

Conta degli elettroni: metodo della donazione di coppie elettroniche

- Il *numero di ossidazione* dell'atomo metallico è dato dalla carica totale del complesso meno le eventuali cariche dei leganti.
- Il *numero di elettroni* forniti dal metallo corrisponde a quello del suo Gruppo meno il suo numero di ossidazione.
- Il *numero totale di elettroni* è la somma del numero di elettroni sull'atomo metallico e del numero di elettroni forniti dai leganti.

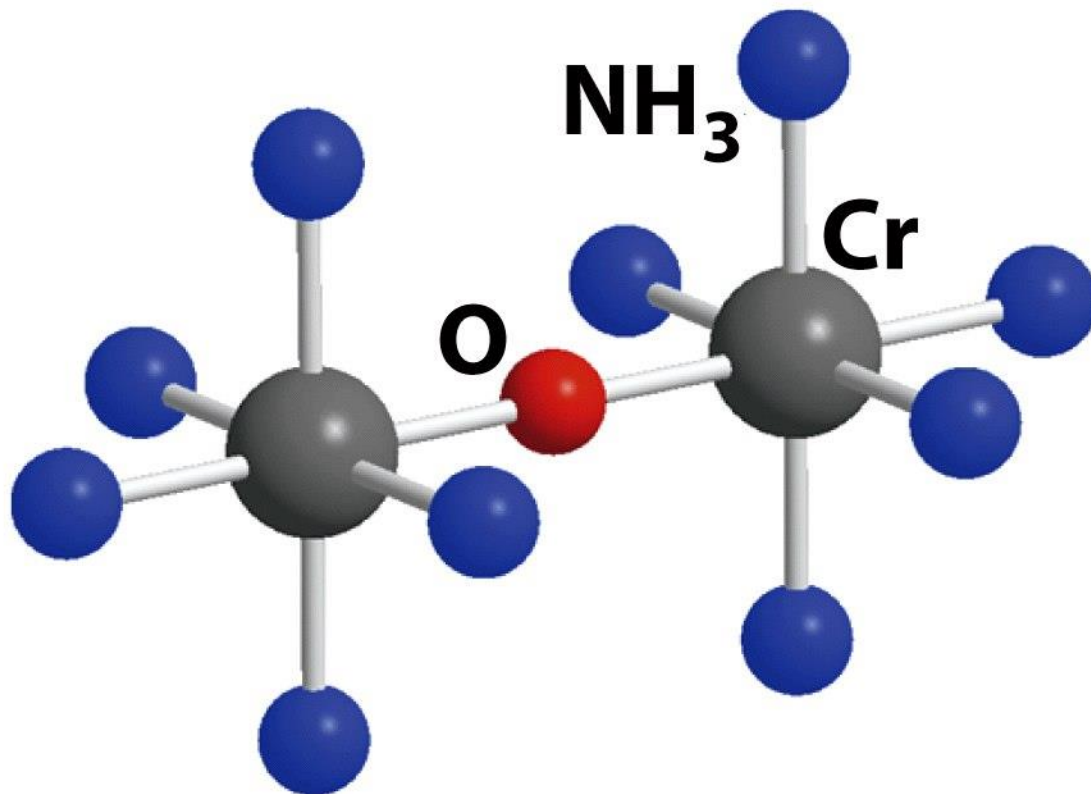
Nomenclatura

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

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

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

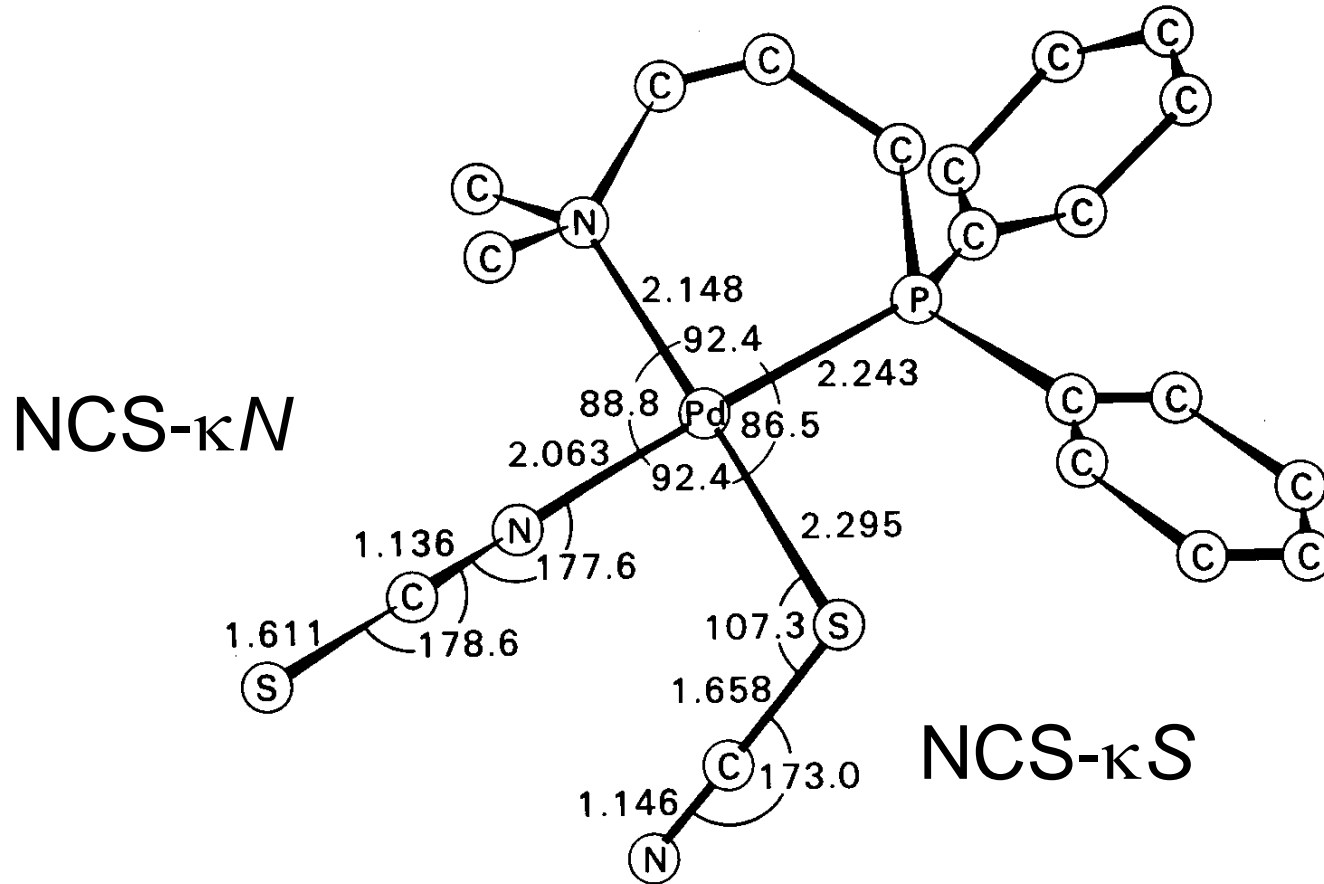
$[\text{RuCl}_2(\text{dmso})_4]$
diclororotetrakisdimetilsolfossidorutenio(II)

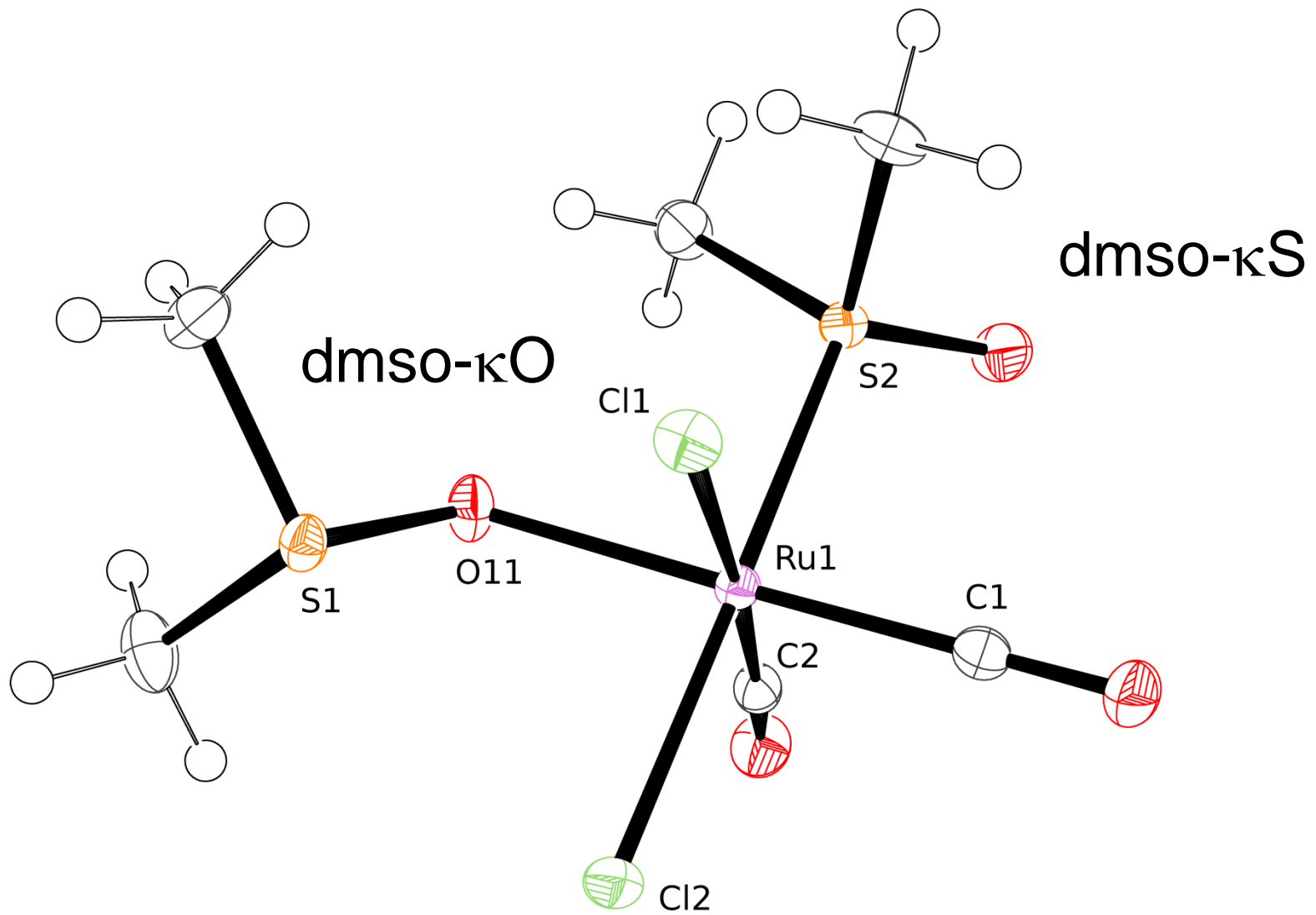


μ -osso-bis(pentaammino)cromo(III)



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 σ (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 π .
- 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)

