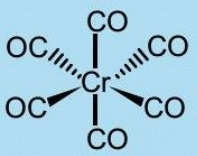
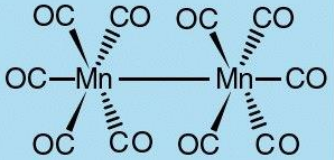
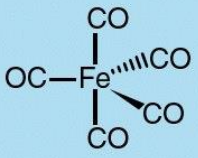
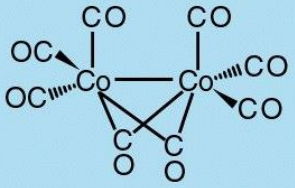
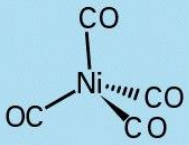
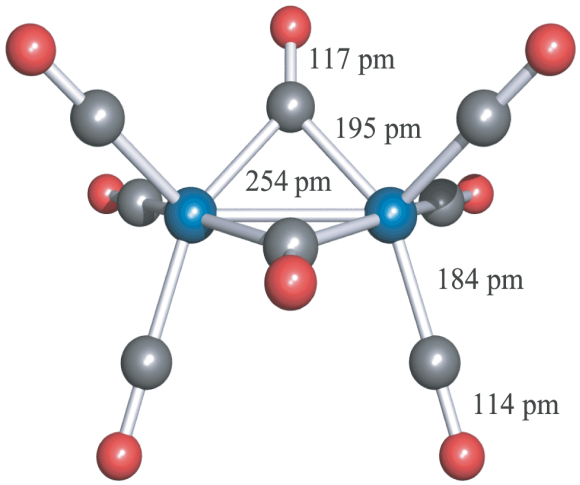
Carbonili omoleptici

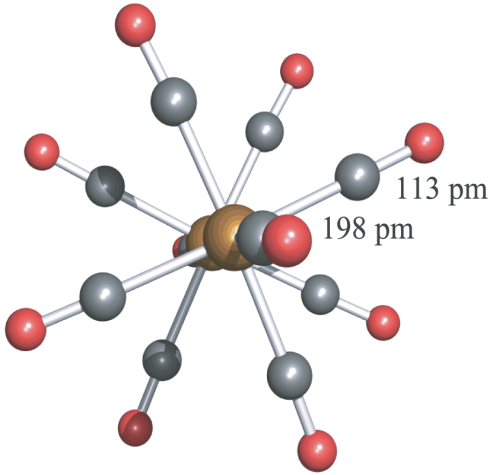
Table 21.5 Formulas and electron count for some 3*d*-series carbonyls

Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr	6	
		6(CO)	12	
			18	
7	$Mn_2(CO)_{10}$	Mn	7	
		5(CO)	10	
		M—M	1	
			18	
8	$Fe(CO)_5$	Fe	8	
		5(CO)	10	
			18	
9	$Co_2(CO)_8$	Co	9	
		4(CO)	8	
		M—M	1	
			18	
10	$Ni(CO)_4$	Ni	10	
		4(CO)	8	
			18	



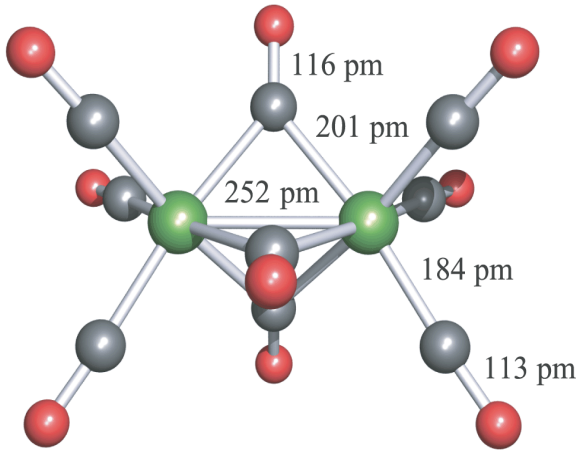
(d)

$Co_2(CO)_8$



(b)

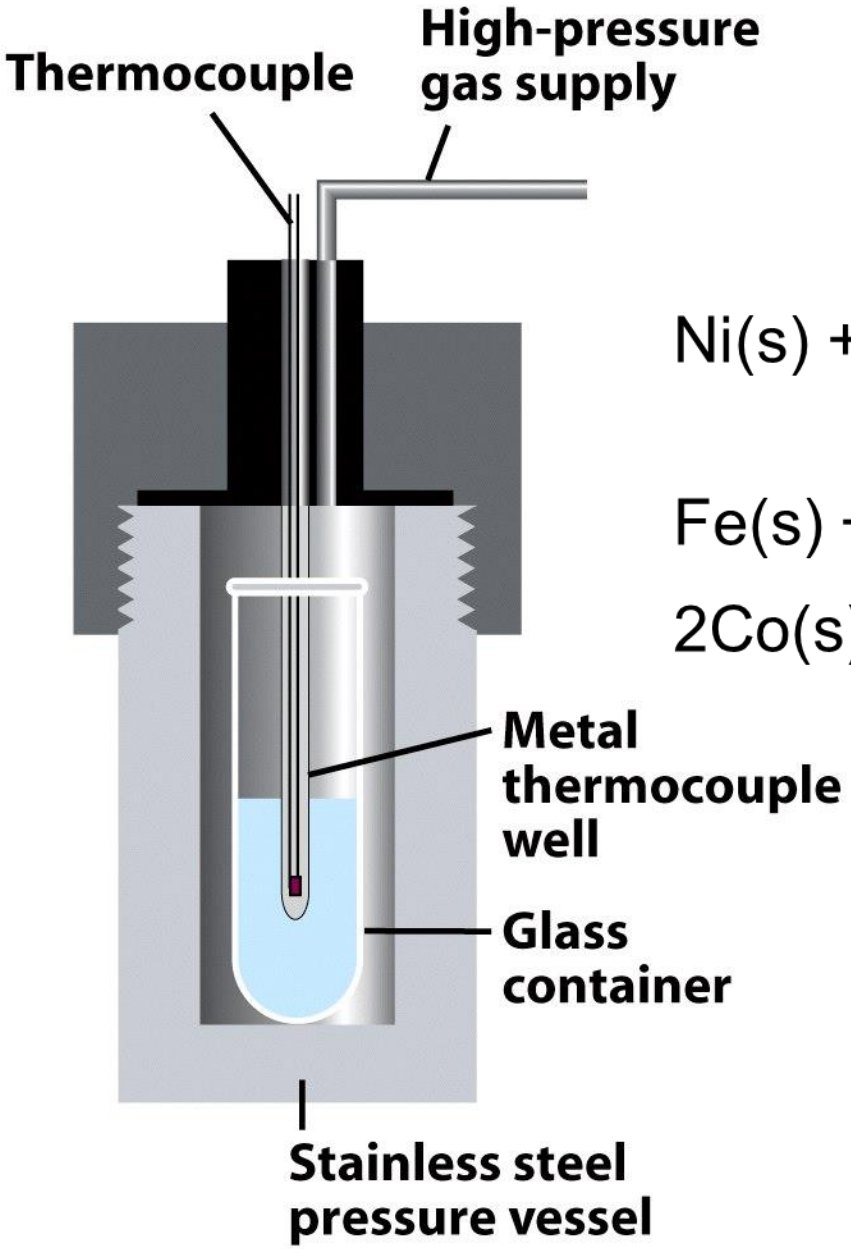
$Re_2(CO)_{10}$



(c)

$Fe_2(CO)_9$

Reazione diretta



$$Ni(s) + 4CO(g) \xrightarrow{50\ °C,1\ atm\ CO} Ni(CO)_4(g)$$

$$Fe(s) + 5CO(g) \xrightarrow{200\ °C,\ 200\ atm} Fe(CO)_5(l)$$

$$2Co(s) + 8CO(g) \xrightarrow{150\ °C,\ 35\ atm} Co_2(CO)_8(s)$$

Carbonilazione riduttiva

$$CrCl_3(s) + Al(s) + 6CO(g) \xrightarrow{AlCl_3,\text{benzene}} AlCl_3(sol) + Cr(CO)_6(sol)$$

