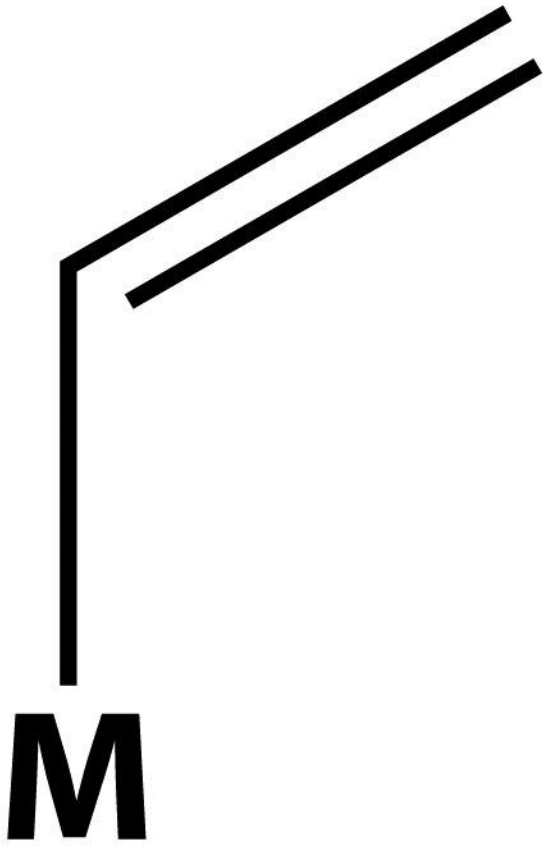
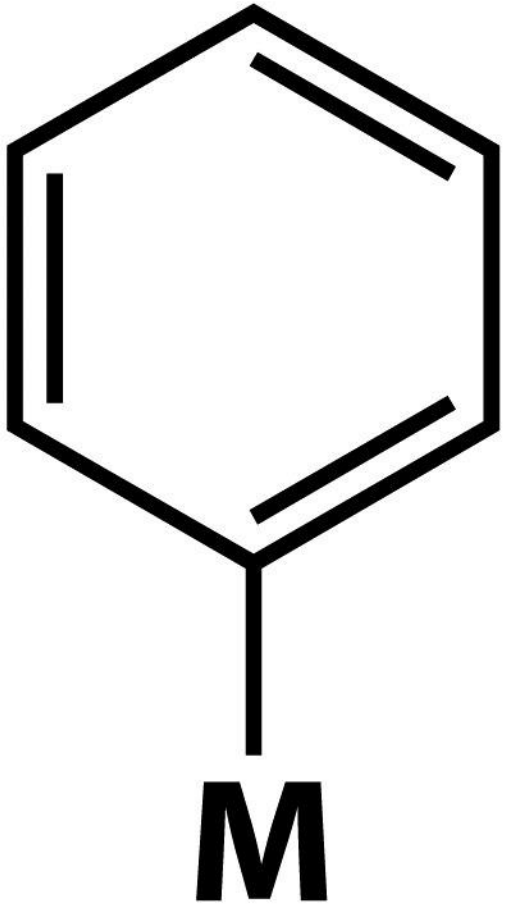


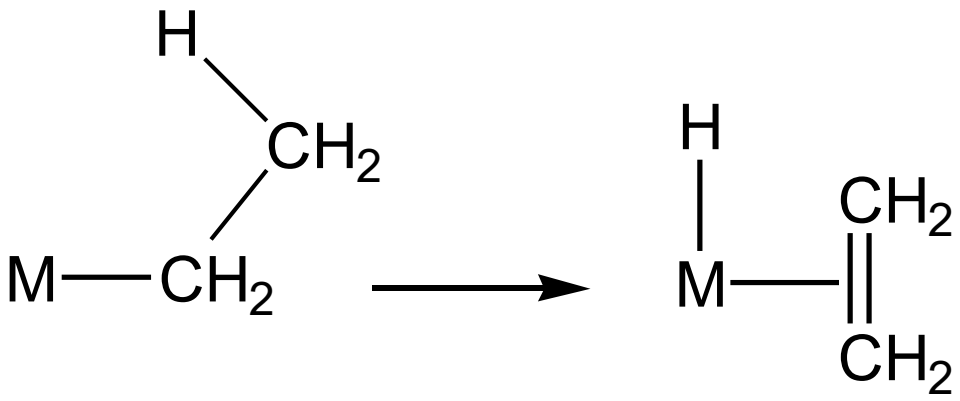
η^1-alkenyl

η^1-alkynyl



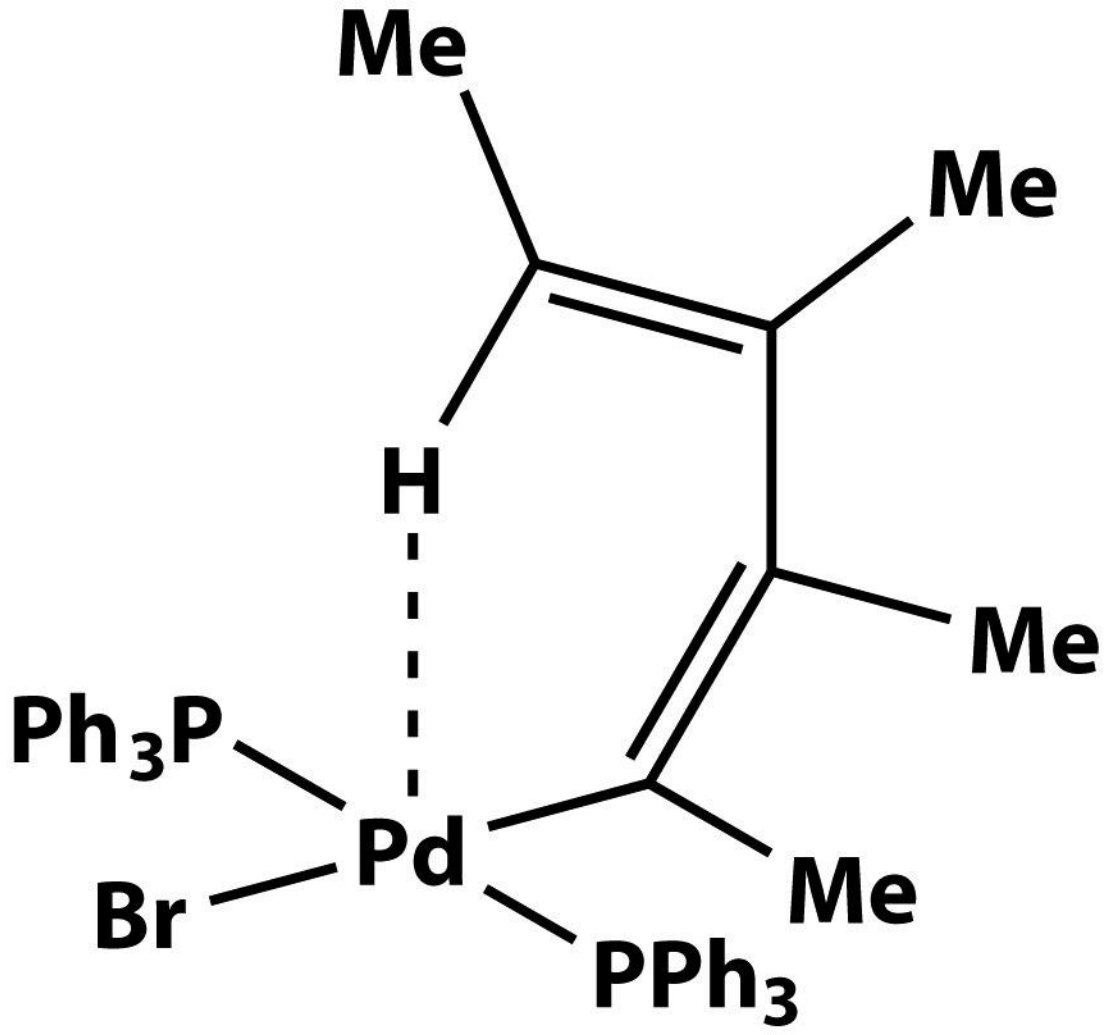
η^1-aryl

Hydride β-elimination



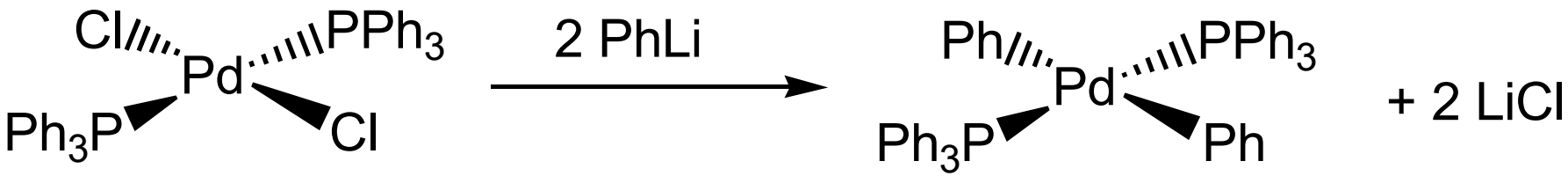
Stabilizing groups:

methyl, benzyl ($CH_2C_6H_5$), neopentyl (CH_2CMe_3), trimethylsilylmethyl (CH_2SiMe_3)

