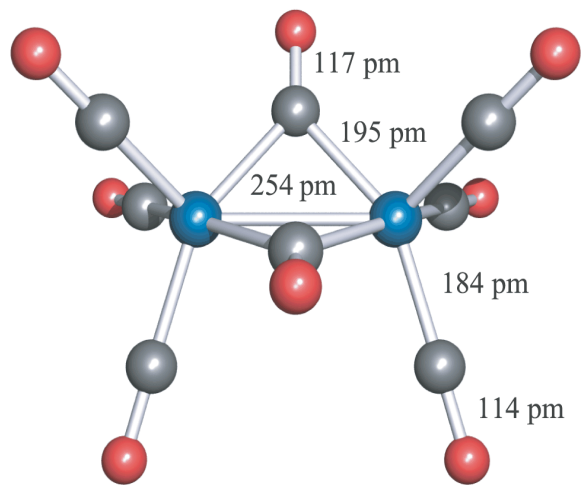


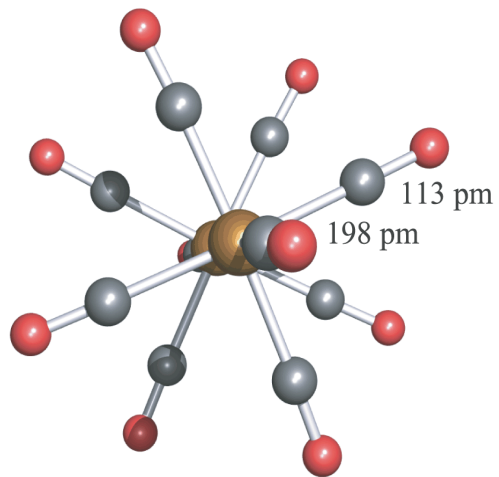
Carbonili omoleptici

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

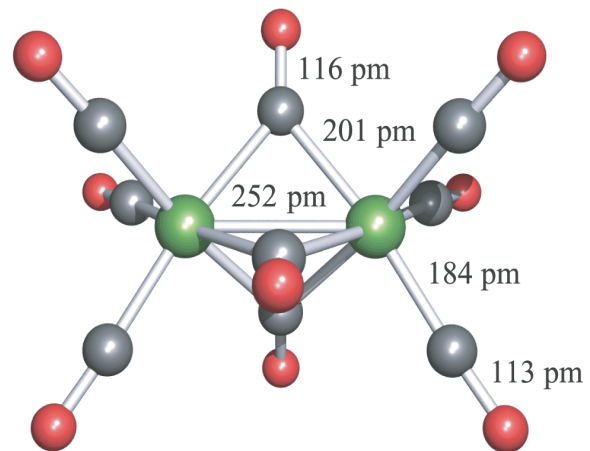
Group	Formula	Valence electrons	Structure
6	$\text{Cr}(\text{CO})_6$	Cr 6(CO) <hr/> 18	
7	$\text{Mn}_2(\text{CO})_{10}$	Mn 5(CO) M—M <hr/> 18	
8	$\text{Fe}(\text{CO})_5$	Fe 5(CO) <hr/> 18	
9	$\text{Co}_2(\text{CO})_8$	Co 4(CO) M—M <hr/> 18	
10	$\text{Ni}(\text{CO})_4$	Ni 4(CO) <hr/> 18	



(d)
 $\text{Co}_2(\text{CO})_8$



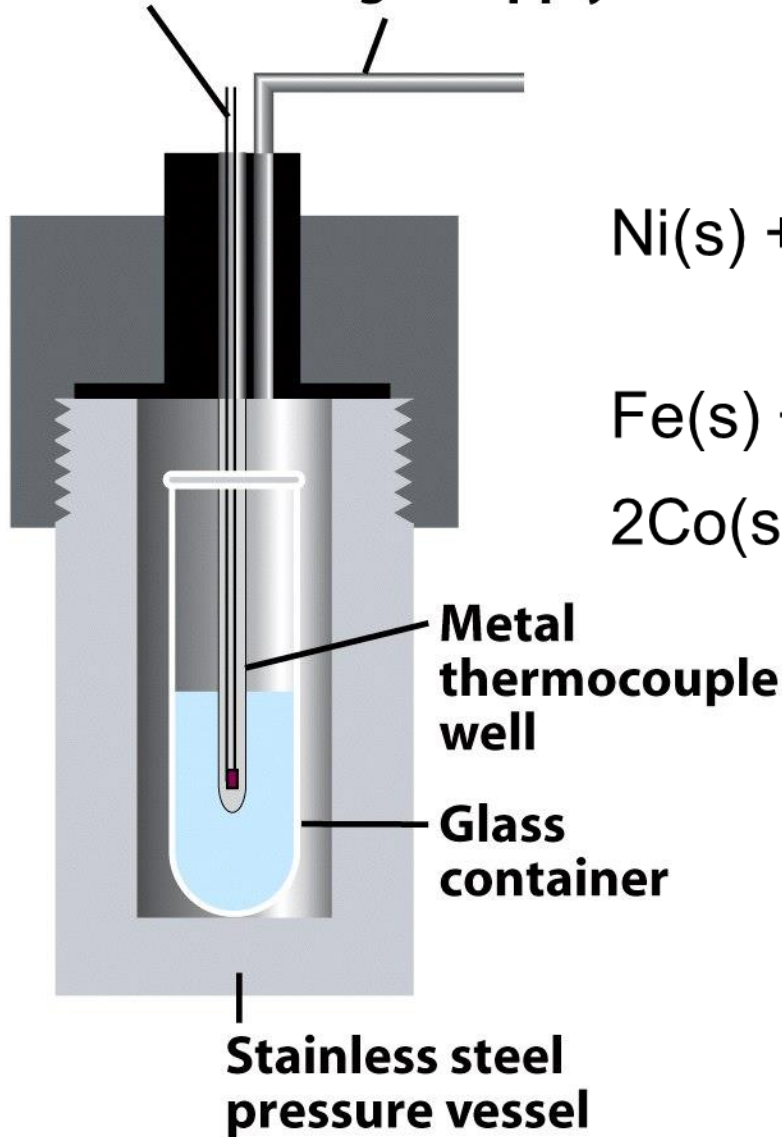
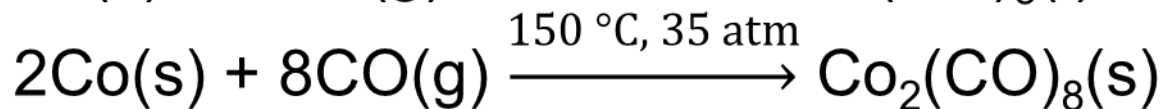
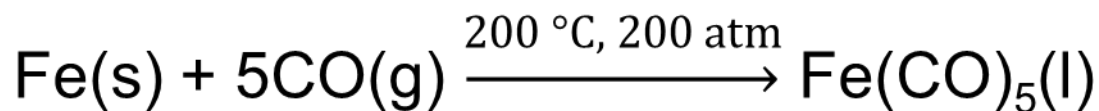
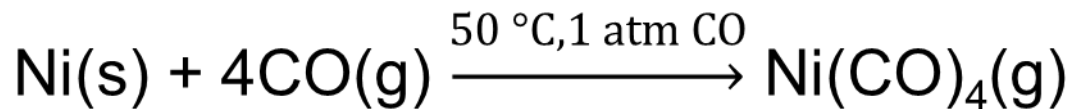
(b)
 $\text{Re}_2(\text{CO})_{10}$