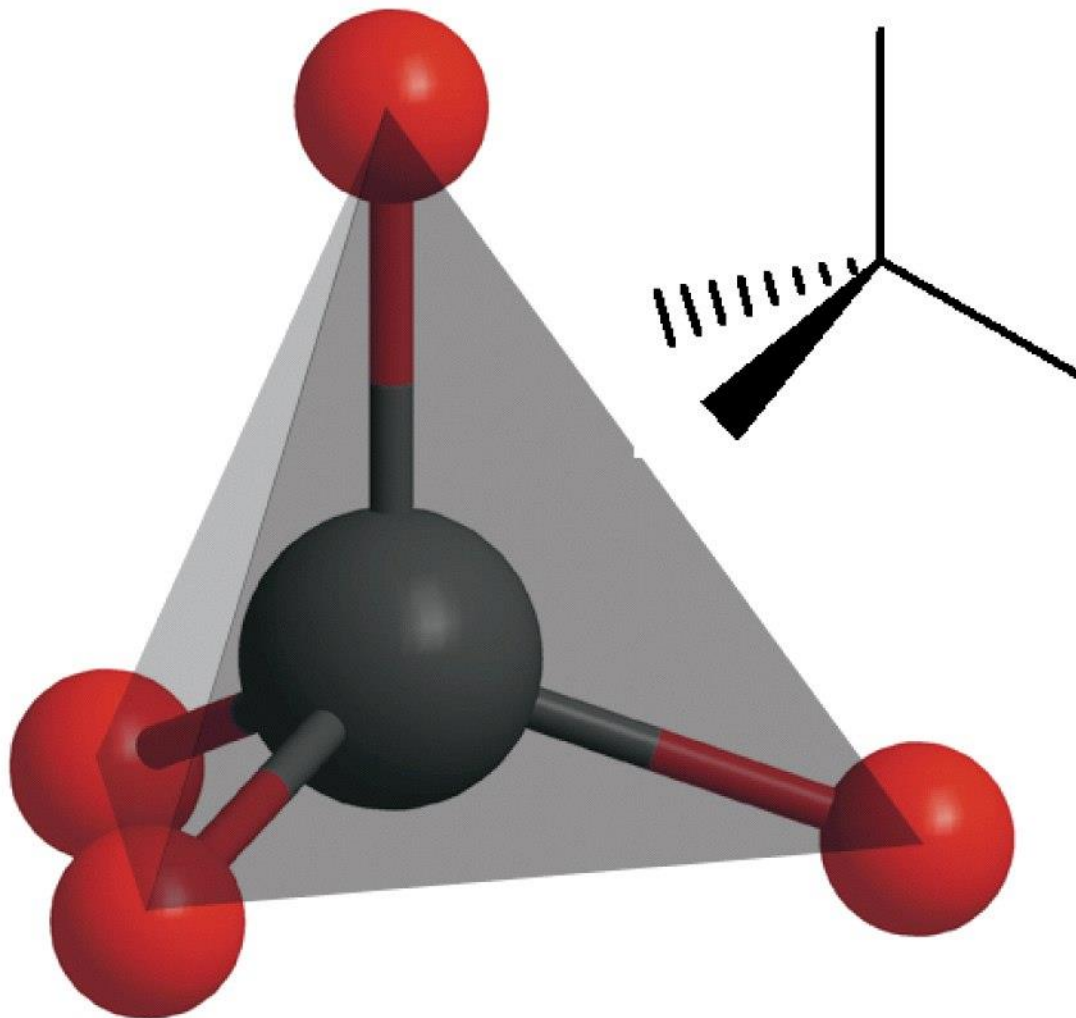


Numero di coordinazione 3
geometria trigonale planare

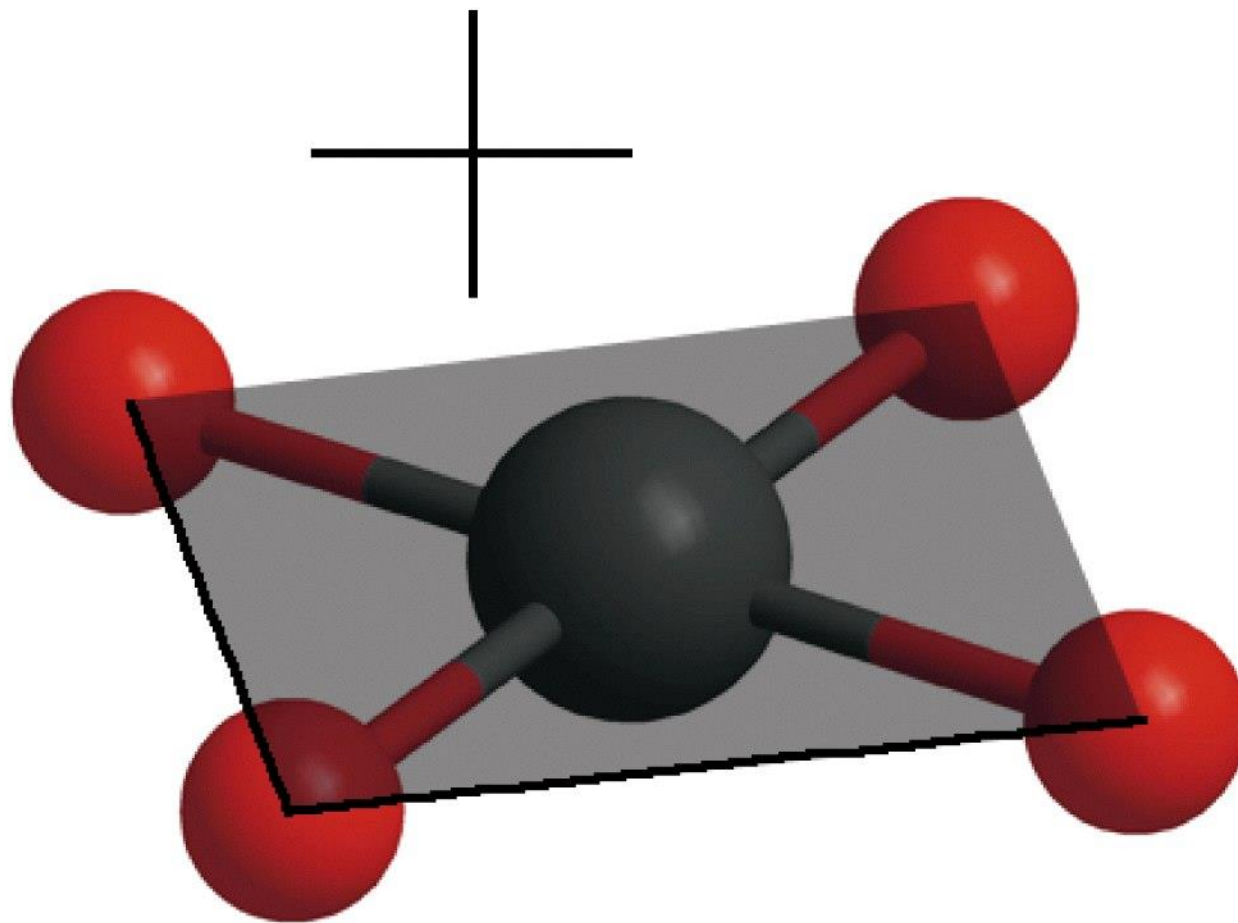
Ioni d^{10} : Cu(I), Au(I), Pt(0)

$[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Au}(\text{PPh}_3)_3]^+$, $[\text{Pt}(\text{PCy}_3)_3]$

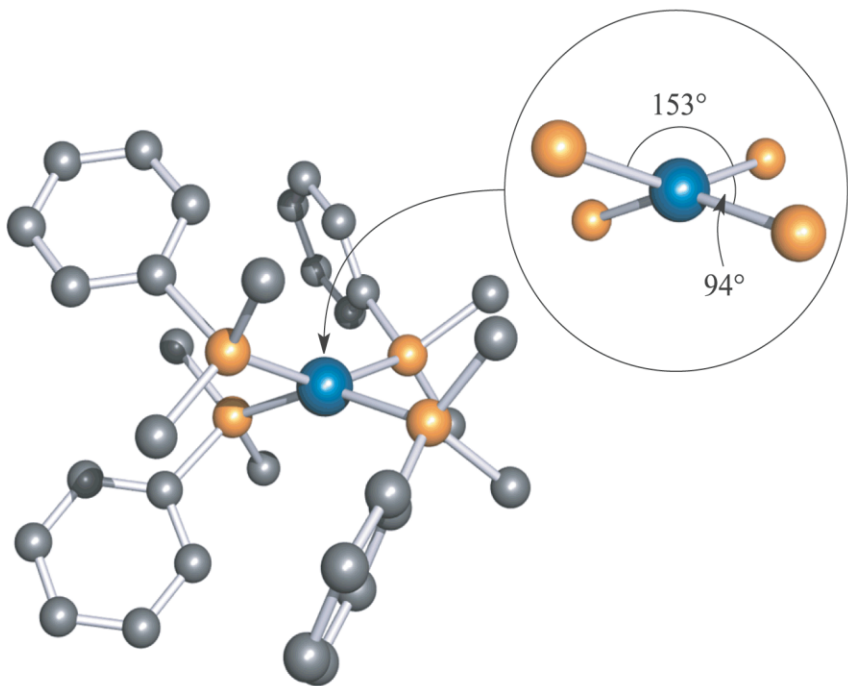
anioni poco coordinanti: NO_3^- , ClO_4^- , CF_3SO_3^- (triflato),
 BF_4^- , PF_6^- , SbF_6^-



Tetrahedral complex, T_d



Square-planar complex, D_{4h}



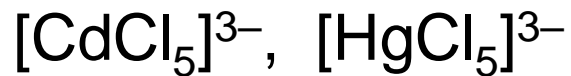
D_{2d}



Distorsione della geometria planare-quadrata causata da leganti voluminosi

Complessi pentacoordinati

Bipiramide trigonale



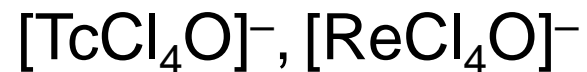
d^{10}

minimizza le repulsioni fra i leganti

Piramide a base quadrata



d^1

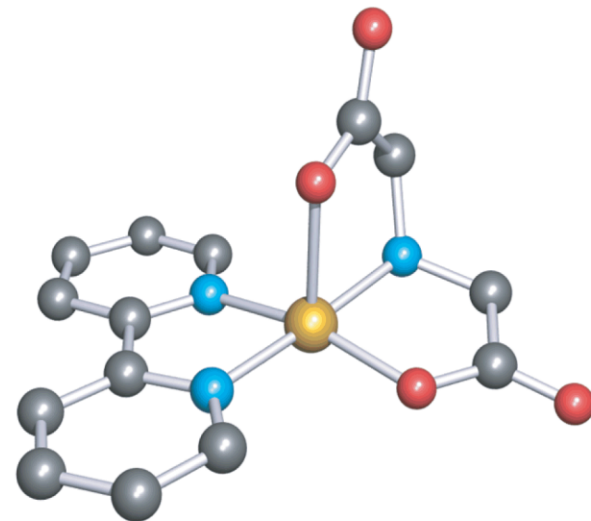
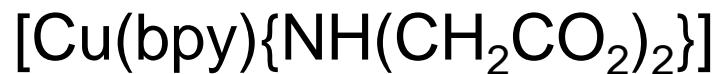
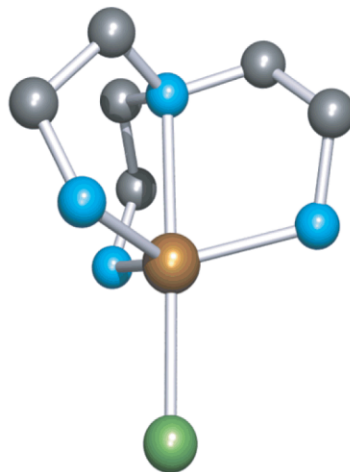


