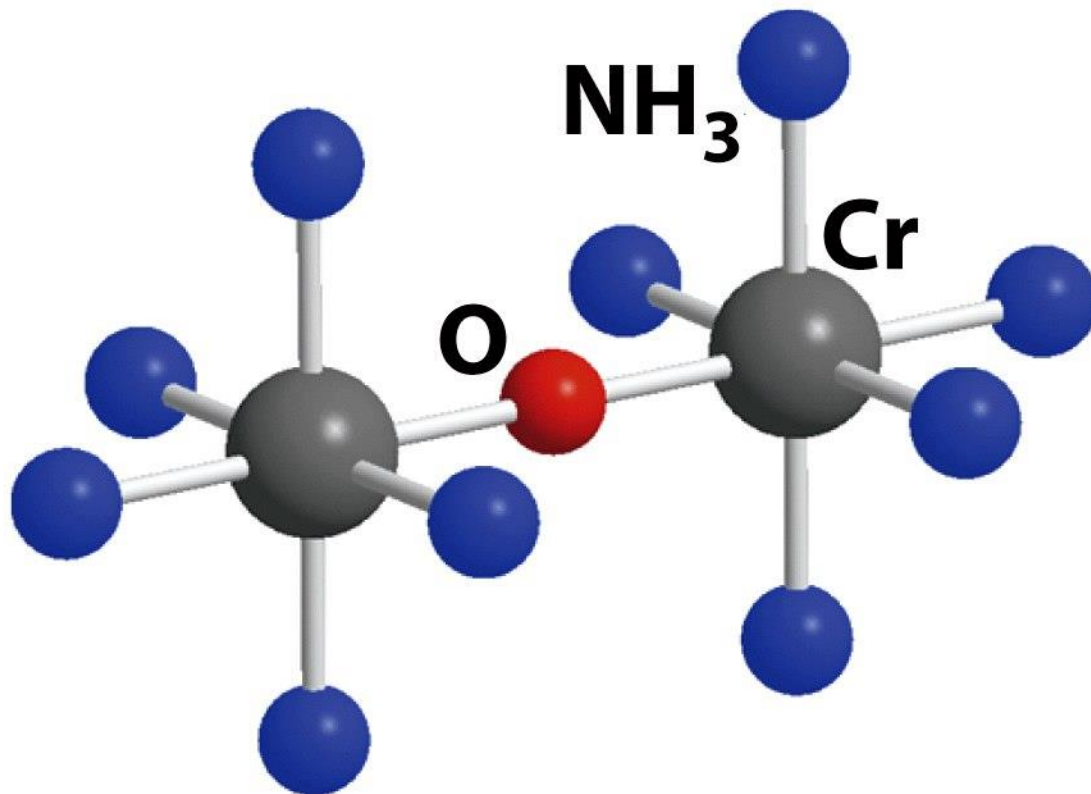


$[\text{Co}(\text{NH}_3)_6]^{3+}$  esaamminocobalto(III)

$[\text{CoCl}_2(\text{NH}_3)_4]^+$  tetraamminodiclorurocobalto(III)

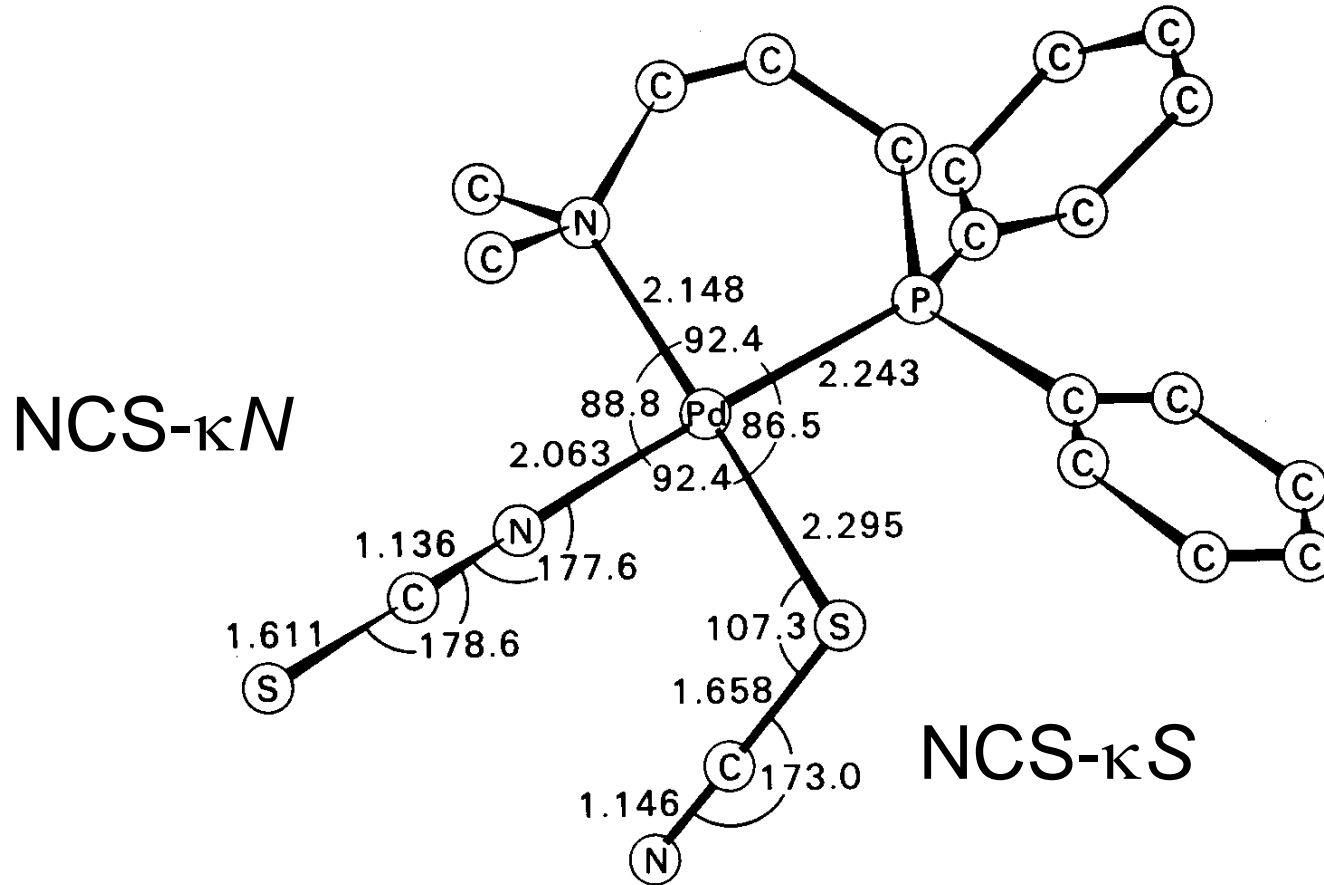
$[\text{PtCl}_4]^{2-}$  tetracloroplatinato(II)

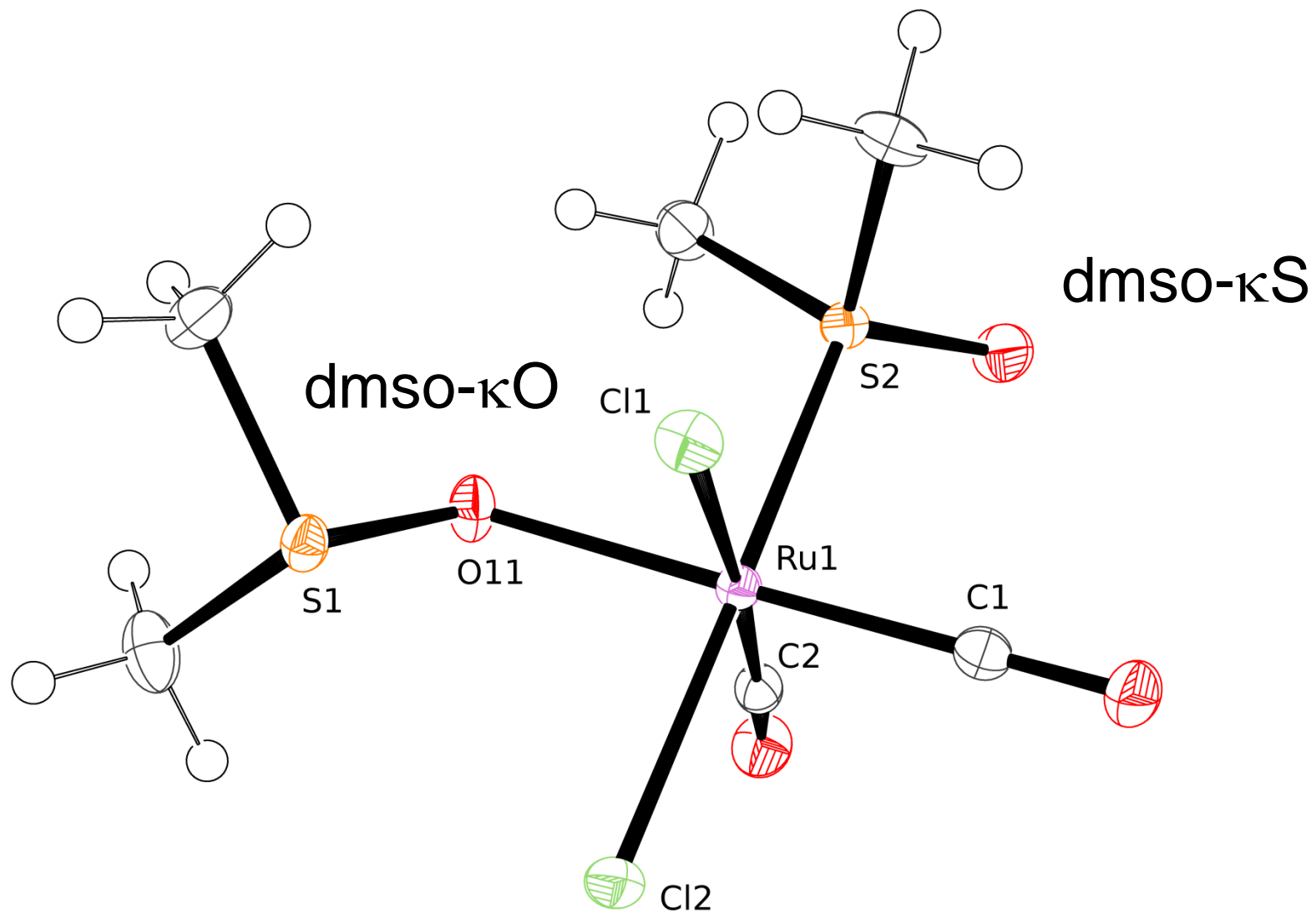


$\mu$ -osso-bis(pentaammino)cromo(III)



# Leganti ambidentati





## **Numeri di coordinazione elevati (e.g. 7, 8):**

- Ioni metallici grandi (*early transition*) e in elevato stato di ossidazione.
- Leganti piccoli e buoni donatori  $\sigma$  (e.g.  $F^-$ ,  $CH_3^-$ ), cioè leganti *hard*.
- Contro-cationi grandi e non acidi.
- I metalli di inizio serie in alto stato di ossidazione tendono a fare legami multipli (e.g. con  $O^{2-}$  o  $N^{3-}$ ).

## **Numeri di coordinazione bassi (e.g. 2, 3):**

- Ioni metallici piccoli (*late transition*) e in basso stato di ossidazione.
- Leganti *soft*, tipicamente buoni accettori  $\pi$ .
- Leganti ingombranti o che facciano legami multipli.
- Contro-anioni non coordinanti.