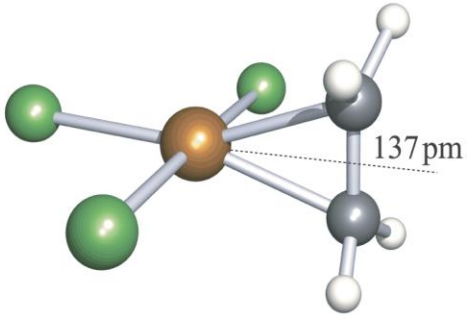


C−H *agostic* interactions

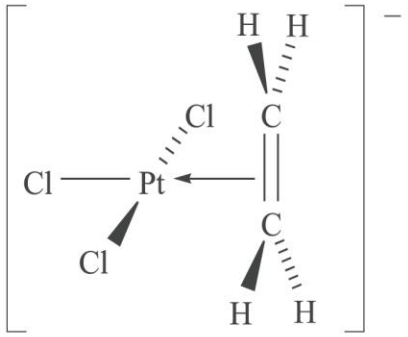
Typical synthetic procedure



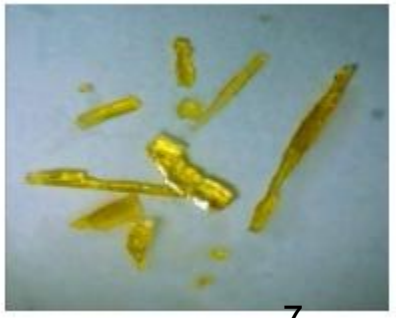
Alternative option: Grignard Reagents

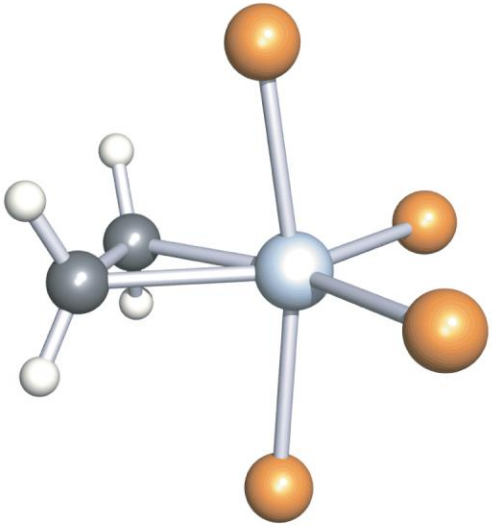


C−C = 137 pm *vs* 134 pm in ethene



η^2-alkene
side-on coordination

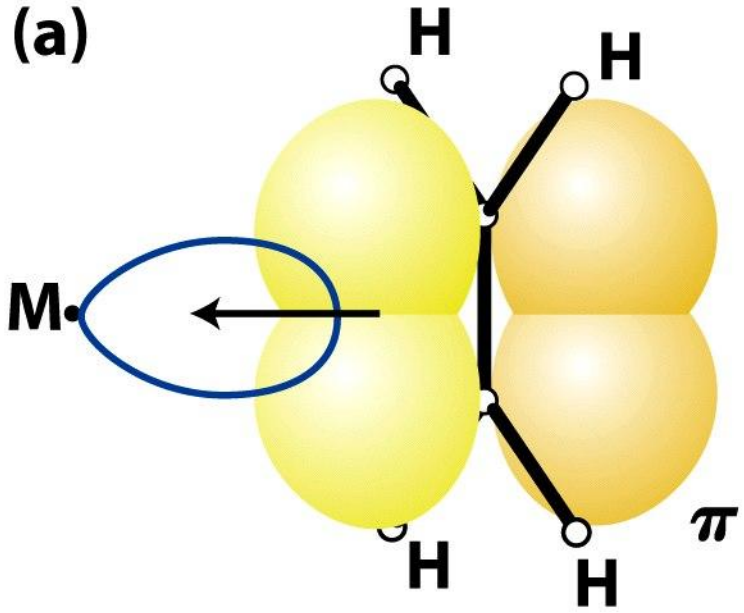




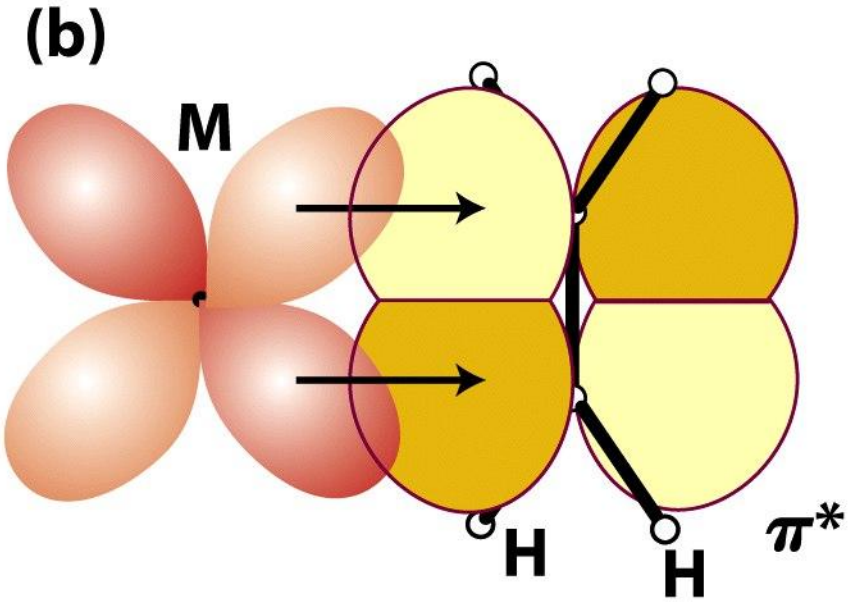
metallacyclopropane

X-ray structure of $Ru(\eta^2\text{-}C_2H_4)(PMe_3)_4$

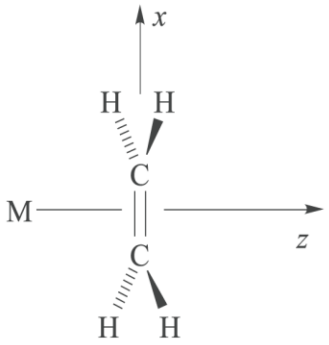
C−C = 144 pm *vs* 134 pm in ethene

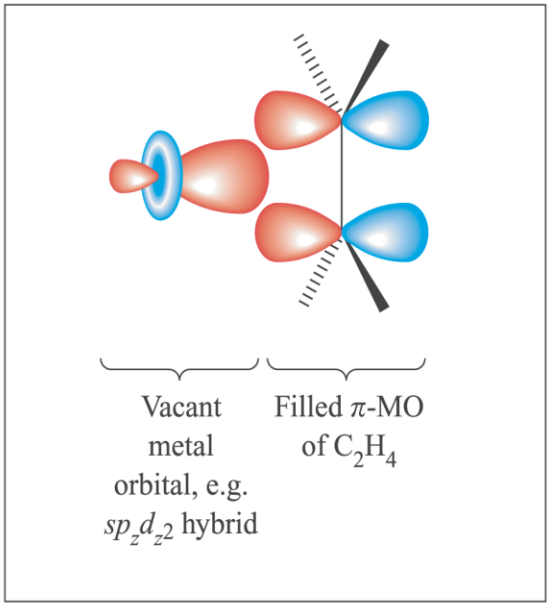


π–symmetry orbital for isolated ethene, σ-symmetry orbital when ethene is coordinated η^2 (*side-on*)

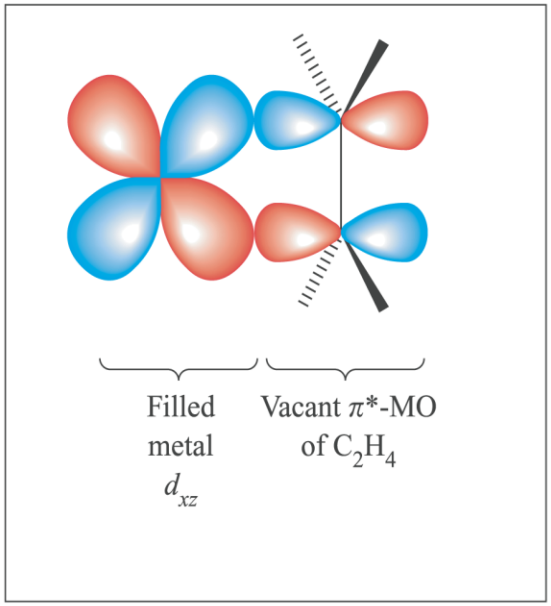


Dewar – Chatt – Duncanson Model



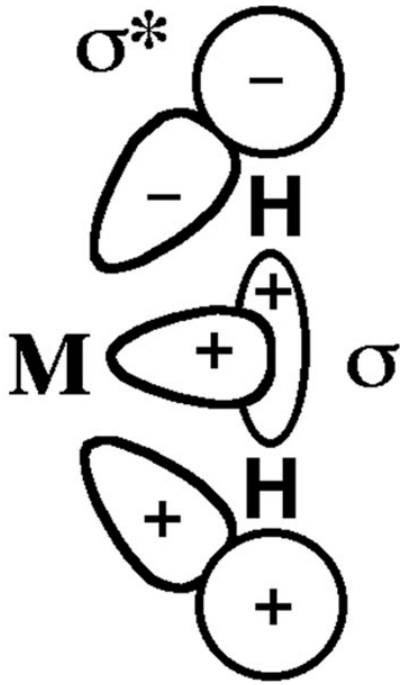


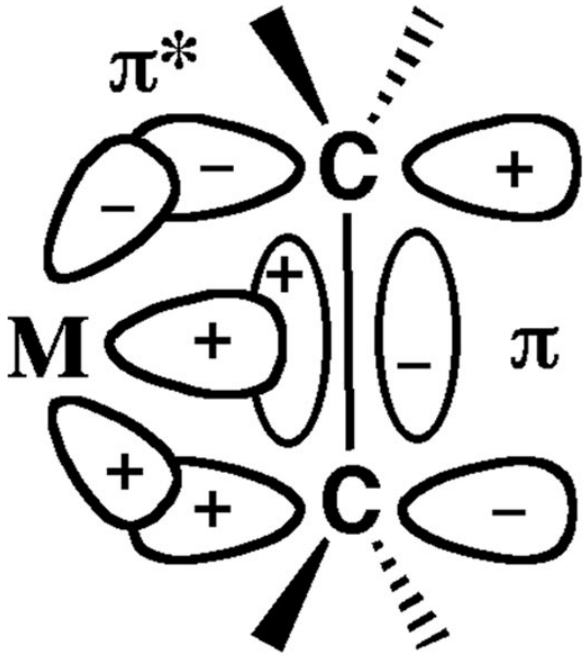
Alkene-to-M donation
(a)

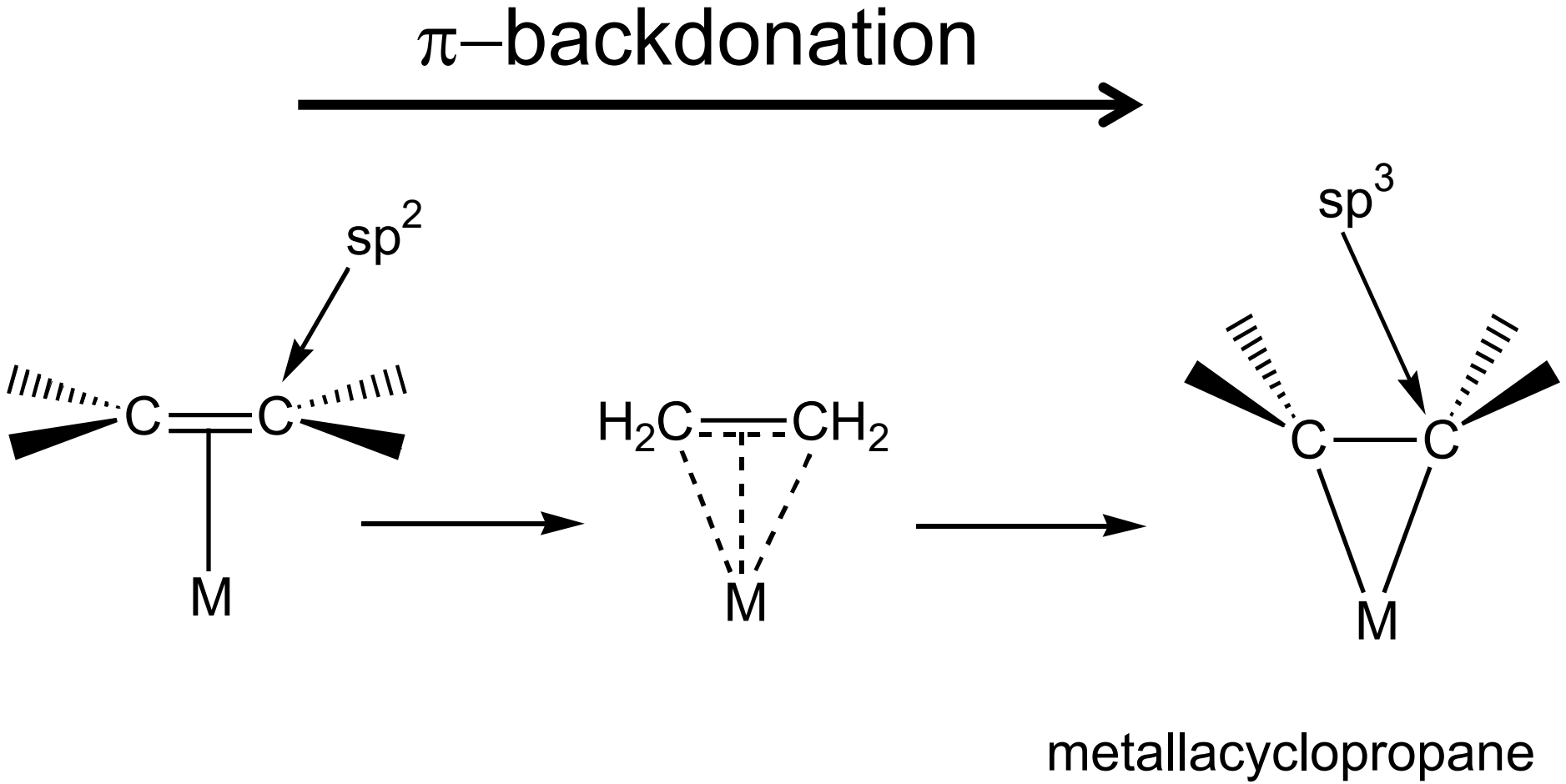


M-to-alkene back-donation
(b)