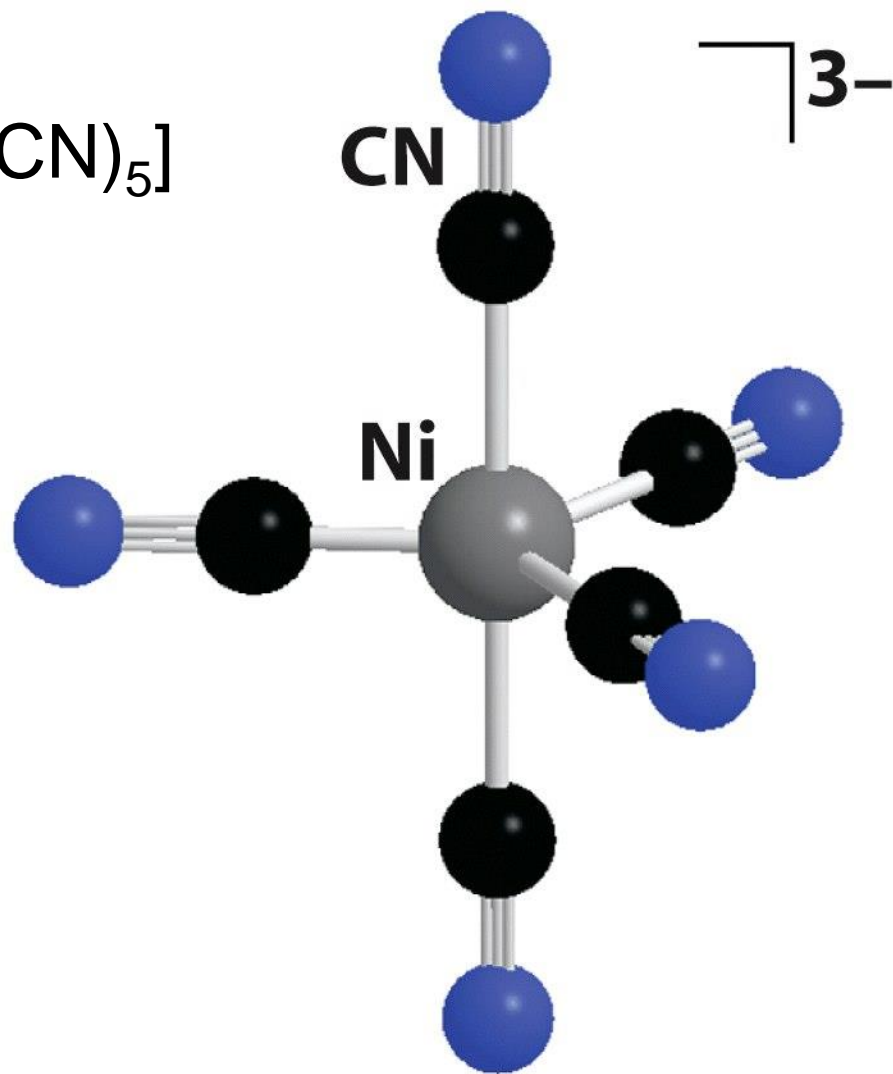
d^2

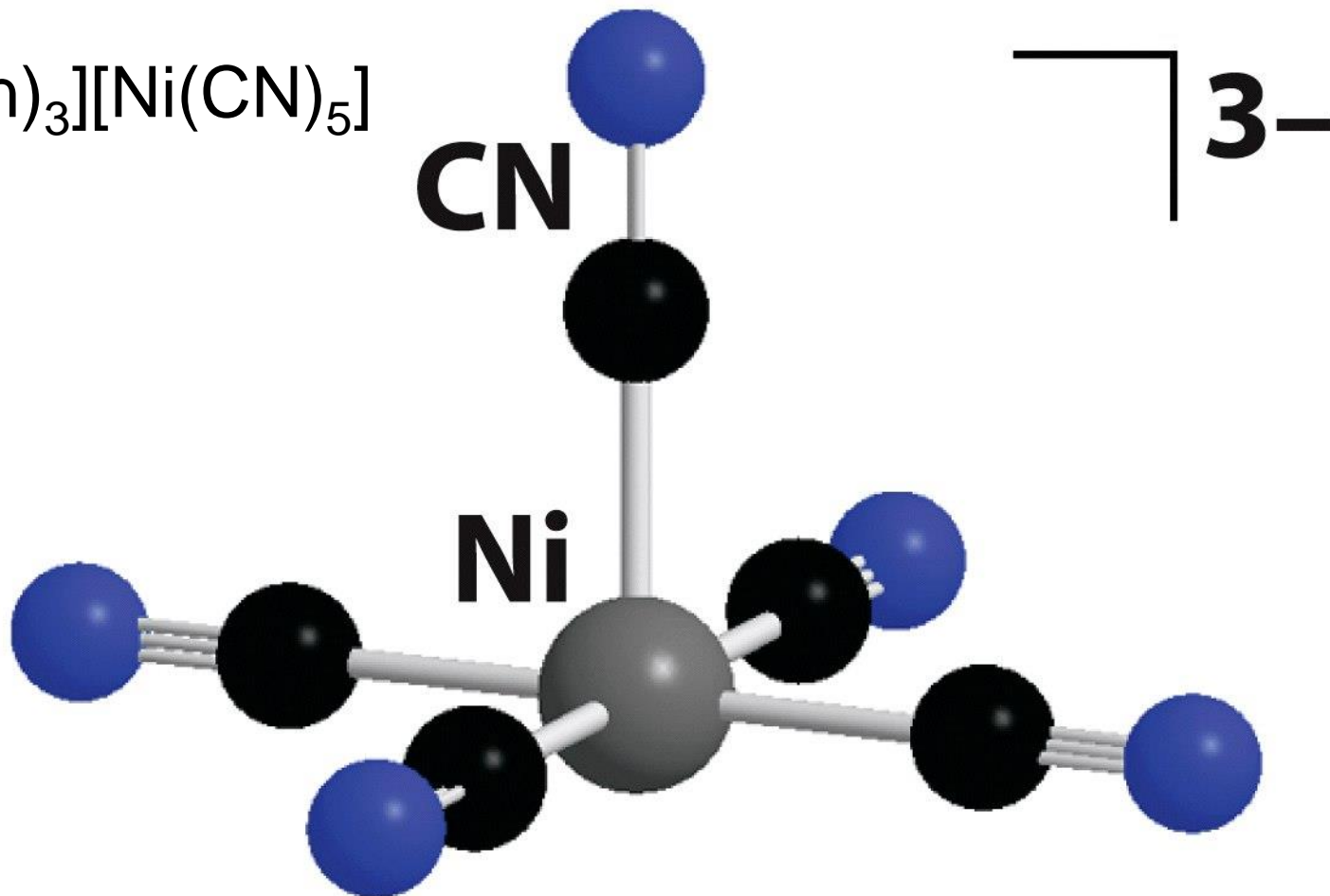
Esempi di complessi pentacoordinati con geometria imposta dai leganti



Legante tripodale



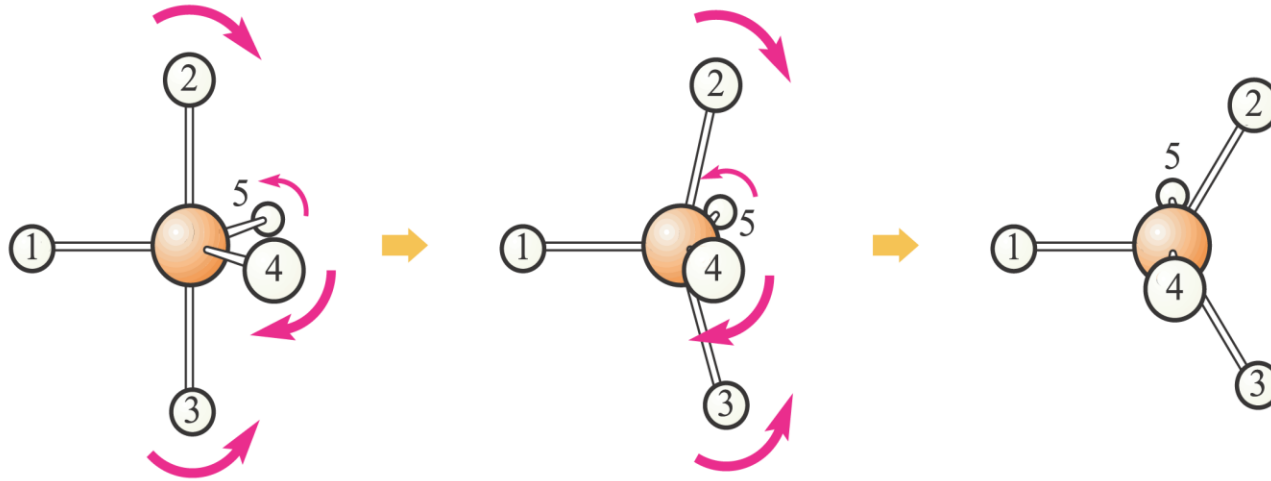




$[\text{Ni}(\text{CN})_5]^{3-}$, square pyramidal

Flussionalità

Pseudo-rotazione di Berry

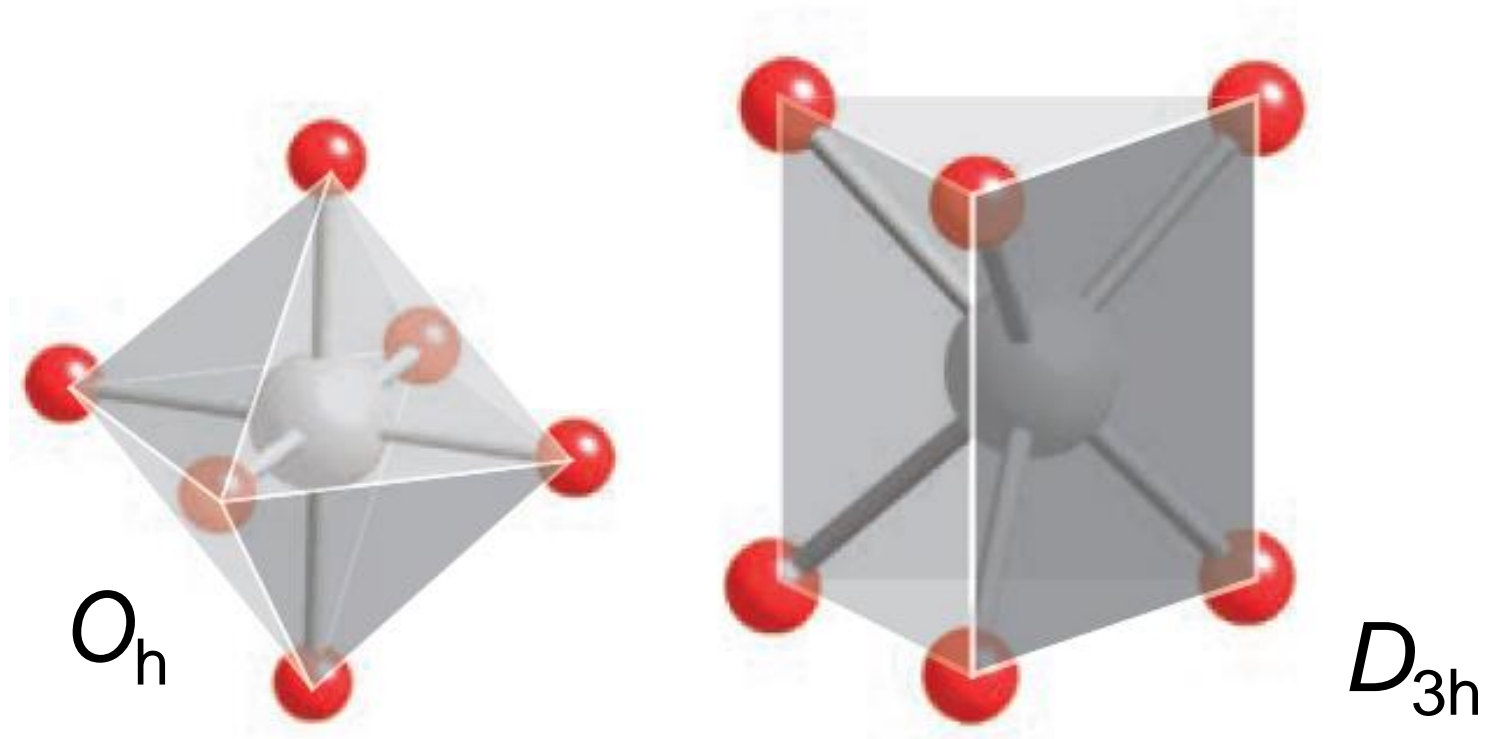


Trigonal bipyramid
(Atoms 2 and 3 are
in axial sites.)

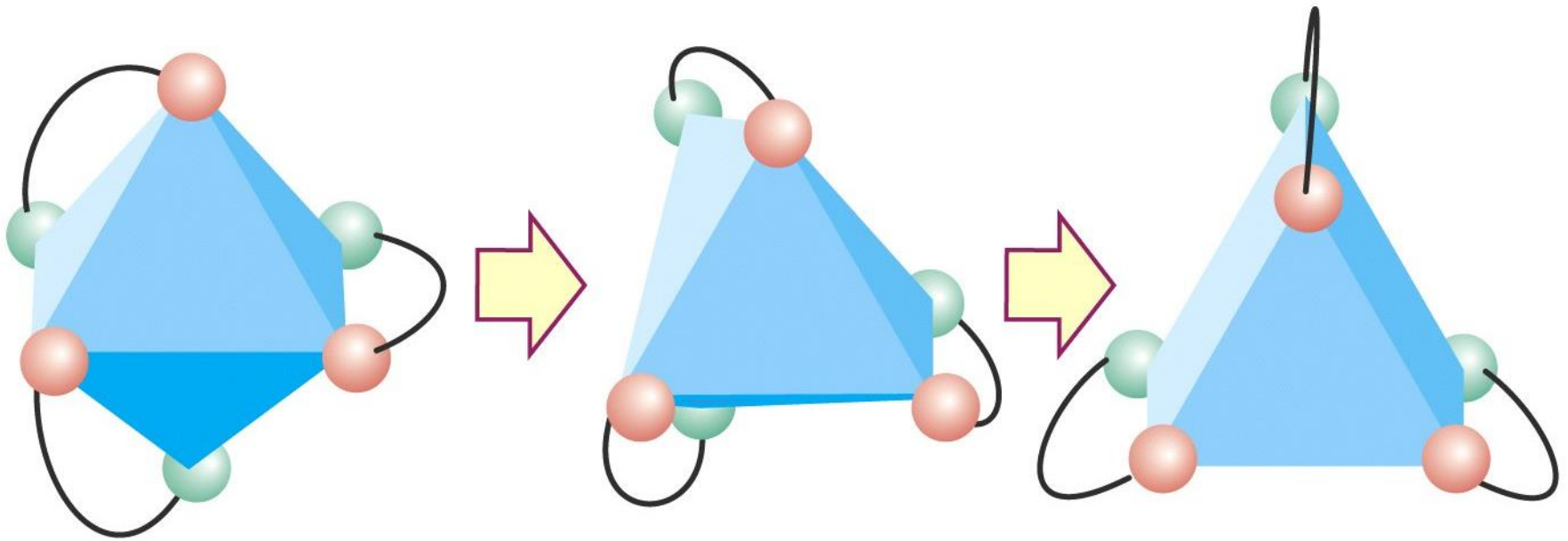
Square-based pyramid

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

Complessi esacoordinati

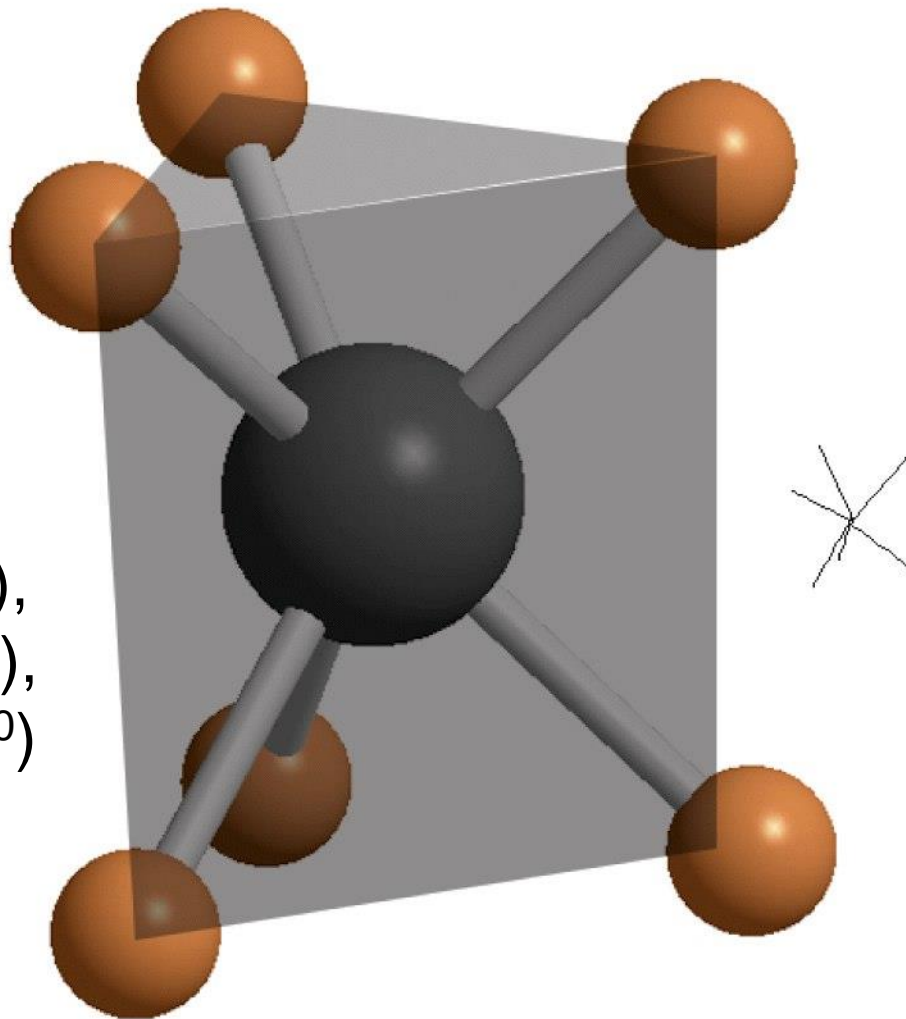


Un ottaedro può essere considerato un anti-prisma trigonale



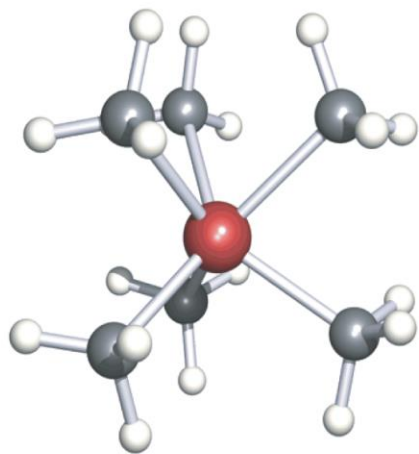
interconversion ottaedro-prisma triangolare per rotazione di 60° di una faccia triangolare rispetto a quella opposta