## **Anioni poco coordinanti:**

$NO_3^-$ ,  $ClO_4^-$ ,  $CF_3SO_3^-$  (triflato),  $BF_4^-$ ,  $B(C_6H_5)_4^-$ ,  $PF_6^-$ ,  
 $SbF_6^-$

# Numero di coordinazione 2 geometria lineare

Ioni  $d^{10}$ : Cu(I), Ag(I), Au(I), Hg(II)

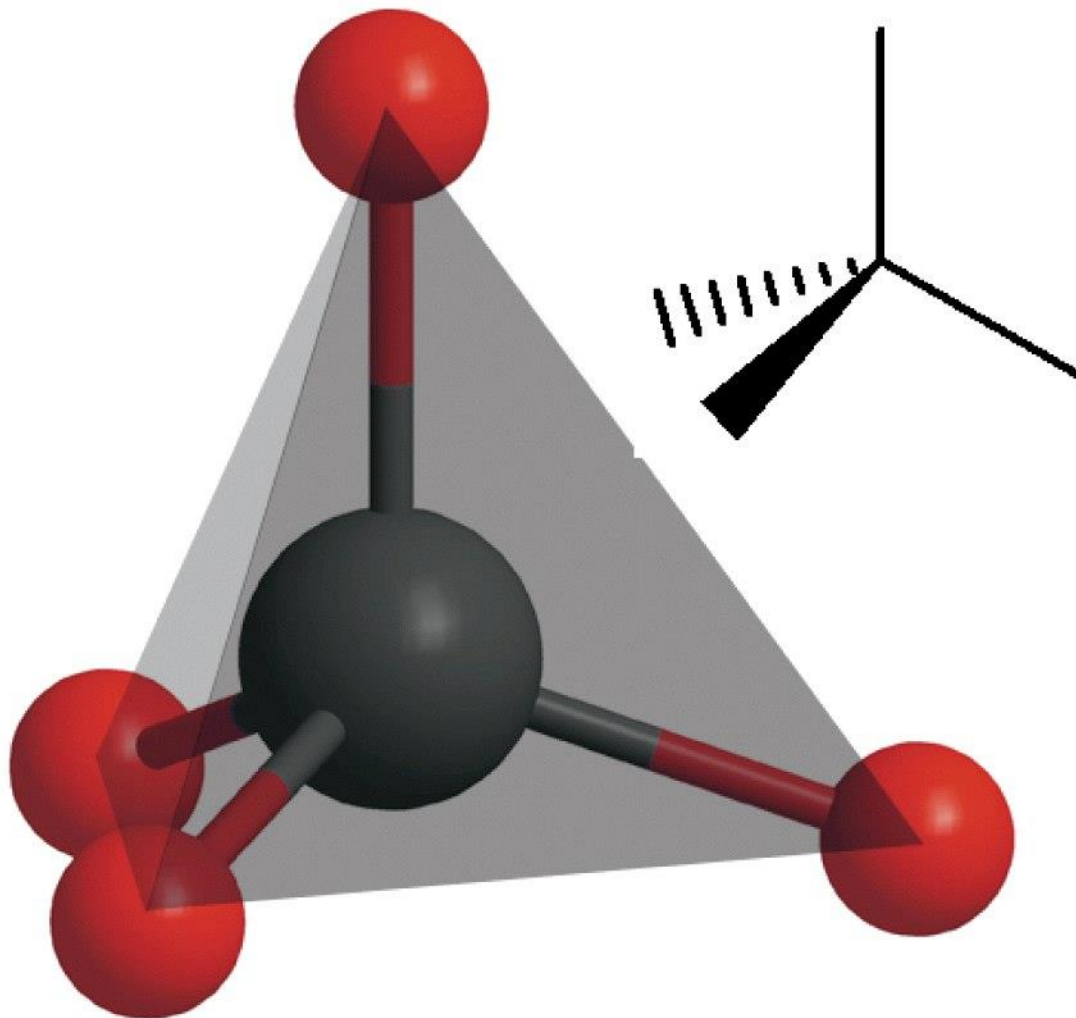


# Numero di coordinazione 3 geometria trigonale planare

**Ioni  $d^{10}$ :** Cu(I), Au(I), Pt(0)

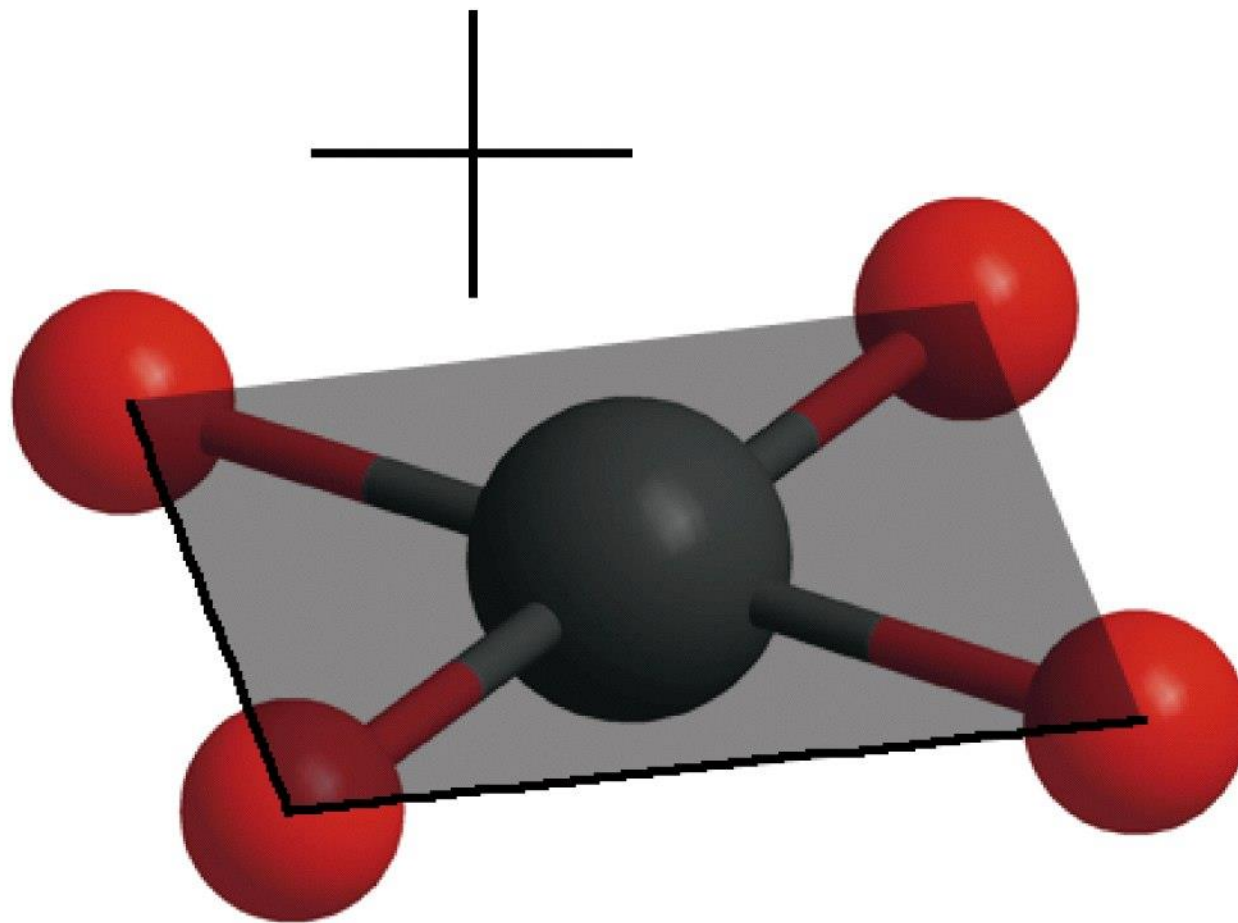


**anioni poco coordinanti:**  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  (triflato),  
 $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$

