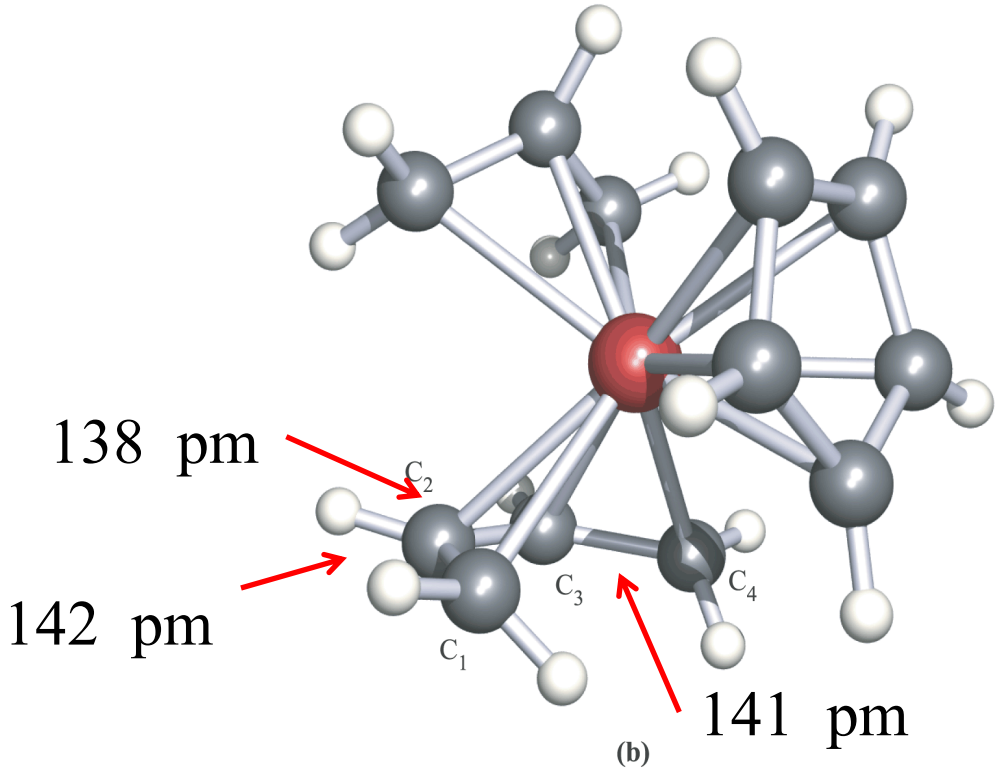
(a)

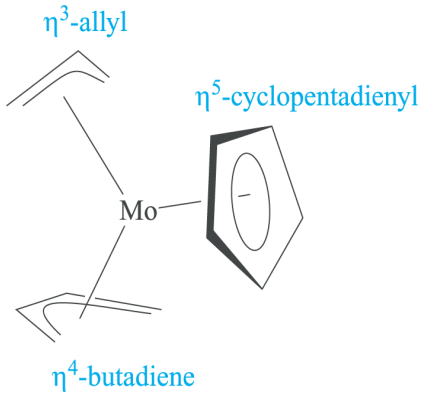

M
C_2
C_3
C_1
C_4
x
y
z


Vacant
sp_zd_z2
Vacant
d_{xz}
ψ_1
ψ_2

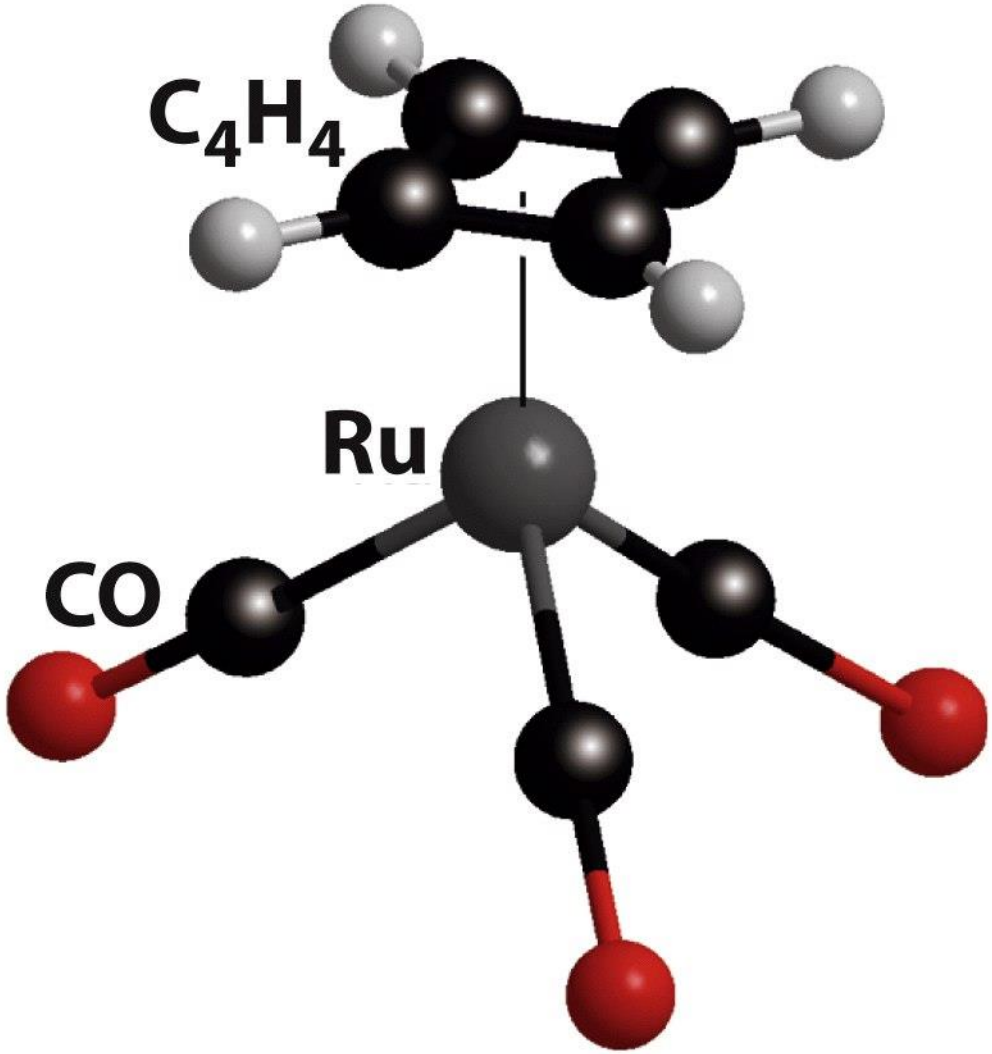

Filled
d_{yz}
Filled
d_{xy}
ψ_3
ψ_4

(b)