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

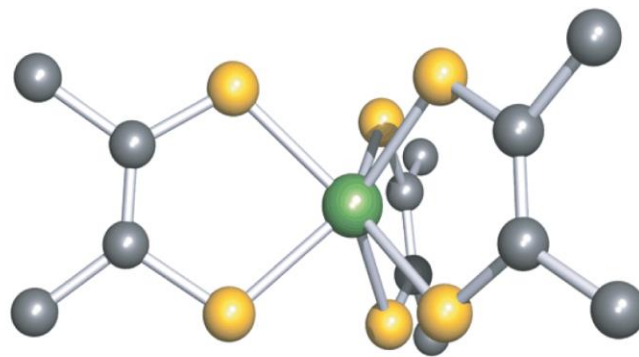


Trigonal prism, D_{3h}

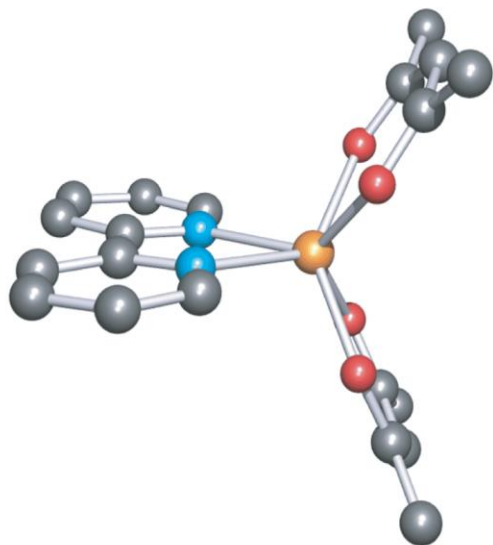
Essenzialmente in complessi di metalli d^0 o d^1
con leganti puri σ -donatori



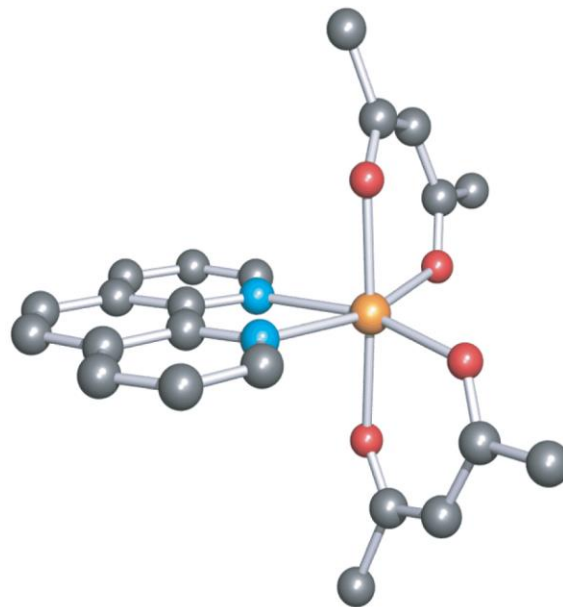
[W(CH₃)₆] (d⁰)



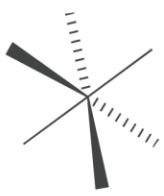
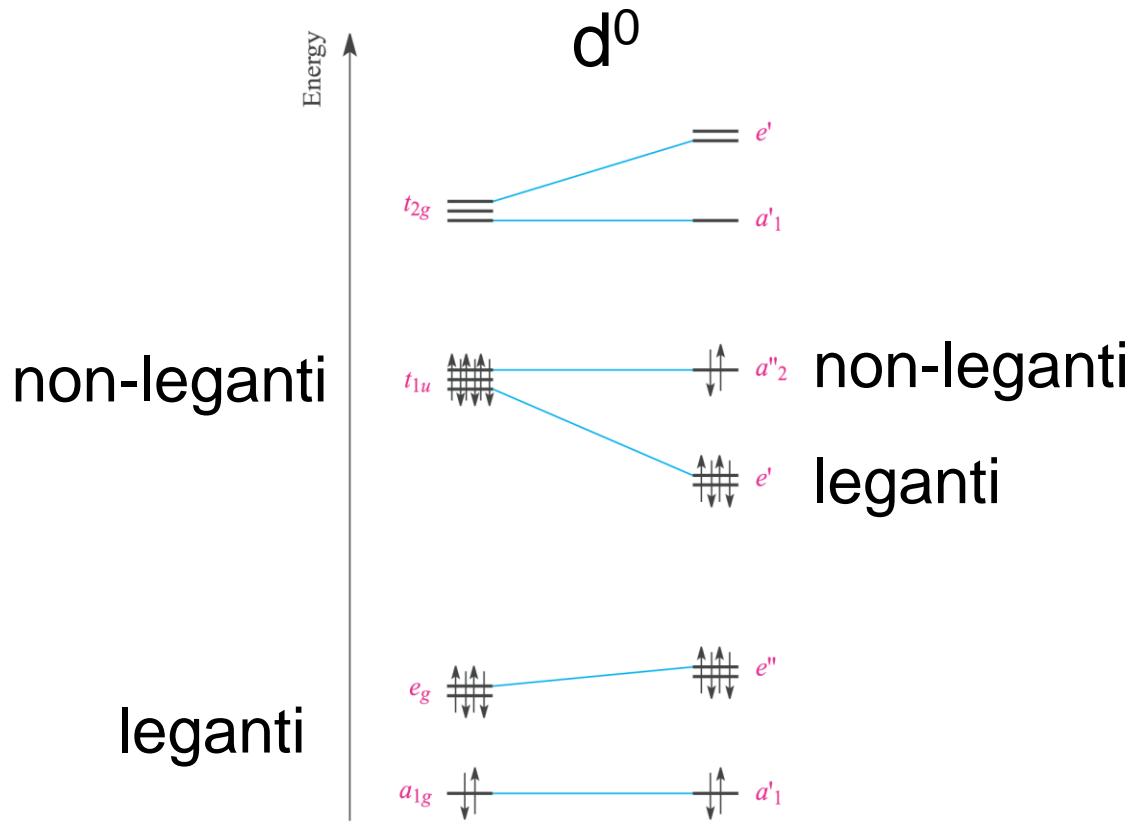
[Re(S₂C₂Ph₂)₃] (d¹)



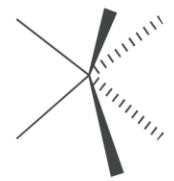
[Mn(acac)₂(bipy)]



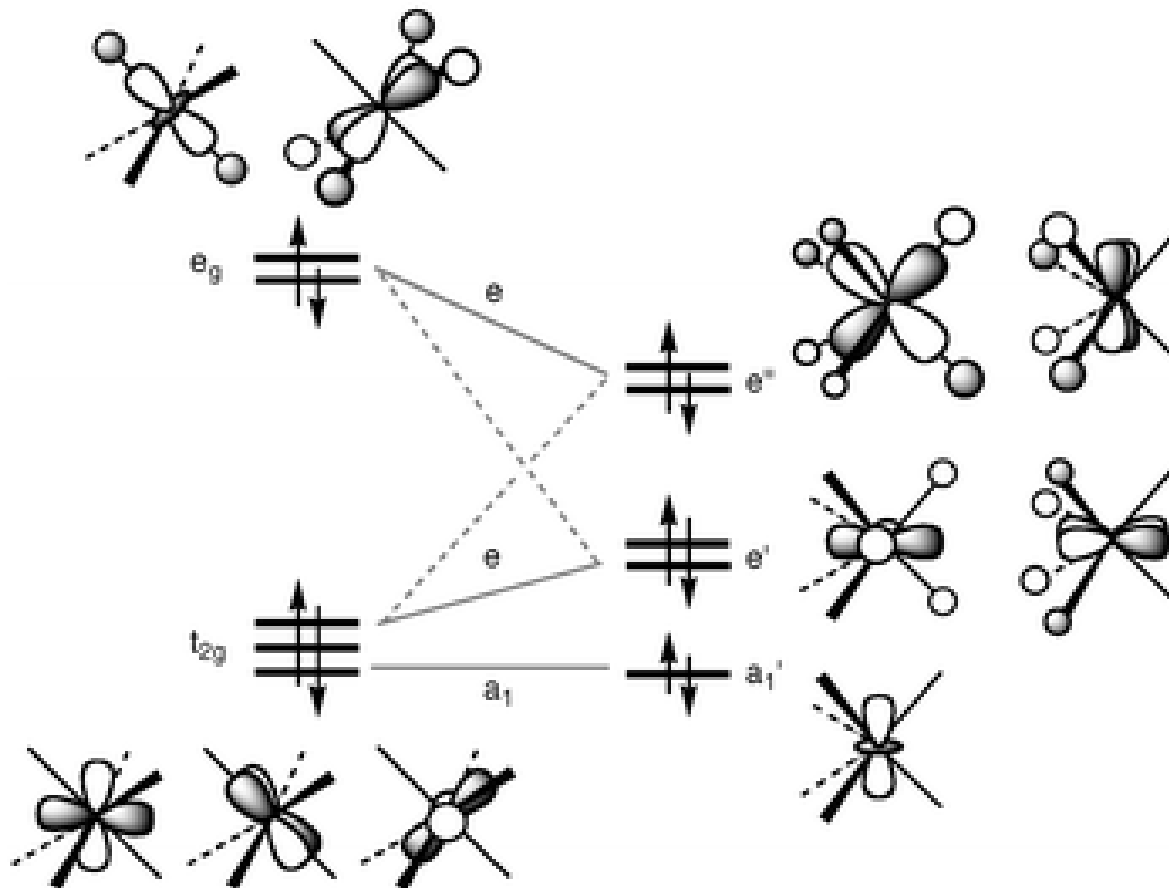
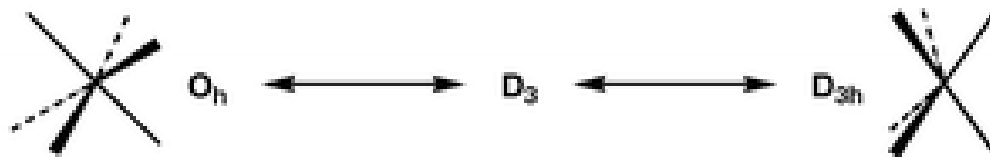
[Mn(acac)₂(phen)]



Octahedral
 O_h

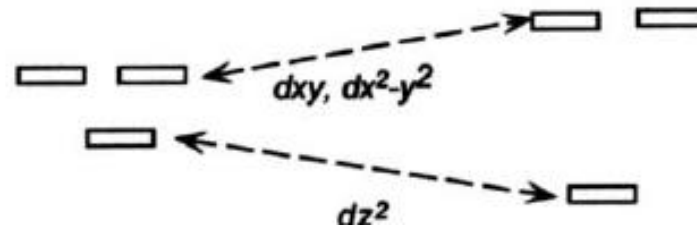
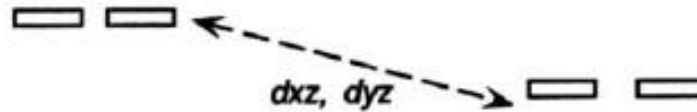
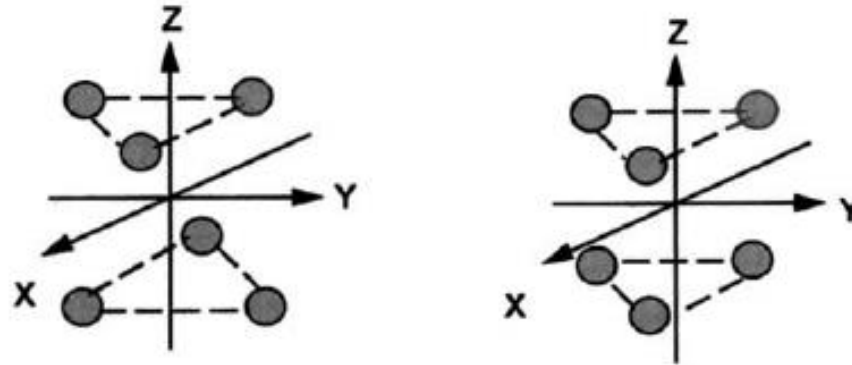