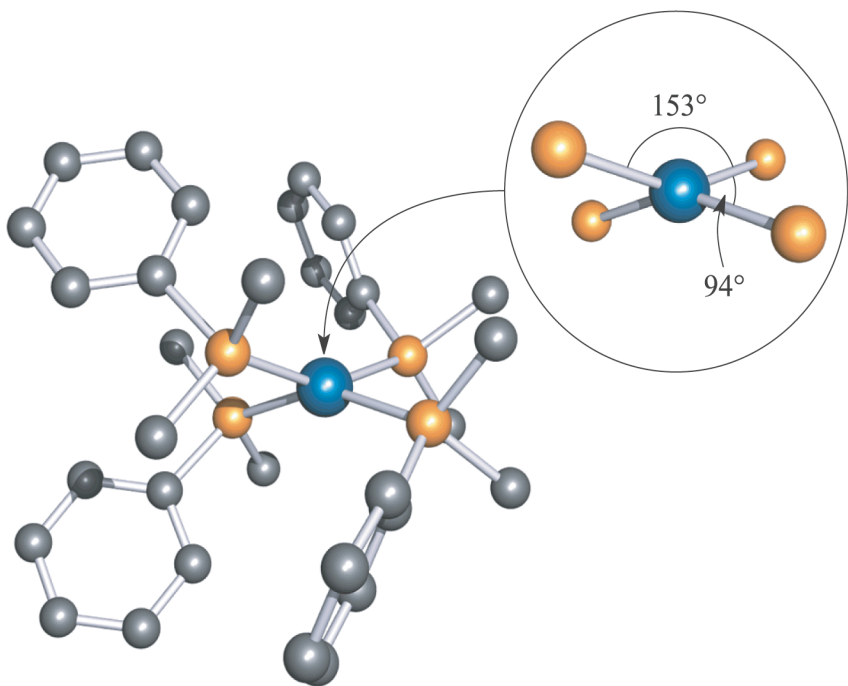


**Tetrahedral complex,  $T_d$**





**Square-planar complex,  $D_{4h}$**



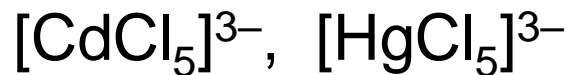
$D_{2d}$



Distorsione della geometria planare-quadrata causata da leganti voluminosi

# Complessi pentacoordinati

Bipiramide trigonale



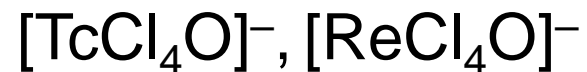
$d^{10}$

*minimizza le repulsioni fra i leganti*

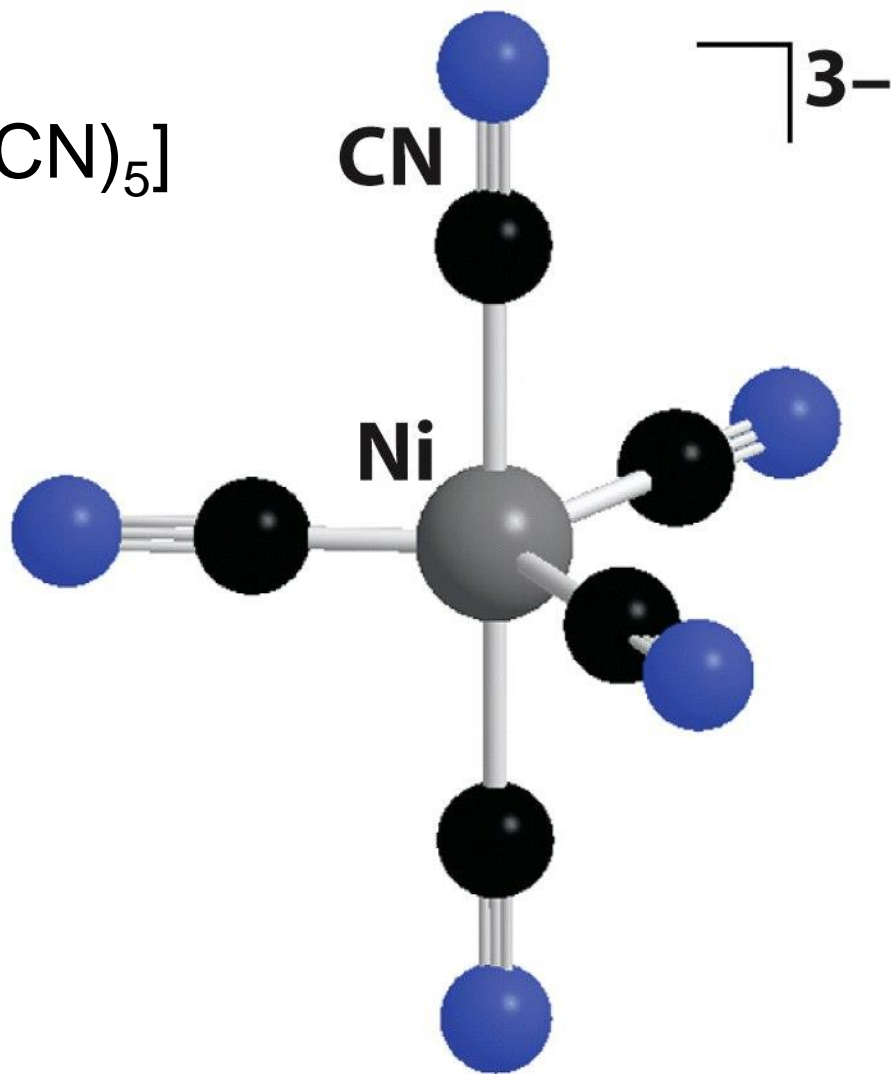
Piramide a base quadrata

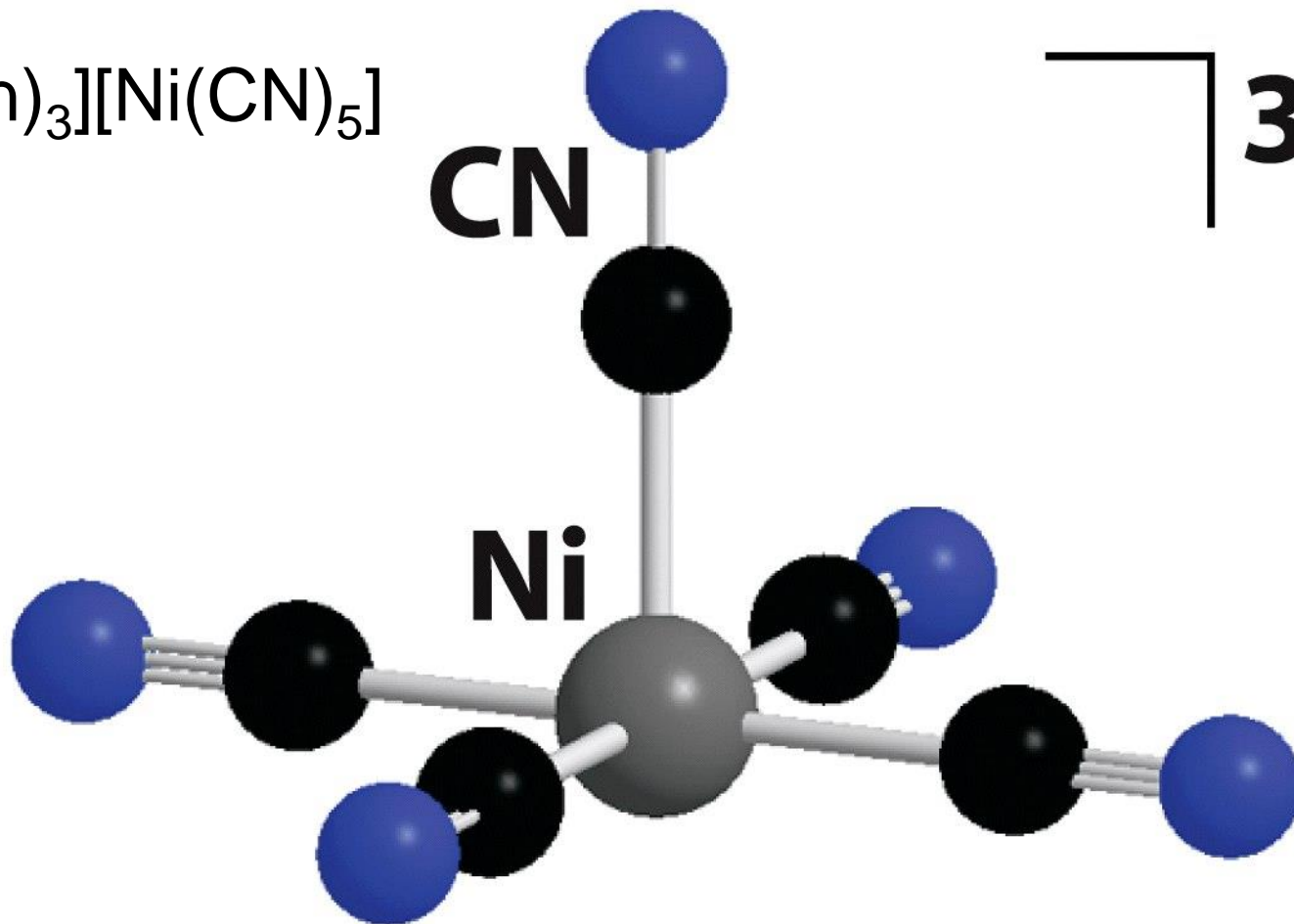


$d^1$



$d^2$

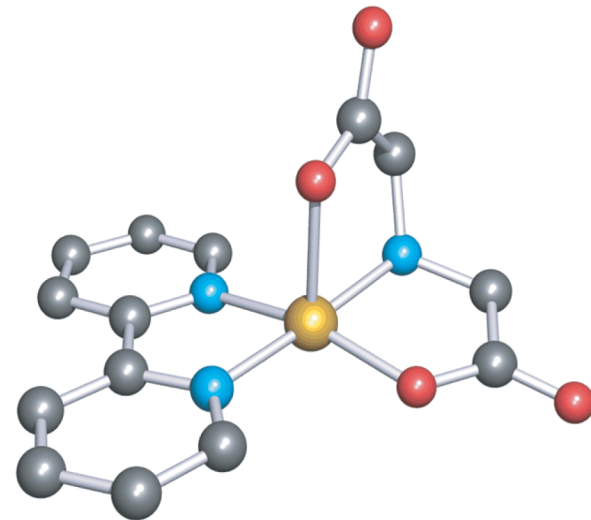
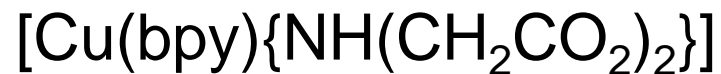
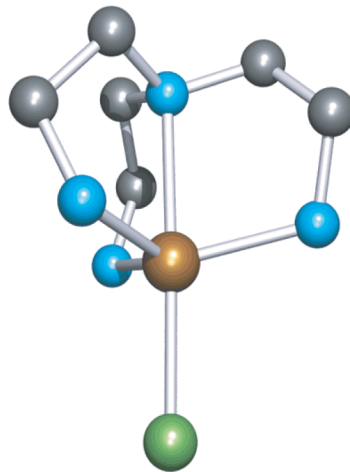




# Esempi di complessi pentacoordinati con geometria imposta dai leganti

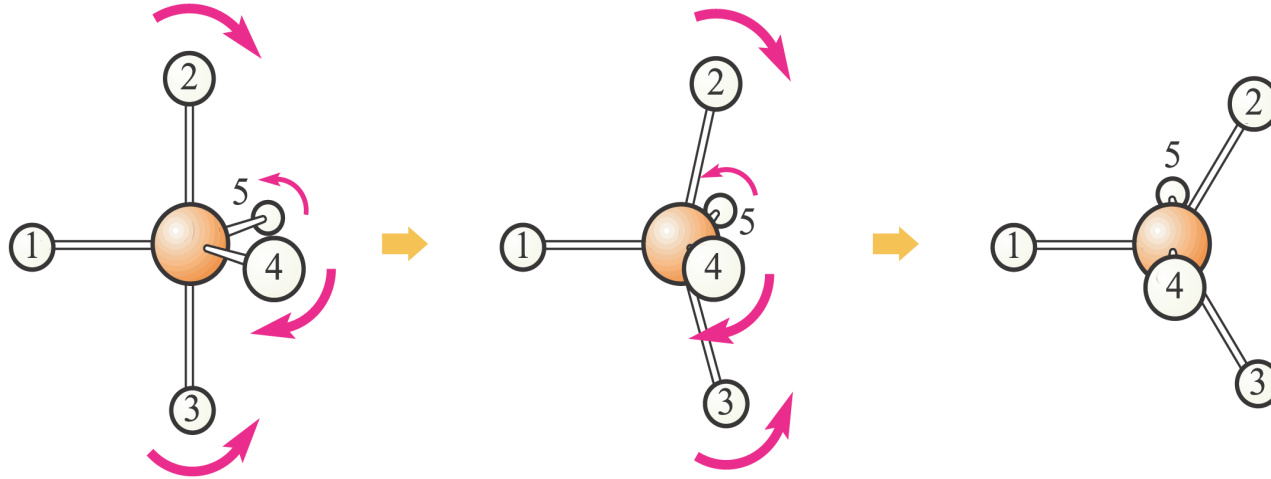


Legante tripodale



# Flussionalità

## Pseudo-rotazione di Berry

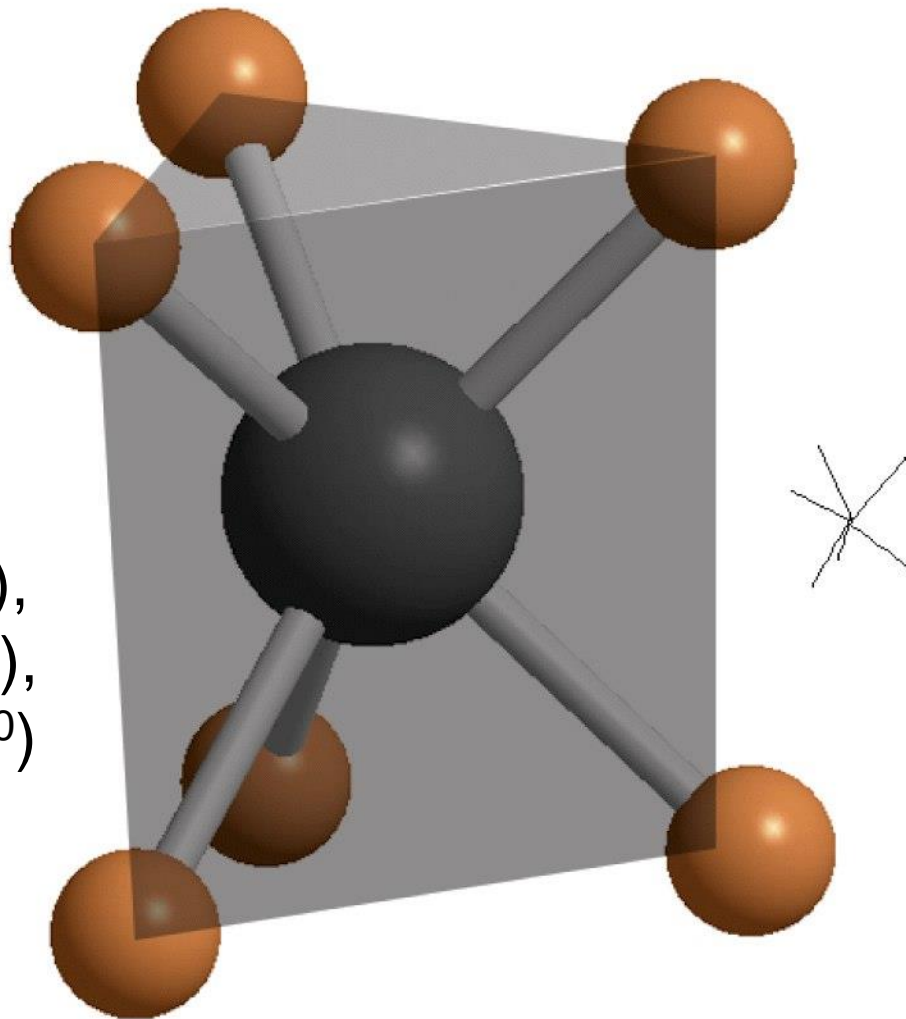


Trigonal bipyramid  
(Atoms 2 and 3 are  
in axial sites.)

Square-based pyramid

Trigonal bipyramid  
(Atoms 4 and 5 are  
in axial sites.)

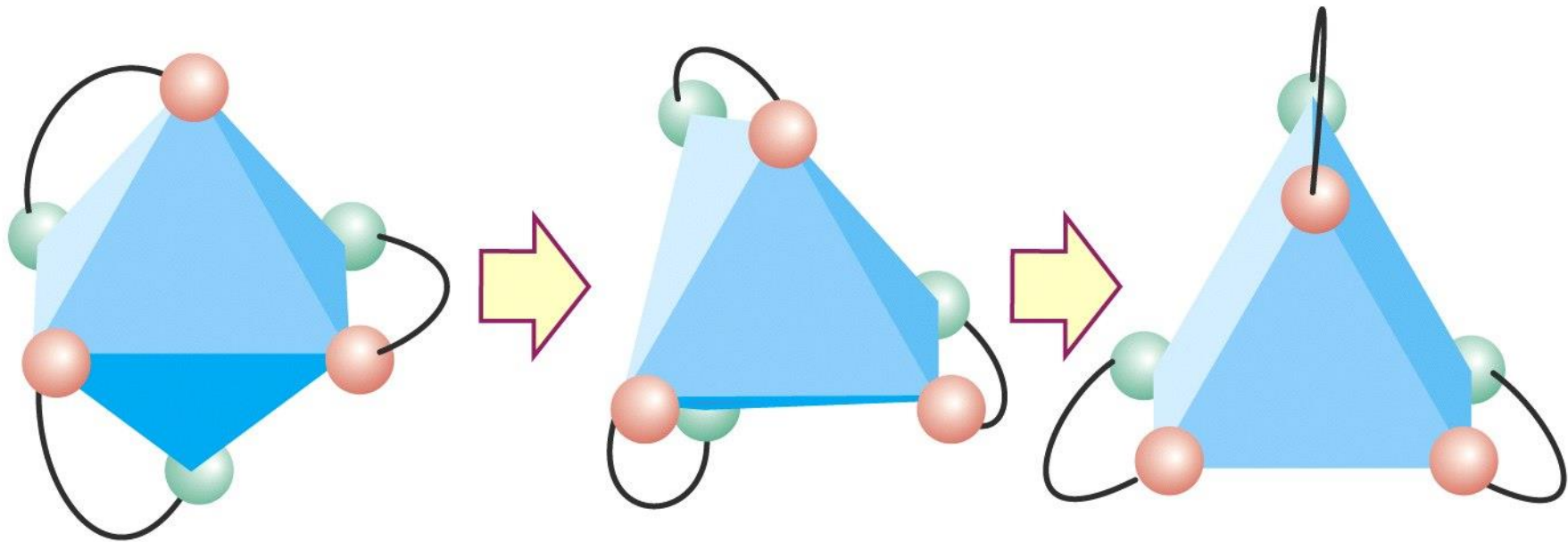
$[\text{Re}(\text{CH}_3)_6]$  ( $d^1$ ),  
 $[\text{Ta}(\text{CH}_3)_6]^-$  ( $d^0$ ),  
 $[\text{Zr}(\text{CH}_3)_6]^{2-}$  ( $d^0$ )