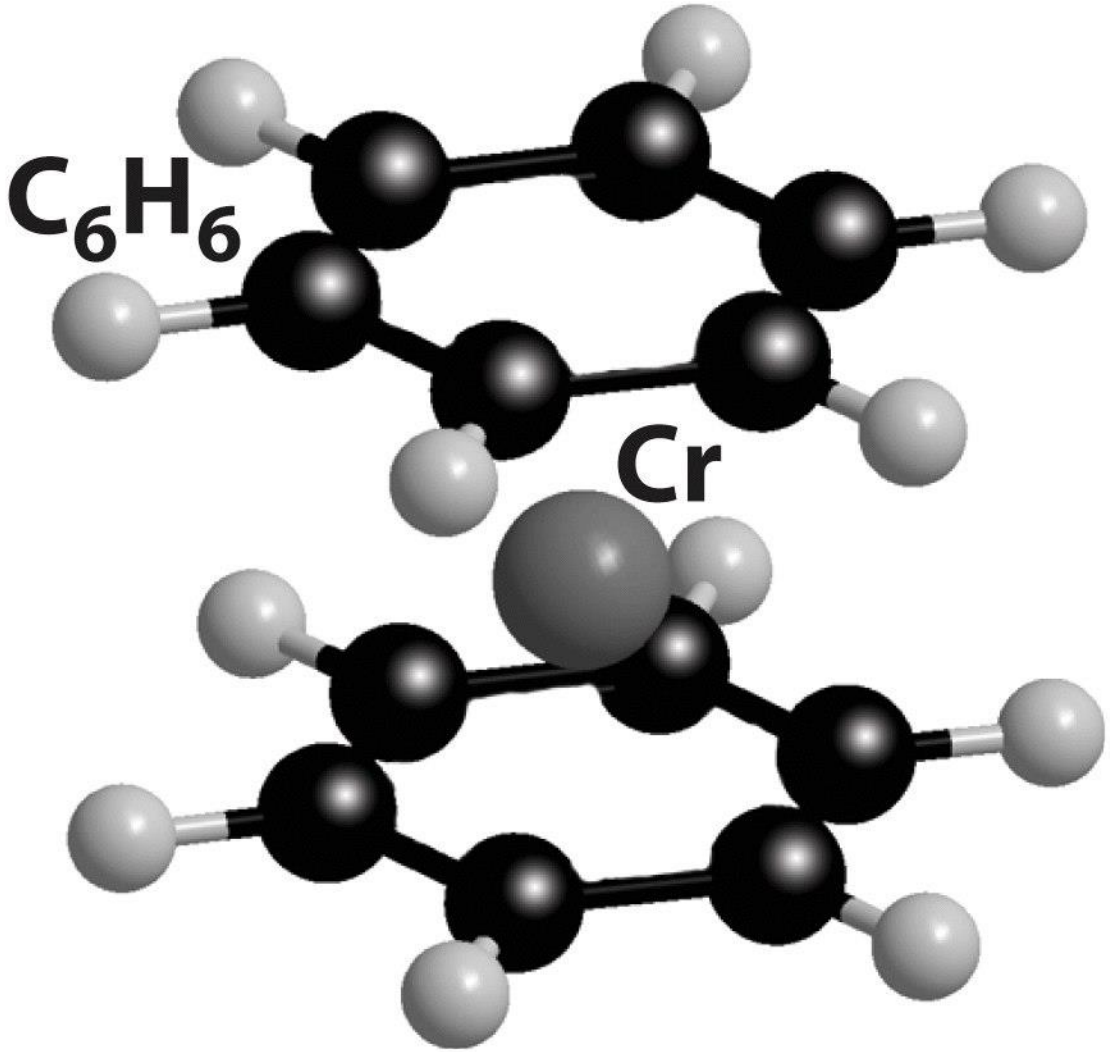


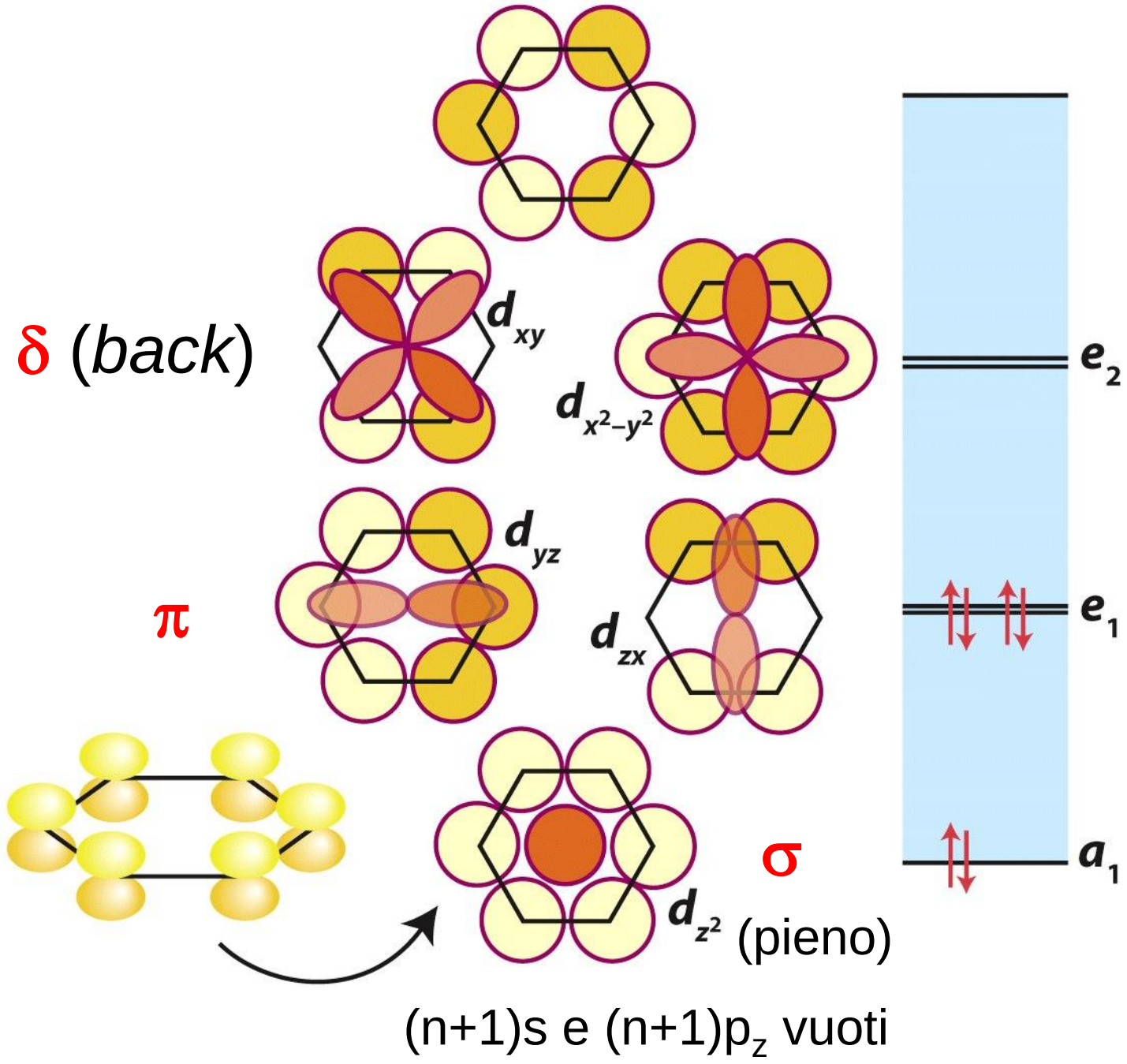


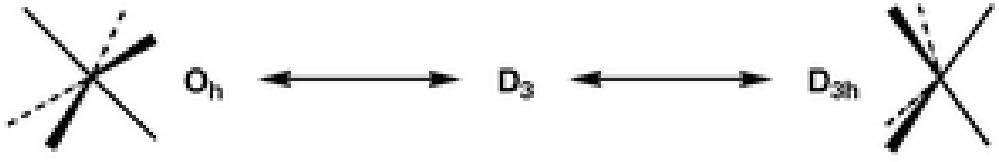
$[Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)]$