Dewar – Chatt – Duncanson Model

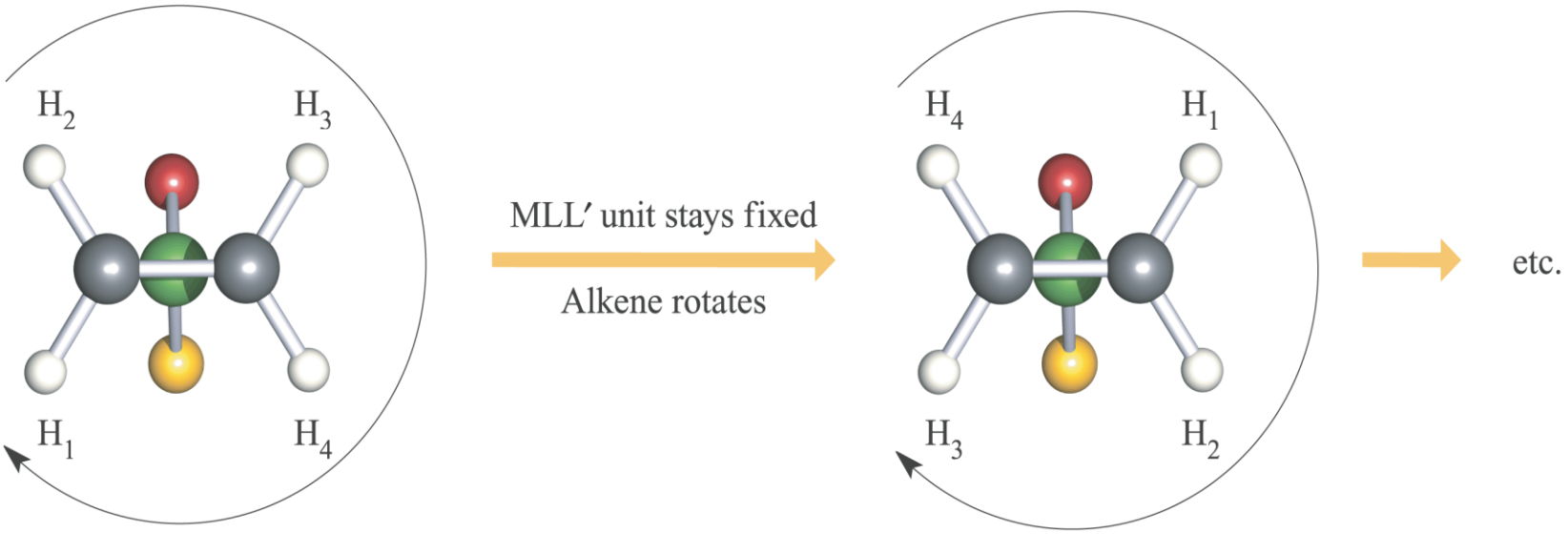

σ*
−
−
H
+
M
+
σ
H
+
+

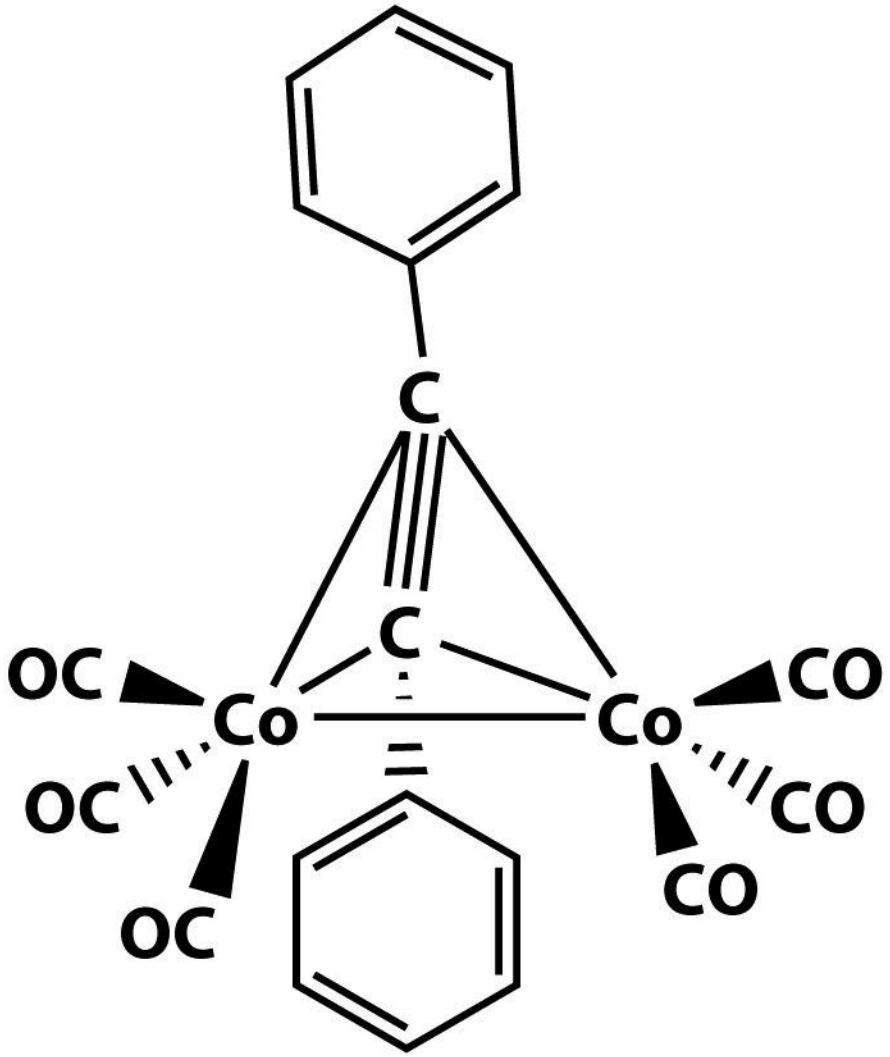

π*
C
−
−
+
+
M
+
−
π
+
+
C
−



metallacyclopropane

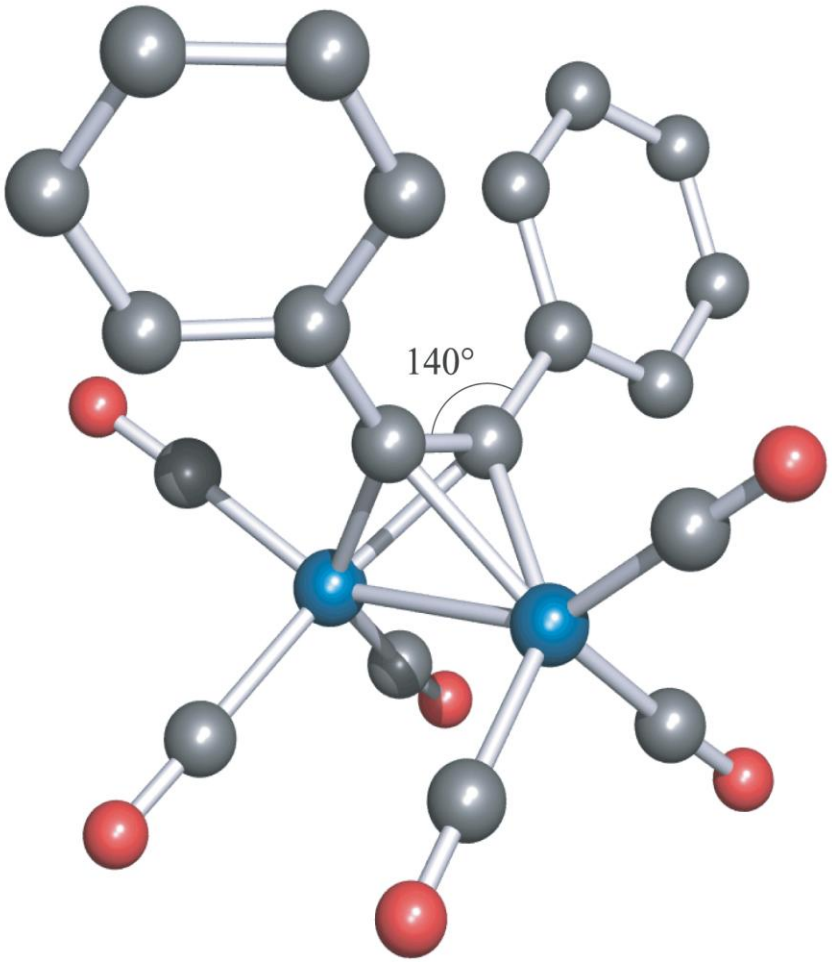
η^2-alkene bond - fluxionality





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

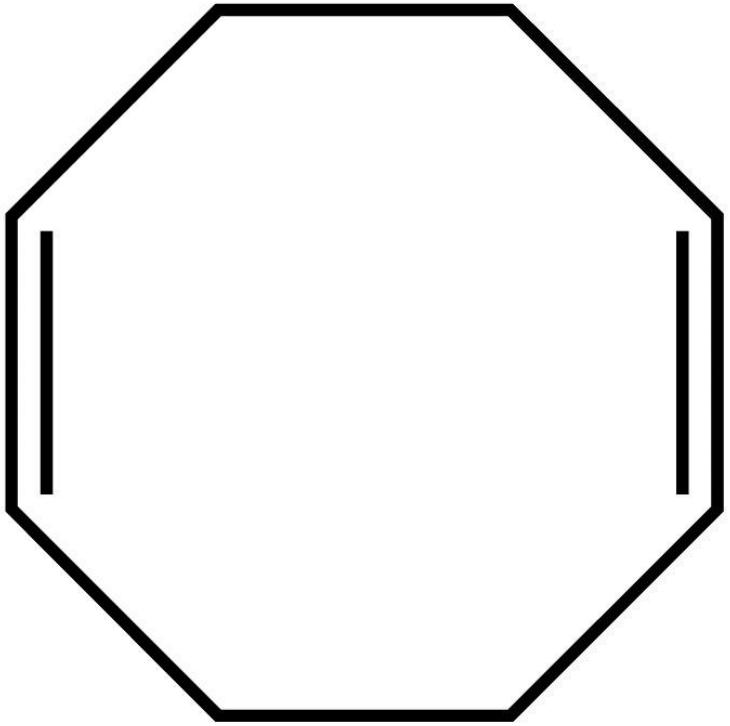
4-electron donor



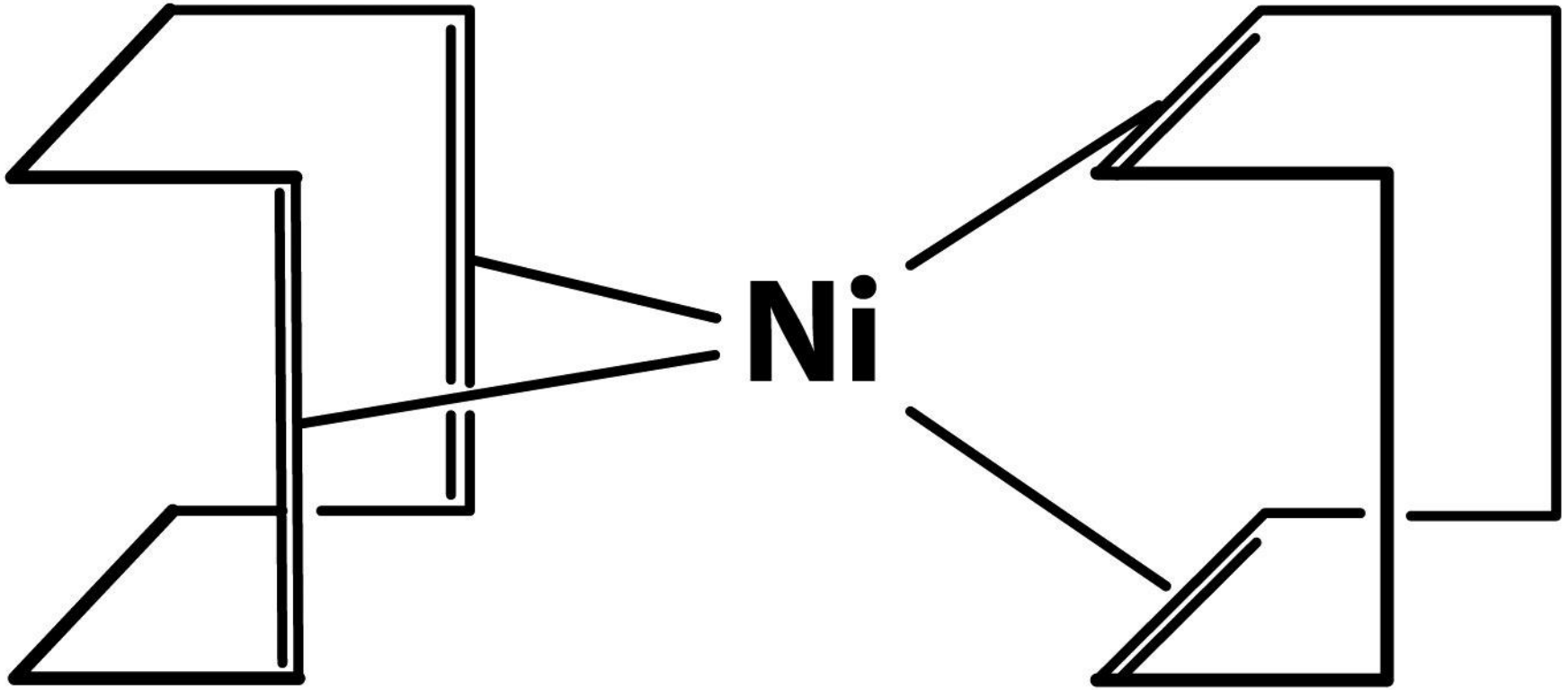
C—C in Co_2C_2-unit = 136 pm *vs* 120 pm in C_2Ph_2