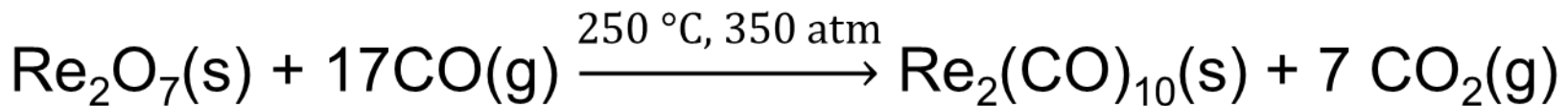
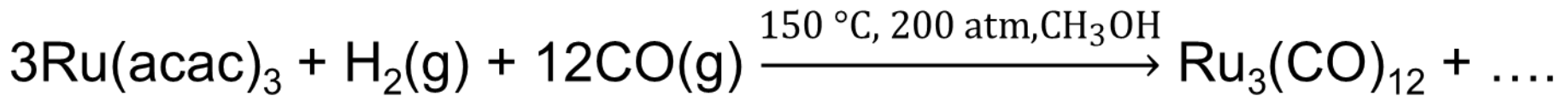
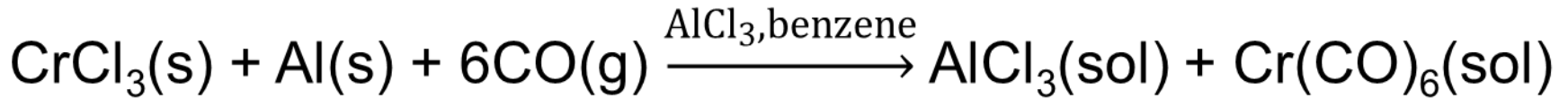
(c)
 $\text{Fe}_2(\text{CO})_9$

Thermocouple
High-pressure
gas supply

Reazione diretta

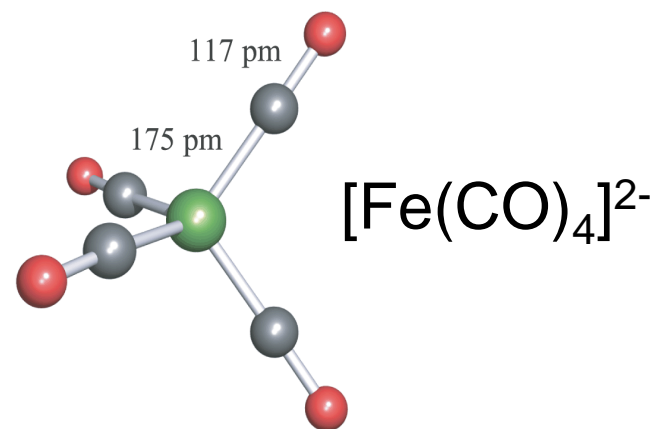
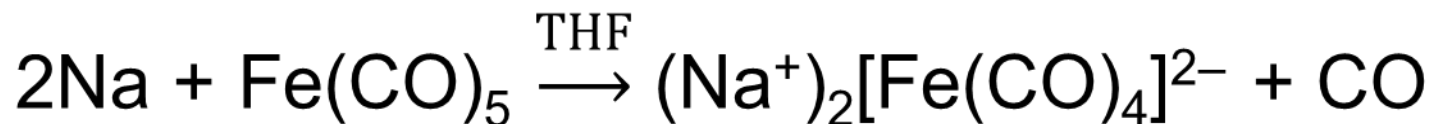


Carbonilazione riduttiva



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 <i>in vacuo</i> ; dec. 403 K	Mn₂(CO)₁₀ Yellow solid; mp 427 K	Fe(CO)₅ Yellow liquid; mp 253 K; bp 376 K		Co₂(CO)₈ Air-sensitive, orange-red solid; mp 324 K	Ni(CO)₄ Colourless, volatile liquid; highly toxic vapour; bp 316 K
Second row metals		Mo(CO)₆ White solid; sublimes <i>in vacuo</i>	Tc₂(CO)₁₀ White solid; slowly dec. in air; mp 433 K	Fe₂(CO)₉ Golden crystals; mp 373 K (dec.) Fe₃(CO)₁₂ Dark green solid; dec. 413 K	Ru(CO)₅ Colourless liquid; mp 251 K; dec. in air at 298 K to Ru ₃ (CO) ₁₂ + CO Ru₃(CO)₁₂ Orange solid; mp 427 K; sublimes <i>in vacuo</i>	Co₄(CO)₁₂ Air-sensitive, black solid Co₆(CO)₁₆ Black solid; slowly dec. in air Rh₄(CO)₁₂ Red solid; >403 K dec. to Rh ₆ (CO) ₁₆ Rh₆(CO)₁₆ Black solid; dec. >573 K	
Third row metals		W(CO)₆ White solid; sublimes <i>in vacuo</i>	Re₂(CO)₁₀ White solid; mp 450 K	Os(CO)₅ Yellow liquid; mp 275 K Os₃(CO)₁₂ Yellow solid; mp 497 K	Ir₄(CO)₁₂ Slightly air-sensitive yellow solid; mp 443 K Ir₆(CO)₁₆ Red solid		

Riduzione dei metallocarbonili a metallocarbonilati



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

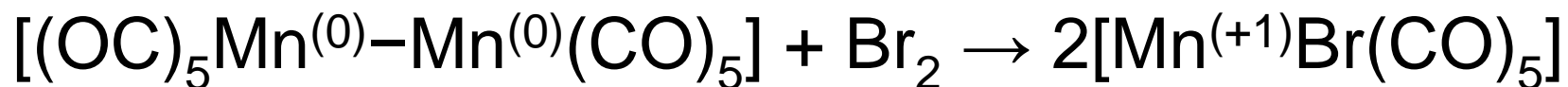
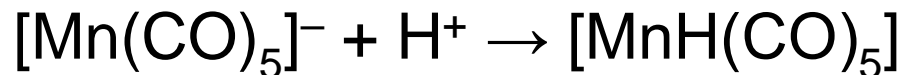


Table 21.6 Acidity constants of *d*-metal hydrides in acetonitrile at 25°C

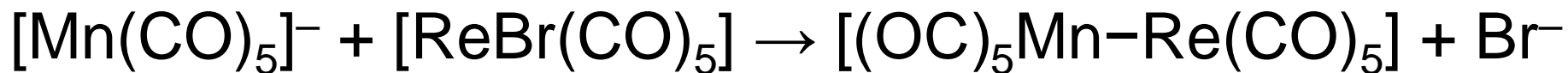
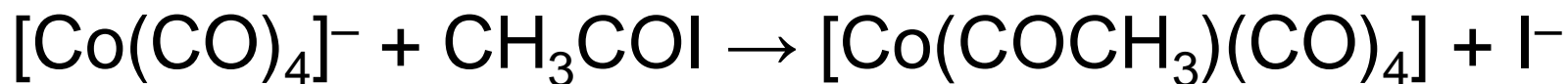
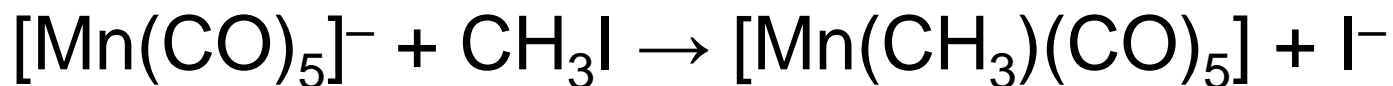
Hydride	pK _a
[CoH(CO) ₄]	8.3
[CoH(CO) ₃ P(OPh) ₃]	11.3
[Fe(H) ₂ (CO) ₄]	11.4
[CrH(Cp)(CO) ₃]	13.3
[MoH(Cp)(CO) ₃]	13.9
[MnH(CO) ₅]	15.1
[CoH(CO) ₃ PPh ₃]	15.4
[WH(Cp)(CO) ₃]	16.1
[MoH(Cp*)(CO) ₃]	17.1
[Ru(H) ₂ (CO) ₄]	18.7
[FeH(Cp)(CO) ₂]	19.4
[RuH(Cp)(CO) ₂]	20.2
[Os(H) ₂ (CO) ₄]	20.8
[ReH(CO) ₅]	21.1
[FeH(Cp*)(CO) ₂]	26.3
[WH(Cp)(CO) ₂ PMe ₃]	26.6