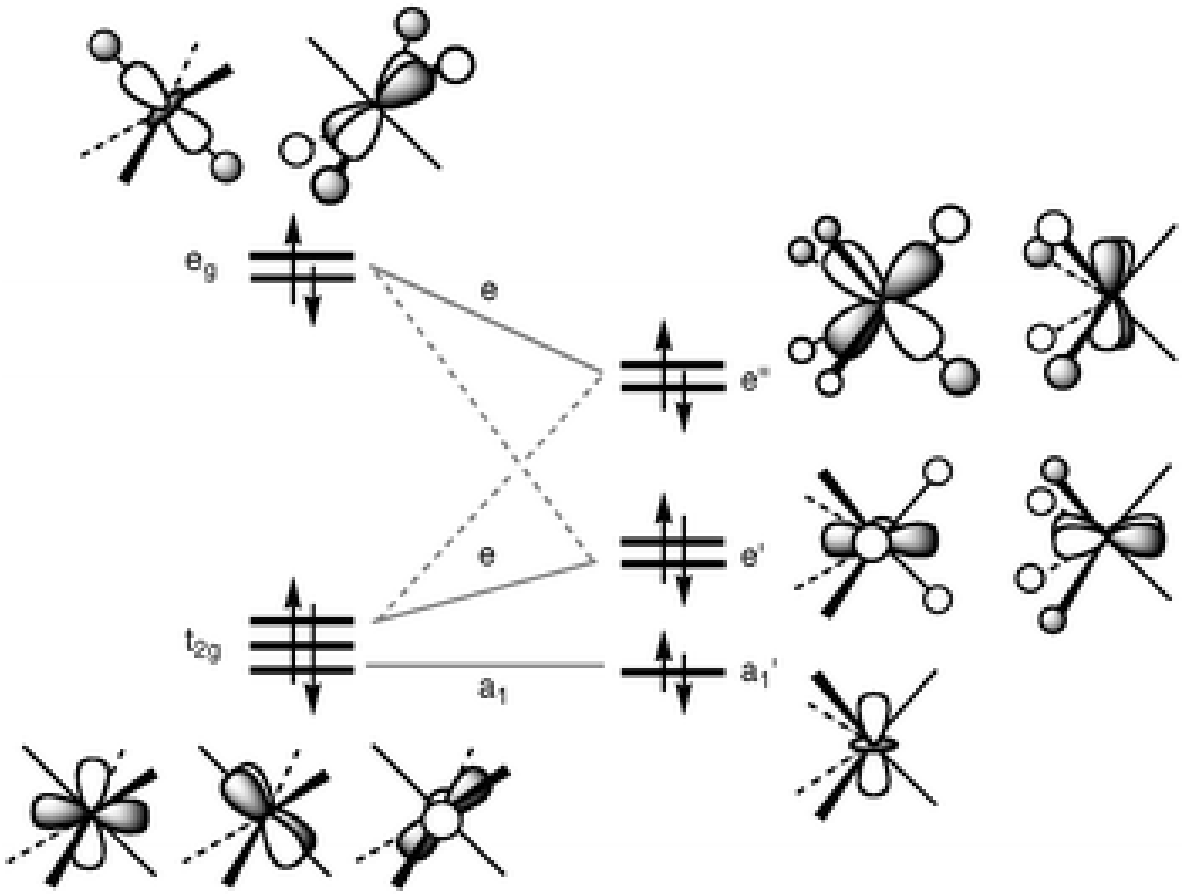


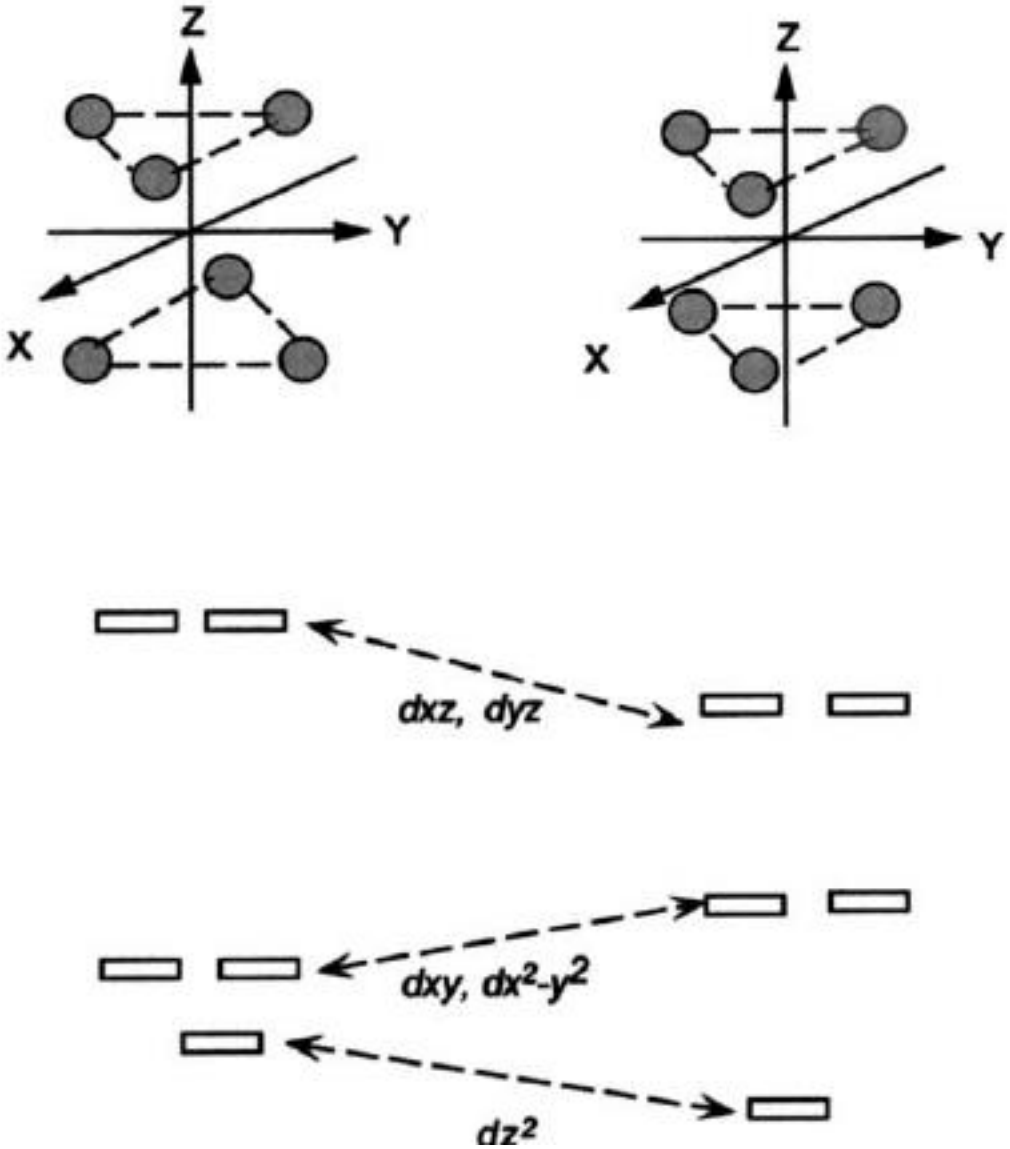
$[Ru(C_4H_4)](CO)_3]$

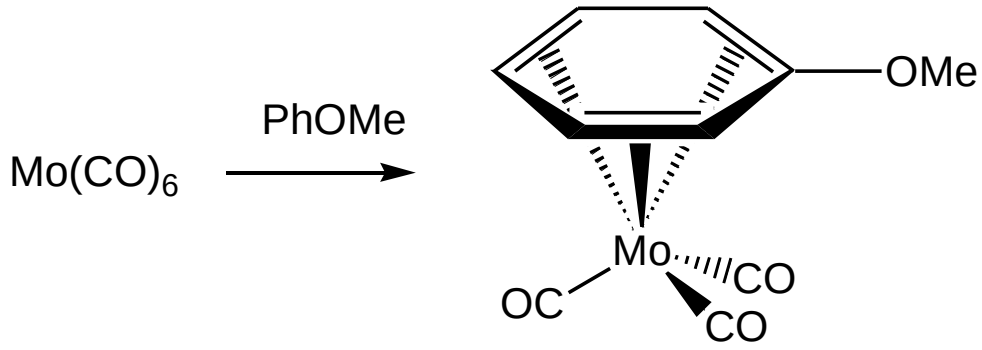

C_6H_6
Cr

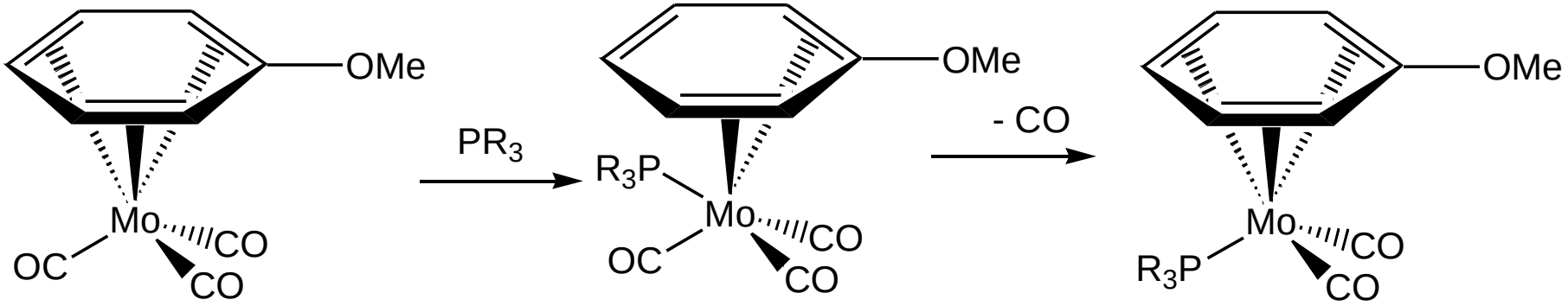

δ (back)
d_{xy}
$d_{x^2-y^2}$
d_{yz}
π
d_{zx}
σ
d_{z^2} (pieno)
e_2
e_1
a_1
(n+1)s e (n+1)p_z vuoti


O_h
D_3
D_{3h}


e_g
e
e''
e
e'
t_{2g}
a_1
a_1'