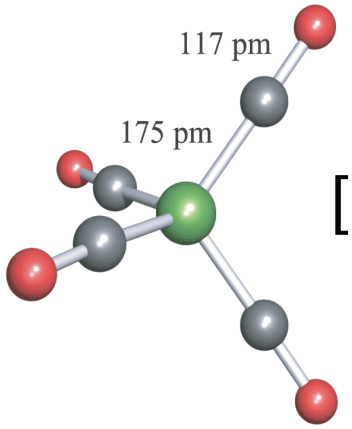
$$3Ru(acac)_3 + H_2(g) + 12CO(g) \xrightarrow{150\ ^\circ C,\ 200\ atm,CH_3OH} Ru_3(CO)_{12} + \ldots.$$

$$Re_2O_7(s) + 17CO(g) \xrightarrow{250\ ^\circ C,\ 350\ atm} Re_2(CO)_{10}(s) + 7\ CO_2(g)$$

Group number	5	6	7	8	9	10
First row metals	$V(CO)_6$ Dark blue solid; paramagnetic; dec. 343 K	$Cr(CO)_6$ White solid; sublimes *in vacuo*; dec. 403 K	$Mn_2(CO)_{10}$ Yellow solid; mp 427 K	$Fe(CO)_5$ Yellow liquid; mp 253 K; bp 376 K	$Co_2(CO)_8$ Air-sensitive, orange-red solid; mp 324 K	$Ni(CO)_4$ Colourless, volatile liquid; highly toxic vapour; bp 316 K
				$Fe_2(CO)_9$ Golden crystals; mp 373 K (dec.)	$Co_4(CO)_{12}$ Air-sensitive, black solid	
				$Fe_3(CO)_{12}$ Dark green solid; dec. 413 K	$Co_6(CO)_{16}$ Black solid; slowly dec. in air	
Second row metals		$Mo(CO)_6$ White solid; sublimes *in vacuo*	$Tc_2(CO)_{10}$ White solid; slowly dec. in air; mp 433 K	$Ru(CO)_5$ Colourless liquid; mp 251 K; dec. in air at 298 K to $Ru_3(CO)_{12} + CO$	$Rh_4(CO)_{12}$ Red solid; >403 K dec. to $Rh_6(CO)_{16}$	
				$Ru_3(CO)_{12}$ Orange solid; mp 427 K; sublimes *in vacuo*	$Rh_6(CO)_{16}$ Black solid; dec. >573 K	
Third row metals		$W(CO)_6$ White solid; sublimes *in vacuo*	$Re_2(CO)_{10}$ White solid; mp 450 K	$Os(CO)_5$ Yellow liquid; mp 275 K	$Ir_4(CO)_{12}$ Slightly air-sensitive yellow solid; mp 443 K	
				$Os_3(CO)_{12}$ Yellow solid; mp 497 K	$Ir_6(CO)_{16}$ Red solid	

Riduzione dei metallocarbonili a metallocarbonilati

$$2Na + Fe(CO)_5 \xrightarrow{THF} (Na^+)_2[Fe(CO)_4]^{2-} + CO$$



$[Fe(CO)_4]^{2-}$

$$2Na + (OC)_5Mn\text{-}Mn(CO)_5 \xrightarrow{THF} 2Na[Mn(CO)_5]$$

Ossidazione (rottura ossidativa) di un legame M−M in metallo-carbonili

$$[(OC)_5Mn^{(0)}{-}Mn^{(0)}(CO)_5] + Br_2 \rightarrow 2[Mn^{(+1)}Br(CO)_5]$$

Table 21.6 Acidity constants of *d*-metal hydrides in acetonitrile at 25°C

Hydride	pK_a
$[CoH(CO)_4]$	8.3
$[CoH(CO)_3P(OPh)_3]$	11.3
$[Fe(H)_2(CO)_4]$	11.4
$[CrH(Cp)(CO)_3]$	13.3
$[MoH(Cp)(CO)_3]$	13.9
$[MnH(CO)_5]$	15.1
$[CoH(CO)_3PPh_3]$	15.4
$[WH(Cp)(CO)_3]$	16.1
$[MoH(Cp^*)(CO)_3]$	17.1
$[Ru(H)_2(CO)_4]$	18.7
$[FeH(Cp)(CO)_2]$	19.4
$[RuH(Cp)(CO)_2]$	20.2
$[Os(H)_2(CO)_4]$	20.8
$[ReH(CO)_5]$	21.1
$[FeH(Cp^*)(CO)_2]$	26.3
$[WH(Cp)(CO)_2PMe_3]$	26.6