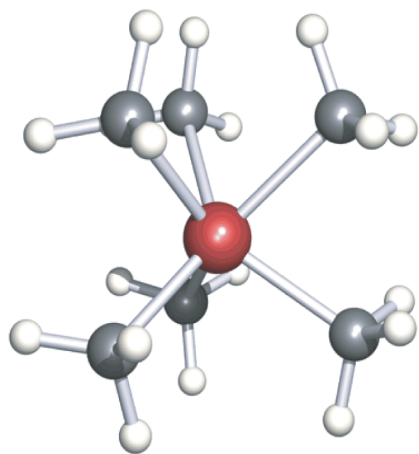


## Trigonal prism, $D_{3h}$

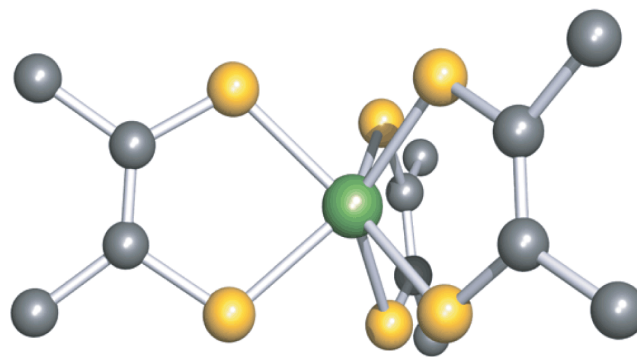
Essenzialmente in complessi di metalli  $d^0$  o  $d^1$   
con leganti puri  $\sigma$ -donatori



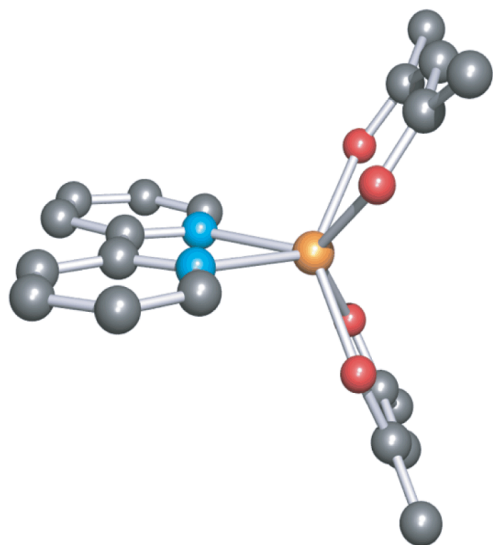




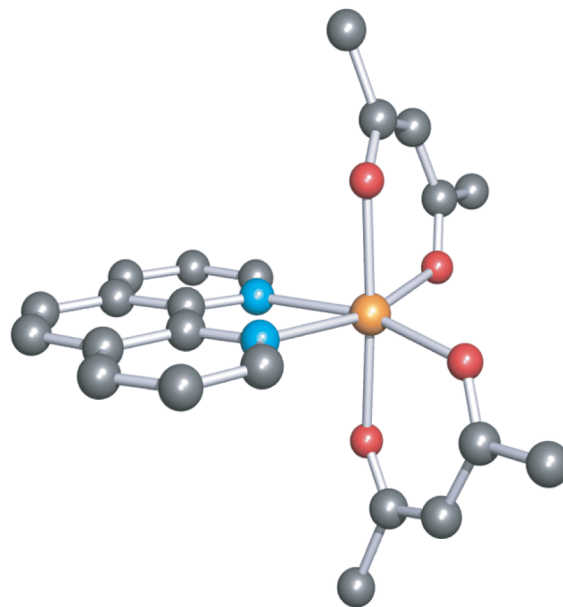
[W(CH<sub>3</sub>)<sub>6</sub>] (d<sup>0</sup>)



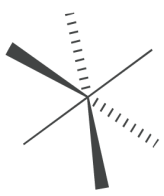
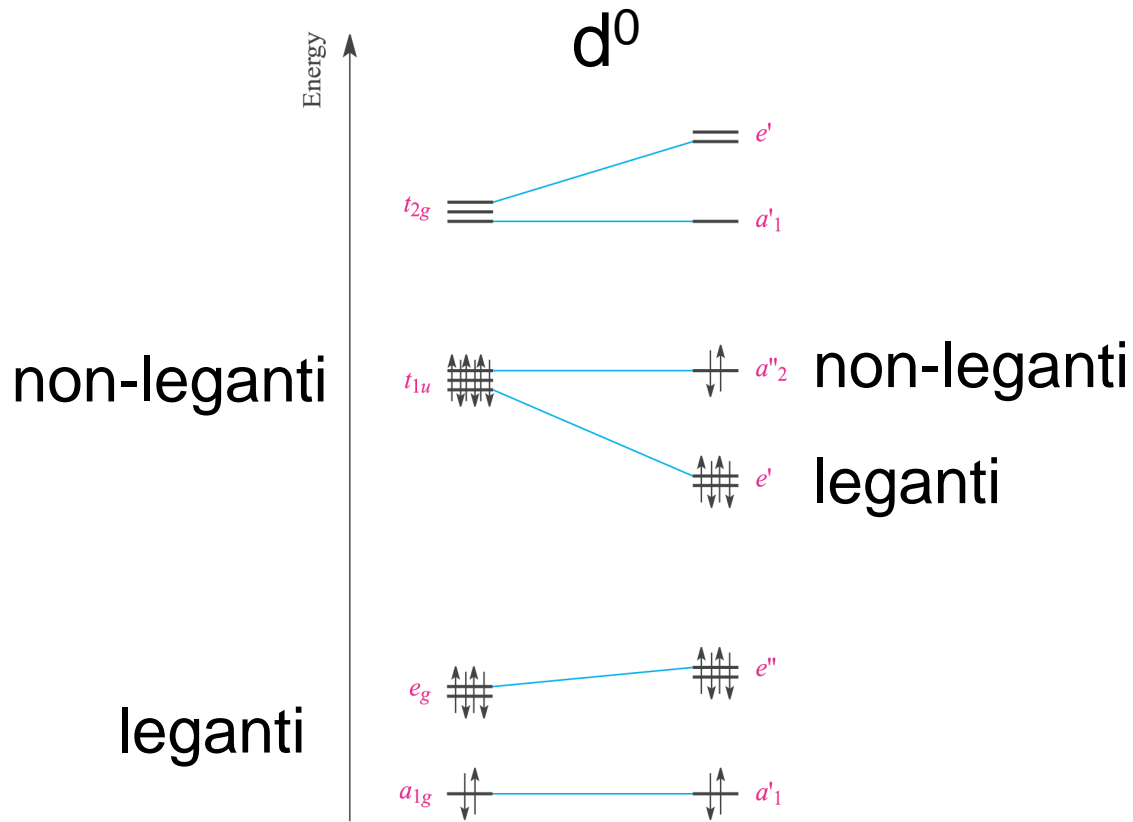
[Re(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>3</sub>] (d<sup>1</sup>)



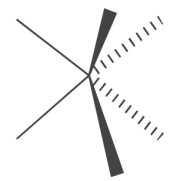
[Mn(acac)<sub>2</sub>(bipy)]



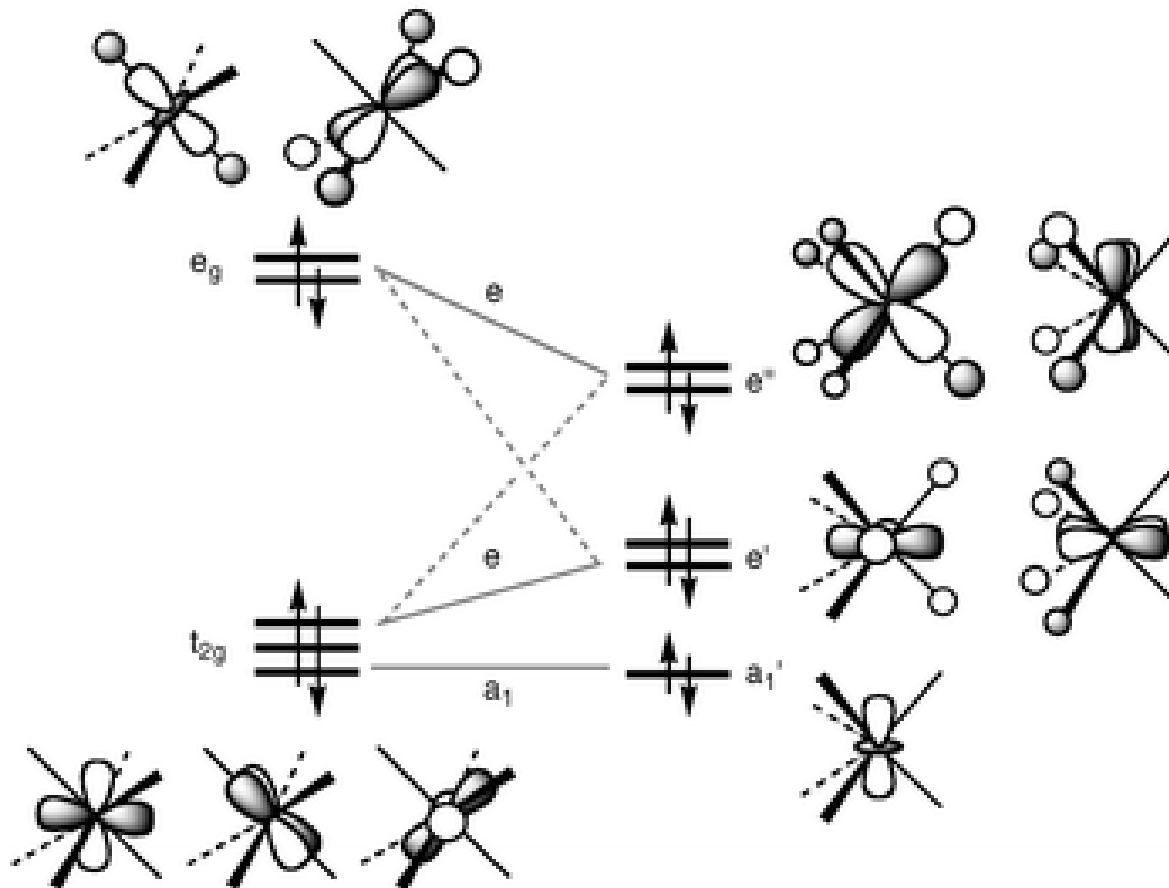
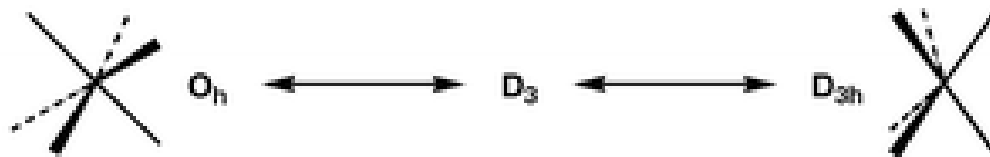
[Mn(acac)<sub>2</sub>(phen)]



Octahedral  
 $O_h$

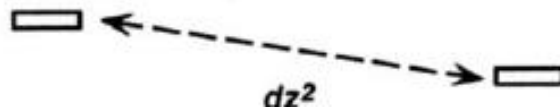
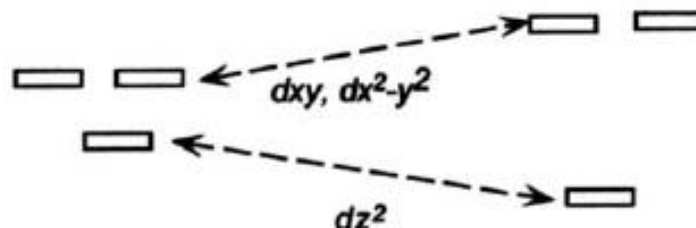
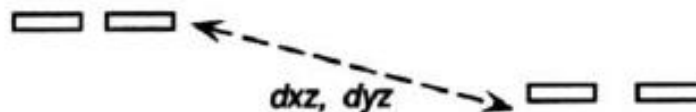
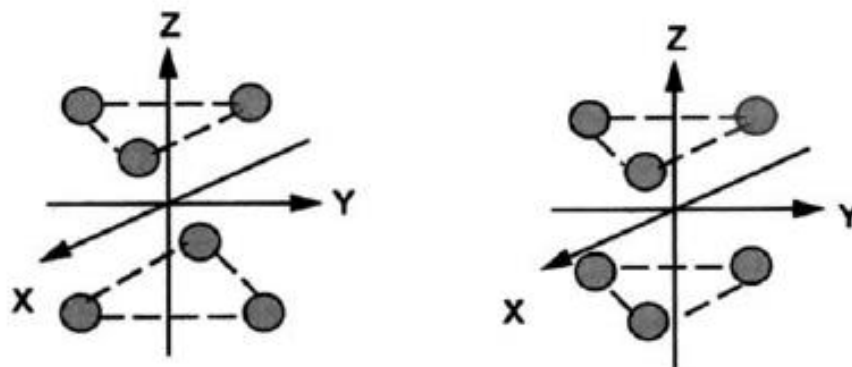


Trigonal prismatic  
 $D_{3h}$

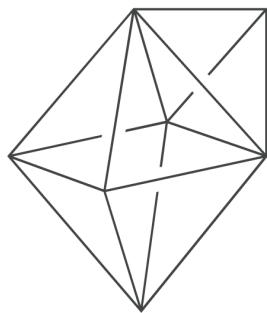


*Diversa orientazione degli assi cartesiani*

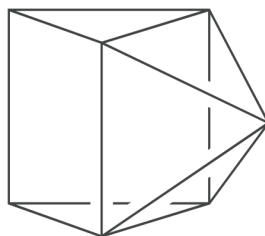
*Splitting degli orbitali d in ottaedro e prisma trigonale mantenendo l'orientazione degli assi cartesiani del prisma*