The two C_2Co planes, *i.e.* the two η^2 bonds, are roughly orthogonal

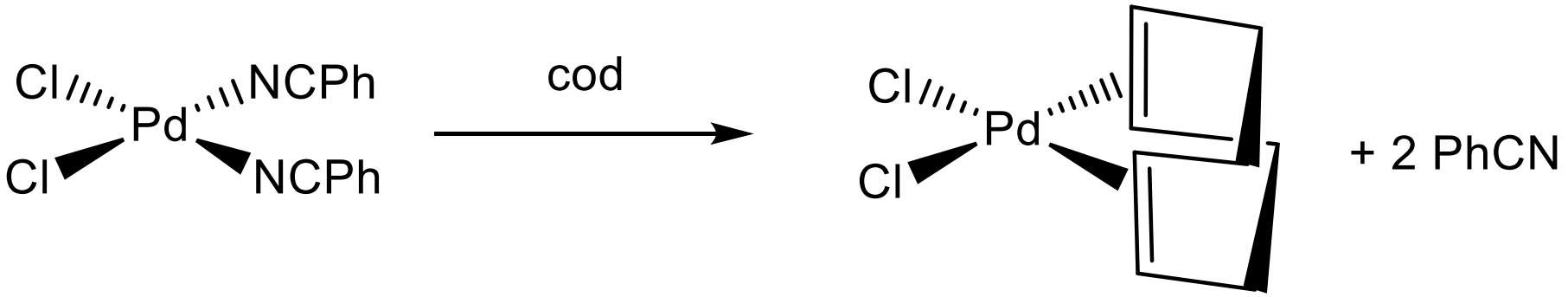
Non-conjugated Dienes

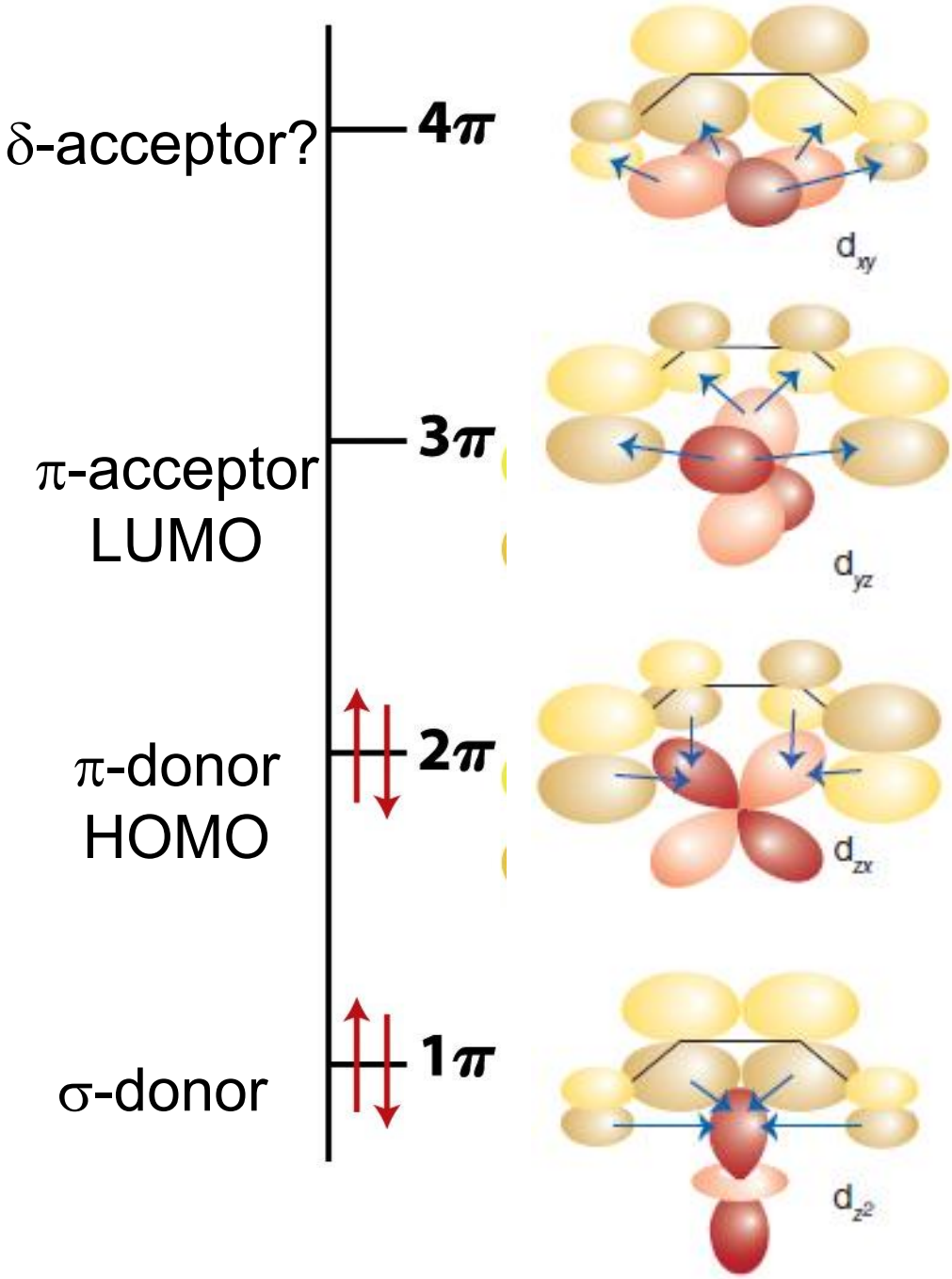


Cycloocta-1,5-diene, cod

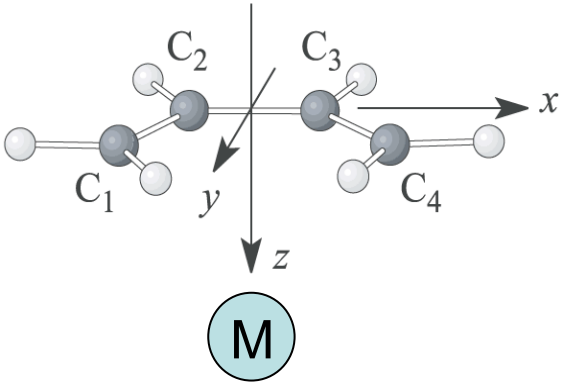


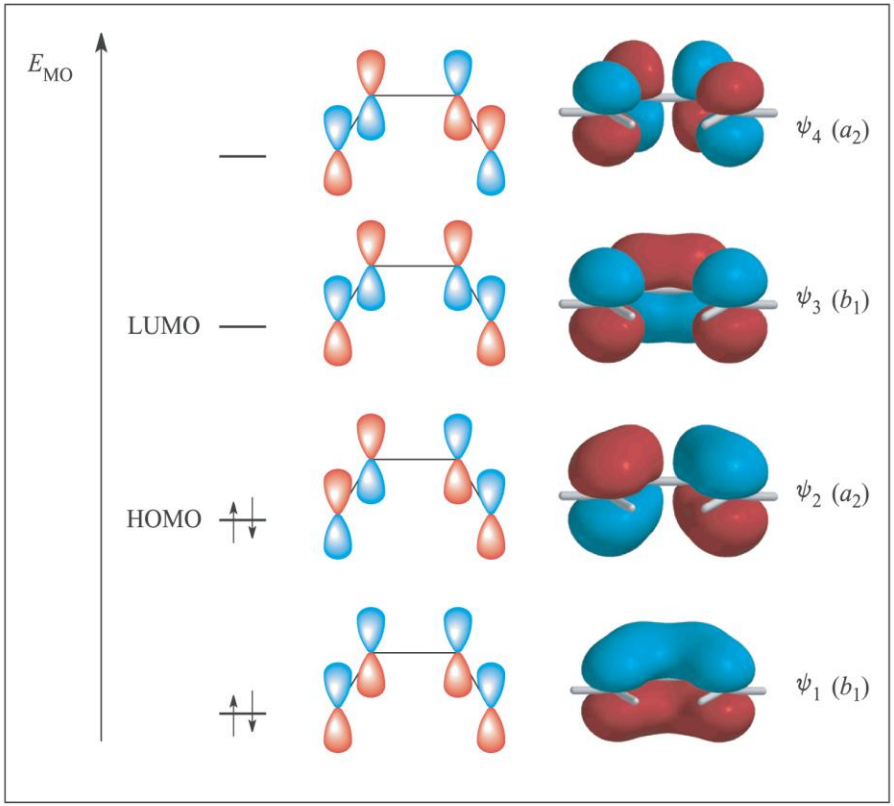
$Ni(cod)_2$


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

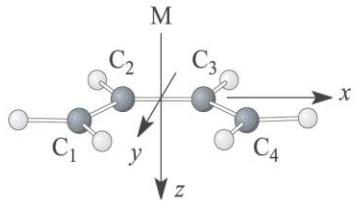


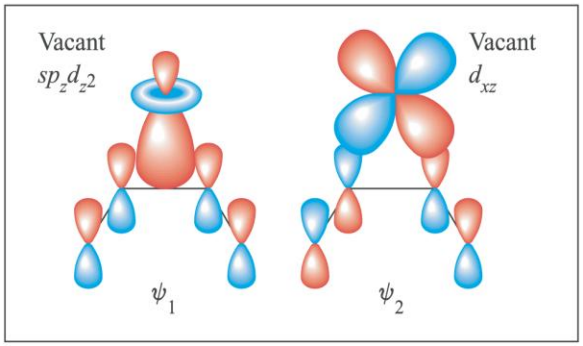
Butadiene - lays on the *xy* plane, above the metal

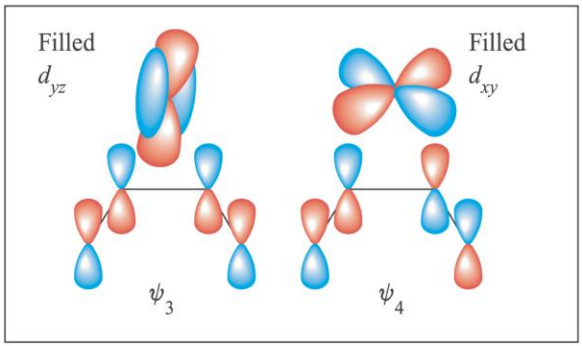



E_{MO}
LUMO
HOMO
ψ_4 (a_2)
ψ_3 (b_1)
ψ_2 (a_2)
ψ_1 (b_1)

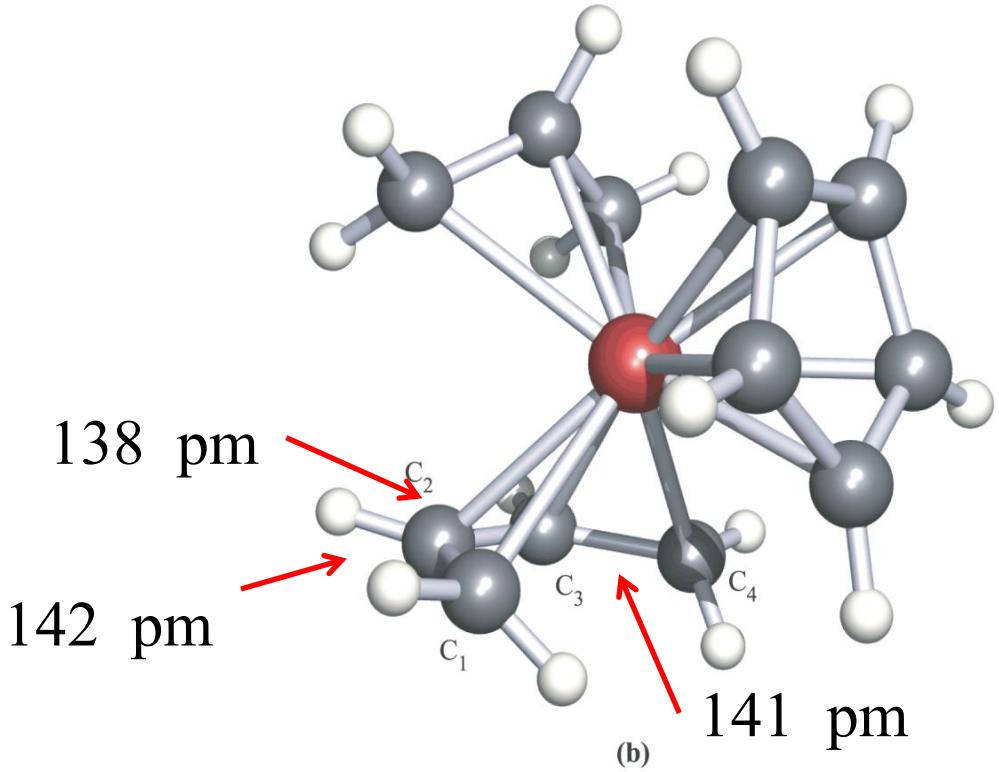
(a)