Protonazione di metallocarbonilati

$$[Mn(CO)_5]^- + H^+ \rightarrow [MnH(CO)_5]$$

Basicità dei metallocarbonilati
Attacco nucleofilo

$[Mn(CO)_5]^- + CH_3I \rightarrow [Mn(CH_3)(CO)_5] + I^-$

$[Co(CO)_4]^- + CH_3COI \rightarrow [Co(COCH_3)(CO)_4] + I^-$

$[Mn(CO)_5]^- + [ReBr(CO)_5] \rightarrow [(OC)_5Mn{-}Re(CO)_5] + Br^-$

Attacchi nucleofili ed elettrofili a carbonili

Metallo elettron-povero: attacco nucleofilo su C

$$Li(CH_3) + [Mo(CO)_6] \rightarrow Li[Mo(COCH_3)(CO)_5]$$

$$[(OC)_nM(CO)] + OH^- \rightarrow [(OC)_nM(COOH)]^-$$

Metallo elettron-ricco: attacco elettrofilo su O

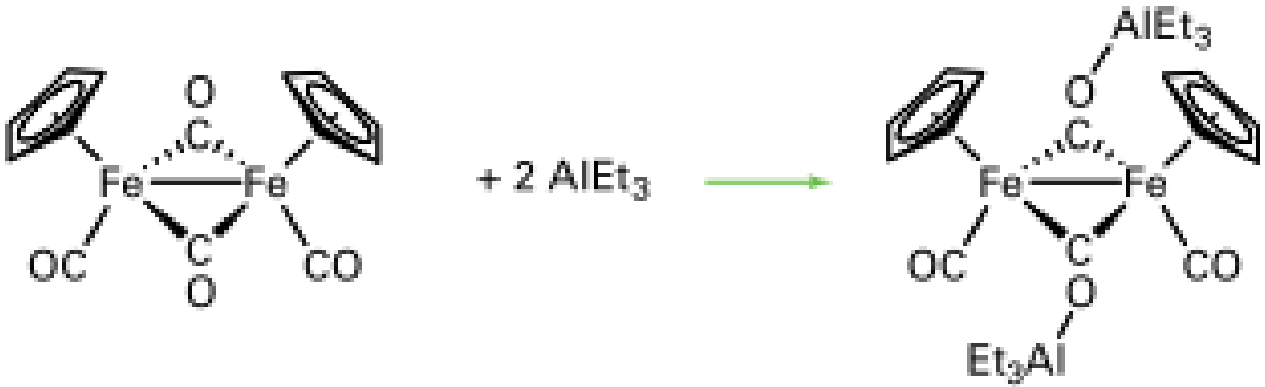
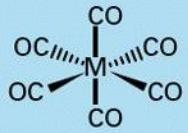
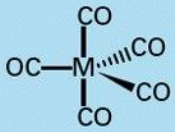
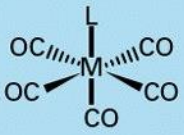
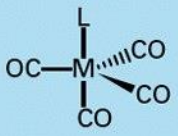
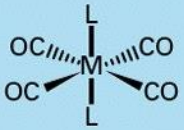
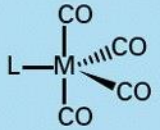
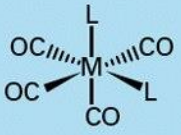
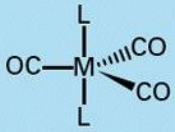
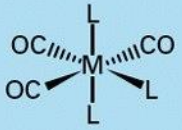
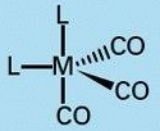
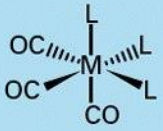
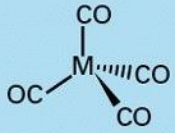
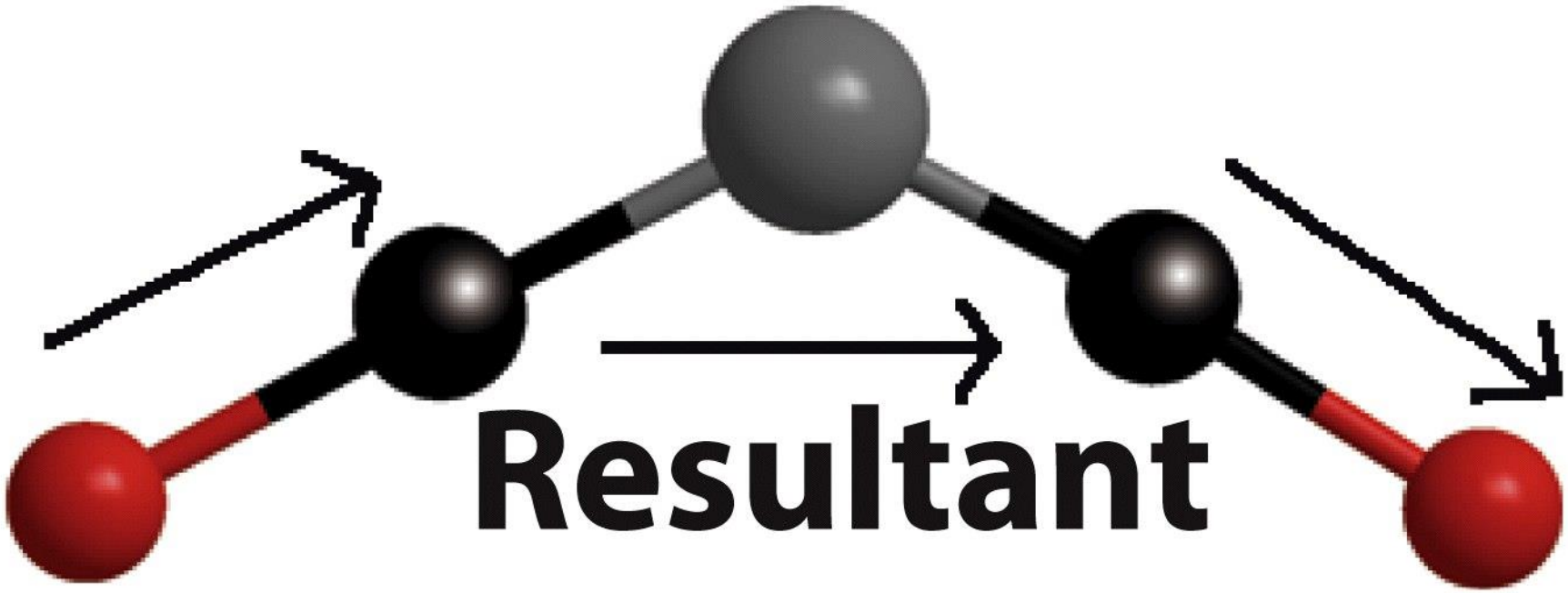


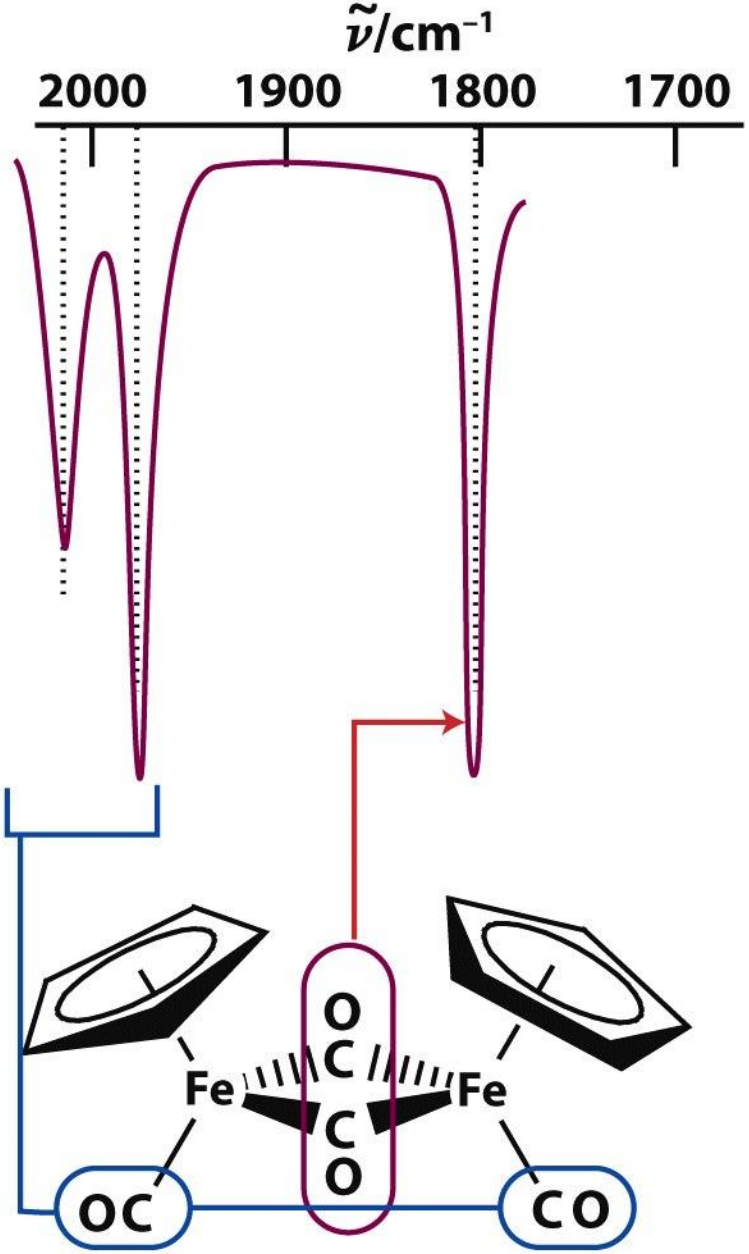
Table 21.7 Relation between the structure of a carbonyl complex and the number of CO stretching bands in its IR spectrum

Complex	Isomer	Structure	Point group	Number of bands*	Complex	Isomer	Structure	Point group	Number of bands*
$M(CO)_6$			O_h	1	$M(CO)_5$			D_{3h}	2
$M(CO)_5L$			C_{4v}	3†	$M(CO)_5$	*ax*		C_{3v}	3§
$M(CO)_4L_2$	*trans*		D_{4h}	1	$M(CO)_4L$	*eq*		C_{2v}	4
$M(CO)_4L_2$	*cis*		C_{2v}	4‡	$M(CO)_3L_2$	*trans*		D_{3h}	1
$M(CO)_3L_3$	*mer*		C_{2v}	3‡	$M(CO)_3L_2$	*cis*		C_s	3
$M(CO)_3L_3$	*fac*		C_{3v}	2	$M(CO)_4$			T_d	1

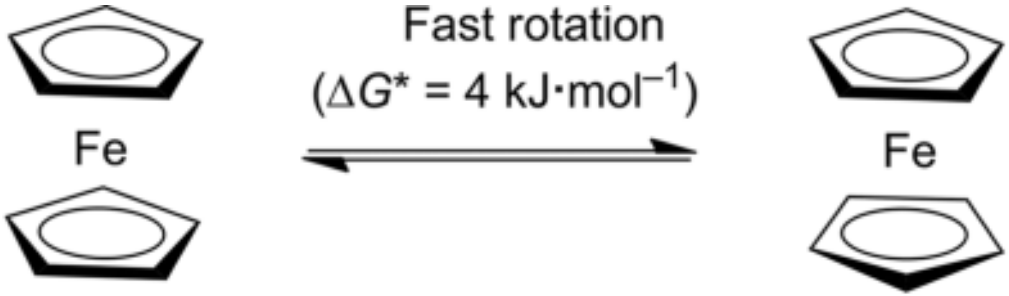
* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained below.
† If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.
‡ If the *trans* CO ligands are nearly collinear, one fewer band will be observed.
§ If the threefold array of CO ligands is nearly planar, only two bands will be observed.