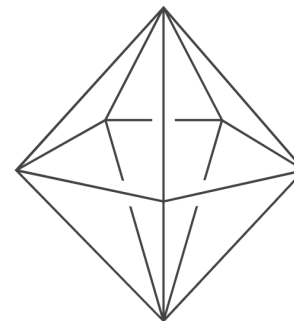
# Geometrie per numero di coordinazione 7



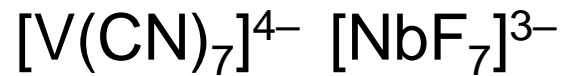
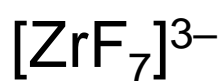
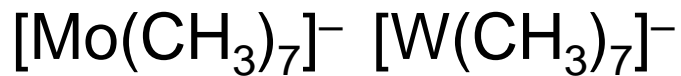
Monocapped  
octahedron



Monocapped trigonal  
prism

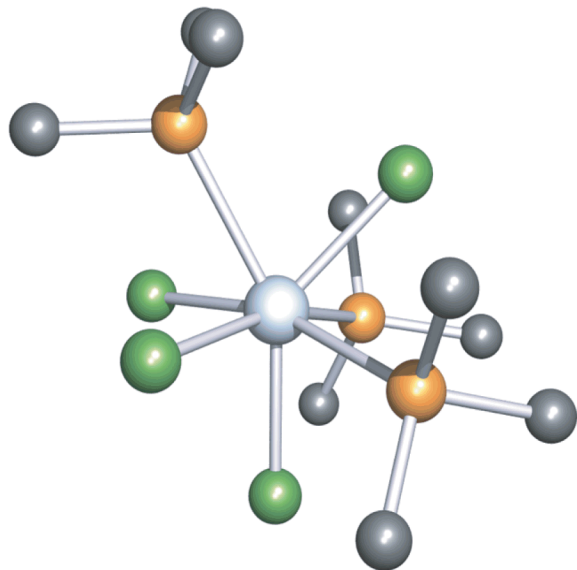


Pentagonal  
bipyramid

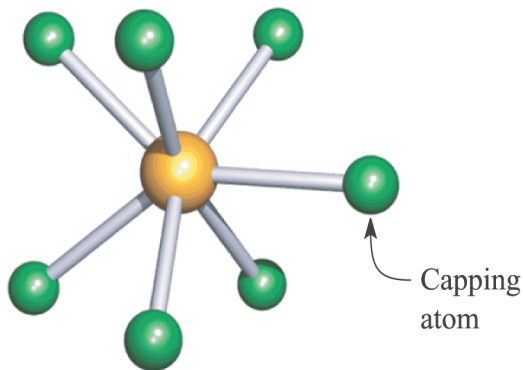


leganti piccoli e/o poco polarizzabili

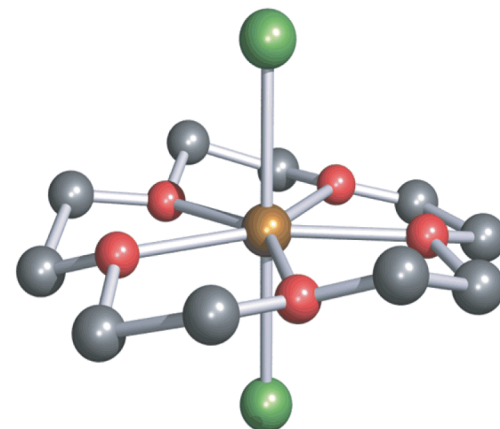
# Esempi di complessi eptacoordinati



$[\text{TaCl}_4(\text{PMe}_3)_3]$   
ottaedro cappato



$[\text{ZrF}_7]^{3-}$   
prisma trigonale cappato

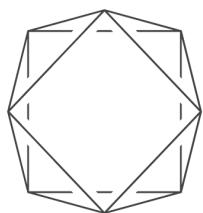


$[\text{ScCl}_2(15\text{-crown-}5)]^+$   
bipiramide pentagonale

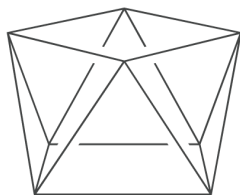
Cationi = acidi di Lewis deboli



# Geometrie per numero di coordinazione 8

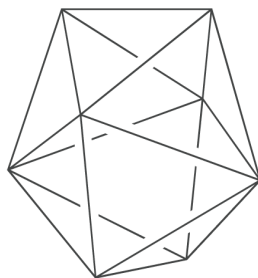
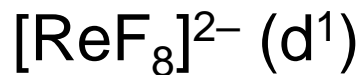
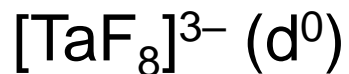


or



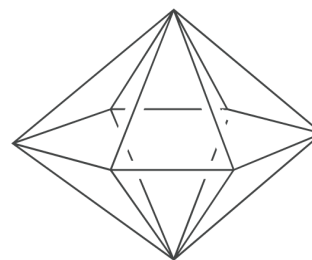
Square antiprism

$D_{4d}$

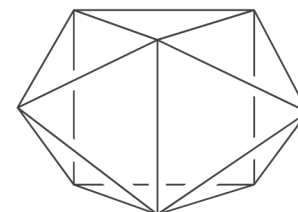


Dodecahedron

$D_{2d}^{(a)}$

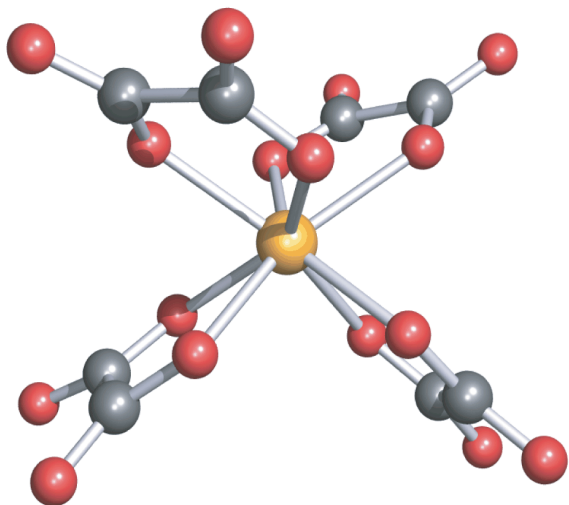


Hexagonal bipyramid

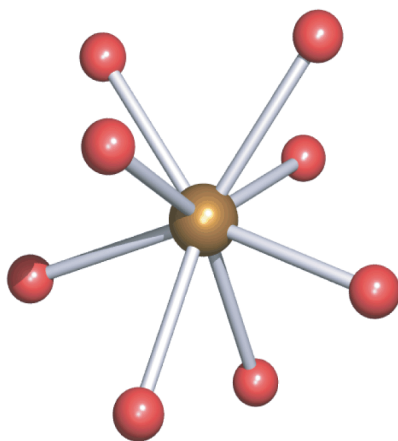


Bicapped trigonal prism

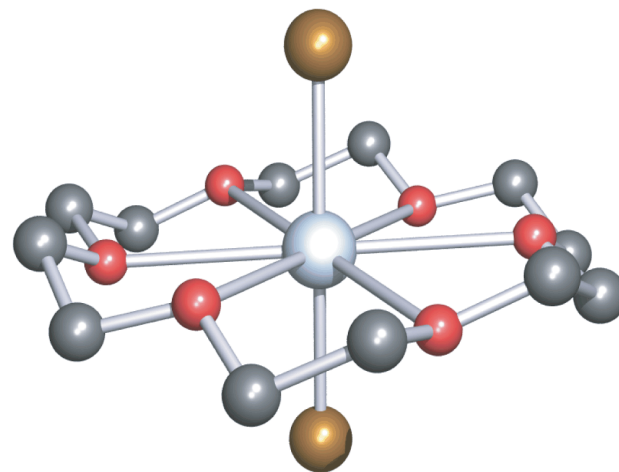
# Esempi di complessi ottacoordinati



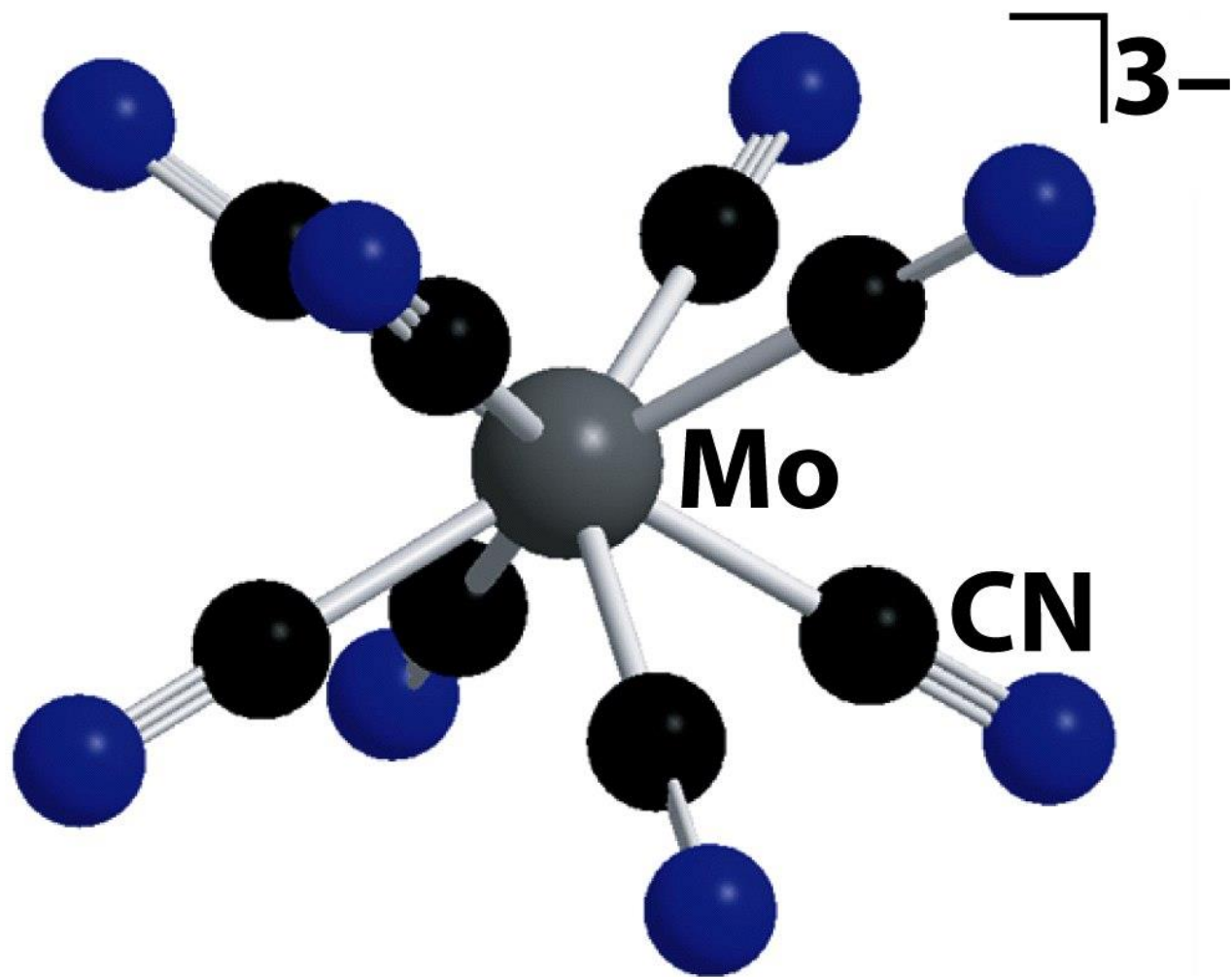
$[\text{Nb}(\text{ox})_4]^{4-}$   
antiprisma quadrato