Protonazione di metallocarbonilati



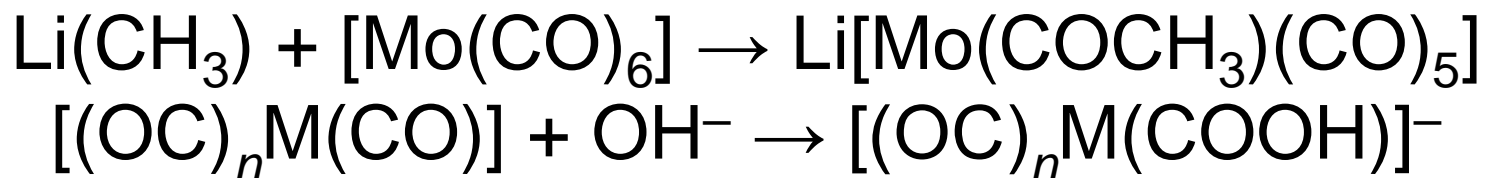
Basicità dei metallocarbonilati

Attacco nucleofilo



Attacchi nucleofili ed elettrofilo a carbonili

Metallo elettrone-povero: attacco nucleofilo su C



Metallo elettrone-ricco: attacco elettrofilo su O

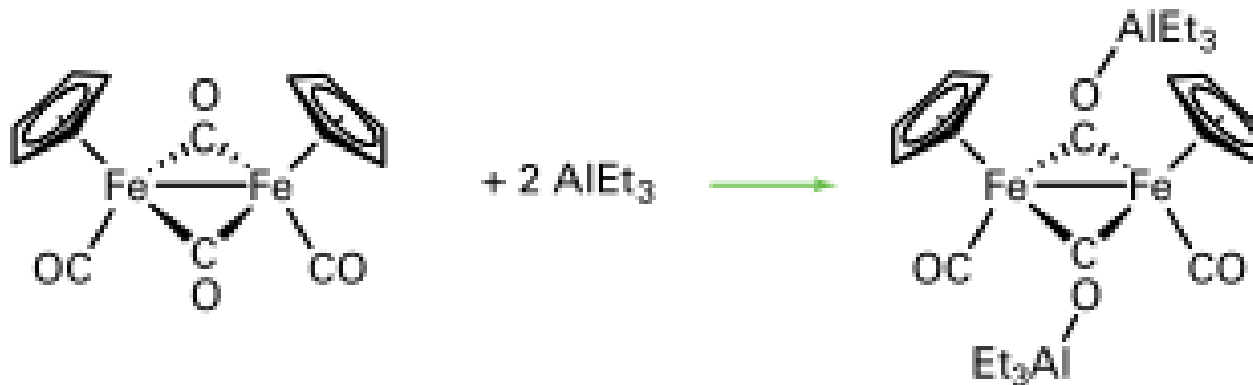


Table 21.7 Relation between the structure of a carbonyl complex and the number of CO stretching bands in its IR spectrum

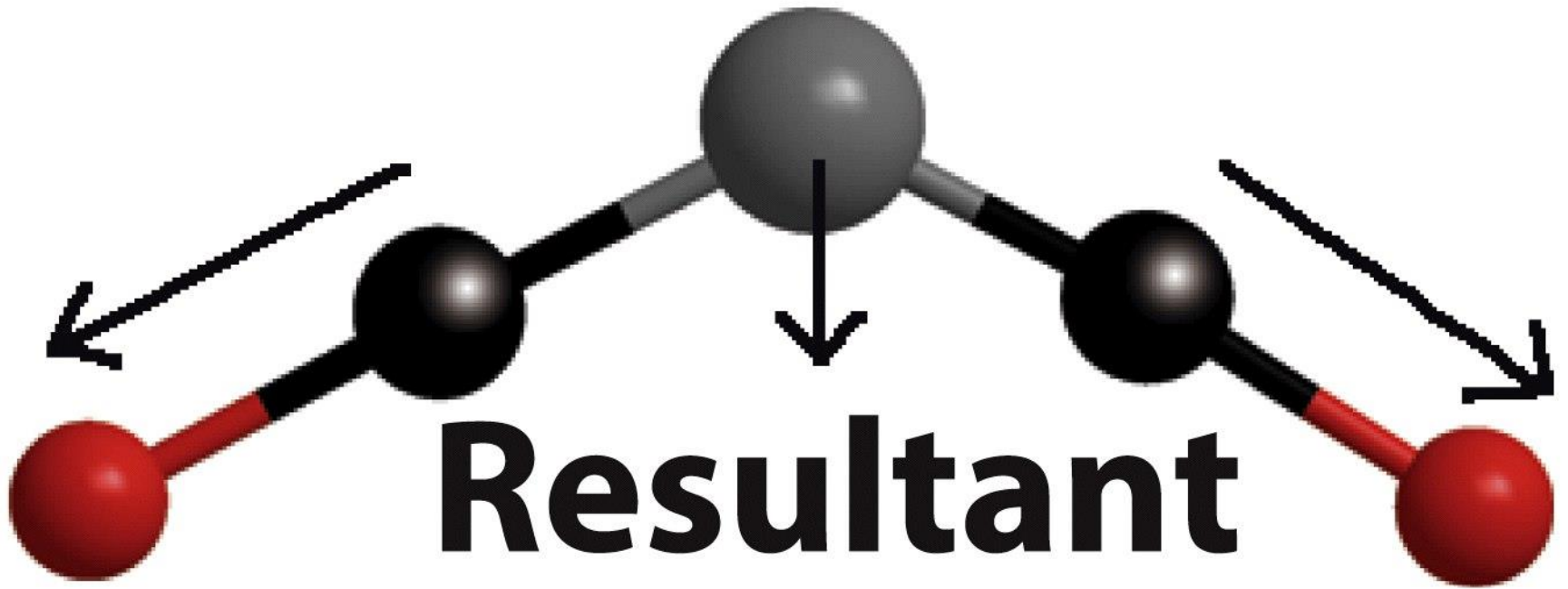
Complex	Isomer	Structure	Point group	Number of bands*	Complex	Isomer	Structure	Point group	Number of bands*
$M(CO)_6$			O_h	1	$M(CO)_5$			D_{3h}	2
$M(CO)_5L$			C_{4v}	3 [†]	$M(CO)_5$	<i>ax</i>		C_{3v}	3 [§]
$M(CO)_4L_2$	<i>trans</i>		D_{4h}	1	$M(CO)_4L$	<i>eq</i>		C_{2v}	4
$M(CO)_4L_2$	<i>cis</i>		C_{2v}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

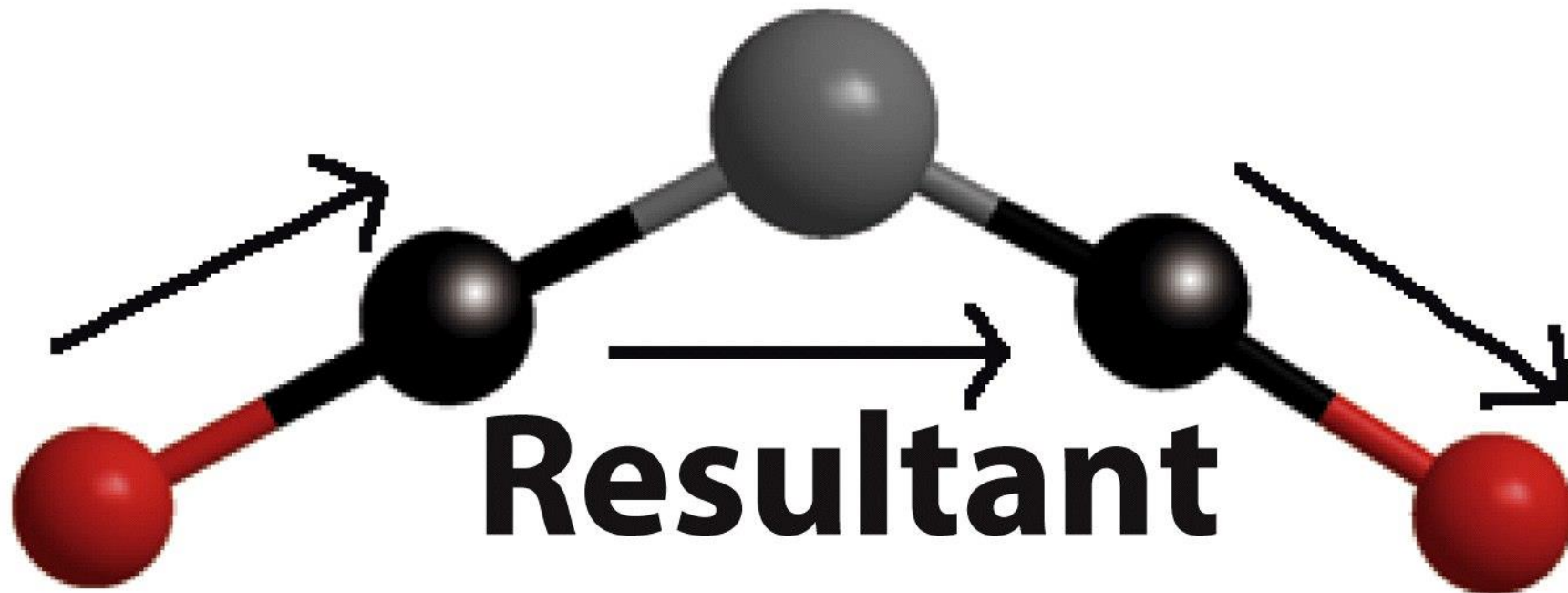
* The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed, as explained below.