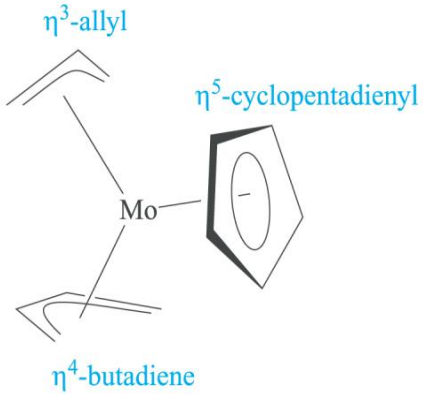

M
C_2
C_3
C_1
C_4
x
y
z


Vacant
$sp_z d_{z^2}$
Vacant
d_{xz}
ψ_1
ψ_2

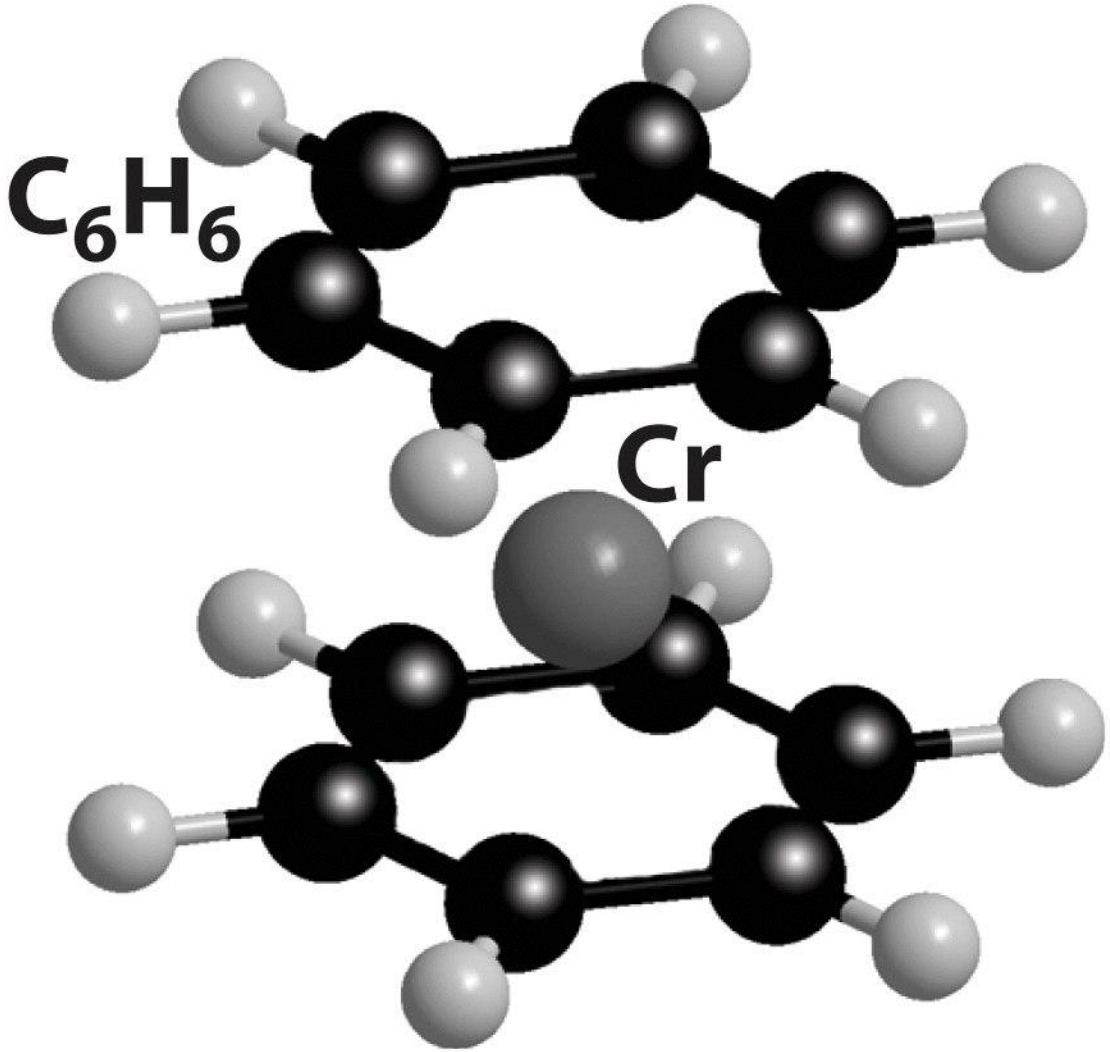

Filled
d_{yz}
Filled
d_{xy}
ψ_3
ψ_4

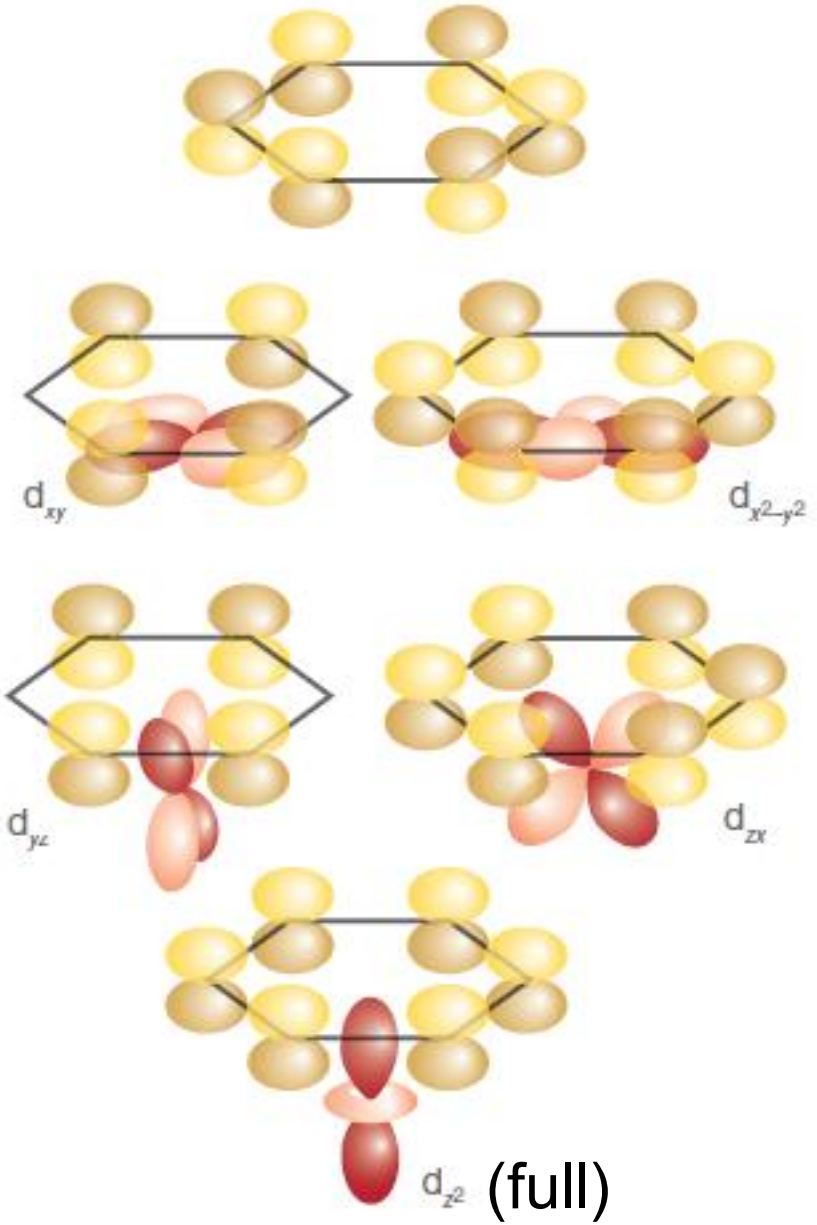
(b)

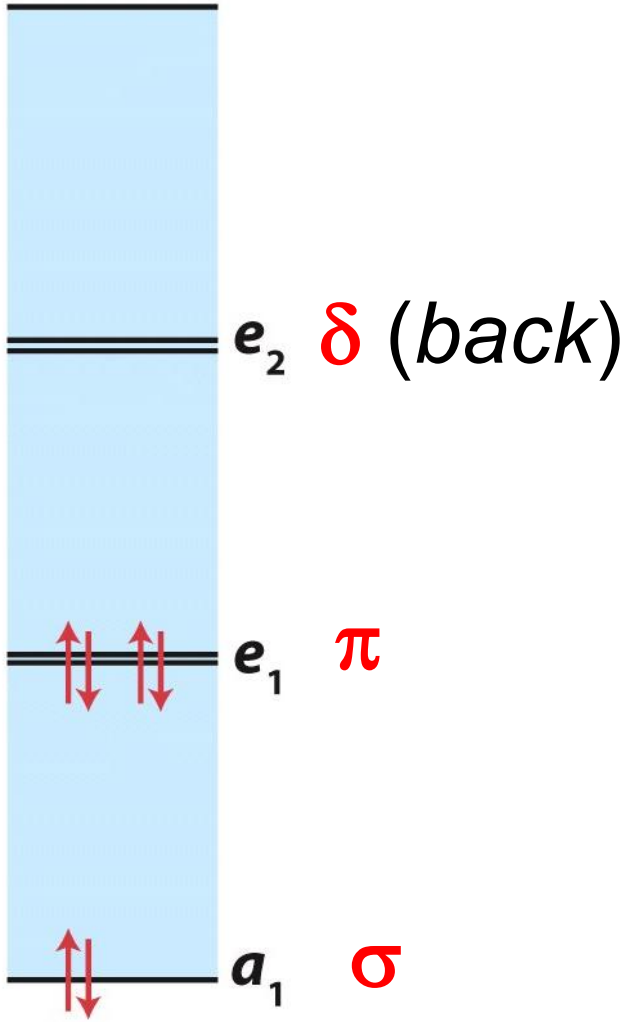




$[Mo(\eta^3\text{-}C_3H_5)(\eta^4\text{-}CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)]$

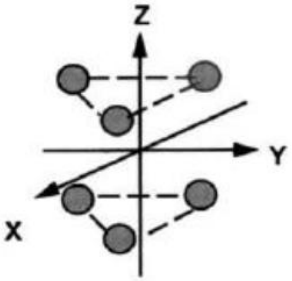

C_6H_6
Cr

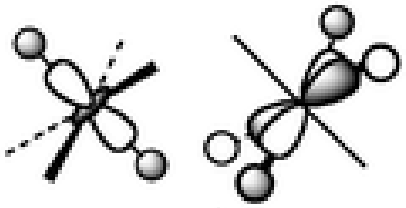




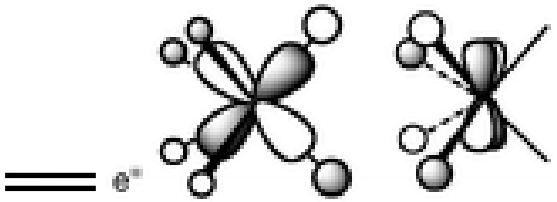
d_{z^2} (full)