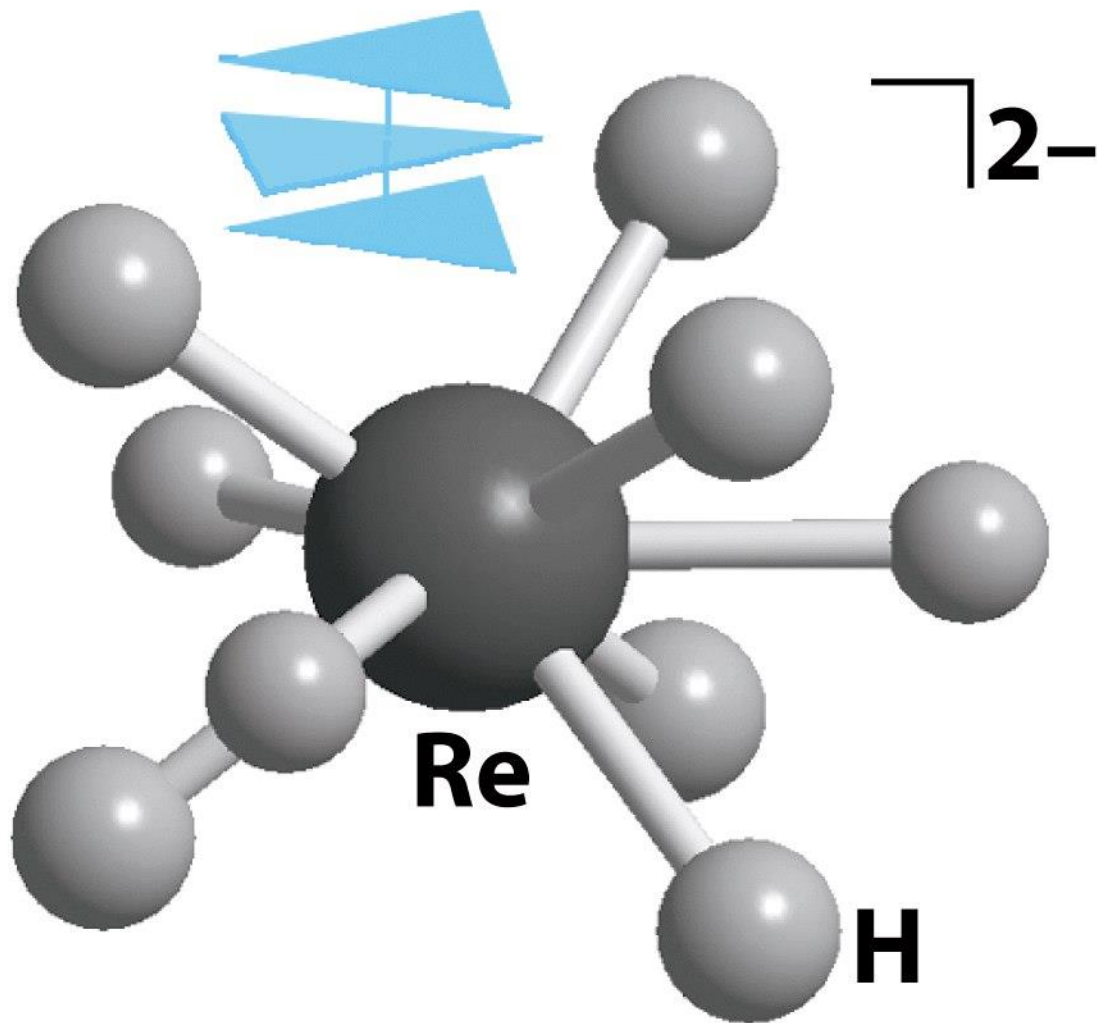


$[\text{Y}(\text{OH}_2)_8]^{3+}$   
dodecaedro

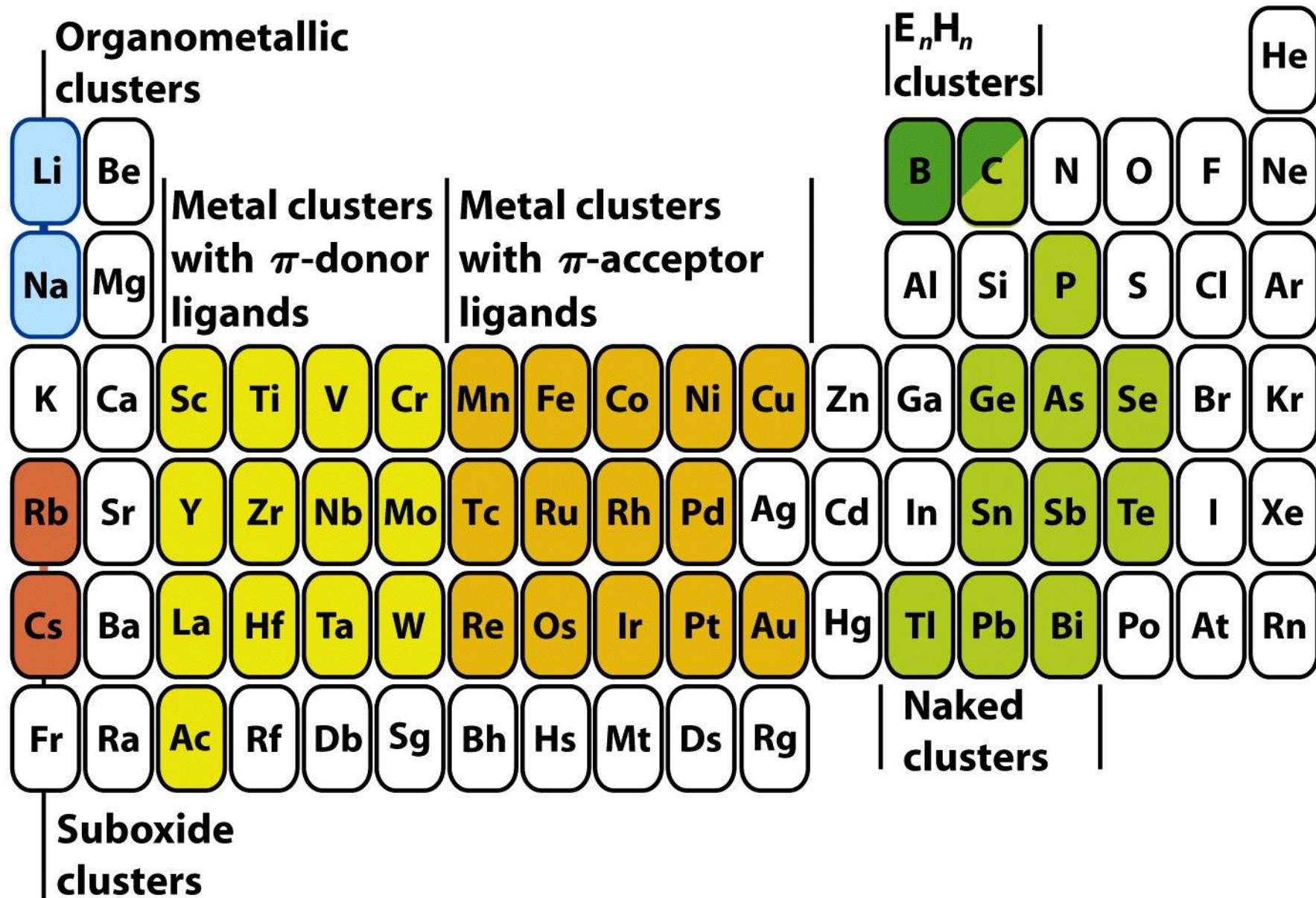


$[\text{CdBr}_2(18\text{-crown-}6)]$   
bipiramide esagonale

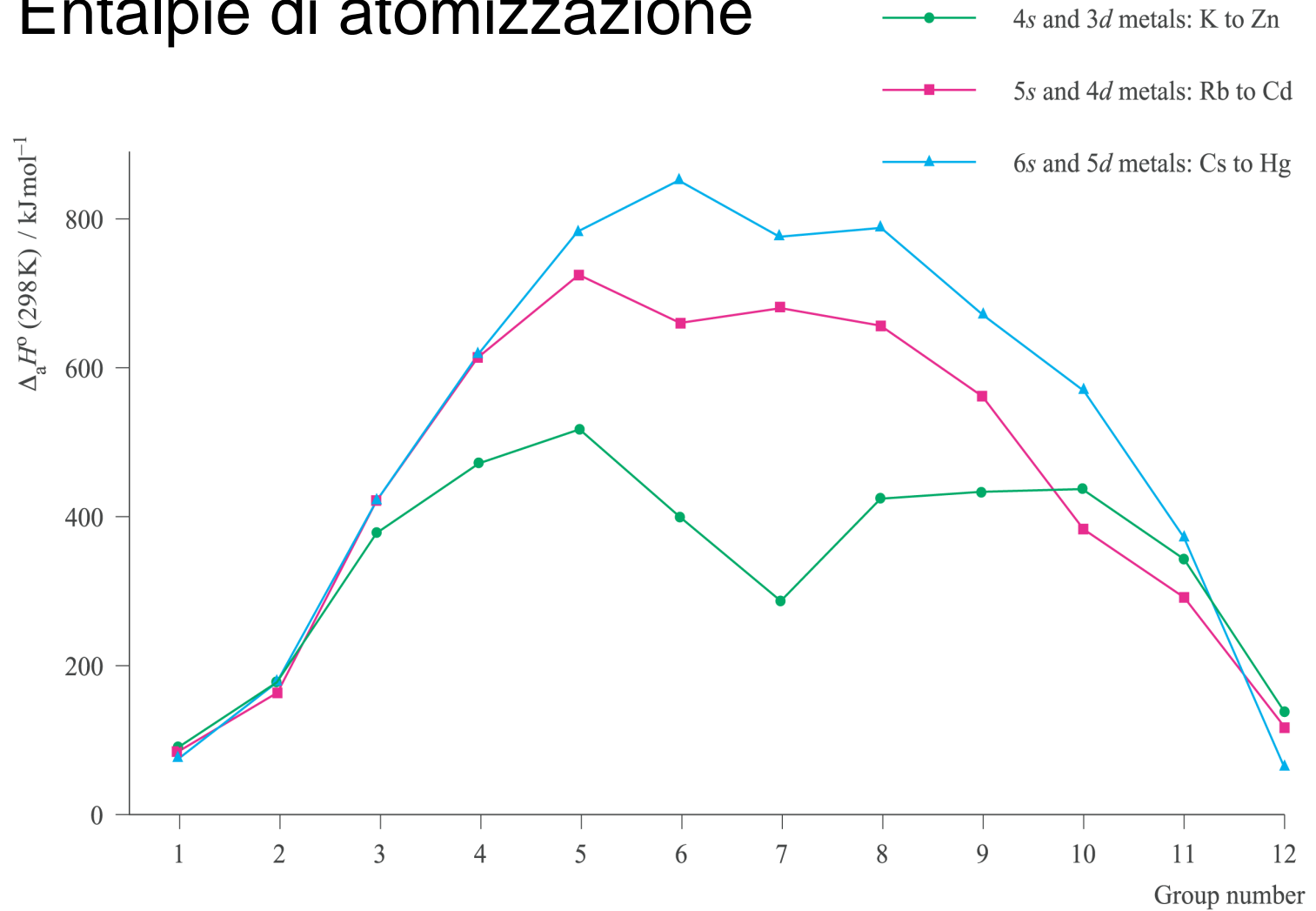


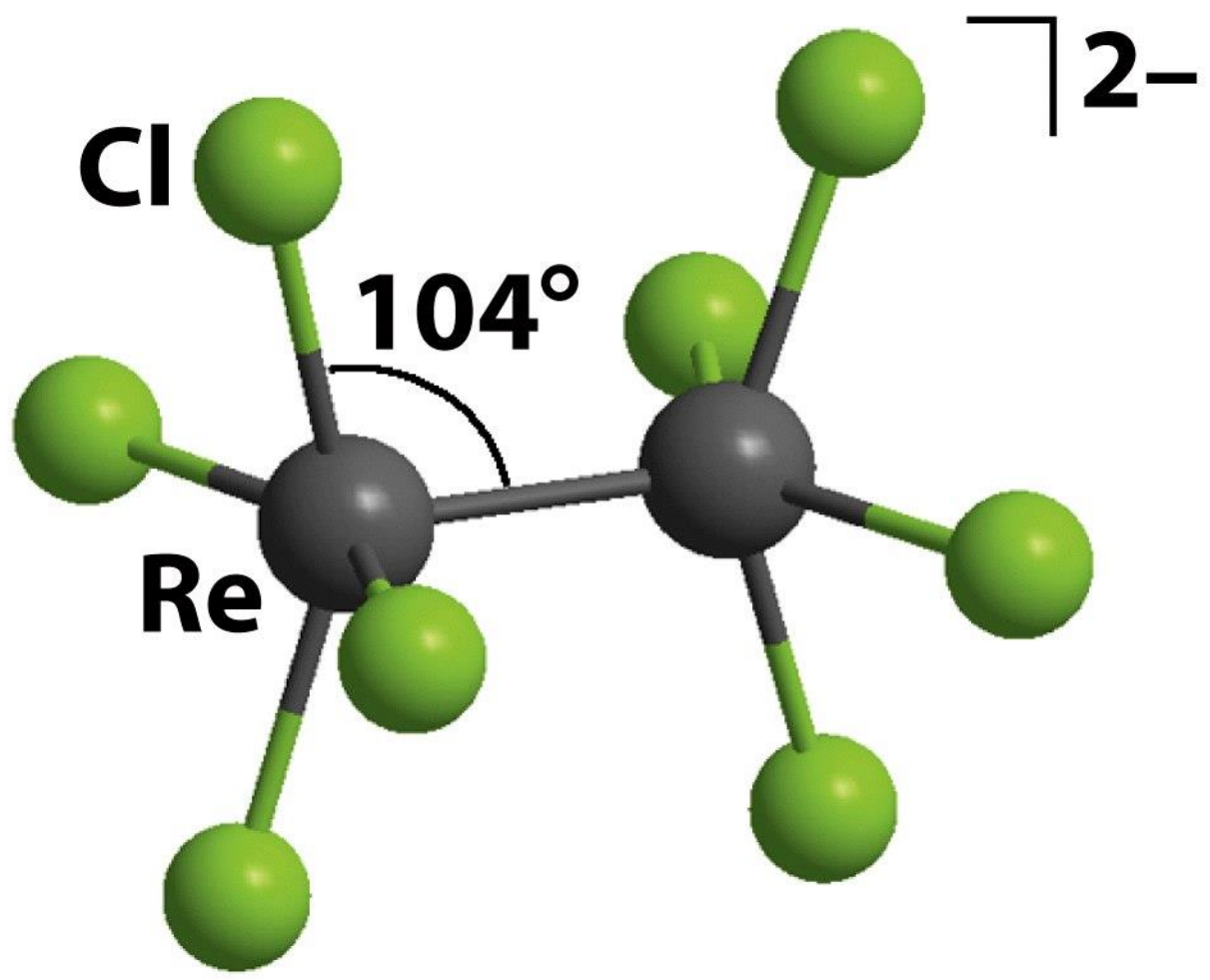


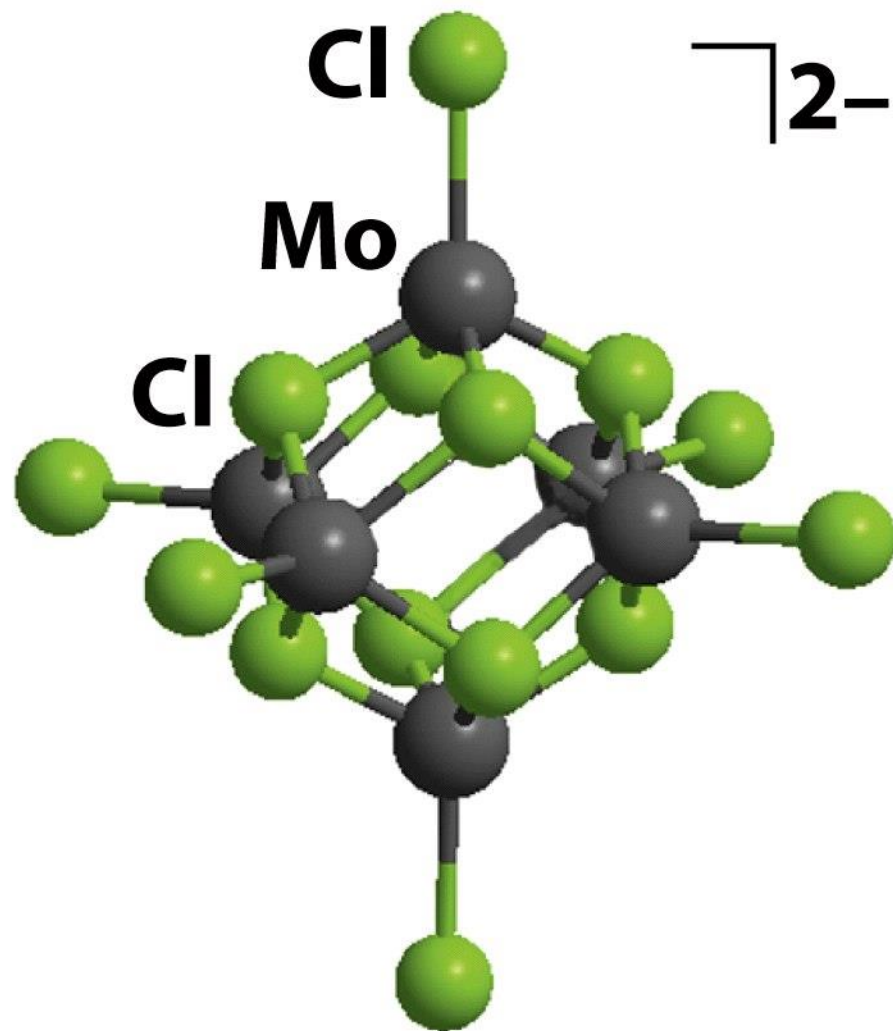
Prisma trigonale tricappato



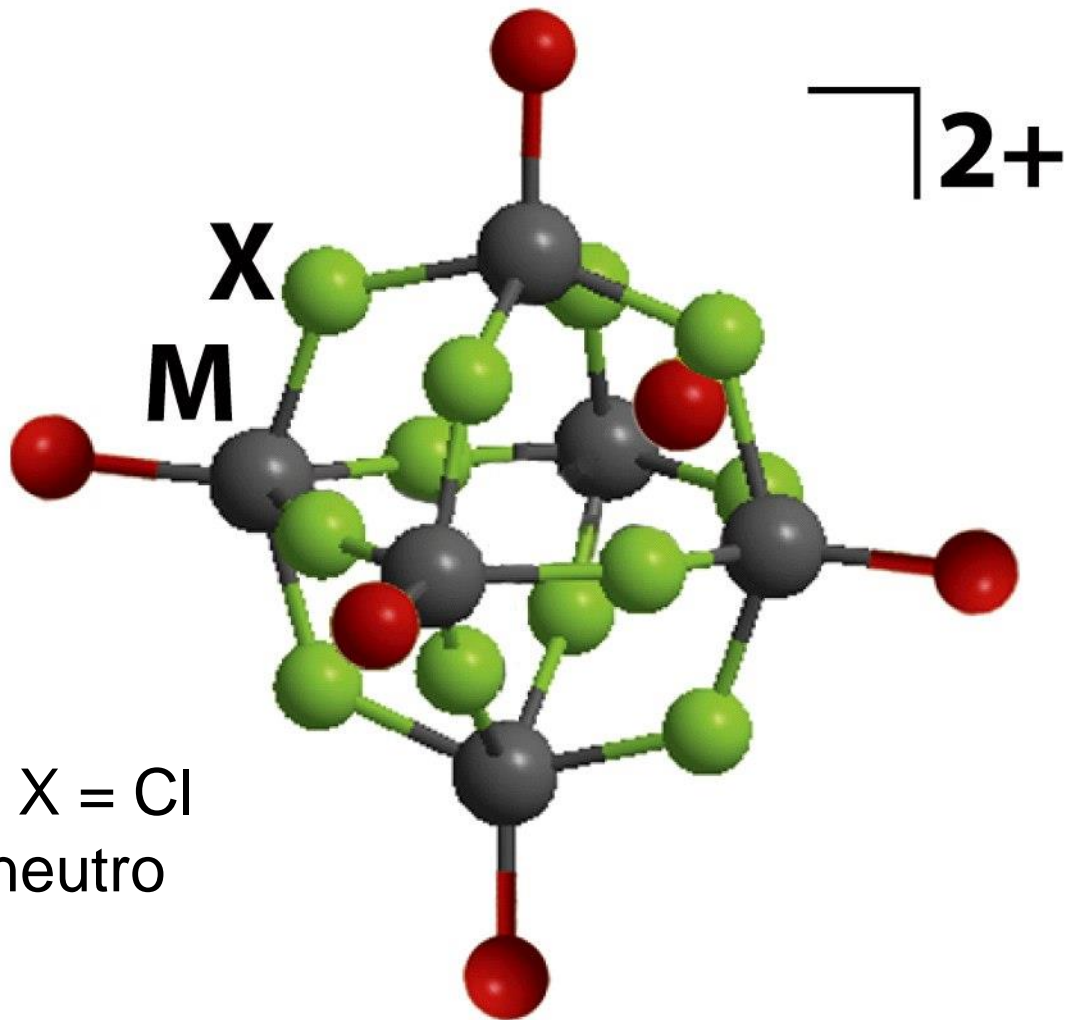
# Entalpie di atomizzazione





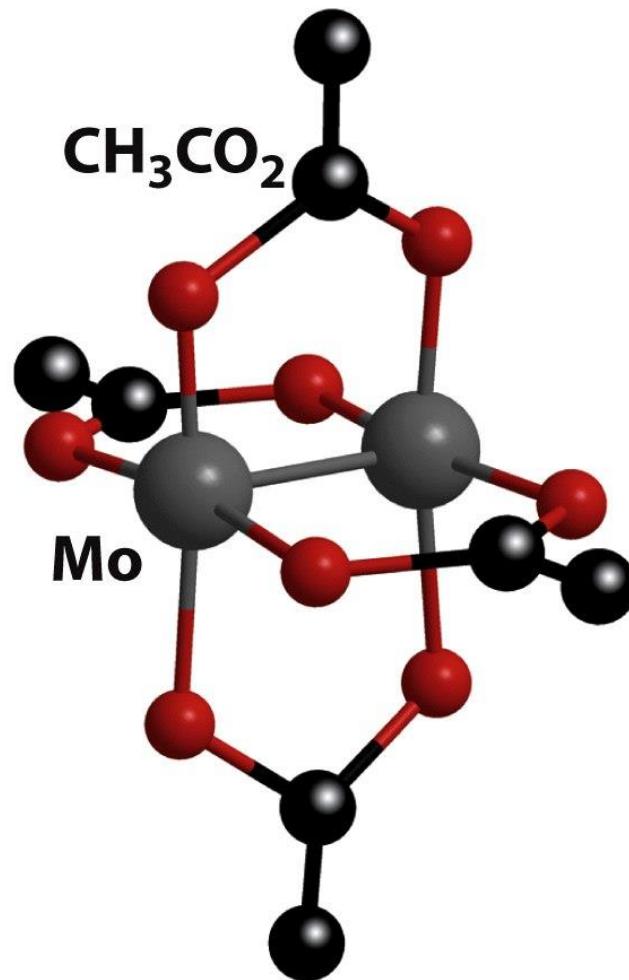






e.g. M = Nb, X = Cl  
L = legante neutro

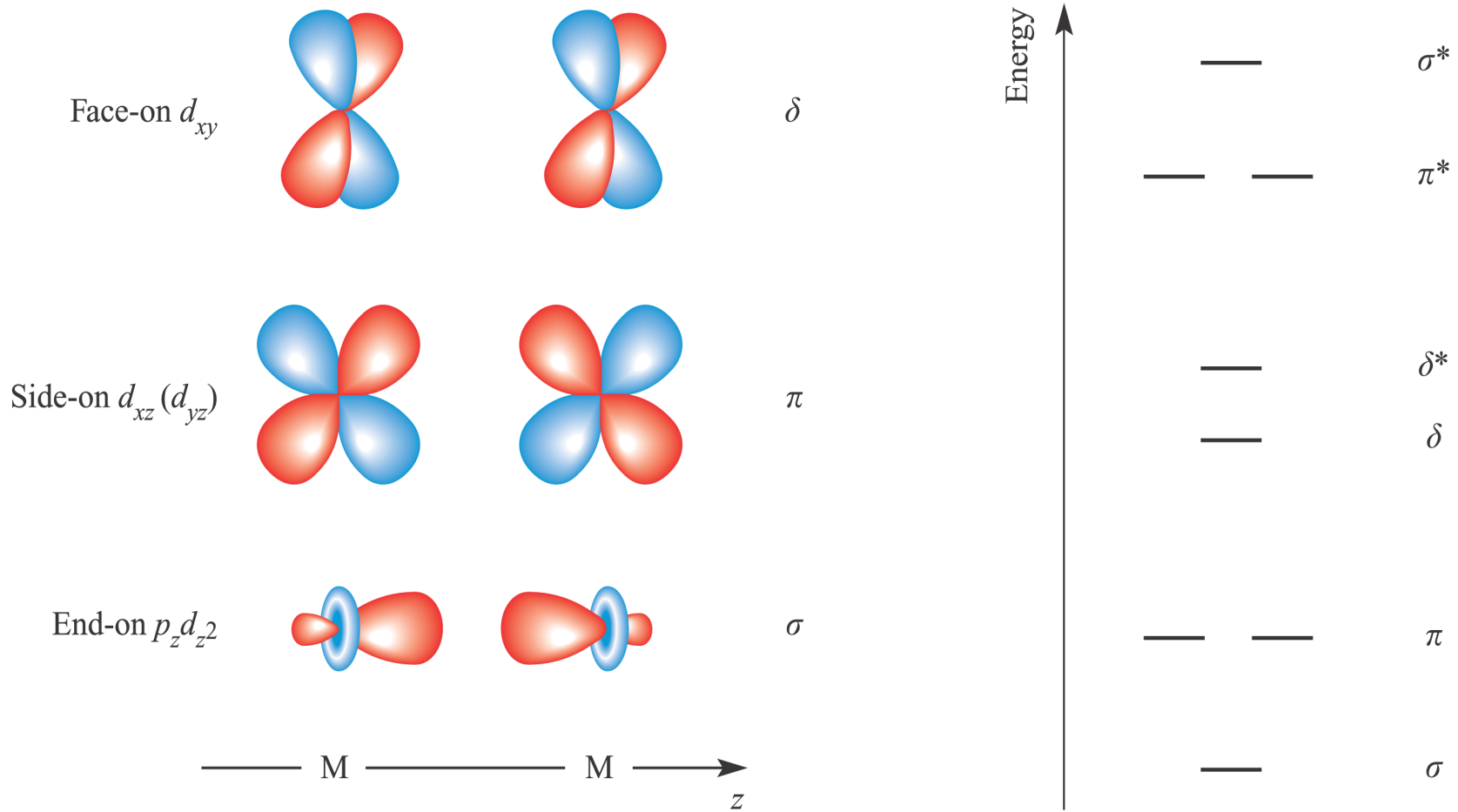


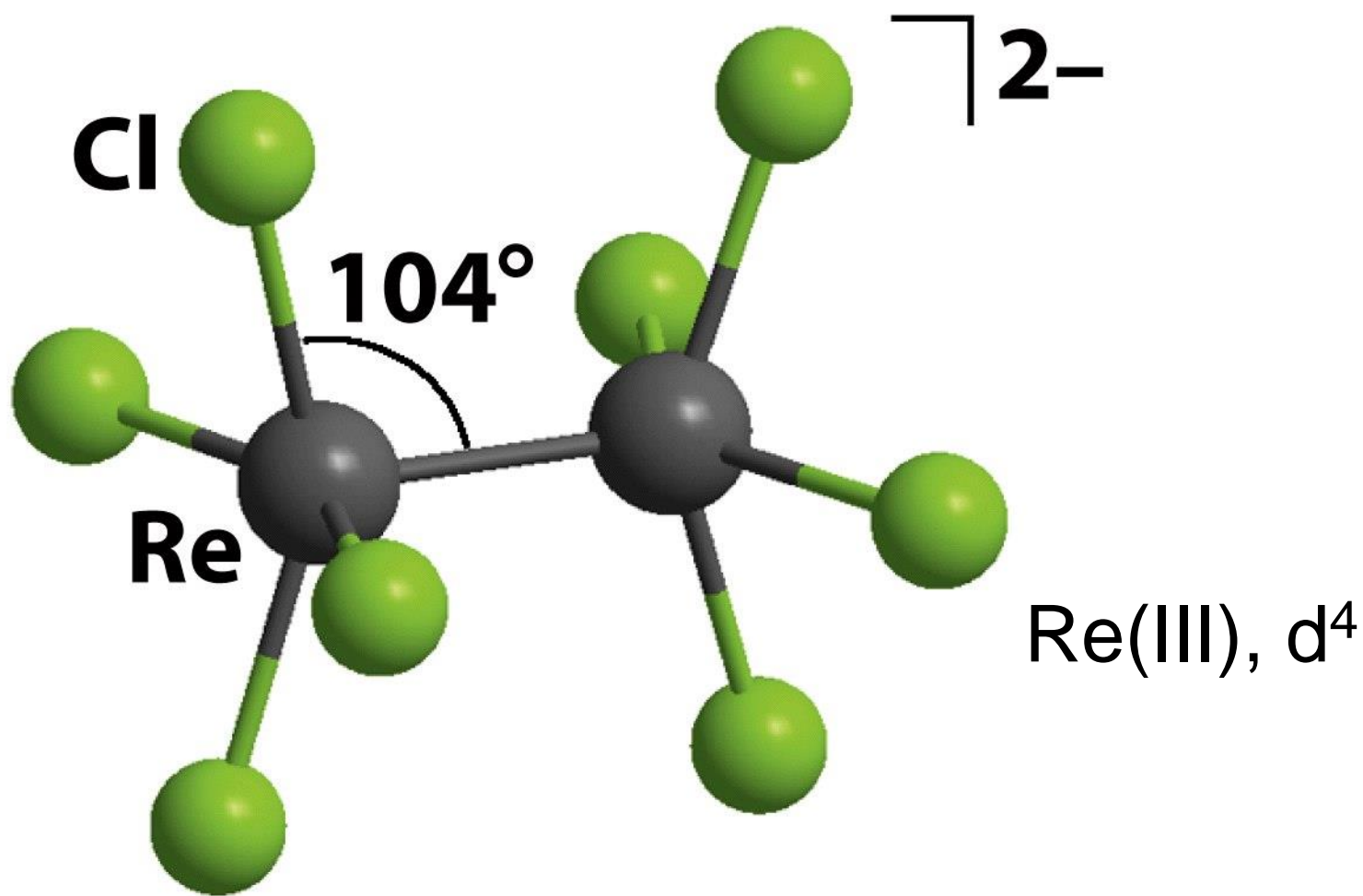


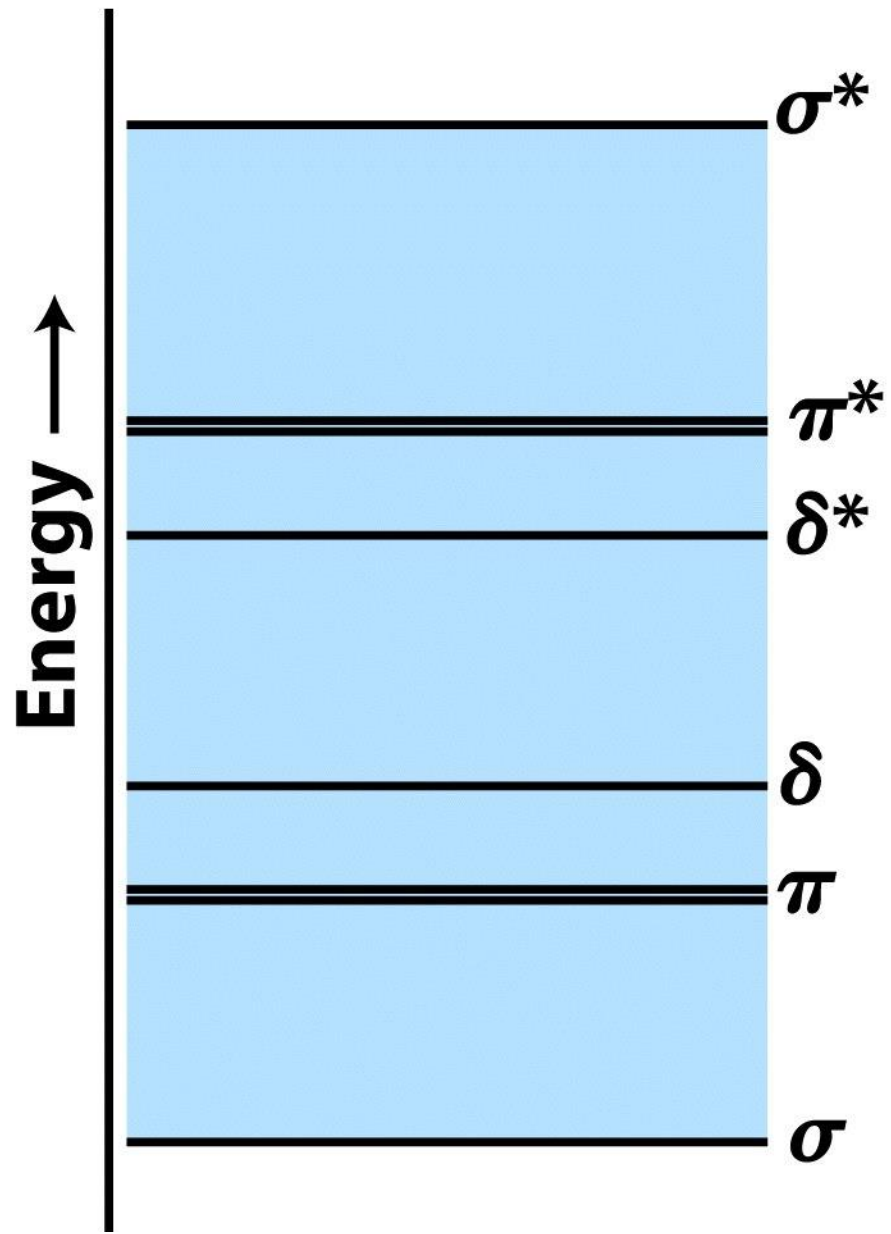