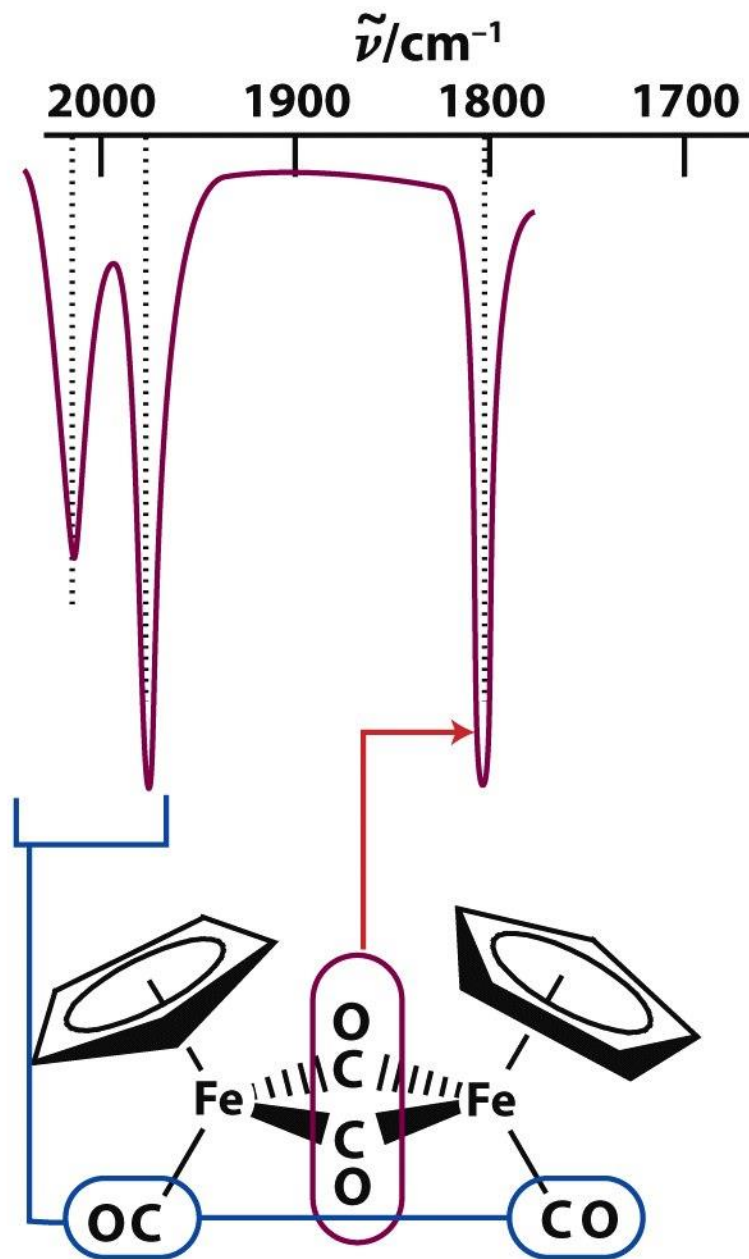
† If the fourfold array of CO ligands lies in the same plane as the metal atom, two bands will be observed.

‡ If the *trans* CO ligands are nearly collinear, one fewer band will be observed.

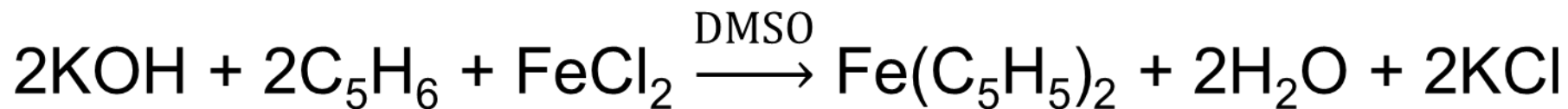
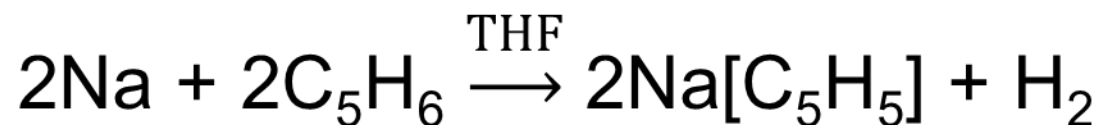
§ If the threefold array of CO ligands is nearly planar, only two bands will be observed.