Z
Y
X
Z
Y
X
dxz, dyz
dxy, dx2-y2
dz2



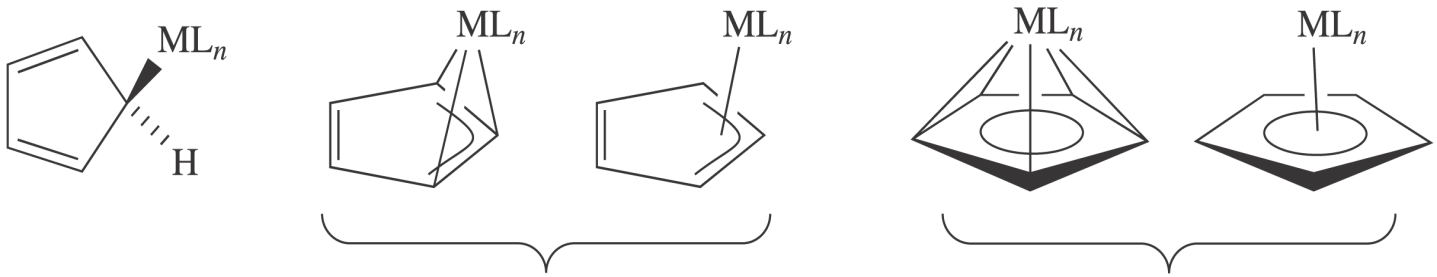


η^6-arene

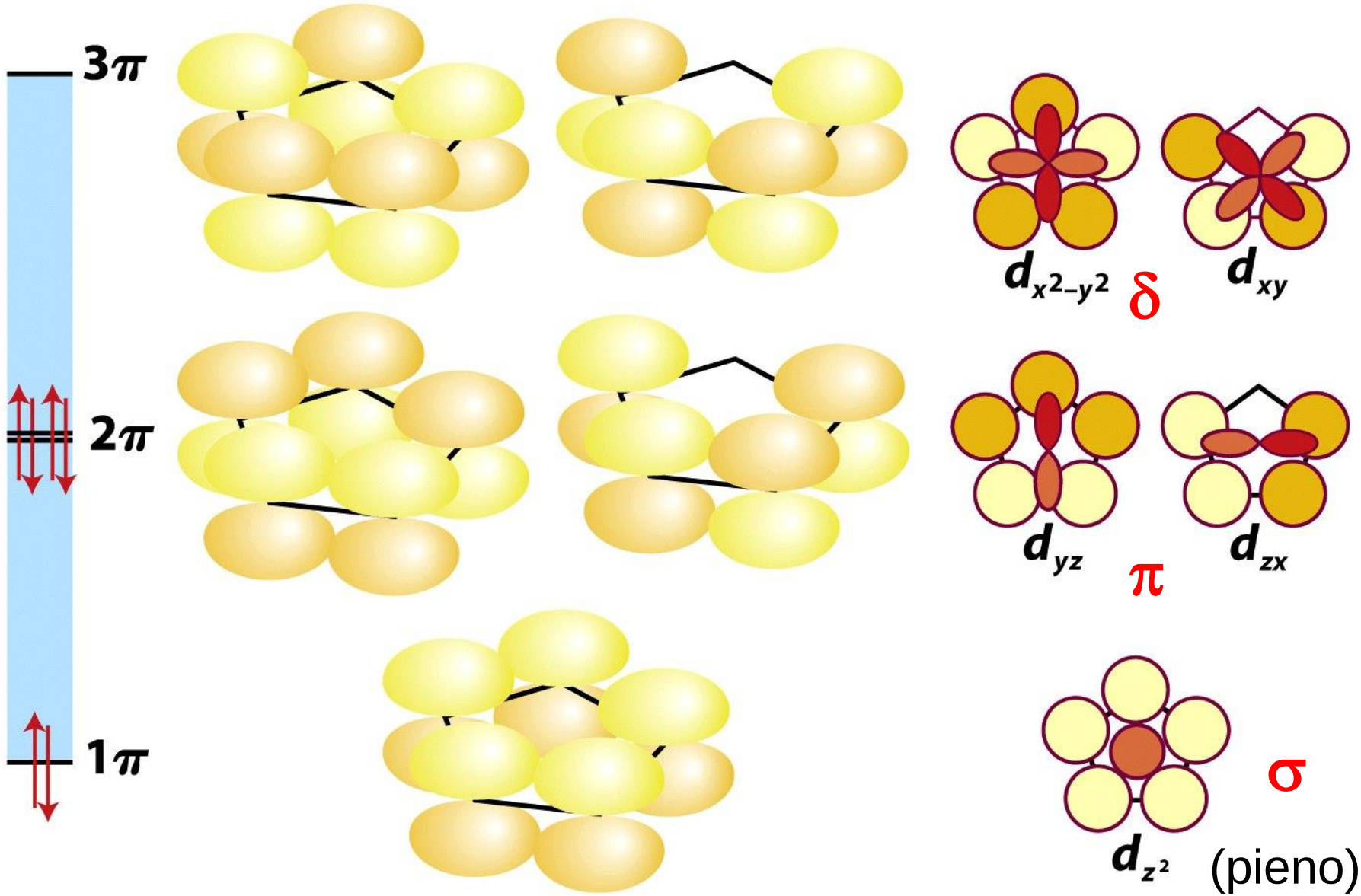
η^4-arene

slipping intermediate

η^6-arene

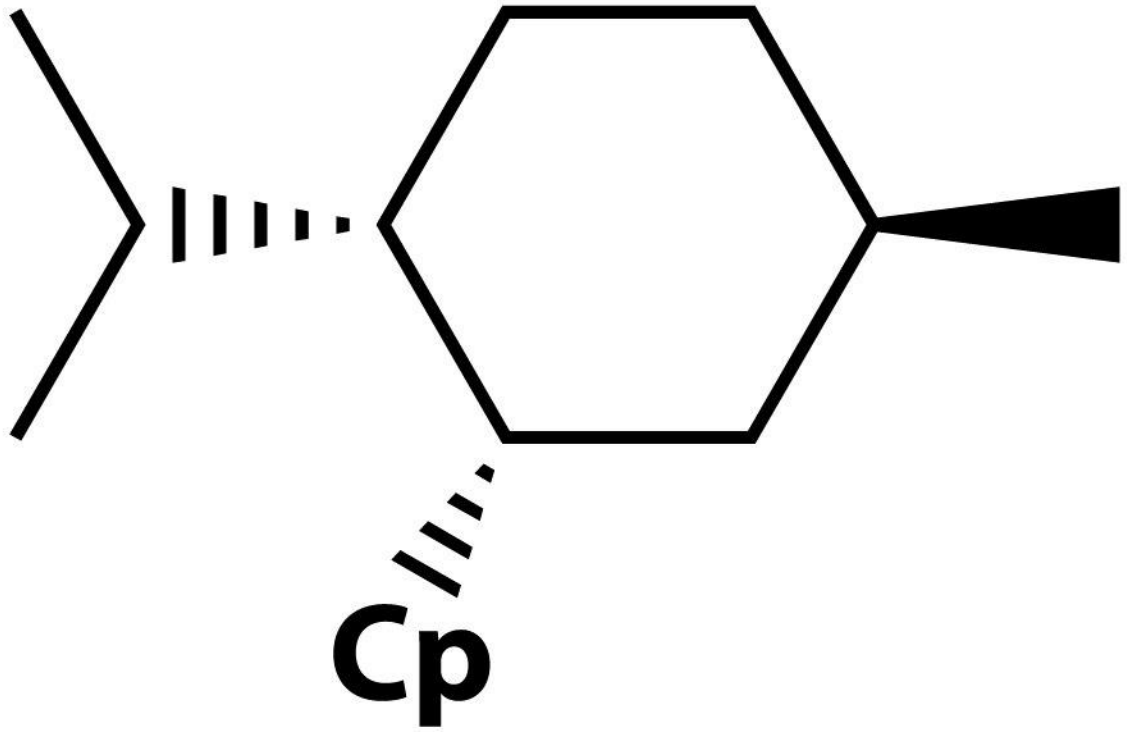


η^1-mode η^3-mode η^5-mode