Resultant


Resultant


$\tilde{\nu}$/cm^{-1}
2000
1900
1800
1700
O
C
Fe
Fe
C
O
OC
CO

Ferrocene e Metalloceni



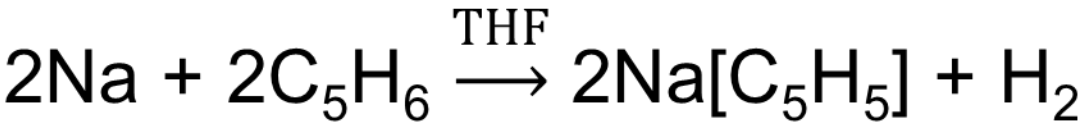
Eclipsed D_{5h} conformation observed in solution by XAFS at very low temperatures[353]

Staggered D_{5d} conformation often observed in crystal structures including for decamethylferrocene

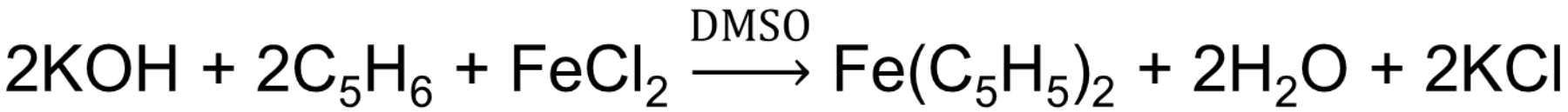
- G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.

- E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, *7*, 377–379.

Nel 2017 si contavano più di 18000 pubblicazioni sui ferroceni

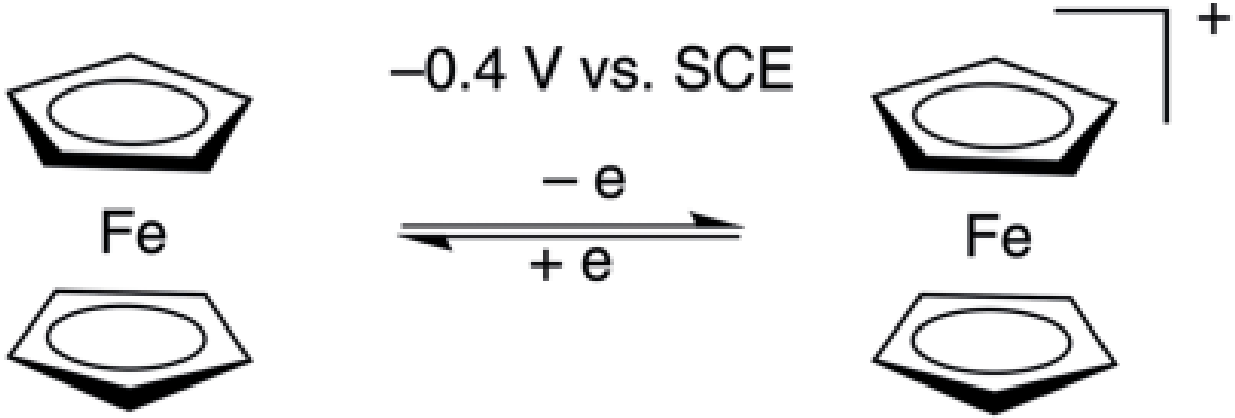


$$2Na + 2C_5H_6 \xrightarrow{THF} 2Na[C_5H_5] + H_2$$



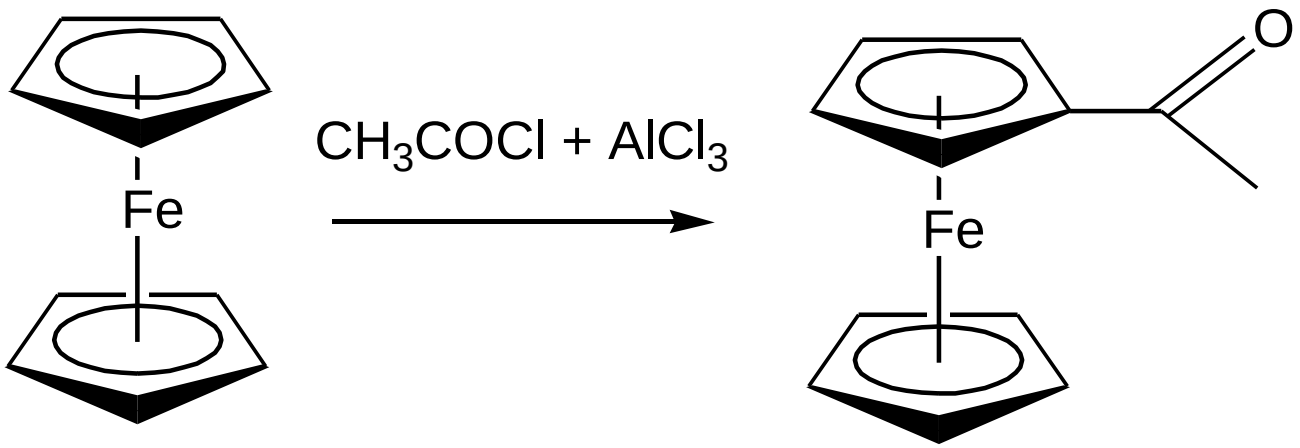
$$2KOH + 2C_5H_6 + FeCl_2 \xrightarrow{DMSO} Fe(C_5H_5)_2 + 2H_2O + 2KCl$$

- Stabile fino a 400 ºC (fonde a 172 ºC)
- Stabile all’aria e solubile in molti solventi organici
- Reattività di un super-elettrofilo aromatico
- Ossidazione reversibile a +0.4 V vs SCE