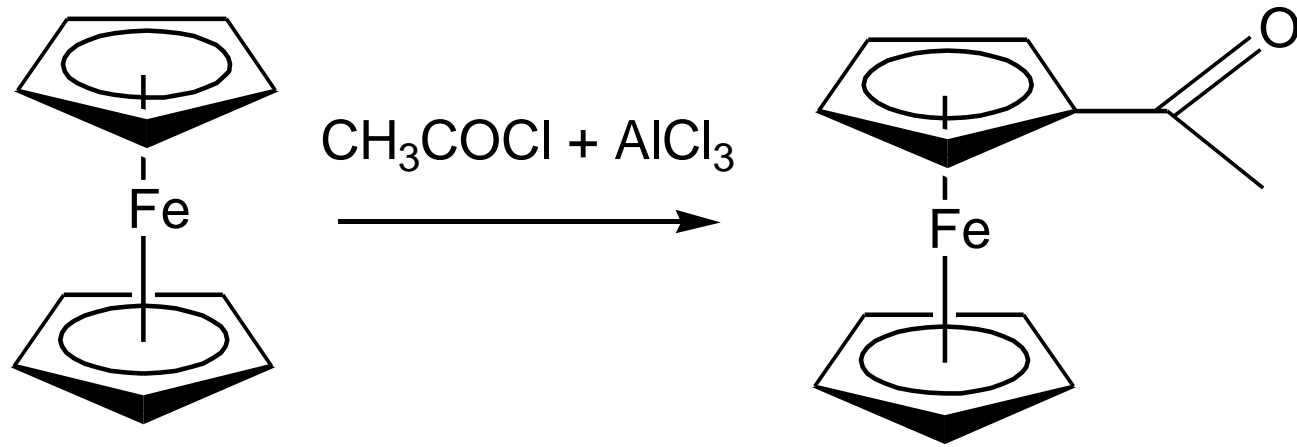




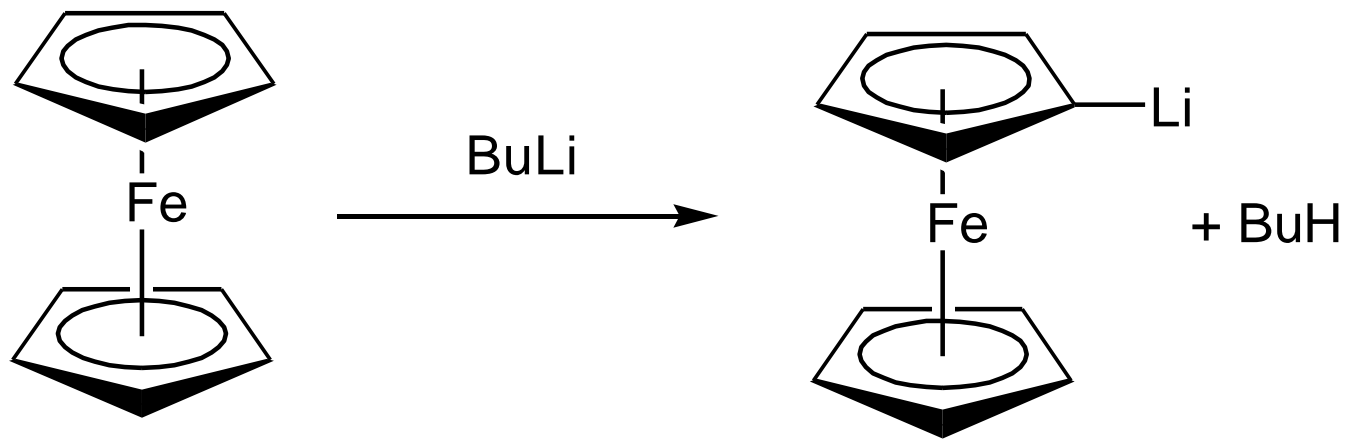


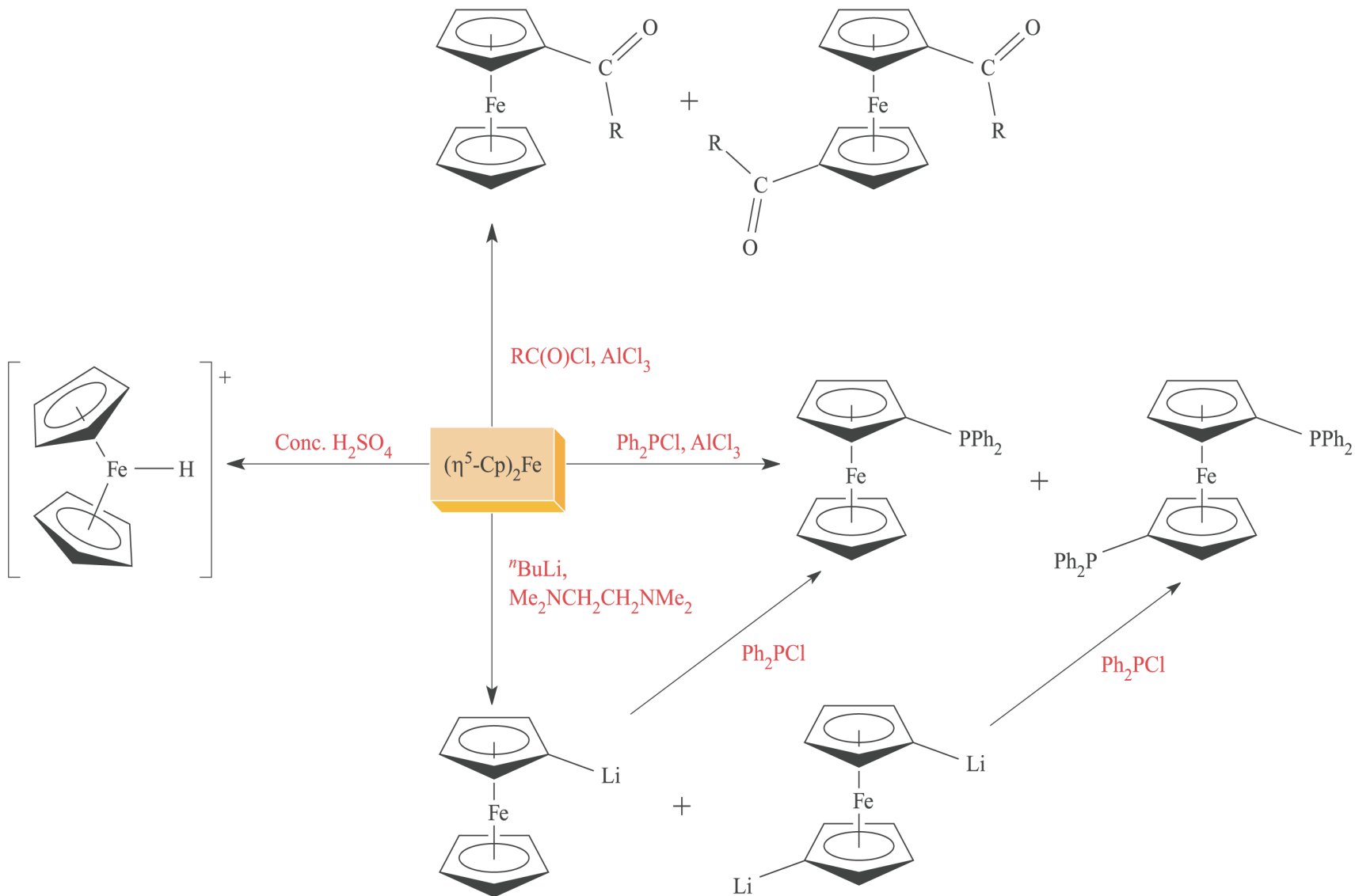
Metalloceni

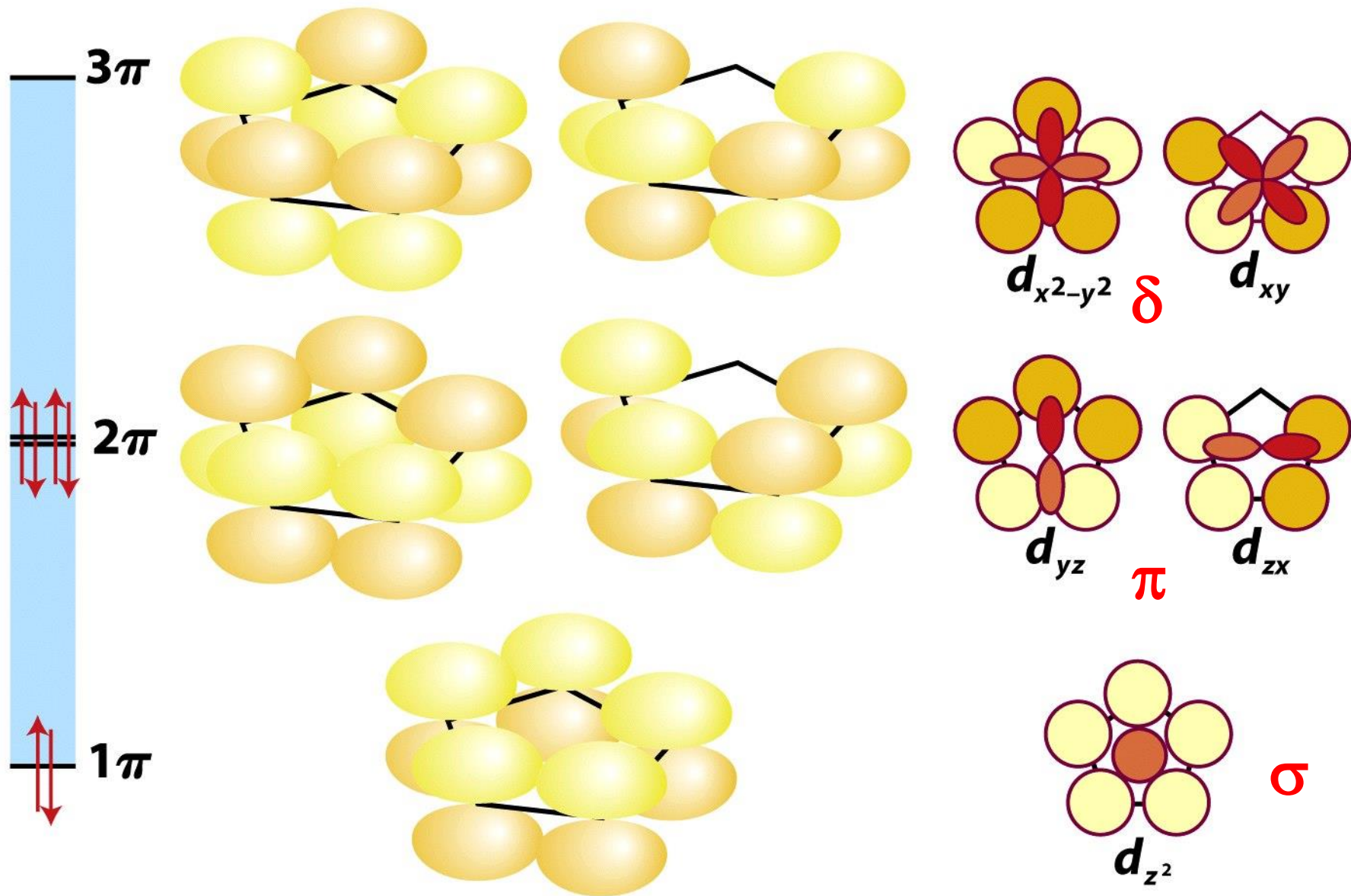