empty *(n+1)s* and *(n+1)*p_z

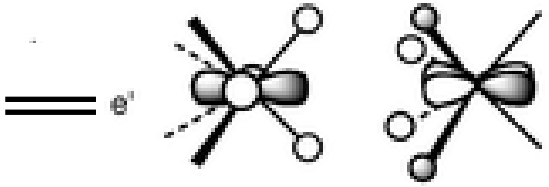




dz^2
$dx^2\text{-}y^2$ e_g



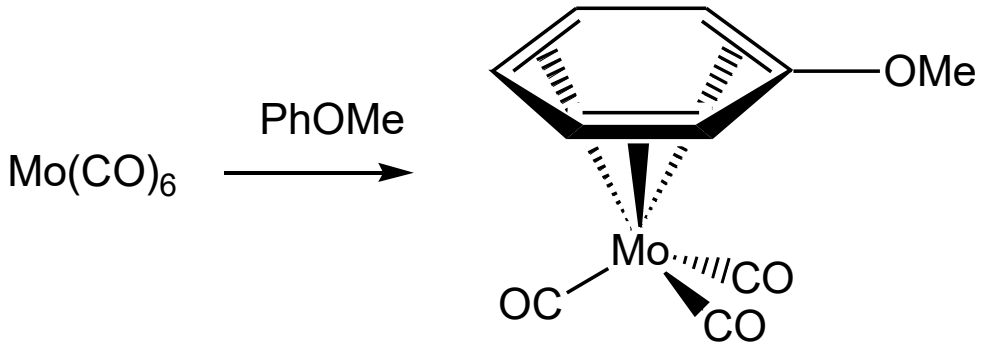
dxz
dyz

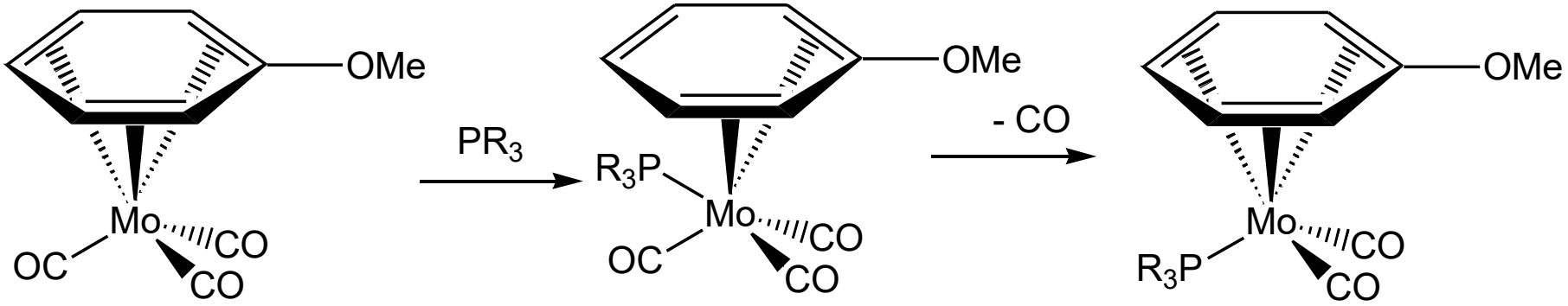


dxy,
$dx^2\text{-}y^2$

dxz
dyz
dxy t_{2g}

dz^2



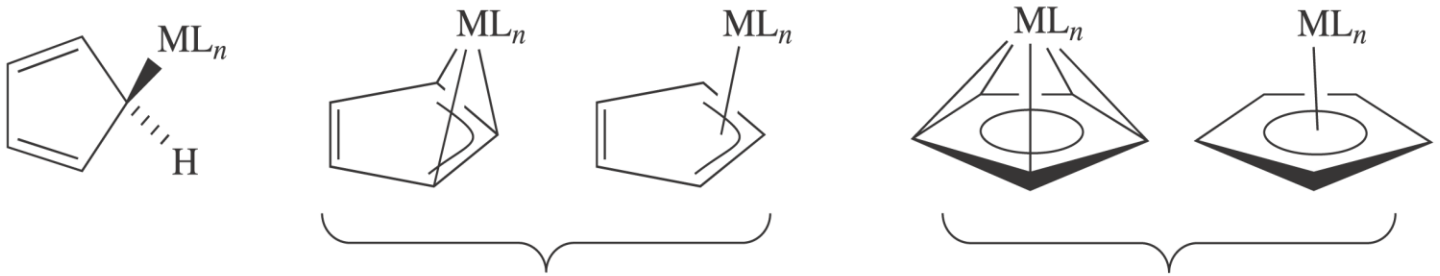


η^6-arene

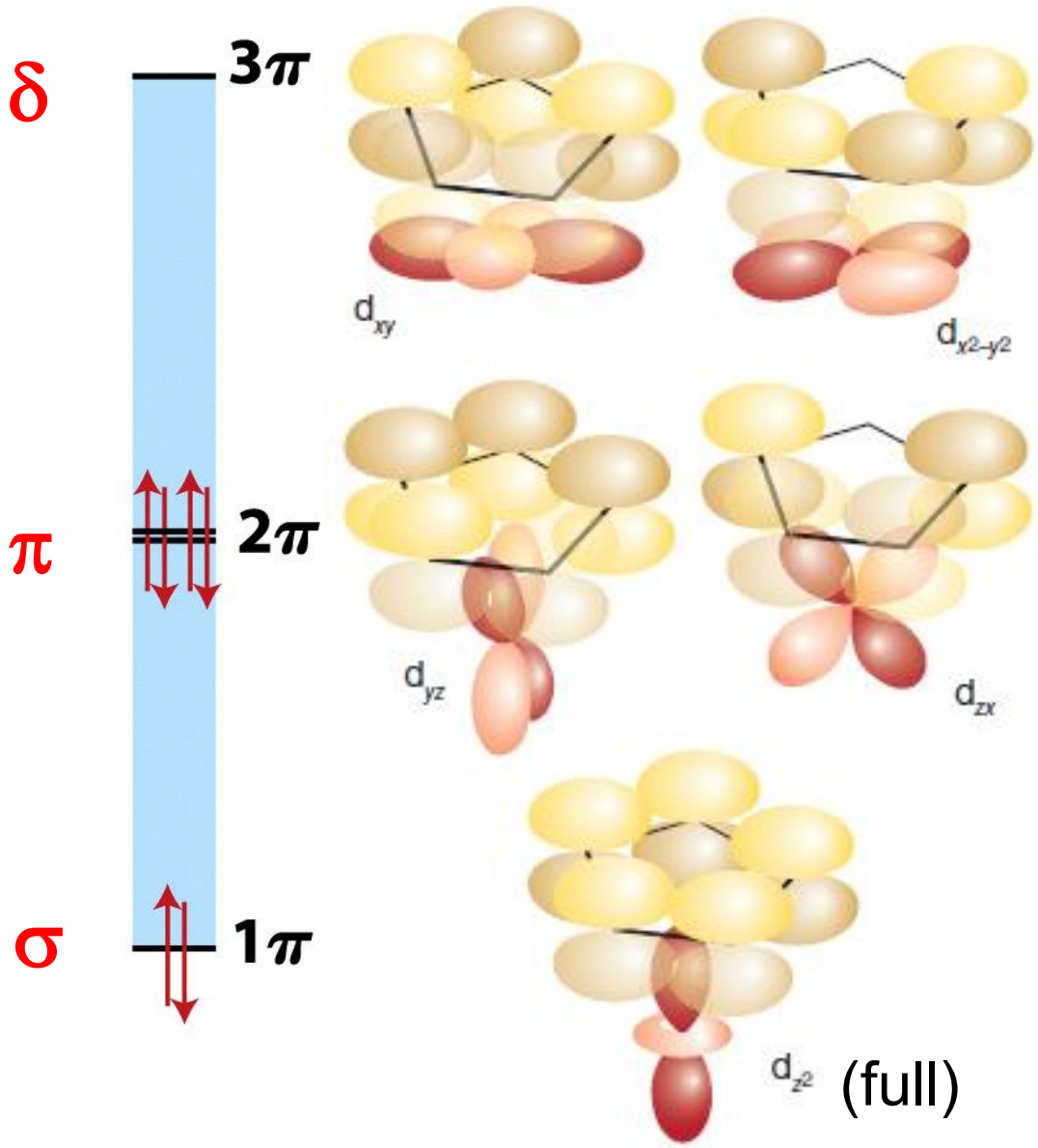
η^4-arene

slipping intermediate

η^6-arene

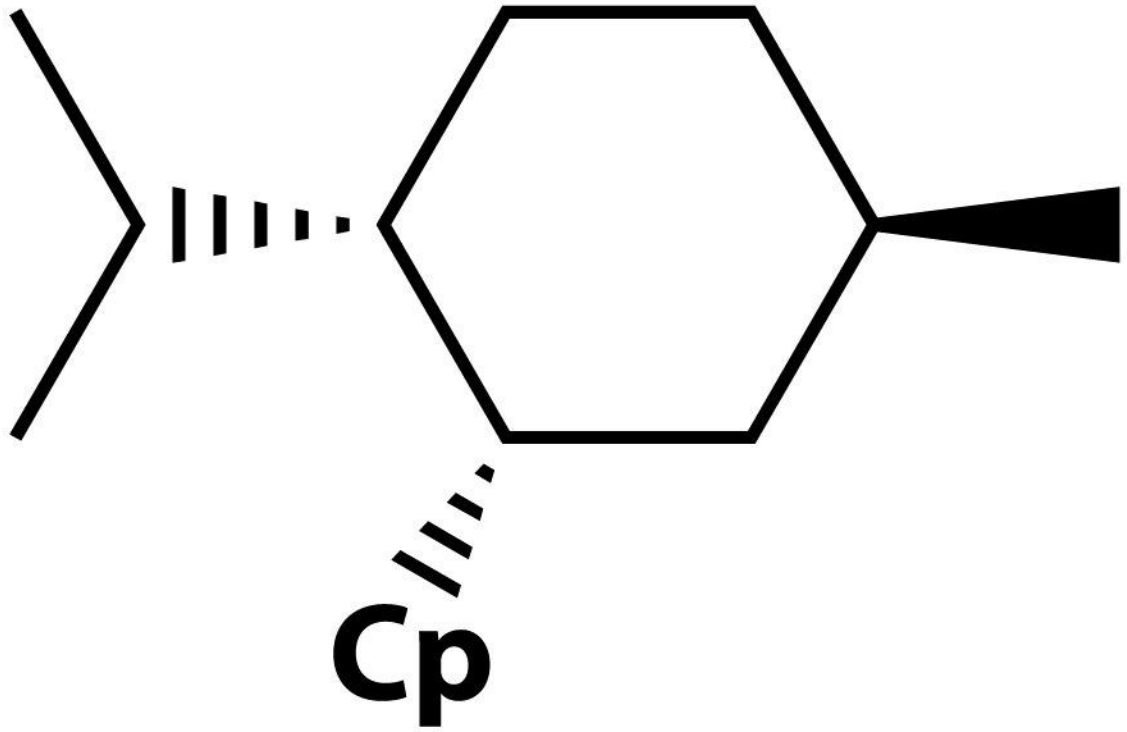


η^1-mode η^3-mode η^5-mode



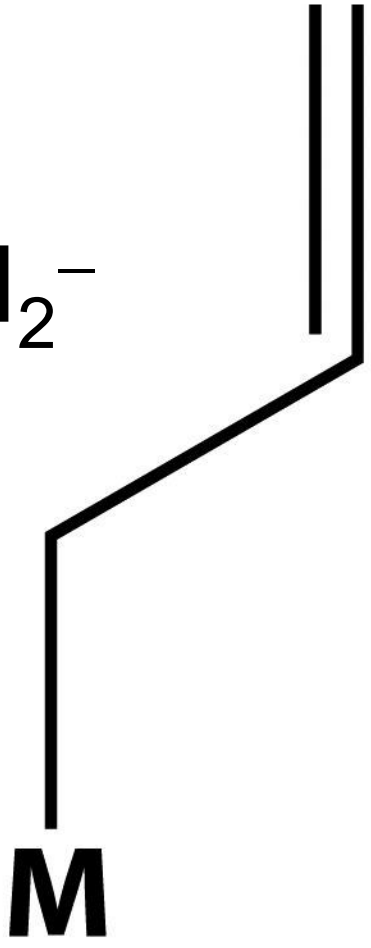
(full)