Trigonal prismatic
 D_{3h}

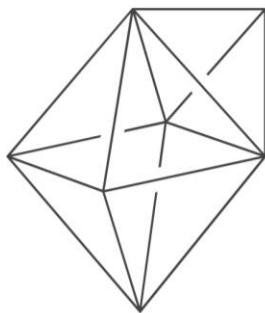


Diversa orientazione degli assi cartesiani

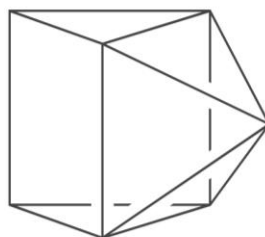
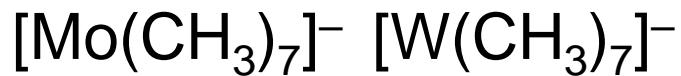
Splitting degli orbitali d in ottaedro e prisma trigonale mantenendo l'orientazione degli assi cartesiani del prisma



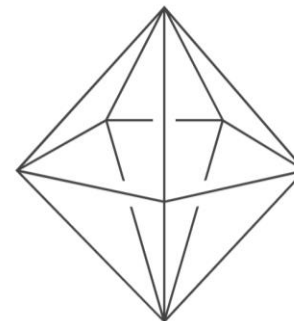
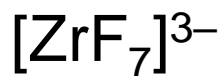
Geometrie per numero di coordinazione 7



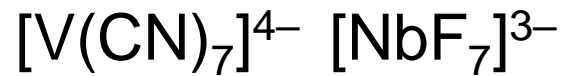
Monocapped
octahedron



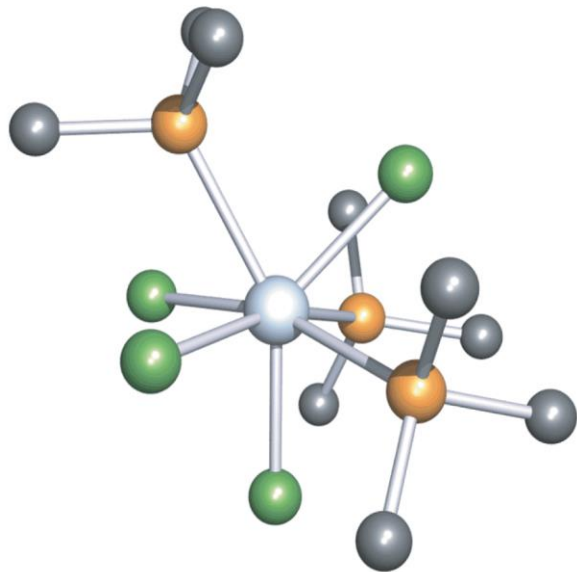
Monocapped trigonal
prism



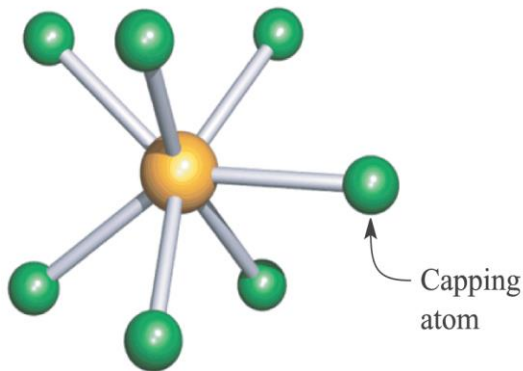
Pentagonal
bipyramid



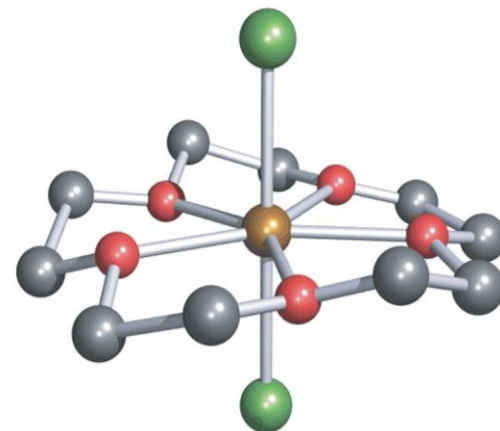
Esempi di complessi eptacoordinati



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



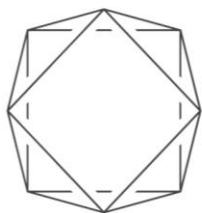
$[\text{ZrF}_7]^{3-}$
prisma trigonale cappato



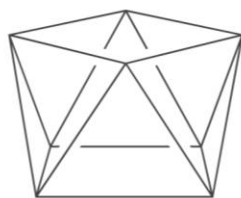
$[\text{ScCl}_2(15\text{-crown-}5)]^+$
bipiramide pentagonale

Cationi = acidi di Lewis deboli

Geometrie per numero di coordinazione 8

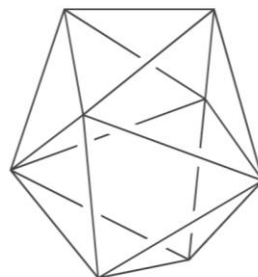
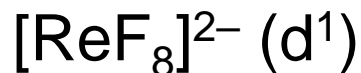
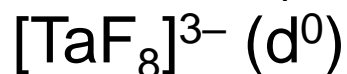


or



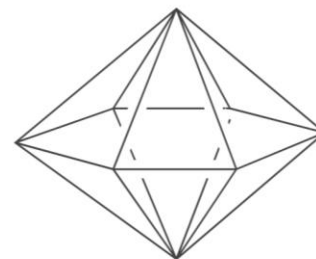
Square antiprism

D_{4d}

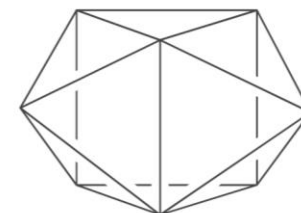


Dodecahedron

D_{2d}

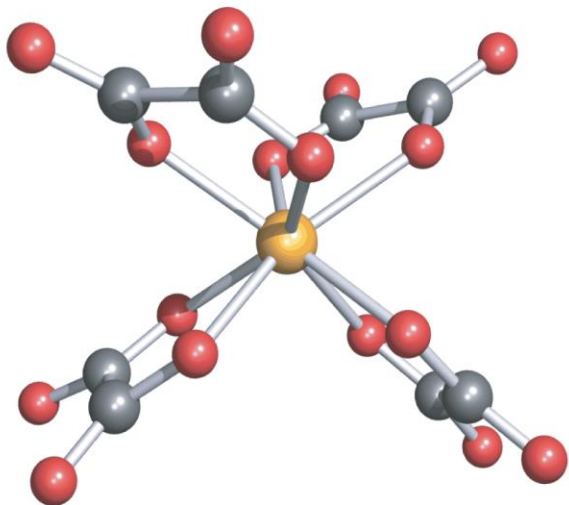


Hexagonal bipyramid

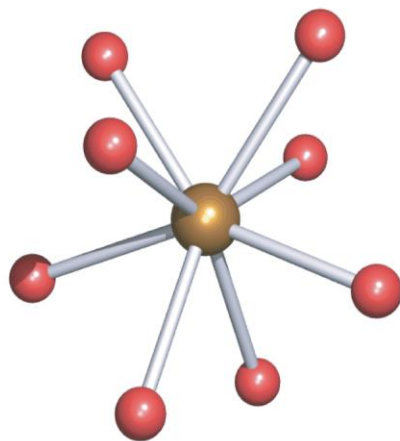


Bicapped trigonal prism

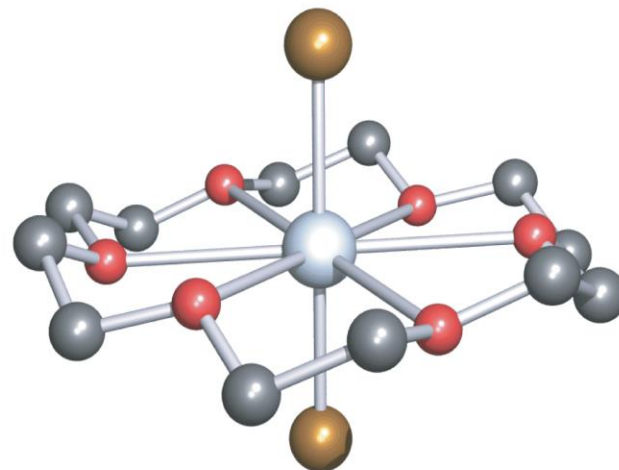
Esempi di complessi ottacoordinati



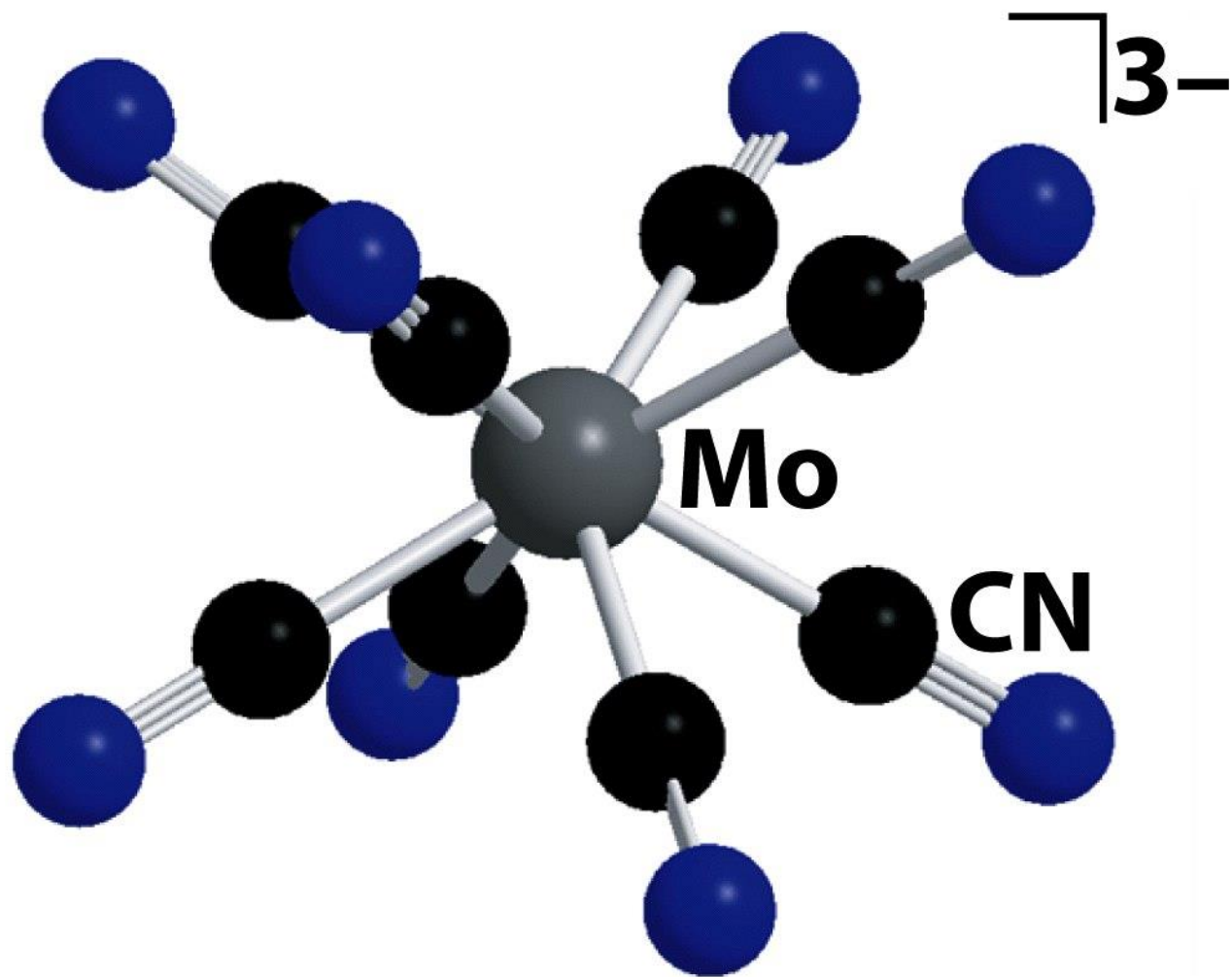
$[\text{Nb}(\text{ox})_4]^{4-}$
antiprisma quadrato



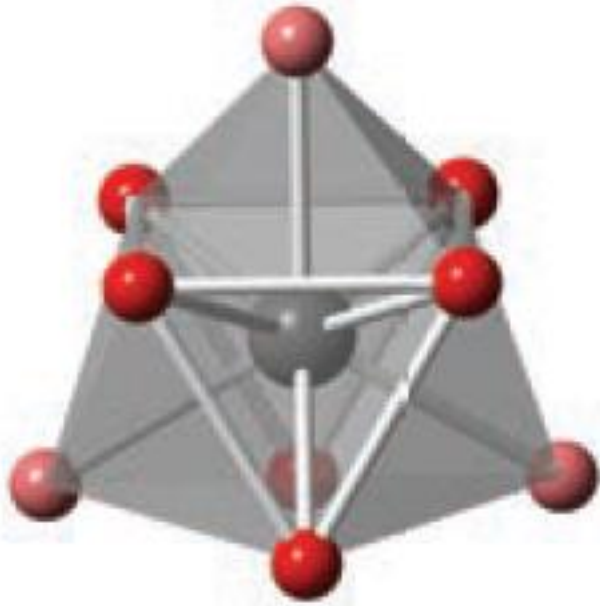
$[\text{Y}(\text{OH}_2)_8]^{3+}$
dodecaedro