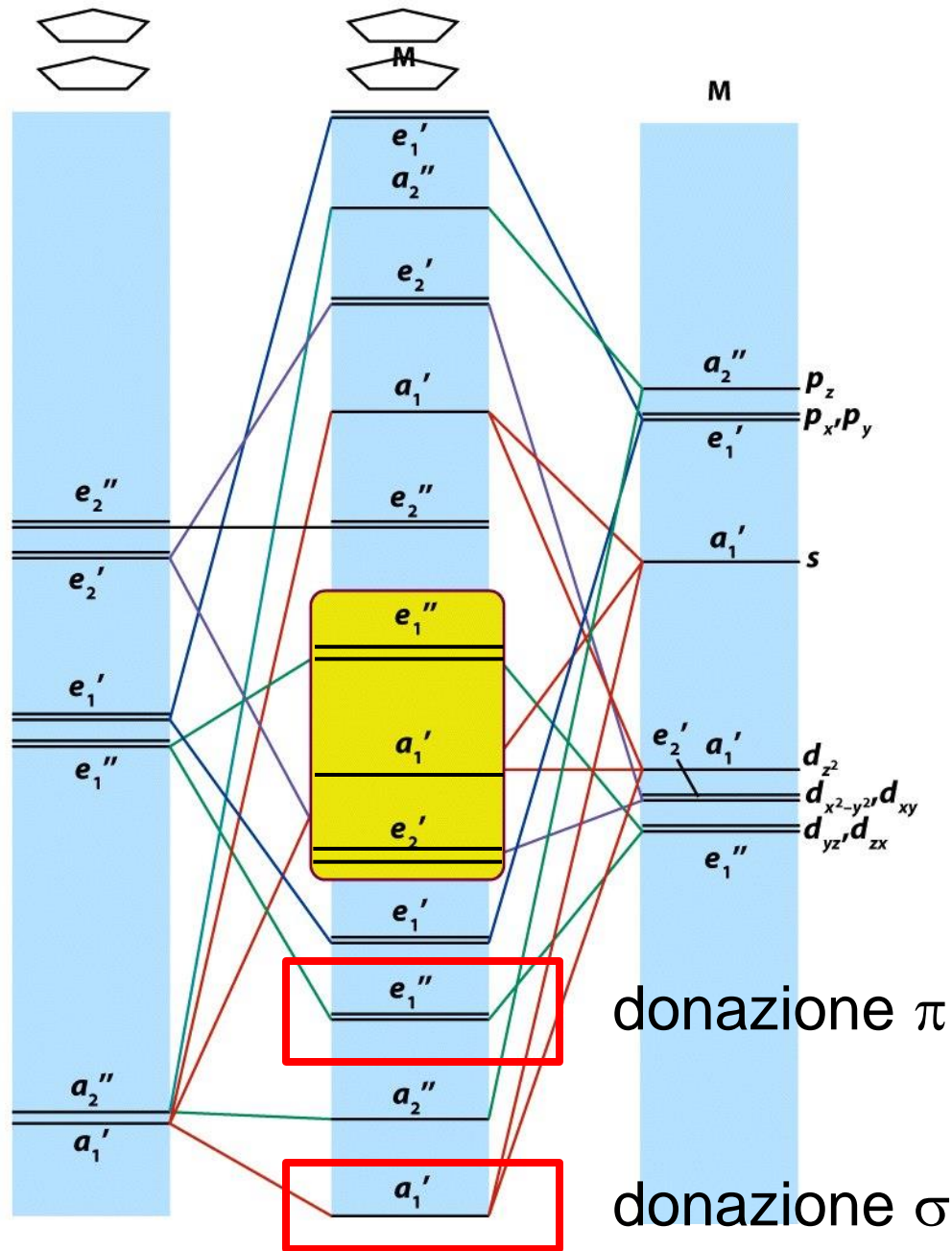


acilazione di Friedel – Crafts









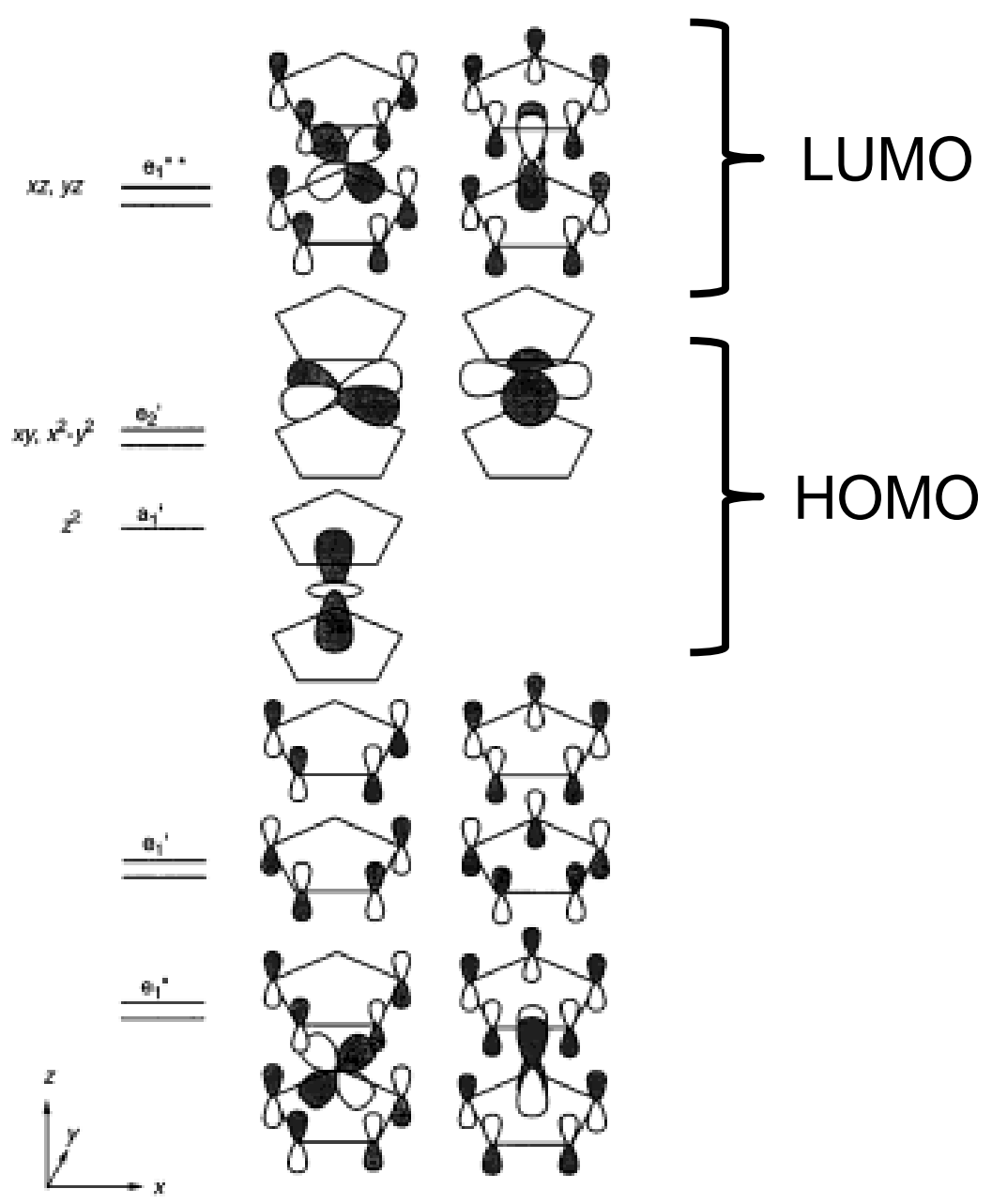
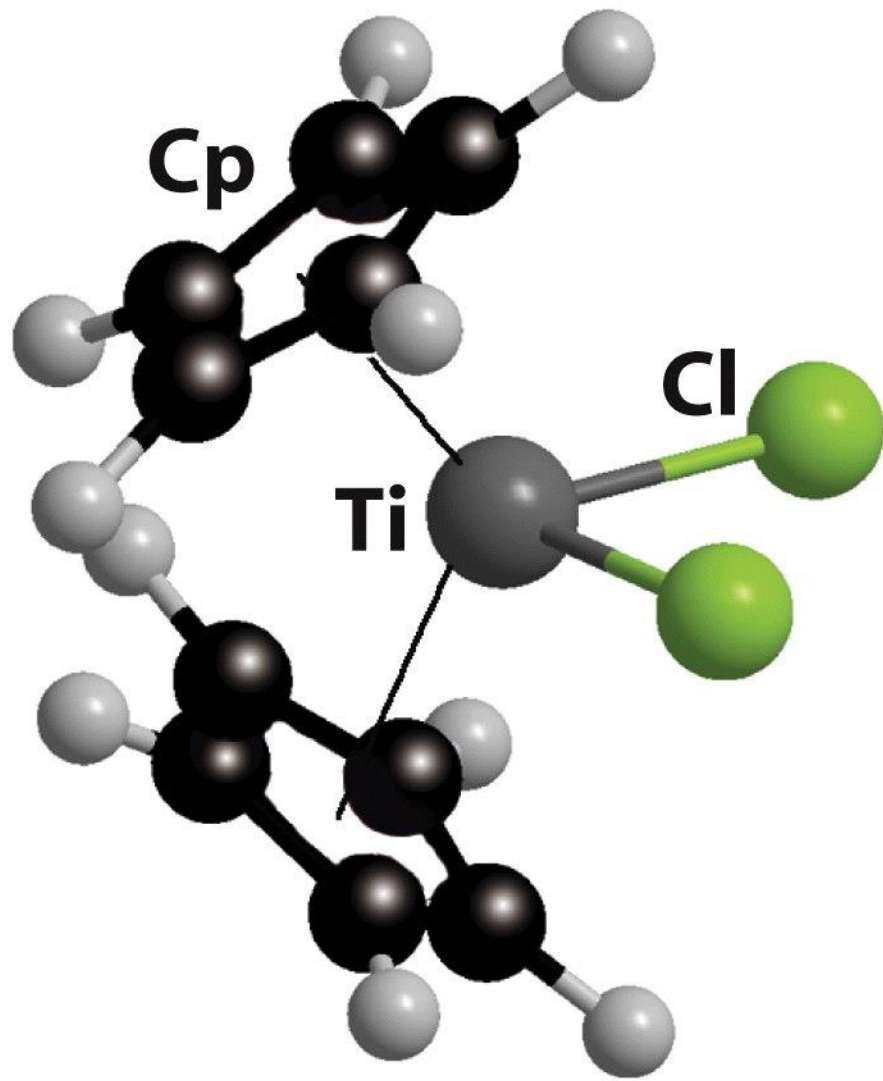