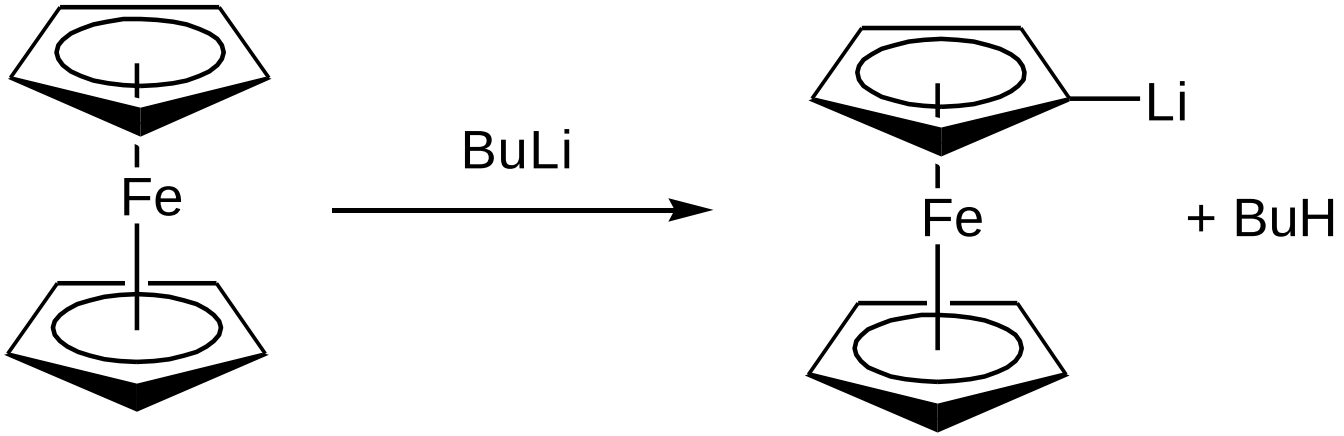


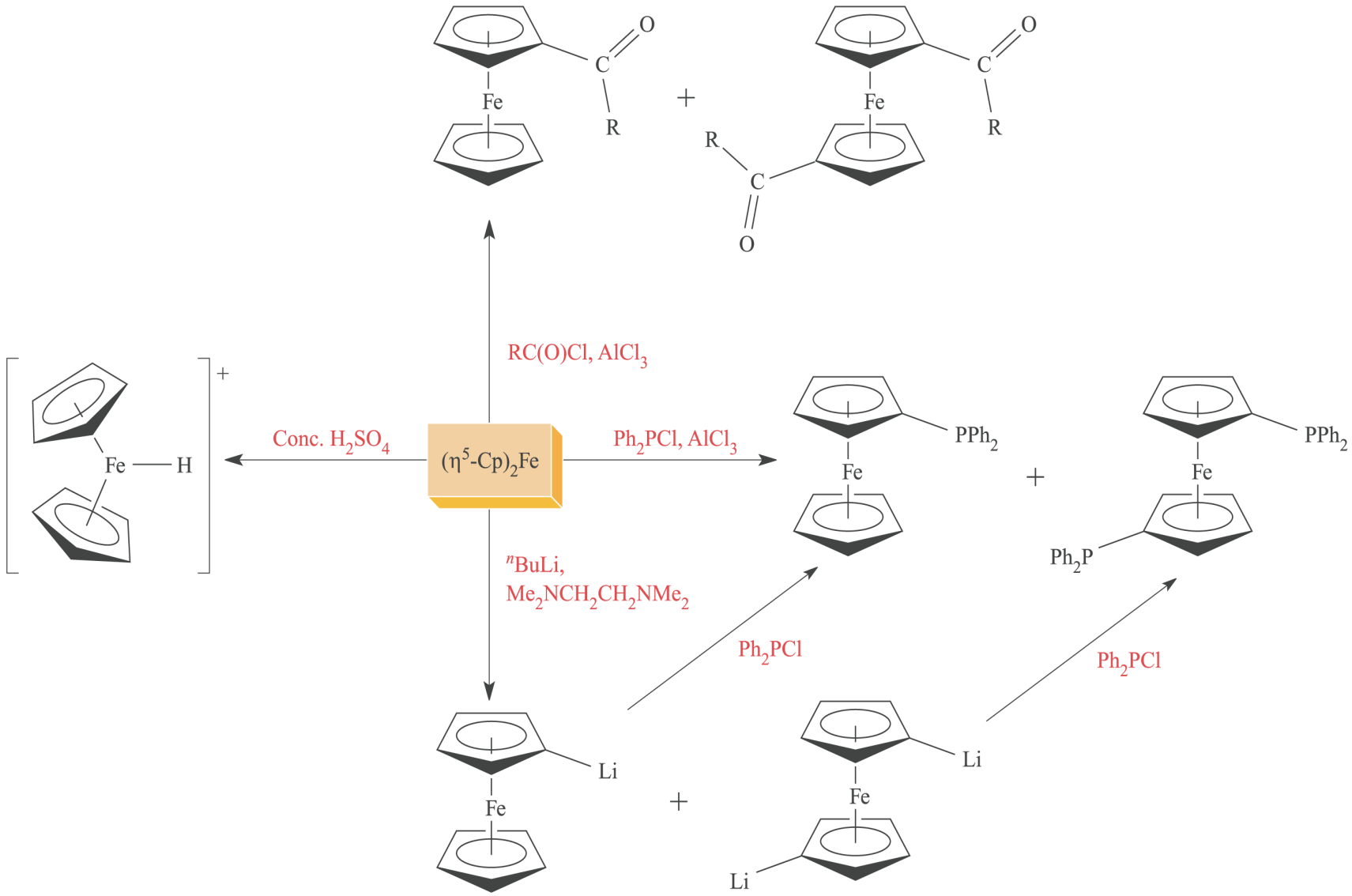
Ferrocene, orange
d^6, Fe^{II}, 18e
Functionalization with
non-oxidizing electrophiles

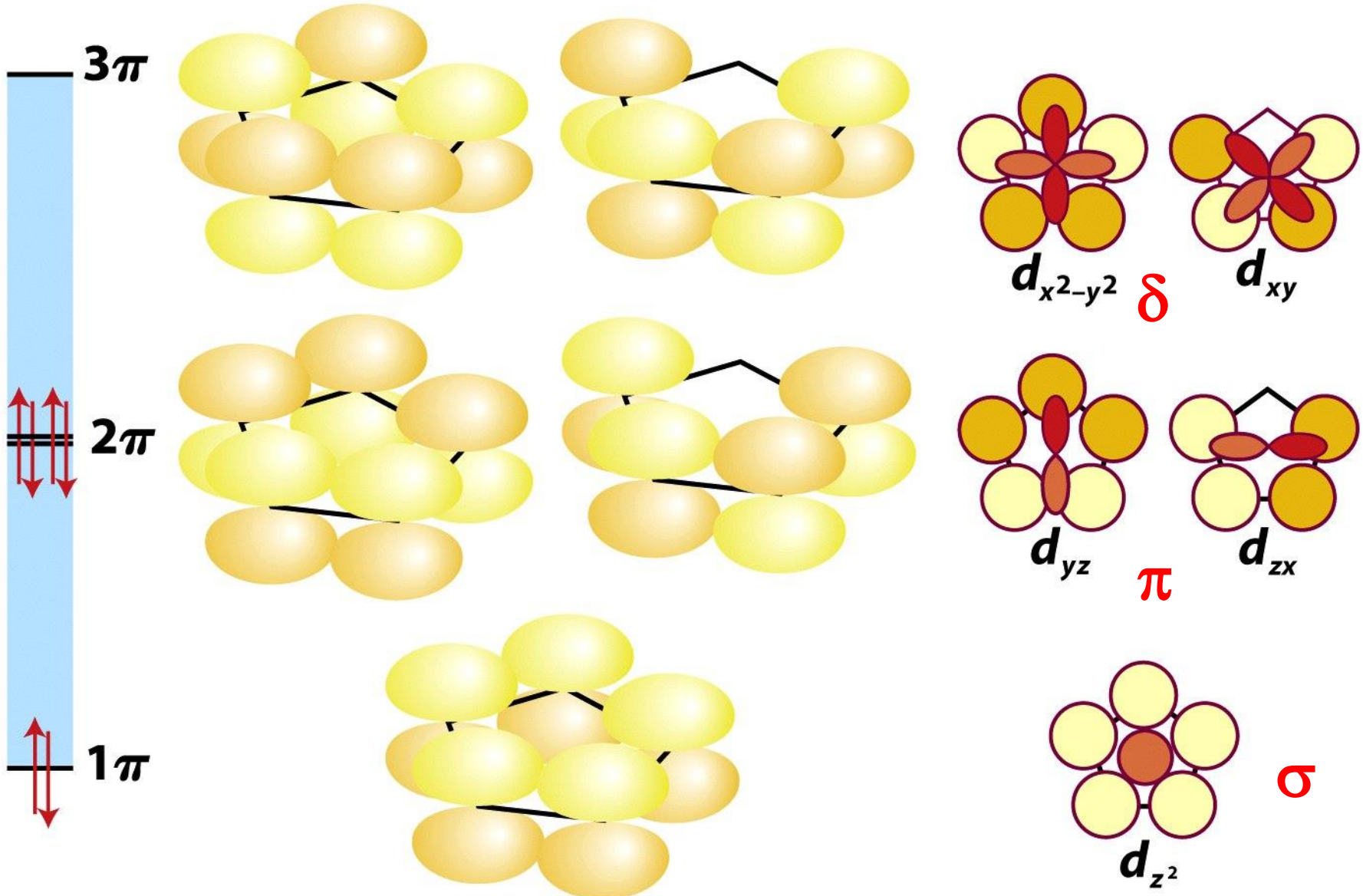
Ferricinium, deep-blue
d^5, Fe^{III}, 17e
Isolable as BF_4^- or PF_6^- salt, etc.
Sensive to O_2 and nucleophiles