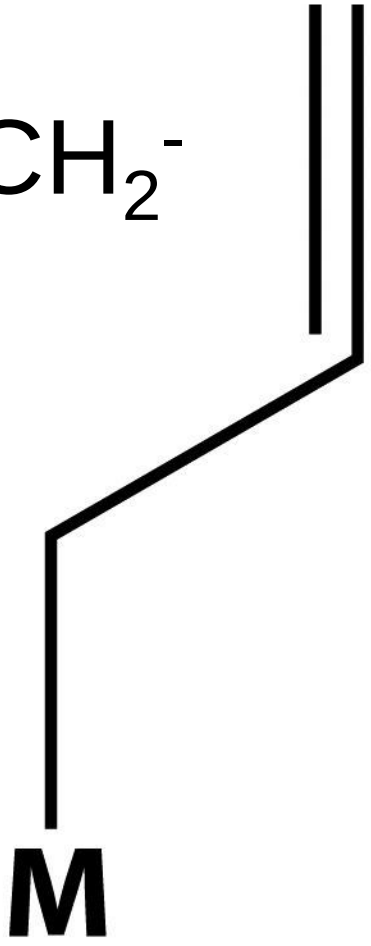
(pieno)

(n+1)s e (n+1)p_z vuoti

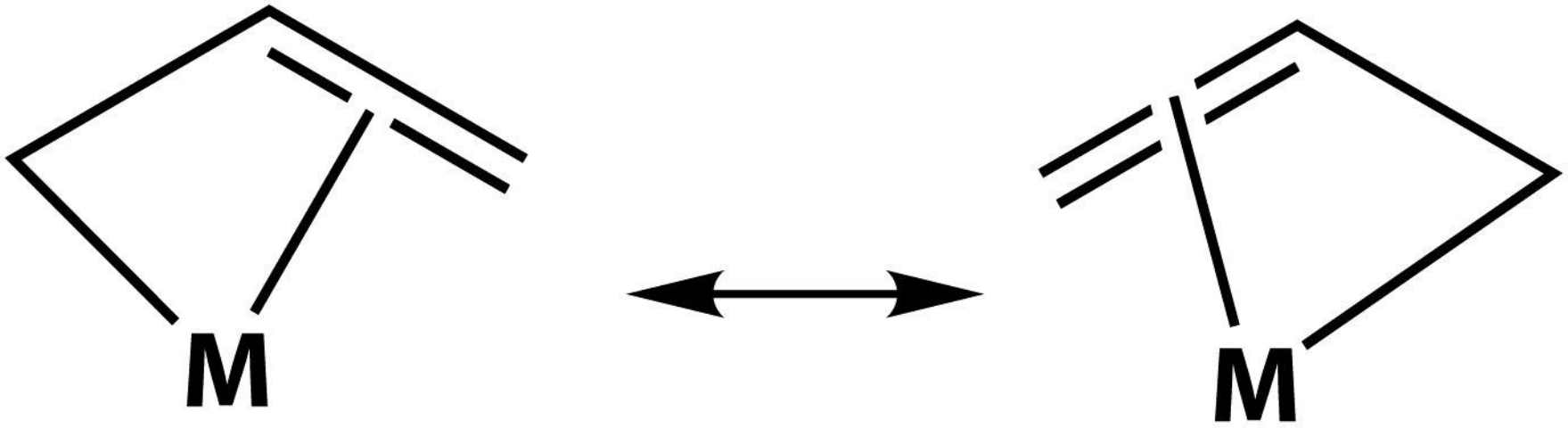


***neo*-Menthylcyclopentadienyl**

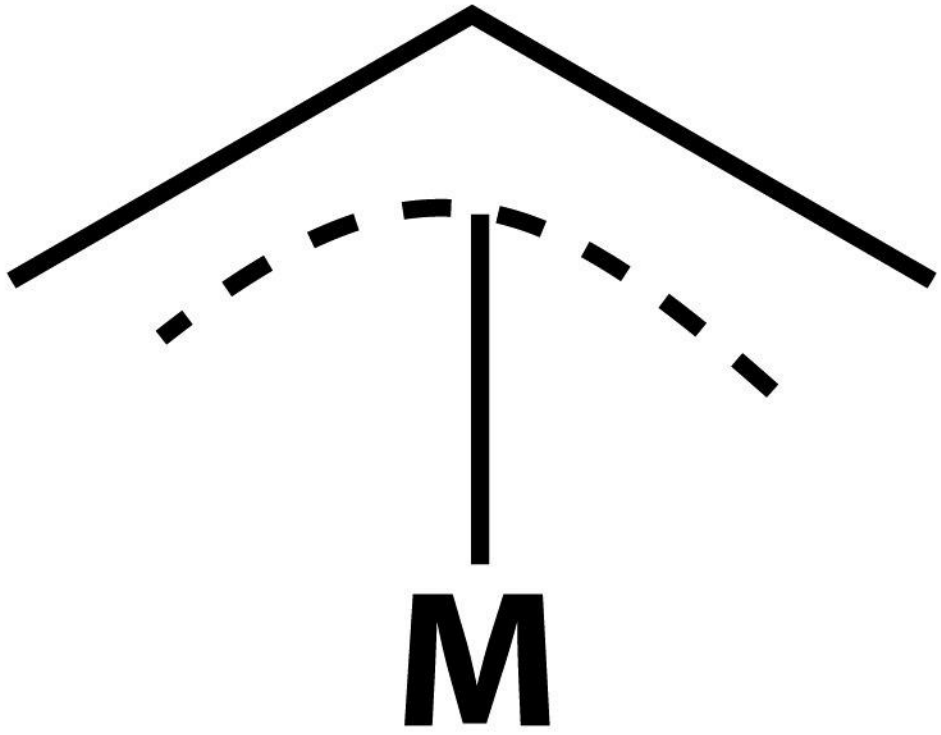
Allile, $CH_2=CH-CH_2^-$



η^1-($CH_2CH=CH_2$)