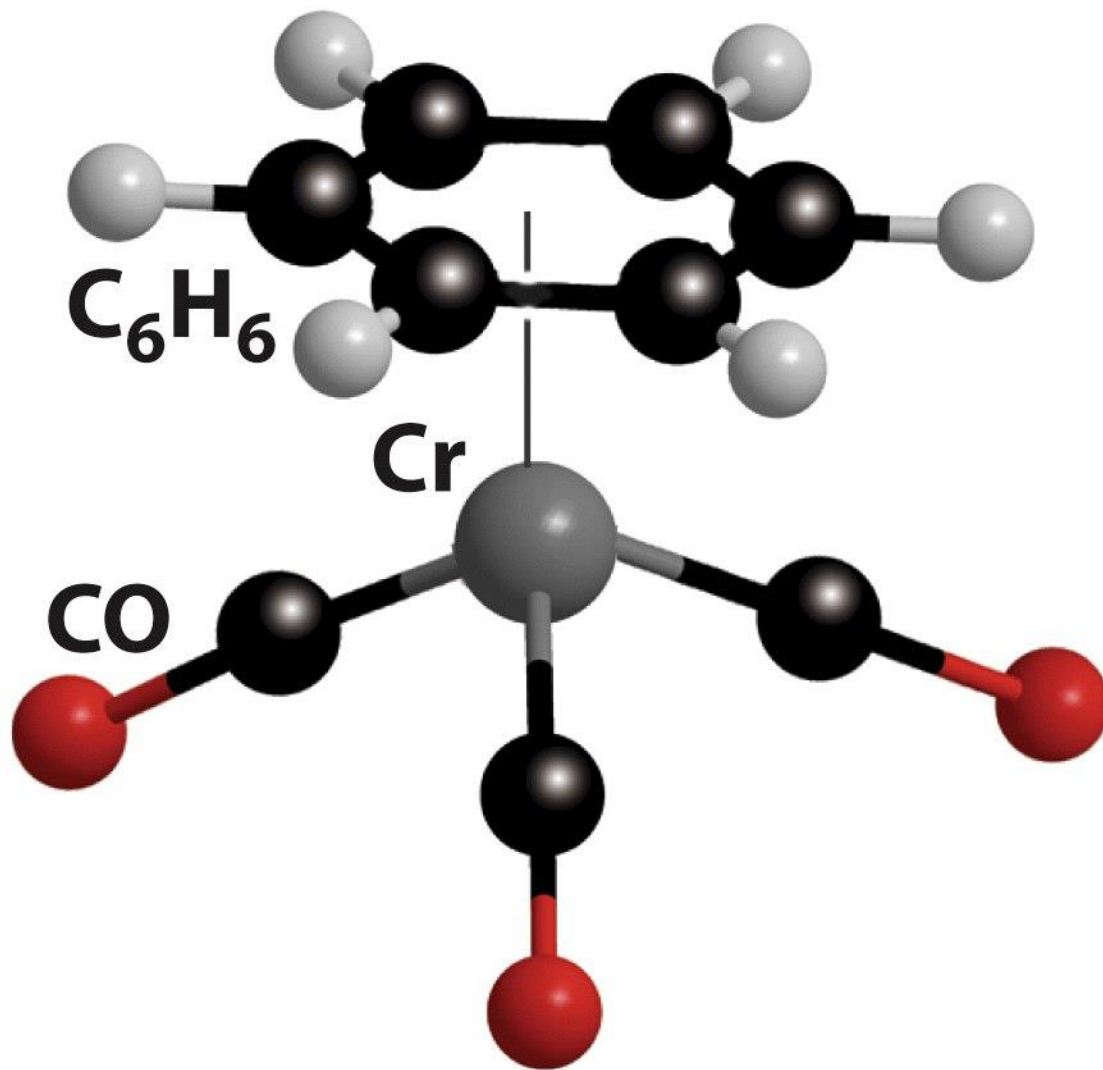
Table 21.8 Electronic configuration and M—C bond length in $[M(\eta^5\text{-Cp})_2]$ complexes

Complex	Valence electrons	Electron configuration	M—C bond length/pm
$[V(\eta^5\text{-Cp})_2]$	15	$e_2'^2 a_1'^1$	228
$[\text{Cr}(\eta^5\text{-Cp})_2]$	16	$e_2'^3 a_1'^1$	217
$[\text{Mn}(\eta^5\text{-Me-C}_5\text{H}_4)_2]^*$	17	$e_2'^3 a_1'^2$	211
$[\text{Fe}(\eta^5\text{-Cp})_2]$	18	$e_2'^4 a_1'^2$	206
$[\text{Co}(\eta^5\text{-Cp})_2]$	19	$e_2'^4 e_1''^1 a_1'^2$	212
$[\text{Ni}(\eta^5\text{-Cp})_2]$	20	$e_2'^4 e_1''^2 a_1'^2$	220