empty *(n+1)s* and *(n+1)*p_z

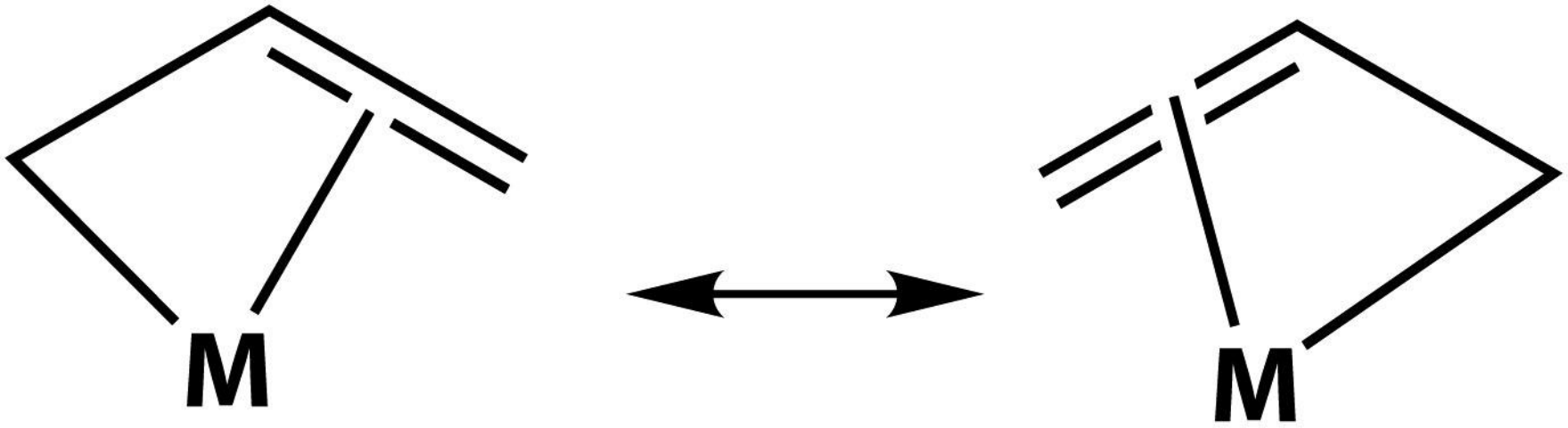


***neo*-Menthylcyclopentadienyl**

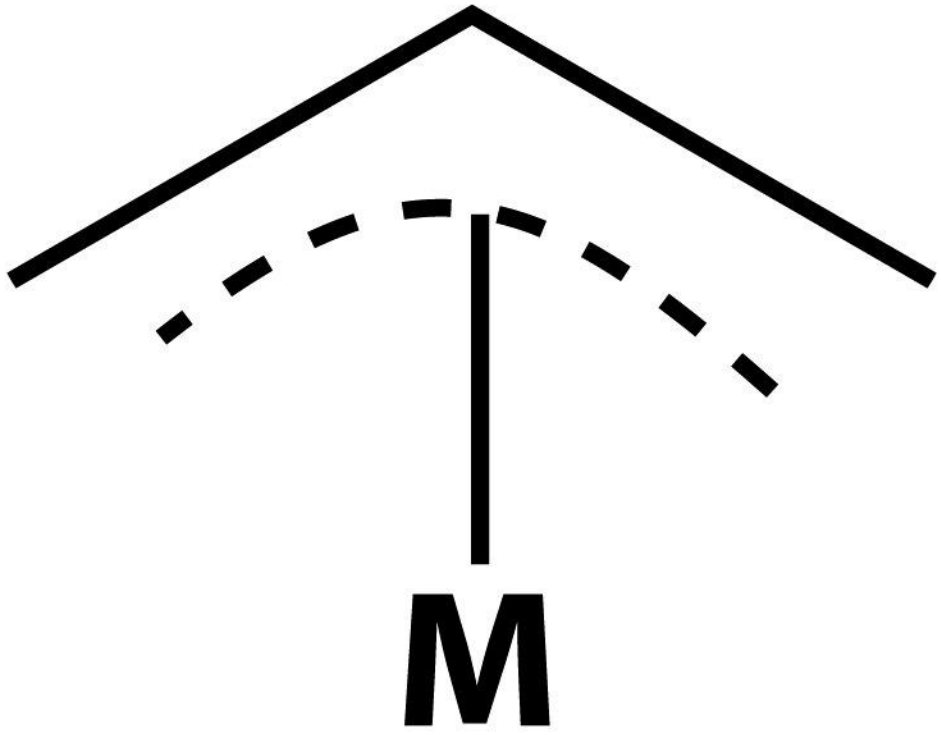
Allyl group,
$CH_2=CH-CH_2^-$



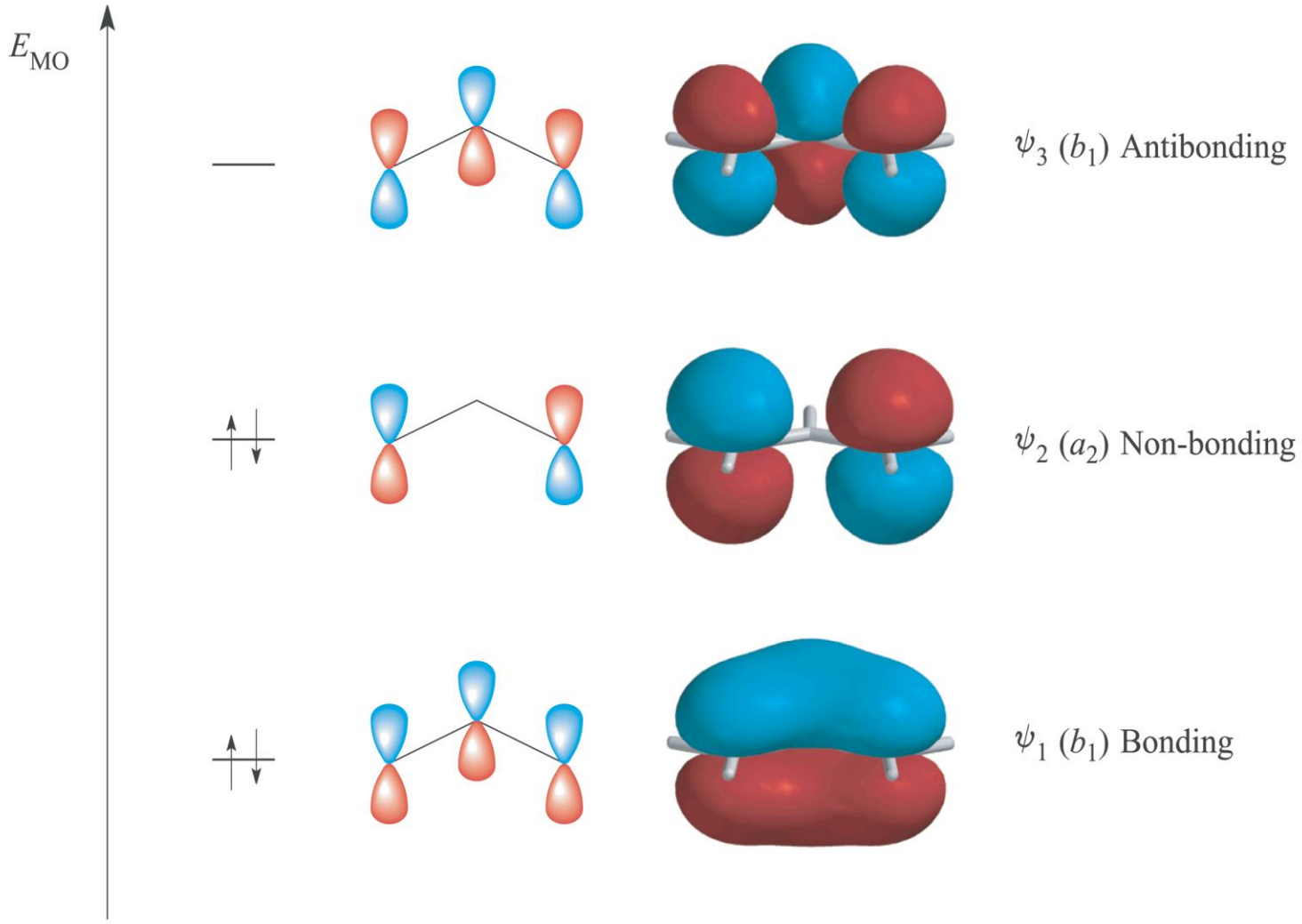
η^1-($CH_2CH=CH_2$)