$$\eta^3(CH_2CH{=}CH_2)^-$$

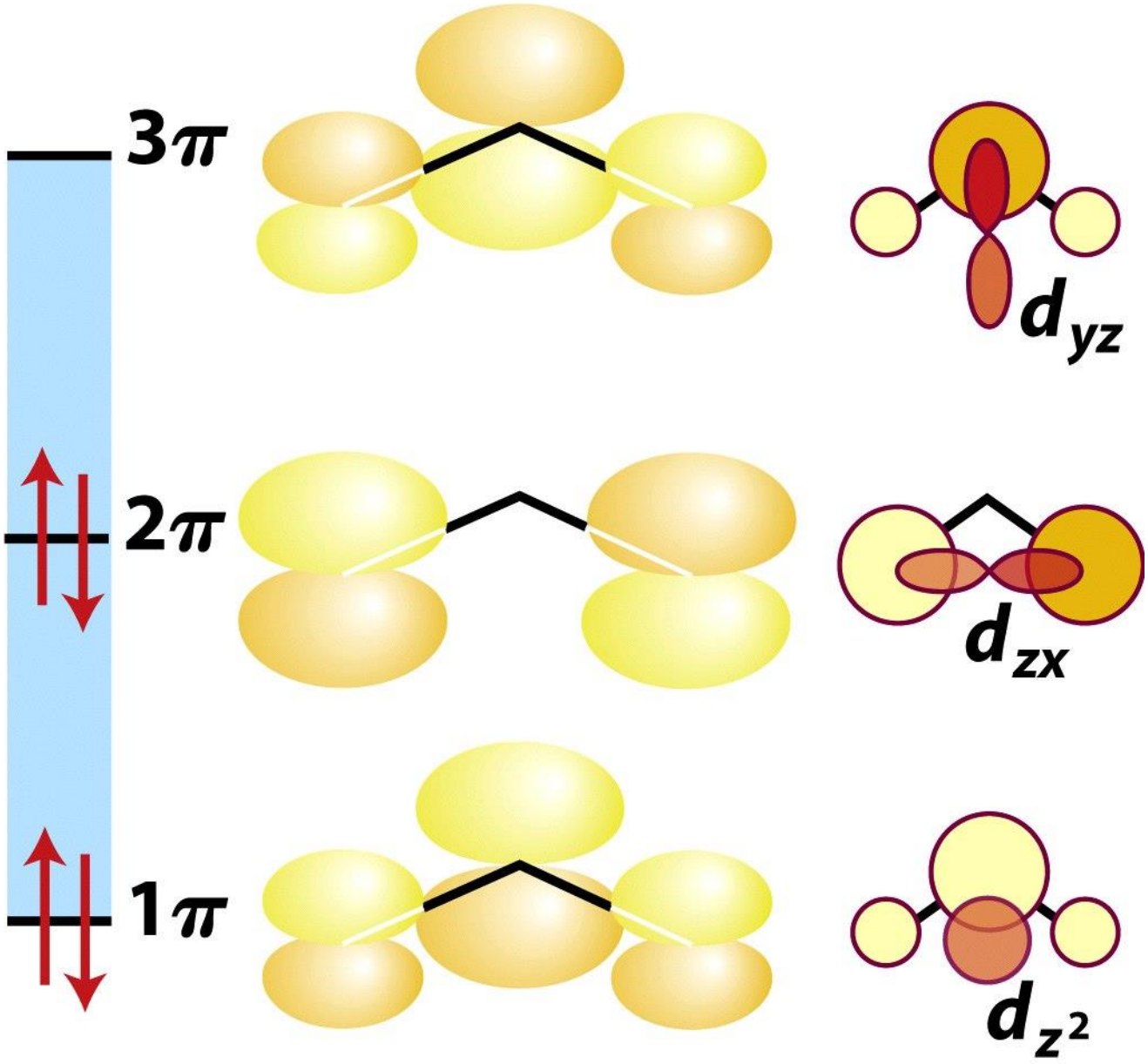


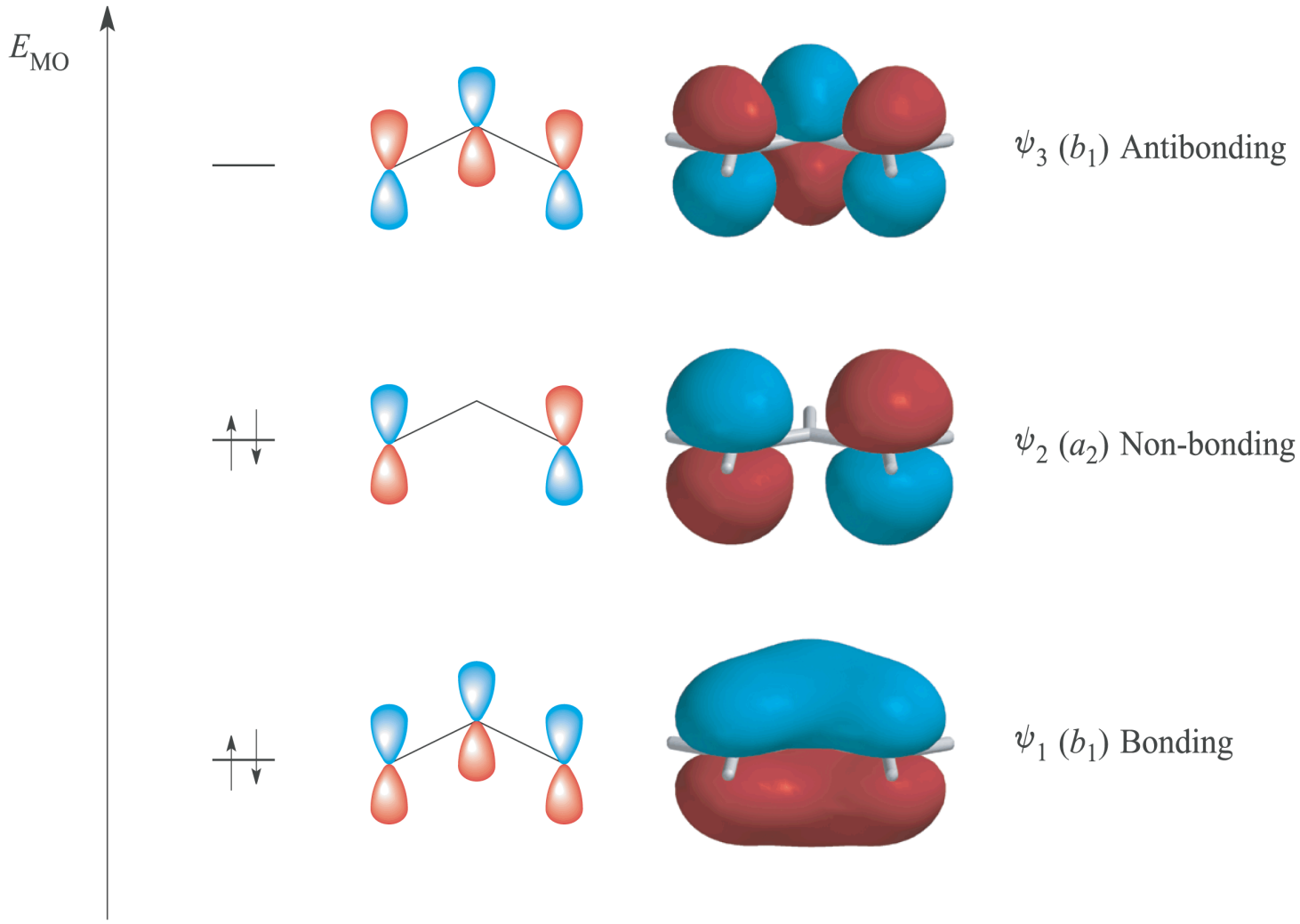
η^3-$(CH_2CH{=}CH_2)^-$

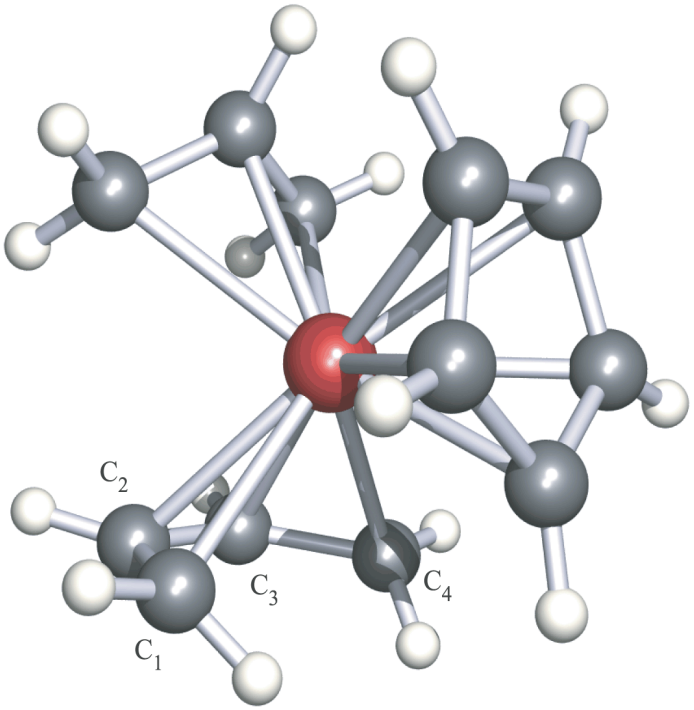
Accettore π