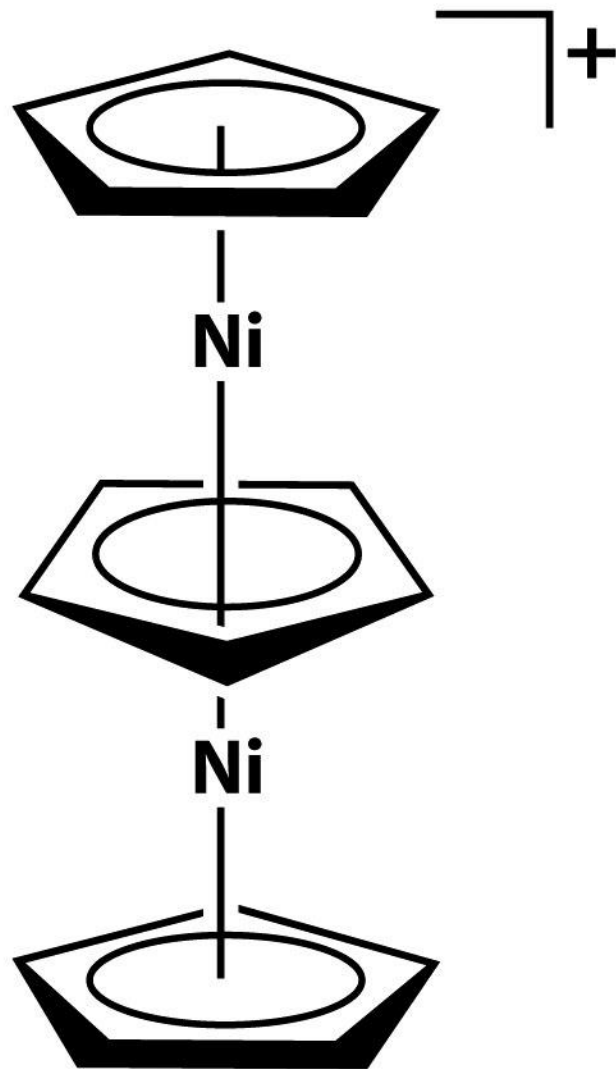
*Data are quoted for this complex because $[\text{Mn}(\eta^5\text{-Cp})_2]$ has a high-spin configuration and hence an anomalously long M—C bond (238 pm).



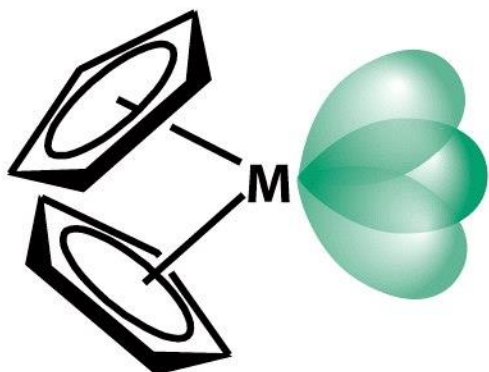
Bent sandwich



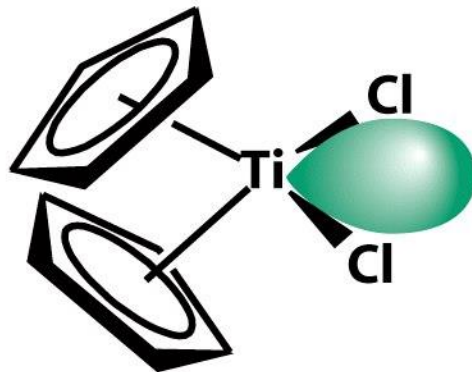
Half sandwich o Piano stool



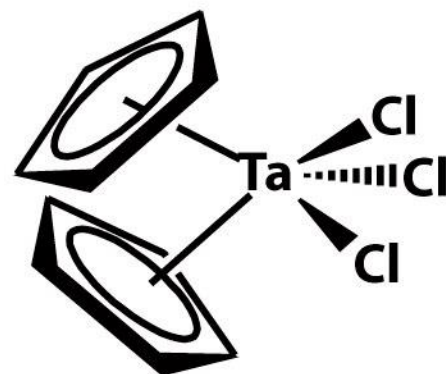
Triple decker o doppio sandwich



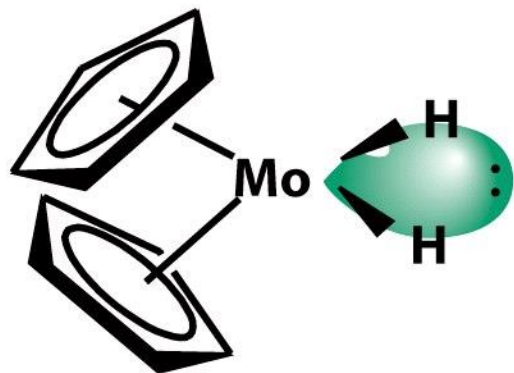
General form



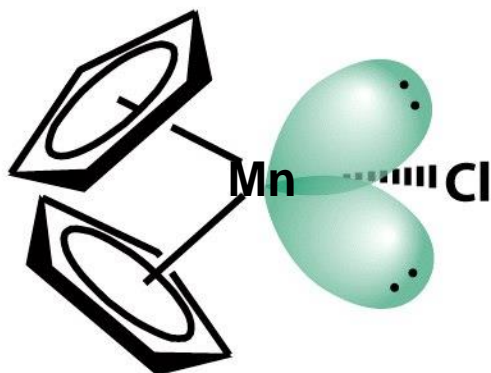
16-electron



18-electron



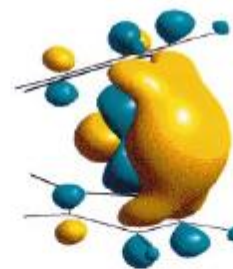
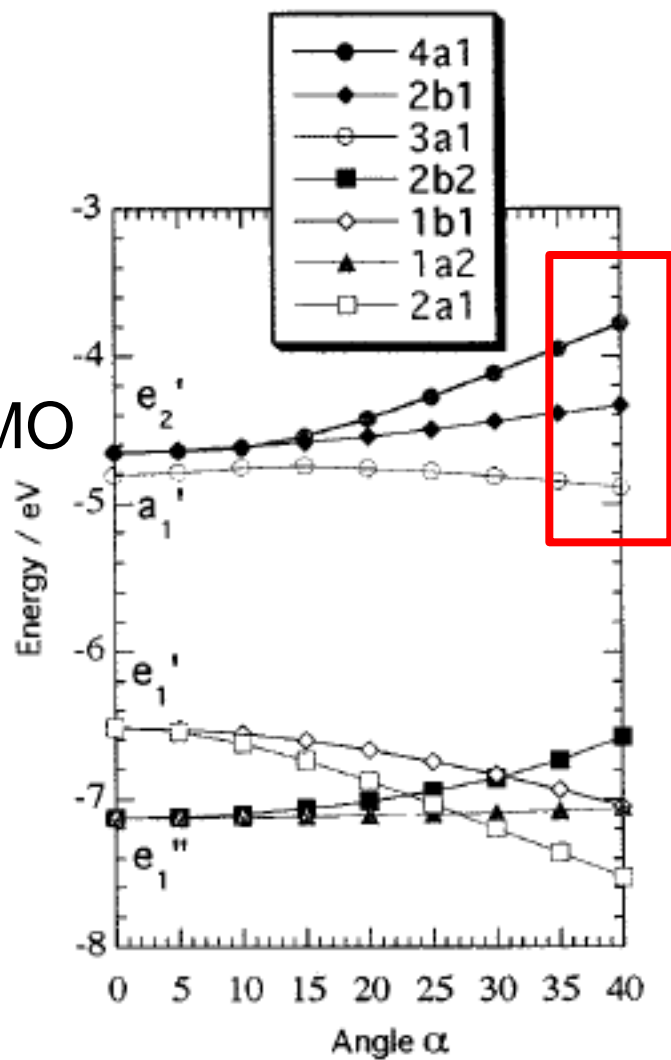
18-electron



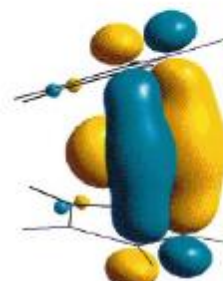
18-electron

Diagramma di Walsh

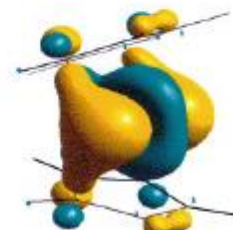
HOMO



4a1



2b1



3a1

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