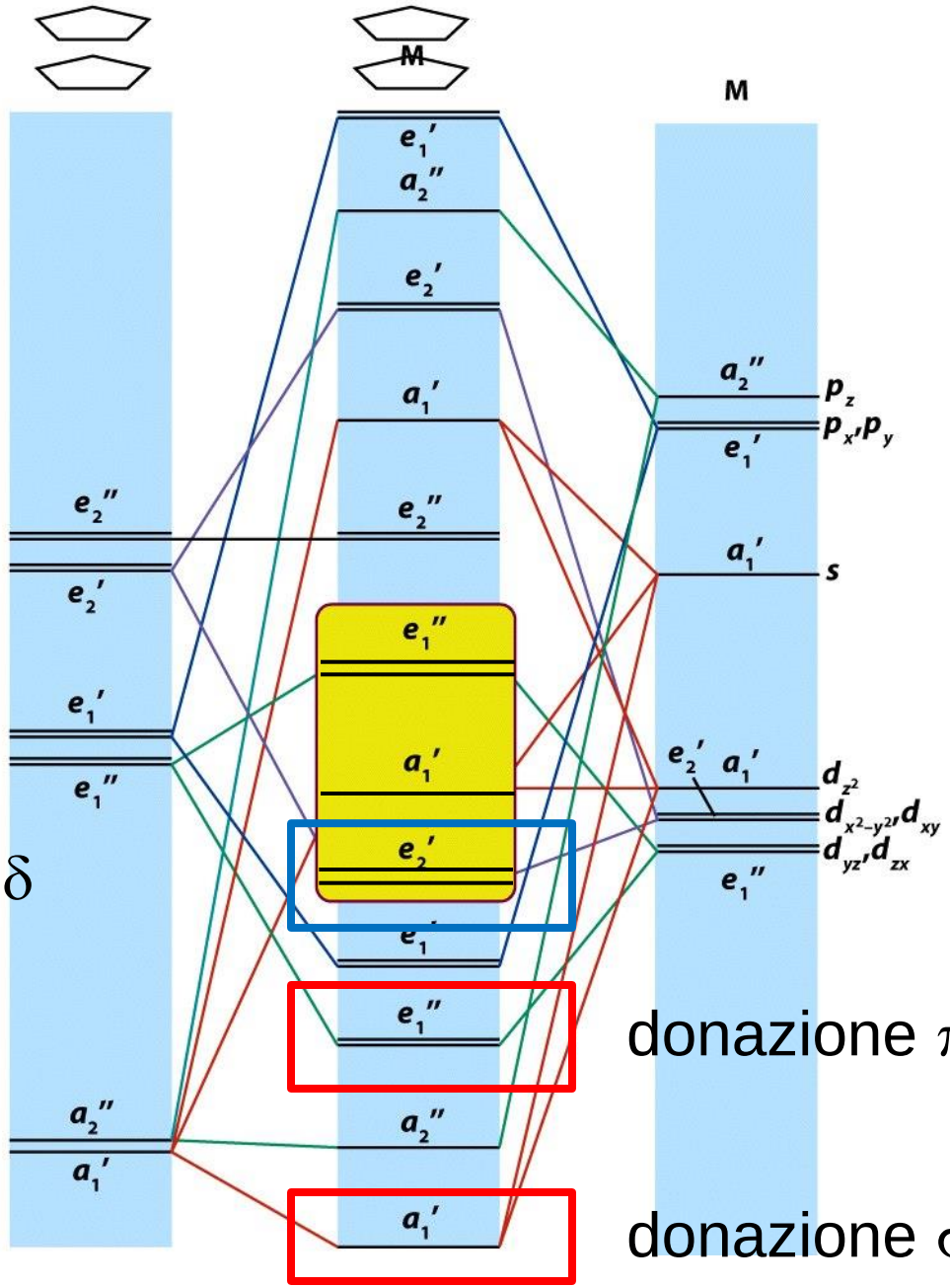
acilazione di Friedel – Crafts




RC(O)Cl, AlCl3
Conc. H2SO4
(η5-Cp)2Fe
Ph2PCl, AlCl3
nBuLi,
Me2NCH2CH2NMe2
Ph2PCl
Ph2PCl
Fe
H
PPh2
Ph2P
Li
O
R


3π
2π
1π
$d_{x^2-y^2}$
δ
d_{xy}
d_{yz}
π
d_{zx}
d_{z^2}
σ

retrodonazione δ



donazione π

donazione σ

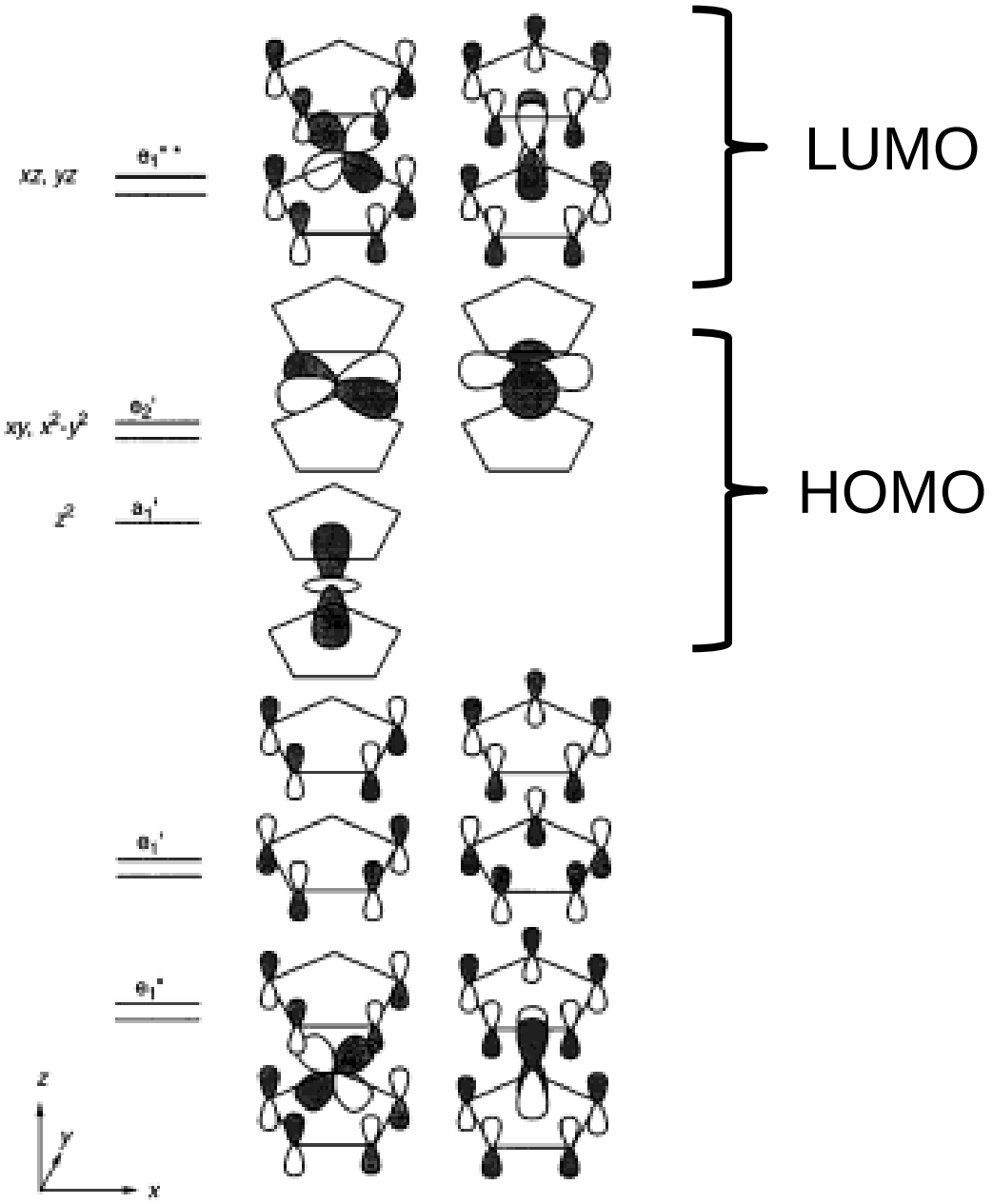
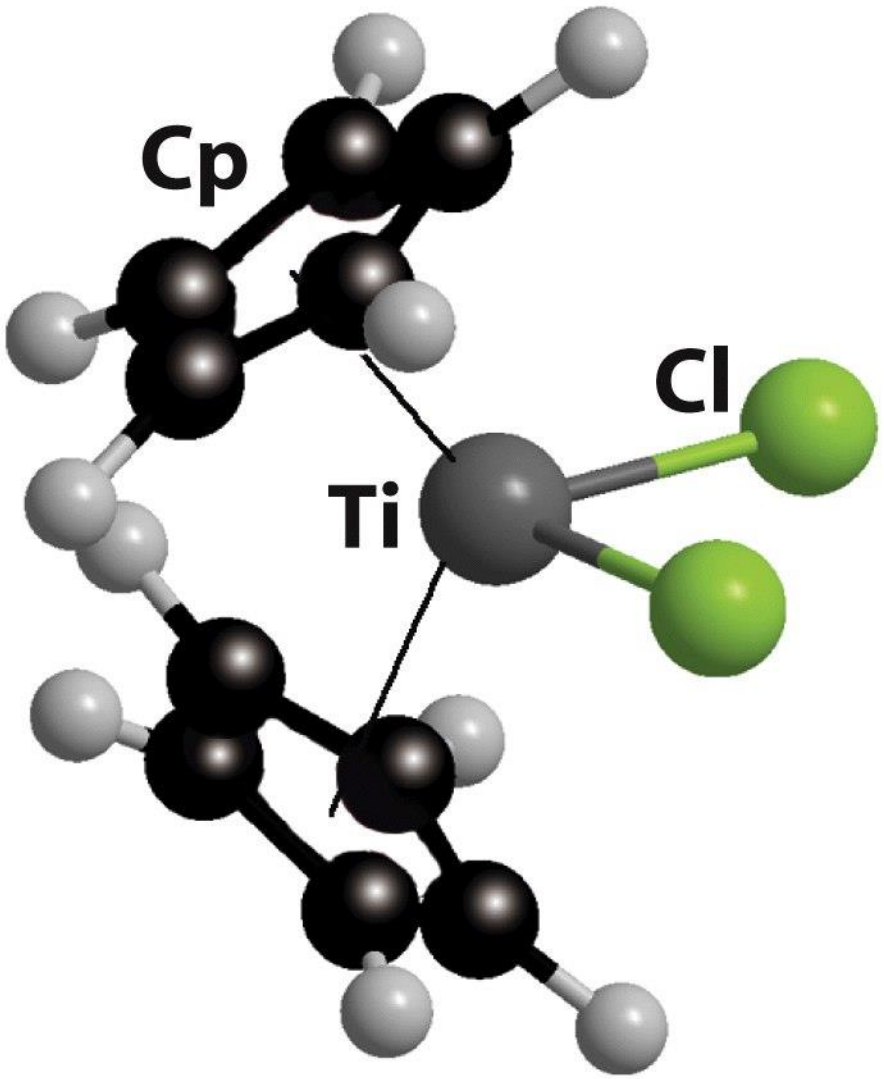