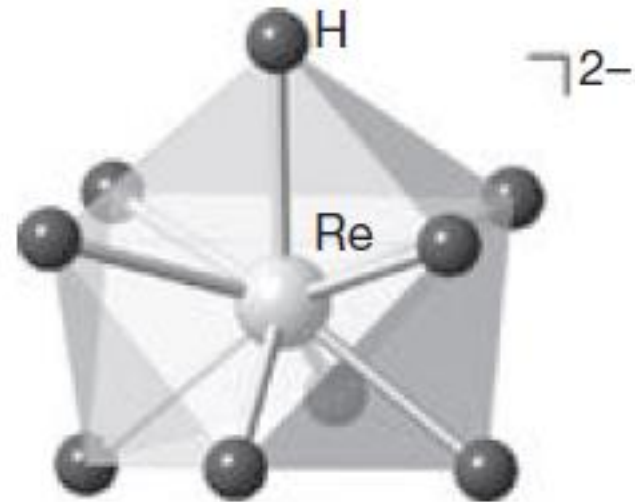
$[\text{CdBr}_2(18\text{-crown-}6)]$
bipiramide esagonale



Geometrie per numero di coordinazione 9

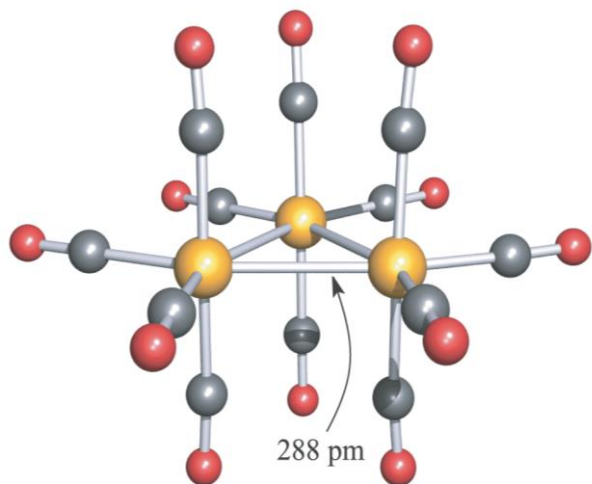


Prisma trigonale tricappato

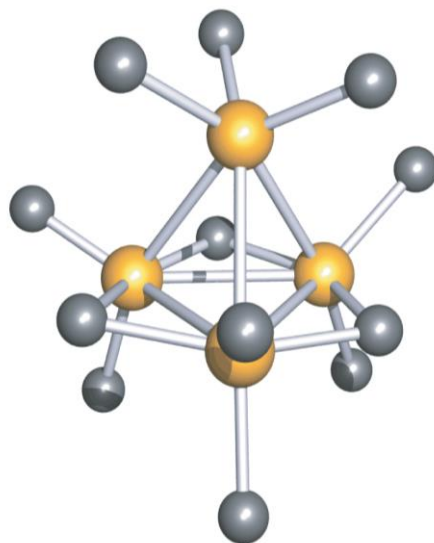


$[\text{ReH}_9]^{2-}$

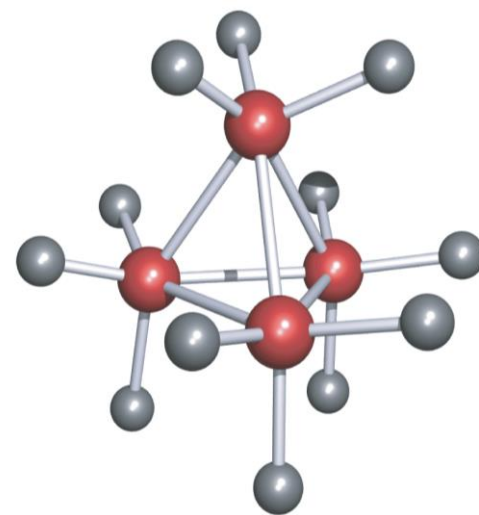
Cluster metallici



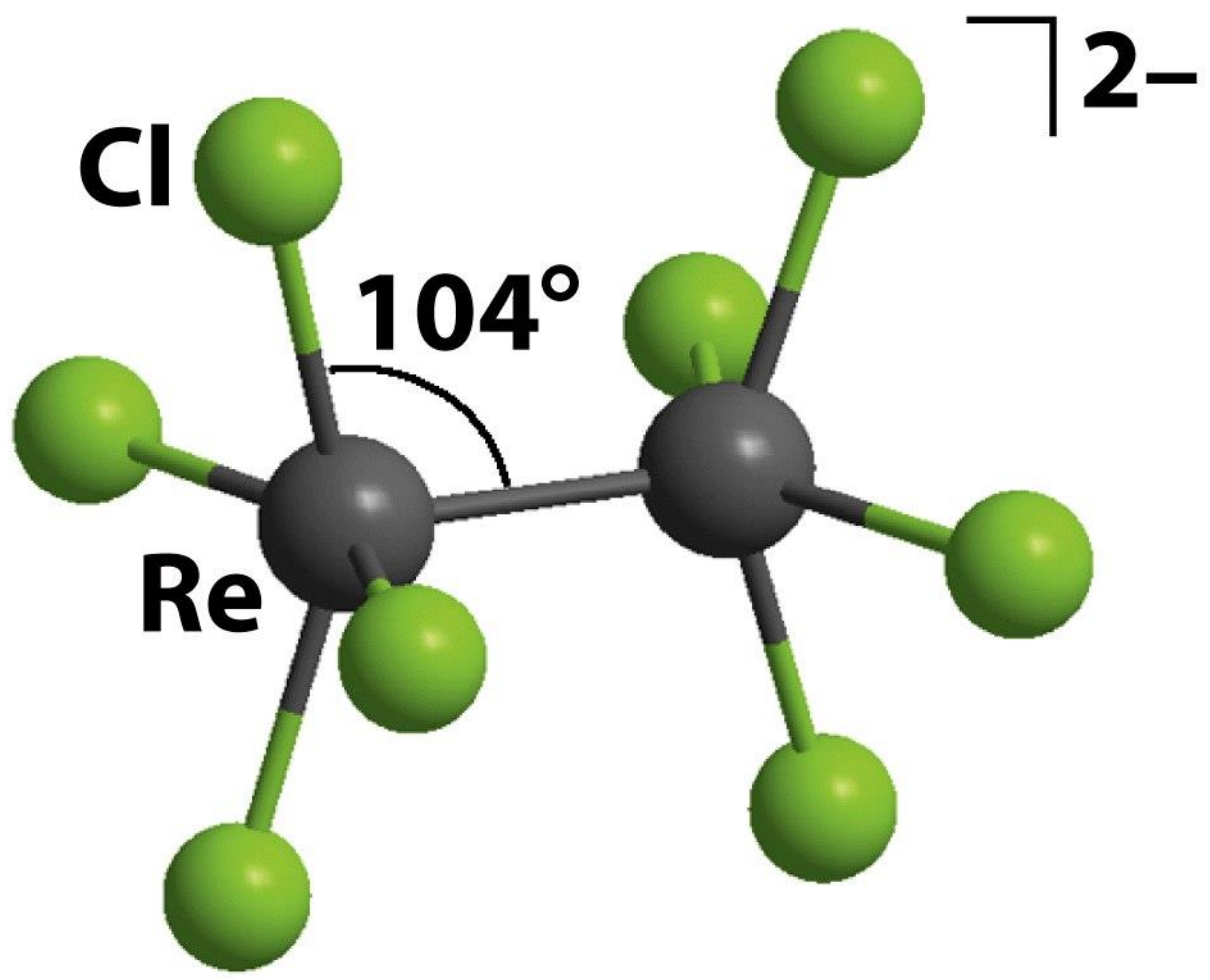
$\text{Os}_3(\text{CO})_{12}$