Donatore π

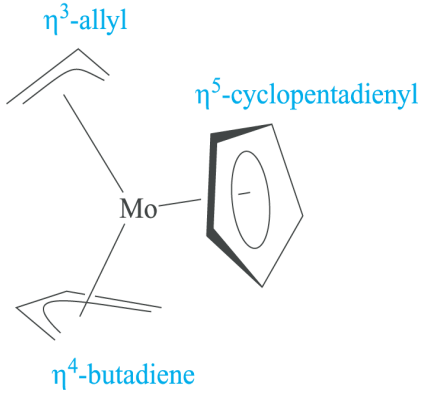
Donatore σ




E_{MO}
ψ_3 (b_1) Antibonding
ψ_2 (a_2) Non-bonding
ψ_1 (b_1) Bonding

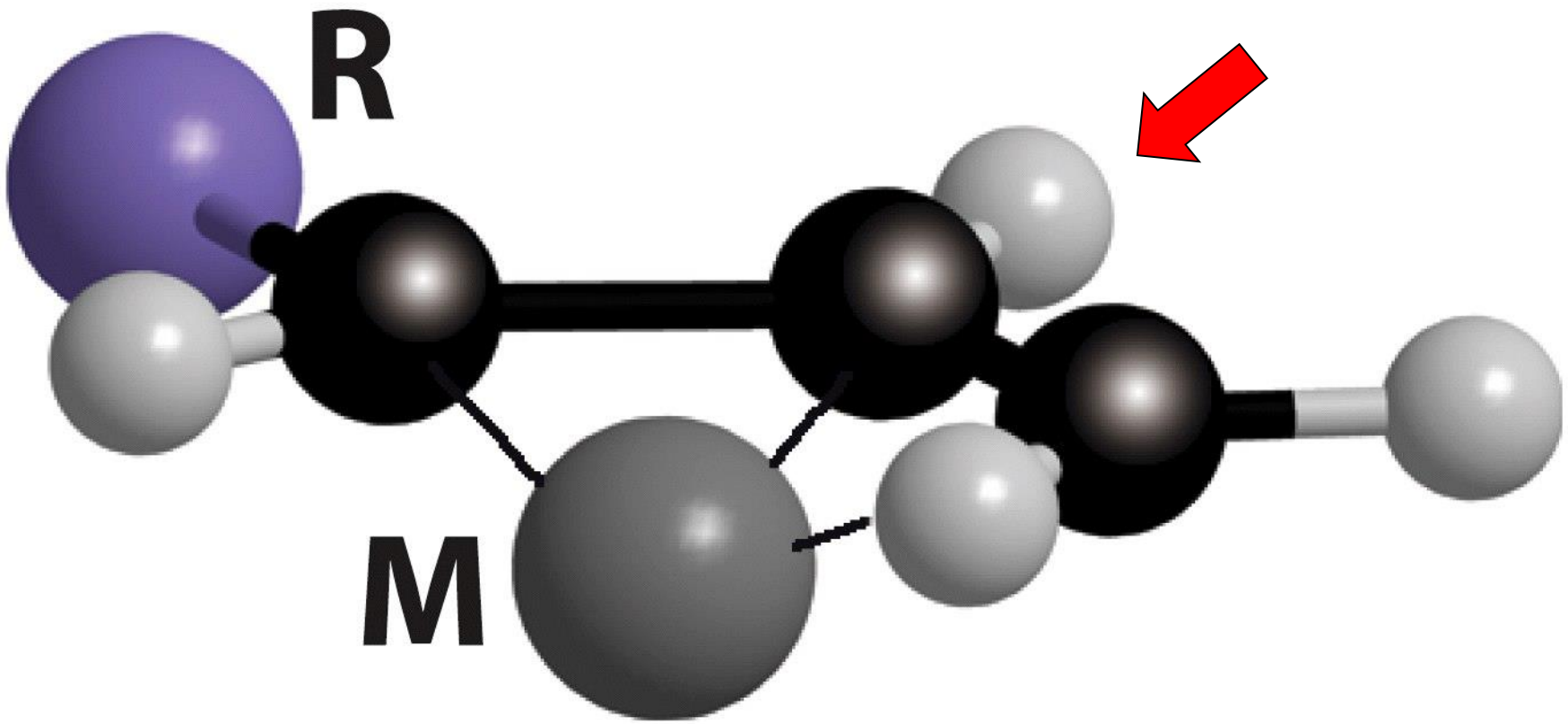


(b)