xz, yz
e_1''
xy, x^2-y^2
e_2'
z^2
a_1'
a_1'
e_1''
z
y
x
LUMO
HOMO

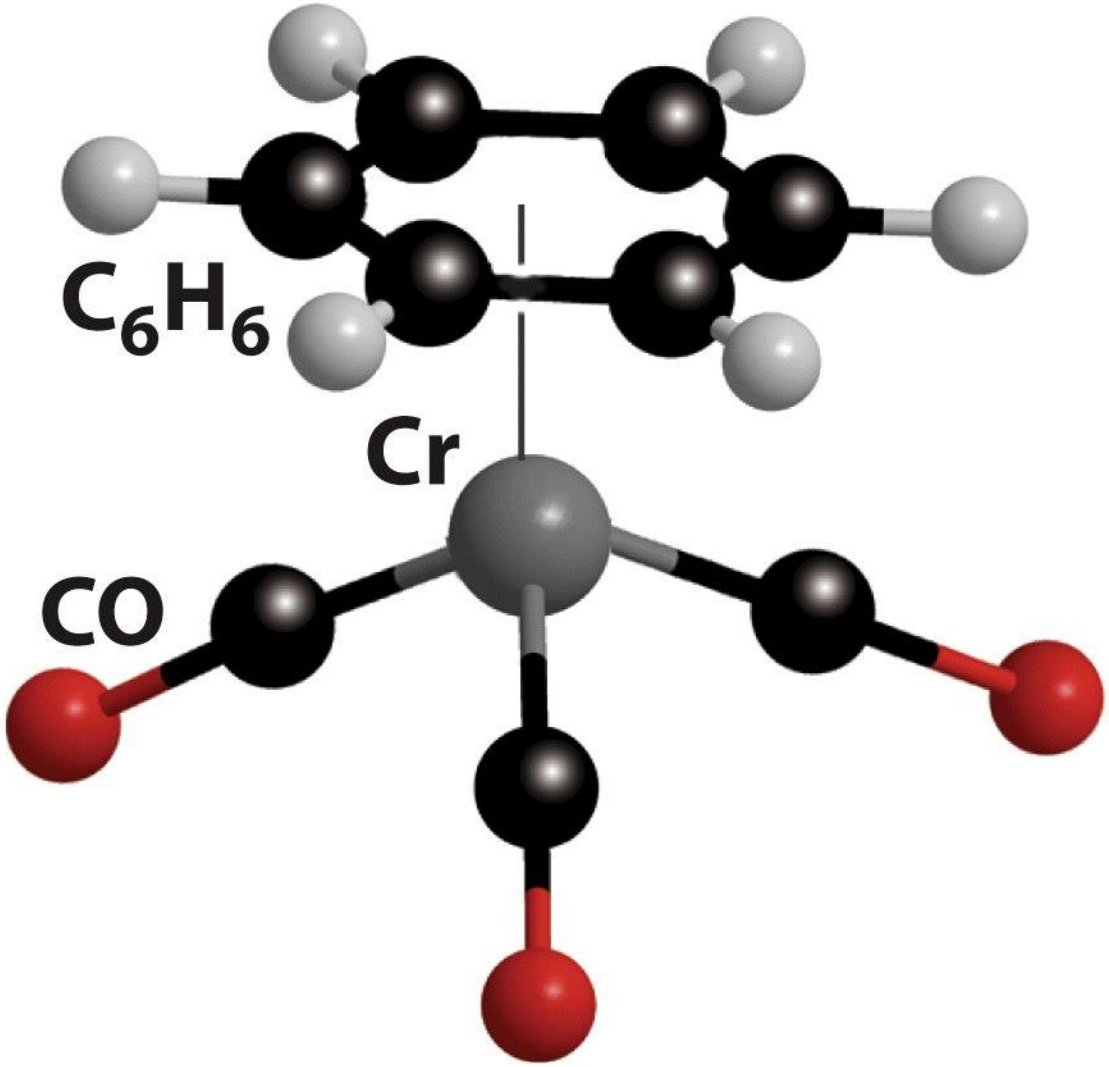
Table 21.8 Electronic configuration and M—C bond length in $[M(\eta^5\text{-Cp})_2]$ complexes

Complex	Valence electrons	Electron configuration	M—C bond length/pm
$[V(\eta^5\text{-Cp})_2]$	15	$e_2'^2 a_1'^1$	228
$[Cr(\eta^5\text{-Cp})_2]$	16	$e_2'^3 a_1'^1$	217
$[Mn(\eta^5\text{-Me-}C_5H_4)_2]$*	17	$e_2'^3 a_1'^2$	211
$[Fe(\eta^5\text{-Cp})_2]$	18	$e_2'^4 a_1'^2$	206
$[Co(\eta^5\text{-Cp})_2]$	19	$e_2'^4 e_1''^1 a_1'^2$	212
$[Ni(\eta^5\text{-Cp})_2]$	20	$e_2'^4 e_1''^2 a_1'^2$	220