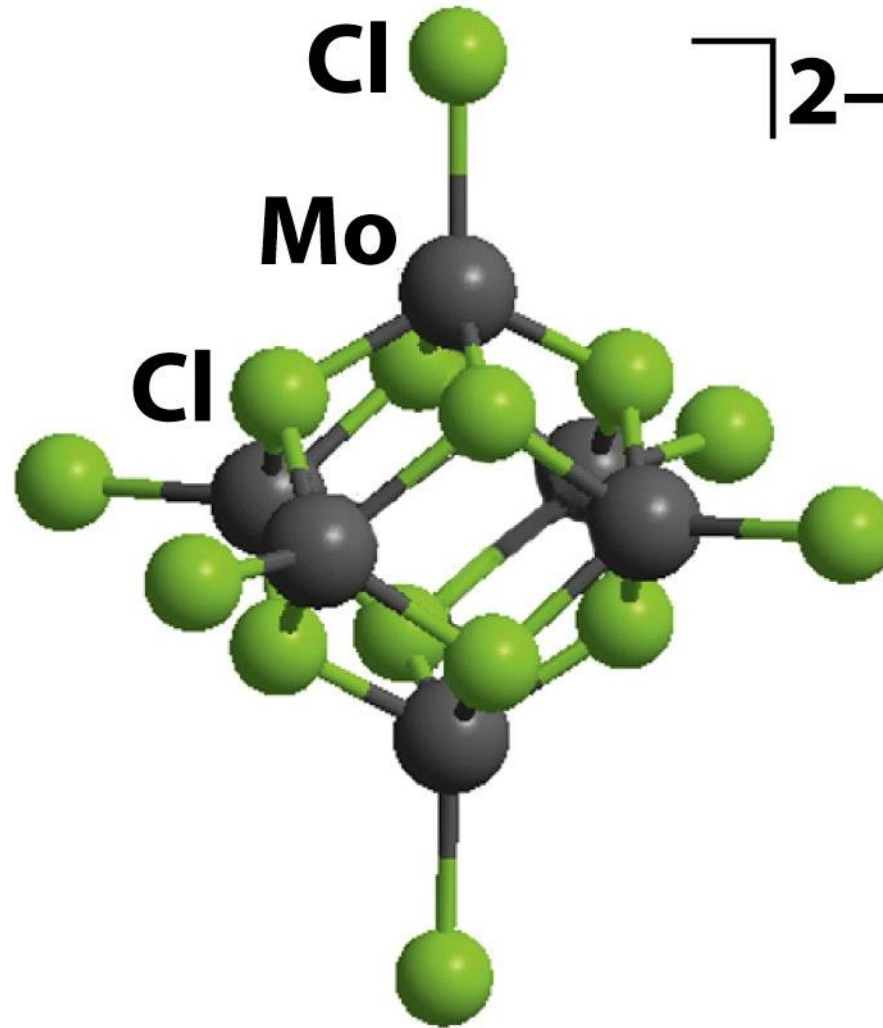
$\text{Rh}_4(\text{CO})_{12}$

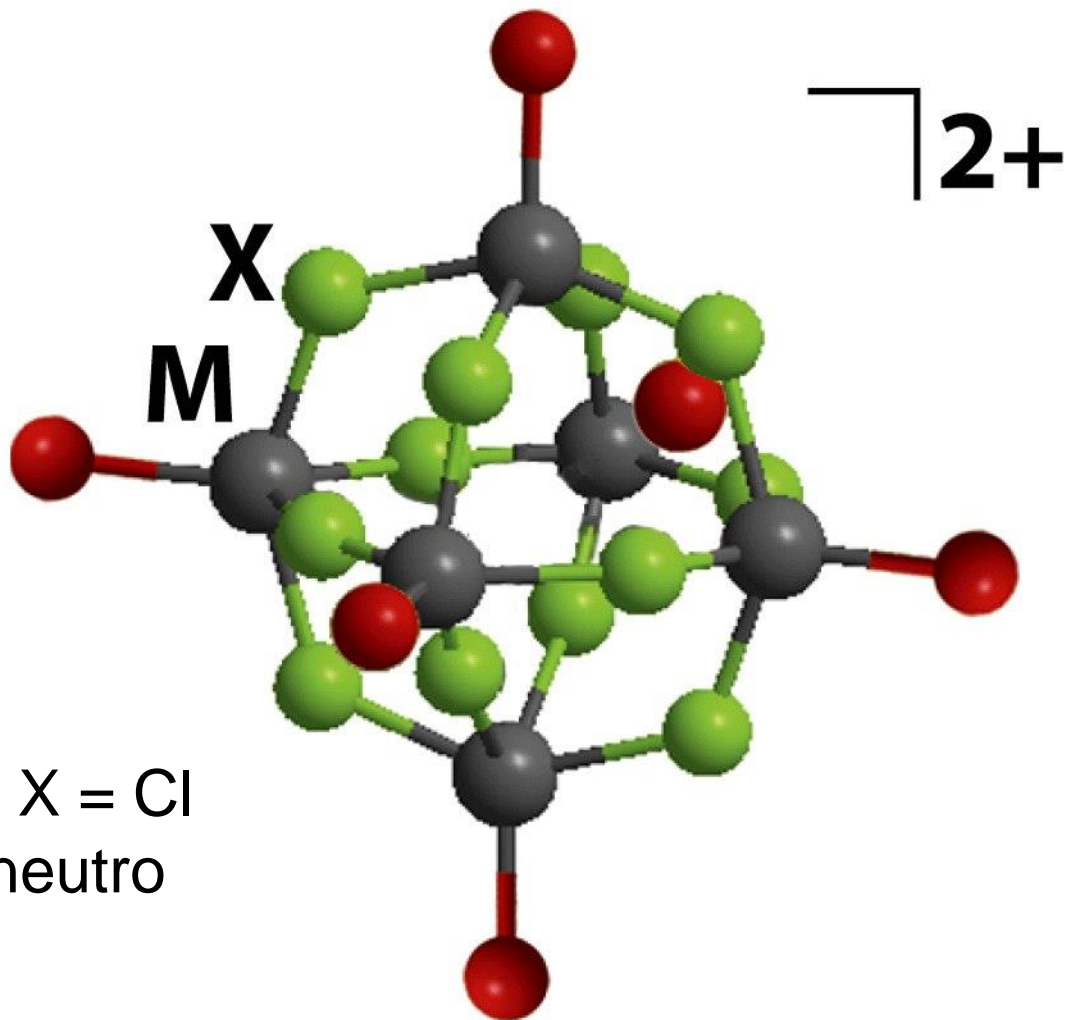


$\text{Ir}_4(\text{CO})_{12}$



Complessi a gabbia



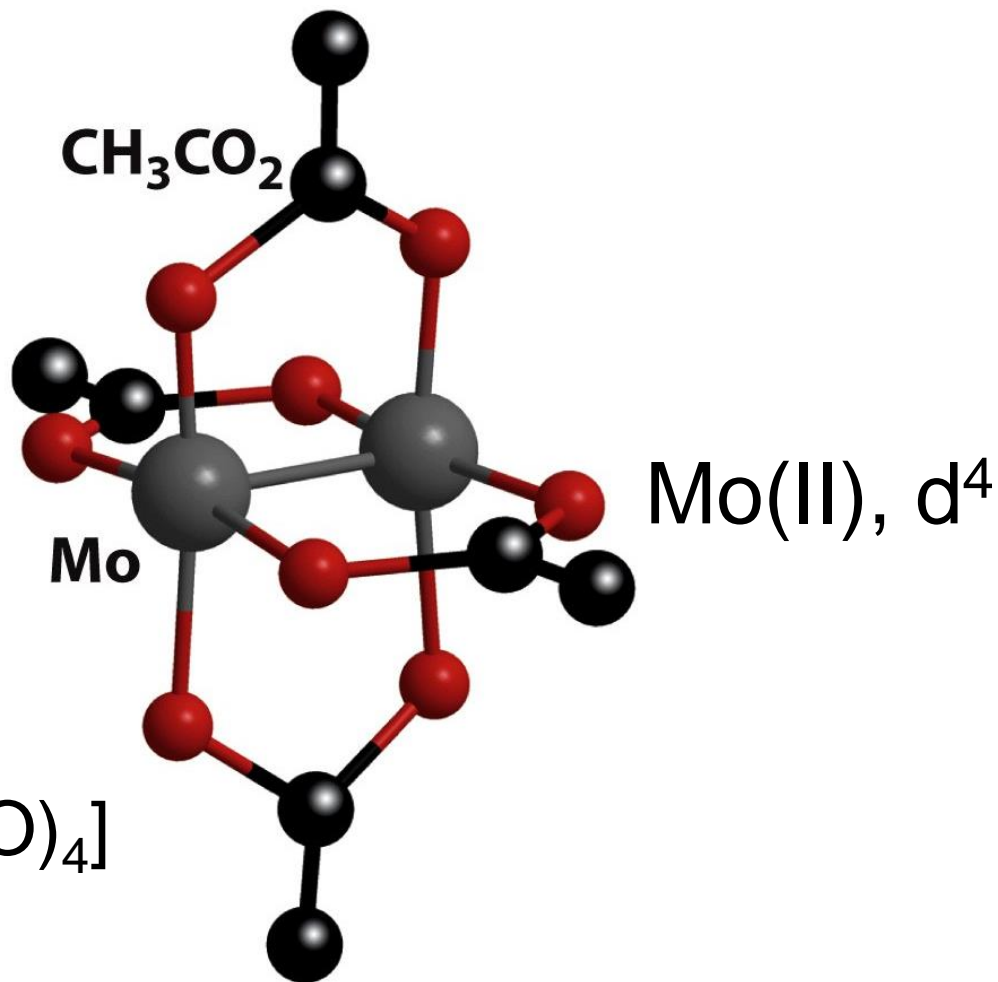


e.g. M = Nb, X = Cl
L = legante neutro



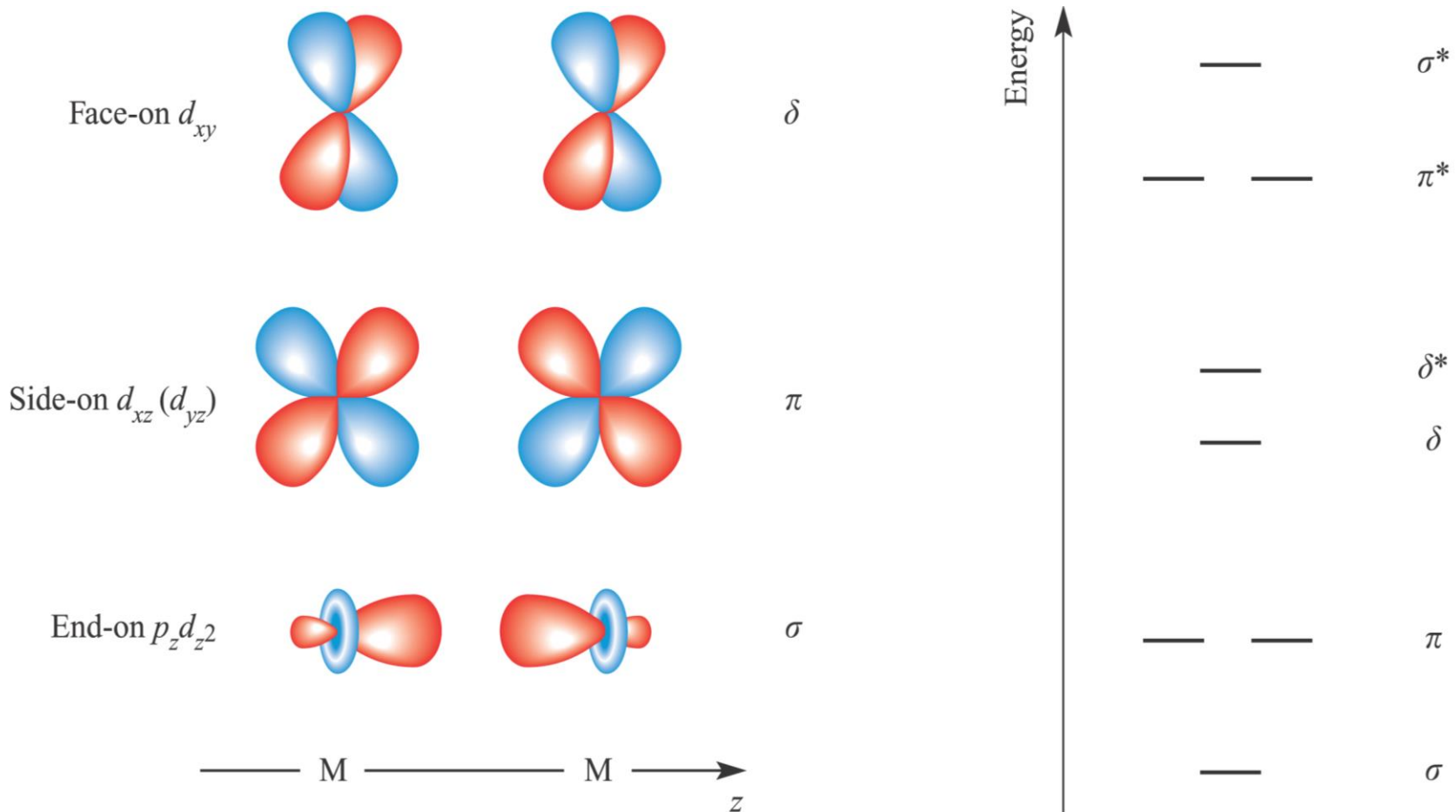
Complesso a gabbia

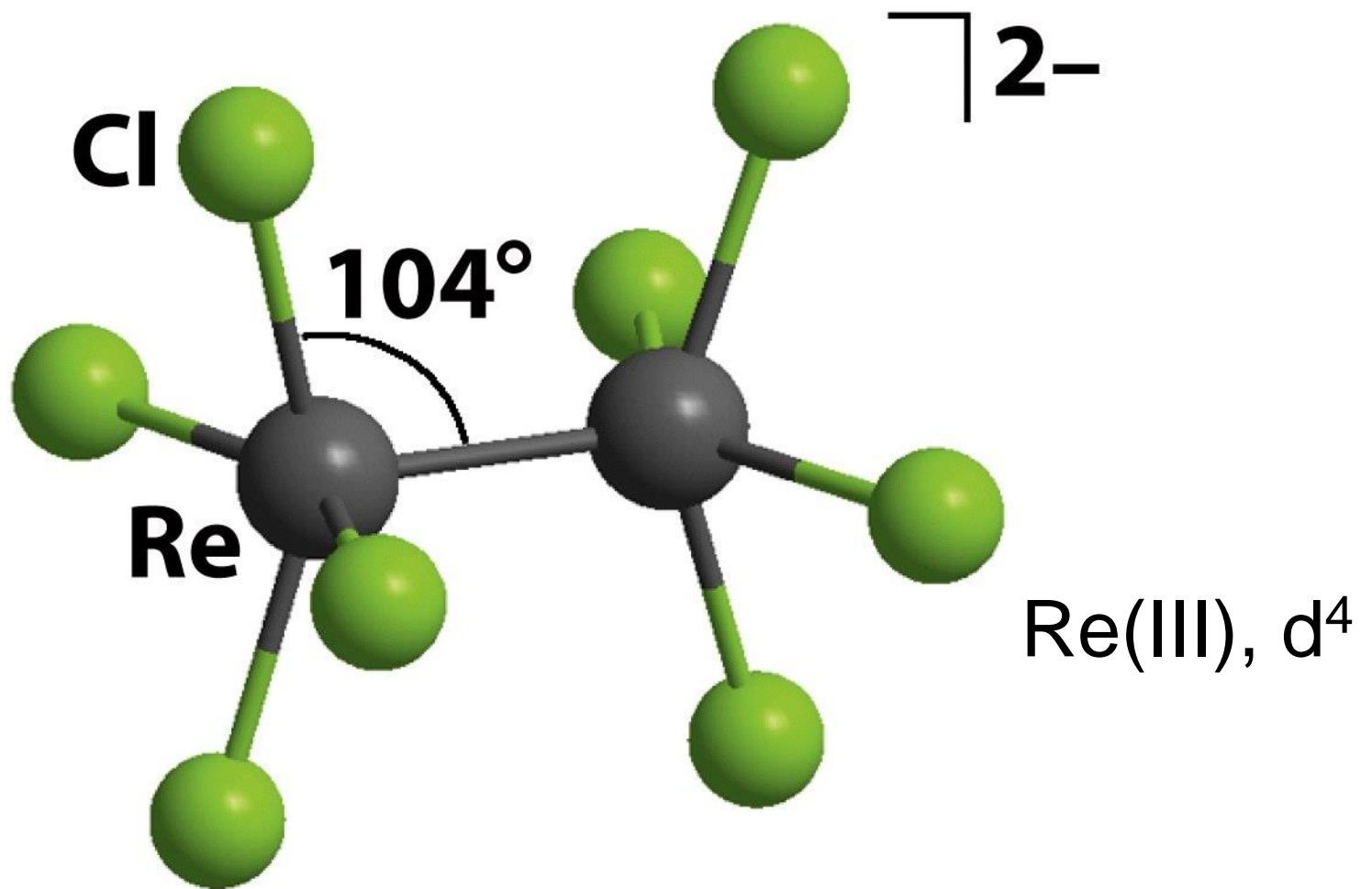
(tipo *a lanterna* o *paddle-wheel*)