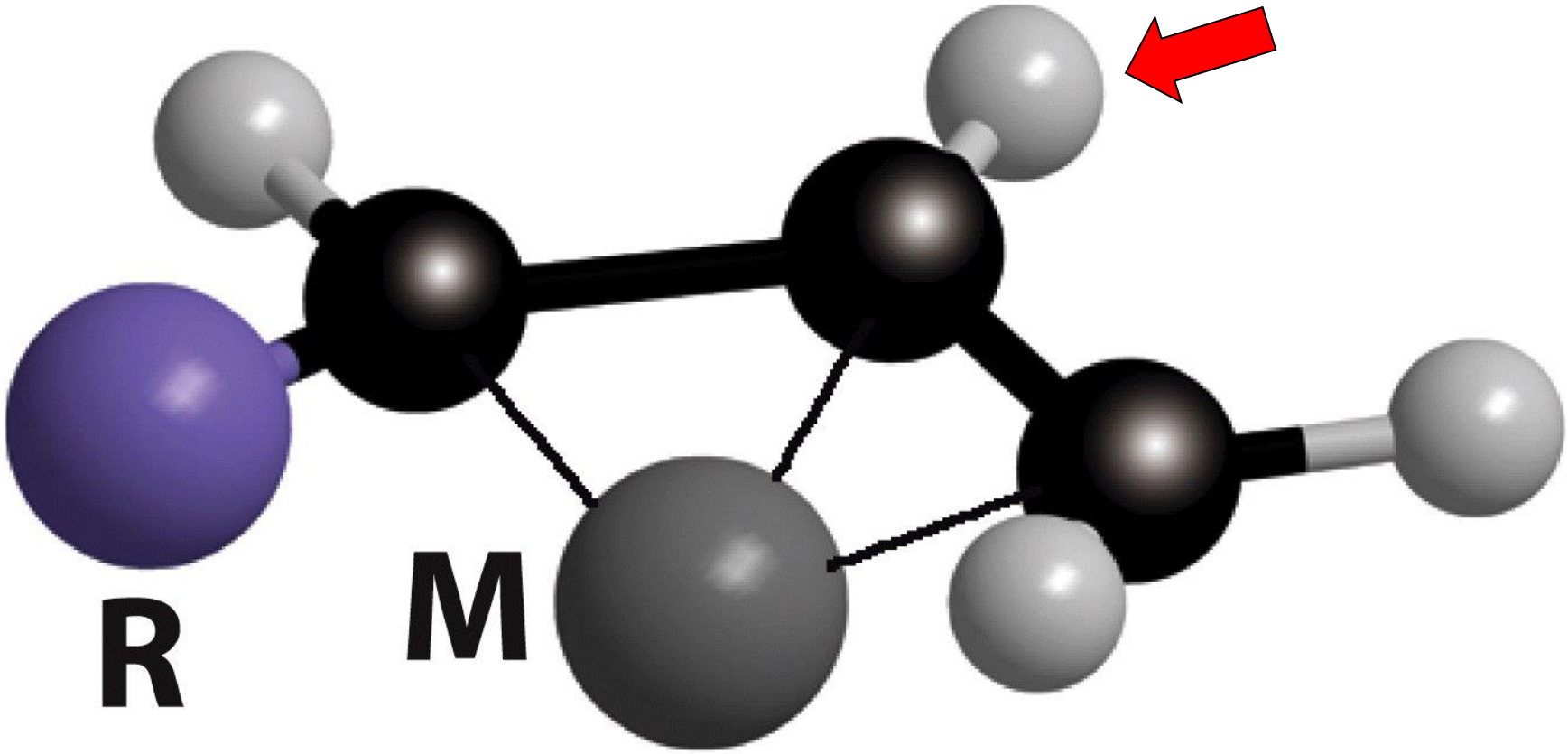


(c)

$[Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)]$



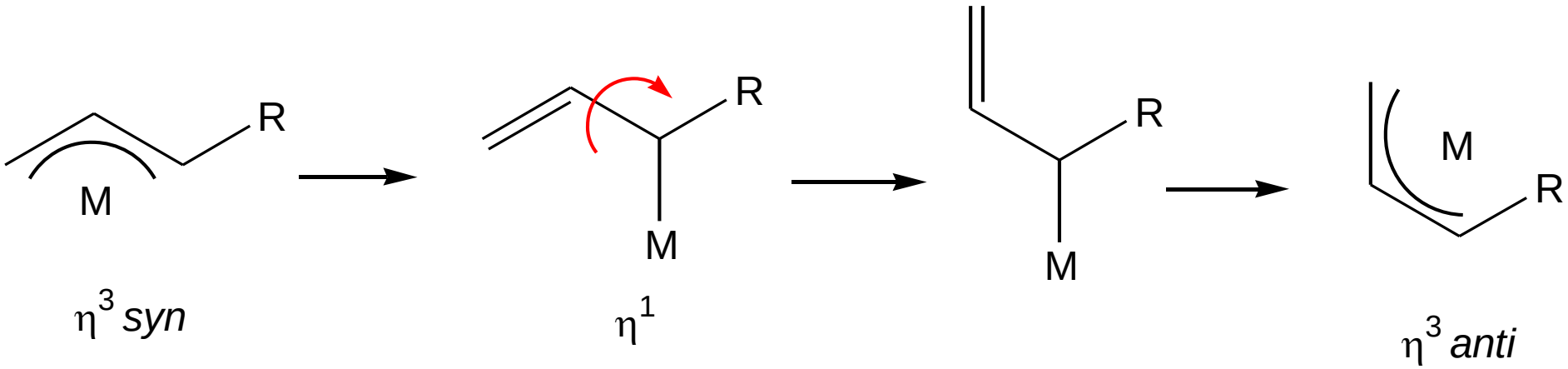
syn



anti

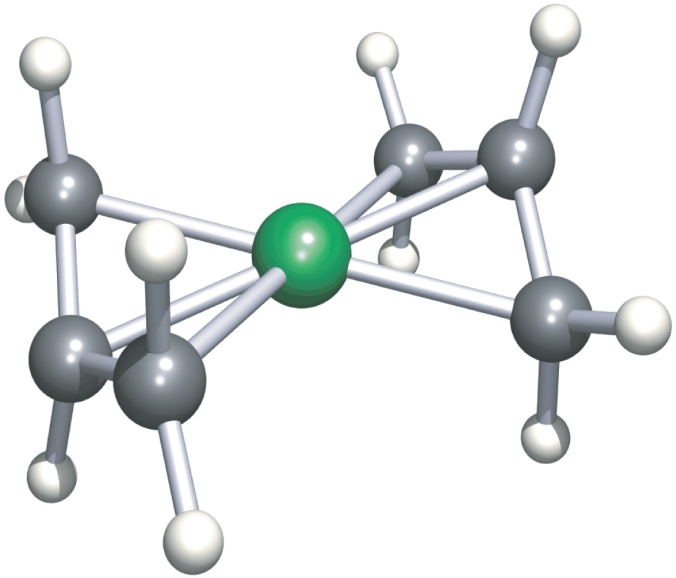
Meccanismo di scambio *syn-anti*

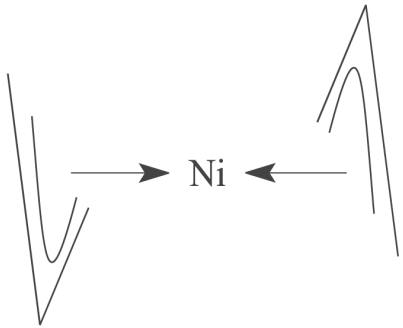
$\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$



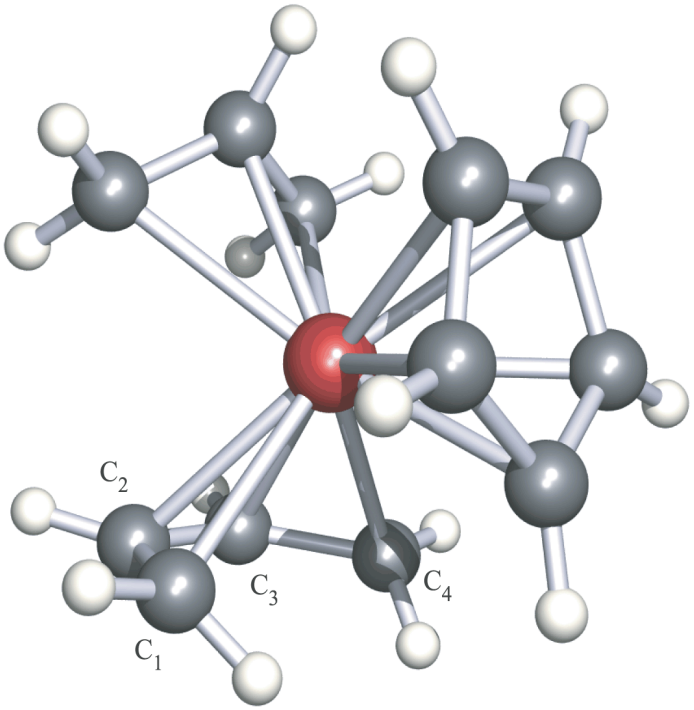
η^3 *syn* η^1 η^3 *anti*

$$2C_3H_5MgBr + NiCl_2 \rightarrow [Ni(\eta^3\text{-}C_3H_5)_2] + 2MgBrCl$$

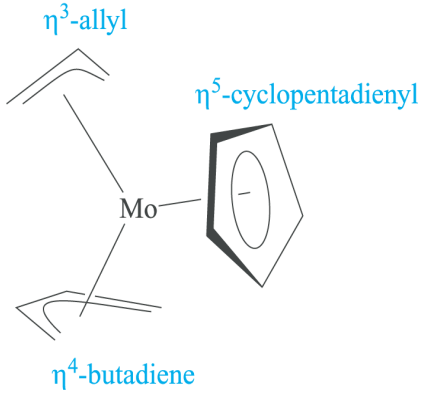




$[Ni(\eta^3\text{-}C_3H_5)_2]$



(b)



(c)

$[Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)]$