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



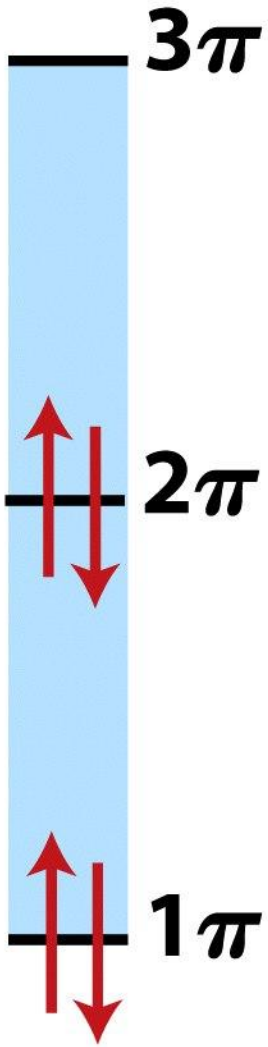
η^3-$(CH_2CH{=}CH_2)^-$

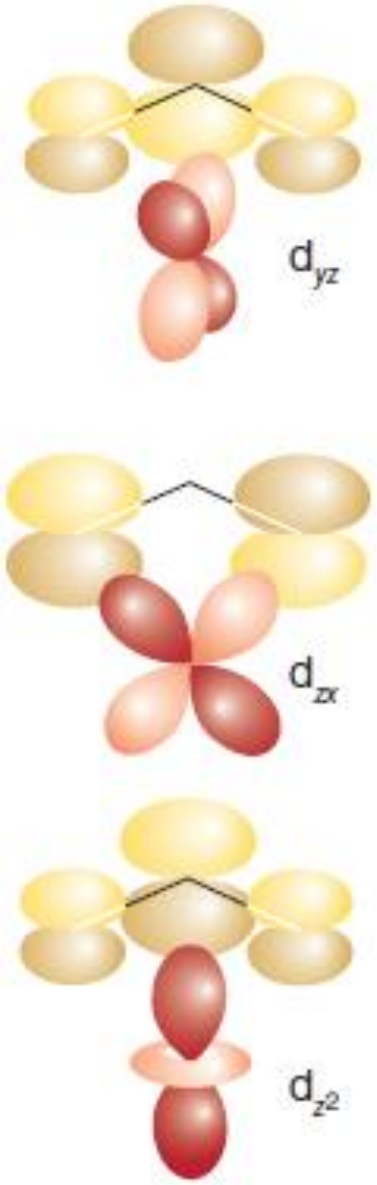

E_{MO}
ψ_3 (b_1) Antibonding
ψ_2 (a_2) Non-bonding
ψ_1 (b_1) Bonding

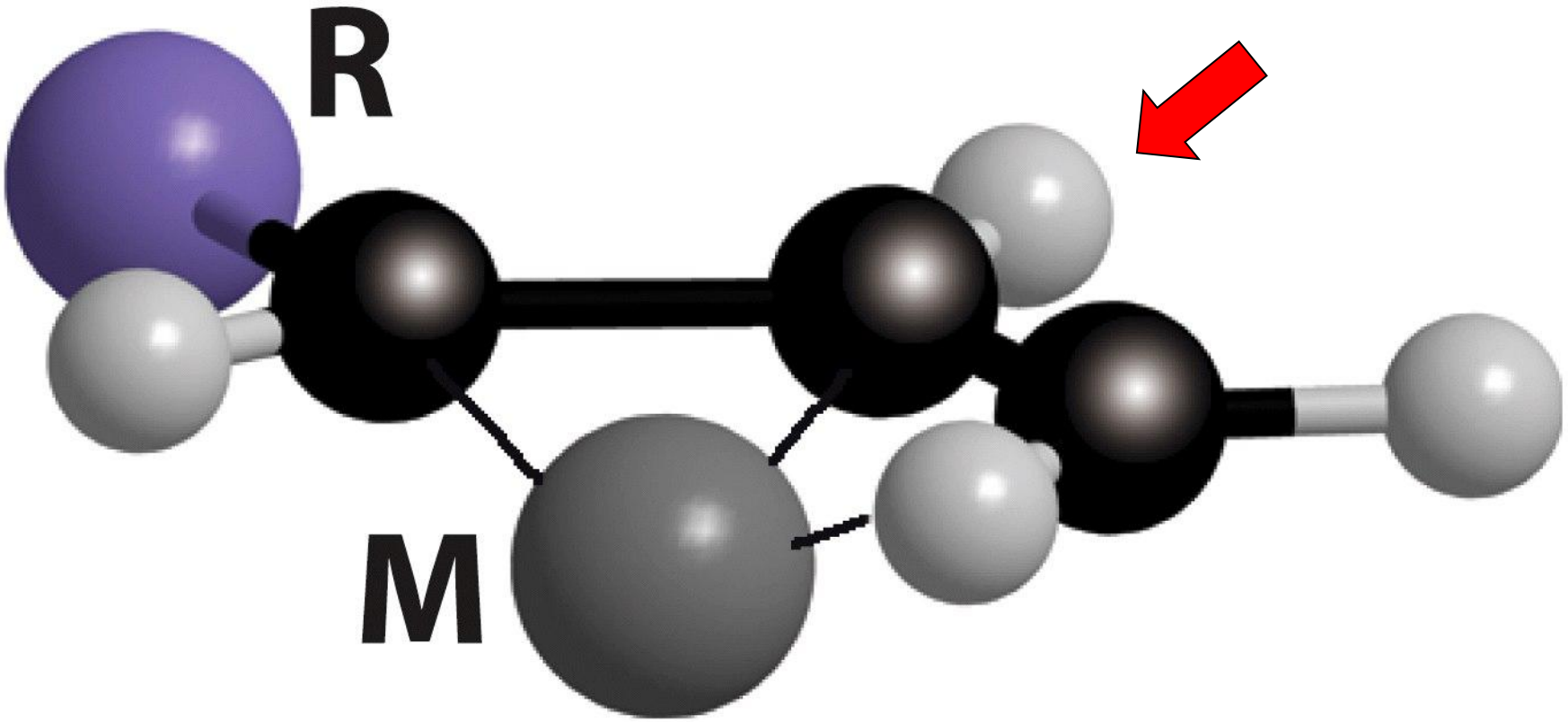
π–acceptor

π-donor

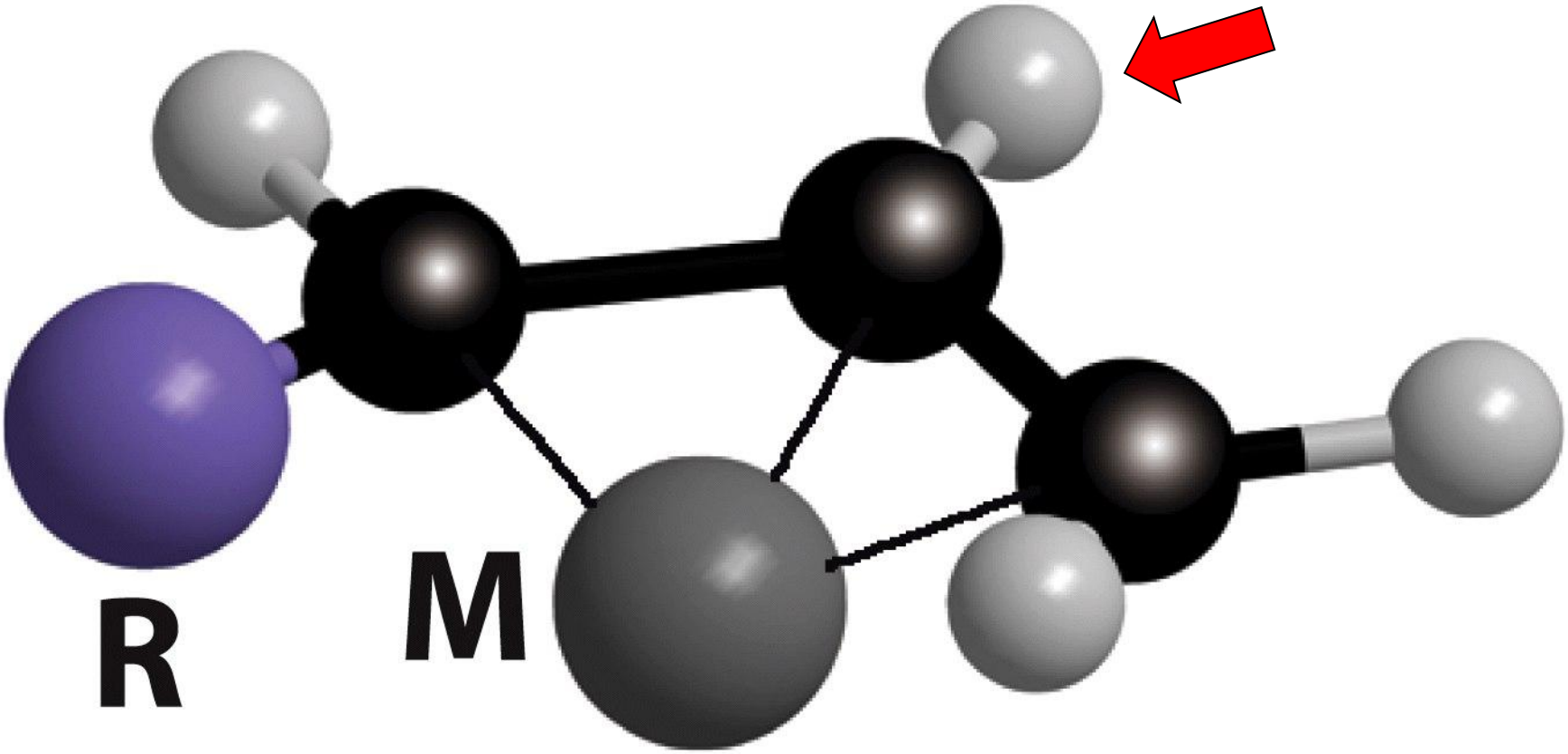
σ-donor







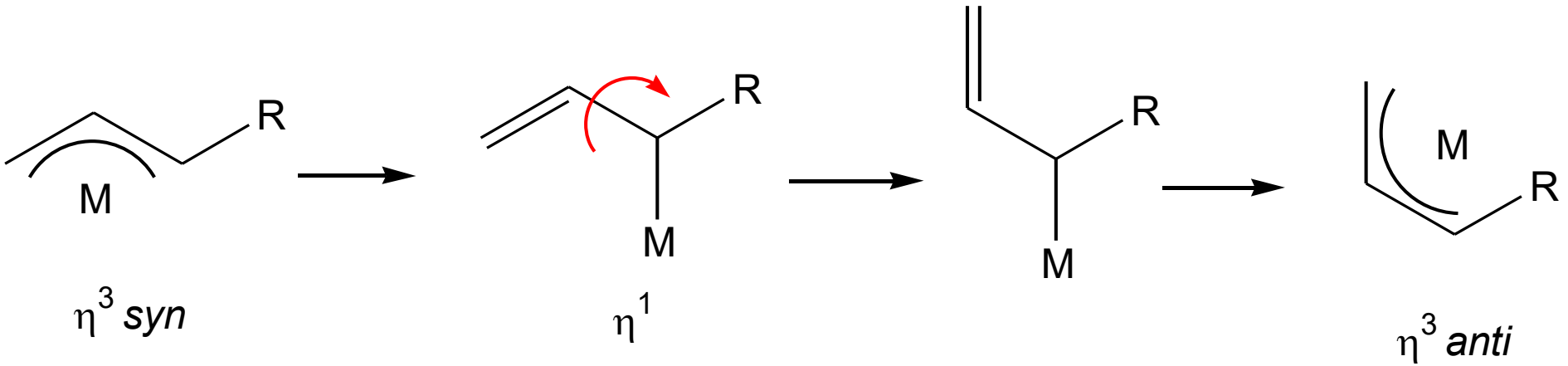
syn



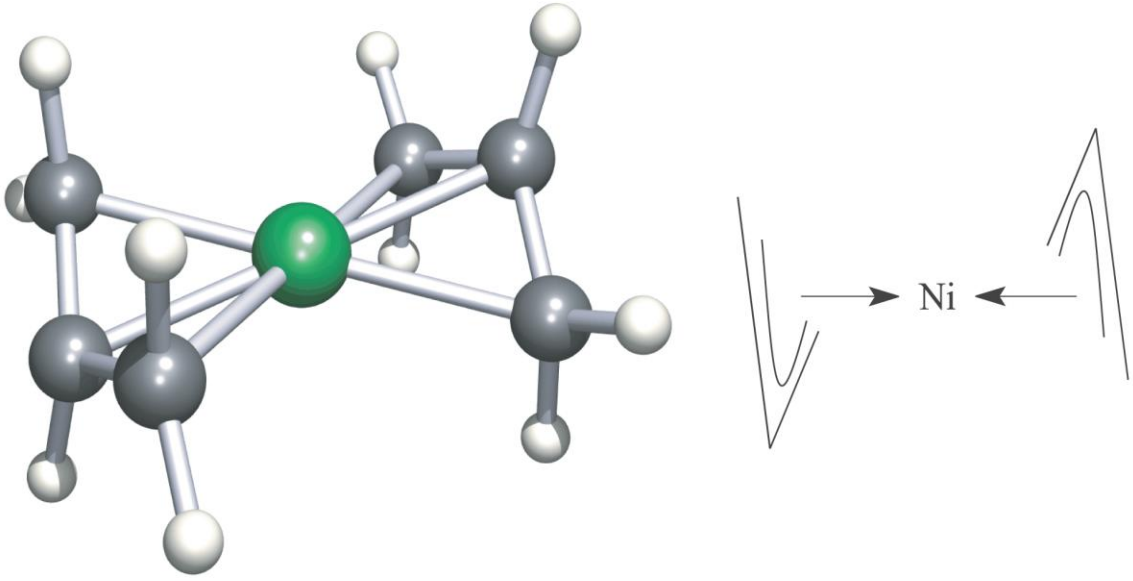
anti

syn-anti exchange mechanism

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

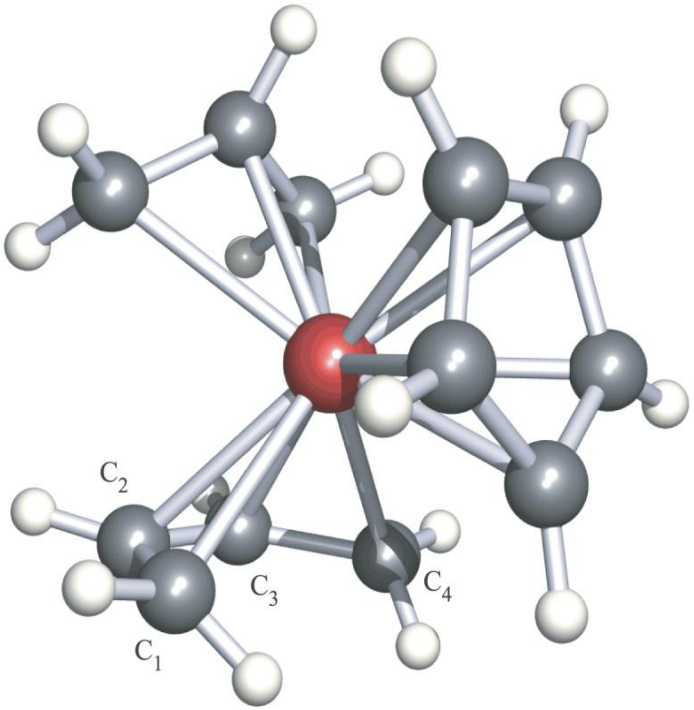


η^3 *syn* η^1 η^3 *anti*

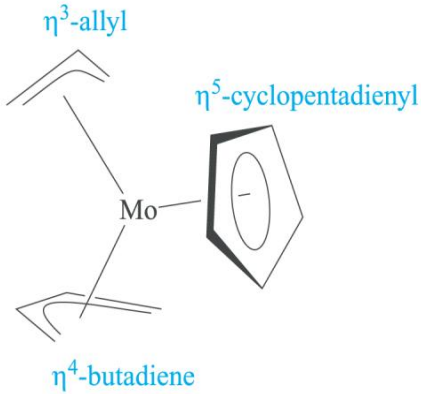


$[Ni(\eta^3\text{-}C_3H_5)_2]$

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

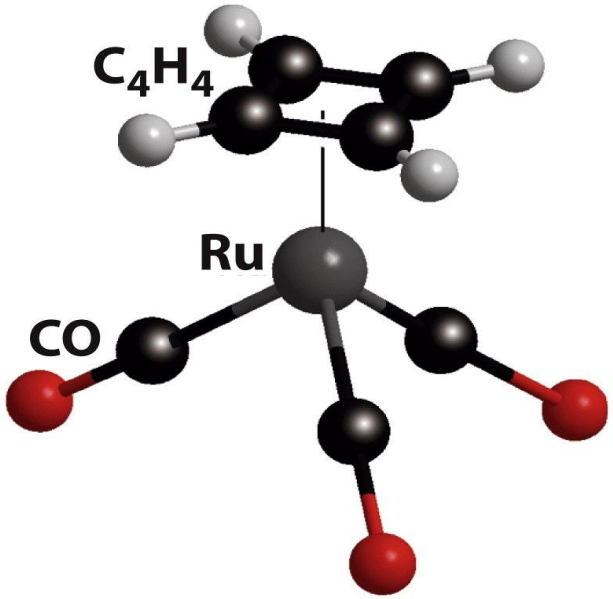


(b)



(c)

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



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

Cyclobutadiene is anti−aromatic (*4π*−electrons), and unstable as a free molecule; but its dianionic form is stable because of being aromatic (*6π*−electrons) - cyclobutadiene is stabilized by significant metal to ligand π−back donation to the vacant ligand orbitals.