Ordine di legame M–M da 1 a 4

Legami multipli M–M con contributo δ





Cloruri eclissati a causa del legame δ

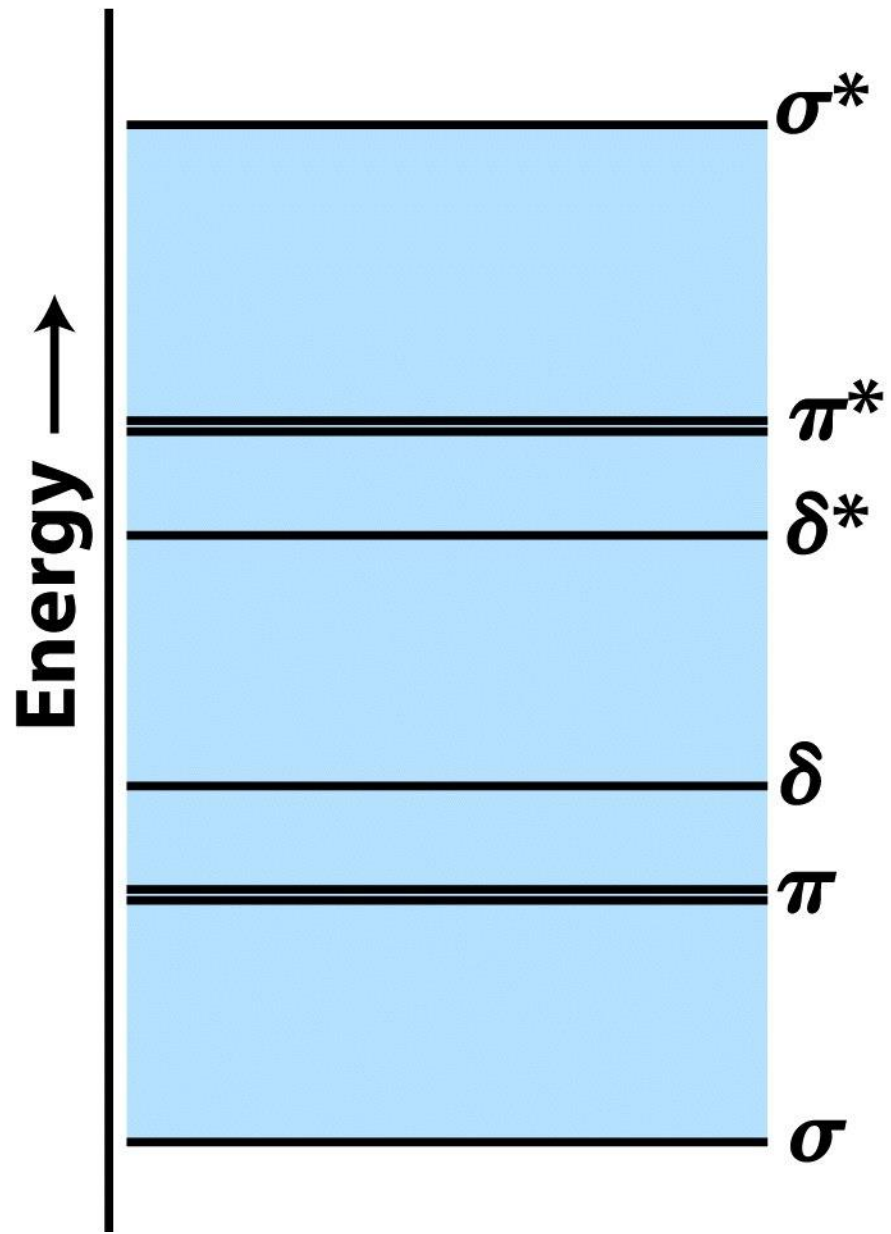


Table 18.9 Examples of metal–metal bonded tetragonal prismatic complexes[†]

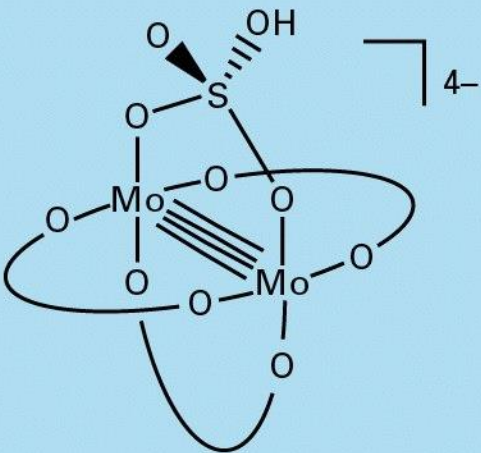
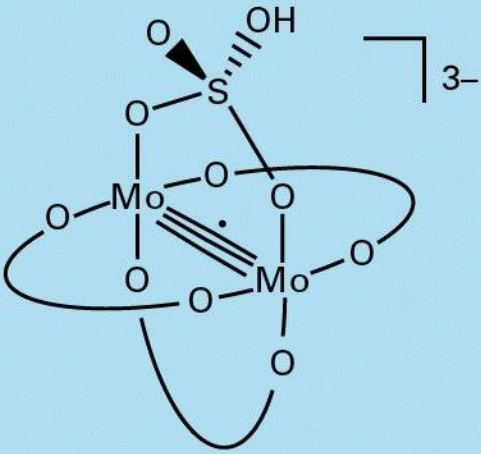
| Complex | Configuration | Bond order | M—M bond length/pm |
|--|-------------------------|------------|--------------------|
|  | $\sigma^2\pi^4\delta^2$ | 4 | 211 |
|  | $\sigma^2\pi^4\delta^1$ | 3.5 | 217 |

Table 18.9 Examples of metal–metal bonded tetragonal prismatic complexes[†]

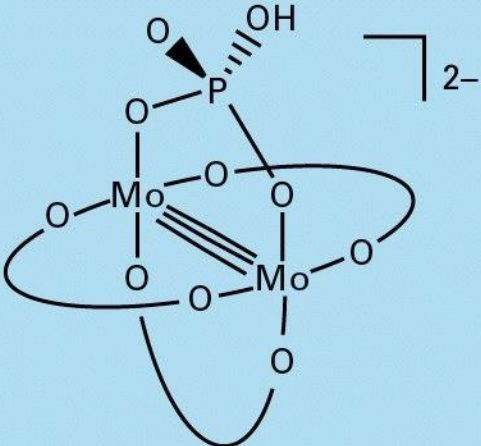
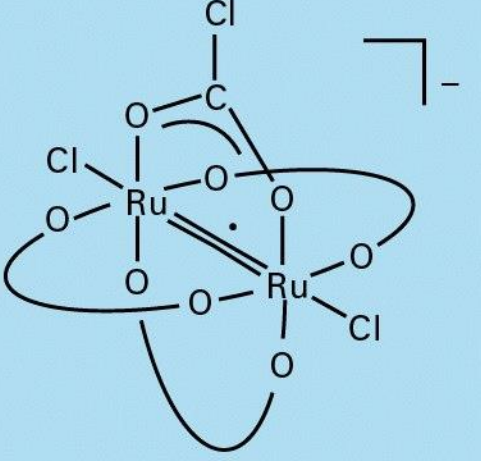
| Complex | Configuration | Bond order | M—M bond length/pm |
|--|--|------------|--------------------|
|  | $\sigma^2\pi^4$ | 3 | 222 |
|  | $\sigma^2\pi^4\delta^2\delta^*1\pi^*2$ | 2.5 | 227 |

Table 18.9 (Continued)

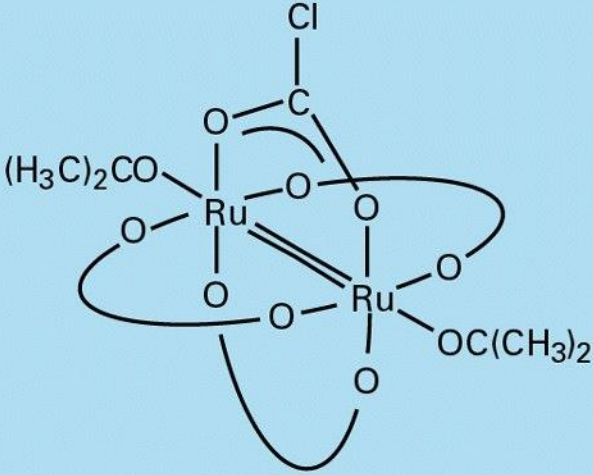
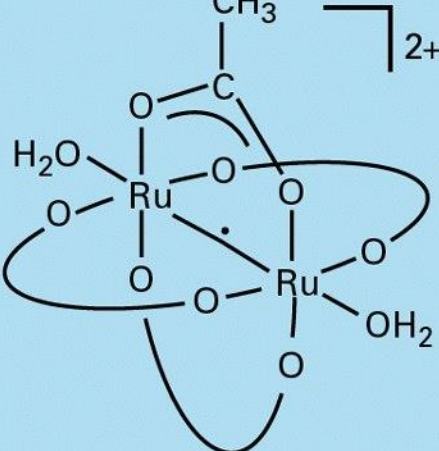
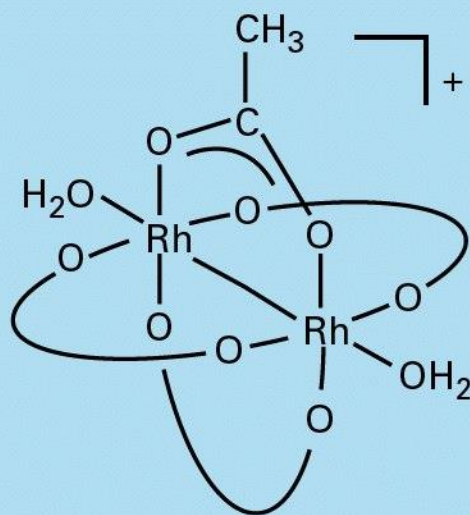
| Complex | Configuration | Bond order | M—M bond length/pm |
|--|--------------------------------------|------------|--------------------|
|  | $\sigma^2\pi^4\delta^2\delta^*\pi^2$ | 2 | 226 |
|  | $\sigma^2\pi^4\delta^2\delta^*\pi^4$ | 1.5 | 232 |

Table 18.9 (Continued)**Complex****Configuration****Bond order****M—M bond length/pm** $\sigma^2\pi^4\delta^2\delta^*\pi^4$

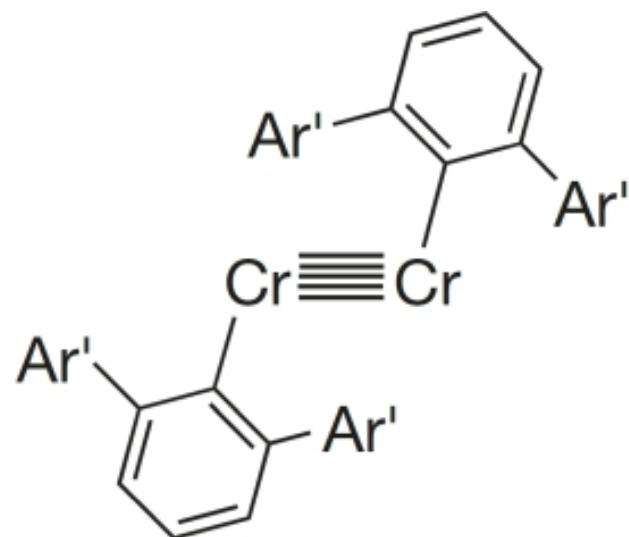
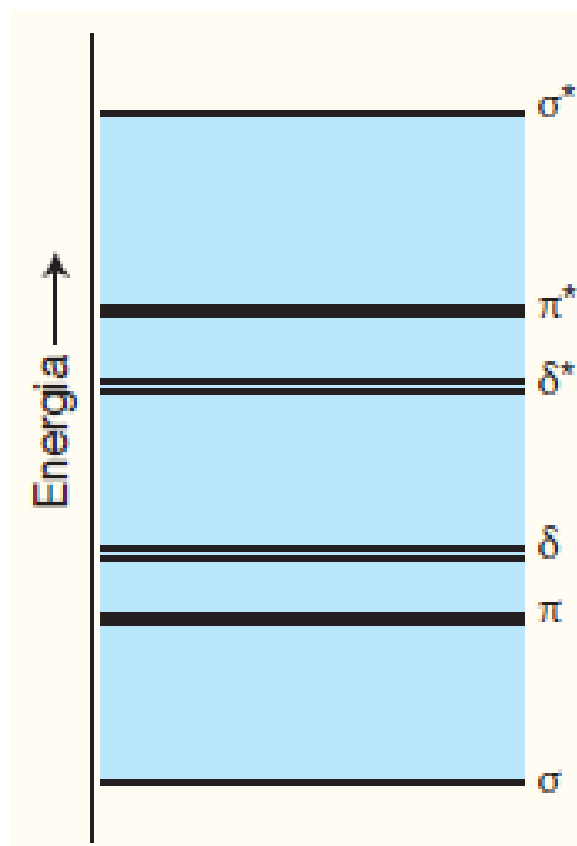
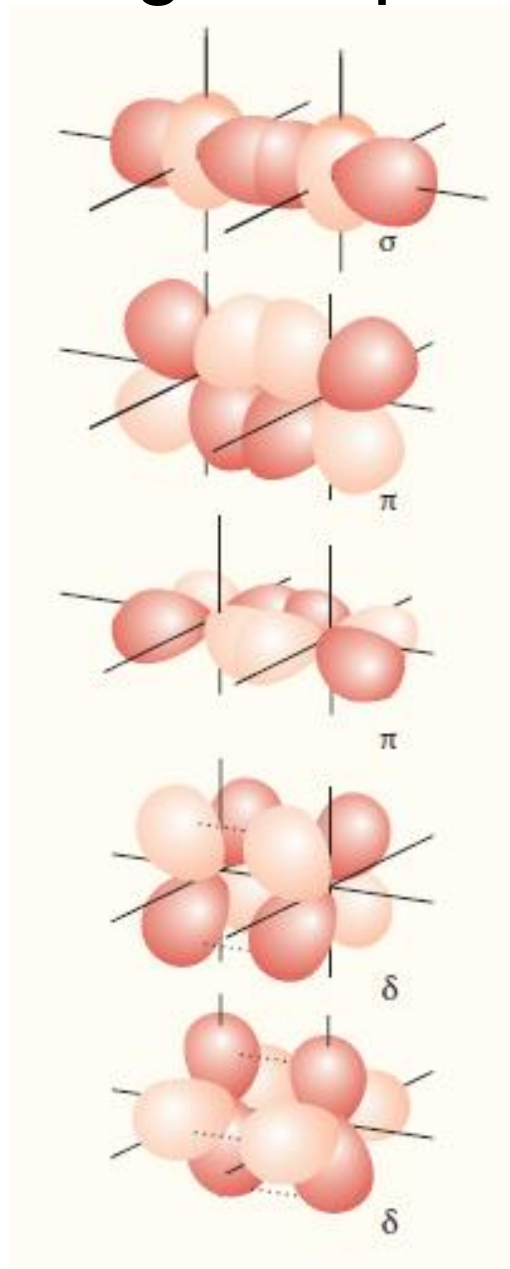
1

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

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

Legami quintupli M–M in complessi di Cr(I), d^5



Distanza Cr–Cr 183.5 pm,
vs 258 pm nel metallo