Mo(II),  $d^4$



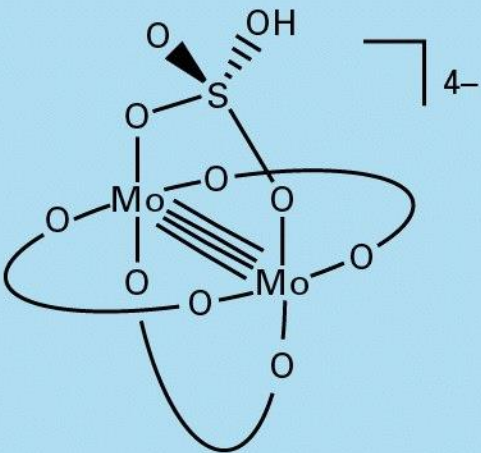
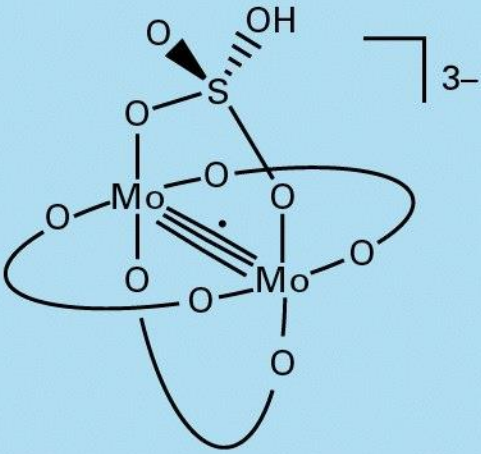
Complesso a gabbia  
(tipo *a lanterna* o *paddle-wheel*)  
Ordine di legame M–M da 1 a 4



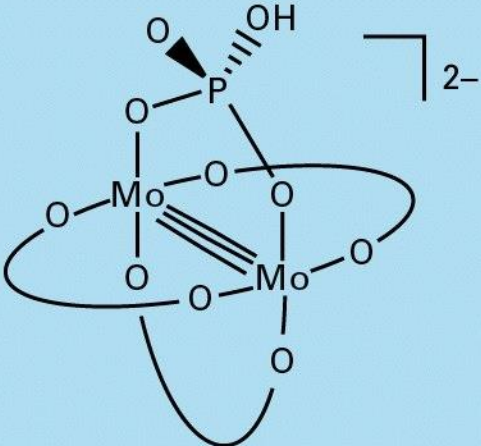
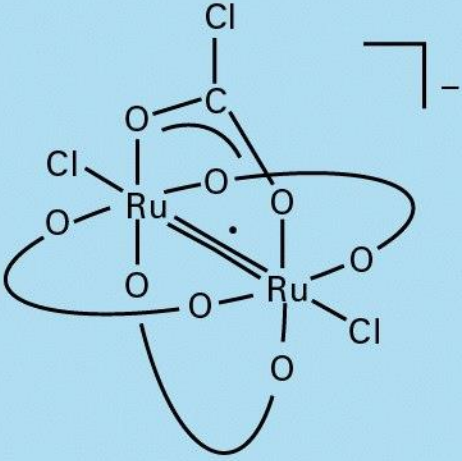




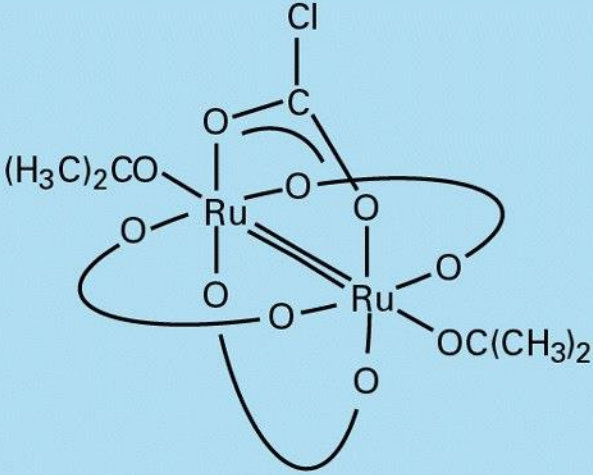
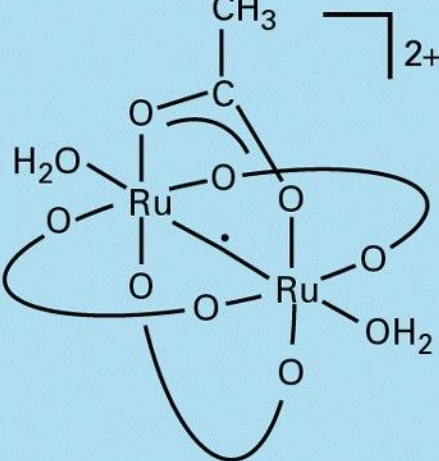
**Table 18.9** Examples of metal–metal bonded tetragonal prismatic complexes<sup>†</sup>

Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2\pi^4\delta^2$	4	211
	$\sigma^2\pi^4\delta^1$	3.5	217