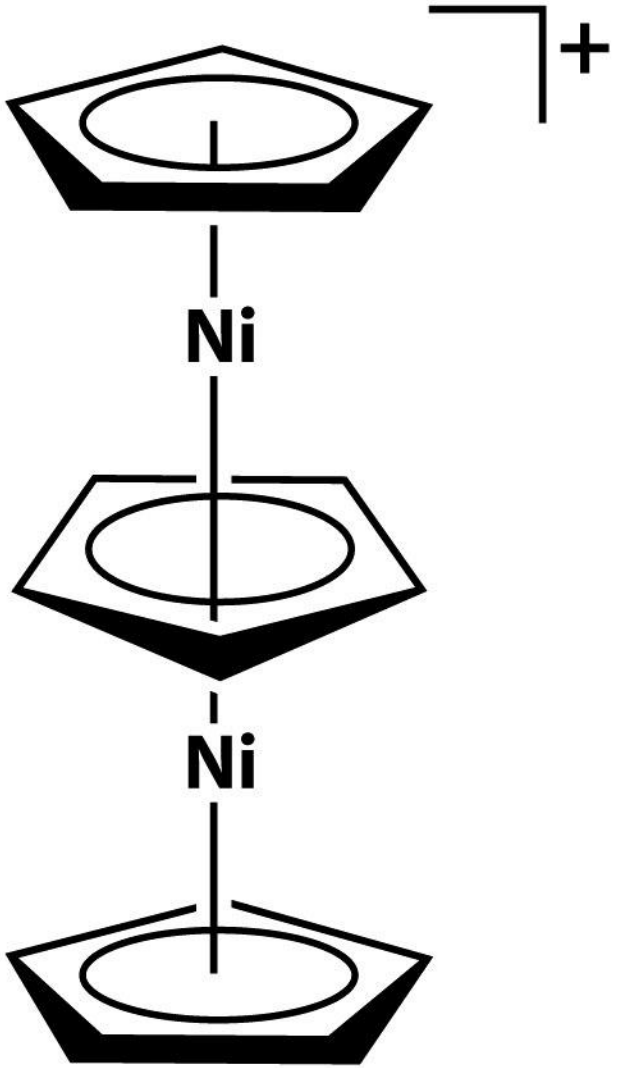
*Data are quoted for this complex because $[Mn(\eta^5\text{-Cp})_2]$ has a high-spin configuration and hence an anomalously long M—C bond (238 pm).



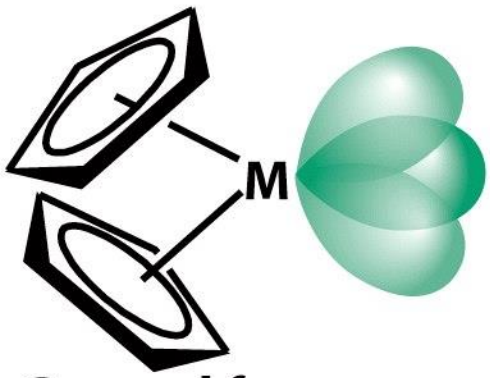
Bent sandwich



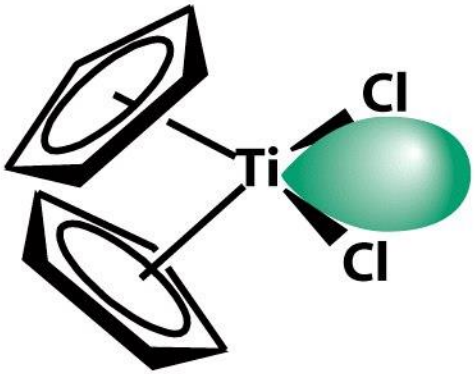
Half sandwich o *Piano stool*



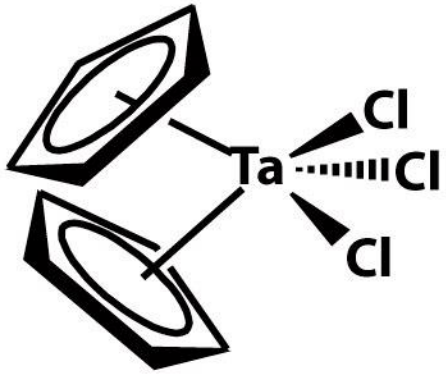
Triple decker o *doppio sandwich*



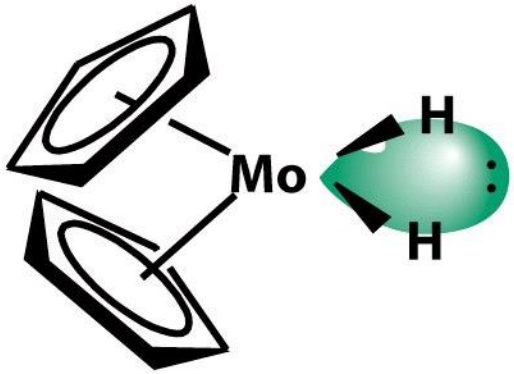
General form



16-electron



18-electron



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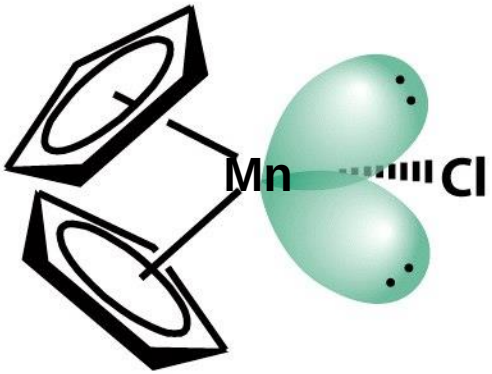
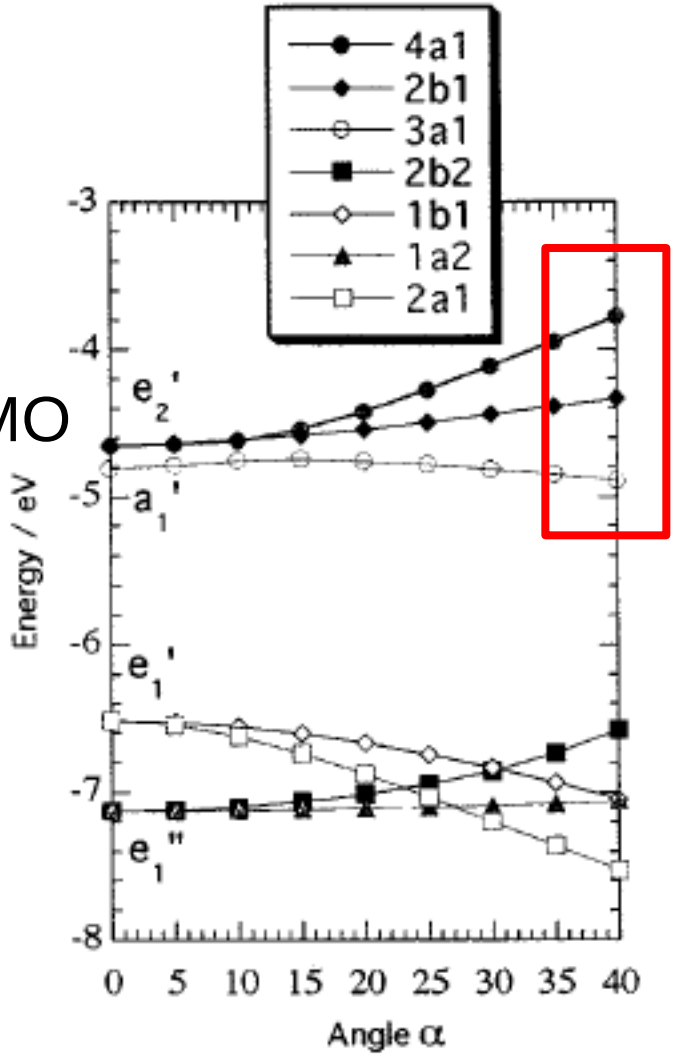
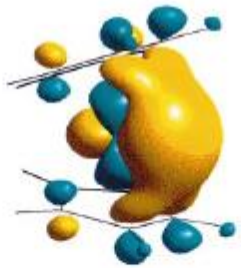


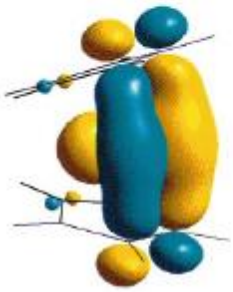
18-electron

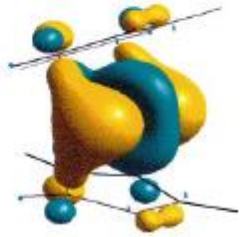
Diagramma di Walsh

HOMO









Cp_2ZrCl_2: catalizzatore tipo Ziegler-Natta per la polimerizzazione di olefine