**Table 18.9** Examples of metal–metal bonded tetragonal prismatic complexes<sup>†</sup>

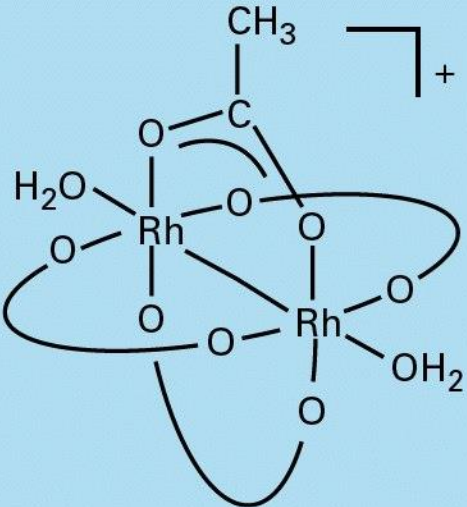
Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2\pi^4$	3	222
	$\sigma^2\pi^4\delta^2\delta^*1\pi^*2$	2.5	227

**Table 18.9** (Continued)

Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2 \pi^4 \delta^2 \delta^* 2 \pi^{*2}$	2	226
	$\sigma^2 \pi^4 \delta^2 \delta^* 1 \pi^{*4}$	1.5	232



**Table 18.9** (Continued)

Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2\pi^4\delta^2\delta^*\pi^4$	1	239

† When multiple bridging ligands are present, only one is shown in detail.

Source: F.A. Cotton, *Chem. Soc. Rev.*, 1983, **12**, 35.